

TRANSCENDING TRANSITION STATE THEORY:  
SOLVENT DYNAMIC EFFECTS IN POLAR REACTIONS AND MACHINE-  
LEARNING TRANSITION STATE THEORY

A Dissertation

by

VLADISLAV ROYTMAN

Submitted to the Office of Graduate and Professional Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Chair of Committee,	Daniel Singleton
Committee Members,	Oleg Ozerov
	David Powers
	Peter Rentzepis
Head of Department,	Simon North

May 2021

Major Subject: Chemistry

Copyright 2021 Vladislav Roytman

## ABSTRACT

Statistical rate theories such as transition state theory (TST) are central to the understanding of the rates of chemical reactions. This dissertation describes an investigation of a variety of observations in simple organic reactions that cannot be understood with statistical rate theories. Such observations are referred to as dynamic effects.

The long history of experimental observations in carbocation reactions has treated ion pairs as ordinary intermediates reacting statistically. The combined experimental, computational, and dynamic trajectory study of one such reaction here suggests that this view is incorrect due to the importance of nonequilibrium solvation and solvent dynamics in the mechanism. This idea complicates our understanding of the nature of charged intermediates in solution and suggests a reinterpretation of a series of historically notable observations in carbocation reactions.

The fundamental idea of symmetry in chemistry breaks down on a sufficiently short time scale, but this theoretical pedantry is assumed to be irrelevant to reactive chemistry. However, for the carboborative ring contraction of cyclohexenes studied here, the apparent symmetry of an intermediate structure is lost due to its short lifetime. This reaction affords an unequal mixture of two equivalent products, and molecular dynamics studies are able to account for the product mixture based on the formation of a nominally symmetrical carbocation structure with a nonsymmetrical distribution of vibrational energy. This *dynamical asymmetry* complicates the understanding and interpretation of stereochemical observations in chemistry.

Machine-learning transition state theory (MLTST) is an approach to the numerical prediction of dynamic effects and their qualitative understanding, while retaining the strengths of statistical rate theories. The central idea of MLTST is that machine learning algorithms are used to divide the transition state hypersurface into regions associated with each possible outcome of a trajectory crossing the transition state. This mapping of the surface allows the prediction of trajectory outcomes from the first point of the trajectory, sidestepping the numerous and computationally expensive trajectories needed to achieve statistical significance. This approach allows for an understanding of selectivity controlling elements outside of the TST paradigm.

## DEDICATION

I could not have gotten this far without the love and support of my Mom and Pop. This dissertation is for them.

## ACKNOWLEDGEMENTS

I would like to thank my graduate advisor Dr. Daniel Singleton for his unwavering support over the last five years. It has been a privilege to have him as a patient mentor, fierce advocate, and equitable role model.

I would also like to thank Dr. David Powers for his mentorship, his support, and investment in my career – all of which he gave freely and without any obligation to do so. I would like to thank Dr. Simon North for his instructive discussions on photodissociation reactions, roaming, and determinism. I am grateful to have the guidance of Drs. Oleg Ozerov and Peter Rentzepis through their roles as dissertation committee members. Drs. Lisa Perez, Greg Wylie, and Doug Elliot have my gratitude for their tireless efforts in training me and troubleshooting my experiments. I am grateful to Sandy Horton for keeping the train on the rails as I transitioned through milestones in my graduate study.

To my current and former labmates: Sherry Alvi, Johnathan Bailey, Christoph Bracher, Andrew Jeffries, Kai-Yuan Kuan, Hiroaki Kurouchi, and Yexenia Nieves-Quinones. Thank you for being my colleagues and my friends, for challenging me and inspiring me. I owe a debt of gratitude to Singleton group alumni Drs. Jennifer Hirschi and Mathew Vetticatt for support and collaboration that far exceeded my expectations when I first began my scientific career as their undergraduate research assistant in 2014.

Angelo, Corrie, Zach – your friendship was the wind in my sails these last few years. I could not have done it without you. Mom, Dad, Julie, Oleg. Thank you for your faith in me and your unconditional love. Finally, thank you Masha for your patience, love, and support. I adore you.

## CONTRIBUTORS AND FUNDING SOURCES

### **Contributors**

This work was supported by a dissertation committee consisting of Dr. Daniel Singleton (advisor), Dr. Oleg Ozerov and Dr. David Powers from the Department of Chemistry, and Dr. Peter Rentzepis. from the Department of Electrical Engineering. All the work done in this dissertation was done by the student independently with the exception of the syntheses and product determination experiments in Chapter III, which were performed by Shengfei Jin, Vu T. Nguyen, and Viet D. Nguyen as a collaboration with Professor Larionov at The University of Texas at San Antonio.

### **Funding Sources**

This graduate study was supported by a Texas A&M Department of Chemistry teaching appointment, in addition to financial support from National Institutes of Health (NIH) Grant Number GM-45617.

## NOMENCLATURE

CVT	Canonical Variational Transition State Theory
DCI	Deuterium Chloride
DCM	Dichloromethane
DEPT	Distortionless Enhancement by Polarization Transfer
DFT	Density Functional Theory
DMSO	Dimethylsulfoxide
DRP	Dynamic Reaction Path
DS	Dividing Surface
ee	enantiomeric excess
EPT	Electron-Proton Transfer
EVB	Empirical Valence Bond
FES	Free Energy Surface
HAT	Hydrogen Atom Transfer
HPLC	High Performance Liquid Chromatography
HSQC	Heteronuclear Single Quantum Coherence
ICT	Intramolecular Charge Transfer
IRC	Intrinsic Reaction Coordinate
IVR	Intramolecular Vibrational Redistribution
KIE	Kinetic Isotope Effect
MD	Molecular Dynamics

MECP	Minimum Energy Crossing Point
MEP	Minimum Energy Path
MK	Merz-Singh-Kollman
ML	Machine Learning
MLTST	Machine Learning Transition State Theory
MM	Molecular Mechanics
NCI	Non-covalent Interaction
NMR	Nuclear Magnetic Resonance
NTST	Nonadiabatic Transition State Theory
PCM	Polarizable Continuum Model
PES	Potential Energy Surface
PMF	Potential of Mean Force
QCT	Quasiclassical Trajectory
QM	Quantum Mechanics
QMT	Quantum Mechanical Tunneling
RC	Reaction Coordinate
RRKM	Rice-Ramsperger-Kassel-Marcus
TFIPA	Trifluoro-isopropanol
THF	Tetrahydrofuran
TS	Transition State
TST	Transition State Theory



## TABLE OF CONTENTS

	Page
ABSTRACT .....	ii
DEDICATION .....	iv
ACKNOWLEDGEMENTS .....	v
CONTRIBUTORS AND FUNDING SOURCES.....	vi
NOMENCLATURE.....	vii
TABLE OF CONTENTS .....	ix
LIST OF FIGURES.....	xii
LIST OF TABLES .....	xix
CHAPTER I INTRODUCTION .....	1
1.1 Chemical Models .....	1
1.2 Transition State Theory.....	1
1.3 Dynamic Effects.....	4
Bifurcating Surfaces .....	5
Nonstatistical Energies and Recrossing .....	7
Entropic Intermediates .....	13
Dynamic Effects in Solvation.....	16
CHAPTER II SOLVATION DYNAMICS AND THE NATURE OF REACTION BARRIERS AND ION-PAIR INTERMEDIATES IN CARBOCATION REACTIONS .....	28
2.1 Introduction .....	28
2.2 Experimental Results and Discussion .....	34
Reaction of 1-methylcyclopentene with DCl .....	34
Reaction of Cyclopentene with DCl.....	36
Reaction of 1,3-pentadiene with DCl .....	38
Reaction of tert-butylethylene with DCl .....	39
Reaction of Norbornene with DCl.....	41
Conclusions .....	43
2.3 Molecular Dynamics Results and Discussion .....	43
Computational Methods Selection .....	43
Implicit Solvation .....	45
Explicit Solvation .....	48

2.4 Conclusions .....	64
2.5 Experimental Procedures.....	71
General Methods .....	71
Reaction of 1-methylcyclopentene with DCl .....	71
Reaction of Cyclopentene with DCl.....	71
Reaction of Cyclopentene with DCl and Tetramethylammonium Chloride .....	72
Reaction of 1,3-pentadiene with DCl.....	72
Synthesis of trans-2-d <sub>1</sub> -cyclopentanol.....	73
Synthesis of Cyclopentan-2-d-ol acetate.....	73
Synthesis of trans-1-toluenesulfonyl-2-d <sub>1</sub> -cyclopentane.....	73
Synthesis of syn-1-chloro-2-d <sub>1</sub> -cyclopentane .....	74
Reaction of Norbornene with DCl.....	74
Reaction of tert-butylethylene with DCl .....	75
2.6 Computational Procedures .....	76
General .....	76
Trajectory Terminology .....	77
Computational Methods Validation Studies.....	78
DRP and Trajectories in Implicit Solvent .....	81
PMF for Protonation in Explicit Solvent.....	84
Trajectories in Explicit Solvent Started from the Area of 10 <sup>‡</sup> .....	88
CHAPTER III BOND MEMORY IN DYNAMICALLY DETERMINED STEREOSELECTIVITY .....	98
3.1 Introduction .....	98
3.2 Computational Results and Discussion.....	102
Initial Exploration of Computational Models .....	102
The Study of (+)-limonene/triethylborane .....	104
3.3 Conclusions .....	113
3.4 Computational Procedures .....	113
Method Validation.....	113
Trajectory Details .....	115
Trajectory Error Analysis.....	116
The Effect of the Isopropenyl Group .....	117
CHAPTER IV MACHINE LEARNING TRANSITION STATE THEORY AND THE DESCENT OF TRAJECTORIES INTO CHAOS .....	119
4.1 Introduction .....	119
Starting at Transition State Theory .....	119
The Limitations of Molecular Dynamics as a Tool for Redeeming TST.....	120
Machine Learning Transition State Theory.....	121
4.2 The Dimerization of Cyclopentadiene .....	123
Introduction .....	123
Computational Results and Discussions.....	125
Computational Procedures .....	131

4.3 The Dissociation of Acetone Cation Radicals.....	133
Introduction .....	133
Computational Results and Discussion .....	138
Initial Trajectory Studies .....	139
Machine Learning Studies.....	143
Computational Procedures .....	147
4.4 The Diels-Alder Reaction of Vinylfuran and Cyclopentadienones .....	150
Introduction .....	150
Experimental Results and Discussion .....	152
Computational Results and Discussion .....	152
Experimental Procedures.....	154
CHAPTER V CONCLUSIONS.....	158
REFERENCES.....	161
APPENDIX A NMR SPECTRA.....	184
APPENDIX B CALCULATED STRUCTURES AND ENERGIES .....	198
APPENDIX C PROGRAMS FOR CALCULATIONS AND SAMPLE INPUT FILES .....	295

## LIST OF FIGURES

	Page
Figure 1 Reaction scheme for the generation and partitioning of diradical 2. ....	6
Figure 2 Computational KIE predictions for diazotization. ....	7
Figure 3 Archetypal recrossing on an idealized PES. ....	8
Figure 4 Reaction scheme for recrossing in the Bergman cyclization. ....	9
Figure 5 Transition states and intermediates for the mechanochemical ring-opening of ladderanes. ....	11
Figure 6 Product distribution from Bauld's stereochemical studies. ....	14
Figure 7 Mechanistic scheme for the Diels-Alder addition of ethylene or cation radical ethylene to cyclopentadiene. ....	15
Figure 8 Mechanistic hypothesis and solvent selection for studying the ring opening of 27. ....	21
Figure 9 Gas phase potential energy surface for the ring opening of 27. Re-printed with permission from "Prediction of Enhanced Solvent-Induced Enantioselectivity for a Ring Opening with a Bifurcating Reaction Path". Carpenter, B. K.; Harvey, J. N.; Glowacki, D. R. <i>Phys. Chem. Chem. Phys.</i> 2015, 17, 8372–8381. Published by the PCCP Owner Societies. <sup>33</sup> ....	22
Figure 10 Mechanistic scheme from Hammes-Schiffer. Re-printed with permission from "Nonadiabatic Dynamics of Photoinduced Proton-Coupled Electron Transfer in a Solvated Phenol–Amine Complex" by Goyal, P.; Schwerdtfeger, C. A.; Soudackov, A. V.; Hammes-Schiffer, S. <i>J. Phys. Chem. B.</i> 2015, 119, 2758–2768. Copyright 2014 American Chemical Society. <sup>38</sup> ....	26
Figure 11 The Markovnikov paradigm for hydrohalogenations. ....	30
Figure 12 The regiochemistry of the addition of hydrogen halides to conjugated dienes. ....	30
Figure 13 Nordlander's model for the regioselectivity of DCl additions to piperylene. ....	31
Figure 14 Reaction stereochemistry from Pocker <i>et al.</i> ....	32

Figure 15 Stereochemistry of hydrochlorination for cyclohexene from Fahey. ....	32
Figure 16 Fahey's proposed AdE3 mechanism. ....	33
Figure 17 A termolecular alternative to the AdE3 mechanism. ....	33
Figure 18 Experimental product distributions from previous and current work. ....	34
Figure 19 $^{13}\text{C}$ spectrum illustrating two disparate triplets belonging to 6/7. ....	35
Figure 20 Observed product ratio in addition of DCl to 1-methycyclopentene. ....	36
Figure 21 $^{13}\text{C}$ DEPT NMR indicating that the regiochemistry of addition to cyclopentene is not consistent with an AdE3 mechanism. ....	37
Figure 22 Experimental product ratios/synthetic protocol for preparing a stereochemistry standard. ....	37
Figure 23 Example $^{13}\text{C}$ spectrum of 2/3 with integration lines shown on critical triplet peaks. ....	39
Figure 24 Compiled product selectivity data for the hydrochlorination of <i>tert</i> - butylethylene. ....	40
Figure 25 $^1\text{H}$ NMR for a 11 + HCl reaction mixture after concentrating. Integration on the left is for the methine C-H on 12, integral on the right is for the 13 isopropyl methine C-H. ....	40
Figure 26 Product ratios from Brown <i>et al.</i> Equates to 58:42. ....	41
Figure 27 Inverse-gated decoupling $^{13}\text{C}$ NMR of the reaction mixture of DCl and norbornene in nitromethane. A 53:47 ratio of 12 to 13 was observed. ....	42
Figure 28 Inverse-gated decoupling $^{13}\text{C}$ NMR of the reaction mixture of DCl and norbornene in dichloromethane. A ~50.1:49.9 ratio of 12 to 13 was observed. ....	42
Figure 29 A demonstrative image of 1,3-pentadiene and HCl immersed in 120 nitromethane molecules. ....	45
Figure 30 The outcomes of several standard computational techniques in implicit solvent. Energies are given in kcal/mol. ....	47
Figure 31 PMF for the protonation of 1,3-pentadiene by $(\text{HCl})_2$ in nitromethane. ....	48
Figure 32 The survival curve for MP2 trajectories in explicit nitromethane solvent. ....	52

Figure 33 Plots of the average values for the incipient ion-pair stabilization parameter $E_{ip}$ versus time for trajectories with differing outcomes. For each trajectory, the $E_{ip}$ was only followed “forward in time”, defined as the direction in which the initial motion of the proton transfer was toward C <sub>1</sub> of the diene. ....	56
Figure 34 Plots of the incipient ion-pair stabilization parameter $E_{ip}$ versus time for individual productive trajectories. ....	59
Figure 35 QM/QM’ PMF for the approach of a chloride ion to either C <sub>2</sub> or C <sub>4</sub> of 4 <sup>+</sup> in explicit nitromethane. The energy scale is relative to a minimum on the surface at $1.85 \pm 0.025$ Å. ....	61
Figure 36 Decay of solvent-equilibrated ion-pairs, and an exponential fit. ....	62
Figure 37 Experimental results from Brown <i>et al.</i> ....	66
Figure 38 Reaction product of propene and brosic acid in trifluoroacetic acid. ....	67
Figure 39 The reaction of the <i>tert</i> -butylethylene with HCl in acetic acid shows formation of a secondary alkyl halide product. ....	69
Figure 40 Isotope scrambling experiments were evidence for Shiner’s concept of “hidden return”. ....	70
Figure 41 Correlation of energies calculated at test DFT MP2/6-31+G** levels versus DLPNO-CCSD(T)/aug-cc-pVTZ for solute points in a sample trajectory. ....	80
Figure 42 Correlation of energies calculated at test DFT M06-2X/6-31+G** levels versus DLPNO-CCSD(T)/aug-cc-pVTZ for solute points in a sample trajectory. ....	80
Figure 43 Correlation of energies calculated at test DFT M06-2X/6-31+G* levels versus DLPNO-CCSD(T)/aug-cc-pVTZ for solute points in a sample trajectory. ....	81
Figure 44 Expanded version of Figure 31 from the main text with no point selection at the edges. ....	86
Figure 45 Expanded version of Figure 31 from the main text with no point selection at the edges, viewed from a higher angle. ....	87
Figure 46 PMF for the addition of one HCl molecule to 1,3-pentadiene, using M06-2X/6-31+G* for the ONIOM high-level method. ....	88
Figure 47 Expanded PMF for Figure 35. ....	92

Figure 48 Analog of Figure 33 from the main text except using ~50% smaller atomic charges for the cationic atoms. ....	94
Figure 49 Histogram showing the range of initial $E_{ip}$ for reactive trajectories. ....	95
Figure 50 Even achiral molecules such as $\text{CH}_2\text{FCl}$ exhibit instantaneous chirality. Over the course of an asymmetric C-H stretch vibration, one C-H bond is short ( $H_s$ ) and another is long ( $H_L$ ), making these bonds connections inequivalent. This asymmetry exists on the femtosecond timescale, but at large time intervals converges to a time-averaged achiral form. ....	98
Figure 51 The proposed mechanism for the carboborative ring contraction reaction, starting at <i>trans</i> -cyclohexene. ....	100
Figure 52. The mechanistic scheme for the reaction of equatorial <i>trans</i> -(+)-limonene (8-eq) with triethylborane. Axial <i>trans</i> -(+)-limonene (8-ax) contributes to the observed product mixture and will be discussed later. ....	101
Figure 53 Stereochemistry of the photoinduced carboborative ring contraction of (+)-limonene. ....	102
Figure 54 The M11/6-31+G** MEP for the reaction of <i>trans</i> -cyclohexene with trimethylborane. ....	103
Figure 55 Lowest-energy calculated mechanism for the reaction of 8-eq with triethylborane. Relative free energies are shown in parentheses in kcal/mol. The energy for non-minimum 14 is based on when the $\text{C}_2\text{-C}_6$ distance is 1.6 Å. ....	105
Figure 56 Composite conformational motion as $13^\ddagger$ descends to 14 and 14 evolves with time. ....	109
Figure 57 Evolution of the average $\text{C}_1\text{-C}_2\text{-C}_6$ and $\text{C}_1\text{-C}_2\text{-C}_3$ angles in inversion and retention trajectories after formation of 14. ....	110
Figure 58 Kinetic energy in selected bonds and attached hydrogens versus time after initial formation of 14. ....	111
Figure 59 Time-smoothed plot of kinetic energy in selected bonds and attached hydrogens versus time after initial formation of 14. ....	112
Figure 60 Much like $\text{CH}_2\text{FCl}$ , ethylmethanamine is chiral as it the nitrogen has four unique substituents in its valence. The pyramidal inversion that interconverts the enantiomeric structures on the picosecond timescale, rendering ethylmethanamine achiral for most purposes. ....	112

Figure 61 Large screen of DFT methods against an <i>ab initio</i> standard across an MEP constructed with M06-2X. Red trace indicated standard. ....	114
Figure 62 Benchmark of the DFT method used for trajectories versus an <i>ab initio</i> standard.....	115
Figure 63 Experiments from the Larionov group show that the product ratio is not sensitive to replacement of the isopropenyl group with a methyl group. ....	117
Figure 64 Trajectory studies on 18 <sup>‡</sup> closely reproduced the experimental selectivity observed with 15. Shifting the methyl group to a remote position also does not affect the sense of stereoselectivity.....	118
Figure 65 The subdivision of the low-dimensional cross-section of the high-dimension hypersurface. ....	122
Figure 66 Experimental and predicted Newtonian KIEs from Kelly <i>et al.</i> Numbers in parentheses represent 95% confidence limits in the last digit. The intramolecular KIEs are defined as $k_{12c}/k_{13c}(a)/k_{12c}/k_{13c}(a')$ , $k_{12c}/k_{13c}(b)/k_{12c}/k_{13c}(b')$ . No noticeable KIE was seen in positions <i>b/b'</i> and <i>e/e'</i> . ....	125
Figure 67 MLTST KIE predictions, sorted by increasing KIE. Vertical bars indicate uncertainties at the 95% confidence interval as calculated by a standard error function.....	129
Figure 68 Displacement vectors for a 84 cm <sup>-1</sup> normal mode in 2 <sup>‡</sup> .....	130
Figure 69 Color coded representation pairing parameter number to descriptors of internuclear relationships along the three key bonds in 2 <sup>‡</sup> . ....	131
Figure 70 The mechanism of the conversion of acetone cation radical to acylium cations and methyl radicals proceeds via intramolecular HAT, followed by an uphill dissociation process. ....	134
Figure 71 Tureček's mechanistic proposal invokes unselective side-reactions to rationalize the monotonic energy trend from experiments. ....	135
Figure 72 Experimental branching ratios from Brauman (left) and Tureček(right). Left figure re-printed with permission from "Infrared Multiple-Photon Dissociation of the Acetone Enol Radical Cation. Dependence of Nonstatistical Dissociation on Internal Energy" by Osterheld, T.H.; Brauman, J.I. <i>J. Amer. Chem. Soc.</i> 1993, 115, 10311-10316. <sup>168</sup> Copyright 1993 American Chemical Society. Right figure re-printed with permission from "Loss of Methyl from [H <sub>2</sub> C=C(OH)-CH <sub>3</sub> ] <sup>+</sup> Ions Prepared by Electron Impact Ionization of Unstable 2-Hydroxypropene"	



by Tureček, F.; Hanuš, V. <i>Org. Mass. Spectrum.</i> 1984, 19, 631-638. <sup>166</sup> Copyright 1984 Wiley Heyden Ltd. ....	136
Figure 73 Energies are B2PLYP/6-31+G** potential energies given in kcal/mol. ....	138
Figure 74 Energies are B2PLYP/6-31+G** potential energies given in kcal/mol. ....	139
Figure 75 The time-evolution of C-C bond lengths in classical trajectories that reach the 1000 fs time constraint. ....	141
Figure 76 MLTST prediction of energy-dependent dissociation selectivity. Error bars calculated at 99% confidence interval. ....	144
Figure 77 Kinetic scenario invoked for RRKM corrections .....	145
Figure 78 Two TS structures for the 1,3-isomerization in the enol. ....	145
Figure 79 MLTST prediction of energy-dependent dissociation selectivity after inclusion of RRKM corrections. Error bars calculated at 99% confidence interval.....	146
Figure 80 A screen of numerous DFT methods against CCSD(T)/aug-CC-pVTZ. Vertical axis units are in kcal/mol. ....	148
Figure 81 Benchmark of B2PLYP/6-31+G* against CCSD(T)/aug-CC-pVTZ. Axis units are in kcal/mol. ....	148
Figure 82 Benchmark of B2PLYP/6-31+G** against CCSD(T)/aug-CC-pVTZ. Axis units are in kcal/mol. ....	149
Figure 83 Mechanistic scheme for Harmata's reaction of 12 and 13.....	151
Figure 84 Time-lapsed (6-days) inverse-gated decoupling <sup>13</sup> C NMR spectra show that the equilibration of 1,2- and 1,4- products takes place at a low rate. This reaction was quenched with acetone enol ether prior to analysis.....	184
Figure 85 Inverse-gated decoupling <sup>13</sup> C NMR for peak assignment. Crude cyclopentene deuteriochlorination reaction mixture (top) and the same mixture doped with authentic <i>syn</i> -1-chloro-2-d <sub>1</sub> -cyclopentane (bottom).....	185
Figure 86 Inverse-gated decoupling <sup>13</sup> C NMR for peak assignment. Crude cyclopentene deuteriochlorination reaction mixture (bottom) and the same mixture doped with authentic <i>trans</i> -1-acetoxy-2-d <sub>1</sub> -cyclopentane (top).....	186
Figure 87 <sup>1</sup> H NMR of <i>syn</i> -2-d <sub>1</sub> -cyclopentanol in CDCl <sub>3</sub> . ....	187

Figure 88 $^1\text{H}$ NMR of synthetic cyclopentan-2- <i>d</i> -ol acetate.....	188
Figure 89 $^{13}\text{C}$ NMR of synthetic cyclopentan-2- <i>d</i> -ol acetate.....	189
Figure 90 $^1\text{H}$ NMR of <i>trans</i> -1-toluenesulfonyl-2- $\text{d}_1$ -cyclopentane in $\text{CDCl}_3$ .....	190
Figure 91 $^1\text{H}$ NMR of <i>syn</i> -1-chloro-2- $\text{d}_1$ -cyclopentane in $\text{CDCl}_3$ . Contains pentane impurities.....	191
Figure 92 Spectral peak assignments in $\text{d}_6$ -benzene .....	192
Figure 93 $^1\text{H}$ spectra in benzene showing that the as the reaction in toluene at 60 °C progresses, the ratio of products does not change appreciably. Spectrum timepoint 3 spectrum is mistitled. These measurements were made 16 hours apart.....	193
Figure 94 $^1\text{H}$ NMR in benzene of 12 + 13 reaction at 23 °C in benzene and tabulated integrations for this sample.....	194
Figure 95 $^1\text{H}$ NMR in benzene of 12 + 13 reaction at 60 °C in benzene tabulated integrations for this sample.....	194
Figure 96 $^1\text{H}$ NMR in benzene of 12 + 13 reaction at -20 °C in toluene and tabulated integrations for this sample.....	195
Figure 97 $^1\text{H}$ NMR in benzene of a reaction running in toluene at 23 °C. Some of shown integrals were determined to be reliable for use in quantifying product ratios. ....	196
Figure 98 $^1\text{H}$ NMR in benzene of a reaction running in toluene at 60 °C. Some of shown integrals were determined to be reliable for use in quantifying product ratios. ....	197

## LIST OF TABLES

	Page
Table 1 Results from Essafi <i>et al</i> and structures of glucose and paniculatine solutes investigated in that study. ....	18
Table 2 Trajectory outcomes for ONIOM simulations in explicit solvent. ....	51
Table 3 Trajectory outcomes for a selection of initialization geometries in implicit solvent.....	82
Table 4 Trajectory outcomes for a comprehensive selection of initialization geometries in implicit solvent.....	84
Table 5 ONIOM trajectory productivity as a function of internal C-H coordinate selection. ....	96
Table 6 ONIOM trajectory productivity as a function of internal C-H coordinate selection. Truncated range of C-H values.....	96
Table 7 ONIOM trajectory productivity as a function of internal C-Cl coordinate selection. ....	97
Table 8 Final trajectory results and comparison with experimental observations from the Larionov group.....	107
Table 9 Trajectory outcomes for standard QCTs initiated at 298 K. ....	126
Table 10 Trajectory outcomes for anharmonicity-corrected QCTs initiated at 298 K. ....	126
Table 11 Trajectory outcomes for anharmonicity-corrected QCTs initiated 298 K. These trajectories are spawned with <sup>14</sup> C at the 10 <sup>th</sup> atomic position, <i>a</i> . ....	126
Table 12 Groundhog trajectory outcomes for <sup>14</sup> C-labeled QCTs at 298 K.....	128
Table 13 Force constants and anharmonic corrections for 2 <sup>‡</sup> .....	131
Table 14 Results from the first runs of reactive trajectories. ....	140
Table 15 Results of investigation of energy/selectivity relationship in classical trajectories.....	142
Table 16 Results of investigation of energy/selectivity relationship in QCTs.....	143

Table 17 Benchmark energetics for stationary points in the conversion of acetone (enol) cation radical to separated fragments. Energies are potential energies in kcal/mol.....	147
Table 18 Force constants and anharmonic corrections for 5 <sup>‡</sup> .....	150
Table 19 Experimental ratios of 15:16 from 1H NMR measurements. ....	152
Table 20 Outcomes and MLTST and accuracy benchmarks for gas phase QCTs at 25 °C. ....	153
Table 21 15:16 ratios from MLTST predictions. ....	153
Table 22 Collected MP2 and M06-2X raw energies.....	198
Table 23 Selected MP2 and M06-2X relative energies (kcal/mol).....	199
Table 24 DLPNO/aug-cc-pVTZ derived energies. ....	200

# CHAPTER I

## INTRODUCTION

### **1.1 Chemical Models**

Dating back its origins in alchemy, a central focus of chemistry has been the transformation of chemical compounds. To understand and control these transformations, early practitioners assembled a body of principles and strategies to guide their experiments. This collection of rules and heuristics is known as a paradigm. The earliest paradigms were simple and shrouded in symbolism, ritual and superstition, e.g., the classical elements of earth, wind, fire, and water. The need for explanations of observations and for testable hypotheses however led to progressively more complex ideas. The iterative process of development, extinction, and adaptation of axioms ushered in new ideas and technological breakthroughs that further feed back into the evolutionary process. Crucial to this process is failure. Schools of thought become obsolete when their models continually fail to rationalize observations or anticipate experimental outcomes. Although modern chemistry is a far cry from the incantations and elixirs of antiquity, its conceptual frameworks and constituent models are still not able to account for all observations. This introduction will briefly discuss the predominant approach for understanding chemical reactions, the reaction mechanism, an associated model, transition state theory, and a collection of chemical phenomena, dynamic effects, that challenge both.

### **1.2 Transition State Theory**

Chemists understand reactions from their mechanism. A mechanism is generally viewed as the sequence of transition states (TS) and intermediates that a reactant must

proceed through as it transforms into the product. These ‘thin’ mechanisms, focused on critical points, are routinely assumed to be sufficient to account for the observations in reactions. Although chemists are taught first about the intermediates in mechanisms, the transition state is an equal partner. The transition state, especially, is used as a conceptual tool in order to understand reactivity trends and tune reaction outcomes.

The theoretical framework for the importance of transition states is Eyring’s transition state theory (TST). TST predicts the absolute rates of reactions from a formal free energy barrier  $\Delta G^\ddagger$  (eq 1).

$$k = \kappa \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}} \quad (\text{eq 1})$$

This model facilitates an intuitive understanding of chemical reactions, as ground-state stereoelectronic, steric, and electrostatic concepts can be applied to the transition state in order to make qualitative predictions about the free energy cost, and by extension, the reaction rate. Using TST is therefore operationally simple, but that simplicity arises from a series of assumptions and approximations.

TST requires knowledge of a reaction’s potential energy surface, a multidimensional topology that connects a molecule’s atomic configuration to an energy value. Such surfaces exist within the Born-Oppenheimer approximation, that is, the surface is valid assuming that the electron wavefunction is separable from the nuclear wavefunction. TST then assumes that the energy of a reacting system at a critical point is statistically distributed. Additionally, TST assumes that all degrees of freedom in the reactant(s) are orthogonal. In solution, this would apply to solvent, and the solvent is assumed to be at equilibrium with respect to the solvent at every geometry. TST models reactions as irreversible equilibria with no recrossing of molecules

traversing the TS. As a quasiclassical model, TST also neglects rate acceleration from quantum mechanical tunneling (QMT).

These assumptions and approximations can fail, requiring adjustments to TST. Nonadiabatic TST (NTST) is an adaptation to handle reactions on excited state surfaces. In NTST, the time course of chemical reaction is reliant not on the TS, but on the crossing between diabatic surfaces that takes place at minimum energy crossing points (MECP) at a shared seam of the surfaces. Theoretical consideration of the MECP's geometric configuration, potential energy, and vibronic coupling permits the calculation of transition probabilities by extension, the rate of a chemical reaction that proceeds through nonadiabatic transitions.

The free energy difference used in the Eyring equation is determined at a TS structure that is a first-order saddle point on the potential energy surface (PES). Recrossing is the traversal of a system through the TS and then back to starting material. This occurs when the barrier on the free energy surface (FES) is higher than the barrier on the PES. As a result, the rates in reactions that recross are then lower than those predicted from TST. Working contemporaneously with Eyring, Wigner devised a pre-exponential recrossing factor,  $\gamma$ , in order to scale TST rate predictions to allow for recrossing. The modern formulation of Eyring's theory, variational transition state theory (VTST) takes a different approach to addressing recrossing. VTST variationally optimizes the position of the TS to minimize the rate constant, effectively measuring the reaction barrier at the free energy maximum. This remedies the mismatch of surfaces and accounts for the rate diminution from statistical recrossing. VTST also makes use of QMT calculations in order to scale reaction rates by the amount of tunneling present at a given temperature.

Rice-Ramsperger-Kassel-Marcus theory (RRKM) is a theory developed to understand the reactivity of molecules that are vibrationally-excited and whose energy distribution deviates

from a Boltzmann distribution. This aids in modeling the kinetics of a thermally or photochemically excited species traversing a TS, however RRKM also makes a series of assumptions that limit its applicability. In RRKM, the collisional excitation and de-excitation, intramolecular vibrational distribution processes are assumed to be much faster than any barrier-crossing process. These assumptions are valid for an excited molecule that decomposes slowly, however, these assumptions are not appropriate for an excited molecule that crosses barriers quickly. And even less appropriate for molecules crossing multiple barriers in rapid succession. In these cases, there is insufficient time for the molecule's kinetic energy to equilibrate to a statistical distribution, and so local excitation of degrees of freedom may influence the rate and ratio of product formation.

The simplicity and generality of TST have made it a uniquely privileged and ubiquitous model whose application spans incongruous areas in chemistry such as mechanistic enzymology, heterogeneous catalysis, total synthesis, and even astrochemistry. Despite this, there exist numerous qualitative failures of TST and the study of these cases will illustrate that 1) these failures become more frequent when one starts to look for them 2) these failures occur for even the most basic reactions 3) adequate simulation of these systems demands techniques not typically employed or developed in physical organic chemistry 4) a successful study ultimately provides an intuitive explanation for results and begins framing the next series of questions and hypotheses.

### **1.3 Dynamic Effects**

Dynamic effects are broadly defined as phenomena that cannot be well described with statistical treatments like TST and its associated models. Dynamic effects appear when the system in question violates the assumptions of TST. This chapter will provide a modern



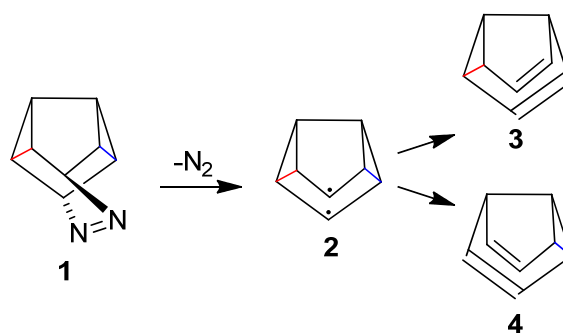
overview of dynamic effects, the conditions under which they arise, and the models constructed in order to understand them.

### *Bifurcating Surfaces*

Early studies of dynamic effects focused on the theoretical simulation of so-called “thick mechanisms” taking place on bifurcating surfaces. In contrast with “thin mechanisms” focused on the identity and energies of critical points along the PES, thick mechanisms describe the reaction’s motion along the contours of the PES, not unlike a motion picture. A bifurcating PES is a reaction pathway that forks into two paths, and with some exceptions, most of these branching points took place at or after the rate-limiting TS. In the new millennium, studies from the Singleton group provided much-needed experimental and computational studies to assess the impact of dynamic effects on experimental observations and develop a conceptual framework for understanding their role in organic chemistry.<sup>1-7</sup> With the initial groundwork laid, the field of dynamic effects blossomed quickly with publications from Houk<sup>8-12</sup>, Tantillo<sup>13-15</sup>, and others<sup>16-19</sup>. While the Singleton group has contributed extensively to this area, this review will focus on recent contributions from other groups.

A recent example of dynamics on a bifurcating surface was published by Mandal *et al.*<sup>20</sup> The authors theoretically modeled a deazetization reaction that leads to two degenerate semibullvalene products (Figure 1).<sup>20</sup> The TS for N<sub>2</sub> expulsion is a synchronous, concerted structure that should lead to a diradical intermediate. This intermediate then travels along a symmetric bifurcating PES falling into either identical bond-rearranged product well. As is often the case, the authors’ study of the minimum energy path offered little insight into the underlying issue of dynamics. An intrinsic reaction coordinate (IRC) calculation follows the

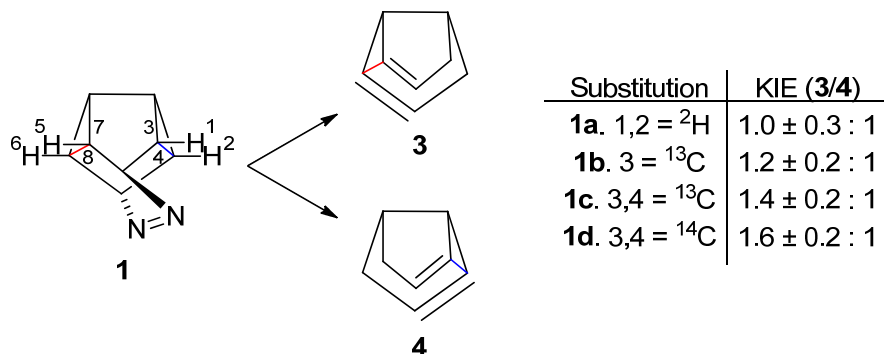
PES straight down the middle, depicting a pathway that starts at the reactant state (0.0 kcal/mol), proceeds through the concerted N<sub>2</sub> extrusion transition state (+12.5kcal/mol), passes a valley-ridge inflection point (+6.8 kcal/mol) and arrives at the submerged transition state for the Cope rearrangement of the products (-41.6 kcal/mol). Any substitution of the starting material breaks the symmetry of the surface and results in an MEP that bypasses the valley-ridge inflection (VRI) and arrives directly at the thermodynamically favored of the two products, suggesting that thermodynamically unfavored products arise solely from Cope rearrangement of the products. To mitigate this failure in TST, quasiclassical trajectory (QCT) molecular dynamics simulations were initiated at the TS for C-N bond cleavage. QCTs are not obligated to follow the minimum energy path and so allow for an analysis of the bifurcating nature of the PES. Their limited run of QCT trajectories gives a 1.03 (±0.32):1 mixture of **3** and **4**, reflecting the expectation from experiments. Because of the bifurcation of the PES, the N<sub>2</sub> extrusion TS can then be classified as then *ambimodal*, capable of forming both products.



**Figure 1** Reaction scheme for the generation and partitioning of diradical **2**.

The authors next probed the effect of isotopic substitution on the bifurcating energy surface. Performing trajectories at 300 K with isotopic substitution at key positions, the

authors were able to predict intramolecular KIEs. Because the product-determining step occurred after the TS, the KIEs did not report on isotopic fractionation occurring at the TS, but rather, these *Newtonian* KIEs (Figure 2) reflect the effect of de-symmetrizing the PES in mass-weighted coordinates.



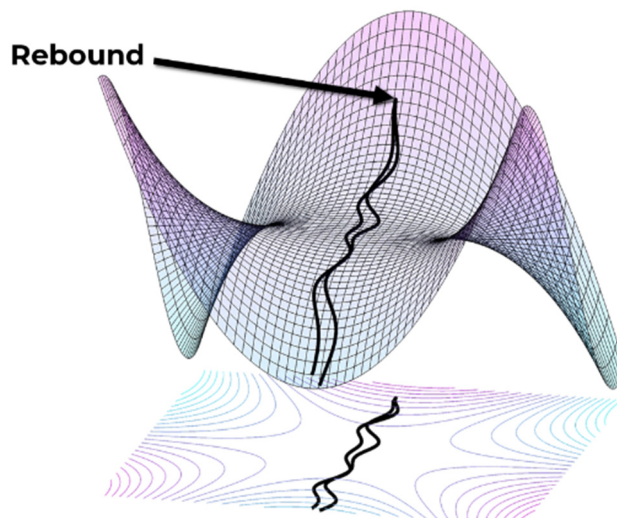
**Figure 2** Computational KIE predictions for diazotization.

The authors interpret the unity KIE for **1a** as arising from the “distal position” of the isotopic substitution, but given the uncertainty, a deeper analysis is not reasonable. For **1b-d**, the trajectories show that bond breaking occurs more frequently on the more side with greater mass. This selectivity is explained as a consequence of the heavier side having the higher gradient on the steepest-descent path in mass-weighted coordinates.

#### *Nonstatistical Energies and Recrossing*

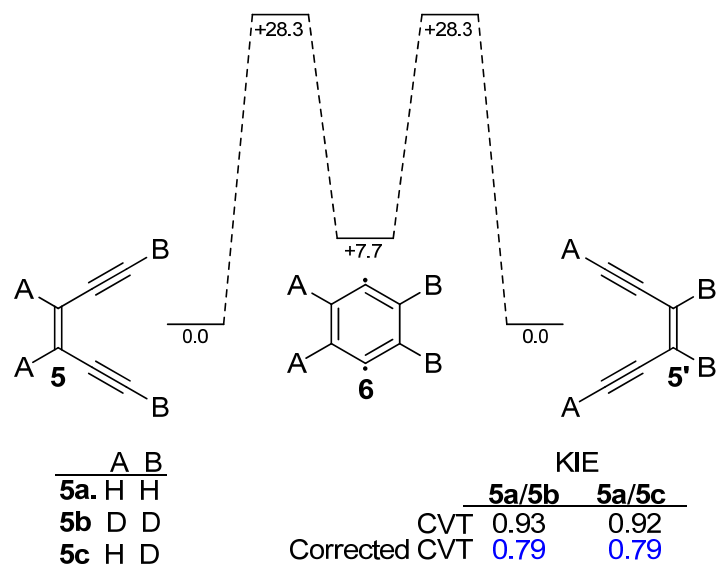
Non-statistical recrossing is a phenomenon in which a trajectory will pass through the TS and rebound off of an obstruction on the surface (Figure 3). This behavior is commonly encountered in the trajectory study of reactions with bifurcating surfaces and/or intermediates on flat regions of the PES. An additional factor that induces recrossing in trajectories is the initiation of trajectories at a point on the PES that does not correlate to the TS on the FES. VTST corrects for this by variationally optimizing the TS to give a

structure that minimizes recrossing, however the effects of non-statistical recrossing cannot be predicted quantitatively with a statistical apparatus like VTST.



**Figure 3** Archetypal recrossing on an idealized PES.

Doubleday *et al*<sup>21</sup> published a theoretical study outlining how nonstatistical recrossing can significantly impact the H/D KIEs in Bergman cyclizations. The reaction of **5** faces a 28.3 kcal/mol enthalpic barrier to form p-benzyne **6**. The newly formed **6** is metastable on the PES, but it is imbued with 20.6 kcal/mol excess thermal energy from the TS, allowing **6** to recross back to **5** or undergo a second barriered reaction to **5'**. Doubleday used the TS for conversion of **5** to **6** to conduct QCT studies at 470 K for three isotopologs of **5** and found that recrossing was sensitive to isotopic substitution.



**Figure 4** Reaction scheme for recrossing in the Bergman cyclization.

Monitoring the decay of **6a** over time, trajectories leaving the TS terminated rapidly by recrossing to **5a** or **5'a**. Exponential fitting of the decay curve to the infinite time asymptote gave an predicted transmission coefficient of 0.68. **6b** and **6c** decayed by recrossing more gradually, giving extrapolated transmission coefficients of 0.84 and 0.82, respectively. In all three cases, recrossing to **5** predominated over recrossing to **5'**. The authors hypothesized that the excess energy was likely localized in the nascent C-C bonds and caused large amplitude C-C motions that facilitated cycloreversion. An extension of this hypothesis was that isotopic substitution influences the rate of energy dissipation from the new C-C bonds.

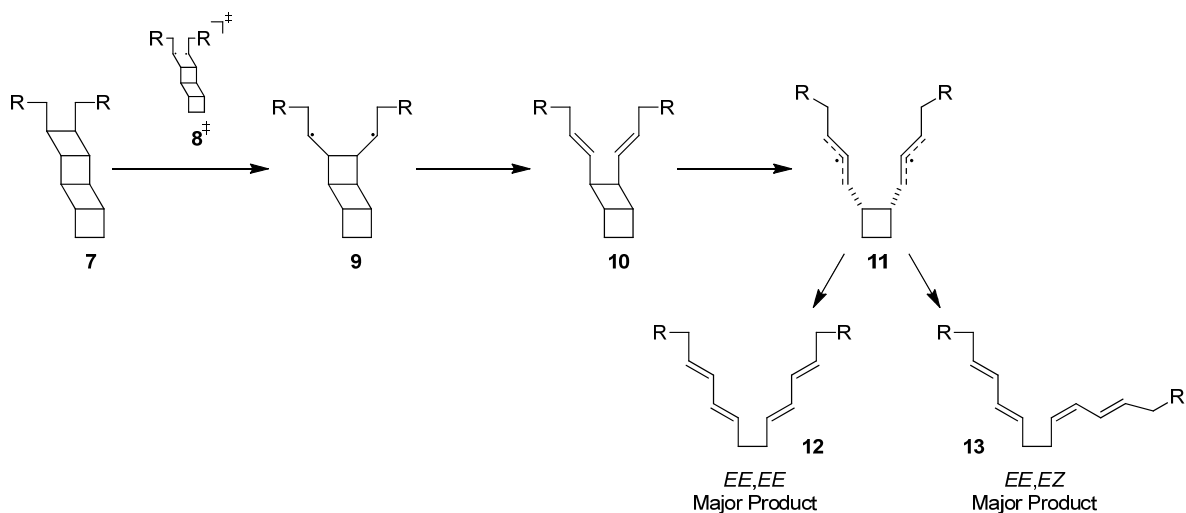
Analysis of vibrational energies in trajectories supported this idea. For **5a**, kinetic energy in symmetric and asymmetric C-C stretching modes remained roughly constant for over 1200 fs. For **5b**, this kinetic energy was rapidly redistributed into C-D stretching and bending motions. The authors interpreted this as a form of Fermi resonance where the

redshifting of the C-H stretch frequency induced by isotopic substitution, aligned the C-H frequency to an overtone of a C-C stretching frequency, increasing energy transfer via vibrational coupling.

The authors also observed that a small proportion of **6** molecules in each system recrossed to **5** and then recrossed again to form **6**. The authors built a kinetic model that predicted the transmission coefficient corrected for single and multiple recrossings. From the model, predicted ratios of transmission coefficients of 0.857 were calculated for both **5a/5b** and **5a/5c**. Canonical variation transition state theory (CVT) was used to calculate the transmission coefficient for each system, giving ratios of transmission coefficients of 0.93 and 0.92, for **5a/5b** and **5a/5c**, respectively. The CVT ratios were interpreted as KIE predictions that accounted for zero-point energy effects in the TS and for statistical recrossing. The clear mismatch of the two sets of ratios indicated that nonstatistical recrossing was occurring to a considerable extent. The two ratios for each system could then be multiplied to give an overall KIE prediction that accounted for statistical isotope effects from TST and Newtonian KIEs isotope effects from trajectories (given in blue in Figure 4). Acknowledging that long QCT simulations were subject to spurious results from ZPE leakage, the authors performed additional simulations with 25% less ZPE in C-H/C-D stretches to find that the final predictions remained unchanged. The authors conclude that unpublished preliminary studies on other Bergman cyclizations suggest that similar nonstatistical behavior.

More recently, mechanochemistry has opened an interesting new avenue of research of dynamic effects. Chen *et al*<sup>22</sup> describes a force-induced reaction cascade in polymer-

grafted ladderanes/enes (Figure 5). The application of tensile strain across the extended bicyclic system was expected to induce two sequential cycloreversions.



**Figure 5** Transition states and intermediates for the mechanochemical ring-opening of ladderanes.

This was indeed the case and the reaction afforded a mixture of alkenes. The experimental product ratios of 79 : 21 for **12** and **13** did not appear to change over the course of the reaction or change in response to varying the reaction temperature. These factors in addition to the absence of the single cycloreversion species in their spectroscopic observations suggested to the authors that the two cycloreversion were dynamically linked and that the intermediate was bypassed.

The authors studied this reaction with MD trajectories that featured varying mechanical forces on the polymer linkages. In MD trajectories from **7**, it became clear that no reaction occurred at <2.9nN of mechanical tension. Trajectories initiated at **8<sup>‡</sup>** exhibited biexponential decay behavior. The rate of the slower process from biexponential fit matched with the monoexponential decay of trajectories initiated at **9**, while the faster process

appeared to be an order of magnitude faster. The slow process was attributed to the decay of the  $\mathbf{8}^\ddagger$  to an equilibrated  $\mathbf{9}$  that slowly underwent the second cycloreversion. The fast process was attributed to a pathway where the residual exotherm from  $\mathbf{8}^\ddagger$  was efficiently transduced into parallel C-C bonds and accelerated the second cycloreversion step, a hallmark dynamic effect referred to as dynamic-matching. In a systematic study of mechanical activation, the dynamic matching pathway appeared to be significantly more sensitive to increased mechanical stress. The trajectories correctly predicted the major product of the first cycloreversion, but the limited dataset did not allow a reliable analysis. The authors claimed that complete *E* stereoselectivity in the first cycloreversion is imparted by the dynamic effect, while stereoselectivity in the second cycloreversion varied little between trajectories initiated at  $\mathbf{8}^\ddagger$  and  $\mathbf{9}$ . Analysis of the MEP under different mechanical stress regimes gave insight to the fundamental changes imparted by external forces. Increasing forces dramatically changes the surface by increasing the reaction exothermicity and flattening topographic features. At 0-2 nN external force, the surface exhibits a caldera at the region of  $\mathbf{11}$  with low (<3 kcal/mol) barriers along the exit channels to products, however the energetics of the barriers are inverted relative to experimental observations. At forces near 3 nN, the surface morphs into a steeply sloped terrain with no barriers after  $\mathbf{8}^\ddagger$ . Dynamics on this surface recovered the experimental product ratio within error. Finally, the authors used logistic regression to delineate the boundary line between the two product regions with a linear combination of torsional angles and velocities during the first C-C bond scission.



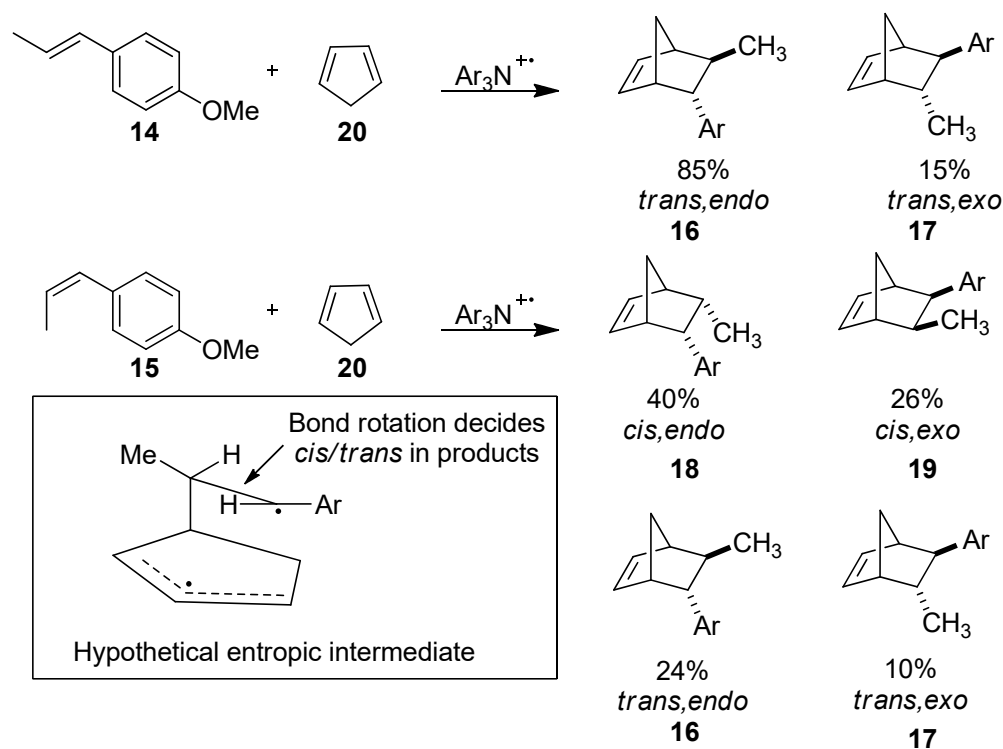
### *Entropic Intermediates*

Entropic intermediates are metastable structures on a FES, but not so on the PES. Put another way, an entropic intermediate is a species that is expected to quickly collapse to another bound state, except that those transformations are barred by an entropic penalty. In Wigner's parlance, the phase space of newly formed intermediate is relatively large and the phase space of each exit channel is sufficiently small that from a statistical standpoint, it is not likely as expected that a trajectory crossing the TS can "thread the needle" (dynamic matching) and proceed directly to the product. The narrowest volumes of phase space are also called "dynamical bottlenecks". Gonzalez-James *et al*<sup>23</sup> first articulated the experimental implications of entropic intermediates in the cycloaddition of dichloroketene to 2-butene. In that case study, the phase space is such that fast-moving trajectories crossing the TS down the center proceed through VRI, and as the first C-C bond continues to contract, climb an energetic barrier that re-directs the momenta backwards towards starting material (nonstatistical recrossing). Trajectories passing the TS symmetrically with low momentum do not ricochet so violently and so once they arrive at the VRI, they sample the available phase space in the region for extended periods of time before proceeding to a PES minimum.

In recent years, the literature has elucidated that bond changes in Diels-Alder reactions are not always concerted as postulated in the Woodward-Hoffmann rules. Reports suggest that these reactions can take place via two sequential steps if the single bond adduct is relatively stable, or alternatively, if the concerted pathway is kinetically unfeasible. The existence of these two pathways has implications for the stereochemistry of Diels-Alder reactions. When both new bonds are made simultaneously, the stereochemistry of the reactants is relayed into the products, that is, the reaction is stereospecific. However,

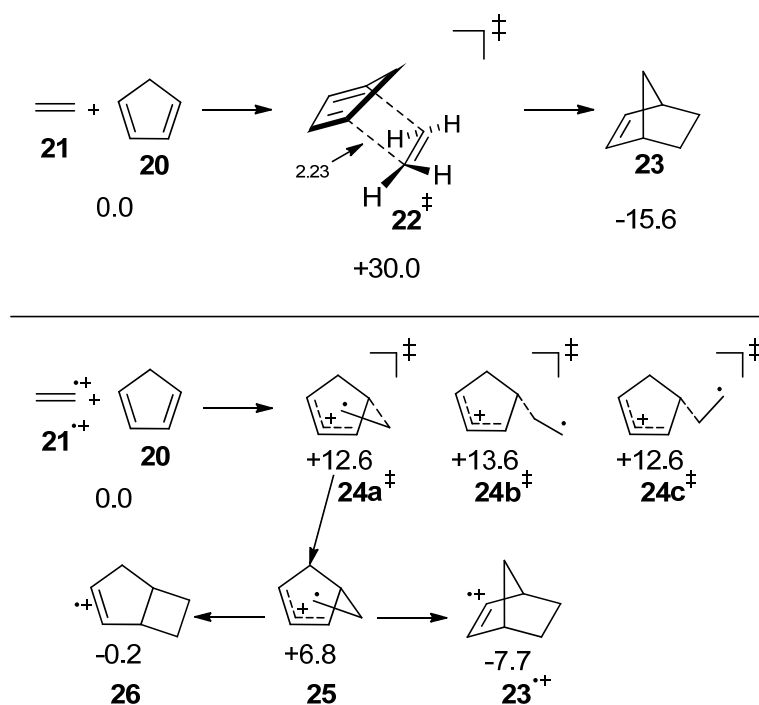
stepwise mechanisms with long-lived intermediates may be subject to a loss of stereochemical information as the intermediates can sample conformational space before forming the second bond.

Recently Tan *et al*<sup>24</sup> performed a theoretical study to understand the lack of stereospecificity in some radical cation Diels-Alder reactions studied by Bauld in the 1990's (Figure 6).<sup>25,26</sup> The authors state prior dynamic effects studies to support a claim that even when calculated TS structures show a favorable concerted bond formation, synchronicity in the two bond formations is not guaranteed. As reported elsewhere, the existence of an entropic intermediates blurs the lines between the extreme concerted and extreme stepwise mechanisms and impacts product selectivity.



**Figure 6** Product distribution from Bauld's stereochemical studies.

To test their hypothesis, the authors truncated the system significantly to the addition of ethylene to cyclopentadiene. In studying the reaction of neutral ethylene and cyclopentadiene at the SMD(DCM)-M06-2X/6-31G\* level of theory, the authors could only locate a TS for concerted bond-formation with a free energy of 22.3 kcal/mol from the encounter complex (29.9 kcal/mol from separate reactants). The addition of radical cation ethylene to cyclopentadiene was found to proceed by three conformers of a single bond formation TS.



**Figure 7** Mechanistic scheme for the Diels-Alder addition of ethylene or cation radical ethylene to cyclopentadiene.

Analysis of the flat PES region between intermediate **25** and product **23<sup>•+</sup>** did not reveal a second TS for the second bond formation. The authors note that the **25** can also give product

**26**, albeit through a TS 2.2 kcal/mol uphill from **25**. In order to understand the decay of **25** into product, the authors conducted QCT studies on the SMD-M06-2X surface using the ProgDyn software with a timestep of 2.5 fs

Of 150 trajectories of the neutral system initiated at **24a**<sup>‡</sup>, 142 completed the Diels-Alder reaction within ~50 fs with an average time gap between bond formations of ~2fs. The remaining trajectories recrossed to a loose reactive complex. Of 150 trajectories of the cation radical system, 110 led to the Diels-Alder product and 40 recrossed. The authors observed that four of the product forming trajectories “roamed” for >1000fs. Although unmentioned in the text, QCTs suffer from the phenomenon known as ZPE-leakage after 500 fs. The product forming trajectories completed after 200-2700 fs with average duration of ~365 fs and gap of 167 fs between bond formations. The authors observed bond rotations that would scramble stereochemistry, but only in trajectories that last well beyond the onset of ZPE-leakage. On the basis of trajectory durations and bond formation time gaps, the authors concluded that **25** was an entropic intermediate and that the two C-C bonds were formed in “dynamically stepwise” fashion. The authors’ classification of **25** as an entropic intermediate appears unusual as the species **25** was calculated as a traditional PES intermediate by the authors prior to their QCT studies.

#### *Dynamic Effects in Solvation*

The study of solvent effects in organic chemistry is typically concerned with the effects of solvent properties on the efficiency and selectivity of reactions. Equilibrium properties such as dielectric strength, hydrogen-bonding capability, and viscosity are traditional parameters for screening conditions for organic reactions. From a physical organic chemistry perspective, a reaction’s sensitivity to the parameters can be leveraged as

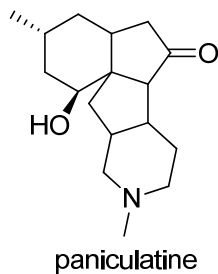
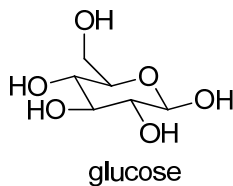
a point of mechanistic inquiry, e.g. distinct mechanisms have different TSs and intermediates that may have differing sensitivity to solvent properties. Marcus theory is a statistical rate theory designed to predict the rates of electron transfers in solution and frames the solvent reorganization as a phenomenon that modulates barrier-heights. More recently, the idea that solvent behavior in the midst of a mechanism need not mimic its equilibrium behavior has appeared in the literature and a handful of studies have suggested that this unusual solvent behavior has significant explanatory power in the interpretation of experimental observations.

It is understood that excess energy in reactive intermediates can have consequences for reaction outcomes, and this behavior falls under the umbrella term “dynamic effects”. Most dynamic effects studies are conducted in the gas phase or with an implicit solvent model, and the origins of these dynamic effects are slowly becoming known. What is relatively less understood is how the solvent impacts the energy content of these intermediates. Currently, the normal assumptions for solution phase reactions are similar to those made in RRKM, that is chemical steps are slow relative to other mechanistic steps such that intermediates in solution are thermally equilibrated and the solvent is organized to match the polarity of intermediates. This approach simplifies the conception of reaction mechanisms in solution and is often sufficient to establish a mechanistic model for reactions. Studies in this area are relatively few due to the computational and conceptual difficulties with considering solvent motion on equal footing with solute motion, but both classic and modern studies have demonstrated that these considerations must be made to understand some simple, even unremarkable, systems.

In order to study the effect of solvation on vibrationally excited solute, Essafi *et al*<sup>27</sup> performed a suite of explicit solvent MD studies at the semi-empirical level of theory. The authors simulated a variety of solutes immersed in a bath of solvent molecules in a periodic boundary box. The boxes were subjected to NVT equilibration followed by production runs as an NVE ensemble. The transfer of energy during MD runs between the solvent and solute was probed through the continuous calculation of the solute internal energy. The time-dependent deviation of solute internal energy from initial conditions was used to calculate a decorrelation time. The decorrelation times and the variances of internal energy (Table 1) permit analysis, although care should be taken in interpreting the results as the simulations utilize the harmonic approximation.

**Table 1** Results from Essafi *et al* and structures of glucose and paniculatine solutes investigated in that study.

Solute	Solvent	Decorrelation time $\tau$ /ps	$\sigma(E)$ /kcal mol <sup>-1</sup>
Ethanol	Ethanol	6.9	2.8
DMSO	DMSO	7.0	2.9
THF	THF	12.1	3.4
d <sub>8</sub> -THF	d <sub>8</sub> -THF	17.8	3.4
n-Pentane	n-Pentane	13.6	4.0
DCM	DCM	74.6	1.9
Glucose	THF	11.0	5.0
Paniculatine	THF	18.7	6.7
THF	DCM	40.4	3.6
THF	Supercritical Ar	238.4	3.3



In pure solvent systems, decorrelation times are quite short. The authors agree with existing literature that energy transfer is facilitated by resonance of vibrational modes between energy acceptors and donors. This energy transfer is especially efficient in pure solvent systems, where the vibrational modes of the donor-accepter pair are identical. This same effect was expected to lead to a shorter decorrelation time in THF than the one shown, so the authors remarked that this effect must not be a major contributor. The decorrelation in ethanol and DMSO is further expedited by intermolecular hydrogen bonding that provides an electrostatic impetus for solvent molecules to collide. The authors do not comment on the small change in decorrelation for pure  $d_8$ -THF, but one possibility is that isotopic substitution stiffens the harmonic potential for the C-D bonds and redshifts their oscillation frequency. This may reduce the vibrational overlap between C-D bonds with other normal mode, reducing efficiency of intermolecular energy transfer and intramolecular vibrational distribution (IVR). The behavior of non-polar n-pentane appears similar to that of polar solvent THF, but this similarity was not investigated. DCM was also not discussed.

In mixed systems, the results do not vary significantly. In discussing glucose and paniculatine, the authors state that these similarities indicate that vibrational relaxation does not depend on the size of the solute and that difference in decorrelation times mirrors the differing hydrogen-bonding capabilities of the solute. The slower relaxation of THF in DCM is again explained with vibrational resonance arguments. Lastly, the vibrational relaxation of THF in supercritical argon is extremely slow due to the lack of resonance between THF and argon normal modes. The authors conclude by stating that chemical steps that occur faster than these decorrelation times, such as ozonolysis,<sup>28</sup> may exhibit non-statistical

dynamic effects. An interesting addition to the study would be to study the relationship between solute temperature and decorrelation time in solvent.

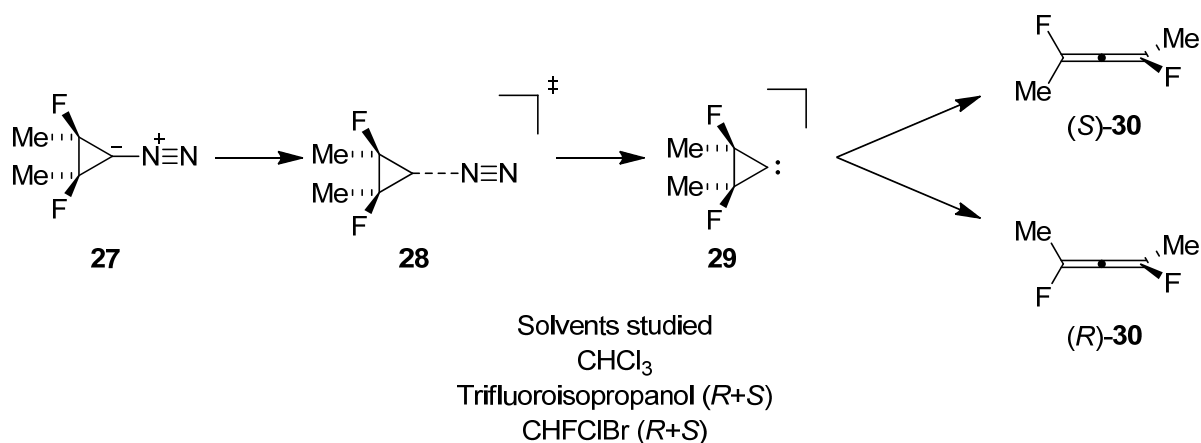
North and Hase have also studied the influence of solvent on the relaxation of vibrationally excited molecules.<sup>29</sup> In the case of 148 kcal/mol excited benzene immersed in a N<sub>2</sub>/benzene bath at 1 atm, it was observed that relaxation occurred by primarily by vibration-vibration resonance and that even after 2 ns excited (apparent temperature 573 K) benzene populations still persisted. The implications of this study emphasize again that relaxation can take considerably longer than some chemical steps, and that reactive intermediates in solution cannot always be generalized as having a single defined structure or thermal energy content.

While not meeting all of the criteria used to define catalysis, solvents can be thought as superstoichiometric catalysts. They increase reaction rates without being consumed. Prior studies have attempted to control the stereochemistry of reactions using chiral solvents. This is theoretically possible, but due to the weak nature of solvent-solute noncovalent interactions (NCI) and the need for tight-binding of solvent to significantly discriminate between enantiomeric TSs, the experimental enantiomeric excesses (*ee*) reported are typically ~1%.<sup>30-32</sup>

Carpenter *et al*<sup>33</sup> published a computational study outlining the effects of chiral solvent on the stereoselectivity of a reaction where the product-determining step takes place on a bifurcating surface. The authors argued that when product selectivity is decided on a flat region of the PES, the small forces exerted by nearby solvent molecules are competitive with the forces of the reacting solute, leading to a stereoselective reaction. The study

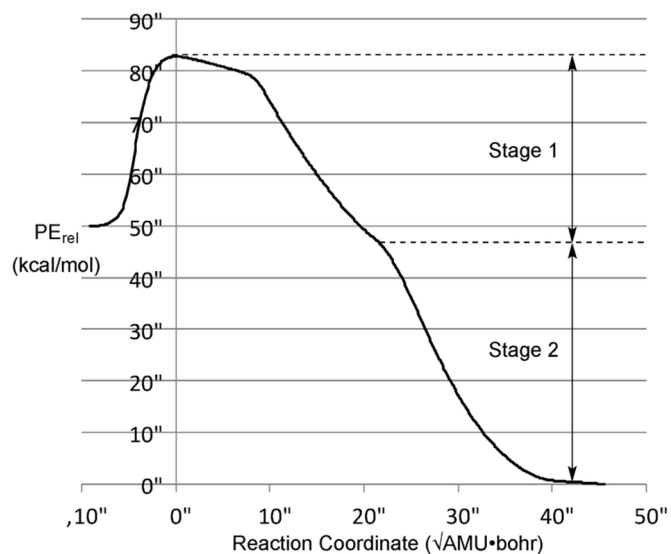


discusses the ring opening of a singlet meso cyclopropanylidene to form chiral allenes (Figure 8).



**Figure 8** Mechanistic hypothesis and solvent selection for studying the ring opening of **27**.

This system has historical significance as one of the earliest bifurcating systems studied theoretically by Valtazanos.<sup>34</sup> It is thought that cyclopropanylidene ring opening proceeds by a single TS for  $\text{N}_2$  extrusion **26** that generates highly unstable carbenoid **29** that rapidly and exothermically rearranges to give a racemic mixture of allenes **30**. **29** is not considered to be an intermediate with an associated energy minimum, but a transient species on a sloped portion of a bifurcating PES. The authors calculated the PES for this system in the gas phase with M06-2X (Figure 9). The surface was considered to have two distinct geometric regimes. Stage 1 is a region of the PES after the TS and is dominated by the C-C bond breaking coordinate, Stage 2 occurs after the C-C bond is fully-broken and is dominated by the torsion of the substituents to form **30** products.



**Figure 9** Gas phase potential energy surface for the ring opening of **27**. Re-printed with permission from “Prediction of Enhanced Solvent-Induced Enantioselectivity for a Ring Opening with a Bifurcating Reaction Path”. Carpenter, B. K.; Harvey, J. N.; Glowacki, D. R. *Phys. Chem. Chem. Phys.* 2015, *17*, 8372–8381. Published by the PCCP Owner Societies.<sup>33</sup>

The authors developed an empirical valence bond (EVB) model to describe the system. Classical reactive trajectories were initiated from the EVB highest-energy structure on the DFT IRC. 1200 simulations in CHCl<sub>3</sub>(control), CHFClBr, and trifluoro-isopropanol (TFIPA) gave a predicted ees of  $1.2 \pm 4.6$  %,  $2.3 \pm 3.7$  %, and  $15.2 \pm 2.1$  %, respectively. The authors discovered the energy dissipation to solvent, especially CHCl<sub>3</sub> and TFIPA, was rapid and trajectories arriving at the product wells were unable to escape, in contrast to the product isomerization observed in gas phase trajectories. In analyzing the solvent motion of TFIPA, the authors found that the solute-solvent interactions were strongest just after C-C rupture, and that solute-solvent motions were not significantly correlated afterwards. The authors concluded that this interaction took place too early to significantly influence the stereochemical outcome and that the **29** core, while eventually cooled by solvent, jettisoned

nearby solvent molecules in the beginning of Stage 1 and limited their influence in Stage 2. From a technical perspective, this level of detail is not possible to gain through the implicit modeling of solvent. Conceptually, this study highlights that solvent equilibration is not always possible during a rapid succession of mechanistic steps, and that solvent dynamic effects do not necessarily make reactions more selective.

The reaction coordinate is a conceptual tool that simplifies the description of a chemical step by ignoring some geometric motions and focusing on one as the single descriptor of reaction progress. As in the case of cyclopropanylidene ring opening, all of the atoms are in flight, but the C-C bond length is considered the geometric coordinate that describes the reaction's progress in Stage 1. This is a logical extension of TST and qualitatively fails when a reaction's location on the PES is controlled by several interwoven geometric changes, e.g., the complete transformation of a cyclopropanylidene to an allene cannot be described by the C-C coordinate alone. An additional complication encountered in simulation reactions in explicit solvent is that the system gains even higher dimensionality and thus demands an even greater trivialization of degrees of freedom in order to arrive at a low-dimensionality representation of reaction progress.

This is an old problem and was encountered by Hynes and coworkers in studying the solvolysis of tert-butylchloride in water.<sup>35</sup> The authors truncated the tertbutyl group into a single carbon atom in order to simplify the reaction into a single reaction coordinate C-Cl. Using semi-empirical methods, the authors calculated a potential of mean force (PMF) free energy surface for the rupture of C-Cl bond. Reactive trajectories were initiated from TS at 2.28 Å and integrated forwards and backwards in time for 1 ps in each direction. For a set of 200 trajectories, 91 completed a transition from neutral reactant to ion-pair and 109

recrossed. Clearly even for a solute with a single degree of freedom, the trajectories were not initiated at the true configuration that exactly divides reactant and product states. One might surmise that an additional dimension such as velocity along the C-Cl coordinate would have allowed a more precise definition of the TS and reduced recrossing, however it is possible that the outcomes of trajectories are under solvent control. In a later computational study Hynes focused on the effect of water libration on methyl chloride energy transfer.<sup>36</sup> Hynes observed that vibrational relaxation in the solute is a complex phenomenon where distant solvent molecules restructure their networks to facilitate energy structure, precluding the possibility of describing the solvent coordinate with a geometric parameter of a single adjacent solvent molecule. In summary, when a mechanistic step in solvent generates or consumes charged species, the step occurs only because the instantaneous solvent configuration allows. Hynes outlines the absence of a well-defined and controllable solvent coordinate as a critical problem that plagues the understanding of molecules crossing the TS in solution and ultimately frames solvent dynamic effects as unexpected deviations from the norm.

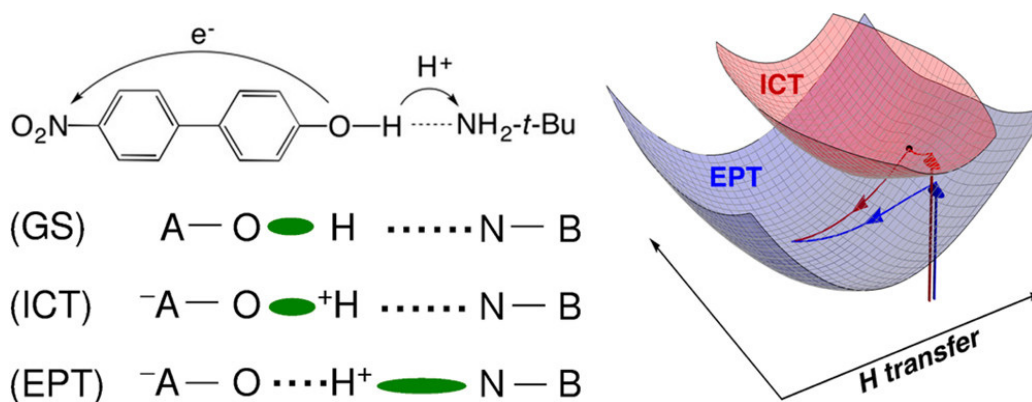
In 2020 Leitold *et al*<sup>37</sup> proposed a general means of constructing solvent coordinates for organic reactions. Studying the degenerate S<sub>N</sub>2 reaction of chloride anions with methyl chloride, the authors used commitor analysis to screen a selection of parameters and determine the parameters' accuracy in predicting the outcome of a trajectory. Ultimately, three parameters were considered sufficient to locate the dividing surface (DS) and judge where an initialized trajectory was relative to it. The first parameter was the difference between the two C-Cl bond lengths, the second was a vector representation of the Walden inversion, and the last was a solvent charge descriptor. To generate this descriptor, the

average atomic charges for each solvent molecule is calculated at each point along the C-Cl dimension. The magnitude of this descriptor is the difference between the instantaneous charge distribution and the average distribution, and the direction of this magnitude is decided by the difference between the instantaneous distribution and the net change in average charges between the two final states. Qualitatively, this solvent coordinate describes the solvent polarization as being either product-like or reactant-like. The statistical analysis showed that the bond length and pyramidalization parameters performed well at predicting the outcome of trajectories initiated far from the DS, while the additional solvent parameter improves prediction accuracy for trajectories initiated close to the DS.

The study of proton-coupled electron transfer, or PCET, reactions has become increasingly common in organic chemistry and biochemistry. The charm of PCET reactions is that electrons and proton move in a concerted fashion, bypassing unfavorable sequential electron-transfer/proton-transfer intermediates or kinetically unfeasible TSs. Because these two translocations of charged particles takes place so rapidly, it was anticipated that non-equilibrium solvation may have an influence on these reactions. And because some biologically relevant PCET reactions are photoinduced, the decay of excited states via vibrational energy transfer to solvent is a promising locus of mechanistic study. The Hammes-Schiffer group has computationally studied the photoinduced PCET reaction of *p*-nitrophenyl-phenol and amine bases in 1,2-dichloroethane and discussed the complex influence of solvation (Figure 10).<sup>38</sup> Proton transfer from oxygen to nitrogen is kinetically and thermodynamically unfavorable on the  $S_0$  surface in solution. Calculations and experiment support that the  $S_1$  state in solution is best described as an electron-proton transfer (EPT) state where the electron from the phenolic ring has shifted to the nitro group

and the proton is closer to oxygen, but electron density around the proton originates from nitrogen. The S<sub>2</sub> manifold is an intramolecular charge transfer state (ICT) where nitro-phenyl electron density shifts to the nitro group and the proton is still covalently bound to oxygen, displaying a much smaller change in dipole than S<sub>1</sub>. Proton transfer in all three manifolds is energetically unfavorable in the gas phase, but S<sub>1</sub> permits proton transfer with low barriers in solution.

Hammes-Schiffer conducted QM/MM simulations in explicit solvent using a surface-hopping algorithm that allowed transitions between electronic states. Trajectories initiated from vertical excitation to S<sub>2</sub> decayed to S<sub>1</sub> in ~100 fs before relaxing back to S<sub>0</sub> equilibrium over the course of ~0.9 ps. Analysis of the trajectories showed that proton transfer did not occur on the S<sub>1</sub> manifold until the first solvation charge reorganized (~250 fs), causing the buildup of negative potential at nitrogen, and tipping the balance to favor the formation of an N-H bond over an O-H bond.



**Figure 10** Mechanistic scheme from Hammes-Schiffer. Re-printed with permission from “Nonadiabatic Dynamics of Photoinduced Proton-Coupled Electron Transfer in a Solvated Phenol–Amine Complex” by Goyal, P.; Schwerdtfeger, C. A.; Soudackov, A. V.; Hammes-Schiffer, S. *J. Phys. Chem. B.* 2015, *119*, 2758–2768. Copyright 2014 American Chemical Society.<sup>38</sup>

Furthermore, their analysis showed that the solvent's response was immediate and acted to negate the reorientation of the solute dipole toward the nitro group. However, solvent dynamics could not explain why roughly half of the trajectories never completed a proton transfer. The authors analyzed the geometric space of the solute and recognized that in nonproductive trajectories the linearity of the O-H-N assembly had broken, and the two fragments separated in space. Solvent dynamics were also used to explain why  $S_2$  decayed to  $S_1$  rather than directly to  $S_0$ . The  $S_1/S_0$  conical intersection for the system lay in a region of geometric space after the proton transfer, so any process accelerating the movement of the proton would do the same for electronic relaxation. This work reiterates the fact that seemingly facile movements of small groups and even electronic transitions are gated by solvent dynamics.

Due to the relatively small number of contributions to this area, the nature and regularity of the experimental consequences of non-equilibrium solvation have not been enumerated so thoroughly as analogous studies in the gas phase. The study of solvent dynamic effects in the literature is limited by a variety of factors, outlined above, but additional issues prevent some existing studies from being included in the physical organic chemistry canon. Many of the reactions studied use small molecules that are irrelevant to organic synthesis in order to draw parallels to significant benchmark gas phase reactions in the chemical physics literature. Additionally, organic chemists may overlook studies conducted in less popular solvents such as water or supercritical argon. A study with the right choice of solutes and solvents will ultimately give solvent dynamic effects greater visibility in the field of organic chemistry, bringing the role of solvation to the forefront of mechanistic inquiry.

CHAPTER II

SOLVATION DYNAMICS AND THE NATURE OF REACTION BARRIERS AND  
ION-PAIR INTERMEDIATES IN CARBOCATION REACTIONS\*

**2.1 Introduction**

As discussed in the previous chapter, the regular mechanistic paradigm fails when the understanding of experimental observations requires the consideration of additional information, such as the multifurcating shape of an energy surface<sup>3,6,23,39-43</sup> the excess energy in an intermediate and its distribution,<sup>9,28,51,52,29,44-50</sup> or the non-equilibrium solvation of structures. We describe all such reactions as involving “dynamic effects” in that they possess experimental characteristics that can be understood by allowance for the motions and momenta of atoms, if not for now by the standard statistical theories of chemistry.

The common denominator for dynamic effects is time. That is, when an experimental observation is associated with the evolution of a sufficiently short-lived structure, whether it is a formal intermediate or simply on the slope of an energy surface, then the inaccuracy or inapplicability of statistical theories is unsurprising. Molecular dynamics is inherently nonlinear, and so chaotic, but the descent into the past-forgetting chaos that engenders statisticality takes time, often multiple picoseconds.

Carbocations are the most studied reactive intermediates in organic chemistry. Over the course of a half-century of experimental observations of carbocation reactions have been

---

\*Adapted with permission from “Solvation Dynamics and the Nature of Reaction Barriers and Ion-Pair Intermediates in Carbocation Reactions” by Roytman, V.A.; Singleton, D.A. *J. Amer. Chem. Soc.* **2020**, *142*,12865-12877. Copyright 2020 American Chemical Society.<sup>184</sup>

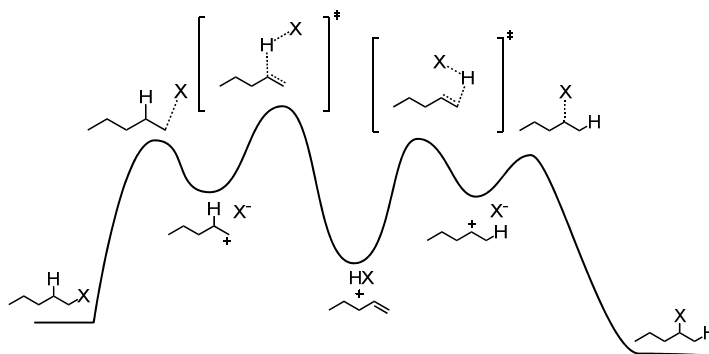


understood within the normal conception of mechanisms; a ‘thin’ mechanism in which the reactions of the carbocation intermediate are governed by the height of surrounding potential energy barriers.<sup>53</sup> Carbocations are often generated from neutral starting materials in polar solutions, and the transition states that form these intermediates from neutral molecules exhibit partial charge separation. The solvation of these transition states is by theorem approximately at equilibrium, the idea being that any departure from equilibrium solvation would raise the barrier. However, downhill progress from these transition states involves rapidly changing charge separation over the course of a few dozen femtoseconds.<sup>54,55</sup> The burden of stabilizing this charge separation falls on the polar solvent, which, moving on the picosecond timescale, is inevitably behind in responding to the progress of the reaction coordinate (RC).<sup>56,57</sup> Carbocations exhibit short lifetimes in solution,<sup>58</sup> making the assumption of equilibrium solvation in later steps appear dubious.

This makes carbocation intermediates<sup>58</sup> make them ripe for dynamic effects.<sup>15,59</sup> The abundant observations in classical carbocation chemistry have usually been fit, by implicit assumption, into a normal mechanistic model in which carbocations and ion pairs act as ordinary intermediates and their reactions are controlled by the barrier heights along exit channels. In some carbocation reactions, however, the observations are more difficult to shoehorn into a standard mechanism. We explore such a case here involving a textbook observation in electrophilic addition reactions. Here, we establish the extent to which solvation dynamics impact regioselectivity of a fundamental organic reaction.

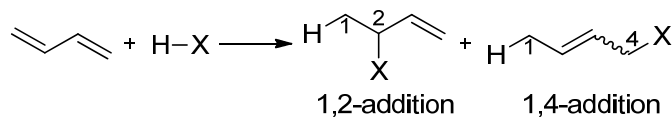
In introductory organic chemistry textbooks, the mechanism of hydrohalogenation of alkenes is often depicted as involved proton transfer from the acid followed by nucleophilic attack by the halide of the resulting carbocation (Figure 11). Regioselectivities

and rates in these reactions can be understood from the analysis of the carbocation intermediate. Pathways proceeding through the more stable carbocation are favored over less stable alternatives because the stability of the carbocation intermediates modulates the kinetic barriers at the rate-limiting TS for alkene protonation.



**Figure 11** The Markovnikov paradigm for hydrohalogenations.

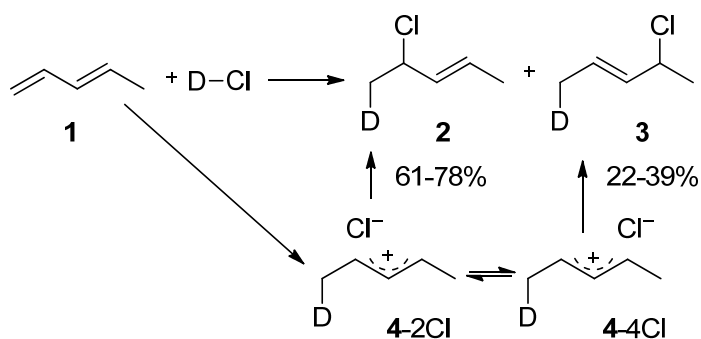
Additions of acids to dienes introduce the added complexity of delocalized carbocation intermediates. The addition of acids to dienes gives products of both 1,2- and 1,4- addition (Figure 12).<sup>60,61</sup> Textbooks provide a standard perspective on the matter, that is, that the 1,2- addition product and the 1,4-addition product are the kinetic and thermodynamic products of nucleophilic trapping of conjugated carbocations, respectively.<sup>62</sup>



**Figure 12** The regiochemistry of the addition of hydrogen halides to conjugated dienes.

In 1979, Nordlander offered a simple means of studying the kinetic selectivity of HCl additions to dienes.<sup>63</sup> Studying the reaction of piperylene (**1**) with deuterium chloride in a range of solvents and temperatures, Nordlander found that the 1,2-addition product (**2**) and

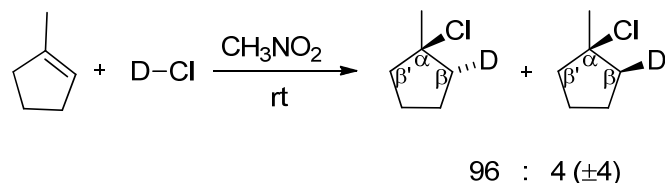
the 1,4-addition product (**3**) were formed in disparate quantities (Figure 13) – an interesting discovery as the dimethylallyl carbocation intermediate should have given equal quantities of 1,2- and 1,4-addition. Nordlander explained that the product ratios were determined by a competition that took place after rate-limiting deuteron transfer from the deuterium chloride: the attack of the chloride on the nascent cation (**4-2Cl**) to form **2** or the isomerization of this cation-anion complex to give an intermediate (**4-4Cl**) that would collapse to give **3**.



**Figure 13** Nordlander's model for the regioselectivity of DCl additions to piperylene.

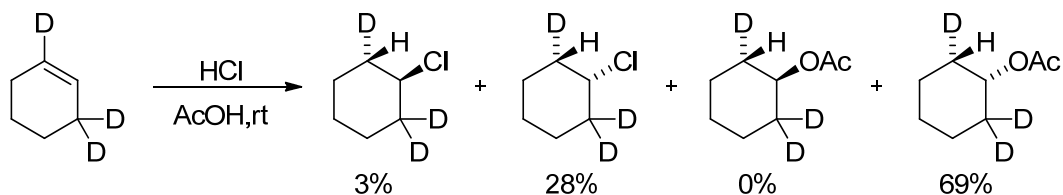
Although Nordlander's explanation invoked a carbocation intermediate, other chemists have proposed mechanisms for hydrochlorinations that forgo reactive intermediates altogether. The Ad<sub>E</sub>3 mechanism was put forth as a possible means of bypassing especially unstable carbocations such as vinyl cations.<sup>64</sup> This mechanism is first order in alkene, second order in HCl and would render products of concerted *trans* addition. An illustrative example was Pocker's study of the addition of HCl to alkenes in nitromethane.<sup>65</sup> After observing a greater than first order dependence of reaction rate on HCl, Pocker investigated the stereochemistry of the addition of deuterium chloride (DCl) to 1-methylcyclopentene. Pocker found that the product was almost exclusively *trans* (Figure 14). It bears mentioning that Pocker's determination of stereochemistry relied on mass

spectrometric analysis of the base elimination product of the hydrochlorination reaction mixture, and as such was reliant on multiple assumptions about stereochemistry, regiochemistry and isotope effects in the basic elimination. These two pieces of evidence provided the most compelling argument for the A<sub>E</sub>3 mechanism in normal alkenes.



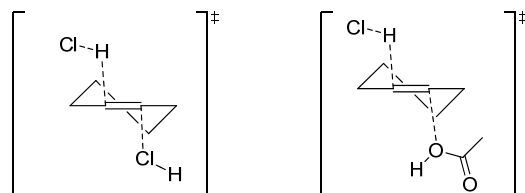
**Figure 14** Reaction stereochemistry from Pocker *et al.*

Fahey too performed crucial studies in this area.<sup>64,66-72</sup> In 1969, Fahey noticed that the addition of hydrogen chloride to cyclohexene was second order in the acid and that adding exogenous chloride anions in the form of tetramethylammonium chloride not only accelerated the rate of the reaction but increased the ratio of hydrochlorination product:acetolysis product in the product mixture.<sup>73</sup> Fahey pursued cyclohexene further and published the stereochemistry of the hydrochlorination of cyclohexene-1,3,3-d<sub>3</sub> in acetic acid (Figure 15).<sup>74</sup> With <sup>1</sup>H{<sup>2</sup>H} NMR, Fahey observed that the hydrochlorination reaction proceeded in a predominately *trans* fashion while the solvolysis product was exclusively *trans*.



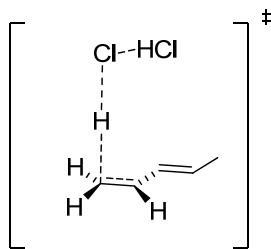
**Figure 15** Stereochemistry of hydrochlorination for cyclohexene from Fahey.

Fahey's two studies on cyclohexene allowed the construction of an  $A_{E3}$  model for the reaction mechanism (Figure 16). The model used to explain the formation of hydrochlorination and solvolysis products from two concerted *trans*-diaxial TSs.



**Figure 16** Fahey's proposed  $A_{E3}$  mechanism.

There is, however, another means by which the observation of termolecular kinetics and *syn* stereoselectivity can be married into a coherent mechanism. Pocker's graduate student, Kenneth Stevens, detailed that he was aware of a proposition made by Mayo that the high order in acid could be explained by a catalytic mechanism where protonation of alkenes is facilitated by an additional molecule of acid as an electrostatic stabilizer for the building charge (Figure 17), however his advisor ultimately sided with Fahey on the mechanism.<sup>75,76</sup>

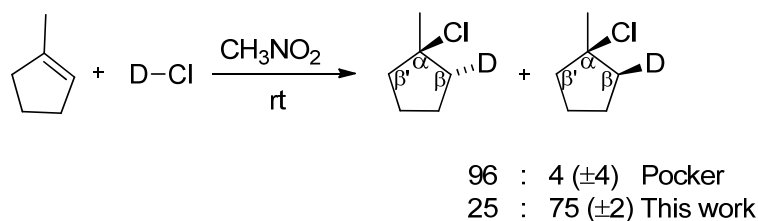


**Figure 17** A termolecular alternative to the  $A_{E3}$  mechanism.

## 2.2 Experimental Results and Discussion

### *Reaction of 1-methylcyclopentene with DCl*

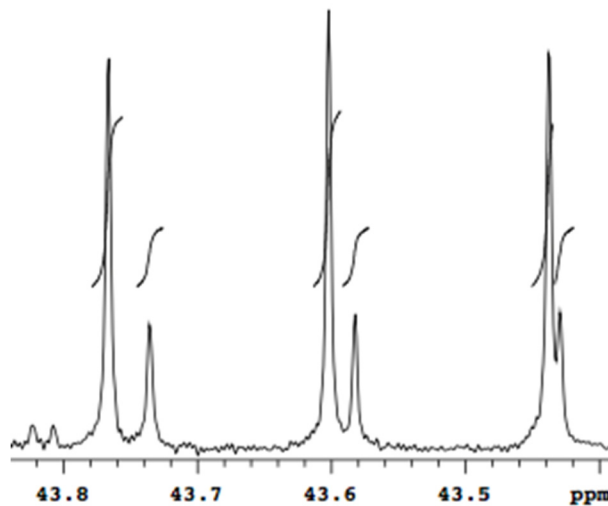
As mentioned before, Pocker *et al* used an indirect measurement of stereoselectivity to support their proposed concerted *trans* addition mechanism for 1-methylcyclopentene in nitromethane. Pocker's method may have been the best approach available at the time, but ultimately a direct analysis of the product mixture would be able to settle the matter and offer a more reliable measurement. With the advantage of modern NMR methodology, we were able to directly examine the concentrated 6/7 mixture (Figure 18).



**Figure 18** Experimental product distributions from previous and current work.

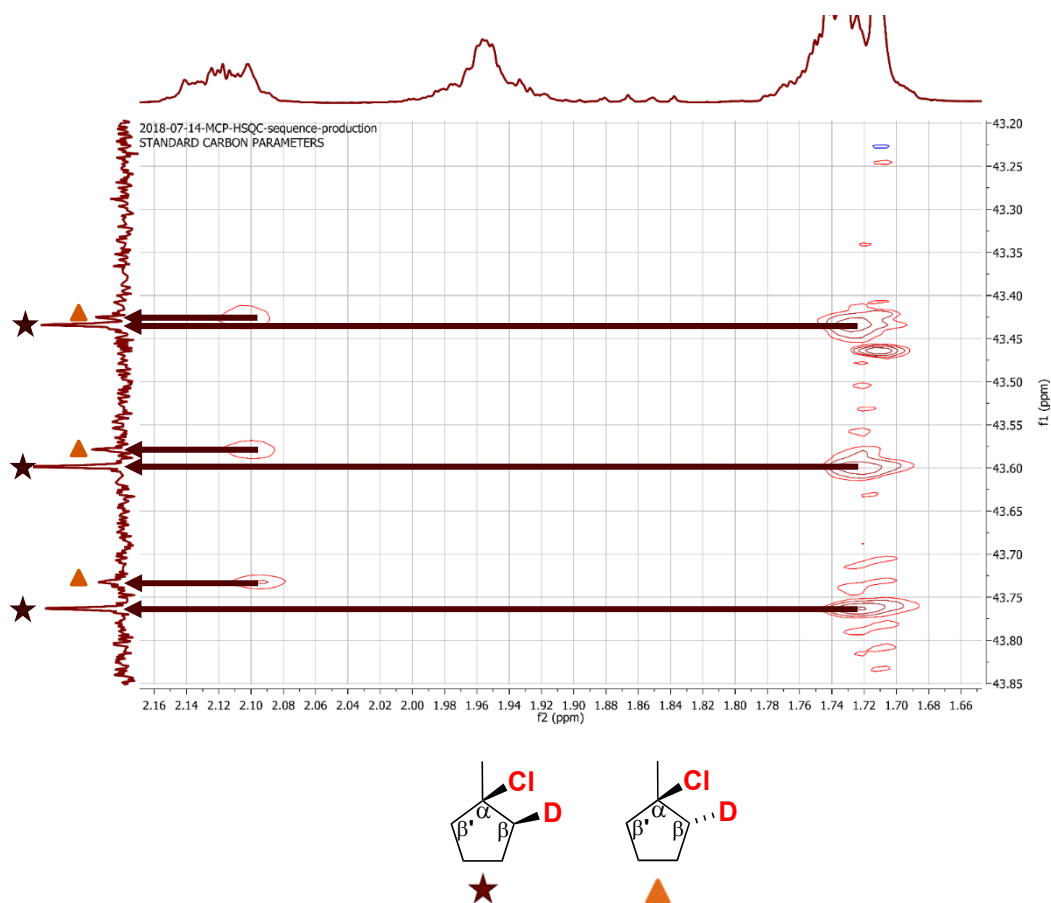
The  $^{13}\text{C}$  NMR of the 6 / 7 mixture was obtained using a 5 second delay between  $90^\circ$  pulses, and with no special precautions for high-accuracy integrations. Since the width of the  $\beta$  carbon signals of interest were indistinguishable for 6 and 7, suggesting similar relaxation rates, this was considered adequate for the purpose at hand of determining an approximate product ratio. As shown in Figure 19, the  $^{13}\text{C}$  NMR of the 6 / 7 mixture exhibits two deuterium-split triplets that are shifted upfield from the otherwise equivalent carbon by  $\sim 0.37$  ppm, in a 75 : 25 ratio. The assignment of these triplets was based on the HSQC spectrum shown below (Figure 20). In this HSQC, it should be understood that the cross peaks are for the  $^1\text{H}$  on the deuterated materials. The HSQC then shows that the larger of the

triplets correlates with the upfield (H *trans* to Cl)  $^1\text{H}$  at  $\delta$  1.73, while the smaller triplet correlates to the downfield (H *cis* to Cl)  $^1\text{H}$  at  $\delta$  2.12. The assignment of the downfield H as *cis* to Cl and the upfield H as *trans* to Cl was initially based on general correlation observations (chlorine atoms shift nearby  $\beta$  hydrogens downfield), but this was also supported by calculated chemical shifts based on WP04/aug-cc-pVDZ/PCM(chloroform) calculations on **6** / **7**, which predicted the *cis* protons to be 0.35 ppm downfield from the *trans* protons.



**Figure 19**  $^{13}\text{C}$  spectrum illustrating two disparate triplets belonging to **6/7**.

The *syn* addition of HCl is thus the major pathway, by a ratio of 75:25 versus the alternative *anti* addition. This is inconsistent with a concerted  $\text{A}_{\text{E}}3$  mechanism. This result is perplexing in the context of existing evidence. A possible explanation for the second order acid dependence is the pathway in which a second molecules HCl acts as a catalyst for protonation. Understanding the regioselectivity, however, will require a new mechanistic paradigm.



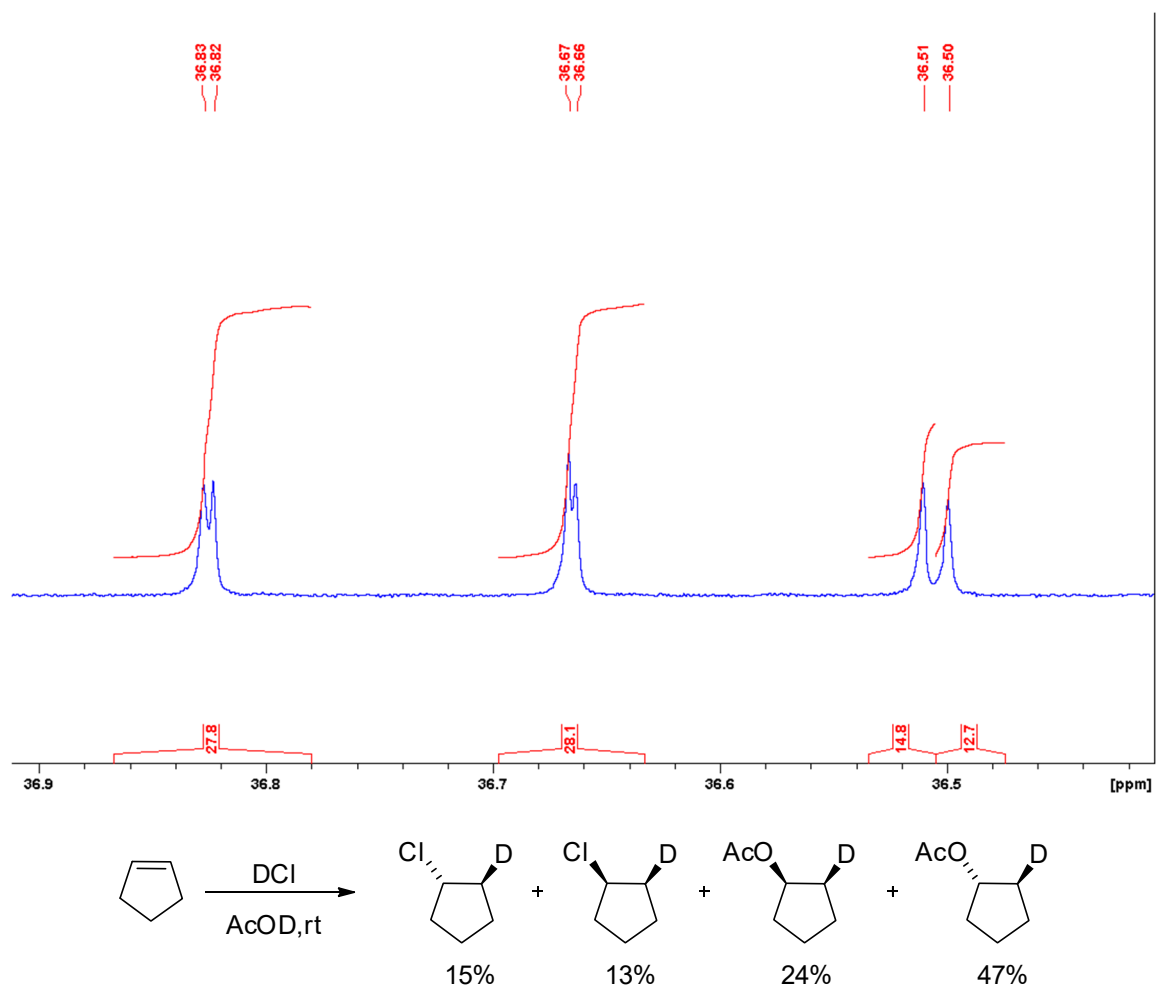
**Figure 20** Observed product ratio in addition of DCl to 1-methycyclopentene.

### *Reaction of Cyclopentene with DCl*

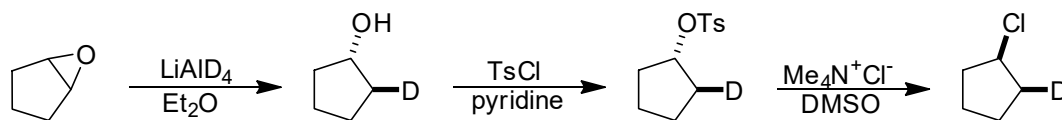
Fahey's choice in alkene may have strongly influenced the results of the study. The cyclohexyl cation's faces are not symmetrical and this manifests in cyclohexenes having a strong preference for *trans* diaxial additions vis à vis the Fürst-Plattner rule.<sup>77</sup> In testing this hypothesis, the stereochemistry of addition to cyclopentene was studied. It was thought that the cyclopentyl cation would have less stereochemical bias than the cyclohexyl cation, though still be equal in reactivity. Distortionless Enhancement by Polarization Transfer (DEPT) NMR analysis offered results that are qualitatively different than Fahey's (Figure



21). The major halogenated product was identified by comparison with a synthetic, diastereopure sample prepared from cyclopentene oxide (Figure 22).



**Figure 21**  $^{13}\text{C}$  DEPT NMR indicating that the regiochemistry of addition to cyclopentene is not consistent with an  $\text{A}_{\text{D}}\text{E}_3$  mechanism.

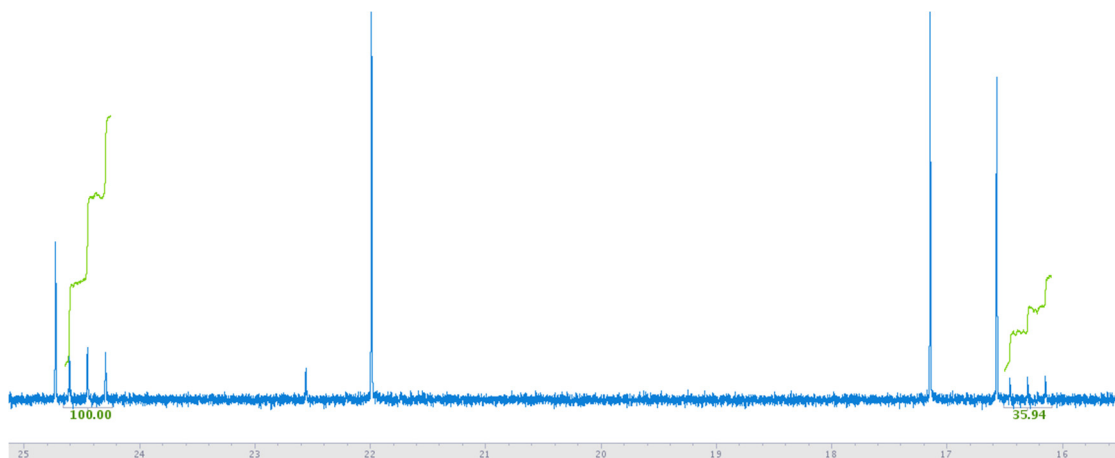


**Figure 22** Experimental product ratios/synthetic protocol for preparing a stereochemistry standard.

### *Reaction of 1,3-pentadiene with DCl*

Nordlander's measurement appeared subject to possible error since it was based on incompletely resolved  $^2\text{H}$  NMR peaks and since the analysis required purified material subject to isomerization under the reaction conditions and in the isolation process. Accordingly, after all of the computations for this project were complete, we undertook a redetermination of the product ratio. The deuterated carbons in **2** and **3** are completely resolved from their unlabeled isotopologs, and their ratio was readily determined by direct  $^{13}\text{C}$  NMR analysis of the reaction mixture without isolation, after quenching of the excess acid with 2-trimethylsiloxyprene. The  $^{13}\text{C}$  NMR of **2** / **3** was obtained under conditions previously found to allow high accuracy integrations, including the use of calibrated  $90^\circ$  pulses, inverse gated decoupling, and with 31.6 s delays between pulses and 4 s acquisitions. Spectra of the sample prepared above were obtained immediately after quenching and at times of 24 h, 72 h, 96 h, and 144 h, and the difference in spectra (due to isomerization) were used to extrapolate a product distribution at the outset of the reaction. The time at the midpoint of each spectrum acquisition was used for the extrapolation. An example spectrum is shown below (Figure 23). The uncertainty associated with the relative integrations was examined in two ways. The first of these was to consider the range of relative integrations that could be obtained using marginally acceptable spectral parameters. For example, the spectrum below changes from 100 : 35.94 (least favorable for agreement with the computational prediction) to 100 : 33.87 using a  $lv1$  parameter of 0.001 (most favorable for agreement with the computational prediction). The second way was to examine the

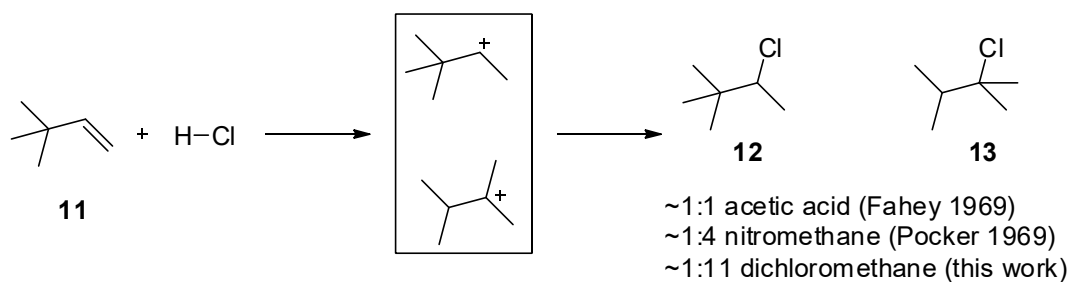
uncertainty expected based on a simulation that allowed for the observed signal-to-noise ratio. The latter gave rise to the larger uncertainty.



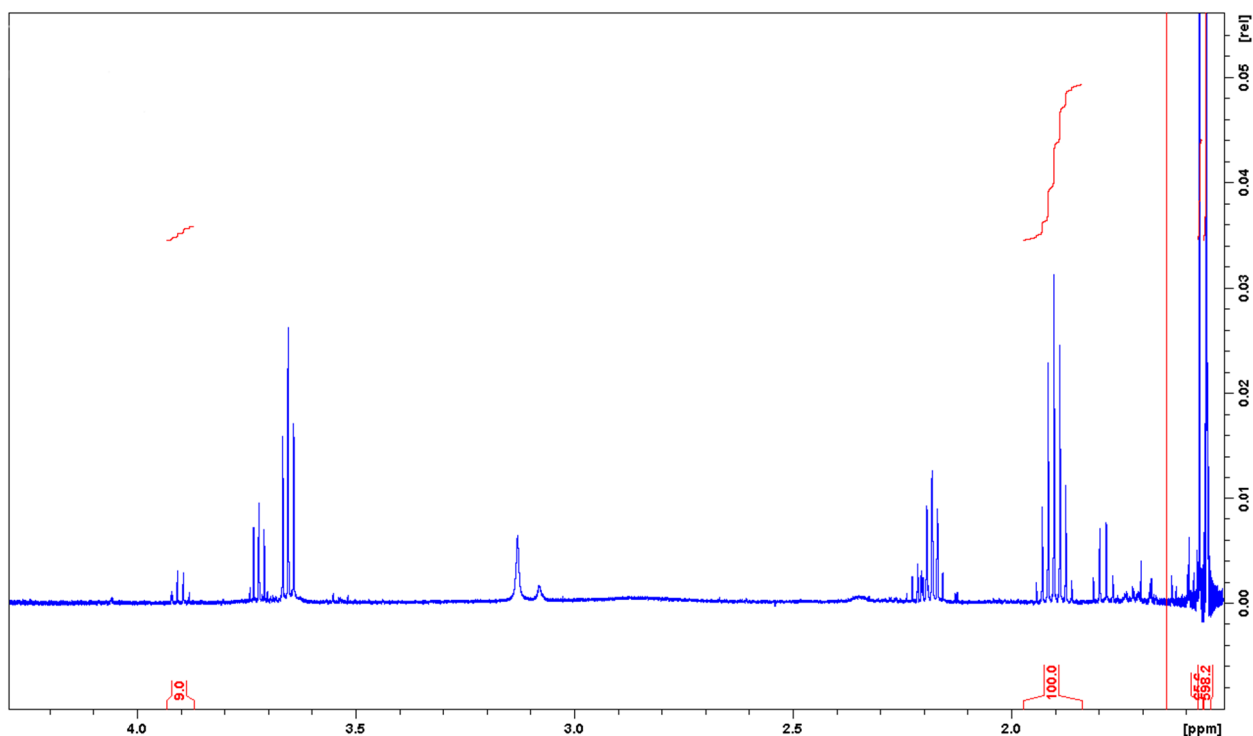
**Figure 23** Example <sup>13</sup>C spectrum of 2/3 with integration lines shown on critical triplet peaks.

#### *Reaction of tert-butylethylene with DCl*

Experiments from Fahey and Pocker reported that the hydrochlorination of *tert*-butylethylene give two alkyl halide products, a tertiary chloride and a secondary chloride.<sup>65,69</sup> The observation of **13** is unusual given that the secondary carbocation intermediate can rearrange to the tertiary carbocation in an exothermic and barrierless methyl shift. Our hypothesis is that after protonation, the surrounding solvent cage has yet to equilibrate and so a true carbocation intermediate is not generated until a few picoseconds later. This structure then has the potential to undergo nucleophilic addition before the solvent cage allows methyl shift to take place.



**Figure 24** Compiled product selectivity data for the hydrochlorination of *tert*-butylethylene.



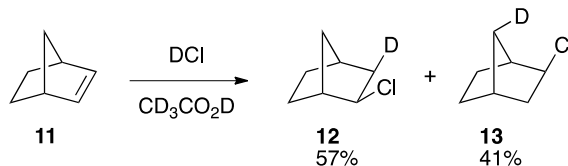
**Figure 25**  $^1\text{H}$  NMR for a **11** + HCl reaction mixture after concentrating. Integration on the left is for the methine C-H on **12**, integral on the right is for the **13** isopropyl methine C-H.

Our own work on this reaction in dichloromethane suggests that solvation dynamics may still influence reactions taking place in considerably less polar and viscous solvents. While it is possible that these product mixtures arise from the competition of  $\text{Ad}_{\text{E}2}$  and  $\text{Ad}_{\text{E}3}$  mechanism, as proposed by Fahey, the  $\text{Ad}_{\text{E}3}$  mechanism does not seem to be likely. Every

ordinary alkene hydrochlorination in this dissertation thus far has not proceeded through an  $\text{Ad}_{\text{E}3}$  mechanism (*vide supra*). Trajectory studies on this reaction in nitromethane are forthcoming.

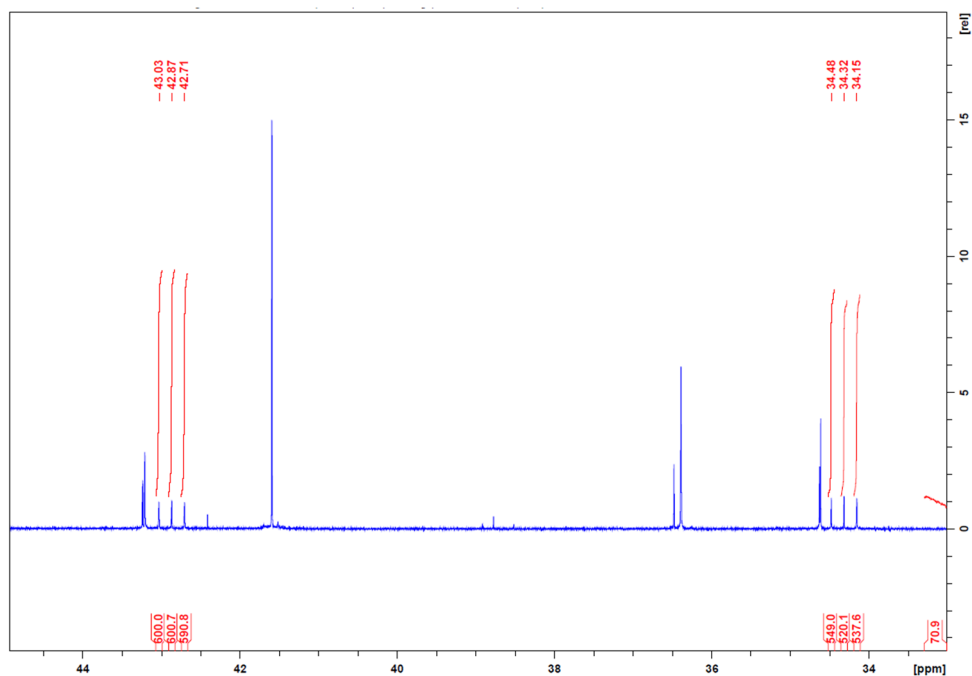
#### *Reaction of Norbornene with DCl*

Brown's observation of unequal mixtures of **12** and **13** from the deuteriochlorination of **11** was leveraged as proof of an equilibrating classical norbornyl carbocation (Figure 26). Another possible explanation for this distribution, much like in the case of symmetrical pentadienyl cation, is the influence of solvent dynamics. Efforts to replicate Brown's experiments of the addition of DCl to norbornene yielded results contradictory to Brown's reported 58:42 ratio in nitromethane.

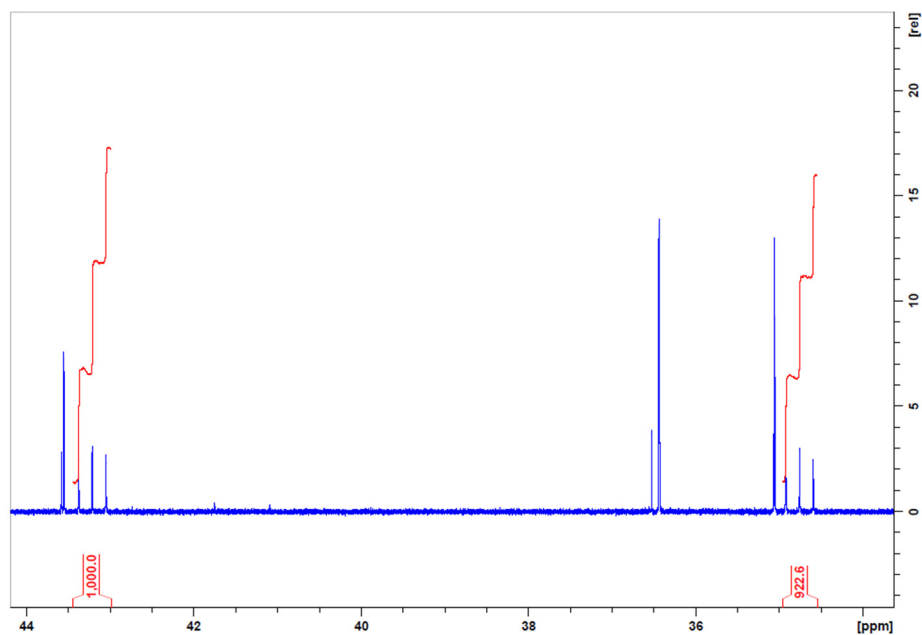


**Figure 26** Product ratios from Brown *et al.* Equates to 58:42.

Despite repeated efforts to reproduce this result at both high and low acid concentrations, and in nitromethane and in dichloromethane, the product ratio never appeared more unequal than ~53:47 (Figure 27). Collection of spectra over the course of a few days showed no change, suggested that the product mixture does not change with time.



**Figure 27** Inverse-gated decoupling  $^{13}\text{C}$  NMR of the reaction mixture of DCl and norbornene in nitromethane. A 53:47 ratio of **12** to **13** was observed.



**Figure 28** Inverse-gated decoupling  $^{13}\text{C}$  NMR of the reaction mixture of DCl and norbornene in dichloromethane. A ~50.1:49.9 ratio of **12** to **13** was observed.

It is not completely certain why these outcomes deviate from Brown's observations, but a likely cause is the inaccuracy of Brown's deconvolution technique which relied on estimates on the extent of overlap between peaks in  $^1\text{H}$  NMR spectra.

### *Conclusions*

Taken together, these results suggest that the  $\text{Ad}_{\text{E}3}$  mechanism is neither the major hydrochlorination pathway in simple alkenes and dienes nor the cause for the unsymmetrical product distributions from nominally symmetric intermediates.<sup>67,69,78</sup> Furthermore, these experiments highlight that control of stereoselectivity is sensitive to the identity of the reacting alkene and solvent. Finally, the results demonstrate that the experimental foundation for classical carbocation chemistry may need re-evaluation as the existing experimental data proved to be qualitatively unreliable.

## **2.3 Molecular Dynamics Results and Discussion**

### *Computational Methods Selection*

DFT methods tend to overestimate the proton affinity of 1,3-pentadiene in comparison with CCSD(T)/aug-cc-pVTZ calculations, most by 6-11 kcal/mol, but M06-2X calculations mirrored the ab initio value within 1 kcal/mol with little dependence on the basis set (see Section 2.6). The proton affinities of  $\text{Cl}^-$  and  $[\text{ClHCl}]^-$  were underestimated by every DFT method explored, by 1-6 kcal/mol and 6-11 kcal/mol, respectively. In contrast, MP2/6-31+G\*\* calculations performed uniformly well, within 1.5 kcal/mol. The MP2/6-31+G\*\* calculations also closely reproduced DLPNO-CCSD(T)/aug-cc-pVTZ energies along a series of 98 points sampled from solution trajectories (see below), with a correlation  $R^2$  of 0.996 and a slope of 0.98. M06-2X/6-31+G\* calculations performed less well on each of these tests but were more practical for large-scale trajectory calculations in explicit

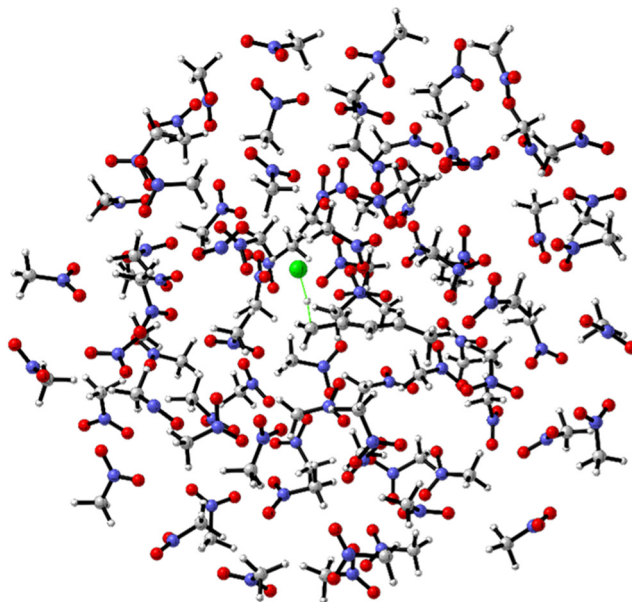
solvent. In practice, both methods were fully explored and gave similar results. We will emphasize the MP2 calculations, since they were notably superior in every comparison with high-level energies from highly correlated methods.

It was anticipated that implicit solvent models would prove inadequate for this reaction, but they provide a baseline for consideration of the reaction in explicit solvent. Four series of stationary points and trajectories were obtained, arising from the use of the MP2 and M06-2X methods in combination with PCM and SMD implicit solvent models. Calculated free energies for stationary points are based on DLPNO-CCSD(T)/aug-cc-pVTZ gas-phase potential energies, with PCM or SMD implicit solvent corrections, and MP2 or M06-2X enthalpies and entropies corrected to a 1 M standard state. The DLPNO-CCSD(T)//MP2/PCM results are presented here, but very similar results were obtained with all the combinations.

For trajectories and free-energy surface calculations in explicit solvent, the computational model consisted of 1,3-pentadiene and either one or two molecules of HCl in a sphere of 120 nitromethane molecules with a diameter of 29.5 Å and a density of 1.18 g/mL (Figure 29). This model was explored on the QM/QM' ONIOM surface, using either MP2/6-31+G\*\* or M06-2X/6-31+G\* for the 1,3-pentadiene and HCl, and using PM6-DH+ for the nitromethane. The low-level component of the ONIOM calculation was supplemented by an additional empirical dispersion term, modeled after the Grimme GD2 dispersion,<sup>79</sup> with a global parameterization to approximate a realistic density and heat of vaporization. A notable limitation of this approach is that the polarizability of the nitromethane is 29% too low, as is normal for semiempirical methods. The PM6-DH+ dipole moment for nitromethane is 3.98, in reasonable agreement with the experimental value of



3.46. The low solvent sensitivity of the Nordlander results suggested that the accuracy of the computational solvent may be adequate, but this will be probed by comparison of computed and experimental observations.



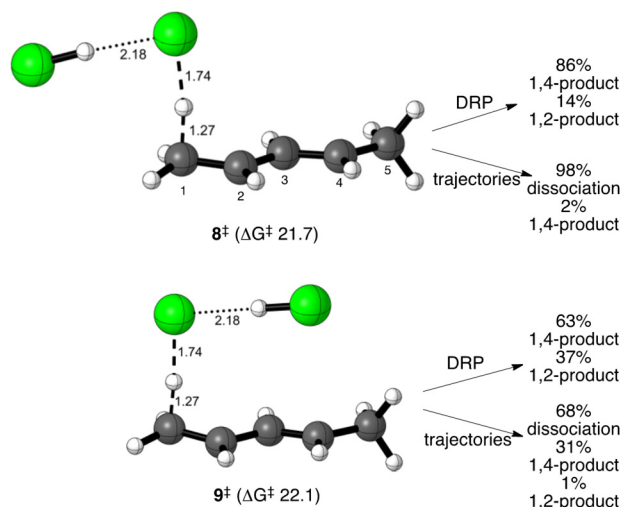
**Figure 29** A demonstrative image of 1,3-pentadiene and HCl immersed in 120 nitromethane molecules.

### *Implicit Solvation*

Transition structures were located in the various calculations for the protonation of 1,3-pentadiene by either one or two molecules of HCl. The lowest-energy structure **8**<sup>o</sup> is predicted to have a  $\Delta G^\ddagger$  of 21.7 kcal/mol at 25 °C and a  $\Delta H^\ddagger$  of only 9.1 kcal/mol. These barriers are consistent with the observation that these reactions occur experimentally at 25 °C. The implicit-solvent calculations thus appear satisfactory for the prediction of the barrier for the addition. However, they fail to account for the observed preponderance of the 1,2-addition product **2**. Two approaches were used to gauge the products from each transition structure.

The first was based on the dynamic reaction path (DRP) method,<sup>80,81</sup> with the variation that the DRP was calculated repeatedly with the addition of a Boltzmann-random amount of energy to the transition vector  $v^\ddagger$ . In the case of  $8^\ddagger$ , the outcome of the DRPs varied with the energy put into  $v^\ddagger$  with 86% 1,4-product and 14% 1,2-product. The alternative transition structure  $9^\ddagger$  is only modestly higher in energy and would contribute significantly to the product mixture. The DRPs from this structure lead consistently to the 1,4-product **3**. Neither prediction fits with the experimental preponderance of **2**.

For a more complete evaluation of the products that would be produced from  $8^\ddagger$  and  $9^\ddagger$  within the implicit solvent model, each was used as the starting point for quasiclassical direct-dynamics trajectories on the MP2/6-31+G\*\*/PCM surface. Each normal mode in the two structures was given its zero-point energy (ZPE) plus a randomized excitation energy based on a Boltzmann distribution, along with a randomized displacement of the modes. The trajectories were then propagated forward and backward in time until **2** or **3** was formed, the  $4^+/\text{ClHCl}^-$  ion pair dissociated (gauged by a minimum C–Cl distance of 5.0 Å), the starting materials were reformed, or a 500 fs time limit was reached. The outcome of these trajectories is summarized in Figure 30. In each case, dissociation of the ions predominated. When a neutral product was formed, it was predominantly the 1,4-product. Clearly, the implicit-solvent approach cannot account for experimental observations. Equivalent results were obtained with the SMD solvent model and in M06-2X/6-31+G\*\* calculations with both the PCM and SMD solvent models. As we observed previously in a study of the nitration of toluene,<sup>82</sup> implicit solvent models appear simply inadequate for the prediction of product mixtures that arise from the dynamics of ionic reactions in solution.

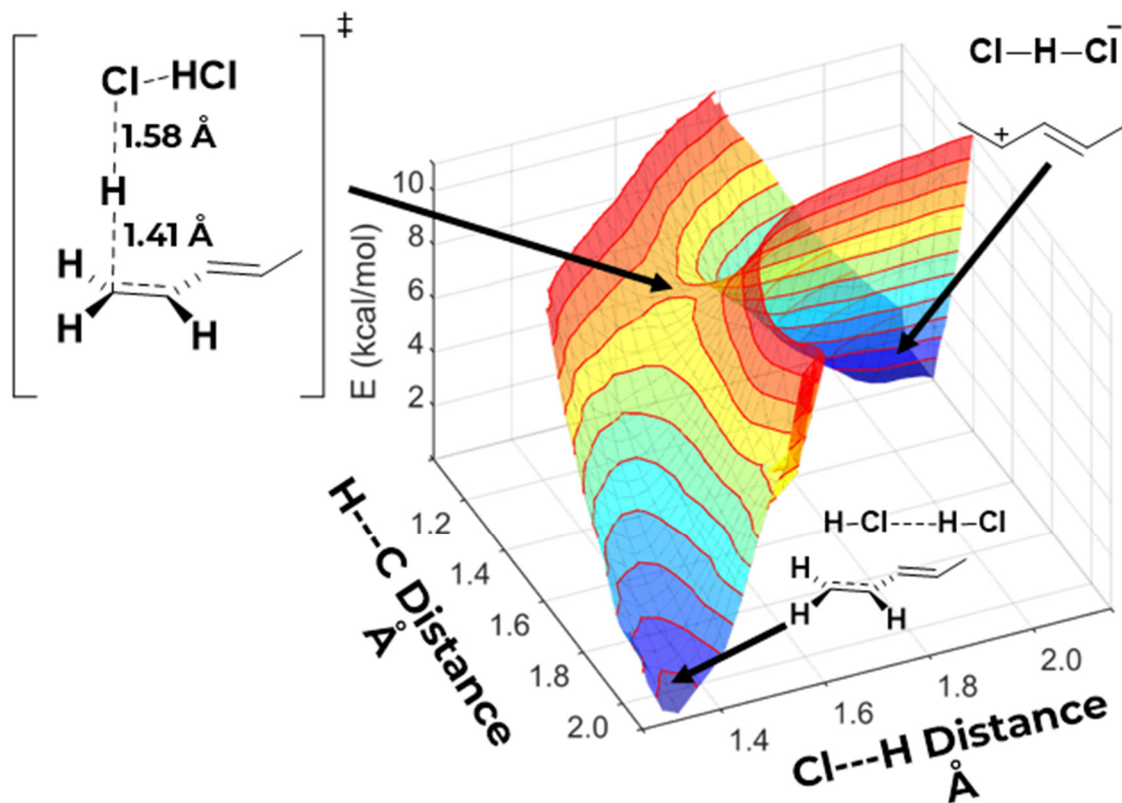


**Figure 30** The outcomes of several standard computational techniques in implicit solvent. Energies are given in kcal/mol.

### Potential of Mean Force Calculations in Explicit Solvent

For the reaction of MP2/6-31+G\*\* **1** with dimeric HCl in PM6D+H 120 nitromethane molecules, the 2-dimensional PMF surface for diene protonation along the C1---H and H---Cl distance dimensions was determined by umbrella sampling in molecular dynamics (MD) calculations over a total of 1.0 ns. The PMF was then calculated by the weighted histogram analysis method.<sup>83</sup> The resulting surface is shown in Figure 31; similar surfaces obtained in M06-2X calculations and for protonation by monomeric HCl are shown in the Section 2.6. A saddle point **10<sup>‡</sup>** on this surface has C1---H and H---Cl distances of approximately 1.29 and 1.68 Å, respectively. The saddle point in explicit solvent is then in reasonable agreement with the implicit-solvent transition structures  $8^\ddagger$  and  $9^\ddagger$ . By adding the free-energy cost of bringing the reactants together to form a pre-reactive complex in MP2/PCM calculations (6.8 kcal/mol) to the PMF barrier for reaching the saddle point (13.4 kcal/mol) from the area of this complex, a total reaction barrier of 20.2 kcal/mol may be

estimated. This barrier is then in good agreement with the implicit solvent calculations and experimental observations.



**Figure 31** PMF for the protonation of 1,3-pentadiene by (HCl)<sub>2</sub> in nitromethane.

### *Explicit Solvation*

By its nature, a PMF surface of this type is a dimensionally trivialized representation of a high-dimensional problem.<sup>84</sup> In this reaction, the unconstrained dimensions include both the motions of the second HCl molecule and the multitude of solvent motions associated with the protonation. The PMF saddle point then presents an incomplete and potentially

misleading picture of the reaction. Our analysis below of trajectories started from the area of  $10^{\ddagger}$  will examine the impact of these additional dimensions on the reaction.

### Trajectories in Explicit Solvent

The protonation of the diene and the subsequent 1,2- versus 1,4-product selectivity were explored in trajectory studies using the same 1,3-pentadiene / two-HCl / 120 nitromethane system as used for the PMF surface. The starting points for trajectories were obtained from a series of independent simulations that were equilibrated at 25 °C with the C1---H and H---Cl distances constrained in the area of  $10^{\ddagger}$  by a harmonic potential. At intervals of 250 fs, structures and velocities were extracted from the equilibrating systems and integrated forward and backward in time with no constraint. For clarity later, we define ‘forward in time’ as the direction in which the transferring proton moves closer to C1 of the diene. The trajectories were then stopped when the products **2** or **3** were formed, the starting materials were re-formed, a time limit of 3000 fs was reached, or the Cl---HCl anion / pentadienyl cation tight ion pair dissociated. Dissociation was defined by the chlorides being  $>5$  Å separated from the cationic carbons. The 5 Å criterion was chosen to delineate approximately the formation of a solvent-separated ion pair.<sup>85</sup>

The trajectories of interest for understanding the rate and selectivity in this reaction are those that fully traverse the protonation transition state, passing from the starting materials to form the pentadienyl cation. We refer to such trajectories as “productive.” An expected but important observation for later analysis is that only a small proportion of the trajectories (22%) started from the area of  $10^{\ddagger}$  are productive. The remainder are recrossing trajectories, passing either from starting materials to starting materials (“SM-SM”, 46%) or

between the differing outcomes (**2, 3**, ion dissociation, time-limited ion pair) on the product-side of **10<sup>3</sup>** (“product-product”, 32%).

### **Comparison with Experiment. Redetermination of the Product Ratio**

A critical issue was whether the explicit-solvent trajectories could account for the experimental product ratio. The productive trajectories include those forming the 1,2- and 1,4-products with either of the two chloride anions along with trajectories that result in dissociation of the ion pair and those reaching the time limit as an associated tight ion pair. Table 2 summarizes the results from trajectories with either MP2 or M06-2X employed as the high-level component of the ONIOM calculations. To predict the product ratio from these results, we make the assumption that the dissociating and time-limited trajectories would ultimately form equal amounts of 1,2 and 1,4 products. The expectation that dissociated ions will reassociate randomly seems evident, but the disposition of the long-lived tight ion pairs will require further consideration below. Allowing for the mixture of products from these trajectories leads to predictions of 77% 1,2-product from the MP2 ONIOM simulation and 69% 1,2-product from the M06-2X ONIOM. The full trajectory count is given below (Table 2).

**Table 2** Trajectory outcomes for ONIOM simulations in explicit solvent.

	MP2 ONIOM	M06-2X ONIOM
% productive	22%	16%
1,2-product	265	94
1,4-product	5	13
dissociation of ions	77	66
ion pair reaches time limit	128	41
predicted % 1,2-product <sup>a</sup>	77% ± 2%	69% ± 3%
	experimental 68%	1,2 selectivity (Nordlander)
	74% ± 2% (this work)	

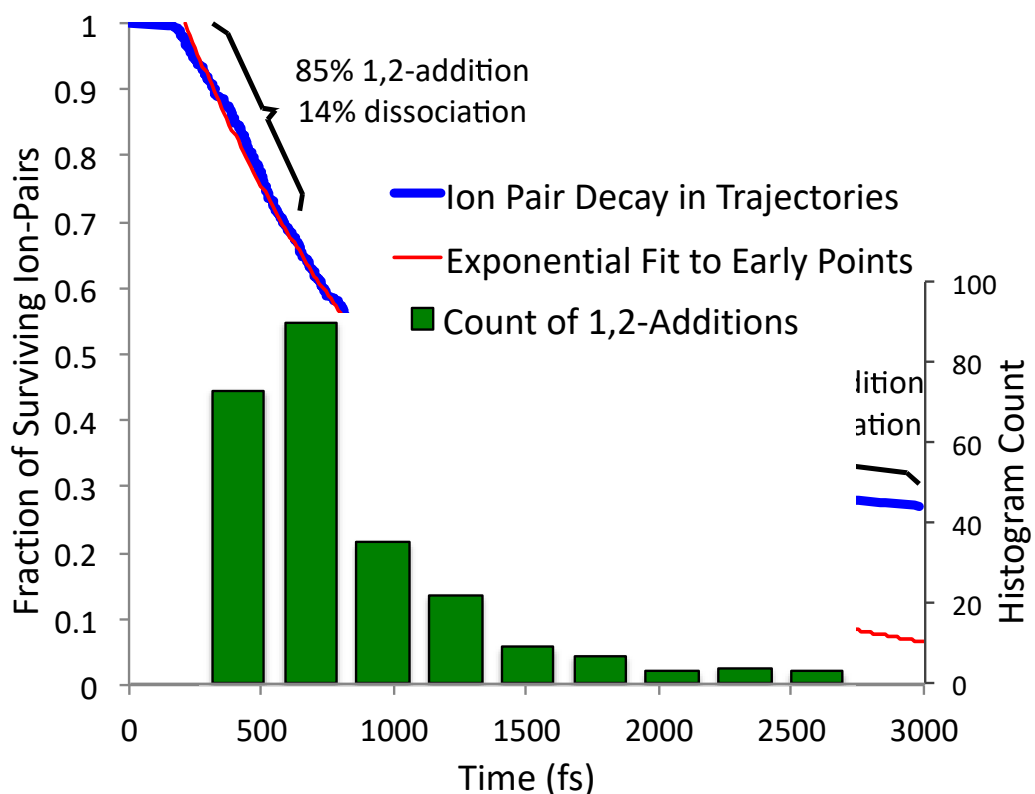
The limited number of solvent molecules and the under-estimation of their polarizability in the ONIOM method employed are significant limitations in the computational models. However, their ability to accurately account for the product selectivity supports the necessity and adequacy of the ONIOM models for understanding the origin of the 1,2-selectivity in these reactions.

### The Multi-Stage Nature of Product Formation

The productive trajectories exhibit two striking features. The first of these is that very few trajectories afford the 1,4-product within the 3000 fs time limit. Only five of the MP2 ONIOM trajectories form the 1,4-product, and two of these involve initial geometries that place the second HCl molecule in a position that is favorable for its chloride to attack C<sub>4</sub> of the diene, leading to product derived from the distal chloride. The low formation of 1,4-product might be understandable if 1,2- and 1,4-ion pairs rarely interconvert, but in fact ion-pair equilibration happens routinely. The ion pairs in trajectories that last to the time limit of 3000 fs undergo isomerization, defined by a switch in whether C<sub>2</sub> versus C<sub>4</sub> is closest to a chloride atom, an average of six times (median of four). This observation supports our

assumption above that the time-limited ion pairs will afford equal amounts of 1,2 and 1,4 products. Equilibration, however, does not lead to much 1,4-product formation within 3000 fs. Instead, the trajectories that last long enough to undergo ion-pair equilibration rarely form either product at all!

This leads to the most intriguing observation for the trajectories, which is that product formation at first occurs rapidly then nearly stops. Half of all of the observed product formation occurs within the first 640 fs, 75% within 1000 fs, and 90% within 1500 fs (Figure 32). Although 50% of the ion pairs survive to 1000 fs, any subsequent product formation is slow and progressively slower, with dissociation of the ions becoming their major decay route.



**Figure 32** The survival curve for MP2 trajectories in explicit nitromethane solvent.



The plot of the fraction of surviving ion pairs versus time after release from the area of  $\mathbf{10}^\ddagger$  in Figure 32 can be divided into three phases. The first is a lag time of approximately 200 fs, required for completion of the proton transfer (see the discussion later) and for the chloride of the HCl performing the protonation to approach C<sub>2</sub> of the diene from a median starting separation of  $\sim 3.6$  Å, requiring a relative motion of  $\sim 1.8$  Å. The second phase involves the rapid decay of ion pairs as chloride attack at C<sub>2</sub> occurs. Dissociation of ions is a minor pathway in this time regime, but it is notable that, like the 1,2-addition, the dissociation process also involves an initial rapid phase. The third phase of ion pair decay is slow, far slower than the illustrated exponential decay fit to the first 800 fs. A double-exponential fit of the data found nominal rate constants of  $1.8 \times 10^{12} \text{ s}^{-1}$  ( $\pm \sim 15\%$ ) and  $1.3 \times 10^{11} \text{ s}^{-1}$  ( $\pm \sim 30\%$ ), with the slow phase roughly thirteen times slower than the rapid-decay phase. Qualitatively, the decay of the tight ion pairs is similar to what might be observed if the protonation step formed two distinct species that react at different rates.

To understand this dichotomous behavior of the trajectories, we examine in more detail the role of the solvent in these reactions. This starts with an examination of how the solvent impacts which trajectories are productive.

### **Solvation Dictates Productive Trajectories**

Only 22% of the trajectories initiated from  $\mathbf{10}^\ddagger$  were productive. The idealized expectation arising from the ‘no-recrossing’ assumption of conventional transition state theory is that trajectories initiated from a transition state and propagated forward and backward in time will all be productive. In practice this does not happen for any modestly complex reaction, even for gas-phase simulations, but trajectory simulations of simple organic reactions started from a well-defined transition state often result in greater than 90%

productive trajectories. An alternative possibility for consideration is that the outcome of the forward and backward branches of trajectories could be independent of each other. If the outcome of each branch were fully random, ~50% would be productive (49% for the observed excess of SM-SM trajectories). The much lower proportion of productive trajectories observed here excludes a random outcome. Instead, there is specific preference for recrossing.

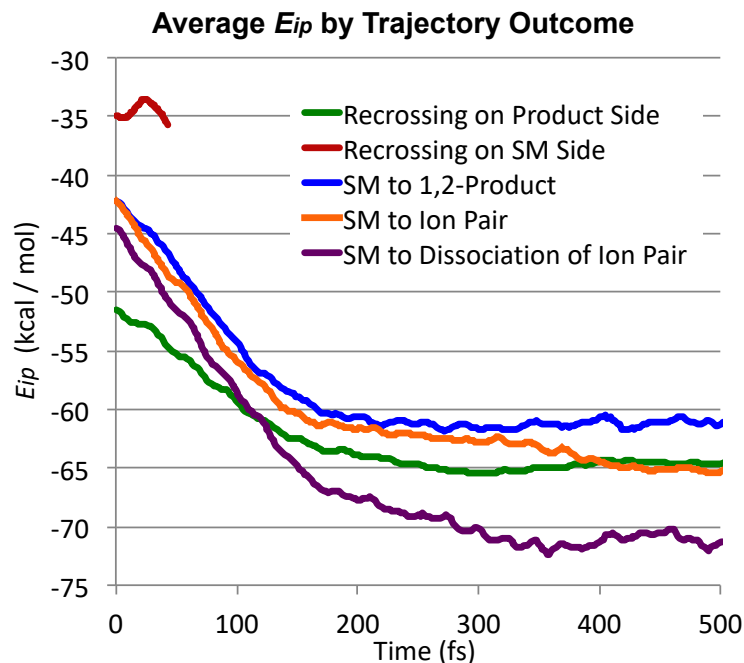
This is unsurprising, especially for a polar reaction in a polar solvent.<sup>86,87</sup> The starting points for trajectories have controlled only two dimensions of a high-dimensional transition state. The many uncontrolled dimensions when starting from  $10^\ddagger$  can readily take on values that displace the trajectory starting points away from the actual transition states. The uncontrolled dimensions then serve as a gate that enforces recrossing most of the time but allows a productive trajectory when these dimensions have values in the area of a true high-dimensional transition state.

This idea is well established but vague. We therefore sought to uncover what aspects of the trajectory starting points dictated whether they were productive versus recrossing. We first explored whether dimensions internal to  $10^\ddagger$ , such as the orientation of the second HCl molecule or the particular starting distances a, b, c, and d affected the likelihood of a trajectory being productive. Within a broad range, the effect of these internal dimensions was minor (see Section 2.6).

The initial orientation of the solvent however had a major effect on the productivity of trajectories and their outcome on the product-side of the transition state. To evaluate the role of solvent, we defined an “incipient ion-pair stabilization parameter”  $E_{ip}$  for each point in the trajectories. The  $E_{ip}$  value, defined by eq 3, represents the hypothetical electrostatic

stabilization that would be present if the solvent atoms were atomic point charges (using equilibrium M06-2X/6-31+G\*\*/MK charges, chosen based on dipole-moment accuracy) and if the solute atoms took on the charges calculated for separated pentenyl cation and [ClHCl]<sup>-</sup> anion (see Section 2.6 for calculational procedures and congruent results obtained by alternative approaches). The  $E_{ip}$  then represents the degree to which the solvent would electrostatically stabilize the protonation of **1** to form an ion pair or the continued presence of the ion pair. An  $E_{ip}$  near zero would mean that the solvent is randomly oriented and unable to stabilize an ion pair, while an  $E_{ip}$  of approximately -72 kcal/mol is the maximum average stabilization of full ion pairs by the solvent. It should be noted that structures in the area of  $10^{\ddagger}$  have taken on only approximately 55% of the charge separation present in the ultimate ion pair (based on MK charges for **8<sup>‡</sup>**). The average starting-point  $E_{ip}$  for all trajectories reflects this partial charge separation, being -39 kcal/mol or a little more than half of the maximum.

A key observation is that the initial  $E_{ip}$  was associated strongly with the outcome of trajectories (Figure 33). For trajectories that underwent recrossing on the starting-material side of the transition state, the average initial  $E_{ip}$  was only -34.9 kcal/mol. This shows that the solvent was on average not well disposed to stabilize the charge separation that would result from proton transfer. Trajectories released from **10<sup>‡</sup>** would take an initial step toward ion-pair formation but the proton transfer could not be completed in trajectories with a low initial  $E_{ip}$ .



**Figure 33** Plots of the average values for the incipient ion-pair stabilization parameter  $E_{ip}$  versus time for trajectories with differing outcomes. For each trajectory, the  $E_{ip}$  was only followed “forward in time”, defined as the direction in which the initial motion of the proton transfer was toward  $C_1$  of the diene.

In contrast, trajectories that underwent recrossing on the product side of the transition state were associated with a high initial  $E_{ip}$  of -51.5 kcal/mol. In these cases, the solvent is initially arranged to strongly stabilize charge separation, making it energetically disfavored for the trajectories to revert to the starting materials. In either case, solvent reorganization simply takes too much time to allow the transition state to be crossed. In Hynes theory the relevant time scale is the longitudinal dielectric solvent relaxation time,  $\tau_L$ .<sup>88,89</sup> The  $\tau_L$  for nitromethane is ~400 fs at 25 °C,<sup>90</sup> and the average decay of  $E_{ip}$  in Figure 33 appears to reflect this reasonably.<sup>91</sup>

The productive trajectories are associated with a “Goldilocks” level of initial electrostatic stabilization of charge separation, with  $E_{ip}$  averaging -42.2 kcal/mol. The

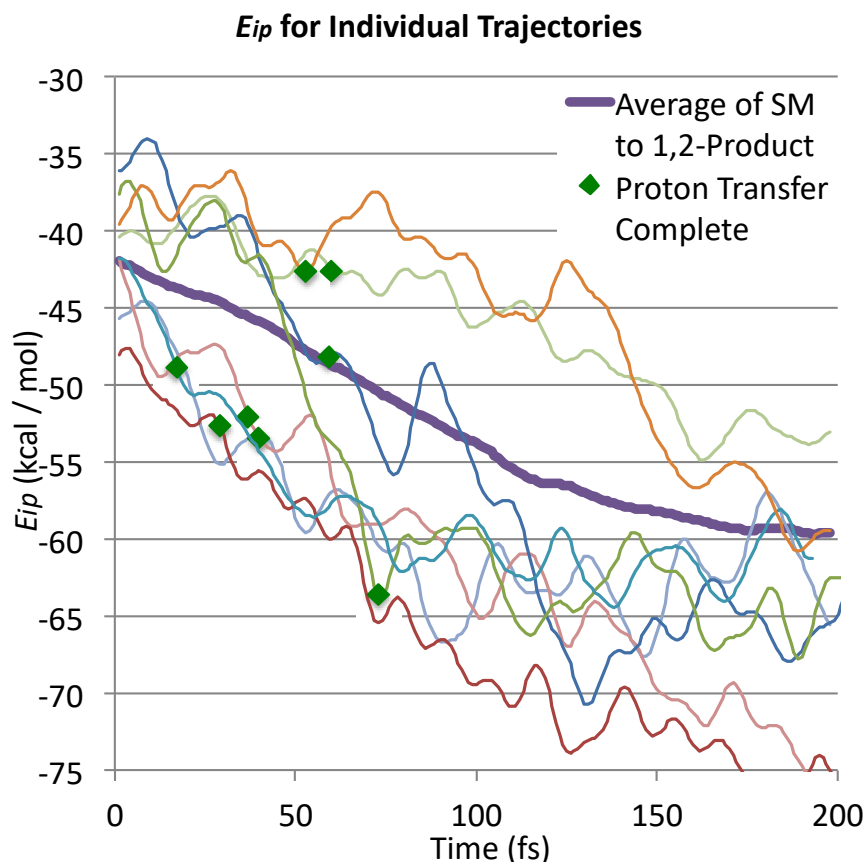
middle range of  $E_{ip}$  appears to provide an energetic balance between reversion to starting material and completing protonation to form the ion pair. This allows trajectories to traverse from one realm to the other.

The time course of the  $E_{ip}$  followed forward in time from  $\mathbf{10}^\ddagger$  also bears an intriguing relationship with the choice of outcomes among productive trajectories. In trajectories that result in ion-pair dissociation, the  $E_{ip}$  rapidly drops to near its terminal value (Figure 33, purple line), indicating that the solvent has become organized to optimally stabilize the separating ions. The solvent organization appears to be a cause, rather than an effect of dissociation, because the greater  $E_{ip}$  shows up in the first 200 fs while the median time for dissociation is 1020 fs. Trajectories that ultimately form the 1,2-product in contrast exhibit a much smaller stabilization of the ion pair (Figure 33, blue line). In such trajectories, the solvent is never fully organized to stabilize an ion pair. The ions are formed in a relatively non-stabilizing “electrostatic hole” in the solvent, then spend their first few hundred femtoseconds pushed toward tight association by this low stabilization. Within 1000 fs, three-quarters of these ion pairs annihilate.

The curves in Figure 33 represent averages of large numbers of trajectories, while individual trajectories vary. The standard deviation for the initial  $E_{ip}$  in each category is  $\sim 7$  kcal/mol. The categories then overlap, but the solvent orientation as gauged by  $E_{ip}$  is a strong predictor of individual trajectory outcomes. For example, a trajectory with a starting  $E_{ip}$  of -51.5 has a 33-fold greater chance of undergoing product-side recrossing than a trajectory with a starting  $E_{ip}$  of -34.9.

Another way in which the solvation influences the reaction in the area of the proton transfer can be seen when individual trajectories are examined. Figure 34 shows the early

time course of the  $E_{ip}$  for a series of 1,2-product forming trajectories with completion times of  $\sim 700$  fs. As the trajectories leave the area of the transition state, the solvation slowly changes in the direction of greater stabilization of the forming ion pair. The proton transfer itself, however, is remarkably slow. To assess this, we examined the time required for the bottom of the proton's energy well, as judged by the forces on the proton, to be at a distance from C1 that is less than 1.14 Å. (It would be misleading to examine the proton position by itself, since it vibrates broadly within its energy well.) Figure 34 shows these proton-transfer completion points on each trajectory, and the median time after release from the TS was  $\sim 50$  fs. For comparison, an ordinary C-H vibration takes  $\sim 11$  fs and moves a proton an equivalent distance within 6 fs. Completion of the proton transfer requires that the solvation first energetically allow it by reorganizing to stabilize the forming ion pair. This takes time, so the simple proton transfer is a surprisingly plodding process.



**Figure 34** Plots of the incipient ion-pair stabilization parameter  $E_{ip}$  versus time for individual productive trajectories.

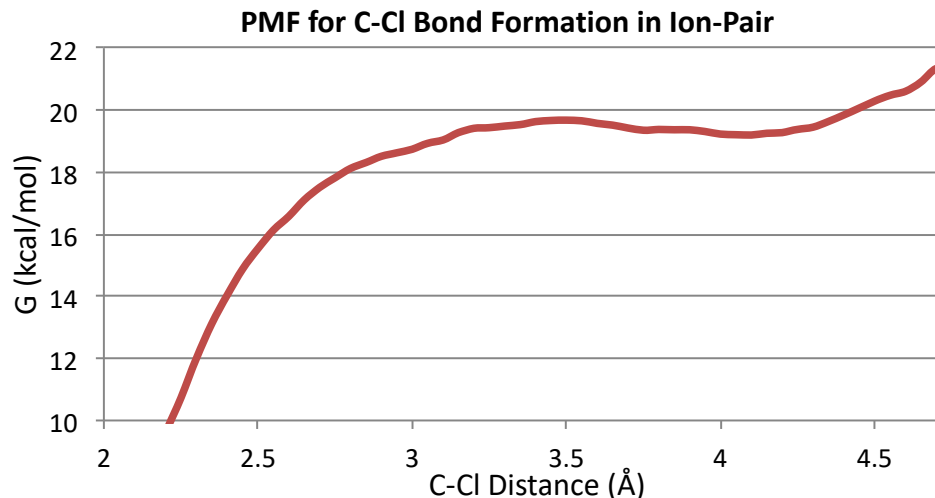
### Is There An Intermediate?

The term “intermediate” can be misleading when applied to the ion-pair structures that are formed after the proton transfer step. An intermediate is defined by IUPAC as a molecular entity in a mechanism that has a lifetime that is “appreciably longer than a molecular vibration” and corresponds to a “local potential energy minimum.” With minimum and median lifetimes of  $\sim 200$  and  $\sim 1000$  fs, the ion pairs are sufficiently long-

lived to be considered intermediates, but whether they exist within energy minima is a more complicated problem on multiple levels. We have argued previously that free energy is more appropriate than potential energy as a defining feature for intermediates.<sup>23</sup> We will follow that definition here, and a species that exists for an extended time in a free-energy well will be described as a “true” intermediate. It should be recognized that free energy is an equilibrium concept that is not rigorously definable at sufficiently short time scales.

To explore the equilibrium free-energy landscape available to the  $4^+$  / ClHCl<sup>-</sup> ion-pair structures, a one-dimensional PMF surface based on the C---Cl distance was determined by umbrella sampling in MD calculations over a total of ~1 ns. The complication that either C<sub>2</sub> or C<sub>4</sub> may undergo bond formation with either of the two chlorine atoms was handled by an interlocking-sphere algorithm,<sup>82</sup> (see Section 2.6) so that the PMF obtained (Figure 35) applies to the shortest of the four relevant C---Cl distances. The PMF has a notable broad minimum at a C---Cl distance of ~4.1 Å. This supports the potential existence of a true intermediate in the system, which we will describe as the “solvent-equilibrated ion pair.” To form the neutral product, the solvent-equilibrated ion pair must surmount a small barrier in the PMF, only 0.5 kcal/mol, to pass through a transition state with a C---Cl distance of 3.5 Å. The ~20 kcal/mol barrier for formation of the solvent-equilibrated ion pair from product is notably in good agreement with the experimental observation that a slow product isomerization occurs at 25 °C.



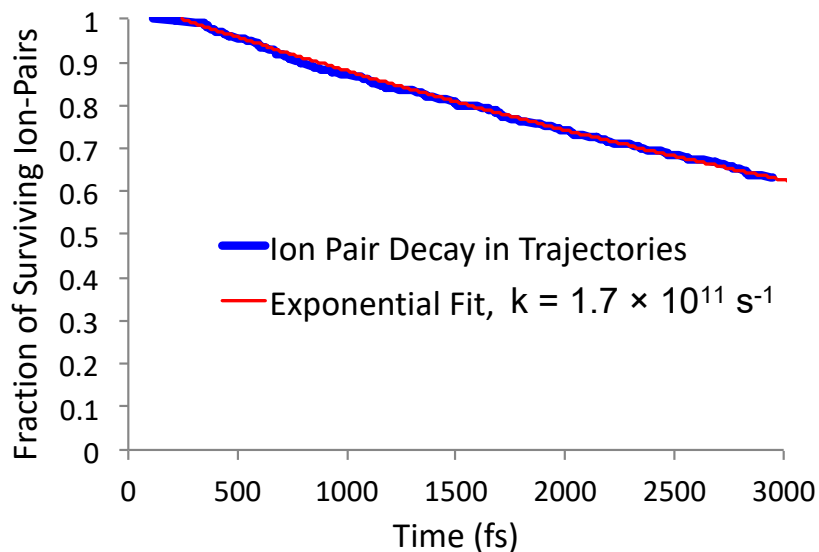


**Figure 35** QM/QM' PMF for the approach of a chloride ion to either C<sub>2</sub> or C<sub>4</sub> of **4**<sup>+</sup> in explicit nitromethane. The energy scale is relative to a minimum on the surface at  $1.85 \pm 0.025$  Å.

The trajectory behavior of solvent-equilibrated ion pairs. The existence of a true intermediate in the system leaves open the question of whether addition pathways actually pass through the intermediate, or alternatively bypass it. To gauge this issue, we studied the behavior of trajectories initiated from the area of the solvent-equilibrated ion pair. The starting points for trajectories were obtained from a series of independent simulations that were equilibrated at 25 °C with the C---Cl distances constrained in the area of the intermediate by a harmonic potential. At intervals of 250 fs, structures and velocities were extracted from the equilibrating systems and integrated forward in time with no constraint. As shown in Figure 36, the resulting trajectories decayed slowly with time to a mixture of the addition product and dissociated ions, but 63% of the solvent-equilibrated ion pairs survive to the time limit of 3000 fs.

The decay fit well with a single exponential with a rate constant of  $1.7 \times 10^{11} \text{ s}^{-1}$  (Figure 36). This may be compared with the  $1.3 \times 10^{11} \text{ s}^{-1}$  observed above for the slower

phase of the double-exponential decay of the original trajectories. Allowing for the uncertainty in each number, particularly the latter due to the double-exponential fitting, the two rate constants are indistinguishable. This agreement supports the idea that the slower phase of the decay of the ion pairs formed on protonation of **1** results from the reaction of species that approximate solvent-equilibrated ion pairs.



**Figure 36** Decay of solvent-equilibrated ion-pairs, and an exponential fit.

### A Consistent Mechanism

The observation in the last section, in combination with the strong and time-dependent effect of solvation in stabilizing the formal ion pairs, supports a mechanism that may be viewed as the combination of two limiting prototypes. At one extreme, the solvation-gated protonation of **1** through **10<sup>‡</sup>** leads in time to solvent-equilibrated ion pairs. Such ion pairs slowly form the addition product in competition with dissociation, and they are representatively viewed as intermediates within the conventional ideas of mechanistic

chemistry. These intermediates have time to geometrically equilibrate, or dissociate, and lead to a mixture of 1,2- and 1,4-addition products by passage over barriers.

At the opposite extreme, the protonation of **1** through **10<sup>‡</sup>** leads to a formal ion pair that is neither fully solvated nor becomes so quickly. The prevalence of such “holes” in the solvation for ion pairs at their creation may be understood from two perspectives. The first is to recognize that the transition state for protonation is not as polar as the ion pair, so solvation that is approximately optimized for the protonation process will not be so for the resulting ion pair. The second perspective is that solvation that strongly stabilizes the ion pair promotes recrossing trajectories, not reactive trajectories. At this extreme, the ion pairs afford the product ~13 times faster than the solvent-equilibrated ion pairs. These ion pairs exist only on the slope of a notional free energy surface that leads inexorably to exclusively 1,2-product formation. This does not make the adduct formation instantaneous; as we have seen previously with nitration reactions, the trajectories of barrierless reactions can proceed slowly as they await solvent reorganization.<sup>82</sup> However, the absence of a barrier for their reaction, or equilibrated solvation as they decay, makes their consideration as conventional mechanistic intermediates misleading.

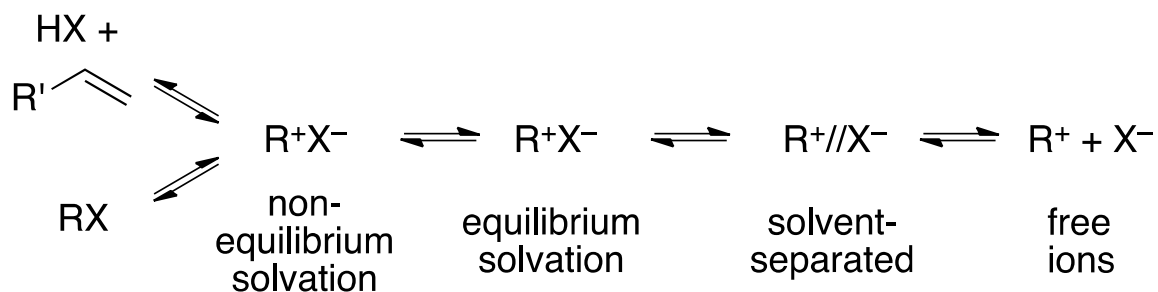
These extremes are likely an incomplete description. The initial  $E_{ip}$  for reactive trajectories is not bimodal, but rather approximates a normal distribution. Ion pairs are formed with a range of solvent stabilizations (with a  $\sigma$  of ~7 kcal/mol) but none have an initial  $E_{ip}$  that is very close to equilibrium. Then, as illustrated in Figure 34, all of the ion pairs tend to show an increase in their solvation over time, at varying rates. The ion-pair decay of Figure 32 was modeled using two exponentials that can be taken as representing the two limiting pathways, but this cannot be cleanly distinguished from a continuum.

A closely analogous mechanism would provide a consistent explanation for *syn* selectivity in the addition of DCl to 5. We would suggest that the protonation step can lead to, at one extreme, a weakly solvated ion pair that collapses without barrier to the major *syn* addition product 7, and, at the other extreme, a highly solvated ion pair that may dissociate or isomerize to afford a mixture of *syn* and *anti* addition products. In this regard, it is notable that the *syn* selectivity with 5 and the 1,2-selectivity with 1 are similar.

## 2.4 Conclusions

The trajectory studies in explicit solvent accurately account for the 1,2 versus 1,4 product selectivity in the addition of DCl to piperylene in nitromethane. In this way, they provide an experimentally consistent model for the mechanism of the reaction, one that differs in fundamental ways from the conventional mechanism. The protonation of the diene is gated by the solvent: solute geometries that nominally appear to be in the area of the transition state mainly lead to recrossing trajectories unless the solvent's ability to stabilize the incipient ion pair is neither too high nor too low.

After the protonation, the solvation of the resulting ion-pairs is not at equilibrium, and equilibrium solvation is on average approached over the course of a few hundred femtoseconds. The ion pairs decay to the product by two limiting processes. The faster of these leads exclusively to the 1,2-addition product, and its rate is inconsistent with that seen after fully equilibrated solvation. The slower decay is at a rate that cannot be distinguished from that of equilibrated ion pairs, and this lower rate appears associated with a barrier that is observed on the PMF surface. These ion pairs lead to a mixture of 1,2 and 1,4 products.

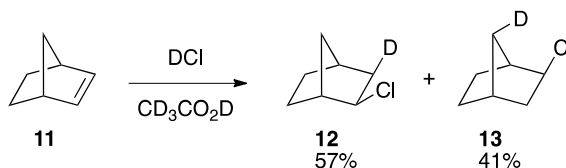


These results suggest a modification of the classical Winstein formulation of the role of ion pairs in carbocation reactions. That is, the tight ion pairs that are produced in ordinary carbocation reactions are initially formed with nonequilibrium solvation, and these species may react differently from solvent-equilibrated ion pairs. Their partitioning between subsequent pathways in particular may not be decided by relative free energy barriers. Whether or not such ion pairs are designated as “intermediates,” their evolution is akin to that of molecules on the slopes of bifurcating energy surfaces.<sup>3,6,93,94,7,10,23,39-41,43,92</sup> With time, these species may lead to tight ion pairs whose solvation is at equilibrium. It then becomes meaningful to describe the ion pair as having a well-defined free energy and having well-defined rates and free energy barriers for its subsequent reactions. As discussed in the introduction for other dynamic effects, the key factor distinguishing these possibilities is time. When the lifetime of an ion pair exceeds a few picoseconds, as is generally true for highly stabilized carbocations, then its internal energy and solvation will reach equilibrium. The conventional Winstein formulation may then apply fully. When the carbocations have shorter lifetimes, the physical reality is just more complex.

We would suggest that this expanded description of ion pairs accounts for many observations in the literature, observations that otherwise appear shoehorned into mechanistic models not considering dynamic effects. We briefly describe here a series of

examples. This is unavoidably speculative, but suggestive of experimental and computational studies that could assess the role of solvation dynamics in fundamental aspects of carbocation reactions.

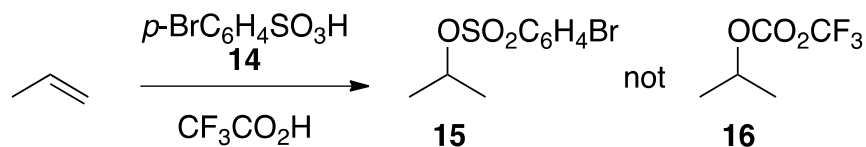
A historically notable example is the addition of DCl to norbornene (**11**). In Brown's hands, this reaction did not give an equal mixture of nonrearranged product **12** and rearranged product **13**,<sup>95</sup> despite extensive evidence that the intermediate "2-norbornyl" cation itself is nonclassical with  $C_s$  symmetry. Our own results call this experimental ratio into question. Nordlander had attempted to explain this observation based on the equilibrating ion-pair ideas that he had used to account for observations with **1**, but the structure and nature of the requisite unsymmetrical but equilibrating ion pair intermediates was nebulous. The experimental observations in fact merely require that the initial positioning of the chloride ion and surrounding solvent molecules be unsymmetrical, as will necessarily follow from the protonation transition state, and that a portion of the initial ion pairs react rapidly before achieving equilibrium solvation. As we have recently shown in another context,<sup>96</sup> when product selectivity is decided without barrier, initial asymmetry in structure readily leads to unequal amounts of otherwise equivalent products.



**Figure 37** Experimental results from Brown *et al.*

A broader if less notorious historical controversy was regarding the origin of  $S_N1$  rate accelerations in nucleophilic solvents and the role of nucleophilic solvation (né

nucleophilic solvent participation<sup>97,98</sup>) versus reversible ionization and “hidden return” of ion pairs.<sup>99,100</sup> A preponderance of data has favored the importance of nucleophilic solvation, at least for secondary substrates, but aspects of the complex debate long persisted.<sup>101</sup> An early lynchpin observation by Shiner, appearing to strongly favor the importance of hidden return, was that the addition of 4-bromobenzenesulfonic acid (**14**) to propene in trifluoroacetic acid affords the isopropyl brosylate **15** instead of the isopropyl trifluoroacetate **16** adduct from solvent (Figure 38).<sup>102</sup> Shiner argued that since the tight ion pair arising from the protonation predominantly collapses to **15** instead of reacting with solvent, then the S<sub>N</sub>1 reaction of **15** must involve a rate-limiting step that is later than formation of the tight ion pair, and so at the formation of a solvent-separated ion pair.



**Figure 38** Reaction product of propene and brosic acid in trifluoroacetic acid.

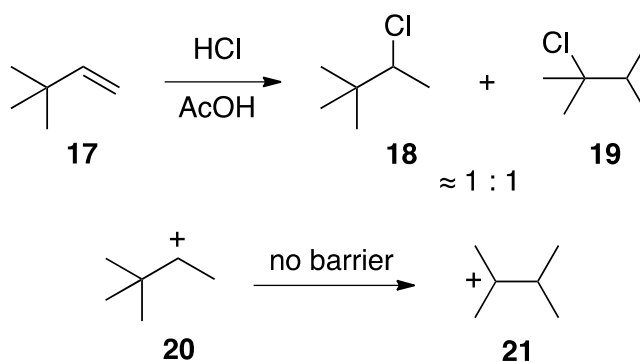
This idea influenced the interpretation of a substantial history of observations.<sup>103–105</sup> The flaw in this argument, as suggested by the present work, is the assumption that there is only one tight ion pair operative in the system. We would suggest that a nonequilibrium solvated ion pair is initially formed from protonation of propene by **14**, and that this ion pair rapidly collapses to **15**. This then undercuts the original support for the importance of solvent-separated ion pairs in the solvolysis of **15** and other secondary systems.<sup>103–105</sup>

We would note that in both of the above controversies, the ultimately disfavored side was supported by observations that could not have been comfortably interpreted otherwise

employing the ideas available at the time. The expansion of ideas to include a role for solvation dynamics then allows explanations that do not conflict with the prevailing view.

Undergraduate organic chemistry textbooks routinely describe the rearrangements of secondary carbocations to tertiary cations that accompany the additions of acids to alkenes.<sup>62</sup> A notable aspect of these rearrangements, exemplified by Fahey's study of the addition of HCl to *tert*-butylethylene (**17**),<sup>69</sup> is that mixtures of nonrearranged and rearranged products (e.g., **18** and **19**) are often produced in acetic (Figure 39). This becomes surprising when it is recognized that there is no calculated barrier for the highly exothermic conversion of **20** to **21**,<sup>106,107</sup> as is typical for secondary to tertiary rearrangements. The cation **20** can only exist dynamically for a short time, with simulations placing the median lifetime at around 300 fs.<sup>107</sup> This is seen again in Pocker's study in nitromethane (1:4 ratio of **18:19**) and our study in dichloromethane. If these reactions involved only solvent-equilibrated ion pairs with lifetimes crudely on the order of that seen for solvent-equilibrated ion pairs here, then significant amounts of unrearranged products could not be formed. We would suggest that these reactions may initially form nonequilibrium solvated ion pairs that react rapidly to mainly afford unrearranged products, then mainly afford rearranged products as solvent-equilibrated ion pairs arise and the ion-pair lifetimes increase. The mixture of products would then be decided dynamically on a bifurcating surface rather than representing the crossing of competing barriers.

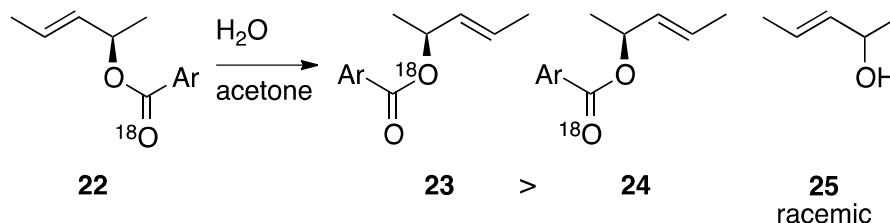




**Figure 39** The reaction of the *tert*-butylethylene with HCl in acetic acid shows formation of a secondary alkyl halide product.

$S_N1$  reactions of RX have often exhibited a striking memory effect when the nature of their ion pairs has been probed. That is, studies of  $^{18}\text{O}$  or  $^{17}\text{O}$  isotopic equilibration and racemization or allylic transposition in recovered reactants have evidenced a definable structure in the ion pairs. The detailed observation varies: sometimes allylic transposition or racemization occurs faster than isotopic equilibration,<sup>108-111</sup> sometimes the reverse is true,<sup>112</sup> sometimes the transposition is accompanied by bond formation to a new oxygen,<sup>108,109</sup> sometimes preferentially to the original oxygen.<sup>111,113</sup> A prominent example occurs in the solvolysis of 2-norbornyl brosylate, where racemization is faster than  $^{17}\text{O}$  exchange.<sup>111</sup> Another example is the solvolysis of **22**, in which racemization from formation of **23** is faster than  $^{18}\text{O}$  equilibration by formation of **24** (Figure 40). This suggests that the ion pairs are very short-lived. In contrast, the products in these reactions, as in 2-norbornyl solvolyses or the formation of **25**, have generally lost all memory of the original structure.<sup>108-112,114</sup> A possible economical explanation for the contrasting features of these reactions is that the return to isomerized reactant involves a short-lived nonequilibrium solvated ion pair, while product formation involves longer-lived equilibrium ion pairs. As is consistent with this idea,

changes in solvent polarity (either by changing the solvent or by adding salts) have a larger effect on the rate of product formation than on isomerization or isotopic equilibration.<sup>108,109,112</sup>



**Figure 40** Isotope scrambling experiments were evidence for Shiner’s concept of “hidden return”.

The era of carbocation chemistry in the twentieth century featured some of the most elegant experiments in chemical history, experiments that defined subtle features of these very complex mechanisms but that occasionally led to conflicting interpretations. We view it as probable that some misinterpretations and conflicts arose from the assumed foundational idea that a reaction mechanism in solution is fully defined by its sequence of intermediates and transition states. This then led to the implicit expectation that identical solute structures should behave identically, and the corollary that differing behavior implied differing intermediates. The nature of an intermediate and its subsequent reactions will however depend on its solvation and its dynamics, which in turn depends of how the intermediate was prepared<sup>115</sup> and its lifetime. The results here show that this can have a substantial effect on observations for short-lived cations, suggesting the need for some modern reconsideration of the results from the era.

## 2.5 Experimental Procedures

### *General Methods*

Nitromethane was dried over activated 4 Å molecular sieves. DCI was prepared by the method of Brown and Groot.<sup>116</sup> Solutions of DCI in nitromethane were freshly prepared and titrated by dilution of an aliquot with excess water and titration using phenolphthalein as indicator. Norbornene from Oakwood Chemical was used without purification. <sup>1</sup>H NMR spectra were taken at 500 MHz and <sup>13</sup>C NMR spectra were taken at 125.7 MHz.

### *Reaction of 1-methylcyclopentene with DCI*

To mimic the conditions of Pocker and Stevens,<sup>65</sup> a mixture of 28.57 mL of 1.4 M DCI in nitromethane (40 mmol of HCl), 10 mL of additional nitromethane, and 5.27 mL (4.11 g, 50 mmol) of 1-methylcyclopentene was diluted to a total volume of 50.0 mL and stirred at 25 °C for 26 h. The reaction mixture was then diluted with 200 mL of 10% by weight NaCl in water, then the organic phase was rinsed with three 100-mL portions of 5% NaHCO<sub>3</sub>. The organic layer was then dried (Na<sub>2</sub>SO<sub>4</sub>), and partially distilled by vacuum transfer to remove additional nitromethane. The residual liquid, including 1-chloro-2-deutero-1-methylcyclopentane (6 and 7 in main text) contaminated with traces of nitromethane, was analyzed by NMR without further purification.

### *Reaction of Cyclopentene with DCI*

13.62 mL of 1.89M DCI (25.8 mmol) in AcOD was added to the flask, followed by 1.13 mL (12.9 mmol) of cyclopentene. The reaction flask was quickly filled to the mark with AcOD, a small stirbar was added. Once sealed with a glass stopper, the flask was inverted several times and allowed to stir on a magnetic stirrer. After two days, the reaction mixture was separated with 100ml of pentane and 100 mL of 10% by weight NaCl in water. The

organic phase was rinsed with three 50-mL portions of 5% NaHCO<sub>3</sub> and dried over Na<sub>2</sub>SO<sub>4</sub>. The reaction mixture was concentrated in vacuo. About ~150 mg of sample was used for NMR analysis in d<sub>6</sub>-benzene.

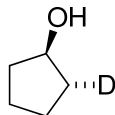
*Reaction of Cyclopentene with DCl and Tetramethylammonium Chloride*

1.1618 grams (10.6 mmol) of tetramethylammonium chloride was dissolved in 8.2 ml of AcOD and the mixture was placed into a 25 mL volumetric flask. 7.67 mL of 1.89M DCl (14.5 mmol) in AcOD was added to the flask, followed by 1.30 mL (14.6 mmol) of cyclopentene. The reaction flask was quickly filled to the mark with AcOD, a small stirbar was added. Once sealed with a glass stopper, the flask was inverted several times and allowed to stir on a magnetic stirrer. After two days, the reaction mixture was separated with 100ml of pentane and 100 mL of 10% by weight NaCl in water. The organic phase was rinsed with three 50-mL portions of 5% NaHCO<sub>3</sub> and dried over Na<sub>2</sub>SO<sub>4</sub>. The reaction mixture was concentrated in vacuo. About ~150 mg of sample was used for NMR analysis in d<sub>6</sub>-benzene.

*Reaction of 1,3-pentadiene with DCl*

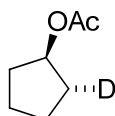
Approximating Nordlander's conditions,<sup>63</sup> a mixture of 0.62 mL of 1.6 M DCl in nitromethane (1 mmol of DCl) and 75 μL (51 mg, 0.75 mmol) of 1,3-pentadiene was added to a Wilmad 528 low pressure valve NMR tube. The NMR tube was sealed and shaken vigorously. After five minutes, the mixture was quenched with 52 μL (40 mg, 0.3 mmol) of 2- (trimethylsiloxy)propene, sealed and shaken again. The tube was then fit with a sealed capillary tube filled to the height of 5 cm with d<sub>6</sub>-acetone, sealed, and analyzed by NMR directly.

### *Synthesis of trans-2-d<sub>1</sub>-cyclopentanol*



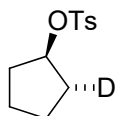
0.624 grams (14.9 mmol) of lithium aluminum deuteride was suspended in 47 ml anhydrous ethyl ether. The mixture was cooled in an ice-water bath. 2.5 grams (29.7 mmol) of cyclopentene oxide was added slowly under nitrogen atmosphere. The reaction was quenched in the manner described by the Merlic group,<sup>117</sup> dried over sodium sulfate, and concentrated in vacuo. The material was further refined by fractional distillation, keeping the mother liquor.

### *Synthesis of Cyclopentan-2-d-ol acetate*



200 ml of dichloromethane, 3.74 ml of pyridine (46.4 mmol), 567 mg of dimethylaminopyridine (46.4 mmol), and a stirbar were added to a 500 ml roundbottom flask. 2.19 ml of acetic anhydride (23.2 mmol) and 2.00 grams of *trans*-2-d<sub>1</sub>-cyclopentanol (23.2 mmol) were added to the flask.

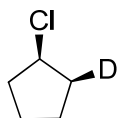
### *Synthesis of trans-1-toluenesulfonyl-2-d<sub>1</sub>-cyclopentane*



11 ml dry pyridine (dried over 4Å mol. sieves) and 4.42 grams (23.2 mmol) tosyl chloride were added to a flask in an ice bath. 1g (11.5 mmol) was added to the flask and the

mixture was stirred for thirty minutes. The reaction was then placed into a -5 °C fridge for two days. The reaction was quenched by slow addition of 1 ml of water (slow addition avoids exotherm and maintain homogeneity). The mixture was poured into a separatory funnel with crushed ice and conc. HCl. The mixture was extracted with 15 ml ether. The ether layer was then washed with 12mL 5% HCl and 12 mL saturated sodium bicarbonate solution. The organic layer was concentrated in vacuo and the product was recrystallized in pentane at -78° C.

*Synthesis of syn-1-chloro-2-d<sub>1</sub>-cyclopentane*



0.25 grams (1 mmol) of the tosylate product and 0.62g (5.7 mmol) of tetramethylammonium chloride was dissolved in 4.7 ml of DMSO. After 48 hours, the reaction reached (conversion measured by <sup>1</sup>H NMR). The reaction mixture was separated with cold water and pentane, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*.

*Reaction of Norbornene with DCl*

A separate solution of 1.83 grams (19.4 mmol) of norbornene dissolved in 5 mL dichloromethane was prepared at room temperature. DCl gas was made through the slow addition of 0.35 ml (19.3 mmol) deuterium oxide to 0.68 ml (7.8 mmol) phosphorus trichloride in Schlenk flask with an outlet to a solution of 19.4 mL dichloromethane and norbornene in a three-neck flask at -78 C. At high gas pressures, the reaction flask was allowed to vent to a mercury bubbler. The reaction was initiated by the addition of a small quantity of the norbornene solution into the reaction flask, followed by the addition of a

small quantity of deuterium oxide into the phosphorus trichloride flask. When the bubbler indicated vacuum inside the reaction flask, more norbornene was added to the reaction flask and more deuterium oxide was added to the phosphorus trichloride flask. After the addition of deuterium oxide was complete, the Schlenk flask was then removed from the ice bath and gas evolution became more vigorous. Once the evolution of gas was complete, the reaction flask was removed from the dry-ice bath and allowed to vent through the bubbler. Once at ambient temperature, the contents of the reaction flask were poured into a separatory funnel and extracted twice with ~30 mL petroleum ether. The organic layer was washed twice with ~30 mL 5% NaHCO<sub>3</sub> to remove traces of acid. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The reaction mixture was analyzed by <sup>13</sup>C NMR without further purification.

*Reaction of tert-butylethylene with DCl*

1.63 grams (19.4 mmol) of tert-butylethylene was pulled up into a plastic syringe. HCl gas was made through the slow addition of 0.19 ml (10.7 mmol) distilled water to 0.68 ml (7.8 mmol) phosphorus trichloride in Schlenk flask with an outlet to a solution of 19.4 mL dichloromethane in a three-neck flask at -78 C. At high gas pressures, the reaction flask was allowed to vent to a mercury bubbler. The reaction was initiated by the addition of a small quantity of the *tert*-butylethylene into the reaction flask, followed by the addition of a small quantity of distilled water into the phosphorus trichloride flask. Unlike in the norbornene case, the reaction of *tert*-butylethylene was very slow and no noticeable vacuum occurred over the course of the experiment. Water and *tert*-butylethylene additions took place dropwise in a staggered pattern over half an hour. After the addition of water was complete, the Schlenk flask was then removed from the ice bath and gas evolution became

more vigorous. Once the evolution of gas was complete, the reaction flask was removed from the dry-ice bath and allowed to vent through the bubbler. Once at ambient temperature, the contents of the reaction flask were poured into a separatory funnel and extracted twice with ~30 mL petroleum ether. The organic layer was washed twice with ~30 mL 5% NaHCO<sub>3</sub> to remove traces of acid. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The reaction mixture was analyzed by <sup>1</sup>H NMR without further purification.

## 2.6 Computational Procedures

### *General*

The calculations of DFT or MP2 structures, energies, and frequencies employed default procedures in Gaussian16<sup>118</sup> unless otherwise noted. DLPNO-CCSD(T) energies were calculated using ORCA.<sup>119</sup> Complete structures and energetics are provided in sections below. All absolute energies are in Hartrees. All relative energies are presented in kcal/mol.

Calculations of trajectories in the gas phase or with implicit solvation models employed the program suite PROGDYN. PROGDYN consists of a series of component programs written as either Unix shell scripts or awk programs. Gaussian16 was used to calculate the forces at each point in trajectories. A full description of PROGDYN can be found in a later section. A full listing of the component programs can be found as a permanent public dataverse set at <https://dataverse.harvard.edu/dataset.xhtml?persistentId=doi:10.7910/DVN/TQZR7E>. The original version of this program was published in the Supporting Information of a previous paper.



Calculations of trajectories in explicit solvent employed the program suite ProgDynONIOM. ProgDynONIOM was previously reported,<sup>82</sup> but the new version contains significant bug fixes important for highly polar reactions and should supersede the prior version. ProgDynONIOM uses a combination of A) Gaussian09 for the DFT or MP2 calculations needed for an ONIOM, and B) MOPAC2016<sup>®120</sup> for all semi-empirical calculations. A full description of ProgDynONIOM can be found in a later section.

A diverse collection of short helper and data-analysis programs were used to aid the running of trajectories and to analyze the data. A later section describes the general purpose, input, and output of each of these programs. A full listing of each can be found in Appendix C.

### *Trajectory Terminology*

An *MD trajectory* is a trajectory in explicit solvent that is equilibrated and run with one or more constraints, typically harmonic constraints on interatomic distances, for the purpose of umbrella sampling. The constraints vary from trajectory to trajectory.

A *feeder trajectory* is similar in that it is a trajectory in explicit solvent that is being equilibrated and run with one or more constraints, but its purpose is to generate the starting points for *spawned trajectories* below. Such trajectories are typically equilibrated and run for tens or hundreds of thousands of fs. The constraints are chosen to place the trajectory in an interesting region, typically the region of a transition state, and the constraints are typically identical for a series of feeders.

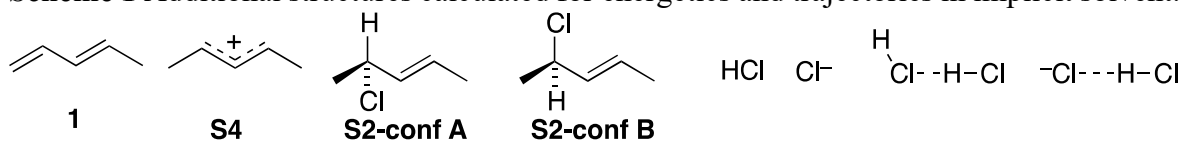
A *spawned trajectory* is one that is created by extracting points from feeder trajectories and continuing them without constraint to see what reaction occurs. Each

spawned trajectory is run in a separate directory until it reaches defined endpoints such as a product formation or time limit.

### *Computational Methods Validation Studies*

To explore the accuracy of computational methods for the addition of HCl to 1,3-pentadiene, a series of structures were first optimized in gas-phase M06-2X/6-31+G\* calculations. This includes 1,3-pentadiene (**1**), pentadienyl cation (**S4**) two different conformations of the addition product (**S2-conf A** and **S2-conf B**), HCl, Cl<sup>-</sup>, the HCl dimer, and the bichloride anion (Cl-H-Cl<sup>-</sup>). Single-point energies for each of these structures were then calculated in CCSD(T)/aug-cc-pVTZ calculations, and the energetics were compared with energetics calculated in a series of DFT calculations, including M062X/6-31+G\*, M11/6-31+G\*\*, wB97xD/6-31+G\*\*, BP86/6-31+G\*\*, B3PW91/6-31+G\*\*, B3P86/6-31+G\*\*, M06/6-31+G\*\*, B97D3/6-31+G\*\*, SOGGA11X/6-31+G\*\*, SOGGA11/6-31+G\*\*, B3LYP/6-31+G\*\*, M06-2X/6-31+G\*\*, M06-2X/6-311+G\*\*, M06-2X/aug-cc-pVDZ, and M06-2X/aug-cc-pVTZ calculations, along with MP2/6-31+G\*\*, MP2/6-31G\*, and MP2/6-31+G\* *ab initio* calculations. Relative potential energy energetics were in each case calculated for the protonation of **1** to give **S4**, the protonation of Cl<sup>-</sup> to give HCl, the protonation of **1** by HCl to give **S4** plus Cl<sup>-</sup>, the overall energetics for the addition of HCl to **1** to give **S2-conf A**, the relative energy of the two product conformations, the energy of dimerization of HCl, and the proton affinity of Cl-H-Cl<sup>-</sup>.

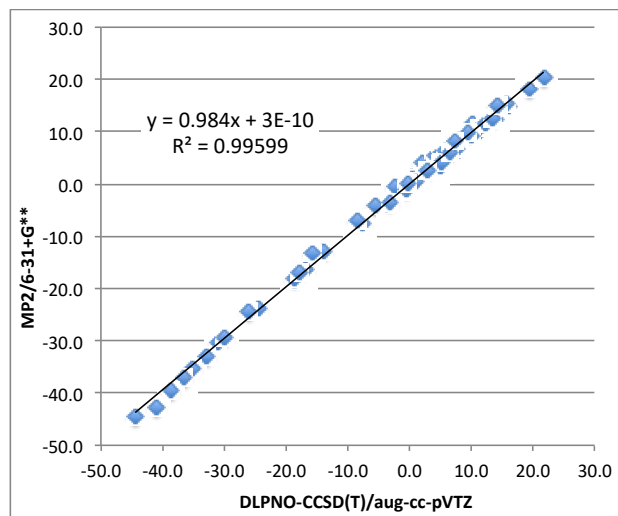
**Scheme 1** Additional structures calculated for energetics and trajectories in implicit solvent.



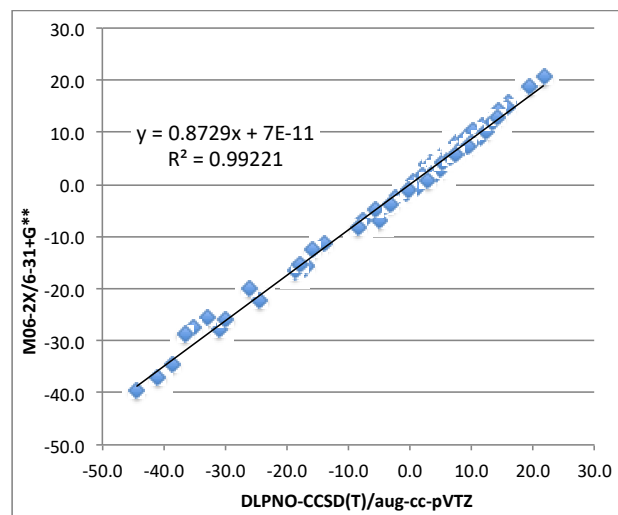
For each calculational method, an RMS error was calculated, treating the CCSD(T)/aug-cc-pVTZ calculations as the standard. The DFT methods in general did not perform very well, giving RMS errors of 5.7 to 7.6 kcal/mol with Pople basis sets, though the M06-2X error went down to 4.7 kcal/mol with an aug-cc-pVDZ basis set and only 2.9 kcal/mol with an aug-cc-pVTZ basis set. MP2 calculations fared much better, with an RMS error of 1.6 kcal/mol for MP2/6-31+G\*\*. M06-2X/6-31+G\* and M06-2X/6-31+G\*\* were only off by 0.2 kcal/mol and 1.0 kcal/mol on the proton affinity of **1**, versus 1.1 kcal/mol for MP2/6-31+G\*\* (though the MP2 calculation is only off from the experimental value by 0.2 kcal/mol), but the M06-2X calculations performed much less well on any calculation involving a Cl atom.

To explore the accuracy of methods for structures directly relevant to trajectories, single-point calculations were carried out on a series of 98 points taken at intervals from a full trajectory in explicit solvent. For the high-level core (1,3-pentadiene + 2 HCl going from reactants to the addition product), single point calculations were carried out using DLPNO-CCSD(T)/aug-cc-pVTZ calculations along with MP2/6-31+G\*\*, M06-2X/6-31+G\*, and M06-2X/6-31+G\*\*. The graphs below (Figure 41) show plots of each, with the DLPNO energies on the horizontal axis. The MP2 calculations are clearly better, both in giving a higher correlation and if giving a slope of energies that is near unity. The M06-2X calculations were considered adequate for structures with separate ions (those in the higher-

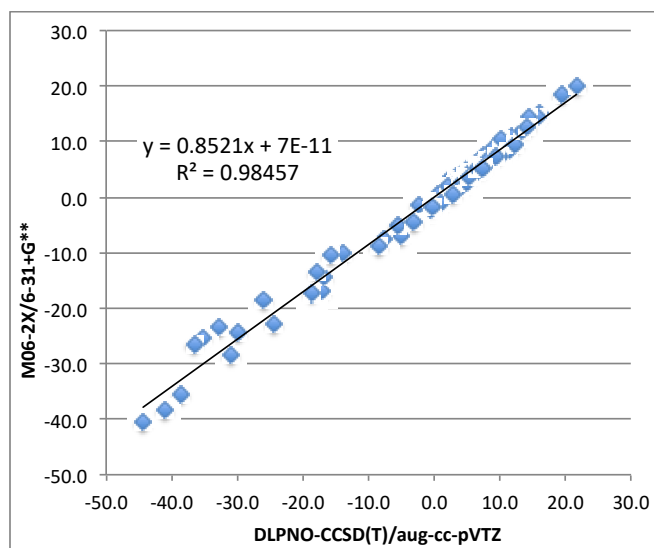
energy range) but they err significantly for the low-energy structures in which the Cl approaches a carbon.



**Figure 41** Correlation of energies calculated at test DFT MP2/6-31+G\*\* levels versus DLPNO-CCSD(T)/aug-cc-pVTZ for solute points in a sample trajectory.



**Figure 42** Correlation of energies calculated at test DFT M06-2X/6-31+G\*\* levels versus DLPNO-CCSD(T)/aug-cc-pVTZ for solute points in a sample trajectory.



**Figure 43** Correlation of energies calculated at test DFT M06-2X/6-31+G\* levels versus DLPNO-CCSD(T)/aug-cc-pVTZ for solute points in a sample trajectory.

#### *DRP and Trajectories in Implicit Solvent*

DRPs starting from **8**<sup>‡</sup> and **9**<sup>‡</sup> on the MP2/6-31+G\*\*/PCM surface as described in the main text were obtained using PROGDYN by using the “classical 4” option. This turns off putting energy in all normal modes except for the imaginary mode associated with the transition vector. The imaginary mode is then given a classical Boltzmann-random sampling of energy in the product-forming direction. The trajectories were then stopped when a chloride bonded with a cationic carbon, as defined by a C-Cl distance of < 1.8 Å. For **8**<sup>‡</sup>, a total of 44 DRPs were run, with 38 undergoing 1,4-addition and 6 undergoing 1,2-addition. For **9**<sup>‡</sup>, a total of 30 DRPs were run, with 19 undergoing 1,4-addition and 11 undergoing 1,2-addition.

The DRPs described above and in the main text are on the MP2/6-31+G\*\*/PCM surface. The table below (Table 3) shows the results of studies with alternative methods and solvent models, starting the DRPs from the various TSs. The listed TS names correspond to structures labeled and depicted in a later section. In each case the major outcome was either ion dissociation or 1,4-addition, and the results do not fit with experimental observations.

**Table 3** Trajectory outcomes for a selection of initialization geometries in implicit solvent.

method / basis set / solvent model	Starting TS	Results
MP2/6-31+G**/SMD	TS / two HCl conf B SMD	18 ion dissociation no addition product
	TS / two HCl conf C SMD	18 ion dissociation
M06-2X/6-31+G**/PCM	TS / two HCl conf A PCM	1 1,2-addition 9 1,2-addition 12 1,4-addition
	TS / two HCl conf B PCM	48 1,4-addition no 1,2-addition
M06-2X/6-31+G**/SMD	TS / two HCl conf A SMD	11 ion dissociation no addition product

Quasiclassical trajectories starting from the area of  $\mathbf{8}^\ddagger$  and  $\mathbf{9}^\ddagger$  on the MP2/6-31+G\*\*/PCM surface as described in the main text were obtained using PROGDYN by using the “classical 0” and “initialdis 2” options. For this, each normal mode is given its zero-point energy (ZPE) plus a randomized excitation energy based on a Boltzmann distribution, along with a randomized displacement of the modes. The phase of each of the normal modes was mapped from Gaussian distribution of random numbers. This distribution is not correct for a classical oscillator but would be approximately correct for a quantum oscillator in its ground state (only ignoring mode displacements outside of the classical limit), and has the advantage that a larger portion of the trajectories start with an energy approximating the initially desired energy. PROGDYN now has the capability to perform a full quantum distribution in its initialization, which would be more accurate physically, but

this capability had not been built into PROGDYN at the time. The trajectories were then propagated forward and backward in time until **2** or **3** was formed or the  $4^+ / \text{ClHCl}^-$  ion pair dissociated (gauged by a minimum C-Cl distance of 5.0 Å) or the starting materials were reformed or a 500 fs time limit was reached. For **8**<sup>‡</sup>, a total of 100 trajectories were run, with 98 undergoing dissociation and 2 undergoing 1,4-addition. For **9**<sup>‡</sup>, a total of 40 trajectories were run, with 27 undergoing dissociation, 12 undergoing 1,4-addition and 1 undergoing 1,2-addition.

The quasiclassical trajectories described above and in the main text are on the MP2/6-31+G\*\*/PCM surface. The table below (Table 4) shows the results of studies with alternative methods and solvent models, starting the trajectories from the various TSs. In listed TS names correspond to structures labeled and depicted in a later section. In each case the major outcome was either ion dissociation or 1,4-addition, and the results do not fit with experimental observations.

**Table 4** Trajectory outcomes for a comprehensive selection of initialization geometries in implicit solvent.

method / basis set / solvent model	Starting TS	Results
MP2/6-31+G**/SMD	TS / two HCl conf B SMD	90 ion dissociation 1 1,4-addition
	TS / two HCl conf C SMD	82 ion dissociation 4 1,4-addition 2 1,2-addition
M06-2X/6-31+G**/PCM	TS / two HCl conf A PCM	217 ion dissociation 2 1,4-addition 1 1,2-addition
	TS / two HCl conf B PCM	129 ion dissociation 58 1,4-addition 2 1,2-addition
M06-2X/6-31+G**/SMD	TS / two HCl conf A SMD	166 ion dissociation 1 1,4-addition
	TS / two HCl conf B SMD	109 ion dissociation 9 1,4-addition 1 1,2-addition
	TS / two HCl conf C SMD	94 ion dissociation 1 1,4-addition

#### *PMF for Protonation in Explicit Solvent*

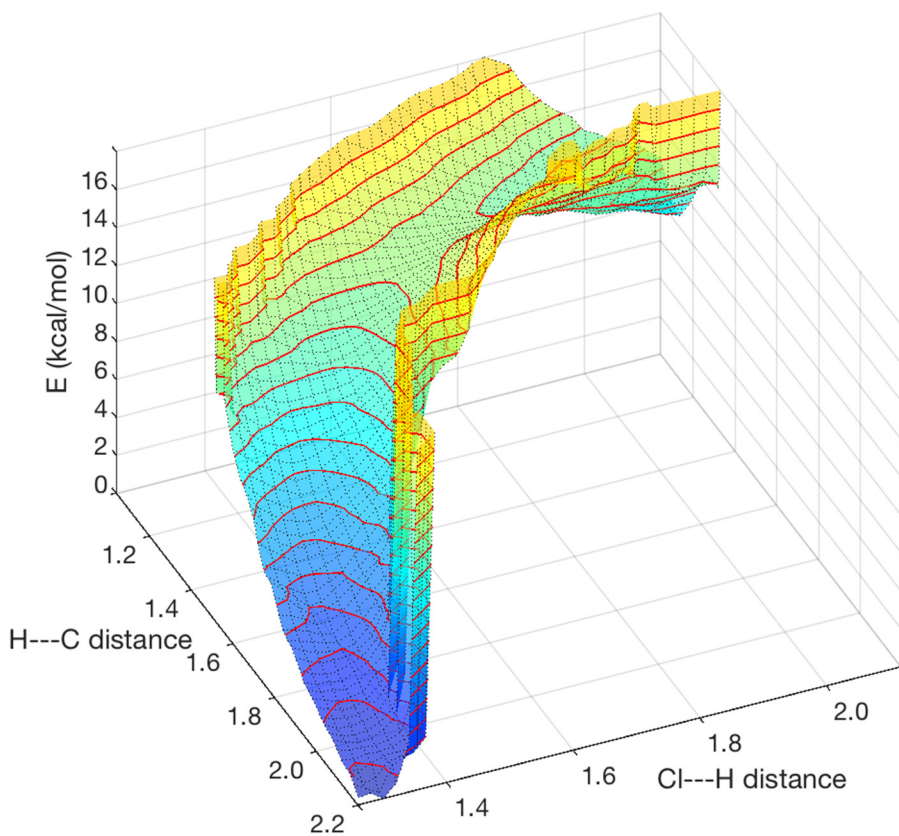
Series of initial structures for molecular dynamics including 1,3-pentadiene, one or two molecules of HCl, and 120 nitromethane molecules was generated using Packmol Version 16.344<sup>121</sup> with an initial sphere radius of 13.66 Å. These structures were used as input to a Gaussian 09 PM3 calculation, which was then used as a *freqinHP* file to initiate trajectories in ProgdynONIOM using the “classical 2” facility. These structures were then equilibrated at 298 while a series of parameters were adjusted to obtain reasonable densities and heats of vaporization while keeping pressures at reasonable values. The parameters explored included the choice of low-level method (PM6, PM6-DH+, PM6-DH2, PM7, finally choosing PM6-DH+), spheresize (finally choosing 14.75), sphereforce (ProgdynONIOM uses a “soft” sphere boundary in which atoms outside of the boundary



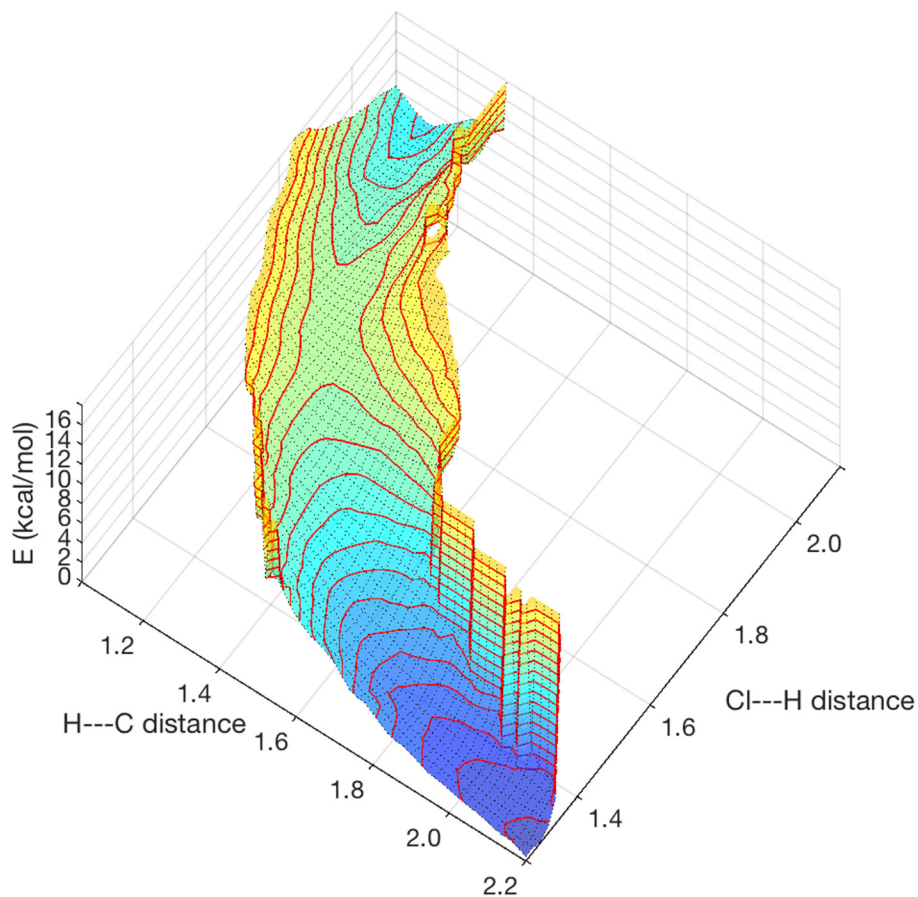
experience an inwardly propelling harmonic potential, final parameter value 0.1), and parameters for the additional empirical dispersion (empiricaldispersion 2.0, radiusmultiplier 1.5, empiricaldispersionb -0.3, radiusmultiplierb 0.8). These parameters led to a median final density (measured for the inner 90% of the sphere) of 1.17 (compared to 1.14 for pure nitromethane), and a median pressure of 174 atm. The initial equilibrations included a weak harmonic potential (with a force constant of 118.58 kcal/mol/Å) that held an HCl molecule with a proton  $\sim 1.4$  Å from C<sub>1</sub> of the diene, a weak quartic potential that held the H of the second HCl molecule at  $\sim 2.1$  Å ( $\pm 0.4$  Å) from the Cl of the first HCl, and a weak harmonic potential that impelled C<sub>2</sub> of the diene toward the center of the sphere ( $\pm 2$  Å) using the “zeroatom” keyword. The total equilibration times for the structures before further use ranged from 80,000 to 150,000 fs.

At this point, these starter trajectories were “dispersed” to create *MD trajectories* for umbrella sampling by applying varying harmonic potentials (with force constants of either 474.32 kcal/mol/Å or 664.05 kcal/mol/Å) at a series of C<sub>1</sub>---H distances (ranging from 1.08 to 1.78 Å) and H---Cl distances (ranging from 1.25 to 2.1 Å). The dispersal was performed in steps of  $<0.2$  Å, followed by equilibrations of  $\sim 1000$  fs, to avoid applying very strong forces to the relevant atoms. After dispersal, equilibrations were continued for 3000 fs before collecting  $\sim 10,000$  fs of data in each umbrella section, with a total time of  $\sim 1$  ns. The raw data was then collected from the *dynfollowfile* outputs for each trajectory and the PMF was calculated using the weighted histogram analysis method<sup>83</sup> employing the program *wham-2d*.<sup>122</sup> Figure 31 of the main text depicts the results within a limited region, with the zero of energy set at a flat region of the surface in the area of a pre-reactive complex. It should be understood that Figure 31 has had selected points on the edge of the energy profile

deleted in order to make the important portion of the energy profile more visible and clear. An expanded depiction of the data, with no point selection along the edge, is given in the two following figures (Figures S4 and S5). For these profiles, points that received no counts in the umbrella sampling were assigned an arbitrary energy value of 25 kcal/mol. The effect of this is that the data shows sharp “cliffs” in passing from populated data points to data points receiving no counts. This makes the edges of the energy surface look unusual, but these edges are not meaningful. The selection of points for Figure 31 and the arbitrary value assignments have no effect on the interpretation of the results.

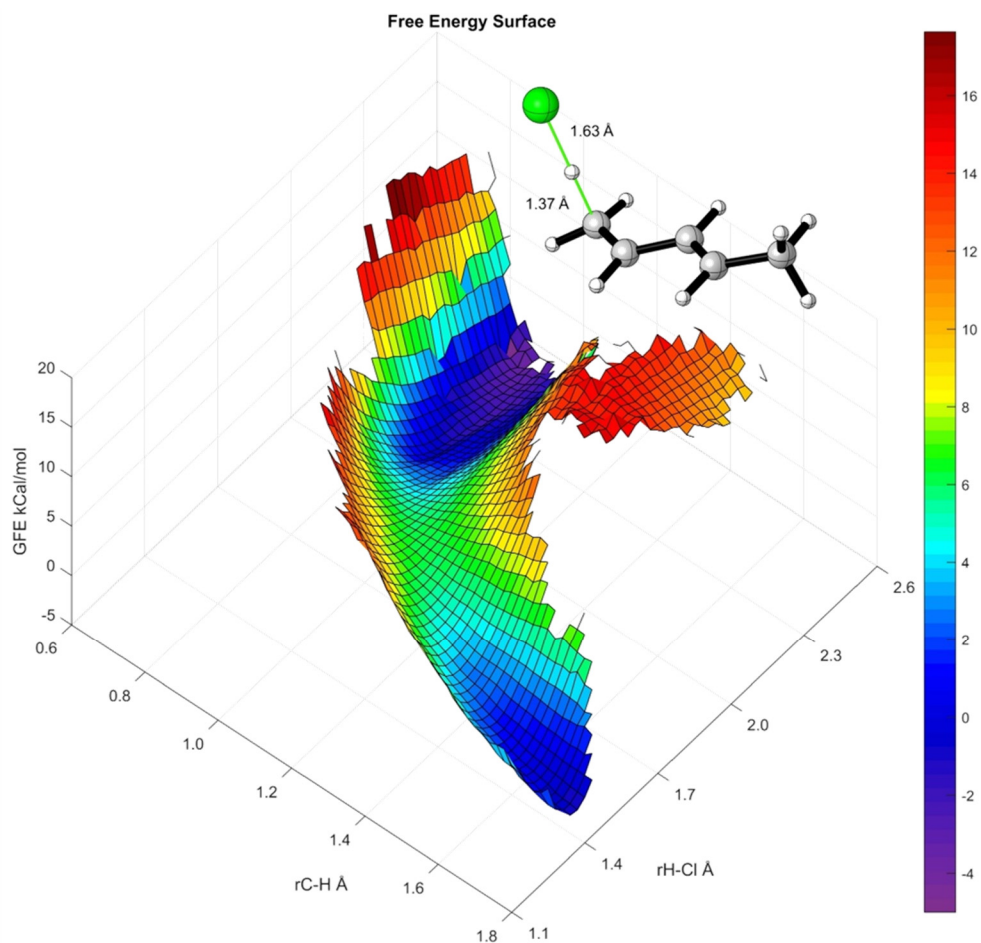


**Figure 44** Expanded version of Figure 31 from the main text with no point selection at the edges.



**Figure 45** Expanded version of Figure 31 from the main text with no point selection at the edges, viewed from a higher angle.

The PMF figures above along with Figure 31 in the main text were obtained in systems using two H-Cl molecules and in which MP2/6-31+G\*\* was used as the high-level method (used for the 1,3-pentadiene and two-HCl solute) for the QM/QM ONIOM. The figure below (Figure 46) shows a similar PMF that was obtained in calculations using only a single HCl molecule and using M06-2X/6-31+G\* for the ONIOM high-level method. The zero of the surface was set arbitrarily at the lowest-energy point.



**Figure 46** PMF for the addition of one HCl molecule to 1,3-pentadiene, using M06-2X/6-31+G\* for the ONIOM high-level method.

*Trajectories in Explicit Solvent Started from the Area of  $10^{\ddagger}$*

**Initialization and Propagation**

A series of 24 *feeder trajectories* were created from independent *MD trajectories* by adjusting the harmonic constraints to the following distances and force-constant values :

C<sub>1</sub>---H 1.28 Å, 1067.22 kcal/mol/Å

(ProgdynONIOM listing: “applyforce 4 0.9 1.28 0.0 40”)

H---Cl 1.68 Å, 711.48 kcal/mol/Å

(ProgdynONIOM listing: “applyforceB 4 0.6 1.68 0.0 1”)

The distance between the Cl of the reacting HCl molecule and the H of the second HCl molecule was constrained by a loose fourth-order constraint to between 1.8 and 2.6 Å, (ProgdynONIOM listing “applyforceC 4 0.00 2.20 0.00 1.0”) to prevent the dissociation of the second HCl molecule (since the experimental kinetics indicate that the reaction is second order in HCl). The H---Cl distance in the second HCl molecule was loosely constrained to less than 1.7 Å (ProgdynONIOM listing “applyforceD 4 0.00 1.30 0.00 1.0”) to prevent a rare protonation of the nitromethane by the HCl (experimental observations of the ion content of the solution suggest that this does not happen significantly experimentally). The *feeder trajectories* were then equilibrated for a minimum of 10,000 fs, then continued for typically 20,000 to 25,000 fs.

At intervals of 250 fs, structures and velocities were extracted from the feeder trajectories to create a *spawned trajectory*. The spawned trajectories were continued without constraint and integrated forward and backward in time. As described in the main text, the trajectories were continued until the products **2** or **3** were formed, the starting materials were reformed, a time limit of 3000 fs was reached, or the Cl---HCl anion / pentadienyl cation tight ion pair “dissociated.” Dissociation was defined by the chlorides being >5 Å separated from the cationic carbons

### **Autocorrelation and the Randomization of Initial Conditions**

Exploratory studies were conducted to examine the rate of randomization of initial trajectory conditions and whether 250 fs was a sufficiently long time between extraction of spawned trajectories to obtain independent results. For one of the feeder trajectories, points

were extracted every 50 fs and the trajectories were integrated without constrain in the normal way. It was then examined whether sequential results were more likely to be the same than would be dictated by random chance. After 50, 100, 150, 200, and 250 fs, the chance that a trajectory result would match the previous result relative to random chance was 1.57, 1.31, 1.22, 1.16, and 1.14, respectively. Because of the limited size of the dataset, there is a significant uncertainty for each number, but the data suggests that the initial substrate / solvent structure does not fully equilibrate over 250 fs. This is unsurprising considering the time required for solvation to relax around charges (see Figure 33 in the main text). However, the degree of autocorrelation after 250 fs was judged to be low enough to not impact significantly the uncertainty in the product ratios obtained from the trajectories.

### **PMF for C-Cl Bond Formation in Ion Pair**

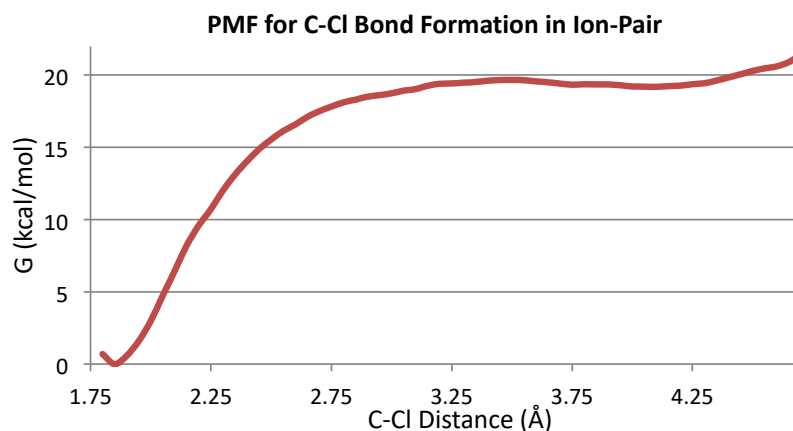
A series of 24 independent starting geometries and velocities for trajectories were obtained by extracting points with appropriate C---Cl distances from the trajectories that had been started in the area of  $\mathbf{10}^\ddagger$ . These trajectories were then dispersed to create 68 MD trajectories for umbrella sampling, setting C---Cl distances in a range from 2.0 to 4.6 Å with a force constant that was either 118.58 kcal/mol/Å or 237.16 kcal/mol/Å. The constraints for these trajectories using the interlocking-sphere biasing potential that we developed in a previous paper.

The idea of the interlocking-sphere potential is that the use of simple biasing potentials based on the distance of a particular Cl atom from a particular carbon atom, such as C<sub>2</sub>, fails. The failure occurs because the Cl remains free to attack C<sub>4</sub> and the other Cl atom can attack either C<sub>2</sub> or C<sub>4</sub>, as happens invariably with only a single bias applied. If four constraints were applied instead, the dimensionality of the data would be too high to

either obtain or interpret. As previously described, the interlocking sphere algorithm gets around this problem by defining a surface of zero potential based on a combination of atoms. In effect, the algorithm works by applying a potential to the shortest (or longest) or a set of relevant distances, while leaving the other distances in the set unconstrained. This allows the two chlorine atoms to roam from  $C_2$  to  $C_4$  in the MD, with the constraint only affecting two atoms at a time.

On rare occasions, a proton transfer would occur from  $C_1$  or  $C_5$  of the diene to one of the Cl atoms. To avoid this outcome, which interferes with the PMF calculation, a second weak (11.8 kcal/mol/Å) interlocking sphere potential was applied to the distance between  $C_1$  or  $C_5$  and their attached hydrogens. This has the effect of preventing deprotonation steps, but otherwise did not unduly affect the MD.

The dispersed MD trajectories in each umbrella section were equilibrated for a minimum of 10,000 fs before collecting data, with a total time of  $\sim 1$  ns. The raw data was then collected from the *dynfollowfile* outputs for each trajectory and the PMF was calculated using the weighted histogram analysis method<sup>83</sup> employing the program *wham*<sup>122</sup>. The zero of energy was assigned to a minimum in the PMF at a nominal C---Cl distance of  $1.85 \pm 0.025$  Å. The result is shown in Figure 7 in the main text and is shown below in more complete form (Figure 47).



**Figure 47** Expanded PMF for Figure 35.

### Trajectories Initiated from Solvent-Equilibrated Ion Pairs in Explicit Solvent

A subset of the MD trajectories, those with C---Cl distance constraints ranging from 3.8 to 4.1 Å, were used directly as the feeder trajectories for spawned trajectories. The spawned trajectories were continued without constraint, and integrated only forward in time. (Since there is no transition state being crossed, integrating both directions in time provides no particular information of value, and since the forward and backward legs are not independent, running both legs provides less information/cost relative to running a new spawned trajectory.) The trajectories were continued until the products **2** or **3** were formed, a time limit of 3000 fs was reached, or the Cl---HCl anion / pentadienyl cation tight ion pair “dissociated.” In no case did the ion pair revert to 1,3-pentadiene. A total of 508 results were obtained, of which 320 reached the 3000 fs time limit, 40 had the ions dissociate, and formed the 1,2 or 1,4 addition product. The ordered raw times used for Figure 8 were:

115, 214, 220, 312, 322, 344, 353, 359, 359, 362, 364, 382, 386, 386, 397, 407, 430, 440, 441, 462, 466, 474, 504, 518, 535, 541, 568, 582, 585, 592, 595, 603, 605, 623, 626, 645, 653, 663, 676, 681, 681, 688, 707, 719, 723, 733, 736, 740, 768, 782, 785, 788, 790, 796, 832, 843, 846, 859, 868, 880, 921, 931, 934, 949, 973, 987,



1007, 1049, 1062, 1080, 1084, 1094, 1103, 1107, 1112, 1115, 1127, 1162, 1162, 1173, 1180, 1180, 1224, 1241, 1296, 1318, 1333, 1347, 1352, 1362, 1367, 1385, 1393, 1421, 1446, 1459, 1485, 1491, 1492, 1494, 1501, 1504, 1591, 1601, 1619, 1653, 1654, 1678, 1680, 1683, 1684, 1696, 1699, 1706, 1707, 1711, 1732, 1748, 1757, 1781, 1797, 1811, 1868, 1877, 1885, 1905, 1932, 1952, 1962, 1966, 1972, 2012, 2023, 2024, 2027, 2041, 2046, 2075, 2112, 2143, 2143, 2162, 2178, 2189, 2193, 2199, 2221, 2258, 2290, 2311, 2331, 2344, 2350, 2360, 2380, 2435, 2455, 2458, 2469, 2473, 2501, 2519, 2550, 2556, 2564, 2588, 2634, 2674, 2680, 2685, 2714, 2722, 2743, 2753, 2765, 2768, 2779, 2793, 2821, 2827, 2831, 2832, 2836, 2837, 2868, 2901, 2937, 2950

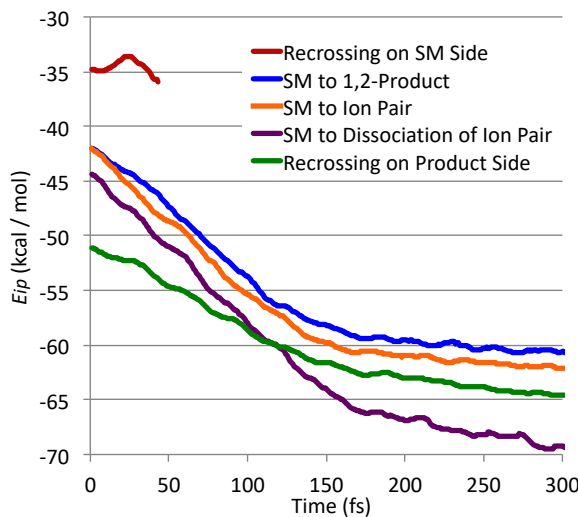
### **Incipient Ion-pair Stabilization Parameter Analyses**

The program *progcharge* that calculates the “incipient ion-pair stabilization parameter”  $E_{ip}$  for each point in a trajectory is described in another section and listed in a separate zip file. Parameters such as the choice of atomic charges can be found in the program. Here, we provide more detail on the calculation and explain the choice of charges employed.

The *progcharge* calculation of  $E_{ip}$  employs constant pre-assigned charges for all of the atoms. For the nitromethane solvent, MP2/6-31+G\*\* overestimates the dipole moment, giving a dipole moment of 4.4 compared to experimental of 3.46 (<https://cccbdb.nist.gov/exp2x.asp?casno=75525&charge=0#NSRDS-NBS10>). This dipole moment was reproduced better by M062X/6-31+G\*\* calculations (3.86), so this method was used to calculate the charges. The charges were calculated by the Merz-Singh-Kollman scheme<sup>123</sup> on gas-phase optimized structures using Gaussian09, and the charges for the equivalent H's were averaged as well as those for the equivalent oxygen atoms.

The choice of atomic charges on the solvent made a change in the  $E_{ip}$  that appeared approximately proportional to the dipole moment, so the use of MP2 charges instead of

M062X charges increased  $E_{ip}$  values but had no qualitative effect. The choice of atomic charges for the incipient ion pair made a nearly negligible effect on the  $E_{ip}$ , so that an initial run with drastically differing charges on the ions (but still adding up to +1 on the pentadienyl cation) did not change averaged  $E_{ip}$  values by more than 2 kcal/mol. The figure below (Figure 48) shows the alternative to Figure 33 using the differing charges.



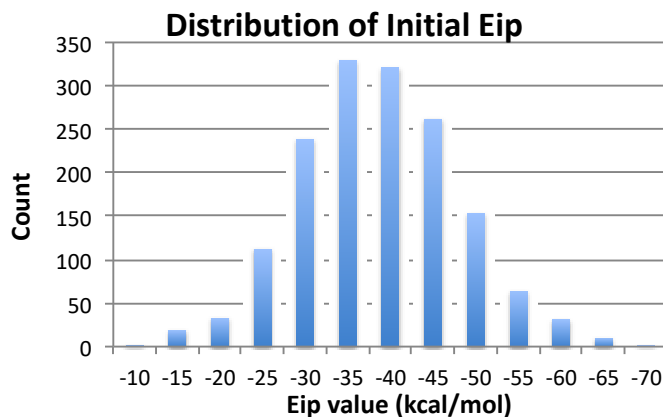
**Figure 48** Analog of Figure 33 from the main text except using ~50% smaller atomic charges for the cationic atoms.

Real charges in the molecules would naturally vary as the geometry varies. Our view was that little could be gained from looking at the fs-by-fs charges since our goal was to recognize overall differences in the solvation and how they vary by time. Limited exploratory studies were carried out using xtb charges for the solute that were calculated at each point, but this led to no qualitative difference versus the simple approach calculating  $E_{ip}$  based on constant charges.

For the trajectories in which the 1,2-product was formed, it was reasoned that the end of these trajectories was misleading with regard to ion-pair stabilization, since the charge

separation goes away as the product is formed. To avoid this problem, the last 25 fs of runs forming the 1,2-product was not used in the calculation of average  $E_{ip}$  values.

As noted in the main text, the initial  $E_{ip}$  for reactive trajectories is not bimodal, but rather approximates a normal distribution. This is illustrated in the figure below (Figure 49), which shows a histogram of the complete set of initial  $E_{ip}$  values.



**Figure 49** Histogram showing the range of initial  $E_{ip}$  for reactive trajectories.

### Exploration of Effect of Solute Internal Dimensions

The effect of a series of variables reflecting internal solute dimensions versus the productivity of the trajectories was explored. The table below (Table 5) shows the effect of the starting C-H for the proton being transferred on the percentage productivity of the trajectories. For the relatively few trajectories outside of this range (~3%), the productivity percentage was lower, but within the range of most trajectories the productivity was approximately equal allowing for the normal statistical variations.

**Table 5** ONIOM trajectory productivity as a function of internal C-H coordinate selection.

C-H distance ( $\pm 0.005$ Å)														
1.23	1.24	1.25	1.26	1.27	1.28	1.29	1.30	1.31	1.32	1.33	1.34	1.35	1.36	1.37
Number of trajectories														
32	30	46	114	167	266	291	287	251	226	167	106	38	17	9
Number productive														
4	5	9	23	33	73	71	70	61	54	39	20	5	3	3
Percentage productive														
13%	17%	20%	20%	20%	27%	24%	24%	24%	24%	23%	19%	13%	18%	33%

The table below (Table 6) shows the effect of the starting H-Cl distance for the proton being transferred on the percentage productivity of the trajectories. The productivity was low, ~1%, for the 6% of trajectories outside of this range. The productivity peaks for distances from 1.62 to 1.78 Å, and this distance is a factor in productivity but not to a major extent within this range.

**Table 6** ONIOM trajectory productivity as a function of internal C-H coordinate selection. Truncated range of C-H values.

H-Cl distance ( $\pm 0.02$ Å)							
1.56	1.6	1.64	1.68	1.72	1.76	1.8	1.84
Number of trajectories							
85	262	586	574	271	99	66	48
Number productive							
9	37	139	160	84	26	12	7
Percentage productive							
11%	14%	24%	28%	31%	26%	18%	15%

The table below (Table 7) shows the effect of the starting Cl---H-Cl distances (the distance to the H of the second HCl molecule to Cl of the HCl doing the proton transfer) on the percentage productivity of the trajectories. Only 0.2% of trajectories were outside of this range. Within this range, there is no discernable effect of this distances on productivity.

**Table 7** ONIOM trajectory productivity as a function of internal C-Cl coordinate selection.

Cl---H-Cl distance ( $\pm 0.025$ Å)											
1.95	2	2.05	2.1	2.15	2.2	2.25	2.3	2.35	2.4	2.45	2.5
Number of trajectories											
27	55	140	184	236	296	348	332	259	169	69	7
Number productive											
7	11	27	43	60	82	67	66	55	39	17	1
Percentage productive											
26%	20%	19%	23%	25%	28%	19%	20%	21%	23%	25%	14%

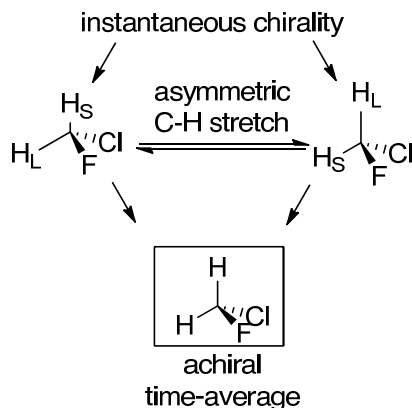
The effect of the general orientation of the second HCl molecule on productivity was explored visually in a qualitative manner by examining productive versus non-productive trajectories, with no discernable effect. A more quantitative examination was hampered by the multiple variables involved in defining the orientation of the second HCl molecule.

## CHAPTER III

### BOND MEMORY IN DYNAMICALLY DETERMINED STEREOSELECTIVITY\*

#### 3.1 Introduction

Much of the understanding of molecular structure in chemistry implicitly assumes time-averaged geometries and statistical distributions of energy in molecules. For example, symmetry-linked bonds to atoms are considered equivalent, even though in individual molecules at any instant the positions and energies of the atoms may be inequivalent.  $\text{CH}_2\text{FCl}$  is not viewed as being chiral in any meaningful sense, because no ordinary experiment can detect the ephemeral positional and energetic differences between the hydrogen atoms (Figure 50).<sup>124</sup>



**Figure 50** Even achiral molecules such as  $\text{CH}_2\text{FCl}$  exhibit instantaneous chirality. Over the course of an asymmetric C-H stretch vibration, one C-H bond is short ( $\text{H}_\text{S}$ ) and another is long ( $\text{H}_\text{L}$ ), making these bonds connections inequivalent. This asymmetry exists on the femtosecond timescale, but at large time intervals converges to a time-averaged achiral form.

---

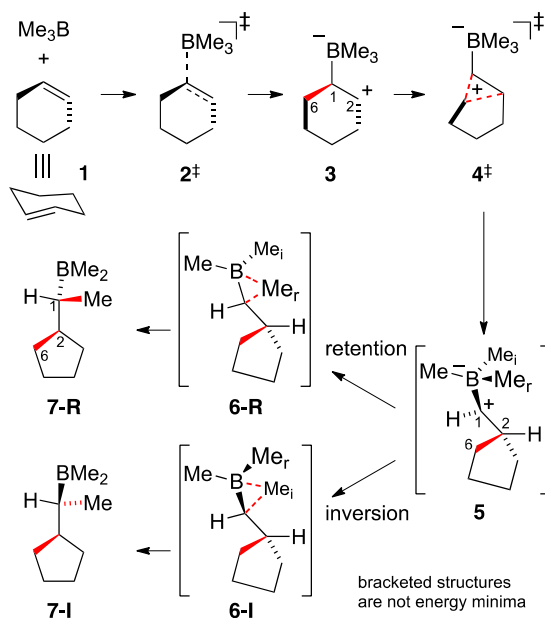
\* Adapted with permission from "Bond Memory in Dynamically Determined Selectivity" by Roytman, V. A.; Jin, S.; Nguyen, V. T.; Nguyen, V. D.; Haug, G. C.; Larionov, O. V.; Singleton, D. A. *J. Amer. Chem. Soc.* **2020**, *142*,85-88. Copyright 2019 American Chemical Society.<sup>96</sup>

On sufficiently short time scales, however, the *de facto* dynamical asymmetry of structures with symmetrical connectivity can influence experimental observations, either through bond breaking in specifically energized fragments of molecules<sup>44,47</sup> or through dynamic matching (see Section 1.3 for a detailed discussion).<sup>9,125–129</sup>

One system where this idea was encountered unexpectedly involves the *E/Z* isomerization of cyclohexenes. Alkenes undergo photoisomerization under radiation with UV light. The *E/Z* isomerization of linear alkenes in chemistry and biology is well-documented, while the photochemical behavior in cyclic structures is less productive.<sup>130–134</sup> In the three to five-membered rings, directly photoexcited cycloalkenes will decompose intramolecularly before intermolecular processes can intercede, precluding any direct or indirect observation of *E/Z* isomerization.<sup>135–137</sup> Six-membered rings are recognized as the smallest cycloalkene to exhibit *E/Z* isomerism – the strained *E*-alkenes serving as reactive intermediates with a lifetime of  $\sim 9 \mu\text{s}$  and barriers to back-isomerization on the order of 8 kcal/mol.<sup>138,139</sup> In the absence of suitable reaction partners, (*E*)-cyclohexenes are prone to non-stereospecific [2 + 2] cyclodimerizations.<sup>140,141</sup> Photosensitizing solvents such as phenols, ketones, and alkylbenzenes have been used to control the extent of photoexcitation of cycloalkenes and impart selectivity to their reactions.<sup>142–144</sup>

The Larionov group recently reported the photoinduced carboborative ring contraction of cyclohexenes to afford chiral cyclopentanes (Figure 51).<sup>145,146</sup> The reaction was proposed to occur by a sensitized *cis/trans* isomerization, giving rise to a strained *trans*-cyclohexene nucleophile (**1**). Electrophilic addition by a tertiary borane via **2**<sup>‡</sup> then forms the zwitterionic adduct **3**. Ring contraction through **4**<sup>‡</sup> leads to the betaine structure **5**. The nature of **5** and its dynamics will be of central importance here. Stereodivergent alkyl

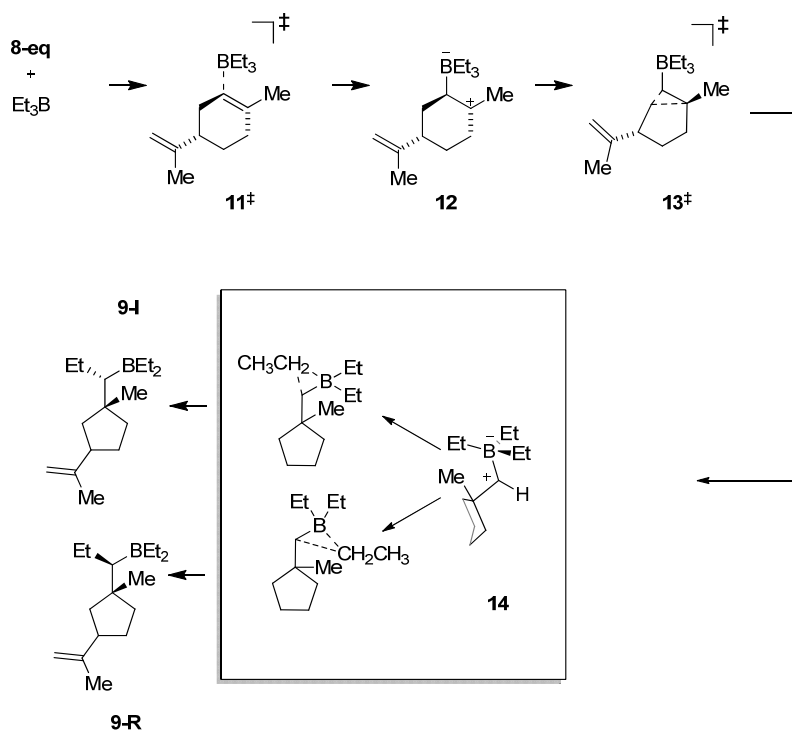
migrations via **6-R** or **6-I** quench the charge separation and give the product cyclopentanes **7-R** and **7-I**. The stereochemistry of the combination of ring contraction and boron–alkyl migration steps cannot be experimentally determined with cyclohexene itself, but a strong preference for inversion is observed with complex substrates.



**Figure 51** The proposed mechanism for the carboborative ring contraction reaction, starting at *trans*-cyclohexene.

Here, we have carefully assigned and quantitated the relatively simple reaction of (+)-limonene with triethylborane (Figure 52).

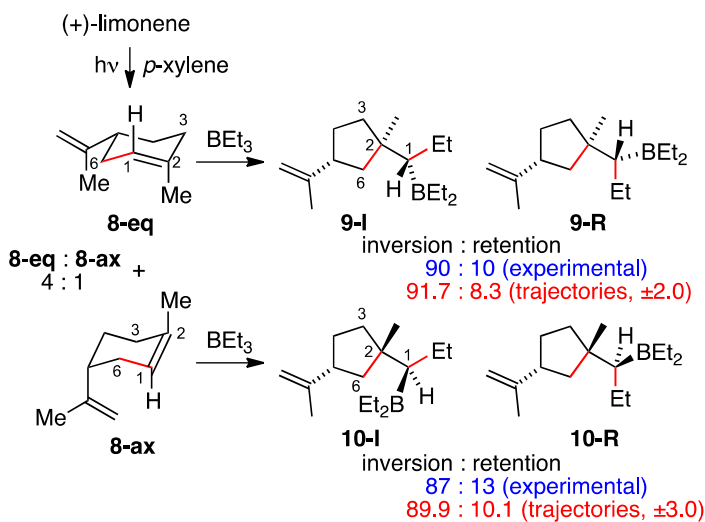




**Figure 52.** The mechanistic scheme for the reaction of equatorial *trans*-(+)-limonene (**8-eq**) with triethylborane. Axial *trans*-(+)-limonene (**8-ax**) contributes to the observed product mixture and will be discussed later.

An unusual experimental observation is that the two rearrangement steps are stereochemically linked, but not completely so. That is, if the bond to C<sub>6</sub> lost in the ring-contraction step is viewed as the “leaving group” and the migrating boron–alkyl is the “nucleophile”, the combination of steps converting the first zwitterion intermediate to the product occurs with preferential, but not exclusive, inversion of configuration at C<sub>1</sub> (see **9-I/10-I** versus **9-R/10-R** in Figure 53). If the two migrations occurred simultaneously, stereospecific inversion would be expected, as in any S<sub>N</sub>2 step. If the ring-contraction step were complete before the boron–alkyl migration, equal inversion and retention might be expected. The high stereoselectivity but absence of S<sub>N</sub>2-like stereospecificity then appears inconsistent with either a concerted or a two-step process. We describe here how the

combination of energetic non-equivalence in newly formed versus pre-existing bonds and the initial geometrical non-equivalence of the two bonds on the slope of an energy surface can direct high stereoselectivity at an adjacent reactive center.



**Figure 53** Stereochemistry of the photoinduced carboborative ring contraction of (+)-limonene.

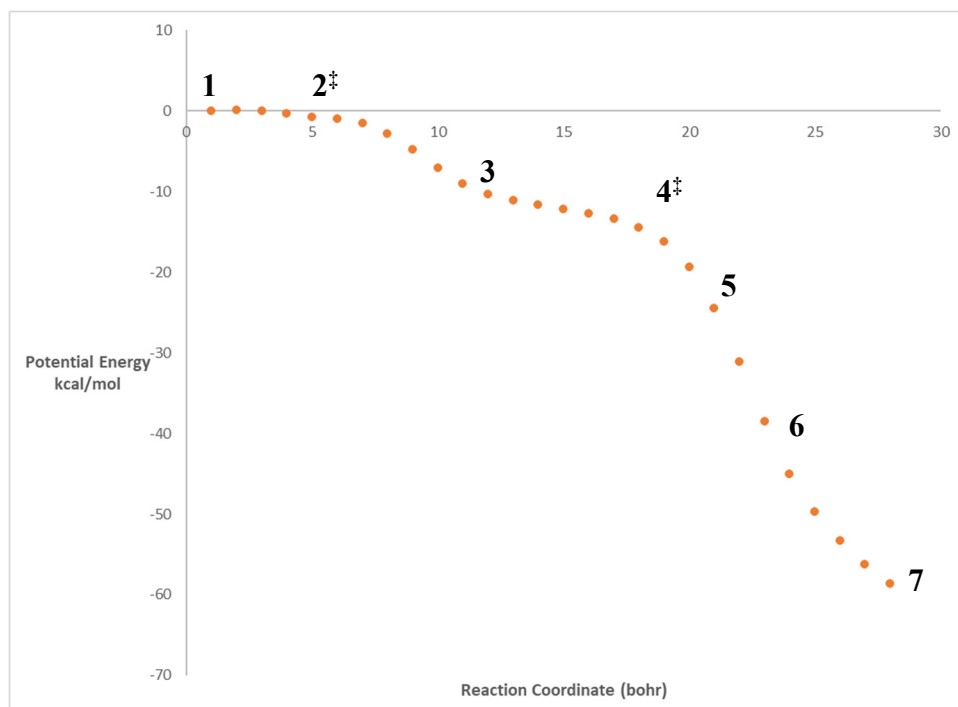
Our hypothesis was that this unexpected stereoselectivity pattern is associated with dynamics on a bifurcating energy surface.<sup>2,3,6,7,10,34,39,40,93,147</sup> The trajectory study here supports this idea but uncovers an origin for the selectivity that is uniquely dynamical in nature. The results complicate the mechanistic interpretation of stereoselectivity in reactions.

### 3.2 Computational Results and Discussion

#### *Initial Exploration of Computational Models*

In order to understand the basics of this reaction, the relatively simple model of the reaction of *trans*-cyclohexene with trimethylborane (as shown in Figure 51) was used for initial exploration of the potential energy surface. After the computational method was

validated (see Section 3.4), GAUSSRATE/POLYRATE was used to calculate the M11/6-31+G\*\* minimum energy path (MEP) connecting **1** to **7** (Figure 54).



**Figure 54** The M11/6-31+G\*\* MEP for the reaction of *trans*-cyclohexene with trimethylborane.

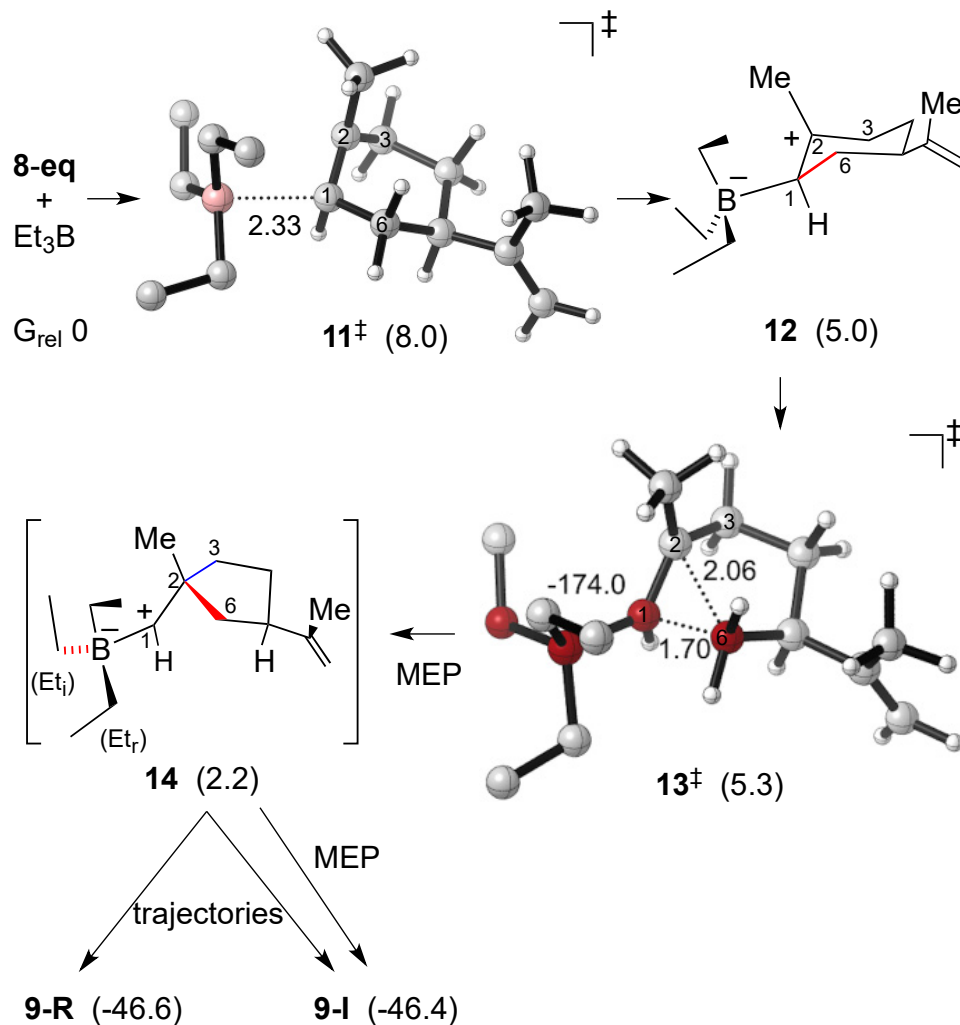
The ring contraction of **3** is barrierless,<sup>148</sup> and the MEP has C<sub>6</sub> migrate from C<sub>1</sub> to C<sub>2</sub> to pass into the area of structure **5**, though **5** is not an energy minimum. The MEP then continues downhill by a boron–alkyl shift to C<sub>1</sub> through **6-I** to afford **7-I**. The energy surface for the ring contraction and boron–alkyl migration is steeply declining, going downhill by 61 kcal/mol overall and 45 kcal/mol from **5** to **7-I**.

### **Potential Energy Surface Studies**

The stereochemically tractable (+)-limonene/triethylborane reaction of Figure 53 was the focus of the calculations here. All calculations discussed hereon were performed with the M11/6-31+G\*\* method validated in the simple model system described above. Unlike the model reaction, this system is configurationally and conformationally complex. The initial *cis/trans* isomerization can occur in two ways, leading to a distorted chair with the isopropenyl group either equatorial (**8-eq**) or axial (**8-ax**). For each, the isopropenyl group and the attacking triethylborane can adopt multiple conformations, and the possibilities were explored systematically (see Section 3.4). Importantly, the conformation of the triethylboryl group later in the mechanism is established in the transition state for its attack on the alkene. The structures subsequent to the initial addition step are extremely short-lived. As a result, their conformations are in a non-Curtin–Hammett regime,<sup>149</sup> and they cannot interconvert prior to the final product formation.

Figure 55 outlines the calculated mechanism. The lowest-energy TS **11**<sup>‡</sup> for the addition of triethylborane to **8-eq** involves a low barrier (8.0 kcal/mol in free energy) despite the steric hindrance. The resulting zwitterion **12** exists in a shallow energy well of only 0.3 kcal/mol versus the subsequent ring-contraction TS **13**<sup>‡</sup>. The MEP forward from **13**<sup>‡</sup> faces no further barrier before arriving at the inversion product **9-I**, so in this respect the two rearrangement steps are concerted. However, the ring contraction is complete in the MEP before any significant motion of a boron–ethyl group, and the MEP passes through the shoulder structure **14** (the limonene analog of **5**, not an energy minimum). Because of the tertiary cation at C<sub>2</sub> in **12**, the ring contraction is less favored than in the unsubstituted model,

and it is only  $\sim 2.8$  kcal/mol downhill from **12** to **14**. The final boron–alkyl migration is extremely exothermic. No TS leading by MEP to **9-R** could be located, and the same was true for the other conformations explored. This absence of TSs leading to retention means that conventional stationary-point calculations cannot account for the experimentally observed minor product.



**Figure 55** Lowest-energy calculated mechanism for the reaction of **8-eq** with triethylborane. Relative free energies are shown in parentheses in kcal/mol. The energy for non-minimum **14** is based on when the C<sub>2</sub>–C<sub>6</sub> distance is 1.6 Å.

## Trajectory Studies

### *Trajectory Results*

To explore whether the retention product could arise from dynamic motions after the ring contraction, trajectory studies were conducted. Quasiclassical direct-dynamics trajectories were initiated from the area of **13<sup>‡</sup>**, a conformational analog of **13<sup>‡</sup>**, and a configurational analog derived from **8-ax**. The choice of TSs used was based on the two lowest-energy **11<sup>‡</sup>** analogs for addition to 8-eq and the lowest-energy analog for addition to **8-ax**. Each normal mode was given its zero-point energy, a Boltzmann-random distribution of thermal energy appropriate for 298.15 K, and a random phase. The trajectories were integrated in 1 fs steps forward and backward in time using a Verlet algorithm and were continued until they terminated at **9/10** or returned to intermediate **12**. Our earliest exploratory studies (using an M06-2X/6-31+G\*\* surface) were initialized at **11<sup>‡</sup>**, and these trajectories afforded a 21:7 mixture of inversion to retention products. However, there were two substantial problems with starting at **11<sup>‡</sup>**. The first problem is that trajectories tended to get stuck in the area of **12**; 53% were still there after 700 fs. The trajectories that did go on to product took a median time of 489 fs after initialization. This is too long because leakage of the zero-point energy out of the C-H stretching vibrations starts to be substantial (our general rule is that quasiclassical trajectories should not be extended beyond 500 fs), making the trajectories too “hot” and unphysical.

The second problem is that the DFT (either M11 or M06-2X) is not very accurate in the area of **11<sup>‡</sup>**, relative to DLPNO-CCSD(T)/aug-cc-pVTZ energies, though they are very good in the area of **13<sup>‡</sup>** and **14**. This is described in Section 3.4 The DFT methods overestimate the energy of **11<sup>‡</sup>**, relative to **13<sup>‡</sup>**, and because of this DFT trajectories started

at **11**<sup>‡</sup> are too hot when they reach **13**<sup>‡</sup>. It might be argued that trajectories started from **11**<sup>‡</sup> are too “cool” since in reality trajectories reaching **13**<sup>‡</sup> would have retained excess energy coming from **11**<sup>‡</sup>. However, the DLPNO-CCSD(T)/aug-cc-pVTZ energies place the change from **11**<sup>‡</sup> to **13**<sup>‡</sup> at less than 1 kcal/mol, making the effect minimal.

Table 8 summarizes the stereochemical results. For both **8-eq** and **8-ax**, the inversion products (**9-I** and **10-I**) were strongly favored, but in each case significant amounts of the retention products were formed. Due to the practicality-limited number of trajectories, the 95% confidence limits on the trajectory ratios are 2.0% and 3.0% for **8-eq** and **8-ax**, respectively. The trajectories overestimate slightly the amount of inversion, but the predicted ratios are within error of the experimental observations.

**Table 8** Final trajectory results and comparison with experimental observations from the Larionov group.

System	Inversion ( <b>9-I</b> / <b>10-I</b> )	Retention ( <b>9-R</b> / <b>10-R</b> )	Ratio
<b>8-eq</b> , TS <b>13</b> <sup>‡</sup>	360	30	92.3 : 7.7
2 <sup>nd</sup> -lowest TS	328	32	91.1 : 8.9
			weighted: 91.7 : 8.3 (±2.0)
			experiment: 90 : 10
<b>8-ax</b> , lowest-energy TS	373	42	89.9 : 10.1 (±3.0)
			experiment: 87 : 13

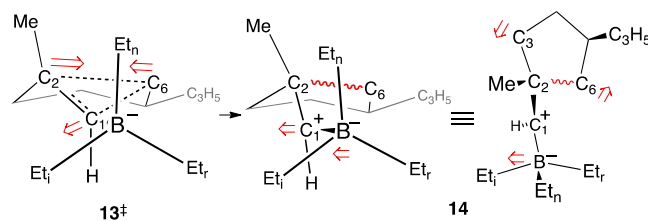
The trajectory results and their close fit with experimental observations support our hypothesis that the reaction involves a bifurcating energy surface and that the inversion and retention products arise from the same ring-contraction transition state. After the ring contraction, a sharply downward-sloping energy surface can lead from **14** to either product. The interesting question then is not why some retention is observed, but rather why inversion is so strongly favored.

A striking feature of the trajectories is that the ring contraction and boron–alkyl shifts are separated in time, eschewing any degree of synchronicity.<sup>150</sup> An average time of 216 fs was required to traverse from **13**<sup>‡</sup> to **9-I/9-R**. This includes on average 78 fs to get to **14** (defined as  $C_2-C_6 < 1.6 \text{ \AA}$  with  $C_1-C_{\text{ethyl}} > 2.3 \text{ \AA}$ ), 107 fs in the area of **14**, and **31** fs for the final highly exothermic boron–alkyl shift (defined by the  $C_1-C_{\text{ethyl}}$  distance reaching an approximate no-return threshold of  $< 2.3 \text{ \AA}$ ). Only 5% of the trajectories involve temporal overlap between the ring contraction and boron–alkyl shifts, as judged by a  $C_1-C_{\text{ethyl}}$  distance of less than  $2.3 \text{ \AA}$  before the  $C_2-C_6$  distance reaches  $< 1.6 \text{ \AA}$ . The remaining 95% of trajectories involve well-separated stages for the ring contraction and boron–alkyl shift, remaining on the edge of an energy cliff near **14** for a remarkable 113 fs on average.

#### *Trajectory Analyses*

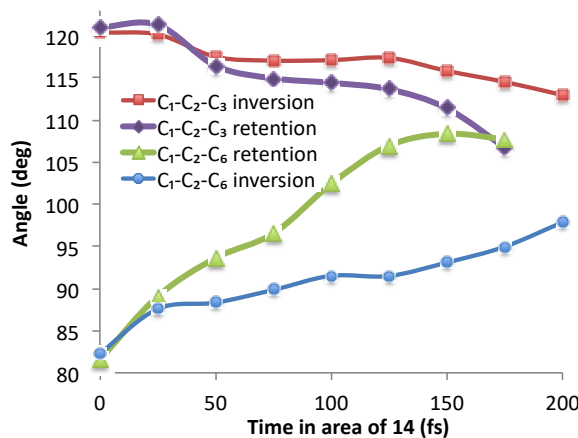
We considered first whether the inversion-engendering ethyl group ( $\text{Et}_i$ , Figure 56) was initially better aligned with the empty p-orbital of  $C_1$  than the alternative ethyl group leading to retention ( $\text{Et}_r$ ). The migration of  $\text{Et}_i$  would then be favored by a steeper, least-motion path. Trajectories, however, initially place the  $\text{Et}_i$  and  $\text{Et}_r$  in nearly equivalent positions with respect to  $C_1$  in the area of **14**. A continuation of  $C_1$  and  $C_2$  motions in the transition vector for **13**<sup>‡</sup> (Figure 56) brings the  $C_1-C_2$  bond and the non-migrating ethyl group ( $\text{Et}_n$ ) into a surprisingly encumbered eclipsed conformation (average  $C_2-C_1-B-Et_n$  dihedral angle  $-4^\circ$  with  $\sigma = 11^\circ$ ) as the trajectories reach **14**. The slightly advantageous alignment of  $\text{Et}_i$  is ephemeral as conformational twisting continues, so that the 93% of the trajectories at some point in the area of **14** have  $\text{Et}_r$  better aligned. Dihedral alignment then cannot account for predominant inversion.





**Figure 56** Composite conformational motion as  $13^\ddagger$  descends to  $14$  and  $14$  evolves with time.

The crux of the problem of understanding inversion is that the nominal structure of  $14$  (or  $5$ ) is misleading. The symmetry of the bond connections to  $C_2$  makes the  $C_2-C_6$  and  $C_2-C_3$  bonds appear equivalent. (See Section 3.4 for evidence that the distant isopropenyl group has a negligible effect on the stereoselectivity.) However,  $14$  is actually highly asymmetric in three subtle but mutually reinforcing ways: (1) the newly formed  $C_2-C_6$  bond is initially vibrationally excited, similarly to what has been seen in the acetone cation radical,<sup>47</sup> and it maintains this local excitation with a time constant of  $\sim 50$  fs, with some energy retained for up to 160 fs; (2) the empty p-orbital of  $C_1$  is initially lined up with the  $C_2-C_6$  bond, and donation from the electrons of the excited bond to  $C_1$  is retained for an extended time; (3) the  $Et_3B$  group as a whole is initially much closer to  $C_6$  than  $C_3$  ( $C_6-B$  averages  $\sim 3.1$  Å,  $C_3-B$  averages  $\sim 4.1$  Å) and the inertial effect of the  $Et_3B$  holds  $C_1$  closer to the  $C_2-C_6$  bond.

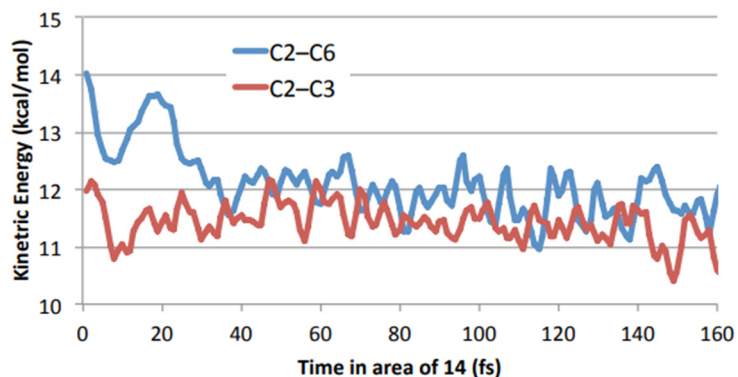


**Figure 57** Evolution of the average C<sub>1</sub>-C<sub>2</sub>-C<sub>6</sub> and C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> angles in inversion and retention trajectories after formation of **14**.

These effects and their dissipation can be seen in the slow evolution of the average C<sub>1</sub>-C<sub>2</sub>-C<sub>6</sub> and C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> angles after the formation of **14** (Figure 57). For trajectories that lead to the inversion product, the average C<sub>1</sub>-C<sub>2</sub>-C<sub>6</sub> angle increases and the C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> angle decreases over time, but the system never reaches approximate symmetry, even after 200 fs. In contrast, the retention product is associated with trajectories that symmetrize the connections to C<sub>2</sub> more rapidly. A low C<sub>1</sub>-C<sub>2</sub>-C<sub>6</sub> angle prevents formation of the retention product. This is understandable as a short-lived steric effect in which the C<sub>6</sub> methylene blocks a migrating Et<sub>r</sub>. Inversion is then favored because ~80% of the trajectories retain asymmetric geometries throughout their time in the area of **14**.

This behavior can also be seen in the kinetic energy content of equivalent bond connections in **14**. In the case of **14**, much of the excess energy appears to pass out of the area of the C<sub>2</sub>-C<sub>6</sub> bond at a faster rate. This is illustrated in Figure 58 and Figure 59. The first of these depicts, in blue, the average of the sum of the kinetic energies in carbons C<sub>2</sub>, C<sub>6</sub>, and the hydrogens attached to C<sub>6</sub> versus time after the formation of **14** (defined as when

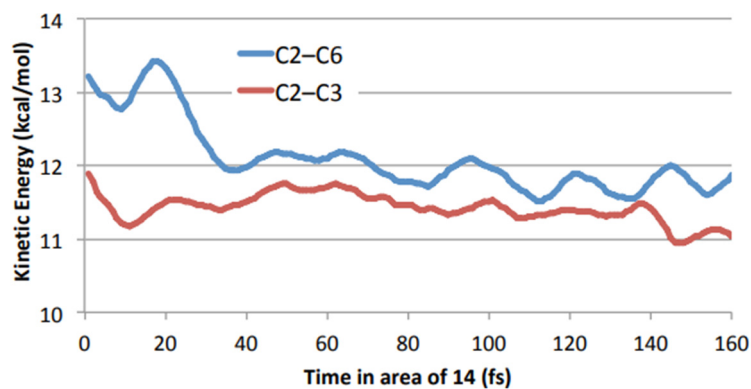
$C_2-C_6 < 1.6 \text{ \AA}$ , excluding the  $\sim 5\%$  of trajectories in which this point has  $C_1\text{-Cethyl} < 2.3 \text{ \AA}$ ), and, in red for comparison, the same quantity for carbons  $C_2$ ,  $C_3$ , and the hydrogens attached to  $C_3$ . It should be noted that initial point in this graph involves a coherence of motion in the  $C_2-C_6$  bond because of the way that **14** is defined.



**Figure 58** Kinetic energy in selected bonds and attached hydrogens versus time after initial formation of **14**.

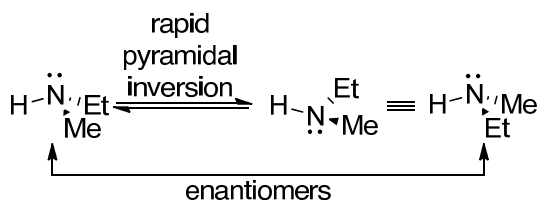
A notable feature of this chart is that it shows that a small amount of excess energy, averaging  $0.46 \text{ kcal/mol}$ , is retained in the  $C_2-C_6$  bond over that in the  $C_2-C_3$  bond for an extended time. This difference is more clearly illustrated in Figure 59, which is just the same as Figure 58 except that the points are time-averaged over a  $\pm 5 \text{ fs}$  range to smooth and filter the raw data. It should be noted that only about 20% of the trajectories survive to 160 fs past the formation of **14**, so that the averaged energies become statistically less meaningful as the chart reaches the end (averaging 150 to 250 trajectories in 60 to 100 fs range but only 70 at 160 fs). The long-term retention of energy  $C_2-C_6$  is possibly in part a manifestation of Newton's law of cooling, where the areas adjacent to the  $C_2-C_6$  bond take up extra energy

themselves very quickly initially, but after warming, they are no longer able to accept energy as quickly.



**Figure 59** Time-smoothed plot of kinetic energy in selected bonds and attached hydrogens versus time after initial formation of **14**.

Symmetry and time are intimately intertwined. Chiral atropisomers are defined by the long time required for their racemization, while the rapidly inverting ethylmethylamine is “operationally” achiral (Figure 60).<sup>124</sup>



**Figure 60** Much like  $\text{CH}_2\text{FCl}$ , ethylmethylamine is chiral as the nitrogen has four unique substituents in its valence. The pyramidal inversion that interconverts the enantiomeric structures on the picosecond timescale, rendering ethylmethylamine achiral for most purposes.

Most “memory effects” impact stereoselectivity through the time persistence of conformations.<sup>151–154</sup> On shorter, sub-picosecond time scale, dynamic matching arises when the symmetry of a short-lived formally symmetrical intermediate is broken by the retained

non-symmetrical momentum of the atoms as they enter the area of the intermediate. The general idea here is the same, but it is taken to its logical extreme since **14** is not an intermediate and since the molecular asymmetry is both energetic and geometrical.<sup>33,155</sup>

### 3.3 Conclusions

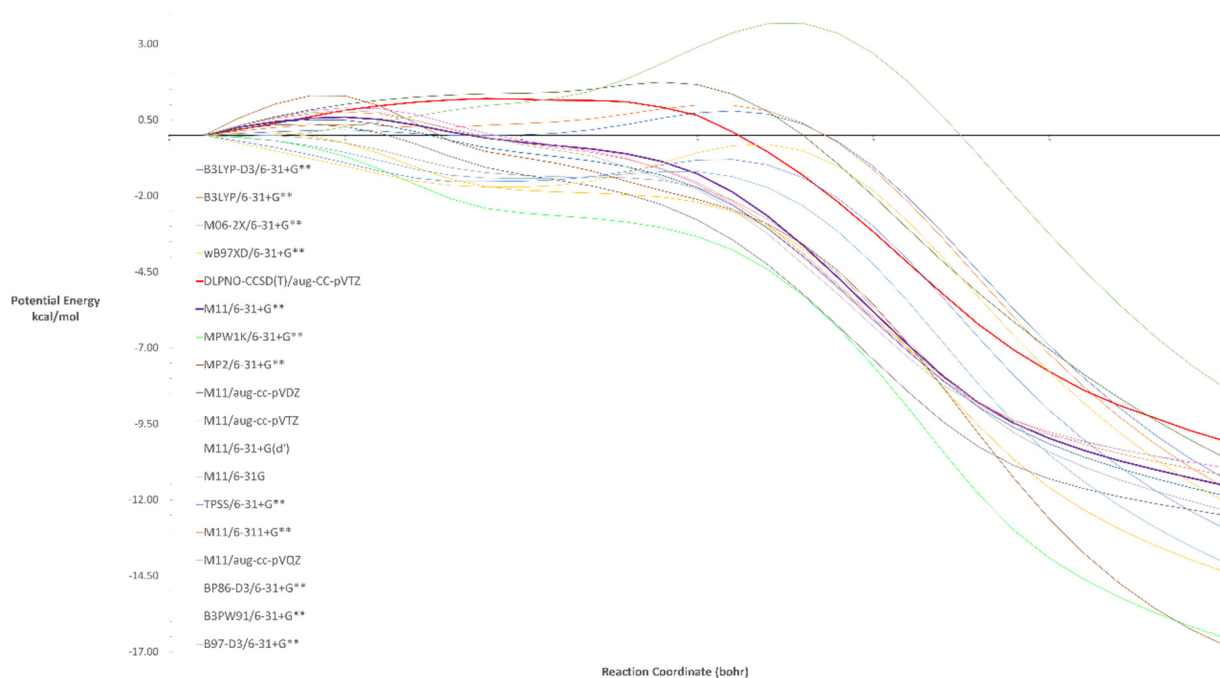
When the products of a reaction are selected within a sufficiently short time, symmetry all but disappears. As a result, molecular events that are separated in time can be interconnected by short-lived dynamical differences. This possibility is not new,<sup>44,47</sup> but here it affects the stereochemistry of an ordinary reaction in solution. This dynamical asymmetry complicates the understanding of stereochemical observations and their origin, since stereospecificity in formally concerted concomitant bonding changes would not necessarily require any degree of temporal overlap.

### 3.4 Computational Procedures

#### *Method Validation*

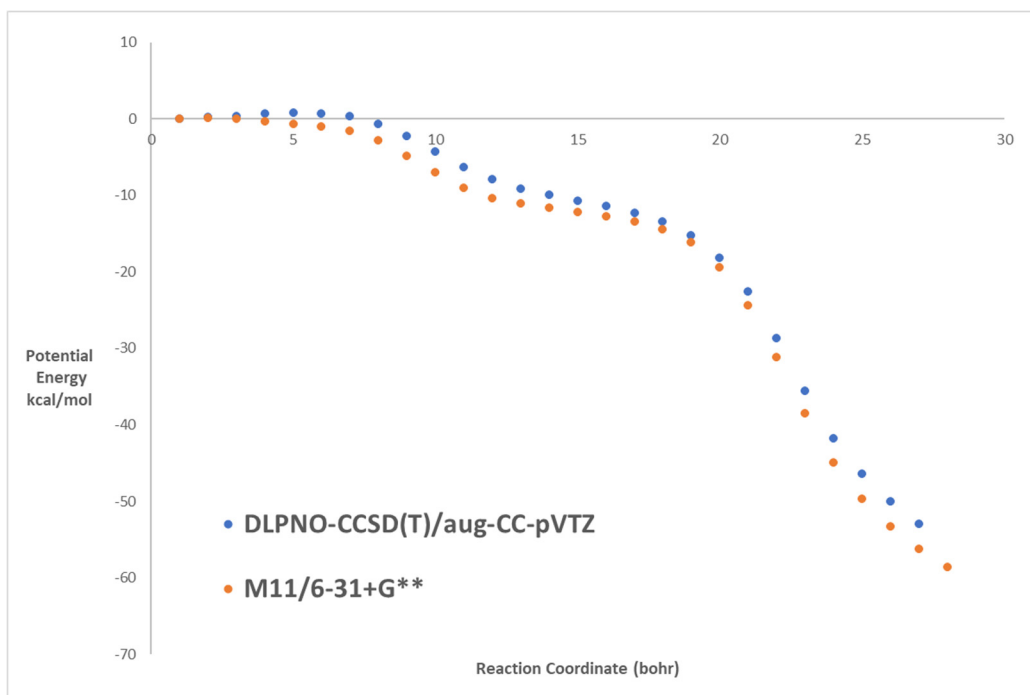
Minimum energy paths (MEPs) for the reaction of trans-cyclohexene with trimethylborane were obtained using GAUSSRATE/POLYRATE, first with M06-2X/6-31+G\*\*. Points were extracted from the latter MEP at regular intervals and subjected to single-point calculations with a large variety of DFT and ab initio methods, including DLPNO-CCSD(T)/aug-cc-pVTZ. The relative energies for the DFT methods were compared against DLPNO-CCSD(T)/aug-cc-pVTZ relative energies to establish which method most closely resembles the DLPNO-CCSD(T)/aug-cc-pVTZ. The first figure below shows a comparison of various DFT methods with the DLPNO results. It is clear that no functional was completely representative of the DLPNO (bold red) results for the entire reaction coordinate, but the M11/6-31+G\*\* (bold purple) energies exhibited a shape in the

key area of the energy surface around structure 5 that was judged to reasonably reflect that exhibited by the high-level energies.



**Figure 61** Large screen of DFT methods against an *ab initio* standard across an MEP constructed with M06-2X. Red trace indicated standard.

The similarity in this key area of the surface is illustrated in the second figure below, which is an GAUSSRATE/POLYRATE MEP recalculated with M11/6-31+G\*\*.



**Figure 62** Benchmark of the DFT method used for trajectories versus an *ab initio* standard.

### *Trajectory Details*

The trajectories were in all cases quasiclassical. For quasiclassical trajectories, each normal mode in the transition structure of interest was given its zero-point energy plus a Boltzmann distribution of quantized vibrational energies. The desired energy in each of the normal modes of the transition structure was mapped from a random number generator to a Boltzmann distribution set at 25 °C. The phase of each of the normal modes was mapped from a Gaussian distribution of random numbers. This distribution is not correct for a classical oscillator but it approximates that for a quantum oscillator in its ground state (only ignoring mode displacements outside of the classical limit), and it has the advantage that a larger portion of the trajectories start with an energy approximating the initially desired energy. By a new algorithm in PROGDYN, the displacement of the normal modes was

performed in internal coordinates. The sign on the velocity of the normal modes was randomized. After an energy/force calculation on the initial geometry, the total initial energy was calculated and the trajectory was thrown out if the energy did not agree satisfactorily (within 2 kcal/mol) with the desired energy. The average energy of accepted trajectories was 1.2 kcal/mol above the desired energy. The mode corresponding to the transition vector was treated classically. A sample PROGDYN parameter file (progdyn.conf) is given in a later section. The specific TS used for the trajectories in the main text are designated TS2-eq-A, TS2- eq-D, and TS2-ax-H. Exploratory trajectory studies were also carried out using the higher energy structures TS2-eq-O and TS2-ax-V, giving inversion to retention ratios of 173:23 and 135:28, respectively.

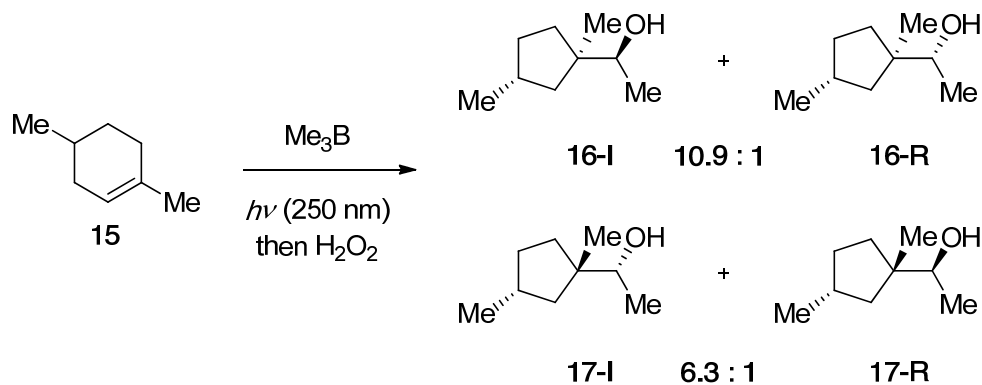
#### *Trajectory Error Analysis*

For the trajectories in the **8-ax** series, started from the area of TS2-ax-H, the standard deviation for the observed ratio of 373 to 42 was calculated from the standard formula:  $\sigma = (p * 1-p * N)^{0.5}$  where p and 1-p are the proportions of each outcome (373/415 and 42/415) and N is the total number (415), giving a  $\sigma$  of 6.14. For a 95% confidence limit, we used  $2\sigma$ , or 12.28. At the limit of this range in both directions, the ratios would be 92.8 : 7.2 and 86.9 : 13.1, giving rise to the  $\pm 3.0$  in the main text. For the trajectories in the **8-eq** series, the TSs used as the starting points are derived from TS1 structures that are very nearly equal in energy (see table in Appendix B) and the results were weighted equally in the error analysis for simplicity. Applying the formula above, we get  $p = 0.917$ ,  $1-p = 0.083$ ,  $N = 750$ , and  $\sigma = 7.54$ . This sets the 95% confidence range between 93.7 : 6.3 and 89.7:10.3, giving rise to the  $\pm 2.0$  in the main text.



### The Effect of the Isopropenyl Group

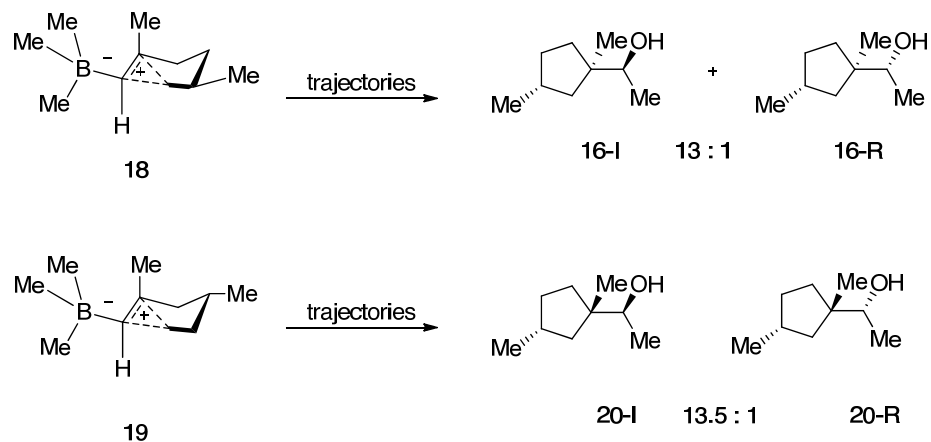
The isopropenyl group of limonene is a stereochemical marker, allowing the experimental observation of the preference for inversion over retention in the carboborative ring contraction. However, the isopropenyl group also clearly desymmetrizes the system, making the C<sub>2</sub>–C<sub>6</sub> and C<sub>2</sub>–C<sub>3</sub> bonds in **14** non-equivalent. In principle, the observed preference for formation of the inversion product could simply be the result of stereochemical induction by the distant isopropenyl group. We addressed this issue both experimentally and computationally. Experimentally, the simplification of system by changing the isopropenyl group to a methyl group and by changing the triethylborane to a trimethylborane, described below (Figure 63) for the reaction of **15**, made very little difference in the stereoselectivity. This showed that the steric size of the substituent group and boron-alkyl groups is not important in the stereoselectivity.



**Figure 63** Experiments from the Larionov group show that the product ratio is not sensitive to replacement of the isopropenyl group with a methyl group.

Computationally, quasiclassical reactive trajectories were initiated from the area of transition structures **18**<sup>‡</sup> and **19**<sup>‡</sup>, with **18**<sup>‡</sup> corresponding to the reaction of **15** and with **19**<sup>‡</sup> having a transposed pseudoequatorial methyl group relative to **18**<sup>‡</sup>. If the methyl group were

controlling the stereochemistry, then **19<sup>‡</sup>** would be expected to exhibit predominant retention. Instead, the stereochemistry is unchanged, at least to the degree that is observable with this limited number of trajectories. This supports the intuitive expectation that the distant alkyl group is not impacting the stereoselectivity to a significant extent.



**Figure 64** Trajectory studies on **18<sup>‡</sup>** closely reproduced the experimental selectivity observed with **15**. Shifting the methyl group to a remote position also does not affect the sense of stereoselectivity.

## CHAPTER IV MACHINE LEARNING TRANSITION STATE THEORY AND THE DESCENT OF TRAJECTORIES INTO CHAOS

### 4.1 Introduction

#### *Starting at Transition State Theory*

Eyring's model of calculating reaction rates, transition state theory, is a cornerstone model in chemistry.<sup>156</sup> The importance of TST in the fields of chemistry and biology cannot be overstated and with the rise of modern supercomputing clusters, this model is becoming increasingly inescapable in the literature. One might argue that the ease of use for TST has become an obstacle to developing a model to supersede it. A fundamental assumption within TST is that molecules traversing the TS do not recross, that is, any that cross the TS proceed to the product well. However, recrossing does happen. By its nature, the rate constant in TST reflects the total number of trajectories that cross the transition state, but since the recrossing trajectories are unproductive, TST in the absence of quantum mechanical tunneling (QMT) is the upper-bound on rate predictions. Working contemporaneously with Eyring, Wigner devised a recrossing factor,  $\gamma$ , in order to match TST rate predictions to experiment. In the modern formulation of the Eyring equation, the effects of recrossing and quantum mechanical tunneling (QMT) are reflected in the transmission coefficient,  $\kappa$  (eq 1).

$$k = \kappa \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}} \quad (\text{eq 1})$$

It is important to point out the free energy difference used in the Eyring equation is determined at a TS structure that is a first-order saddle point on the potential energy surface (PES). Statistical recrossing events occur when there is a mismatch between the PES and the

free energy surface (FES). Neglecting rate acceleration from QMT,  $\kappa$  is adjusted to compensate for this discrepancy and match the prediction to the phenomenological rate.

Variational transition state theory (VTST) addresses this issue in a different way. The reaction barrier is determined by the free energy change at the free energy saddle point. This remedies the aforementioned mismatch and accounts for the rate diminution from statistical recrossing. The Singleton group has been investigating reactions that exhibit dynamic effects.<sup>3,5,94,157–160</sup> One such dynamic effect is non-statistical recrossing, a phenomenon in which a trajectory will pass through the and ricochet off of a feature on the FES. This behavior is prevalent in reactions with trajectories on bifurcating surfaces and reactions with intermediates that react before they can thermalize. The effects of non-statistical recrossing cannot be predicted quantitatively even from a FES as VTST is still a statistical apparatus.

In Wigner's formulation of TST, phase space TST (PSTST), the TS is not a geometry, it is an entity described with coordinates and momentum. PSTST accommodates non-statistical recrossing through its explicit consideration of momentum and affords the most complete description of a reaction coordinate's dividing surface, the separatrix. PSTST is not attractive to the computational community as it constitutes a problem of  $6N-9$  dimensionality. A possible means of grappling with this dimensionality problem is the use of machine learning

### *The Limitations of Molecular Dynamics as a Tool for Redeeming TST*

The studies mentioned in the previous chapters illustrate that molecular dynamics simulations are a critical tool for understanding reactions that exhibit dynamic effects. However, the practitioners of reactive molecular dynamics strike a Faustian bargain. The

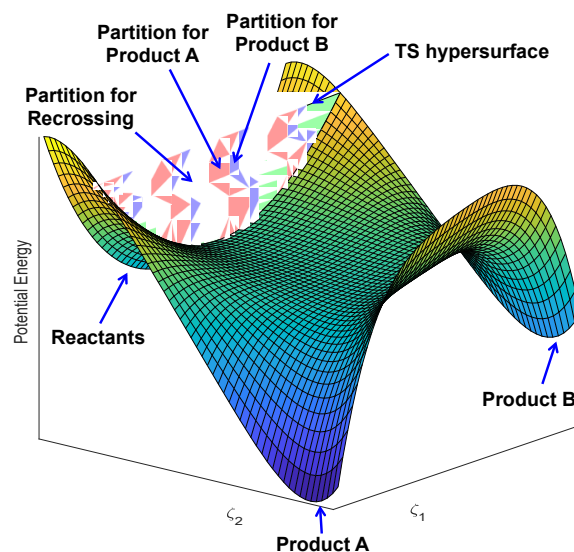
ability to predict non-TST behaviors requires simulations that are orders of magnitude more computationally expensive than traditional DFT calculations – up to 1000 DFT calculations are required for a single trajectory. Furthermore, a large dataset of trajectories is required to achieve statistical significance, on the order of  $10^2$ - $10^6$  trajectories. Users seeking to establish trends across varying conditions (e.g., temperature and energy) are burdened with the generation of multiple datasets. And most importantly, these simulations offer little direct insight to users.

In contrast to TST, where structure-activity relations are quantitative, establishing causality or correlation in trajectory outcomes is immensely difficult. The understanding of the trajectories' outcomes requires significant human effort and is not practical except in simple systems. More specifically, it is not normally possible to investigate the ensemble of initial configurations (floating points) and make a correlation to the classification of the trajectory outcome (a string). Even then, this understanding is qualitative. The high-cost, and nontrivial interpretation of reactive dynamics makes this technique impractical for most circumstances, except to domain experts. This situation obviates the need for an approach that reduces the computational cost of the simulations and increases the simulations' capacity to provide chemical ideas.

#### *Machine Learning Transition State Theory*

This methodology is inspired by Carpenter's work on three-body trajectories on double Morse potentials.<sup>161</sup> Carpenter's initial publication introduced the possibility of constructing a phase space coordinate system and predicting a trajectory outcome from the initial configuration in phase space. Our current efforts are to adopt a similar approach on systems with higher degrees-of-freedom in order to answer a fundamental question: which

trajectories will recross? This is done by subdividing the TS phase space region into segments that define trajectories that have a defined outcome such as a specific reaction product or recrossing (Figure 65). In machine-learning a model that can predict non-statistical recrossing from initial configurations, it may be possible to predict  $\kappa$  across a broad temperature range. The key advantage to such a development precludes the need for propagating a statistical ensemble of dynamics at the same temperature at which the prediction of  $\kappa$  is desired. Additionally, this methodology bypasses the variational nature of VTST altogether or a direct calculation of a FES. More broadly, this technique can be used to make predictions without using a TS structure at all – the relative energy of the starting point and this  $\kappa$  are sufficient for rate predictions. This  $\kappa$  can then be subdivided into  $\kappa$ s for each possible outcome from the TS.



**Figure 65** The subdivision of the low-dimensional cross-section of the high-dimension hypersurface.

The protocol for harvesting training set data has been developed. Upon running a large set of trajectories at some temperature, the redundant coordinates and velocities of the initial points, a TS structure, are extracted. These phase space data are associated with a reaction outcome; e.g. product A, product B, recrossing, and then formatted into a feature matrix for input into a neural network (NN). The NNs are constructed from a series of nodes that connected in a somewhat rhizomic fashion, each layer communicating some permutation of the input data to the next layer of the NN. Dropout and L2 regularization are employed in order to avoid overfitting and to minimize the number of parameters necessary to make a prediction. This model is trained for accuracy against a large set of input data. After training, the NN's robustness is determined through stratified cross-validation against data not used for learning. In order to make a prediction for another temperature, a large series of QCTs are spawned at that temperature, but not run. As with the training set, the initial configuration data is extracted. The NN accepts this data and its model predicts an outcome for each trajectory. This will be referred to as "Level-1" or "Level-2" accuracy. Level-1 accuracy is the network's ability to predict product-forming and recrossing trajectories in a test set. Level-2 accuracy is the network's accuracy in predicting subclasses within the same test set. These trajectory subclasses make a distinction between reactant-side recrossing and product-side recrossing. "Level-3" accuracy is the ML function's ability to make predictions across varying temperature or energy conditions.

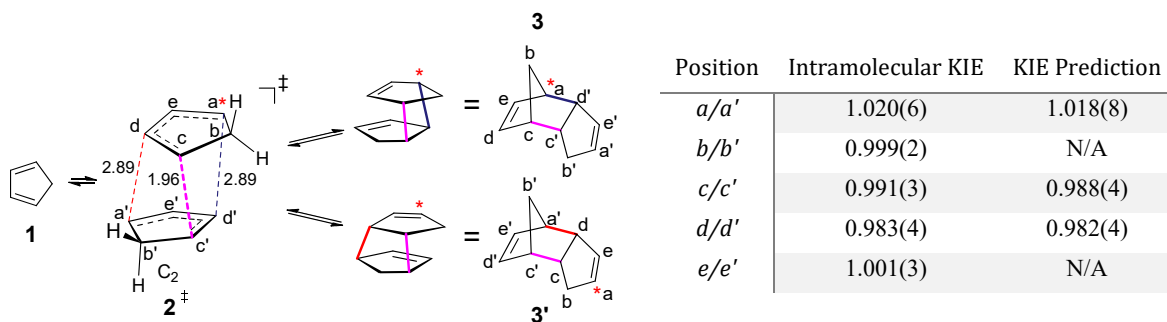
## **4.2 The Dimerization of Cyclopentadiene**

### *Introduction*

The Diels-Alder dimerization of cyclopentadiene is mechanistically unique. Both cyclopentadiene reactants can react as either diene or dienophile and the reaction proceeds

through a  $C_2$ -symmetric, bispericyclic TS. This highly symmetric TS structure is understood to decompose along a bifurcating surface into a 1:1 mixture of degenerate products. However, isotopic labeling at any position of the reactants would desymmetrize the PES and lead to isotopomeric products. In an exhaustive study, the Singleton group characterized this TS structure and examined its ambimodal nature.<sup>7</sup> Experimental KIEs were readily determined from the product mixture in an intramolecular fashion. Isotopic substitution desymmetrizes this bifurcating surface in mass-weighted coordinates, leading to steeper gradient along the path that gives  $^{12}\text{C}$  priority in reacting. Because this Newtonian isotope effect does not stem from ZPE effects at the TS, it is not possible to predict it with conventional approaches such as applying the Bigeleisen-Mayer equation,<sup>162</sup> which are reliant on the validity of the assumptions and approximations inherent to TST. The prediction of  $^{12}\text{C}/^{13}\text{C}$  KIEs from isotopically labeled MD trajectories is possible, however it requires a prohibitively large number of trajectories ( $\sim 10^6$ ) to render a KIE prediction with acceptable precision. The authors devised an elegant solution: perform a small number of trajectories with a series of superheavy carbon isotopes and extrapolate to the results of  $^{12}\text{C}/^{13}\text{C}$  system.





**Figure 66** Experimental and predicted Newtonian KIEs from Kelly *et al.* Numbers in parentheses represent 95% confidence limits in the last digit. The intramolecular KIEs are defined as  $k_{12c}/k_{13c(a)}/k_{12c}/k_{13c(a')}$ ,  $k_{12c}/k_{13c(b)}/k_{12c}/k_{13c(b')}$ . No noticeable KIE was seen in positions *b/b'* and *e/e'*.

The analyses in this work suggest that the observed KIEs arise from the desymmetrization of steepest descent paths in mass-weighted coordinates for  $^{13}\text{C}$  in *a*, *c*, and *d*. With this perturbation to the steepest descent path,  $^{13}\text{C}$  atoms in positions *a* and *d* must travel further than analogous  $^{12}\text{C}$  atoms to complete the bond formation process. The KIE observed at position *c* reflects the issue that heavier atoms at this position slow the bond-forming motion of the adjacent *d* position and exert an influence on the overall product selectivity.

### Computational Results and Discussions

#### Trajectory Studies

A variety of room temperature B3LYP/6-31G\* QCTs were initiated at  $2^\ddagger$  (Table 9-Table 11). The first set of trajectories are standard QCTs, the second set are anharmonicity-corrected QCTS, and the third set are anharmonicity-correct QCTs with the *a* position labeled with  $^{14}\text{C}$ . The results of these trajectories are shown below.

**Table 9** Trajectory outcomes for standard QCTs initiated at 298 K.

Trajectory	Counts	Percentage
SM to $a$	14771	43.7%
SM to $a'$	14839	43.9%
Starting Material Recrossing	1141	3.4%
Product Recrossing	3018	8.9%
Total Trajectories	33769	
Predicted "KIE"	0.995±0.01	

**Table 10** Trajectory outcomes for anharmonicity-corrected QCTs initiated at 298 K.

Trajectory	Counts	Percentage
SM to $a$	20901	46.8%
SM to $a'$	21331	47.8%
$a$ to SM	92	0.2%
$a'$ to SM	75	0.2%
Starting Material Recrossing	1395	3.1%
Product Recrossing	855	1.9%
Total Trajectories	44649	
Predicted "KIE"	<b>0.980±0.01</b>	

**Table 11** Trajectory outcomes for anharmonicity-corrected QCTs initiated 298 K. These trajectories are spawned with  $^{14}\text{C}$  at the 10<sup>th</sup> atomic position,  $a$ .

Trajectory	Counts	Percentage
SM to $a$	2489	45.9%
SM to $a'$	2436	44.9%
$a$ to SM	11	0.2%
$a'$ to SM	11	0.2%
Starting Material Recrossing	217	4.0%
Product Recrossing	263	4.8%
Total Trajectories	5427	
Predicted $^{12}\text{C}/^{14}\text{C}$ KIE	<b>1.022 ± 0.06</b>	

The predicted KIE in Table 11 is as close to the experimental 1.020(6) as the prediction (1.018(8)) from the original paper (a  $^{13}\text{C}/^{12}\text{C}$  KIE), however, the KIE prediction here is subject to significant uncertainty.

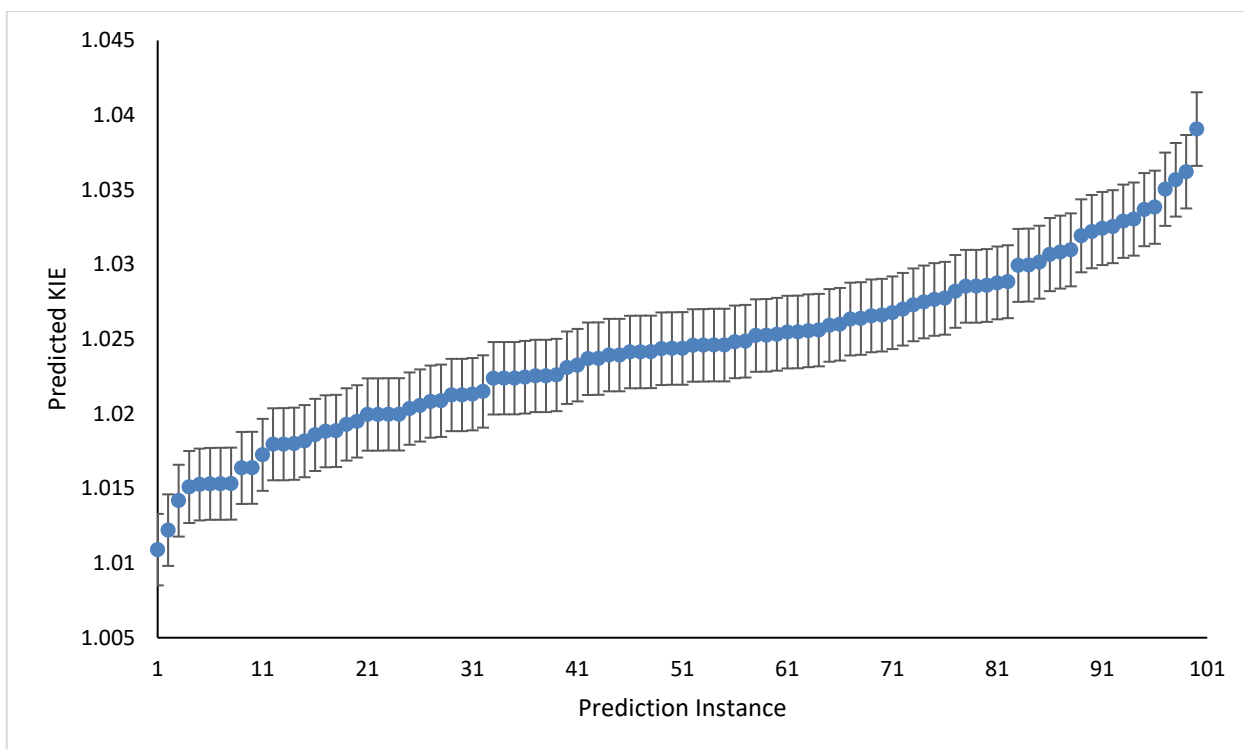
## Machine Learning Studies – Groundhog

The Groundhog algorithm uses a training set of  $^{14}\text{C}$ -labeled anharmonicity-corrected trajectories to train a neural network model. The features used for training include the velocity of all real and imaginary modes (60), displacement of all real modes (59), and a handful of handmade measures of the structure's symmetry (more on this later). As new  $^{14}\text{C}$  trajectories are spawned, the neural network predicts the outcome of the trajectory. If the neural network is greater than 60% (called the "interesting" parameter in the PROGDYN software) certain about the trajectory outcome, the trajectory is discarded. Trajectories whose outcomes are less certain are allowed to run. Once completed, the trajectory's initial phase space features and outcome are extracted and added to the training set. The effect of this algorithm is to run trajectories that are especially difficult to make predictions about. This enhanced sampling technique eventually leads to finer definition of boundaries between regions of phase space that lead to different trajectory outcomes. An additional benefit of this approach is that the new data collected is not redundant with data in the training set. An indirect consequence of this approach is that the outcome of Groundhog trajectories has an increased population of rare-event trajectories such as recrossing, and the ratio of products does not represent the mixture predicted by a traditional Boltzmann ensemble of trajectories. Table 12, below, shows that in Groundhog trajectories, recrossing trajectories are  $\sim 2.5\times$  more abundant than in the trajectories in Table 11. The large KIEs observed in these trajectories pose an interesting question: what about the "SM to  $\alpha$ " trajectories is so difficult to predict that the Groundhog algorithm preferentially spawns them? The answer is not yet clear. Table 11 **Trajectory outcomes for anharmonicity-corrected QCTs initiated 298 K. These trajectories are spawned with  $^{14}\text{C}$  at the 10<sup>th</sup> atomic position,  $\alpha$ .**

**Table 12** Groundhog trajectory outcomes for  $^{14}\text{C}$ -labeled QCTs at 298 K.

Trajectory	Counts	Percentage
SM to $a$	8592	39.7%
SM to $a'$	7995	36.9%
Starting Material Recrossing	2755	12.7%
Product Recrossing	2317	10.7%
Total Trajectories	21659	
Predicted "KIE"	1.075±0.03	

Monitoring the accuracy over time, the Groundhog NN model begins at 22.3% accuracy in predicting the outcome of trajectories from an outside test set, but after a few hundred trajectories the accuracy improves to 83% and slowly reaches 88.5% accuracy (Level 2). A Level-1 accuracy of 95.5 was calculated separately. Finally, the neural network model was trained on the Groundhog trajectory dataset (21308 datapoints) was used to predict the outcome of 3,092,142  $^{14}\text{C}$ -labeled trajectories. This was performed 100 times in order to ascertain the precision in this prediction (Figure 67).

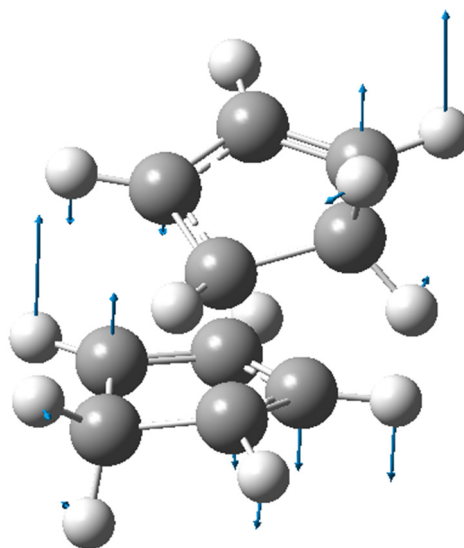


**Figure 67** MLTST KIE predictions, sorted by increasing KIE. Vertical bars indicate uncertainties at the 95% confidence interval as calculated by a standard error function.

The predictions carried an average 95% confidence interval of 0.002. This free lunch amplification offers a precision far exceeding that of any practical QCT dataset. The average  $^{14}\text{C}/^{12}\text{C}$  KIE from these predictions is  $1.024 \pm 0.001$ . This uncertainty offers a metric of the variance in the predictions caused by variance in the model construction, but does not account for the variance due to insufficient sampling in the training data, therefore does not reflect the expected variance of the training data were harvested from scratch.

Satisfied with the accuracy and precision of the KIE prediction, the neural network model analyzed for insight into important correlations. This was initially done by removing one input feature from the neural network, re-training the network, and checking for any large changes in accuracy. A systematic screen of all input features suggested that besides

the velocity of the first real mode (Figure 68), no single feature had a strong impact on prediction accuracy. This does not mean that only mode 1 is important, it is possible that a collection of seemingly unimportant features combine in a nonlinear fashion to produce an accurate model.

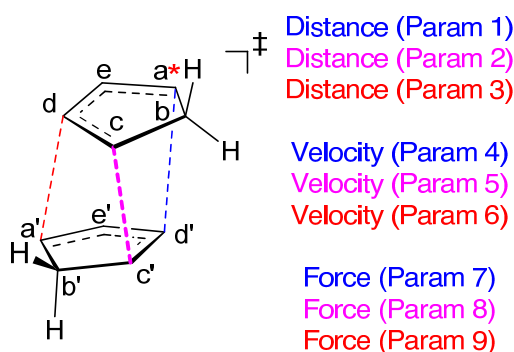


**Figure 68** Displacement vectors for a  $84\text{ cm}^{-1}$  normal mode in  $2^\ddagger$ .

Mode 1 is a low frequency ( $84\text{ cm}^{-1}$ ) torsional mode that desymmetrizes the  $C_2$  symmetric transition state structure. Depending on its phase, motion along this most places atoms  $a$  and  $d'$  in proximity, while distancing atoms  $a'$  and  $d$ , or vice versa. There are other low frequency modes in  $2^\ddagger$  that distort the inter-atomic distances in a similar fashion, further investigations will focus on why mode 2 is particularly important for prediction accuracy.

A separate analysis of which input features are decisive in  $a$  vs  $a'$  selectivity was conducted through the binning of input feature values into numerical ranges and comparing them against the probability of a trajectory terminating with either  $a$  or  $a'$  product formation. Like the previous analysis, this analysis suggested that the velocity of real mode 1 is

important for product selectivity. The analysis also suggested that the displacement in this mode decisive as well. Of the custom-defined features, the displacement and velocity along the  $a-d'$  (Param 1,4) and  $a'-d$  (Param 3,6) internuclear axes also seemed to toggle the trajectory outcome.



**Figure 69** Color coded representation pairing parameter number to descriptors of internuclear relationships along the three key bonds in  $2^\ddagger$ .

### *Computational Procedures*

#### **Anharmonicity Corrections**

Anharmonicity corrections are performed by taking the structure for  $2^\ddagger$  and systematically varying the phase of each real normal mode. As each mode is varied, a single point energy calculation is performed. The energy from this calculation is compared to the energy predicted via the harmonic force constants from the frequency analysis. The difference in these energies, as well as the change in normal mode phase, are used to fit a first order correction to the harmonic force constants (Table 13).

**Table 13** Force constants and anharmonic corrections for  $2^\ddagger$

Mode	Force Constant	Force Constant Correction
2	2.397	-0.017
3	2.889	-0.045
4	5.121	-1.729

Table 13 continued from above

Mode	Force Constant	Force Constant Correction
5	9.543	-0.178
6	16.544	0.009
7	14.917	0.285
8	16.107	-0.396
9	37.923	2.581
10	36.433	0.573
11	27.856	0.558
12	26.824	-0.125
13	32.275	0.374
14	34.542	0.756
15	82.24	-0.773
16	111.231	-4.627
17	129.138	6.328
18	119.374	3.376
19	69.568	-13.382
20	69.629	2.728
21	59.619	1.871
22	55.026	0.489
23	54.734	-1.683
24	61.524	2.004
25	67.074	4.72
26	78.502	-6.782
27	60.577	6.034
28	68.251	-0.848
29	97.606	-22.01
30	61.38	-1.658
31	59.165	-2.983
32	66.264	-2.929
33	69.227	10.317
34	73.173	6.921
35	62.683	7.099
36	72.889	2.029
37	134.072	11.919
38	127.233	8.206
39	102.723	0.577
40	115.259	-4.412



Table 13 continued from above

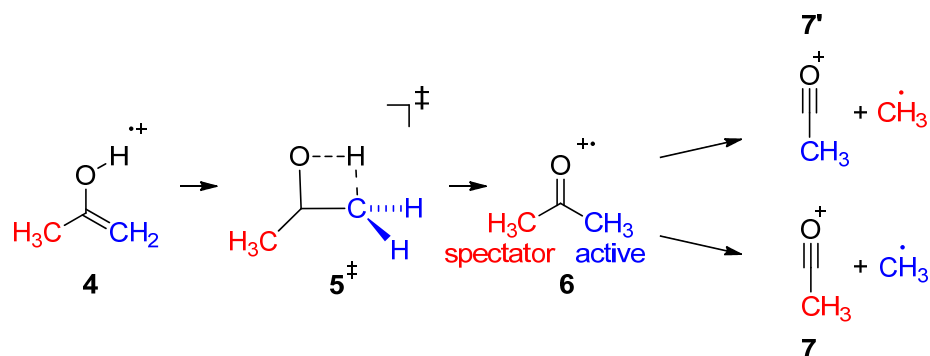
Mode	Force Constant	Force Constant Correction
41	239.01	-49.04
42	249.121	-33.704
43	213.918	61.729
44	226.389	70.293
45	106.668	15.729
46	105.634	12.989
47	351.787	162.289
48	429.288	-337.378
49	418.313	620.581
50	412.795	-17.36
51	452.294	-662.682
52	450.549	9.984
53	471.849	1.848
54	463.889	669.967
55	479.512	67.921
56	488.624	-671.12
57	486.697	-633.783
58	491.956	744.092
59	500.596	699.963
60	498.458	-742.886

### 4.3 The Dissociation of Acetone Cation Radicals

#### *Introduction*

McLafferty rearrangement has frustrated chemists for the last forty years. Ubiquitous in mass spectrometry, this reaction generates acetone cation radicals in the enol form (**4**). The enol rearranges to the keto-form (**6**) via hydrogen atom transfer (HAT) (**5<sup>‡</sup>**) in a highly exothermic fashion, imbuing the keto intermediate with excess energy. This intermediate rapidly fragments into acylium cations and methyl radicals. Although the acetone cation radical is a symmetrical intermediate, a large body of experimental literature suggests that

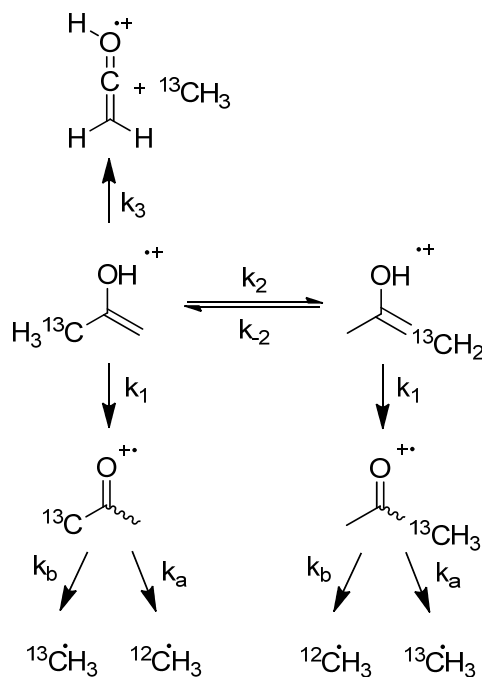
the “active” carbon that receives the hydrogen atom is more likely to dissociate than the “spectator” carbon.



**Figure 70** The mechanism of the conversion of acetone cation radical to acylium cations and methyl radicals proceeds via intramolecular HAT, followed by an uphill dissociation process.

At room temperature, the product mixture from metastable ion and collision induced dissociation experiments is ~1.4:1 active : spectator.<sup>163–166</sup> Brauman performed continuous wave infrared multiple-photon dissociation experiments to measure a rather uncertain minimum selectivity of 1.17. Brauman’s metastable ion and pulsed laser experiments placed the selectivity at 1.36 and 1.55, respectively. These methods were expected to imbue 4 with greater energy upon formation and grant a more selective fragmentation. Tureček’s work in this area studied this energy-activity relationship with isotopically labeled hydrogen and carbon systems. Key observations from the study were that the dissociations experienced a quick rise and extended fall with increasing electron impact energy. Tureček proposed a kinetic scenario (Figure 71) in which reaction selectivity ( $k_a$  vs  $k_b$ ) was complicated by the convergence of three pathways. The formed acetone enol cation radical could 1) fragment directly to give exclusively spectator methyl dissociation ( $k_3$ ) 2) undergo 1,3-isomerization

to scramble the isotope labels in the enol ( $k_2$  and  $k_{-2}$ ) 3) isomerize to the keto form and fragment from there ( $k_1$ ).

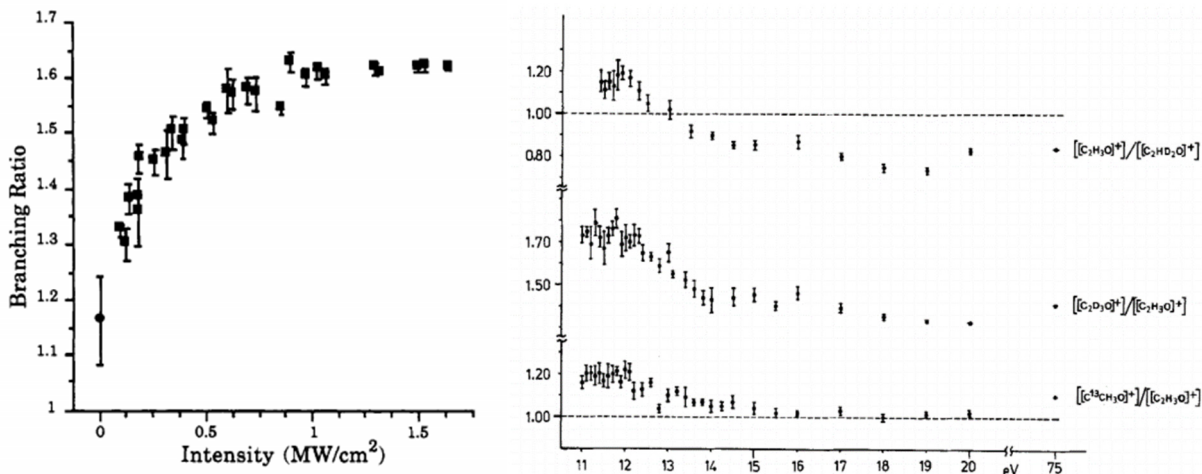


**Figure 71** Tureček's mechanistic proposal invokes unselective side-reactions to rationalize the monotonic energy trend from experiments.

Tureček proposed that reaction selectivity reaches a point of diminishing returns because the more energetically costly  $k_3$  and  $k_2$  pathways become more competitive with  $k_1$  as the system energy increased. Direct dissociation via  $k_3$  was judged to be least competitive with the productive reaction, in agreement with previous work from McLafferty. Attempts to understand this energy trend with RRKM theory produced predictions inconsistent with the observations.<sup>167</sup> It was understood that these failures reflected the non-ergodic (nonstatistical) nature of the acetone cation radical intermediate.

There is not a consensus on the relationship between energy and selectivity between Brauman's and Tureček's studies. Figure 72 shows the qualitatively different trends for the

branching selectivity as a function of energy. A complicating factor is that correlating the energy of the ionization source to the energy of the formed ion is not straightforward and not readily done for comparison between ionization conditions, even with identical precursors for the ions.



**Figure 72** Experimental branching ratios from Brauman (left) and Tureček (right). Left figure re-printed with permission from “Infrared Multiple-Photon Dissociation of the Acetone Enol Radical Cation. Dependence of Nonstatistical Dissociation on Internal Energy” by Osterheld, T.H.; Brauman, J.I. *J. Amer. Chem. Soc.* 1993, *115*, 10311-10316.<sup>168</sup> Copyright 1993 American Chemical Society. Right figure re-printed with permission from “Loss of Methyl from  $[\text{H}_2\text{C}=\text{C}(\text{OH})-\text{CH}_3]^+$  Ions Prepared by Electron Impact Ionization of Unstable 2-Hydroxypropene” by Tureček, F.; Hanuš, V. *Org. Mass. Spectrum.* 1984, *19*, 631-638.<sup>166</sup> Copyright 1984 Wiley Heyden Ltd.

More recent reactive dynamics studies from Carpenter and Schlegel give a qualitative perspective on the behavior of this intermediate.<sup>47,169,170</sup> Carpenter’s study of the PES accurately describes that the HAT is highly exothermic and that the dissociation of methyl radicals from the acetone intermediate is uphill with respect to the intermediate. Conducting reactive QCTs starting at the TS for HAT, Carpenter observed a branching ratio of  $1.13 \pm 0.09$  favoring the active methyl group. The analysis of trajectories suggested that

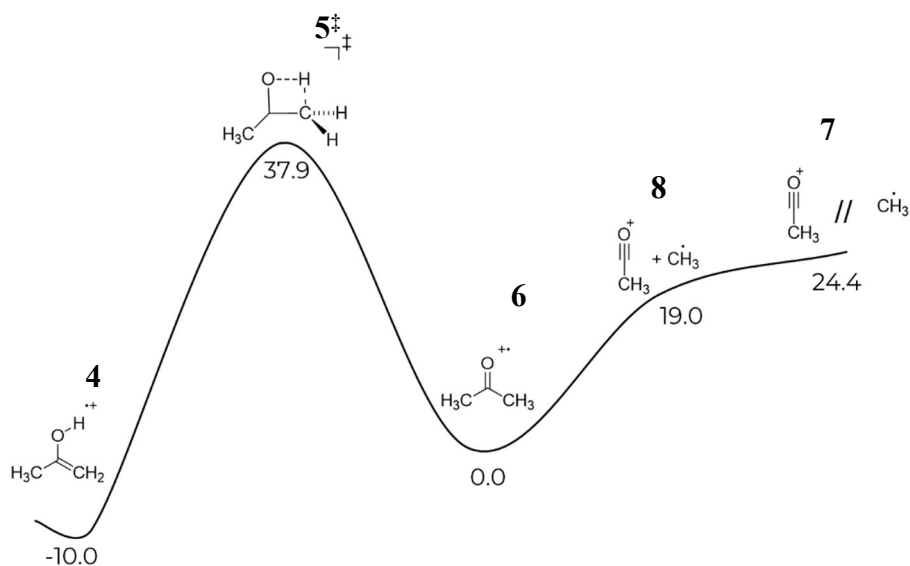
after HAT, active methyl dissociation trajectories never truly visit the geometric space defined for the symmetrical keto intermediate before fragmenting. Trajectories initiated at the **6** with additional energy commensurate to **5<sup>‡</sup>** fragmented in a 1.01 : 1 ± 0.01 ratio. While the significance of this result is questionable, the fact that any trajectories from **5<sup>‡</sup>** exhibited dissociation at all agrees with the suggestion from experimentalists that the acetone cation radical keto form retains with sufficient excess energy to rapidly surmount a steep energetic barrier to dissociation.

Schlegel's work is similar to Carpenter's in most respects. Trajectories starting at **5<sup>‡</sup>** with an additional 10kcal/mol of excess energy predicted a branching ratio of 1.53:1 ± 0.20, in good agreement with a ratio of 1.55 : 1 from Brauman's experiments. Schlegel's trajectory analysis showed that, on average, ~50% of energy available after the cleavage is converted to vibrational energy in the acylium fragment and ~25% is converted to translational energy in the methyl radical fragment, with dissociation active methyl groups receiving ~0.8 kcal/mol more translational energy than their dissociating spectator counterparts. In trajectories initialized at **5<sup>‡</sup>** with excess energy, Schlegel observed greater selectivity for the active methyl group, especially when this energy was localized to normal modes that involved stretching or bending of methyl group bonds.

This body of evidence suggests that selectivity in this dissociation originates in **5<sup>‡</sup>** as a bond-memory effect, much like the one seen in Chapter III. This is not a radical idea and some form of this notion has existed in the literature consensus for decades. Still, quantitative relationships between energy and selectivity for this simple unimolecular reaction elude chemists.

### Potential Energy Surface Studies

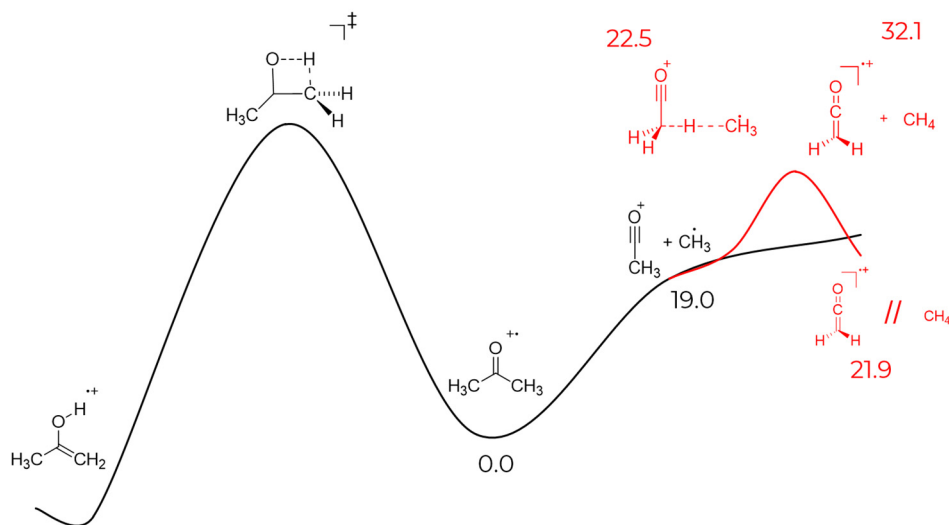
After extensive benchmarking of methods against a set of CCSD(T)/aug-CC-pVTZ calculations, the B2PLYP double hybrid DFT method and 6-31+G\*\* basis set proved to be sufficiently accurate for the description of PES for entire mechanism. The stationary points along the pathway connecting the acetone radical cation (enol) to dissociated acylium ion and methyl radical are shown in Figure 73.



**Figure 73** Energies are B2PLYP/6-31+G\*\* potential energies given in kcal/mol.

This surface shows that, classically, the keto isomer **6** is formed with 37.9 kcal/mol excess energy. If this energy is retained, the intermediate can escape the potential well and go on to dissociation, calculated to have a potential energy of 24.4 kcal/mol at infinite separation. With the inclusion of ZPE, this exothermicity and exit barrier decrease to 35.1 and 19.5 kcal/mol, respectively. An additional pathway is available to **6**, whereby the

dissociated radical is capable of abstracting a hydrogen from acylium to form an ketene radical cation/methane pair (Figure 74).



**Figure 74** Energies are B2PLYP/6-31+G\*\* potential energies given in kcal/mol.

### *Initial Trajectory Studies*

#### **Trajectory Results**

Three different approaches to study the behavior of **5<sup>‡</sup>** were made. QCTs at 298K and anharmonicity-corrected QCTs at 298K were initiated at **5<sup>‡</sup>**. Anharmonicity parameters (described in Section “Computational Methods”) improve the initial structure guess in trajectory initializations, but do not qualitatively change the behavior of trajectories. Classical reactive trajectories that treat the TS as a classical harmonic oscillator, were also initiated. Aside from the quantization of displacements and velocities in QCTS, an important distinction between quasiclassical and classical trajectories is that quasiclassical trajectories include quantum mechanical ZPE in the calculation of kinetic energy in each mode, whereas

classical trajectories only provide an average of RT kinetic energy to each normal mode. Although classical trajectories can be run indefinitely, these trajectories were terminated at 1000 fs. QCTs were limited to a maximum duration of 500 fs to avoid the spurious transfer of ZPE into kinetic energy. Trajectories that reached the time limit for any series were assumed to have undergone IVR and expected to partition equally between the spectator and active pathways. A trajectory's selectivity was judged by which bond had reached a length of 5 Å first. The results of these three trajectories studies are below (Table 14).

**Table 14** Results from the first runs of reactive trajectories.

Outcome	Quasiclassical	Quasiclassical w/ anharmonicity	Classical
Active Dissociation	64	338	41
Spectator Dissociation	8	51	20
Reached Time Limit	98	614	234
Recrossed to Enol	6	29	7
Percent Recrossing	3.4%	2.8%	2.3%
Total Trajectories	176	1032	302
Ratio	$1.98 \pm 0.13$	$1.80 \pm 0.05$	$1.15 \pm 0.05$

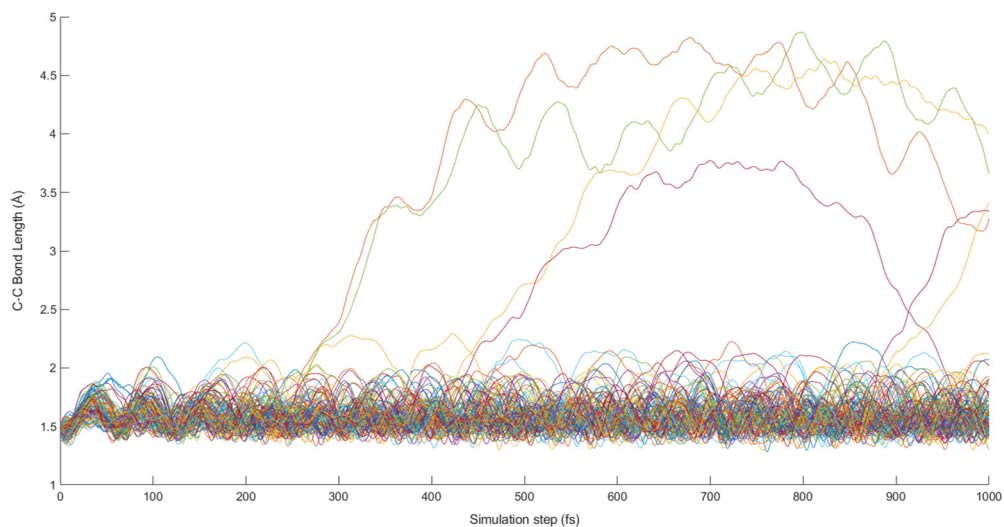
### Trajectory Analysis

All three methods of simulating the dissociation after  $5^\ddagger$  arrive at the same qualitative conclusion; the active methyl group dissociates at a higher frequency than the spectator methyl group. The selectivities from trajectories show significant deviation from experimental observations, however these trajectories will form the basis of a more robust approach.

No reactivity along the ketene radical cation pathway was as observed with any method. A small portion of trajectories recrossed back to the enol structure, typically within 50 fs. This recrossing did not vary significantly between the methods. The classical trajectory



method, although inferior to the other methods, when compared to the QCTs demonstrates that the reaction selectivity is dependent on the energy content available initialization. This can be gleaned from the number of trajectories reaching the maximum duration threshold for each method. In classical trajectories the barrier to exit relative to the excess energy is greater than in QCTs. Classical trajectories arriving at the structure **6** lack the energy to continue to dissociation. A few of these trajectories do exhibit C-C cleavage, however the fragments lack the momentum to escape the potential well centered at **6** and persist on a nearly flat region of the potential energy surface between **7** and **8** (Figure 75).



**Figure 75** The time-evolution of C-C bond lengths in classical trajectories that reach the 1000 fs time constraint.

This behavior, aptly named “roaming” by Bowman,<sup>171</sup> has been implicated in numerous experimental and theoretical studies of aldehyde and ketone photodissociation in the gas phase.<sup>172–179</sup> The fragments in these roaming trajectories will reach a separation of almost 5Å between fragments, liberating and orbiting each other for hundreds of

femtosecond, before coalescing to reform the acetone keto structure. This is because the fragments lack the energy and velocity coherence to cross the dynamical bottleneck between loose complexation of the two fragments and freely dissociated fragments. This behavior calls previous studies from Schlegel and Carpenter into question, as those trajectories were terminated prematurely at inter-fragment distances of 2.0Å.

The effect of energy on selectivity and recrossing was indirectly investigated by performing trajectory at a range of temperatures. Classical trajectories conducted at 1094 K displayed even greater selectivity than their 298 K counterparts (Table 15), but the small sample size renders any discussion of recrossing speculative.

**Table 15** Results of investigation of energy/selectivity relationship in classical trajectories.

Outcome	298 K Classical	1094 K Classical
Active Dissociation	41	68
Spectator Dissociation	20	37
Reached 500 fs	234	3
Recrossed to Enol	7	5
Percent Recrossing	2.3%	4.4%
Total Trajectories	302	113
Ratio	$1.15 \pm 0.05$	$1.81 \pm 0.12$

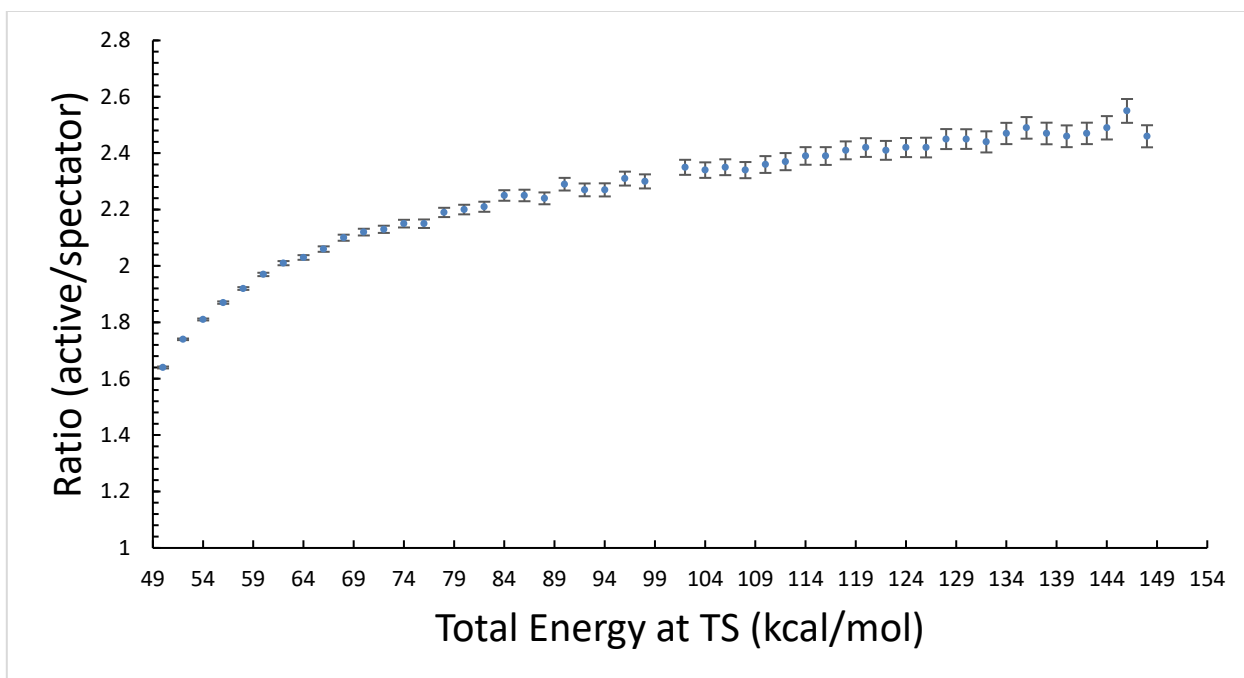
In anharmonicity-corrected QCTs (Table 16), the influence of energy is more lucid. Even at absolute zero, trajectories display a preference for active methyl group dissociation. The trajectories become more selective with increasing energy, a promising result in light of the mismatch with experimental selectivity at 298 K. Recrossing and long-lived trajectories become less frequent as the simulation temperature increases.

**Table 16** Results of investigation of energy/selectivity relationship in QCTs.

Outcome	0 K	298 K	1500 K
Active Dissociation	23	338	377
Spectator Dissociation	8	51	104
Reached Time Limit	102	614	204
Recrossed to Enol	318	29	15
Percent Recrossing	70.5%	2.8%	2.1%
Total Trajectories	451	1032	700
Ratio	$1.25 \pm 0.08$	$1.80 \pm 0.05$	$2.33 \pm 0.13$

### *Machine Learning Studies*

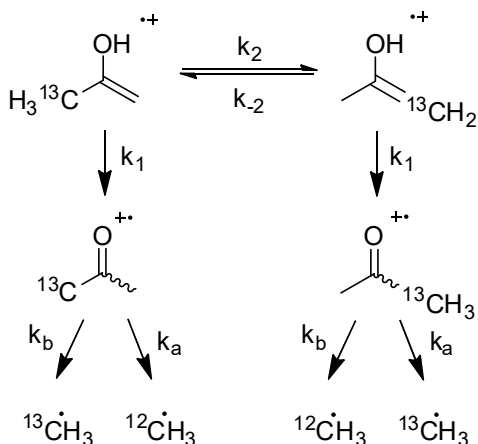
A training set of 4417 anharmonicity-corrected QCTS at 298 K (including 2660 Groundhog trajectories), 1000 K, and 1500 K were combined in order to train a neural network model. Neural network was trained on thirty phase space features of the input data and classified by outcome as “active”, “spectator”, or “time limit reached”. Even for a simple such as this, the testing accuracy for the neural network was ~60%. It was judged that this was acceptable as the classification errors largely canceled out to give predicted ratios that matched the input set ratios. The reason for this error cancelation is not entirely clear, but it is possible that the “reached time limit” trajectories act as a quantitative cushion as error in predicting these only contributes “half” trajectory to both active and spectator classes. The trained neural network was then fed  $10^7$  initial trajectory points and used to make predictions of trajectory outcomes in 2kcal/mol increments from 49 kcal/mol to 147 kcal/mol.



**Figure 76** MLTST prediction of energy-dependent dissociation selectivity. Error bars calculated at 99% confidence interval.

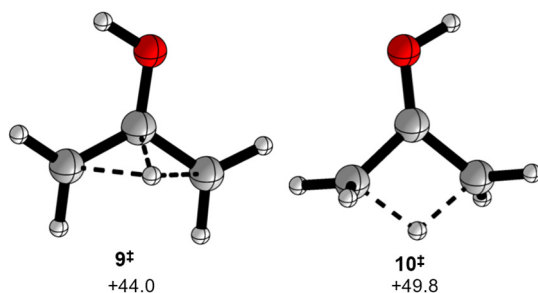
The results produce an energy-selectivity trend that matches with expectations from the Brauman and with the intuition afforded by these and other trajectory studies. The issue however remains that the most physically accurate trajectories, those anharmonicity-corrected QCTs at 298 K, are not a quantitative match with experiment.

In order to see if higher energy pathways might affect the agreement with experiment, a basic kinetic model was constructed (Figure 77).



**Figure 77** Kinetic scenario invoked for RRKM corrections

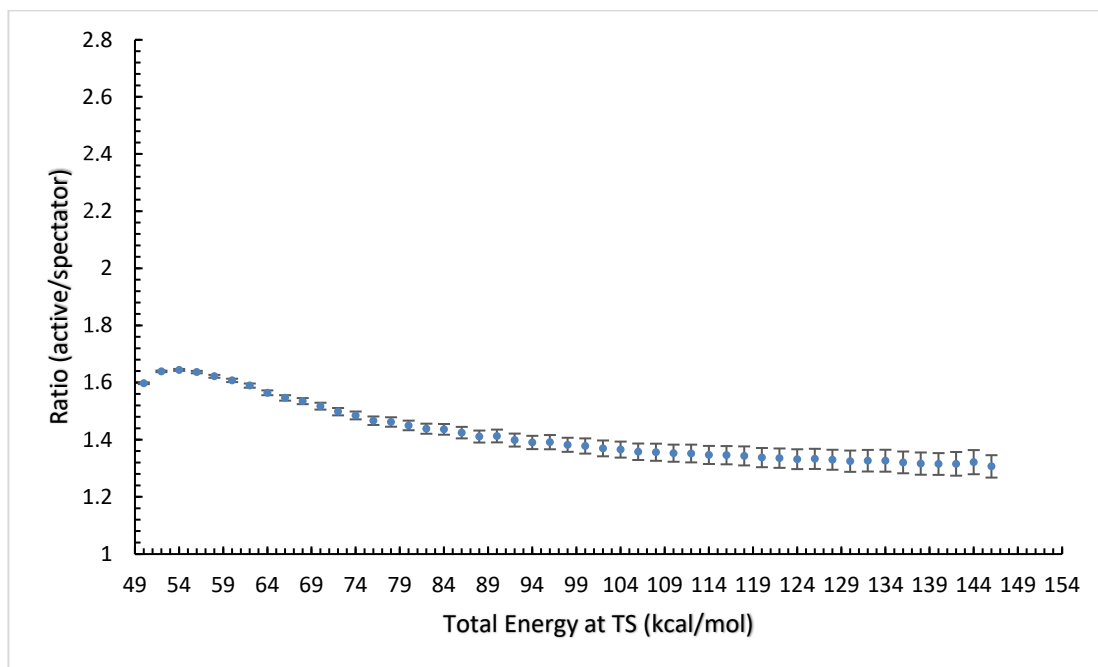
Structures **9<sup>‡</sup>** and **10<sup>‡</sup>** were located with standard techniques (Figure 78) and **9<sup>‡</sup>** was used to calculate the ratio of microcanonical rate constants  $k_1$  and  $k_2$  in 2 kcal/mol energy increments with Hase's QCPE 644 RRKM program.<sup>180</sup> The  $k_2$  (via **10<sup>‡</sup>**) and  $k_3$  pathway were judged to be too energetically uphill to contribute significantly in the energy range of interest. The values of  $k_a$  and  $k_b$  are predicted from MLTST.



**Figure 78** Two TS structures for the 1,3-isomerization in the enol.

The value of  $k_1/k_2$  was then used for kinetic simulations to scale the predicted active:spectator ratio at each energy interval. The resulting selectivity profile, shown below, indicates that while the intrinsic selectivity increases with energy, hydrogen atom scrambling

becomes increasingly competitive. This model is then in agreement with the trend observed by Tureček. The net effect is that the growing selectivity of the dissociation process is negated by the scrambling of active/spectator positions via 1,3-isomerization.



**Figure 79** MLTST prediction of energy-dependent dissociation selectivity after inclusion of RRKM corrections. Error bars calculated at 99% confidence interval.

MLTST allows the prediction of product ratios without the high computational cost associated with high precision. However, additional experiments are necessary to elucidate what the intrinsic branching ratio of the reaction is and to what extent side reactions impact the apparent selectivity.

## Computational Procedures

### Method Validation

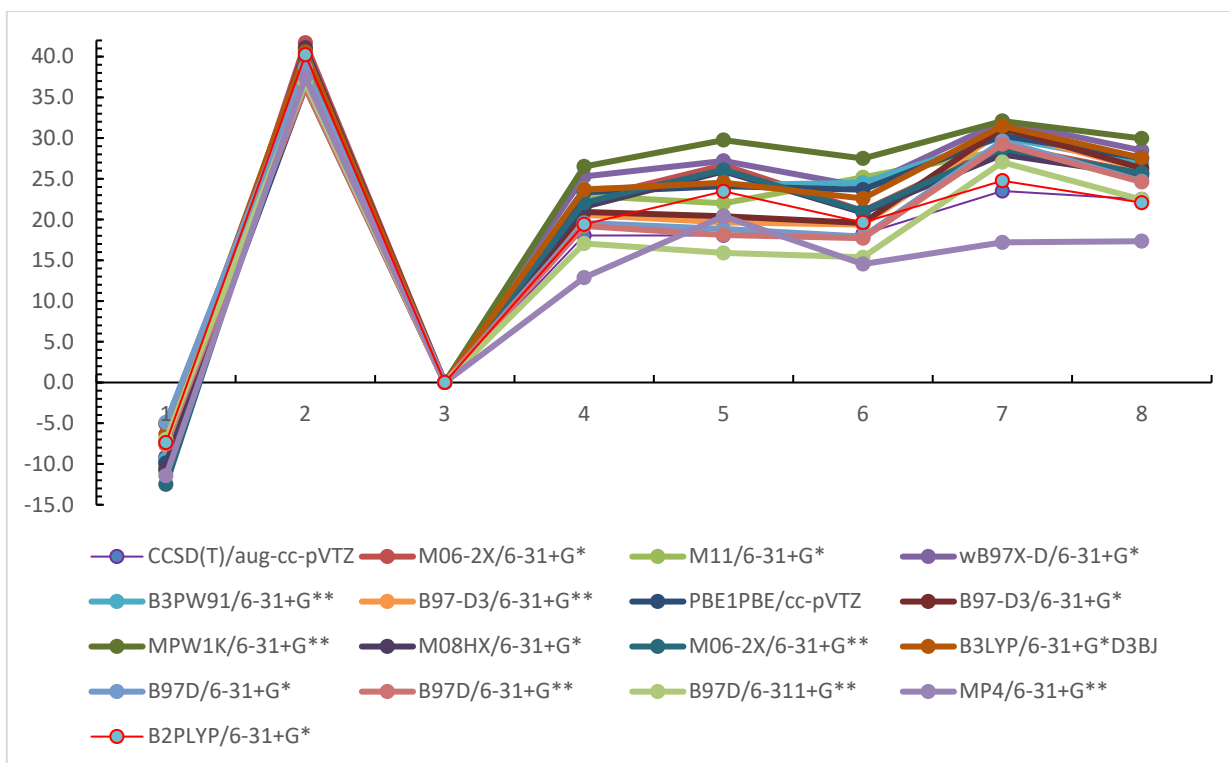
Initial benchmarks against CCSD(T)/aug-CC-pVTZ (Table 17, shown graphically in Figure 80), suggested that B97D/6-31+G\*\* was an acceptable method for further computational studies, but later B2PLYP/6-31+G\*\* proved to have higher accuracy across the various stationary point structures as well as trajectory points (Figure 81, Figure 82). B2PLYP/6-31+G\*\* was used for all trajectories mentioned in the main text.

**Table 17** Benchmark energetics for stationary points in the conversion of acetone (enol) cation radical to separated fragments. Energies are potential energies in kcal/mol.

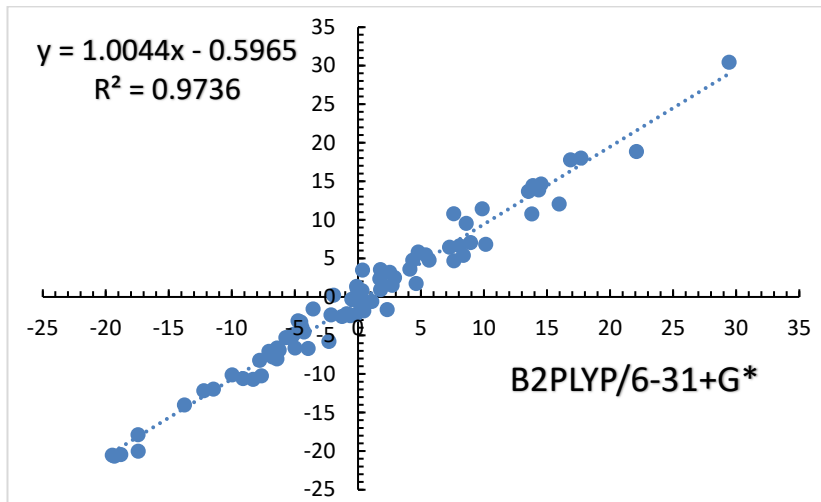
Structure	CCSD(T)/a ug-cc- pVTZ	M06- 2X/6- 31+G*	M11/6- 31+G*	wB97X- D/6- 31+G*	B3PW91 /6- 31+G**	B97- D3/6- 31+G**	PBE1PB E/cc- pVTZ	B97- D3/6- 31+G*	MPW1K /6- 31+G**	M08HX /6- 31+G*	M06- 2X/6- 31+G**
enol	-9.2	-9.8	-10.0	-7.2	-9.4	-7.7	-9.9	-5.1	-10.8	-10.6	-12.5
TS1	38.5	41.7	39.1	40.9	36.5	36.2	36.3	38.6	39.7	41.1	39.2
keto	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
acylium complex	18.0	22.5	22.9	25.3	23.7	20.6	23.3	20.9	26.5	21.6	22.1
TS3	18.0	26.7	22.0	27.2	24.2	19.7	24.1	20.4	29.8	25.9	26.1
ketene complex	18.2	21.1	25.2	24.0	24.5	19.4	23.7	19.6	27.5	20.8	21.0
dissociated acylium complex	23.5	29.1	28.5	32.0	30.1	30.8	30.3	31.2	32.1	28.0	28.7
dissociated ketene complex	22.5	25.7	25.7	28.5	26.9	26.2	27.5	26.3	29.9	25.4	25.7
tw strucs	0.0	7.6	5.5	9.6	7.7	4.8	7.5	3.0	9.7	6.1	4.8
ts vs exit chan	15.0	12.6	10.6	8.8	6.4	5.3	5.9	7.3	7.6	13.1	10.5
ts vs complex	20.4	19.2	16.2	15.6	12.8	15.6	12.9	17.6	13.2	19.5	17.2
TS-endo	49.6										
TS-exo	41.8										
protonated ketene with methyl radical	66.4										

Structure	CCSD(T)/a ug-cc- pVTZ	M06- 2X/6- 31+G**	B3LYP/6- 31+G*D3 BJ	B97D/6- 31+G*	B97D/6- 31+G**	B97D/6- 31+G* *	MP4/6- 31+G**	B2PLYP /6- 31+G*	B3LYP/6 -31+G**	MP2/6- 31+G**	B2PLYP/ 6- 31+G**
enol	-9.2	-12.5	-6.4	-4.9	-7.6	-7.0	-11.5	-7.4	-9.0	15.8	-10.0
TS1	38.5	39.2	40.6	38.6	36.2	36.8	37.5	40.2	38.0	35.1	37.9
keto	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
acylium complex	18.0	22.1	23.7	19.6	19.2	17.1	12.9	19.4	21.9	8.2	19.0
TS3	18.0	26.1	24.5	18.8	18.1	15.9	20.4	23.5	23.0	15.8	22.5
ketene complex	18.2	21.0	22.6	17.9	17.7	15.4	14.5	19.6	21.9	10.8	32.1
dissociated acylium complex	23.5	28.7	31.5	29.6	29.2	27.0	17.2	24.8	28.5	12.5	24.4
dissociated ketene complex	22.5	25.7	27.6	24.7	24.6	22.4	17.3	22.1	24.8	13.7	21.9
main 3 strucs error	0.0	2.5	2.8	1.9	0.9	1.0	2.5	1.0	1.3	11.6	0.6
tw strucs	0.0	4.8	7.7	1.7	3.4	2.6	6.2	3.1	4.4	13.3	1.5
ts vs complex	20.4	17.2	16.9	19.0	17.0	19.8	24.6	20.8	16.0	26.9	18.9
TS-endo	49.6										49.8
TS-exo	41.8										44.0
protonated ketene with methyl radical	66.4										66.5

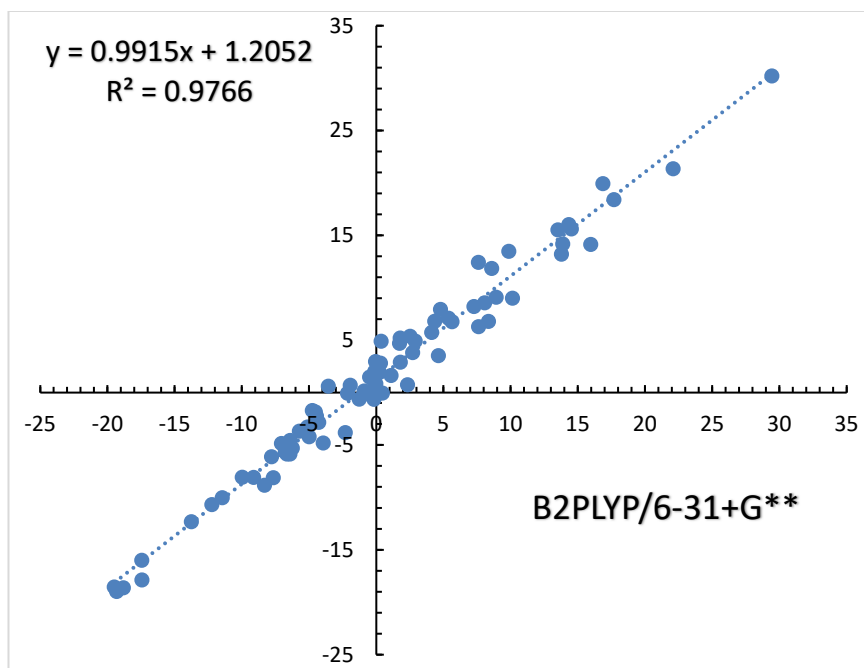


**Figure 80** A screen of numerous DFT methods against CCSD(T)/aug-CC-pVTZ. Vertical axis units are in kcal/mol.



**Figure 81** Benchmark of B2PLYP/6-31+G\* against CCSD(T)/aug-CC-pVTZ. Axis units are in kcal/mol.





**Figure 82** Benchmark of B2PLYP/6-31+G\*\* against CCSD(T)/aug-CC-pVTZ. Axis units are in kcal/mol.

### Anharmonicity Corrections

Anharmonicity corrections are performed by taking the structure for  $5^\ddagger$  and systematically varying the phase of each real normal mode. As each mode is varied, a single point energy calculation is performed. The energy from this calculation is compared to the energy predicted via the harmonic force constants from the frequency analysis. The difference in these energies, as well as the change in normal mode phase, are used to fit a first order correction to the harmonic force constants (Table 18).

**Table 18** Force constants and anharmonic corrections for **5<sup>‡</sup>**

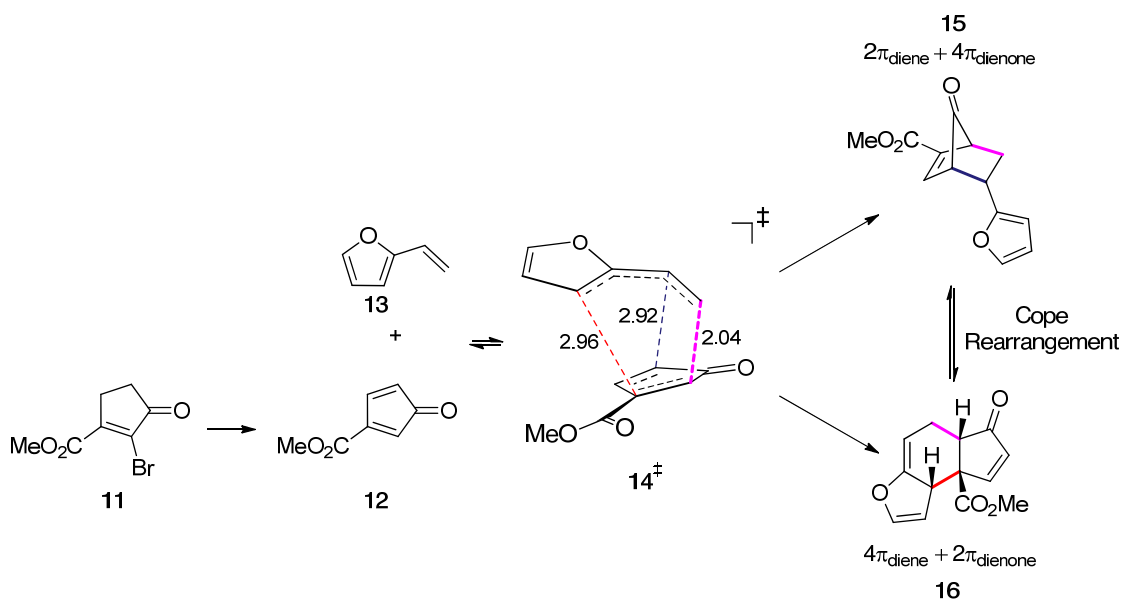
Normal Mode	Force Constant	Force Constant Correction
2	3.974	0.003
3	27.523	-61.05
4	228.487	2.733
5	216.999	1.869
6	82.1	-1.578
7	40.6	0.024
8	151.893	-98.993
9	55.244	-0.077
10	63.254	6.513
11	56.252	0.08
12	318.281	-4.225
13	134.261	25.182
14	101.647	-9.172
15	176.666	32.604
16	110.423	0.53
17	94.454	0.031
18	322.872	518.972
19	175.271	75.024
20	414.643	-492.738
21	461.456	1.61
22	447.724	629.533
23	492.965	781.025
24	515.274	2.861

#### 4.4 The Diels-Alder Reaction of Vinylfuran and Cyclopentadienones

##### *Introduction*

The Diels-Alder reaction of conjugated dienes with cyclopentadienones developed by the Harmata group was studied by the Singleton group in 2008.<sup>158,181</sup> The study found that both possible cycloadditions,  $2\pi_{\text{diene}} + 4\pi_{\text{dienone}}$  and  $4\pi_{\text{diene}} + 2\pi_{\text{dienone}}$ , were formed by the same ambimodal TS. In the case of the reaction of vinylfuran (**13**) with **12**, products **15** and **16** arise from a PES bifurcation at **14<sup>‡</sup>**. An experimental ratio of 1.6 to 1 (**15** to **16**) was

observed for the reaction in toluene, at room temperature. This ratio was found to be stable with respect to Cope rearrangement – no product interconversion (conversion of **15** to more stable **16**) was observed over the course of two months at room temperature, indicating that this ratio was indeed a kinetic ratio.



**Figure 83** Mechanistic scheme for Harmata's reaction of **12** and **13**.

Gas phase MPW1K/6-31+G\*\* QCTs initiated at **14<sup>‡</sup>** gave a prediction of 1.58 to 1 (**15** to **16**), although this number is subject to appreciable uncertainty due to the limited trajectory dataset. The high computational cost of these trajectories prevented a more detailed investigation of the Newtonian dynamics controlling the partitioning of **14<sup>‡</sup>** into **15** and **16**. This chapter will discuss how MLTST can ease the computational burden of this study and permit analysis.

### *Experimental Results and Discussion*

Given that selectivity in this reaction is not governed by the competition of transition states, predicting the effect of temperature on selectivity in the addition of **12** with **13** is not simple. Experiments were conducted at 273 K and 333 K, and 298K and 333 K, in toluene and benzene, respectively. The results are shown below (Table 19).

**Table 19** Experimental ratios of **15:16** from <sup>1</sup>H NMR measurements.

Temperature (° C)	Toluene	Benzene
-20	1.62	x
23	1.66	1.49
60	1.86	1.62

The trend seen in both solvents is that reaction selectivity increases with temperature and the magnitude of this change does not track with the exponential dependence given by TST. This because the selectivity does *not depend on the competition between transition states* – it depends on the bifurcating surface after the ambimodal transition state. No change in the product mixture was seen at extended reaction times, suggesting that the reaction mixture does not equilibrate over time. This trend will be used to validate the performance of MLTST.

### *Computational Results and Discussion*

Gas phase MN15/6-31G\* QCTs were initiated at **14**<sup>‡</sup>. Due to the size of this system (29 atoms), only a limited set of trajectories was collected at 298 K. The results closely match the published experimental and predicted product ratios, albeit at higher precision (Table 20).

**Table 20** Outcomes and MLTST and accuracy benchmarks for gas phase QCTs at 25 °C.

Outcome	Percentage
15	57.3%
16	36.0%
Starting material recrossing	4.8%
Product recrossing	1.4%
Double recross	0.1%
Level-1 Accuracy	90.4%
Level-2 Accuracy	83.4%
Total trajectories	11,482
Predicted 15/16 ratio	1.59 ±0.06

These trajectories were used to train a neural network. The neural networks proved to be effective, as judged by the Level-1 and 2 accuracy metrics. Afterwards, the neural network predicted the outcome of new trajectory points generated at 298 K and 333 K. The predicted product selectivity is shown below.

**Table 21** 15:16 ratios from MLTST predictions.

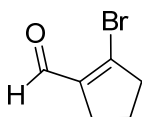
Temperature (° C)	MLTST Gas Phase
23	1.48
60	1.54

While these predictions are not a quantitative match for the experimental data, it is clear that MLTST allows a prediction of product ratios that simply cannot be made with conventional TST. A surprising aspect of this is that the increased selectivity at high temperature was predicted at all. The neural network was trained on trajectories conducted at 23 °C and so the neural network is not expected to encounter relatively energetic trajectories during training. Further inspection of neural network model and its sensitivity to the selection of input features will permit the understanding of which normal mode

displacements and velocities are important to prediction accuracy and to deciding whether a trajectory forms **15** or **16**. Another important question to answer is whether or not the measured Level-2 accuracy is sufficient to accurately predict product ratios and transmission coefficients across a broad range. This will depend on the extent of error cancellation in the neural network, an analysis that remains nebulous.

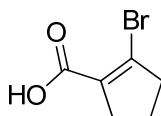
### *Experimental Procedures*

#### **Preparation of 11-1**



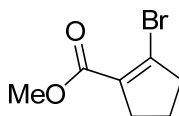
A solution of 11.6 ml dimethylformamide and 40 ml chloroform was prepared in a round bottom flask. The flask was fitted with a stirbar and cooled to 0° C. 11.8 ml fresh phosphorus tribromide (125 mmol) was added to this flask dropwise. In a separate flask, 4.43 ml of cyclopentanone (50 mmol) was dissolved in 20 ml chloroform. The cyclopentanone solution was slowly added to the reaction flask. The reaction was allowed to stir and warm to room temperature. The reaction was then concentrated on a rotary evaporator. Generous quantities of ice and dry sodium bicarbonate were added to the flask. Once the suspended solids settled or dissolved, the solution was subjected to vacuum filtration. The filter solution was extracted twice with diethyl ether. The collected organics were washed with 5% aqueous potassium carbonate and then with distilled water. The solution was then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through glass wool and concentrated *in vacuo*. The crude oily material was taken on to the next step without purification.

### Preparation of 11-2



5.00 grams of **11-1** (28.6 mmol) and 28ml acetonitrile were added to a 100 ml round bottom flask and the flask was fitted with a stirbar. In a separate vial, 0.773 grams of sodium phosphate was dissolved in 4.3 ml distilled water. The salt solution was added to the reaction flask. The flask was cooled to  $-10^{\circ}\text{C}$  with a salt-ice bath. In a beaker, a sodium chlorite solution was prepared through the slow addition of 3.61 grams (40 mmol) of sodium chlorite to 28 ml distilled water. The sodium chlorite solution was added to the reaction flask dropwise over the course of two hours via pressure-equalizing addition funnel. The reaction was stirred for 6 hours. The reaction was quenched by the addition of 10% HCl solution until pH test strips showed a pH of  $\sim 3$ . The mixture was extracted thrice with 75 mL diethyl ether, before being dried over  $\text{Na}_2\text{SO}_4$ , filtered through glass wool and concentrated *in vacuo*. The crude solid material was taken on to the next step without purification.

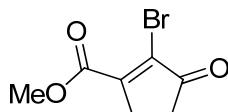
### Preparation of 11-3



4.34 grams of **11-2** was dissolved in 50 ml of methanol. The reaction was fitted with a stirbar and water condenser and then brought to reflux for 24 hours. Afterwards, the

reaction mixture was poured into 100 mL of saturated brine and extracted thrice with 70 ml of diethyl ether. The collected organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through glass wool and concentrated *in vacuo*. The crude material was purified over a 200 grams of silica with 1:1 hexanes:ethyl acetate to give a crystalline material.

### Preparation of 11



11.56 grams of pyridinium dichromate (30.7 mmol), 2.36 grams of potassium carbonate (17.1 mmol), 7.00 grams of **11-4** (34.1 mmol), and 70 ml of dichloromethane were added to a 250 mL round bottom. The flask was fitted with a stirbar, cooled in an ice bath and purge with nitrogen gas. While the flask was cooling, 31 mL of 5-6M tertbutyl hydrogen peroxide in decane was added to 10.5 mL of dichloromethane. Once the reaction flask was ready, half of the peroxide solution was added dropwise under positive nitrogen pressure. The reaction was stirred for 24 hours. The reaction flask was cooled again, followed by the addition of another 11.56 grams of pyridinium dichromate and second dropwise addition of peroxide solution. After an additional 24 hours, the reaction was filtered through a Celite pad. The pad was rinsed with diethyl ether. The filtered solution was concentrated *in vacuo* and then re-suspended in 100 ml fresh diethyl ether. The solution was washed twice with 100 ml of saturated ammonium chloride, followed by a single wash with 100 ml saturated brine. The organic solution was then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through glass wool and concentrated *in vacuo*. The crude material was purified over silica with 6:1 hexanes:ethyl acetate to give a white solid.



### **Preparation of Vinylfuran (13)**

Vinylfuran was prepared via Peterson olefination, described by Waser *et al.*<sup>182</sup>

### **Reaction of Vinylfuran with Cyclopentadienone**

A mixture of 100 mg of vinylfuran (**13**) (1 mmol) and 49 mg of **11** (0.2 mmol) was dissolved in 3.6 mL of deuterated benzene or toluene solvent under N<sub>2</sub> at, and 89  $\mu$ L (1 mmol) of triethylamine was added and left to stir for 2 days at room temperature. Reaction aliquots were quenched with 5ml saturated NaCl, extracted with more deuterated solvent as needed to separate layers, then dried over NaSO<sub>4</sub>, and then analyzed by <sup>1</sup>H NMR.

## CHAPTER V

### CONCLUSIONS

Transition state theory is the central physical model for predicting the rates of chemical reactions, and its applicability is implicitly assumed in the depiction of reaction mechanisms. Some flaws in TST were known at its conception, but recent years have seen a rising recognition of experimental observations that cannot be understood within the limitations and assumptions of TST. These “dynamic effects” have been the subject of this dissertation, and it has illustrated how dynamic effects impact the understanding of reaction mechanisms and other fundamental chemical ideas. Through the exposition of dynamic effects in diverse reactions, this dissertation illustrates how quickly the standard understanding of mechanisms falls apart, even for simple reactions.

Intermediates in reaction mechanisms are implicitly assumed to be equivalent to reactants from the perspective of being energetically equilibrated and equilibrated with respect to the surrounding solvent structure. This assumption can be misleading for reactions forming ionic intermediates because the solvation of these intermediates takes time. While awaiting solvent equilibration, the reactive behavior of an ion pair is not subject to a well-defined barrier and cannot be well-described by TST. This becomes apparent in the regiochemistry of the addition of hydrogen chloride to 1,3-pentadiene in nitromethane. The carbocation intermediate is symmetric, meaning there is no distinction between thermodynamic and kinetic products, but the product ratio is 74:26 1,2-addition to 1,4-addition. Detailed experiments and computational simulations suggest that this is due to a dynamic effect in the solvation. On one extreme, the solute’s reaction is exceedingly fast, the solvent is not able to reorient itself in time to stabilize the ionic intermediates, and the

chloride anion rapidly binds the allylic cation at the 2 position. On the other extreme, the solvent dipoles synchronize with the reaction, pry the chloride away from the cation, and over the course of picoseconds equilibrate to form a true ion-pair intermediate. Remarkably, the 1,2-addition product is formed by both the “dynamical” and ion-pair pathways, while the 1,4-addition product is produced almost exclusively by the ion-pair mechanism. This solvation effect is not limited to dienes, 1D and 2D NMR techniques and theoretical calculations suggest that the product mixtures of the addition of HCl to 1-methylcyclopentene and *tert*-butylethylene may also be controlled by solvent dynamics. The reinterpretation of experimental results from the classic physical organic literature sheds light on the generality of this dynamic effect in solution chemistry.

The photoinduced carboborative ring contraction of cyclohexenes is a reaction in which the experimental stereochemistry of additions to a carbocation is not controlled by competing transition states. Existing on a sheer slope on the potential energy surface, the key structure in this mechanism rearranges to the final product so rapidly that equivalent bond connections never symmetrize in geometry or vibrational motion. This period of dynamical asymmetry only lasts about 50 femtoseconds, the duration of just 5 C-H bond oscillations, but it strongly influences the geometric symmetry about the carbocation center such that one enantiotopic alkyl migration is significantly favored.

MLTST is a 21<sup>st</sup> century revision to transition state theory that has special practicality for studying reactions that exhibit dynamic effects. These dynamic effects are poorly described by TST. This methodology redeems the failures of statistical rate theories, opening new means to understand reactivity and selectivity. In addition to its success in predicting observables, MLTST provides detailed understanding of causal relationships in trajectories.

After an analysis of correlations, it was confirmed that the phases and velocities of normal modes orthogonal to the transition vector were decisive in the outcome of trajectories. This insight suggests the possibility of controlling the outcomes of dynamically controlled reactions through the modulation of the nature and population of the vibrational normal modes.

The design of reactions is predicated on knowing the sequence of events known as the reaction mechanism – understanding the logic of a reaction invites means to control its outcome. More deeply, mechanisms are a necessary symbolism bridging structure with activity, and allowing the understanding of complex biological transformations with same principles as simple acid/base reactions. To that end, TST is an immensely useful model. Nonetheless, it is still a shadow on the wall of the cave. After almost a century of TST, chemistry needs a model that permits better understanding and offers more agency in controlling the outcome of chemical transformations. It is by understanding these dynamics effects, that this new model can be brought about, and organic chemistry can transcend transition state theory.

## REFERENCES

- (1) Singleton, D. A.; Schulmeier, B. E.; Hang, C.; Thomas, A. A.; Leung, S. W.; Merrigan, S. R. Isotope Effects and the Distinction between Synchronous, Asynchronous, and Stepwise Diels-Alder Reactions. *Tetrahedron* **2001**, *57*, 5149–5160.
- (2) Singleton, D. A.; Hang, C.; Szymanski, M. J.; Meyer, M. P.; Leach, A. G.; Kuwata, K. T.; Chen, J. S.; Greer, A.; Foote, C. S.; Houk, K. N. Mechanism of Ene Reactions of Singlet Oxygen. A Two-Step No-Intermediate Mechanism. *J. Am. Chem. Soc.* **2003**, *125*, 1319–1328.
- (3) Singleton, D. A.; Hang, C.; Szymanski, M. J.; Greenwald, E. E. A New Form of Kinetic Isotope Effect. Dynamic Effects on Isotopic Selectivity and Regioselectivity. *J. Am. Chem. Soc.* **2003**, *125*, 1176–1177.
- (4) Ussing, B. R.; Singleton, D. A. Isotope Effects, Dynamics, and the Mechanism of Solvolysis of Aryldiazonium Cations in Water. *J. Am. Chem. Soc.* **2005**, *127*, 2888–2899.
- (5) Ussing, B. R.; Hang, C.; Singleton, D. A. Dynamic Effects on the Periselectivity, Rate, Isotope Effects, and Mechanism of Cycloadditions of Ketenes with Cyclopentadiene. *J. Am. Chem. Soc.* **2006**, *128*, 7594–7607.
- (6) Thomas, J. B.; Waas, J. R.; Harmata, M.; Singleton, D. A. Control Elements in Dynamically Determined Selectivity on a Bifurcating Surface. *J. Am. Chem. Soc.* **2008**, *130*, 14544–14555.
- (7) Kelly, K. K.; Hirschi, J. S.; Singleton, D. A. Newtonian Kinetic Isotope Effects.

- Observation, Prediction, and Origin of Heavy-Atom Dynamic Isotope Effects. *J. Am. Chem. Soc.* **2009**, *131*, 8382–8383.
- (8) Suhrada, C. P.; Selçuki, C.; Nendel, M.; Cannizzaro, C.; Houk, K. N.; Rissing, P. J.; Baumann, D.; Hasselmann, D. Dynamic Effects on [3,3] and [1,3] Shifts of 6-Methylenebicyclo[3.2.0]Hept- 2-Ene. *Angew. Chemie - Int. Ed.* **2005**, *44*, 3548–3552.
- (9) Doubleday, C.; Suhrada, C. P.; Houk, K. N. Dynamics of the Degenerate Rearrangement of Bicyclo[3.1.0]Hex-2-Ene. *J. Am. Chem. Soc.* **2006**, *128*, 90–94.
- (10) Patel, A.; Chen, Z.; Yang, Z.; Gutiérrez, O.; Liu, H. W.; Houk, K. N.; Singleton, D. A. Dynamically Complex [6+4] and [4+2] Cycloadditions in the Biosynthesis of Spinosyn A. *J. Am. Chem. Soc.* **2016**, *138*, 3631–3634.
- (11) Pham, H. V.; Houk, K. N. Diels-Alder Reactions of Allene with Benzene and Butadiene: Concerted, Stepwise, and Ambimodal Transition States. *J. Org. Chem.* **2014**, *79*, 8968–8976.
- (12) Xue, X. S.; Jamieson, C. S.; Garcia-Borràs, M.; Dong, X.; Yang, Z.; Houk, K. N. Ambimodal Trispericyclic Transition State and Dynamic Control of Periselectivity. *J. Am. Chem. Soc.* **2019**, *141*, 1217–1221.
- (13) Hong, Y. J.; Tantillo, D. J. A Potential Energy Surface Bifurcation in Terpene Biosynthesis. *Nat. Chem.* **2009**, *1*, 384–389.
- (14) Pemberton, R. P.; Hong, Y. J.; Tantillo, D. J. Inherent Dynamical Preferences in Carbocation Rearrangements Leading to Terpene Natural Products. *Pure Appl. Chem.* **2013**, *85*, 1949–1957.
- (15) Hare, S. R.; Tantillo, D. J. Dynamic Behavior of Rearranging Carbocations -

- Implications for Terpene Biosynthesis. *Beilstein J. Org. Chem.* **2016**, *12*, 377–390.
- (16) Black, K.; Liu, P.; Xu, L.; Doubleday, C.; Houk, K. N. Dynamics, Transition States, and Timing of Bond Formation in Diels-Alder Reactions. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 12860–12865.
- (17) Martín-Sómer, A.; Yáñez, M.; Hase, W. L.; Gaijeot, M. P.; Spezia, R. Post-Transition State Dynamics in Gas Phase Reactivity: Importance of Bifurcations and Rotational Activation. *J. Chem. Theory Comput.* **2016**, *12*, 974–982.
- (18) Litovitz, A. E.; Keresztes, I.; Carpenter, B. K. Evidence for Nonstatistical Dynamics in the Wolff Rearrangement of a Carbene. *J. Am. Chem. Soc.* **2008**, *130*, 12085–12094.
- (19) Mauguière, F. A. L.; Collins, P.; Kramer, Z. C.; Carpenter, B. K.; Ezra, G. S.; Farantos, S. C.; Wiggins, S. Phase Space Structures Explain Hydrogen Atom Roaming in Formaldehyde Decomposition. *J. Phys. Chem. Lett.* **2015**, *6*, 4123–4128.
- (20) Mandal, N.; Datta, A. Dynamical Effects along the Bifurcation Pathway Control Semibullvalene Formation in Deazetization Reactions. *J. Phys. Chem. B* **2018**, *122*, 1239–1244.
- (21) Doubleday, C.; Boguslav, M.; Howell, C.; Korotkin, S. D.; Shaked, D. Trajectory Calculations for Bergman Cyclization Predict H/D Kinetic Isotope Effects Due to Nonstatistical Dynamics in the Product. *J. Am. Chem. Soc.* **2016**.
- (22) Chen, Z.; Zhu, X.; Yang, J.; Mercer, J. A. M.; Burns, N. Z.; Martinez, T. J.; Xia, Y. The Cascade Unzipping of Ladderane Reveals Dynamic Effects in Mechanochemistry. *Nat. Chem.* **2020**, *12*, 302–309.

- (23) Gonzalez-James, O. M.; Kwan, E. E.; Singleton, D. A. Entropic Intermediates and Hidden Rate-Limiting Steps in Seemingly Concerted Cycloadditions. Observation, Prediction, and Origin of an Isotope Effect on Recrossing. *J. Am. Chem. Soc.* **2012**, *134*, 1914–1917.
- (24) Tan, J. S. J.; Hirvonen, V.; Paton, R. S. Dynamic Intermediates in the Radical Cation Diels-Alder Cycloaddition: Lifetime and Suprafacial Stereoselectivity. *Org. Lett.* **2018**, *20*, 2821–2825.
- (25) Bauld, N. L.; Yang, J. Stereospecificity and Mechanism in Cation Radical Diels-Alder and Cyclobutane Reactions. *Org. Lett.* **1999**, *1*, 773–774.
- (26) Bauld, N. L.; Gao, D. Approaching a Possible Stepwise/Concerted Mechanistic Crossover Point in the Cation Radical Cycloadditions of Cis- and Trans-Anethole. *J. Chem. Soc. Perkin Trans. 2* **2000**, No. 5, 931–934.
- (27) Essafi, S.; Harvey, J. N. Rates of Molecular Vibrational Energy Transfer in Organic Solutions. *J. Phys. Chem. A* **2018**, *122*, 3535–3540.
- (28) Quijano, L. M. M.; Singleton, D. A. Competition between Reaction and Intramolecular Energy Redistribution in Solution: Observation and Nature of Nonstatistical Dynamics in the Ozonolysis of Vinyl Ethers. *J. Am. Chem. Soc.* **2011**, *133*, 13824–13827.
- (29) Paul, A. K.; West, N. A.; Winner, J. D.; Bowersox, R. D. W.; North, S. W.; Hase, W. L. Non-Statistical Intermolecular Energy Transfer from Vibrationally Excited Benzene in a Mixed Nitrogen-Benzene Bath. *J. Chem. Phys.* **2018**, *149*, 134101.
- (30) Faljoni, A.; Zinner, K.; Weiss, R. G. An Attempt to Influence the Decay Modes 1, 2-Diphenylcyclopropane Excited States with Optically Active Solvents.



- Tetrahedron Lett.* **1974**, *15*, 1127–1130.
- (31) Boyd, D. R.; Neill, D. C. Asymmetric Synthesis at a Pyramidal Nitrogen Centre in a Chiral Medium. *J. Chem. Soc. Chem. Commun.* **1977**, No. 2, 51–52.
- (32) Laarhoven, W. H.; Cuppen, T. J. H. M. Chiral Solvent-Induced Asymmetric Synthesis; Photosynthesis of Optically Enriched Hexahelicene. *J. Chem. Soc. Chem. Commun.* **1977**, No. 2.
- (33) Carpenter, B. K.; Harvey, J. N.; Glowacki, D. R. Prediction of Enhanced Solvent-Induced Enantioselectivity for a Ring Opening with a Bifurcating Reaction Path. *Phys. Chem. Chem. Phys.* **2015**, *17*, 8372–8381.
- (34) Valtazanos, P.; Elbert, S. T.; Ruedenberg\*, K. Ring Opening of Cyclopropylidenes to Allenes: Reactions with Bifurcating Transition Regions, Free Internal Motions, Steric Hindrances, and Long-Range Dipolar Interactions. *J. Am. Chem. Soc.* **1986**, *108*, 3147–3149.
- (35) Keirstead, W. P.; Wilson, K. R.; Hynes, J. T. Molecular Dynamics of a Model SN1 Reaction in Water. *J. Chem. Phys.* **1991**, *95*, 5256–5267.
- (36) Whitnell, R. M.; Wilson, K. R.; Hynes, J. T. Vibrational Relaxation of a Dipolar Molecule in Water. *J. Chem. Phys.* **1992**, *96*, 5354–5369.
- (37) Leitold, C.; Mundy, C. J.; Baer, M. D.; Schenter, G. K.; Peters, B. Solvent Reaction Coordinate for an SN2 Reaction. *J. Chem. Phys.* **2020**, *153*, 24103–24111.
- (38) Goyal, P.; Schwerdtfeger, C. A.; Soudackov, A. V.; Hammes-Schiffer, S. Nonadiabatic Dynamics of Photoinduced Proton-Coupled Electron Transfer in a Solvated Phenol-Amine Complex. *J. Phys. Chem. B* **2015**, *119*, 2758–2768.
- (39) Metiu, H.; Ross, J.; Silbey, R.; George, T. F. On Symmetry Properties of Reaction

- Coordinates. *J. Chem. Phys.* **1974**, *61*, 3200–3209.
- (40) Kraus, W. A.; DePristo, A. E. Reaction Dynamics on Bifurcating Potential Energy Surfaces. *Theor. Chim. Acta* **1986**, *69*, 309–322.
- (41) Hong, Y. J.; Tantillo, D. J. Biosynthetic Consequences of Multiple Sequential Post-Transition-State Bifurcations. *Nat. Chem.* **2014**, *6*, 104–111.
- (42) Hong, Y. J.; Tantillo, D. J. Branching out from the Bisaboly Cation. Unifying Mechanistic Pathways to Barbatene, Bazzanene, Chamigrene, Chamipinene, Cumacrene, Cuprenene, Dunningene, Isobazzanene, Iso- $\gamma$ -Bisabolene, Isochamigrene, Laurene, Microbiotene, Sesquithujene, Sesquisabinene, T. *J. Am. Chem. Soc.* **2014**, *136*, 2450–2463.
- (43) Chen, S.; Yu, P.; Houk, K. N. Ambimodal Dipolar/Diels-Alder Cycloaddition Transition States Involving Proton Transfers. *J. Am. Chem. Soc.* **2018**, *140*, 18124–18131.
- (44) Rynbrandt, J. D.; Rabinovitch, B. S. Intramolecular Energy Relaxation. Nonrandom Decomposition of Hexafluorobicyclopropyl. *J. Phys. Chem.* **1971**, *75*, 2164–2171.
- (45) Carpenter, B. K. Dynamic Matching: The Cause of Inversion of Configuration in the [1, 3] Sigmatropic Migration? *J. Am. Chem. Soc.* **1995**, *117*, 6336–6344.
- (46) Reyes, M. B.; Lobkovsky, E. B.; Carpenter, B. K. Interplay of Orbital Symmetry and Nonstatistical Dynamics in the Thermal Rearrangements of Bicyclo[n.1.0]Polyenes. *J. Am. Chem. Soc.* **2002**, *124*, 641–651.
- (47) Nummela, J. A.; Carpenter, B. K. Nonstatistical Dynamics in Deep Potential Wells: A Quasiclassical Trajectory Study of Methyl Loss from the Acetone Radical Cation. *J. Am. Chem. Soc.* **2002**, *124*, 8512–8513.

- (48) Kless, A.; Nendel, M.; Wilsey, S.; Houk, K. N. Origin of the Preference for the Orbital Symmetry Forbidden Stereochemistry of the 1,5-Sigmatropic Shift of Substituted Norcaradienes. *J. Am. Chem. Soc.* **1999**, *121*, 4524–4525.
- (49) Sun, L.; Song, K.; Hase, W. L. A SN2 Reaction That Avoids Its Deep Potential Energy Minimum. *Science (80-. )*. **2002**, *296*, 875–878.
- (50) Oyola, Y.; Singleton, D. A. Dynamics and the Failure of Transition State Theory in Alkene Hydroboration. *J. Am. Chem. Soc.* **2009**, *131*, 3130–3131.
- (51) Kurouchi, H.; Andujar-De Sanctis, I. L.; Singleton, D. A. Controlling Selectivity by Controlling Energy Partitioning in a Thermal Reaction in Solution. *J. Am. Chem. Soc.* **2016**, *138*, 14534–14537.
- (52) Bailey, J. O.; Singleton, D. A. Failure and Redemption of Statistical and Nonstatistical Rate Theories in the Hydroboration of Alkenes. *J. Am. Chem. Soc.* **2017**, *139*, 15710–15723.
- (53) Hendry, R. F.; Needham, P.; Woody, A. I. Introduction. *Philos. Chem.* **2012**, 3–18.
- (54) Bertrán, J.; Sanchez Burgos, F. The Question of Equilibrium in Transition State Solvation. *J. Chem. Educ.* **1984**, *61*, 416–417.
- (55) Tucker, S. C.; Truhlar, D. G. Effect of Nonequilibrium Solvation on Chemical Reaction Rates. Variational Transition-State-Theory Studies of the Microsolvated Reaction  $C1-(H_2O)_n + CH_3Cl$ . *J. Am. Chem. Soc.* **1990**, *112*, 3347–3361.
- (56) Fawcett, W. R.; Foss, C. A. Role of the Solvent in the Kinetics of Heterogeneous Electron and Ion Transfer Reactions. *Electrochim. Acta* **1991**, *36*, 1767–1774.
- (57) Struve, W. S.; Rentzepis, P. M.; Jortner, J. Solvent Reorganization around a "giant Dipole" Molecule. *J. Chem. Phys.* **1973**, *59*, 5014–5019.

- (58) Toteva, M. M.; Richard, J. P. Mechanism for Nucleophilic Substitution and Elimination Reactions at Tertiary Carbon in Largely Aqueous Solutions: Lifetime of a Simple Tertiary Carbocation. *J. Am. Chem. Soc.* **1996**, *118*, 11434–11445.
- (59) Clarke, J.; Bonney, K. J.; Yaqoob, M.; Solanki, S.; Rzepa, H. S.; White, A. J. P.; Millan, D. S.; Braddock, D. C. Epimeric Face-Selective Oxidations and Diastereodivergent Transannular Oxonium Ion Formation Fragmentations: Computational Modeling and Total Syntheses of 12-Epoxyobtusallene IV, 12-Epoxyobtusallene II, Obtusallene X, Marilzabicycloallene C, and Marilzabi. *J. Org. Chem.* **2016**, *81*, 9539–9552.
- (60) Kharasch, M. S.; Margolis, E. T.; Mayo, F. R. The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. XIII. The Addition of Hydrogen Bromide to Butadiene. *J. Org. Chem.* **1936**, *1*, 393–404.
- (61) Kharasch, M. S.; Kritchevsky, J.; Mayo, F. R. The Addition of Hydrogen Chloride to Butadiene. *J. Org. Chem.* **1937**, *2*, 489–496.
- (62) McMurry, J. E. *Organic Chemistry*, 8th ed.; Cengage Learning: Belmont, CA, 2007.
- (63) Nordlander, J. E.; Owuor, P. O.; Haky, J. E. Regiochemistry of the Addition of Hydrochloric Acid-D to Trans-1, 3-Pentadiene. *J. Am. Chem. Soc.* **1979**, *101*, 1288–1289.
- (64) Fahey, R. C.; Lee, D. J. Polar Additions to Olefins and Acetylenes. IV. Evidence for Synchronous C-H and C-Cl Bond Formation in the Trans Addition of Hydrogen Chloride to 3-Hexyne. *J. Am. Chem. Soc.* **1967**, *89*, 2780–2781.
- (65) Pocker, Y.; Stevens, K. D. Kinetics and Mechanism of Addition of Acids to Olefins. IV. The Addition of Hydrogen and Deuterium Chloride to 3-Methyl-1-Butene, 3,3-

Dimethyl-1 -Butene, 1-Methylcyclopentene, and 1 -Methylcyclopentene-2,5,5-D3.

*J. Am. Chem. Soc.* **1969**, *91*, 4205–4210.

- (66) Fahey, R. C.; Smith, R. A. The Polar Addition of Hydrogen Bromide to Cyclohexene. *J. Am. Chem. Soc.* **1964**, *86*, 5035–5036.
- (67) Fahey, R. C.; Lee, D. J. Polar Additions to Olefins and Acetylenes. III. The Kinetics and Stereochemistry of Addition in the System 1-Phenylpropyne-Hydrogen Chloride-Acetic Acid. *J. Am. Chem. Soc.* **1966**, *88*, 5555–5560.
- (68) Fahey, R. C.; Lee, D. J. Polar Additions to Olefins and Acetylenes. V. Bimolecular and Termolecular Mechanisms in the Hydrochlorination of Acetylenes. *J. Am. Chem. Soc.* **1968**, *90*, 2124–2131.
- (69) Fahey, R. C.; McPherson, C. A. The Mechanism of the Hydrochlorination of T-Butylethylene and Styrene in Acetic Acid. *J. Am. Chem. Soc.* **1969**, *91*, 3865–3869.
- (70) Fahey, R. C.; Schneider, H. J. The Kinetics and Stereochemistry of the Reaction of Diethyl Maleate and Diethyl Fumarate with Hydrogen Chloride in Acetic Acid. *J. Am. Chem. Soc.* **1970**, *92*, 6885–6893.
- (71) Fahey, R. C.; McPherson, C. A. Kinetics and Stereochemistry of the Hydrochlorination of 1,2-Dimethylcyclohexene. *J. Am. Chem. Soc.* **1971**, *93*, 2445–2453.
- (72) Fahey, R. C.; McPherson, C. A.; Smith, R. A. Reaction of Alkenes with Hydrogen Bromide in Acetic Acid. Polar Addition via the Ad3 Mechanism. *J. Am. Chem. Soc.* **1974**, *96*, 4534–4542.
- (73) Fahey, R. C.; Monahan, M. W.; McPherson, C. A. Hydrochlorination of Cyclohexene in Acetic Acid. Kinetic and Product Studies. *J. Am. Chem. Soc.* **1970**,

- 92, 2810–2815.
- (74) Fahey, R. C.; Monahan, M. W. Stereochemistry of the Hydrochlorination of Cyclohexene-1,3,3-D<sub>3</sub> in Acetic Acid. Evidence for Termolecular Anti Addition of Acids to Olefins. *J. Am. Chem. Soc.* **1970**, *92*, 2816–2820.
- (75) Mayo, F. R.; Katz, J. J. The Addition of Hydrogen Chloride to Isobutylene. *J. Am. Chem. Soc.* **1947**, *69*, 1339–1348.
- (76) Mayo, F. R.; Savoy, M. G.; Savoy, M. G. The Addition of Hydrogen Bromide to Propylene. *J. Am. Chem. Soc.* **1947**, *69*, 1348–1351.
- (77) Fürst, A.; Plattner, P. A. Über Steroide Und Sexualhormone. 160. Mitteilung. 2 $\alpha$ , 3 $\alpha$ - Und 2 $\beta$ , 3 $\beta$ -Oxido-cholestane; Konfiguration Der 2-Oxy-cholestane. *Helv. Chim. Acta* **1949**, *32*, 275–283.
- (78) Dewar, M. J. S.; Fahey, R. C. Electrophilic Addition to Olefins. II. Addition of Deuterium Halides to Indene; the Mechanism of Addition. *J. Am. Chem. Soc.* **1963**, *85*, 2248–2252.
- (79) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- (80) Stewart, J. J. P.; Davis, L. P.; Burggraf, L. W. Semi-empirical Calculations of Molecular Trajectories: Method and Applications to Some Simple Molecular Systems. *J. Comput. Chem.* **1987**, *8*, 1117–1123.
- (81) Taketsugu, T.; Gordon, M. S. Dynamic Reaction Path Analysis Based on an Intrinsic Reaction Coordinate. *J. Chem. Phys.* **1995**, *103*, 10042–10049.
- (82) Nieves-Quinones, Y.; Singleton, D. A. Dynamics and the Regiochemistry of Nitration of Toluene. *J. Am. Chem. Soc.* **2016**, *138*, 15167–15176.

- (83) Kumar, S.; Rosenberg, J. M.; Bouzida, D.; Swendsen, R. H.; Kollman, P. A. THE Weighted Histogram Analysis Method for Free-energy Calculations on Biomolecules. I. The Method. *J. Comput. Chem.* **1992**, *13*, 1011–1021.
- (84) Bolhuis, P. G.; Chandler, D.; Dellago, C.; Geissler, P. L. Transition Path Sampling: Throwing Ropes over Rough Mountain Passes, in the Dark. *Annu. Rev. Phys. Chem.* **2002**, *53*, 291–318.
- (85) Jorgensen, W. L.; Buckner, J. K.; Huston, S. E.; Rossky, P. J. Hydration and Energetics for (CH<sub>3</sub>)<sub>3</sub>CCl Ion Pairs in Aqueous Solution. *J. Am. Chem. Soc.* **1987**, *109*, 1891–1899.
- (86) Hynes, J. T. Crossing the Transition State in Solution. In *Solvent Effects and Chemical Reactivity*; Tapia, O., Bertrán, J., Eds.; Springer Netherlands: Dordrecht, 2005; pp 231–258.
- (87) Solà, M.; Lledós, A.; Duran, M.; Bertrán, J.; Abboud, J. L. M. Analysis of Solvent Effects on the Menshutkin Reaction. *J. Am. Chem. Soc.* **1991**, *113*, 2873–2879.
- (88) Hynes, J. T. Outer-Sphere Electron-Transfer Reactions and Frequency-Dependent Friction. *J. Phys. Chem.* **1986**, *90*, 3701–3706.
- (89) Fawcett, W. R.; Foss, C. A. Solvent Effects on Simple Electron Transfer Reactions. A Comparison of Results in Debye and Non-Debye Solvents. *J. Electroanal. Chem.* **1991**, *306*, 71–85.
- (90) Nazet, A.; Weiß, L.; Buchner, R. Dielectric Relaxation of Nitromethane and Its Mixtures with Ethylammonium Nitrate: Evidence for Strong Ion Association Induced by Hydrogen Bonding. *J. Mol. Liq.* **2017**, *228*, 81–90.
- (91) Auer, B.; Soudackov, A. V.; Hammes-Schiffer, S. Nonadiabatic Dynamics of

- Photoinduced Proton-Coupled Electron Transfer: Comparison of Explicit and Implicit Solvent Simulations. *J. Phys. Chem. B* **2012**, *116*, 7695–7708.
- (92) Valtazanos, P.; Ruedenberg, K. Bifurcations and Transition States. *Theor. Chim. Acta* **1986**, *69*, 281–307.
- (93) Wang, Z.; Hirschi, J. S.; Singleton, D. A. Recrossing and Dynamic Matching Effects on Selectivity in a Diels-Alder Reaction. *Angew. Chemie - Int. Ed.* **2009**, *48*, 9156–9159.
- (94) Biswas, B.; Collins, S. C.; Singleton, D. A. Dynamics and a Unified Understanding of Competitive [2,3]- and [1,2]-Sigmatropic Rearrangements Based on a Study of Ammonium Ylides. *J. Am. Chem. Soc.* **2014**, *136*, 3740–3743.
- (95) Brown, H. C.; Liu, K. T. Additions to Bicyclic Olefins. VII. Electrophilic Additions of Hydrogen Chloride and Deuterium Chloride to Norbornene, 2-Methylenenorbornane, and Related Bicyclic Olefins. Evidence for a Carbonium Ion Process and the Capture of Unsymmetrical (Classical) 2. *J. Am. Chem. Soc.* **1975**, *97*, 600–610.
- (96) Roytman, V. A.; Jin, S.; Nguyen, V. T.; Nguyen, V. D.; Haug, G. C.; Larionov, O. V.; Singleton, D. A. Bond Memory in Dynamically Determined Stereoselectivity. *J. Am. Chem. Soc.* **2020**, *142*, 85–88.
- (97) Richard, J. P.; Toteva, M. M.; Amyes, T. L. What Is the Stabilizing Interaction with Nucleophilic Solvents in the Transition State for Solvolysis of Tertiary Derivatives: Nucleophilic Solvent Participation or Nucleophilic Solvation? *Org. Lett.* **2001**, *3*, 2225–2228.
- (98) Amyes, T. L.; Toteva, M. M.; Richard, J. P. Crossing the Borderline between SN1



- and SN2 Nucleophilic Substitution at Aliphatic Carbon. In *Reactive Intermediate Chemistry*; John Wiley & Sons, Ltd, 2005; pp 41–68.
- (99) Bentley, T. W.; Schleyer, P. V. R. The Sn2-Sn1 Spectrum. 1. Role of Nucleophilic Solvent Assistance and Nucleophilically Solvated Ion Pair Intermediates in Solvolyses of Primary and Secondary Arenesulfonates. *J. Am. Chem. Soc.* **1976**, *98*, 7658–7666.
- (100) Bentley, T. W.; Liggero, S. H.; Imhoff, M. A.; Schleyer, P. v. R. Evidence Against Appreciable Hidden Return in Solvolyses of Simple Secondary Substrates. *J. Am. Chem. Soc.* **1974**, *96*, 1970–1973.
- (101) Gajewski, J. J. Is the Tert-Butyl Chloride Solvolysis the Most Misunderstood Reaction in Organic Chemistry? Evidence against Nucleophilic Solvent Participation in the Tert-Butyl Chloride Transition State and for Increased Hydrogen Bond Donation to the 1-Adamantyl Chloride Solvolysis Transition State. *J. Am. Chem. Soc.* **2001**, *123*, 10877–10883.
- (102) Shiner, V. J.; Dowd, W. The Addition of Undissociated Strong Acids to Alkenes. “Hidden Return” Revealed. *J. Am. Chem. Soc.* **1969**, *91*, 6528–6529.
- (103) Shiner, V. J.; Nollen, D. A.; Humski, K. Multiparameter Optimization Procedure for the Analysis of Reaction Mechanistic Schemes. Solvolyses of Cyclopentyl p-Bromobenzenesulfonate. *J. Org. Chem.* **1979**, *44*, 2108–2115.
- (104) Humski, K.; Sendjarević, V.; Shiner, V. J. Stereochemistry of Solvolytic Substitution of Cyclopentyl P-Bromobenzenesulfonate. *J. Am. Chem. Soc.* **1976**, *98*, 2865–2868.
- (105) Seib, R. C.; Humski, K.; Shiner, V. J.; Sendjarević, V. Solvolysis of Cyclopentyl P-

- Bromobenzenesulfonate in Aqueous Hexafluoroisopropyl Alcohol. Deuterium Rate Effects, Stereochemistry of Substitution and Elimination, and Reaction Mechanism. *J. Am. Chem. Soc.* **1978**, *100*, 8133–8137.
- (106) Ammal, S. C.; Yamataka, H.; Aida, M.; Dupuis, M. Dynamics-Driven Reaction Pathway in an Intramolecular Rearrangement. *Science (80-. )*. **2003**, *299*, 1555–1557.
- (107) de Souza, M. A. F.; Ventura, E.; do Monte, S. A.; Riveros, J. M.; Longo, R. L. Dynamic Effects Dictate the Mechanism and Selectivity of Dehydration-Rearrangement Reactions of Protonated Alcohols [Me<sub>2</sub> (R)CCH(OH<sub>2</sub><sup>+</sup>)Me]<sup>+</sup> (R=Me, Et, IPr) in the Gas Phase. *Chemistry* **2014**, *20*, 13742–13754.
- (108) Goering, H. L.; Pombo, M. M.; McMichael, K. D. Stereochemistry of Allylic Rearrangements. XIII. The Racemization, Carboxyl-Oxygen Equilibration and Solvolysis of Trans- $\alpha,\gamma$ -Dimethylallyl p-Nitrobenzoate in Aqueous Acetone. *J. Am. Chem. Soc.* **1963**, *85*, 965–970.
- (109) Goering, H. L.; Pombo, M. M. Stereochemistry of Allylic Rearrangements. X. The Isomeric Rearrangement and Solvolysis of Trans- $\alpha,\gamma$ -Dimethylallyl p-Nitrobenzoate in Aqueous Acetone. *J. Am. Chem. Soc.* **1960**, *82*, 2515–2521.
- (110) Goering, H. L.; Humski, K. Ion-Pair Return Associated with Solvolysis of 1,2-Dimethyl-Exo-2-Norbornyl p-Nitrobenzoate-18O. *J. Org. Chem.* **1975**, *40*, 920–922.
- (111) Chang, S.; le Noble, W. J. Study of Ion-Pair Return in 2-Norbornyl Brosylate by Means of 17O NMR. *J. Am. Chem. Soc.* **1983**, *105*, 3708–3709.
- (112) Goering, H. L.; Anderson, R. P. Stereochemistry of Allylic Rearrangements. 16.

- Ion-Pair Return Associated with Solvolysis of Exo- and Endo-Bicyclo[3.2.1]Oct-3-En-2-Yl p-Nitrobenzoate in Aqueous Acetone. *J. Am. Chem. Soc.* **1978**, *100*, 6469–6474.
- (113) Allen, A. D.; Fujio, M.; Mohammed, N.; Tidwell, T. T.; Tsuji, Y. 3-(Trifluoromethyl)Indenyl Cation: Ion Pair Return in the Formation of an Antiaromatic and Electron-Deficient Doubly Destabilized Carbocation. *J. Org. Chem.* **1997**, *62*, 246–252.
- (114) Goering, H. L.; Doi, J. T.; McMichael, K. D. Stereochemistry of Allylic Rearrangements. XIV. Ion-Pair Return Associated with the Solvolysis of Cis-5-Methyl-2-Cyclohexenyl p-Nitrobenzoate in Aqueous Acetone. *J. Am. Chem. Soc.* **1964**, *86*, 1951–1957.
- (115) Kurouchi, H.; Singleton, D. A. Labelling and Determination of the Energy in Reactive Intermediates in Solution Enabled by Energy-Dependent Reaction Selectivity. *Nat. Chem.* **2018**, *10*, 237–241.
- (116) Brown, H. C.; Groot, C. A Convenient Procedure for the Preparation of Deuterium Chloride. *J. Am. Chem. Soc.* **1942**.
- (117) Merlic Lab Notes  
[http://www.chem.ucla.edu/research/org/MERLIC\\_GROUP/Lab\\_Notes.html#Workup\\_Aluminum](http://www.chem.ucla.edu/research/org/MERLIC_GROUP/Lab_Notes.html#Workup_Aluminum) (accessed Dec 21, 2020).
- (118) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.;

- Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian16 (Revision A.03)*, Gaussian Inc. Wallingford CT. *Gaussian16 (Revision A.03)*. 2016.
- (119) Neese, F. Software Update: The ORCA Program System, Version 4.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**.
- (120) Stewart, J. J. P. MOPAC2016. *Stewart Computational Chemistry*. 2016.
- (121) Martinez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: A Package for Building Initial Configurations for Molecular Dynamics Simulations. *J. Comput. Chem.* **2009**, *30*, 2157–2164.
- (122) Grossfield, A. The Weighted Histogram Analysis Method. *Frequenz* **2003**, *65*, 307–311.
- (123) Singh, U. C.; Kollman, P. A. An Approach to Computing Electrostatic Charges for Molecules. *J. Comput. Chem.* **1984**, *5*, 129–145.
- (124) Mislow, K.; Bickart, P. An Epistemological Note on Chirality. *Isr. J. Chem.* **1976**, *15*, 1–6.
- (125) Carpenter, B. K. Dynamic Behavior of Organic Reactive Intermediates. *Angew.*

*Chemie - Int. Ed.* **1999**, *37*, 3340–3350.

- (126) Collins, P.; Kramer, Z. C.; Carpenter, B. K.; Ezra, G. S.; Wiggins, S. Nonstatistical Dynamics on the Caldera. *J. Chem. Phys.* **2014**, *141*.
- (127) Leber, P.; Kidder, K.; Viray, D.; Dietrich-Peterson, E.; Fang, Y.; Davis, A. Stereoselectivity in a Series of 7-Alkylbicyclo[3.2.0]Hept-2-Enes: Experimental and Computational Perspectives. *J. Phys. Org. Chem.* **2018**, *31*.
- (128) Debbert, S. L.; Carpenter, B. K.; Hrovat, D. A.; Borden, W. T. The Iconoclastic Dynamics of the 1,2,6-Heptatriene Rearrangement. *J. Am. Chem. Soc.* **2002**, *124*, 7896–7897.
- (129) Doubleday, C.; Bolton, K.; Hase, W. L. Direct Dynamics Study of the Stereomutation of Cyclopropane. *J. Am. Chem. Soc.* **1997**, *119*, 5251–5252.
- (130) Kandori, H.; Shichida, Y.; Yoshizawa, T. Review: Photoisomerization in Rhodopsin. *Biokhimiya* **2001**, *66*, 1483–1498.
- (131) TURRO, N. J. MECHANISMS OF SENSITIZED PHOTOCHEMICAL Cis-trans-ISOMERIZATION IN SOLUTION. *Photochem. Photobiol.* **1969**, *9*, 555–563.
- (132) Dugave, C.; Demange, L. Cis-Trans Isomerization of Organic Molecules and Biomolecules: Implications and Applications. *Chem. Rev.* **2003**, *103*, 2475–2532.
- (133) Gozem, S.; Luk, H. L.; Schapiro, I.; Olivucci, M. Theory and Simulation of the Ultrafast Double-Bond Isomerization of Biological Chromophores. *Chem. Rev.* **2017**, *117*, 13502–13565.
- (134) Huppert, D.; Rentzepis, P. M.; Kliger, D. S. Picosecond and Nanosecond Tsomerization Kinetics of Protonated 11-Cis Retinylidene Schiff Bases. *Photochem. Photobiol.* **1977**, *25*, 193–197.

- (135) Zimmerman, H. E.; Bunce, R. A. Cyclopropene Photochemistry. Mechanistic and Exploratory Organic Photochemistry. *J. Org. Chem.* **1982**, *47*, 3377–3396.
- (136) Leigh, W. J.; Postigo, J. A. Cyclobutene Photochemistry. Steric Effects on the Photochemical Ring Opening of Alkylcyclobutenes. *J. Am. Chem. Soc.* **1995**, *117*, 1688–1694.
- (137) Leigh, W. J.; Postigo, J. A.; Venneri, P. C. Orbital Symmetry and the Photochemical Ring Opening of Cyclobutene. *J. Am. Chem. Soc.* **1995**, *117*, 7826–7827.
- (138) Bonneau, R.; Jousset-Dubien, J.; Salem, L.; Yarwood, A. J. A Trans Cyclohexene. *J. Am. Chem. Soc.* **1976**, *98*, 4329–4330.
- (139) Dauben, W. G.; Van Riel, H. C. H. A.; Hauw, C.; Leroy, F.; Jousset-Dubien, J.; Bonneau, R. Photochemical Formation of Trans-1-Phenylcyclohexene. Chemical Proof of Structure. *J. Am. Chem. Soc.* **1979**, *101*, 1901–1903.
- (140) Snyder, J. J.; Rawlings, P. C.; Fravel, H. G.; Kropp, P. J. Photochemistry of Cycloalkenes. 9. Photodimerization of Cyclohexene<sup>1</sup>. *J. Org. Chem.* **1980**, *45*, 4471–4474.
- (141) Day, J. I.; Singh, K.; Trinh, W.; Weaver, J. D. Visible Light Mediated Generation of Trans-Arylcyclohexenes and Their Utilization in the Synthesis of Cyclic Bridged Ethers. *J. Am. Chem. Soc.* **2018**, *140*, 9934–9941.
- (142) Salomon, R. G.; Folting, K. Copper(I) Catalysis in Photocycloadditions. II. Cyclopentene, Cyclohexene, and Cycloheptene. *J. Am. Chem. Soc.* **1974**, *96*, 1145–1152.
- (143) Kropp, P. J. Photochemistry of Cycloalkenes. V. Effects of Ring Size and Substitution. *J. Am. Chem. Soc.* **1969**, *91*, 5783–5791.

- (144) Kropp, P. J. Photochemistry of Cycloalkenes. VII. Limonene. *J. Org. Chem.* **1970**, *35*, 2435–2436.
- (145) Jin, S.; Nguyen, V. T.; Dang, H. T.; Nguyen, D. P.; Arman, H. D.; Larionov, O. V. Photoinduced Carboborative Ring Contraction Enables Regio- and Stereoselective Synthesis of Multiply Substituted Five-Membered Carbocycles and Heterocycles. *J. Am. Chem. Soc.* **2017**, *139*, 11365–11368.
- (146) Nguyen, V. D. V. T.; Nguyen, V. D. V. T.; Jin, S.; Dang, H. T.; Larionov, O. V. Organoboron Chemistry Comes to Light: Recent Advances in Photoinduced Synthetic Approaches to Organoboron Compounds. *Tetrahedron* **2019**, *75*, 584–602.
- (147) Hare, S. R.; Tantillo, D. J. Post-Transition State Bifurcations Gain Momentum—Current State of the Field. *Pure Appl. Chem.* **2017**, *89*, 679–698.
- (148) Hong, Y. J.; Tantillo, D. J. A Maze of Dyotropic Rearrangements and Triple Shifts: Carbocation Rearrangements Connecting Stemarene, Stemodene, Betaerdene, Aphidicolene, and Scopadulanol. *J. Org. Chem.* **2018**, *83*, 3780–3793.
- (149) Seeman, J. I. Effect of Conformational Change on Reactivity in Organic Chemistry. Evaluations, Applications, and Extensions of Curtin-Hammett/Winstein-Holness Kinetics. *Chem. Rev.* **1983**, *83*, 83–134.
- (150) Dewar, M. J. S. Multibond Reactions Cannot Normally Be Synchronous. *J. Am. Chem. Soc.* **1984**, *106*, 209–219.
- (151) Zhao, H.; Hsu, D. C.; Carlier, P. R. Memory of Chirality: An Emerging Strategy for Asymmetric Synthesis. *Synthesis (Stuttg.)* **2005**, No. 1, 1–16.
- (152) Griesbeck, A. G.; Mauder, H. Intersystem Crossing in Triplet 1,4-Biradicals:

- Conformational Memory Effects on the Stereoselectivity of Photocycloaddition Reactions. *Acc. Chem. Res.* **1994**, *27*, 70–75.
- (153) Berson, J. A. Memory Effects and Stereochemistry in Multiple Carbonium Ion Rearrangements. *Angew. Chemie Int. Ed. English* **1968**, *7*, 779–791.
- (154) Ghigo, G.; Maranzana, A.; Tonachini, G. Memory Effects in Carbocation Rearrangements: Structural and Dynamic Study of the Norborn-2-En-7-Ylmethyl-X Solvolysis Case. *J. Org. Chem.* **2013**, *78*, 9041–9050.
- (155) Hare, S. R.; Pemberton, R. P.; Tantillo, D. J. Navigating Past a Fork in the Road: Carbocation- $\pi$  Interactions Can Manipulate Dynamic Behavior of Reactions Facing Post-Transition-State Bifurcations. *J. Am. Chem. Soc.* **2017**, *139*, 7485–7493.
- (156) Eyring, H. The Activated Complex in Chemical Reactions. *J. Chem. Phys.* **1935**, *3*, 107–115.
- (157) Bekele, T.; Christian, C. F.; Lipton, M. A.; Singleton, D. A. “Concerted” Transition State, Stepwise Mechanism. Dynamics Effects in C2-C6 Enyne Allene Cyclizations. *J. Am. Chem. Soc.* **2005**, *127*, 9216–9223.
- (158) Thomas, J. B.; Waas, J. R.; Harmata, M.; Singleton, D. A. Control Elements in Dynamically Determined Selectivity on a Bifurcating Surface. *J. Am. Chem. Soc.* **2008**, *130*, 14544–14555.
- (159) Bogle, X. S.; Singleton, D. A. Dynamic Origin of the Stereoselectivity of a Nucleophilic Substitution Reaction. *Org. Lett.* **2012**, *14*, 2528–2531.
- (160) Biswas, B.; Singleton, D. A. Controlling Selectivity by Controlling the Path of Trajectories. *J. Am. Chem. Soc.* **2015**, *137*, 14244–14247.
- (161) Carpenter, B. K.; Ezra, G. S.; Farantos, S. C.; Kramer, Z. C.; Wiggins, S. Empirical



- Classification of Trajectory Data: An Opportunity for the Use of Machine Learning in Molecular Dynamics. *J. Phys. Chem. B* **2018**, *122*, 3230–3241.
- (162) Bigeleisen, J.; Mayer, M. G. Calculation of Equilibrium Constants for Isotopic Exchange Reactions. *J. Chem. Phys.* **1947**, *15*, 261–267.
- (163) Depke, G.; Lifshitz, C.; Schwarz, H.; Tzidony, E. Non-Ergodic Behavior of Excited Radical Cations in the Gas Phase. *Angew. Chemie Int. Ed. English* **1981**, *20*, 792–793.
- (164) McAdoo, D. J.; McLafferty, F. W.; Smith, J. S. Ketonization of Gaseous Enol Ions. *Journal of the American Chemical Society*. October 1, 1970, pp 6343–6345.
- (165) McLafferty, F. W.; McAdoo, D. J.; Smith, J. S.; Kornfeld, R. The Enolic C<sub>3</sub>H<sub>6</sub>O<sup>•+</sup> + Ion Formed from Aliphatic Ketones. *J. Am. Chem. Soc.* **1971**, *93*, 3720–3730.
- (166) Tureček, F.; Hanuš, V. Loss of Methyl from [H<sub>2</sub>C=C(OH)CH<sub>3</sub>]<sup>•+</sup> Ions Prepared by Electron Impact Ionization of Unstable 2-hydroxypropene. *Org. Mass Spectrom.* **1984**, *19*, 631–638.
- (167) Lifshitz, C.; Tzidony, E. Kinetic Energy Release Distributions for C<sub>3</sub>H<sub>6</sub>O<sup>•+</sup>-Dissociations: A Further Test of the Applicability of the Energy-Randomization Hypothesis to Unimolecular Fragmentations. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 181–195.
- (168) Osterheld, T. H.; Brauman, J. I. Infrared Multiple Photon Dissociation of Acetone Radical Cation. An Enormous Isotope Effect with No Apparent Tunneling. *J. Am. Chem. Soc.* **1992**, *114*, 7158–7164.
- (169) Anand, S.; Schlegel, H. B. Dissociation of Acetone Radical Cation (CH<sub>3</sub>COCH<sub>3</sub><sup>•+</sup> → CH<sub>3</sub>CO<sup>++</sup>+CH<sub>3</sub><sup>•</sup>): An Ab Initio Direct Classical Trajectory Study. *Phys. Chem.*

- Chem. Phys.* **2004**, *6*, 5166–5171.
- (170) Zhou, J.; Schlegel, H. B. Dissociation of Acetone Radical Cation ( $\text{CH}_3\text{COCH}_3^{+\bullet} \rightarrow \text{CH}_3\text{CO}^+ + \text{CH}_3^{\bullet}$ ): An Ab Initio Direct Classical Trajectory Study of the Energy Dependence of the Branching Ratio. *J. Phys. Chem. A* **2008**, *112*, 13121–13127.
- (171) Bowman, J. M. Roaming. *Mol. Phys.* **2014**, *112*, 2516–2528.
- (172) Suits, A. G. Roaming Atoms and Radicals: A New Mechanism in Molecular Dissociation. *Acc. Chem. Res.* **2008**, *41*, 873–881.
- (173) Heazlewood, B. R.; Jordan, M. J. T.; Kable, S. H.; Selby, T. M.; Osborn, D. L.; Shepler, B. C.; Braams, B. J.; Bowman, J. M. Roaming Is the Dominant Mechanism for Molecular Products in Acetaldehyde Photodissociation. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 12719–12724.
- (174) Rehbein, J.; Wulff, B. Chemistry in Motion - Off the MEP. *Tetrahedron Lett.* **2015**, *56*, 6931–6943.
- (175) Mauguière, F. A. L.; Collins, P.; Kramer, Z. C.; Carpenter, B. K.; Ezra, G. S.; Farantos, S. C.; Wiggins, S. Phase Space Barriers and Dividing Surfaces in the Absence of Critical Points of the Potential Energy: Application to Roaming in Ozone. *J. Chem. Phys.* **2016**, *144*.
- (176) Mauguière, F. A. L.; Collins, P.; Kramer, Z. C.; Carpenter, B. K.; Ezra, G. S.; Farantos, S. C.; Wiggins, S. Roaming: A Phase Space Perspective. *Annu. Rev. Phys. Chem.* **2017**, *68*, 499–524.
- (177) Bowman, J. M.; Houston, P. L. Theories and Simulations of Roaming. *Chem. Soc. Rev.* **2017**, *46*, 7615–7624.
- (178) Toulson, B. W.; Fishman, D. A.; Murray, C. Photodissociation Dynamics of

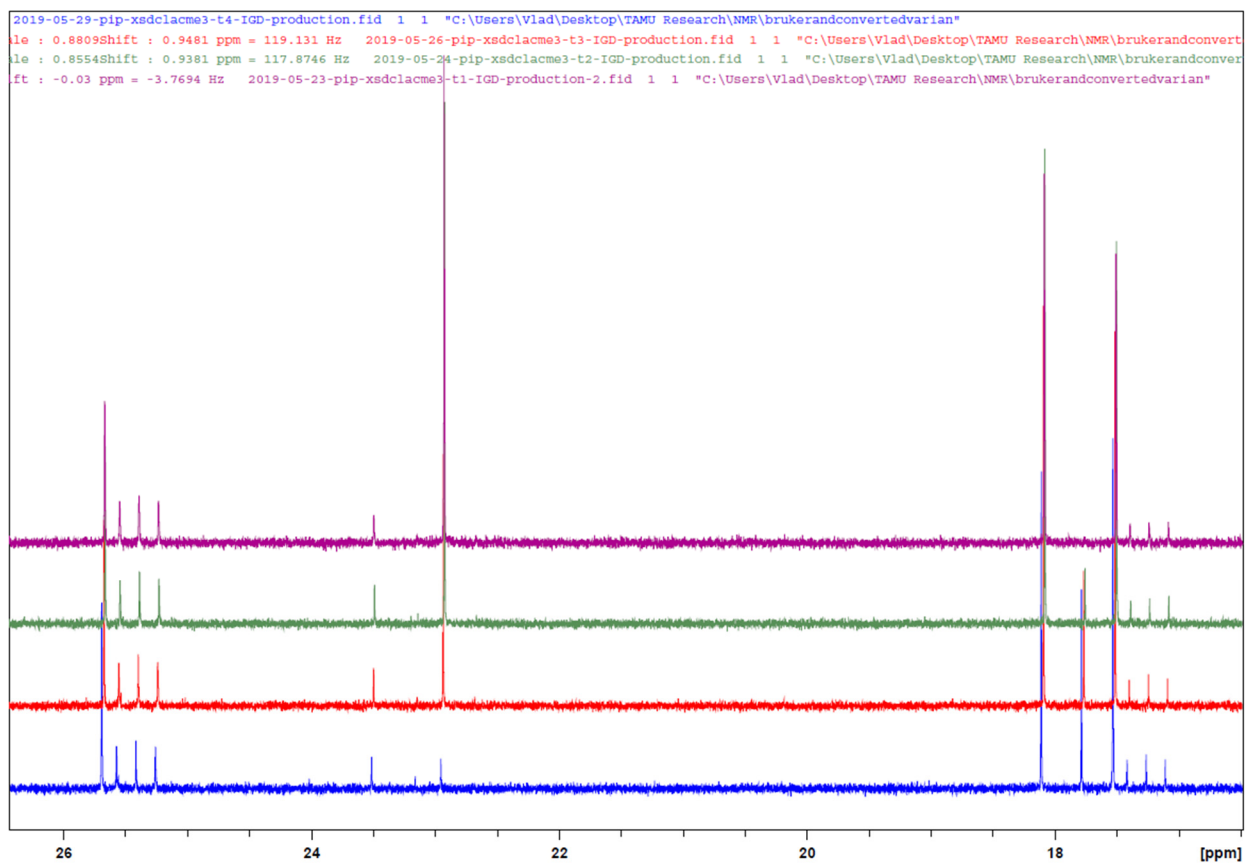
Acetone Studied by Time-Resolved Ion Imaging and Photofragment Excitation Spectroscopy. *Phys. Chem. Chem. Phys.* **2018**, *20*, 2454–2469.

- (179) Carpenter, B. K.; Ezra, G. S.; Farantos, S. C.; Kramer, Z. C.; Wiggins, S. Dynamics on the Double Morse Potential: A Paradigm for Roaming Reactions with No Saddle Points. *Regul. Chaotic Dyn.* **2018**, *23*, 60–79.
- (180) Zhu, L.; Hase, W. L. . *QCPE Bull* **1994**, *14*, 644.
- (181) Harmata, M.; Gomes, M. G. Intermolecular [4+2] Cycloadditions of a Reactive Cyclopentadienone. *European J. Org. Chem.* **2006**, *2006*, 2273–2277.
- (182) Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. Hydrazines and Azides via the Metal-Catalyzed Hydrohydrazination and Hydroazidation of Olefins. *J. Am. Chem. Soc.* **2006**, *128*, 11693–11712.
- (183) Antony, J.; Grimme, S. Density Functional Theory Including Dispersion Corrections for Intermolecular Interactions in a Large Benchmark Set of Biologically Relevant Molecules. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5287–5293.
- (184) Roytman, V. A.; Singleton, D. A. Solvation Dynamics and the Nature of Reaction Barriers and Ion-Pair Intermediates in Carbocation Reactions. *J. Am. Chem. Soc.* **2020**, *142*, 12865–12877.

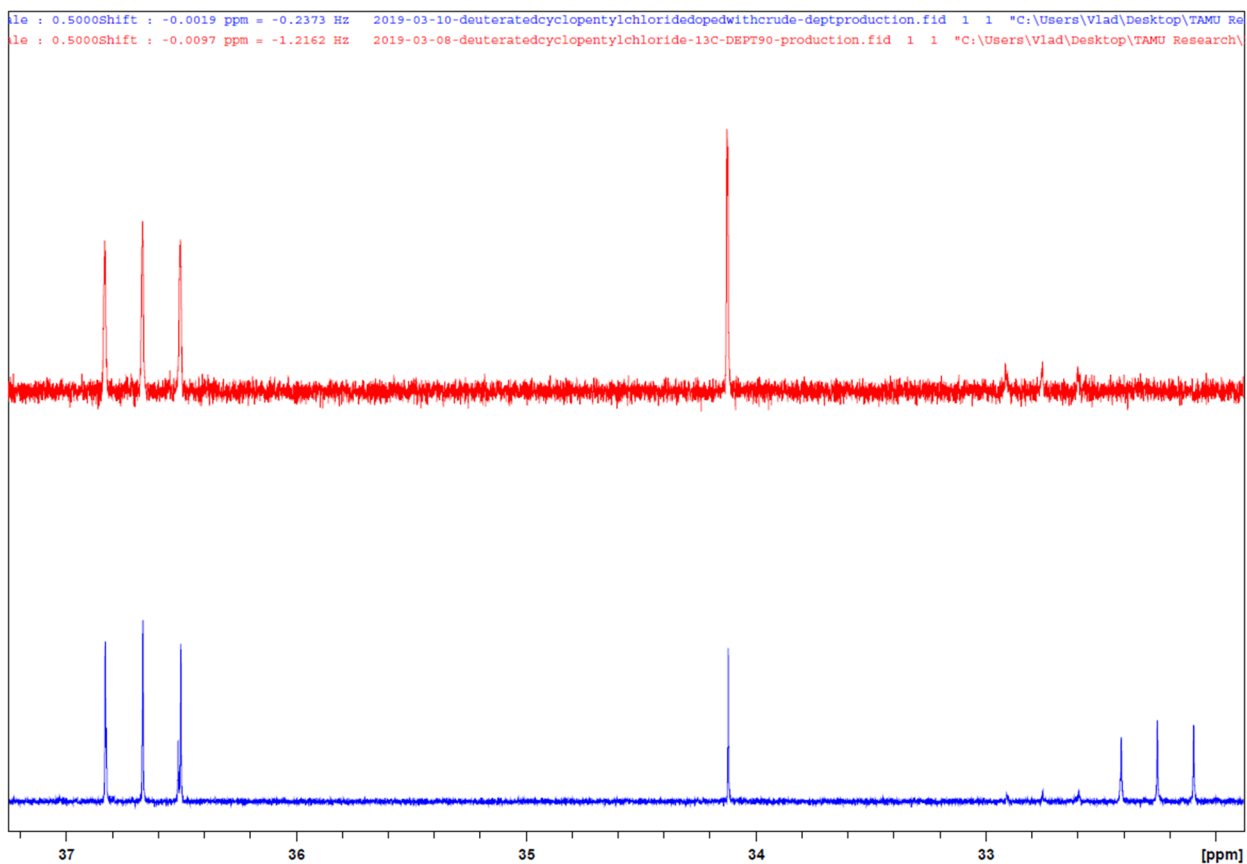
## APPENDIX A

### NMR SPECTRA

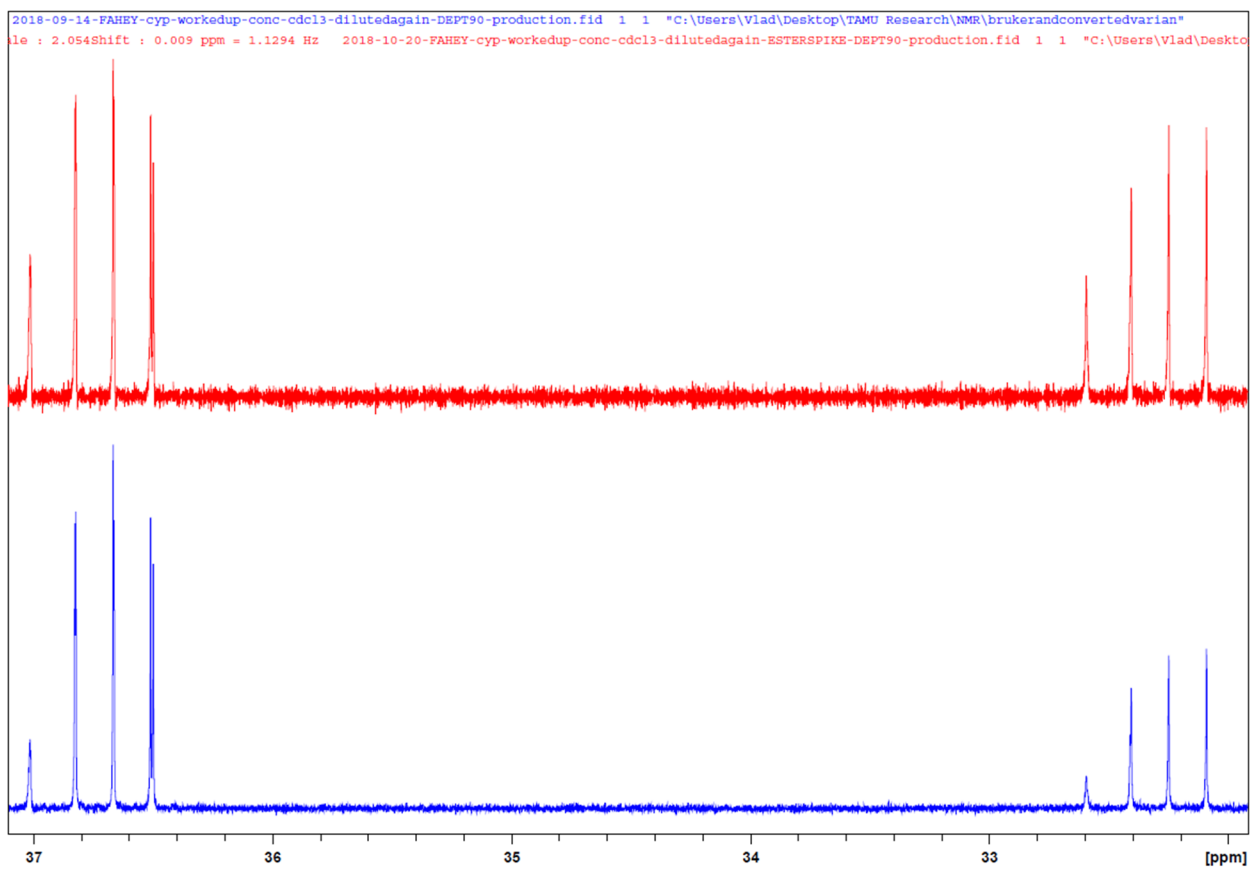
#### NMR Spectra for Chapter II



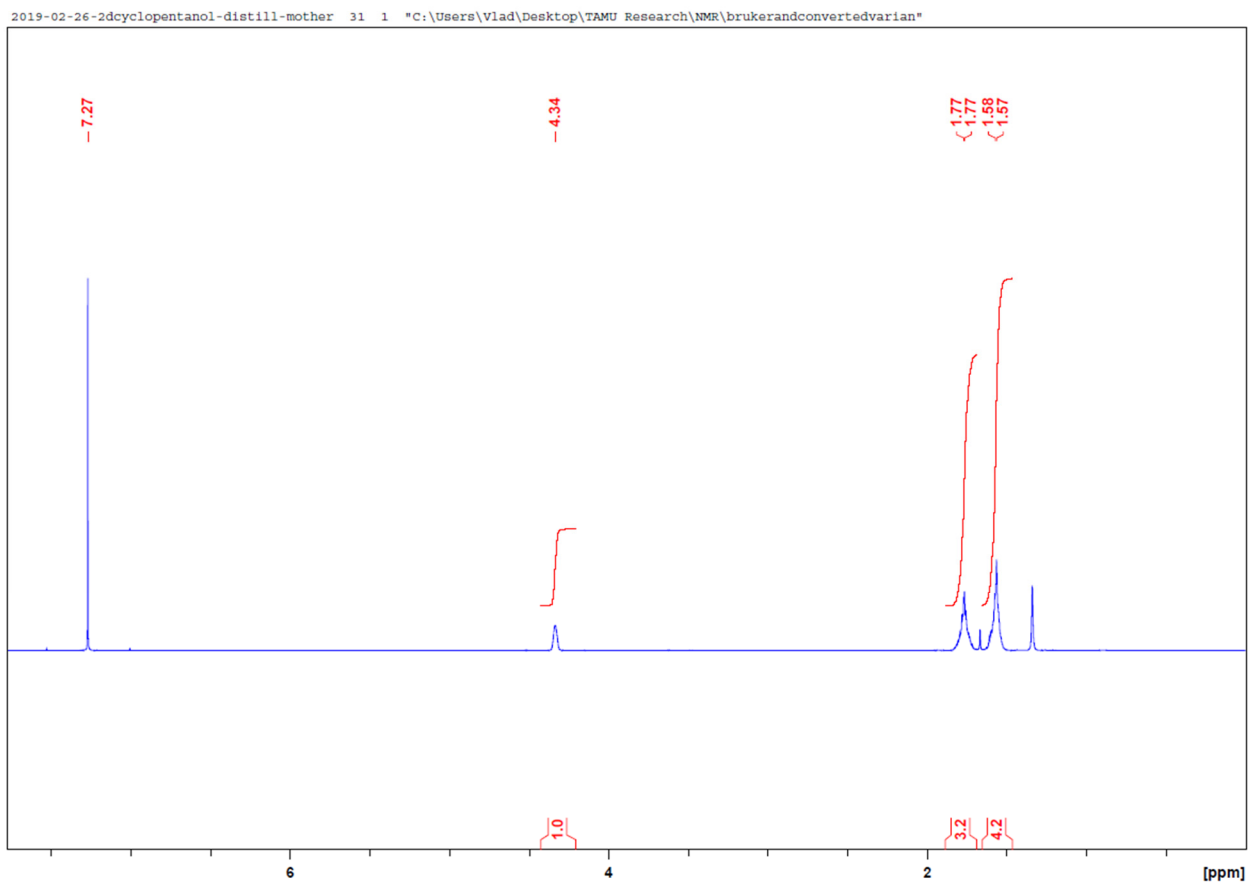
**Figure 84** Time-lapsed (6-days) inverse-gated decoupling  $^{13}\text{C}$  NMR spectra show that the equilibration of 1,2- and 1,4- products takes place at a low rate. This reaction was quenched with acetone enol ether prior to analysis.



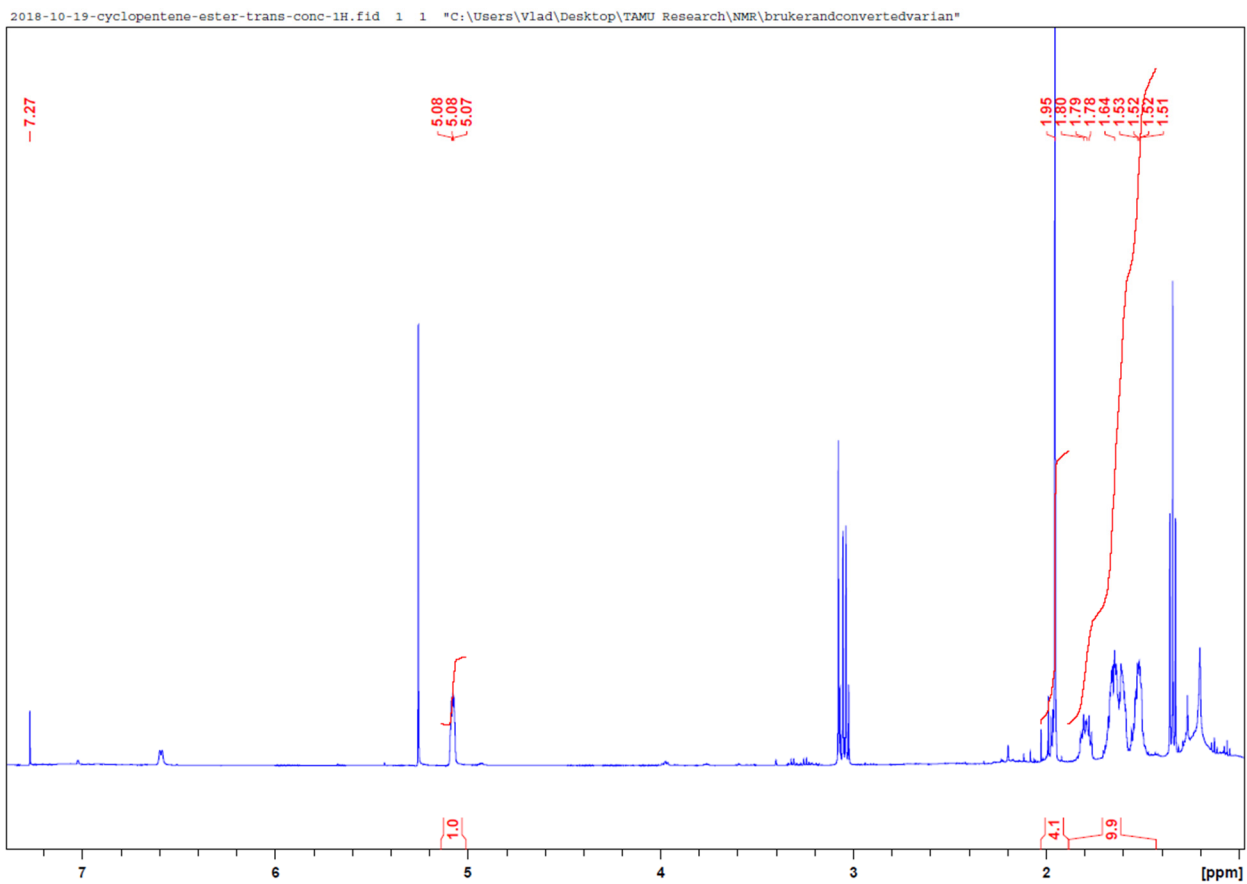
**Figure 85** Inverse-gated decoupling  $^{13}\text{C}$  NMR for peak assignment. Crude cyclopentene deuteriochlorination reaction mixture (top) and the same mixture doped with authentic *syn*-1-chloro-2- $\text{d}_1$ -cyclopentane (bottom)



**Figure 86** Inverse-gated decoupling  $^{13}\text{C}$  NMR for peak assignment. Crude cyclopentene deuteriochlorination reaction mixture (bottom) and the same mixture doped with authentic *trans*-1-acetoxy-2- $\text{d}_1$ -cyclopentane (top).

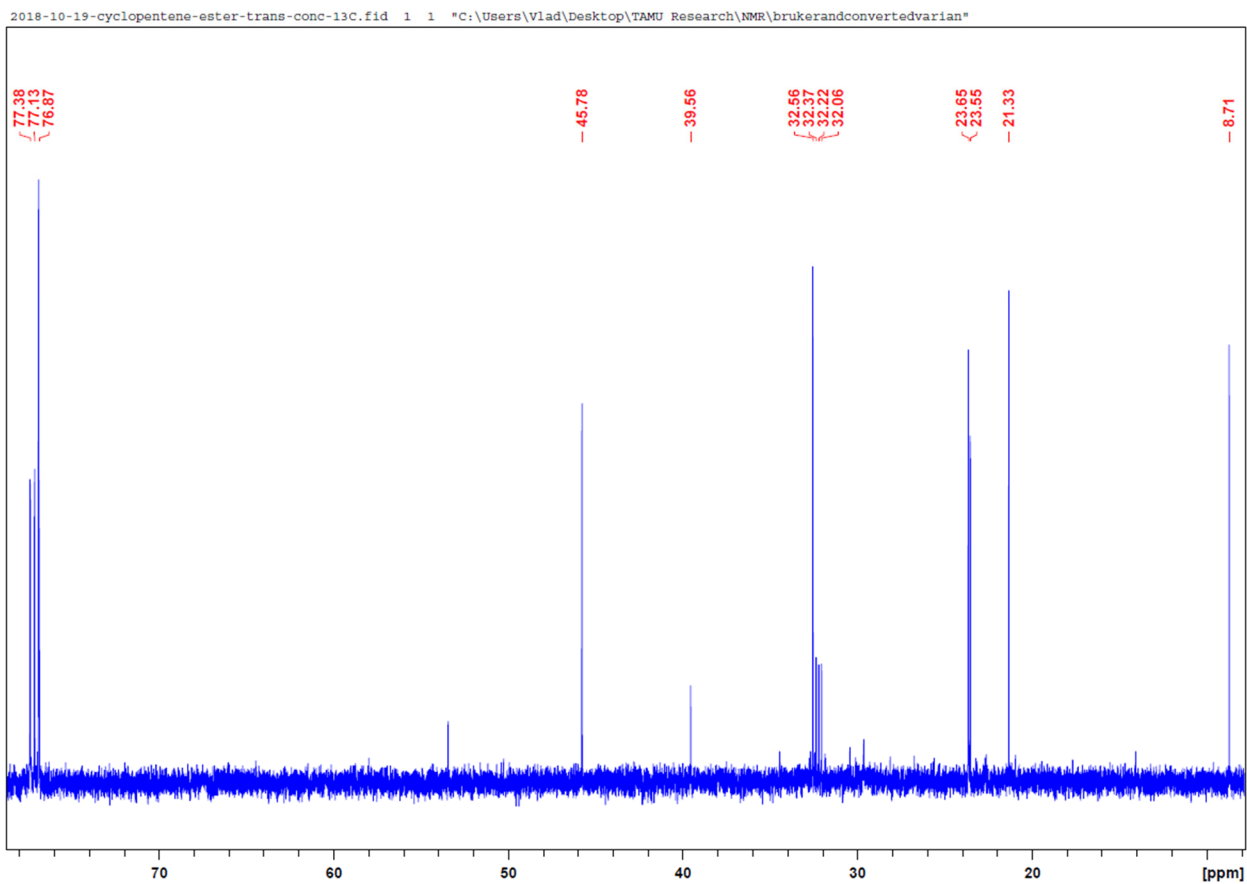


**Figure 87**  $^1\text{H}$  NMR of *syn*-2- $\text{d}_1$ -cyclopentanol in  $\text{CDCl}_3$ .

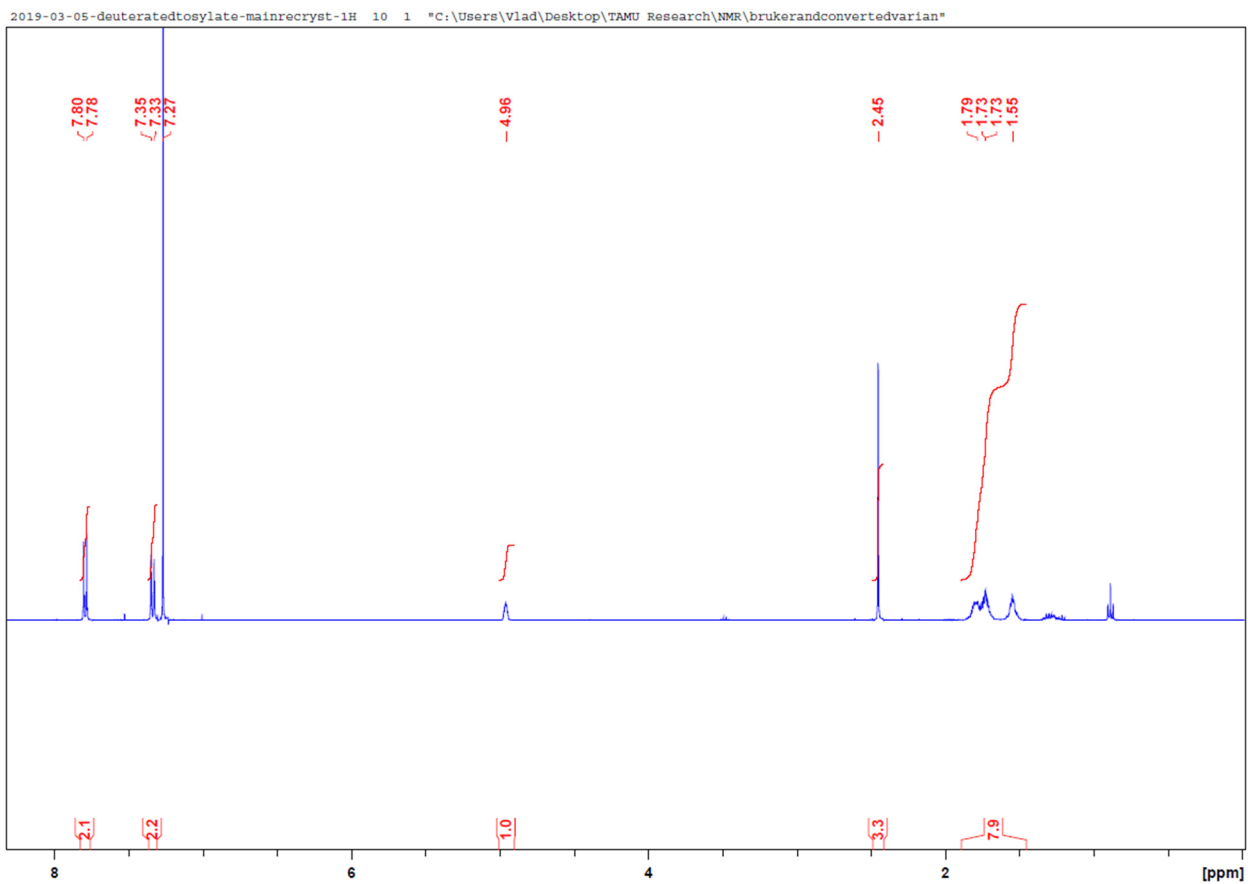


**Figure 88**  $^1\text{H}$  NMR of synthetic cyclopentan-2-*d*-ol acetate.

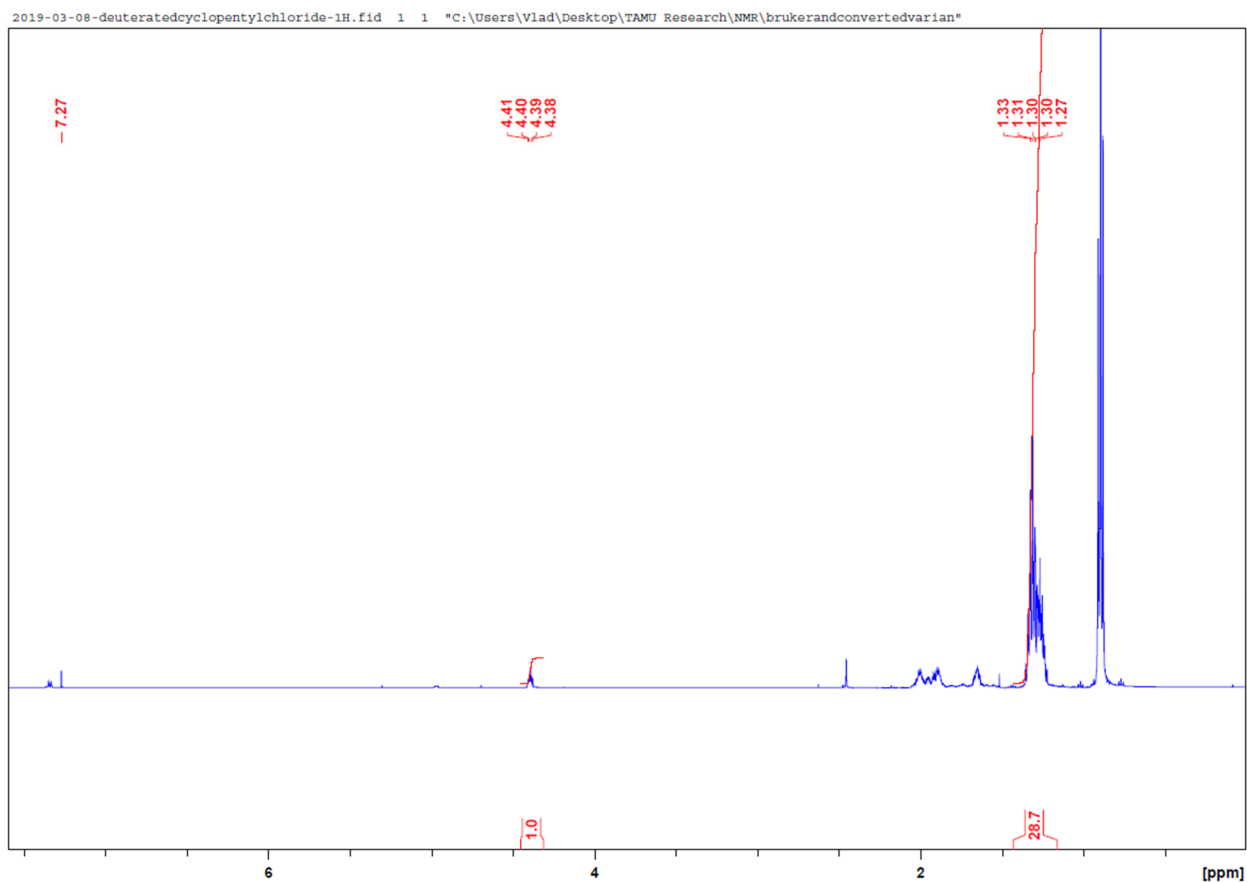




**Figure 89**  $^{13}\text{C}$  NMR of synthetic cyclopentan-2-*d*-ol acetate.



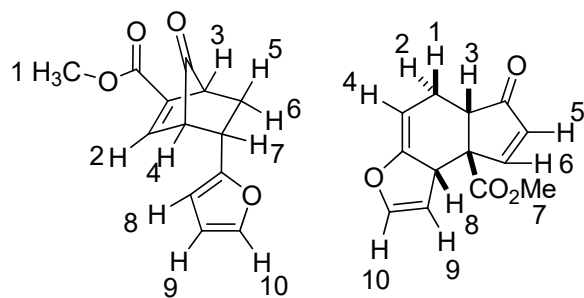
**Figure 90** <sup>1</sup>H NMR of *trans*-1-toluenesulfonyl-2-d<sub>1</sub>-cyclopentane in CDCl<sub>3</sub>.



**Figure 91**  $^1\text{H}$  NMR of *syn*-1-chloro-2- $\text{d}_1$ -cyclopentane in  $\text{CDCl}_3$ . Contains pentane impurities.

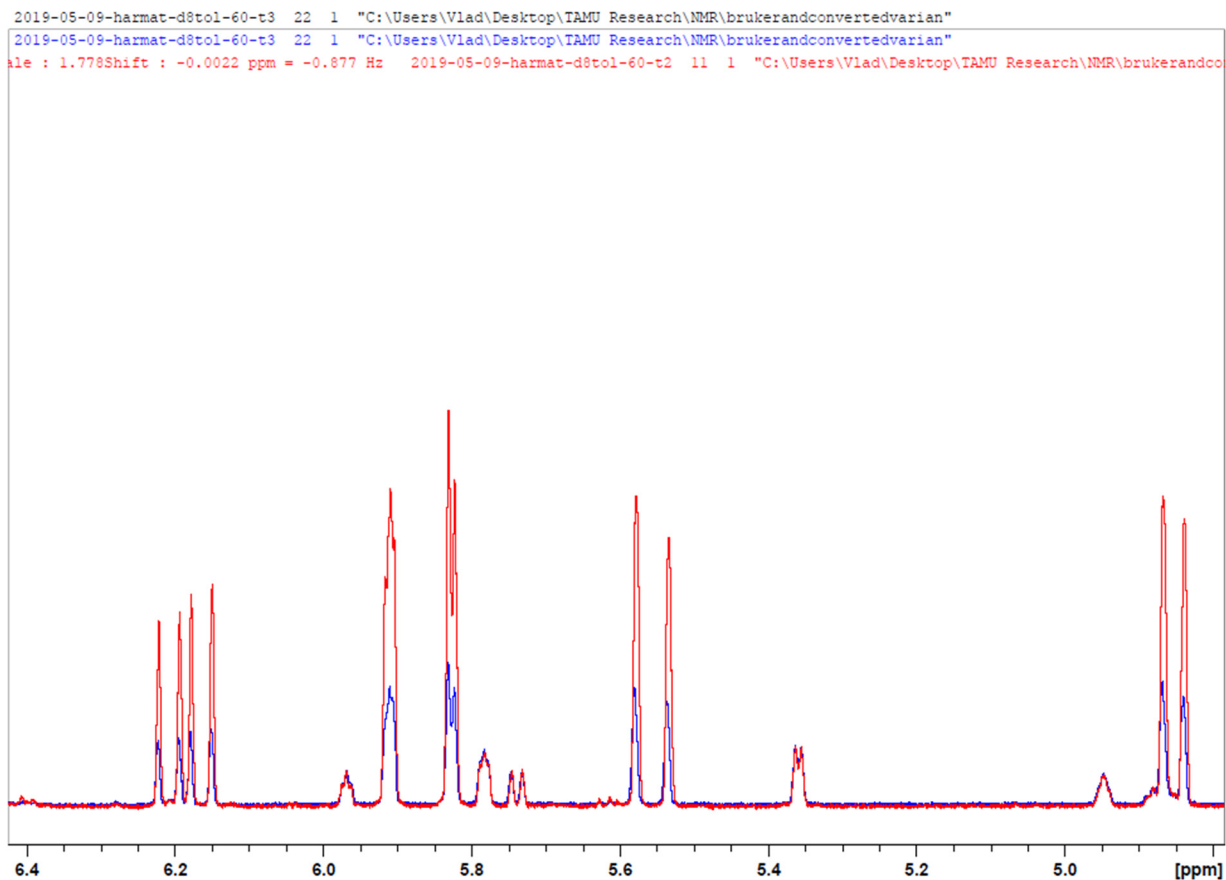
## NMR Spectra for Chapter IV

Reaction of Vinylfuran (**12**) with Cyclopentadienone **13**

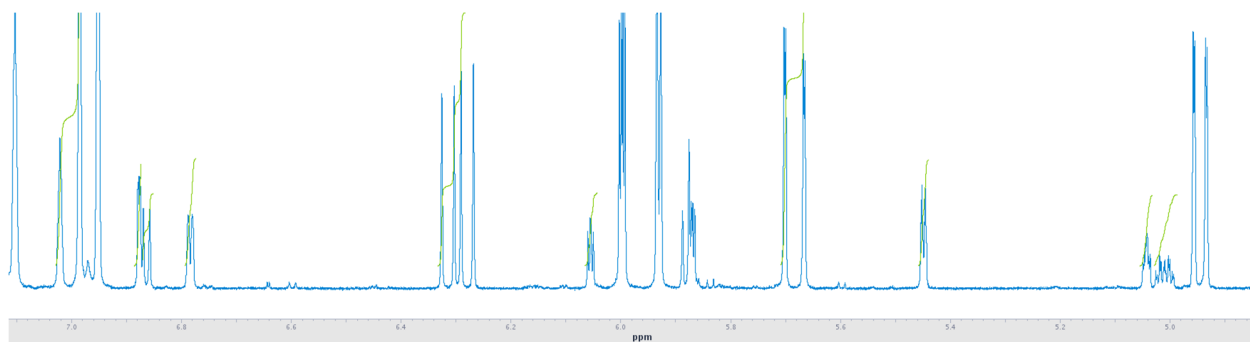


1.	3.27	1.	1.71
2.	6.89	2.	2.72
3.	3.35	3.	2.68
4.	3.01	4.	5.00
5.	1.84	5.	5.88
6.	1.15	6.	6.91
7.	3.13	7.	3.21
8.	5.45	8.	3.40
9.	5.89	9.	5.09
10.	6.8	10.	6.05

**Figure 92** Spectral peak assignments in d<sub>6</sub>-benzene

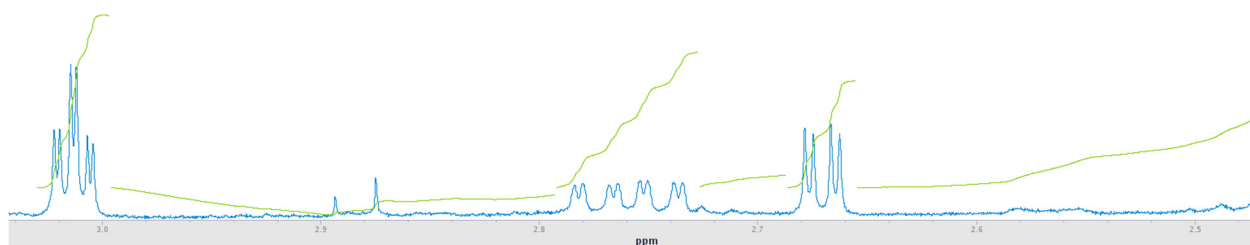


**Figure 93** <sup>1</sup>H spectra in benzene showing that the as the reaction in toluene at 60 °C progresses, the ratio of products does not change appreciably. Spectrum timepoint 3 spectrum is mistitled. These measurements were made 16 hours apart.



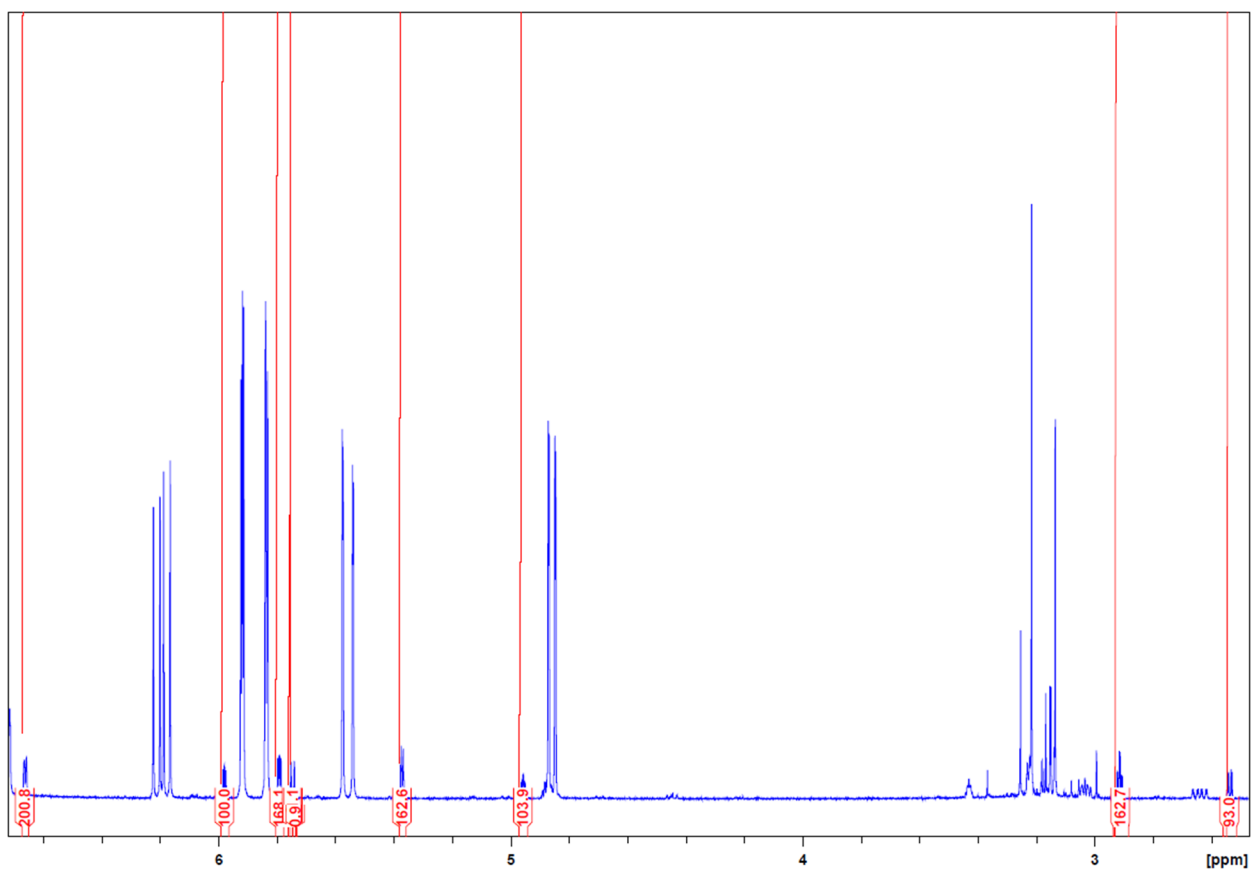
Compound	Peak	Integral
15	6.79	100
16	6.05	68.116
15	5.44	98.716
16	5.04	65.688
16	5.01	66.251
Ratio		1.49

**Figure 94**  $^1\text{H}$  NMR in benzene of **12** + **13** reaction at 23 °C in benzene and tabulated integrations for this sample.



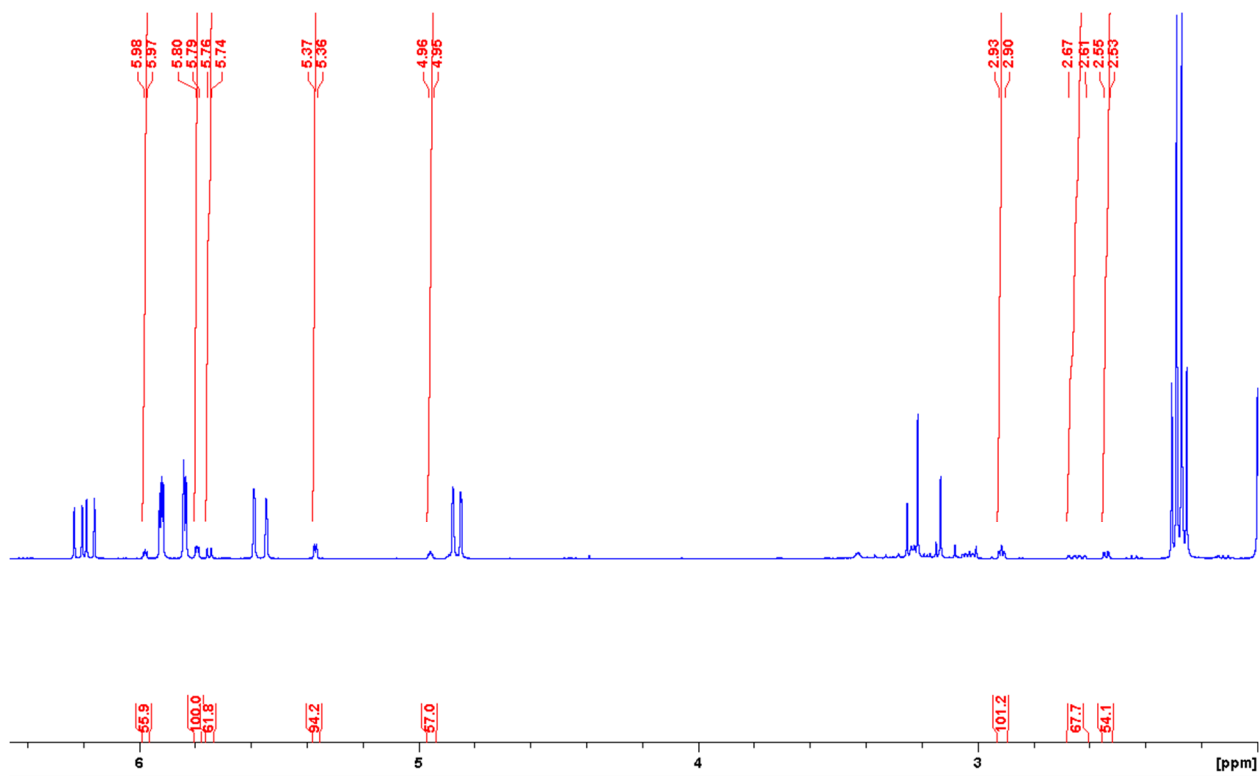
Compound	Peak	Integral
15	3.05	100
16	2.75	61.667
Ratio		1.62

**Figure 95**  $^1\text{H}$  NMR in benzene of **12** + **13** reaction at 60 °C in benzene tabulated integrations for this sample.



Compound	Peak	Integral
16	5.98	100
15	5.78	168.1
15	5.37	162.7
16	4.96	103.9
Ratio		1.62

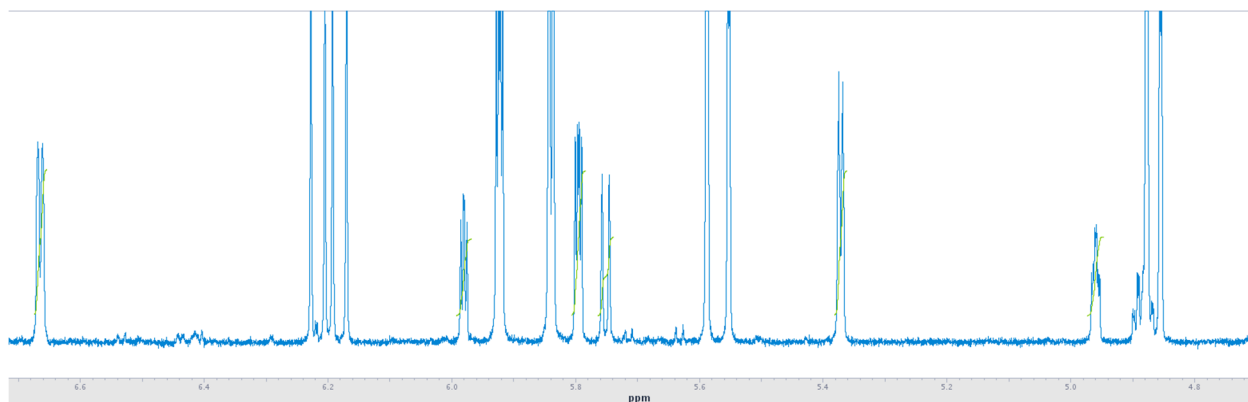
**Figure 96** <sup>1</sup>H NMR in benzene of **12** + **13** reaction at -20 °C in toluene and tabulated integrations for this sample.



Compound	Peak	Integral
16	5.98	55.91
15	5.79	100.00
16	5.75	61.82
15	5.37	94.19
16	4.96	57.04
15	2.91	101.17
16	2.64	67.72
16	2.54	54.13
Ratio		1.66

**Figure 97**  $^1\text{H}$  NMR in benzene of a reaction running in toluene at 23 °C. Some of shown integrals were determined to be reliable for use in quantifying product ratios.





Compound	Peak	Integral
15	6.66	100.0
16	5.98	52.7
15	5.79	99.3
16	5.75	53.9
15	5.37	99.2
16	4.96	54.2
Ratio		1.86

**Figure 98**  $^1\text{H}$  NMR in benzene of a reaction running in toluene at 60 °C. Some of shown integrals were determined to be reliable for use in quantifying product ratios.

## APPENDIX B

### CALCULATED STRUCTURES AND ENERGIES

#### Calculated Structures and Complete Energies for Chapter II

##### *Guide to Structures and Structure Titles*

The structure titles below are in most cases self-explanatory. PCM and SMD refer to structures optimized with the PCM and SMD implicit solvent model. TS refers to transition structures in which the 1,3-pentadiene is being protonated at C1, and this was explored with both one HCl and two HCl molecules present. When two HCl molecules are present, the second HCl may be located in varying positions and these are designated as “Conf A”, “Conf B”, etc. Not every conformation was located for every computational method / solvent model combination, despite careful searches in each case. For the product (E)-4-chloropent-2-ene, three conformations were located but only the lowest-energy conformation is presented here. Bichloride refers to the Cl—H—Cl anion, which was generally unsymmetrical in implicit solvent but was symmetrical for M06-2X calculations in the gas phase.

##### *Tables of Energies*

**Table 22** Collected MP2 and M06-2X raw energies.

	Pot. E.	E+zpe	H	G	S (E.U.)	G 1 M
<b>MP2/6-31+G** structures</b>						
HCl-gas phase	-460.207617	-460.200527	-460.197223	-460.218391	44.55	-460.215373
HCl SMD	-460.213106	-460.206156	-460.202851	-460.224030	44.58	-460.221012
HCl PCM	-460.211164	-460.204120	-460.200815	-460.221987	44.56	-460.218969
HCl Dimer-gas phase	-920.418518	-920.402724	-920.396567	-920.430797	72.04	-920.427779
HCl Dimer SMD	-920.427032	-920.411759	-920.405431	-920.440047	72.86	-920.437029
HCl Dimer PCM	-920.424550	-920.408716	-920.402680	-920.436479	71.14	-920.433461
Chloride anion – gas phase	-459.671145	-459.671145	-459.668785	-459.686168	36.59	-459.683150
Chloride anion – SMD	-459.775357	-459.775357	-459.772996	-459.790380	36.59	-459.787362
Chloride anion – PCM	-459.780255	-459.780255	-459.777895	-459.795278	36.59	-459.792260
Bichloride anion SMD	-920.000061	-919.991806	-919.987619	-920.015845	59.41	-920.012827
Bichloride anion PCM	-920.002148	-919.995235	-919.990657	-920.014395	49.96	-920.011377
Pentadienyl cation – gas phase	-194.998888	-194.871875	-194.864144	-194.901797	79.25	-194.898779
Pentadienyl cation – SMD	-195.095043	-194.968443	-194.960645	-194.998474	79.62	-194.995456
Pentadienyl cation – PCM	-195.078935	-194.951888	-194.944081	-194.981965	79.73	-194.978947
1,3-pentadiene – gas phase	-194.669694	-194.554659	-194.547457	-194.583755	76.40	-194.580737
1,3-pentadiene – SMD	-194.674749	-194.559992	-194.552815	-194.589016	76.19	-194.585998
1,3-pentadiene – PCM	-194.671881	-194.557010	-194.549798	-194.586133	76.47	-194.583115
(E)-4-chloropent-2-ene – gas phase	-654.910587	-654.779735	-654.771254	-654.811787	85.31	-654.808769
(E)-4-chloropent-2-ene – SMD	-654.919429	-654.788938	-654.780450	-654.820975	85.29	-654.817957
(E)-4-chloropent-2-ene – PCM	-654.914356	-654.783702	-654.775207	-654.815754	85.34	-654.812736
TS / one HCl SMD	-654.867425	-654.744800	-654.735952	-654.778580	89.72	-654.775562

TS / one HCl PCM	-654.859761	-654.736546	-654.727737	-654.770334	89.65	-654.767316
TS / two HCl conf B SMD	-1115.090018	-1114.958685	-1114.947012	-1114.998187	107.71	-1114.995169
TS / two HCl conf C SMD	-1115.090006	-1114.958721	-1114.947045	-1114.999134	109.63	-1114.996116
TS / two HCl conf A PCM	-1115.079533	-1114.947843	-1114.936062	-1114.988721	110.83	-1114.985703
TS / two HCl conf B PCM	-1115.081097	-1114.949254	-1114.937593	-1114.988789	107.75	-1114.985771
<b>M06-2X/6-31+G** structures</b>						
HCl-gas phase	-460.762018	-460.755187	-460.751882	-460.773067	44.59	-460.770049
HCl SMD	-460.767806	-460.761125	-460.757820	-460.779017	44.61	-460.775999
HCl PCM	-460.765738	-460.758967	-460.755662	-460.776851	44.60	-460.773833
(HCl) <sub>2</sub> dimer-gas phase	-921.527331	-921.512445	-921.505984	-921.542172	76.16	-921.539154
(HCl) <sub>2</sub> dimer SMD	-921.536203	-921.521639	-921.515214	-921.550656	74.59	-921.547638
(HCl) <sub>2</sub> dimer PCM	-921.533574	-921.518915	-921.513401	-921.546204	69.04	-921.543186
Chloride anion – gas phase	-460.235297	-460.235297	-460.232937	-460.250320	36.59	-460.247302
Chloride anion – SMD	-460.339779	-460.339779	-460.337419	-460.354802	36.59	-460.351784
Chloride anion – PCM	-460.344843	-460.344843	-460.342483	-460.359866	36.59	-460.356848
Bichloride anion – SMD	-921.124048	-921.121093	-921.116239	-921.141285	52.71	-921.138267
Bichloride anion – PCM	-921.125594	-921.120193	-921.115949	-921.144165	59.39	-921.141147
Pentadienyl cation – gas phase	-195.547125	-195.422385	-195.414674	-195.452204	78.99	-195.449186
Pentadienyl cation – SMD	-195.642802	-195.518575	-195.510778	-195.548562	79.52	-195.545544
Pentadienyl cation – PCM	-195.626628	-195.501984	-195.494175	-195.531989	79.59	-195.528971
1,3-pentadiene – gas phase	-195.218451	-195.104296	-195.097236	-195.133135	75.56	-195.130117
1,3-pentadiene – SMD	-195.224268	-195.110463	-195.103413	-195.139270	75.47	-195.136252
1,3-pentadiene – PCM	-195.221028	-195.107071	-195.099997	-195.135938	75.65	-195.132920
(E)-4-chloropent-2-ene – gas phase	-656.014201	-655.885432	-655.876904	-655.917521	85.49	-655.914503
(E)-4-chloropent-2-ene – SMD	-656.023907	-655.895665	-655.887090	-655.927814	85.71	-655.924796
(E)-4-chloropent-2-ene – PCM	-656.018604	-655.890154	-655.881580	-655.922305	85.71	-655.919287
TS / one HCl SMD	-655.982935	-655.862335	-655.853519	-655.895980	89.37	-655.892962
TS / one HCl PCM	-655.975242	-655.853793	-655.844992	-655.887611	89.70	-655.884593
TS / two HCl conf A SMD	-1116.758546	-1116.630365	-1116.618501	-1116.671075	110.652	-1116.668057
TS / two HCl conf B SMD	-1116.759243	-1116.631206	-1116.619365	-1116.670544	107.71	-1116.667526
TS / two HCl conf C SMD	-1116.759577	-1116.631063	-1116.619388	-1116.669688	105.87	-1116.666670
TS / two HCl conf A PCM	-1116.74942	-1116.620670	-1116.608870	-1116.661239	110.22	-1116.658221
TS / two HCl conf B PCM	-1116.750787	-1116.622070	-1116.610328	-1116.661010	106.669	-1116.657992

In the last column, “1 M” refers to free energies adjusted for a standard state of 1 M instead of the default standard state of 1 atm by adding  $0.001987 \times 298.15 \times \ln(24.5)/627.509$ .

**Table 23** Selected MP2 and M06-2X relative energies (kcal/mol).

	MP2 gas phase	MP2 SMD	MP2 PCM	M06-2X gas phase	M06-2X SMD	M06-2X PCM
Chloride proton affinity (H)	331.6			325.6		
1,3-pentadiene proton affinity (H)	198.7			199.2		
HCl dimer versus monomer (G, 1M)	1.9	3.1	2.8	0.6	2.7	2.8
Bichloride vs chloride + HCl		-2.8	-0.1		-6.6	-6.6
Diene + HCl -> cation + Cl (G, 1M)	134.4	15.2	19.4	127.8	9.4	13.1
Product from HCl + diene (G, 1 M)	-7.9	-6.9	-6.7	-9.0	-7.9	-7.9

TS / one HCl vs diene + HCl (G, 1 M)	19.7	21.8	11.9	14.1
TS / two HCl vs diene + (HCl) <sub>2</sub> (G, 1 M)	17.5	19.3	10.9	11.5
TS / two HCl vs diene + HCl + HCl (G, 1 M)	20.6	22.1	13.7	14.3

All energies here refer to a standard state of 1 M. For reactions involving competitive transition states, the barrier for only the lowest-energy transition state is shown. The “1M” refers to free energies adjusted for a standard state of 1 M instead of the default standard state of 1 atm.

**Table 24** DLPNO/aug-cc-pVTZ derived energies.

Structure	DLPNO/aug-cc-pvtz Pot. En.	Pot. Energy MP2 gas phase	G, MP2, solution, 1 Atm	G, DLPNO, solution, 1 M <sup>a</sup>	E <sub>rel</sub> (kcal/mol) <sup>b</sup>
<b>MP2 PCM Structures</b>					
HCl PCM	-460.343187	-460.207614	-460.221987	-460.354540	
1,3-pentadiene – PCM	-194.950054	-194.669687	-194.586133	-194.863480	
HCl Dimer PCM	-920.689674	-920.418458	-920.436479	-920.704675	2.8
TS / one HCl PCM	-655.249629	-654.832479	-654.770334	-655.184464	21.1
TS / two HCl conf B PCM	-1115.613100	-1115.061527	-1114.988801	-1115.537354	22.1
TS / two HCl conf A PCM	-1115.609916	-1115.057592	-1114.988721	-1115.538025	21.7
pentadienyl_cation_mp2Pspcm	-195.277765	-194.998813	-194.981965	-195.257898	
Bichloride anion PCM	-920.182229	-919.911814	-920.014395	-920.281791	
Chloride anion – PCM	-459.804960	-459.671145	-459.795278	-459.926072	
(E)-4-chloropent-2-ene – PCM	-655.321443	-654.910510	-654.815754	-655.223668	-3.5
<b>MP2 SMD Structures</b>					
HCl SMD	-460.343210	-460.207586	-460.224030	-460.356634	
1,3-pentadiene – SMD	-194.950047	-194.669675	-194.589016	-194.866368	
HCl Dimer SMD	-920.689713	-920.418445	-920.440047	-920.708295	3.1
TS / one HCl SMD	-655.251698	-654.834675	-654.778580	-655.192583	19.1
TS / two HCl conf C SMD	-1115.614326	-1115.062741	-1114.999134	-1115.547699	20.0
TS / two HCl conf B SMD	-1115.614586	-1115.063111	-1114.998187	-1115.546642	20.7
Pentadienyl cation – SMD	-195.277748	-194.998765	-194.998474	-195.274437	
Bichloride anion SMD	-920.182843	-919.912226	-920.015845	-920.283442	
Chloride anion – SMD	-459.804960	-459.671145	-459.790380	-459.921174	
(E)-4-chloropent-2-ene – SMD	-655.321421	-654.910443	-654.820975	-655.228934	-3.7
<hr/>					
Structure	DLPNO/aug-cc-pvtz Pot. En.	Pot. Energy M062X gas phase	G, MP2, solution, 1 Atm	G, DLPNO, solution, 1 M <sup>a</sup>	E <sub>rel</sub> (kcal/mol) <sup>b</sup>
<b>M06-2X PCM Structures</b>					
HCl PCM	-460.343198	-460.762013	-460.776851	-460.355016	
1,3-pentadiene – PCM	-194.950058	-195.218440	-195.135938	-194.864536	
(HCl) <sub>2</sub> dimer PCM	-920.689726	-921.527173	-921.546204	-920.705737	2.7
TS / one HCl PCM	-655.249637	-655.947052	-655.887611	-655.187176	20.3
TS / two HCl conf B PCM	-1115.616602	-1116.733211	-1116.661010	-1115.541381	20.8
TS / two HCl conf A PCM	-1115.613848	-1116.729518	-1116.661239	-1115.542548	20.1
Pentadienyl cation – PCM	-195.277803	-195.547055	-195.531989	-195.259717	
Bichloride anion – PCM	-920.184919	-921.038543	-921.144165	-920.287521	

Chloride anion – PCM	-459.804960	-460.235297	-460.359866	-459.926508	
(E)-4-chloropent-2-ene – PCM	-655.321441	-656.014068	-655.922305	-655.226658	-4.5
<b>M06-2X SMD Structures</b>					
HCl SMD	-460.343151	-460.761979	-460.779017	-460.357169	
1,3-pentadiene – SMD	-194.950042	-195.218422	-195.139270	-194.867869	
(HCl) <sub>2</sub> dimer SMD	-920.689669	-921.527233	-921.550656	-920.710072	2.7
TS / one HCl SMD	-655.252939	-655.949817	-655.895980	-655.196083	18.2
TS / two HCl conf C SMD	-1115.618684	-1116.734578	-1116.669688	-1115.550774	19.7
TS / two HCl conf A SMD	-1115.616859	-1116.731929	-1116.671075	-1115.552986	18.3
TS / two HCl conf B SMD	-1115.619081	-1116.734827	-1116.670544	-1115.551778	19.1
Pentadienyl cation – SMD	-195.277747	-195.547016	-195.548562	-195.276273	
Bichloride anion – SMD	-920.185002	-921.038981	-921.141285	-920.284286	
Chloride anion – SMD	-459.804960	-460.235297	-460.354802	-459.921444	17.1
(E)-4-chloropent-2-ene – SMD	-655.321341	-656.013975	-655.927814	-655.232160	-4.5

<sup>a</sup>Calculated as Column 3 – Column 2 + Column 1 + 0.001987\*298.15\*ln(24.5)/627.509 (the last term corrects from 1 atm to 1 M). <sup>b</sup>Relative to separate starting materials.

### MP2/6-31+G\*\* structures

#### HCl-gas phase

MP2/6-31+G\*\*

EUMP2 = -0.46020761713804D+03

Zero-point correction= 0.007090 (Hartree/Particle)  
 Thermal correction to Energy= 0.009450  
 Thermal correction to Enthalpy= 0.010394  
 Thermal correction to Gibbs Free Energy= -0.010774  
 Sum of electronic and ZPE= -460.200527  
 Sum of electronic and thermal Energies= -460.198167  
 Sum of electronic and thermal Enthalpies= -460.197223  
 Sum of electronic and thermal Free Energies= -460.218391

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 5.930	4.968	44.553

Cl<sub>0</sub>, -0.3873357934, -3.152125816, 0.7128749805  
 H<sub>0</sub>, -1.2288842066, -2.308634184, 0.2732650195

#### HCl SMD

MP2/6-31+G\*\*

EUMP2 = -0.46021310572512D+03

Zero-point correction= 0.006950 (Hartree/Particle)  
 Thermal correction to Energy= 0.009311  
 Thermal correction to Enthalpy= 0.010255  
 Thermal correction to Gibbs Free Energy= -0.010924  
 Sum of electronic and ZPE= -460.206156  
 Sum of electronic and thermal Energies= -460.203795  
 Sum of electronic and thermal Enthalpies= -460.202851  
 Sum of electronic and thermal Free Energies= -460.224030

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K

Total 5.843 4.968 44.575

Cl<sub>0</sub>, -0.3850243313, -3.1544426155, 0.7140824473  
 H<sub>0</sub>, -1.2311956687, -2.3063173845, 0.2720575527

#### HCl PCM

MP2/6-31+G\*\*

EUMP2 = -0.46021116360143D+03

Zero-point correction= 0.007044 (Hartree/Particle)  
 Thermal correction to Energy= 0.009404  
 Thermal correction to Enthalpy= 0.010348  
 Thermal correction to Gibbs Free Energy= -0.010824  
 Sum of electronic and ZPE= -460.204120  
 Sum of electronic and thermal Energies= -460.201760  
 Sum of electronic and thermal Enthalpies= -460.200815  
 Sum of electronic and thermal Free Energies= -460.221987

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 5.901	4.968	44.560

Cl<sub>0</sub>, -0.3865779149, -3.1528854445, 0.7132708828  
 H<sub>0</sub>, -1.2296420851, -2.3078745555, 0.2728691172

#### HCl Dimer-gas phase

MP2/6-31+G\*\*

EUMP2 = -0.92041851838371D+03

Zero-point correction= 0.015795 (Hartree/Particle)  
 Thermal correction to Energy= 0.021008  
 Thermal correction to Enthalpy= 0.021952  
 Thermal correction to Gibbs Free Energy= -0.012278  
 Sum of electronic and ZPE= -920.402724  
 Sum of electronic and thermal Energies= -920.397511  
 Sum of electronic and thermal Enthalpies= -920.396567

Sum of electronic and thermal Free Energies= -920.430797

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 13.183 13.288 72.044

H,0,-2.0505141611,0.4812496329,-0.2640794703  
Cl,0,-2.7018667446,-0.5920673714,-0.4630106611  
Cl,0,-0.2658837139,-3.33122548,0.7701505738  
H,0,-1.1237053804,-2.4929567815,0.3448895576

### HCl Dimer SMD

MP2/6-31+G\*\*  
EUMP2 = -0.92042703189231D+03

Zero-point correction= 0.015272 (Hartree/Particle)  
Thermal correction to Energy= 0.020657  
Thermal correction to Enthalpy= 0.021601  
Thermal correction to Gibbs Free Energy= -0.013016  
Sum of electronic and ZPE= -920.411759  
Sum of electronic and thermal Energies= -920.406375  
Sum of electronic and thermal Enthalpies= -920.405431  
Sum of electronic and thermal Free Energies= -920.440047

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 12.962 13.493 72.856

H,0,-2.0312533251,0.4508446608,-0.2538150919  
Cl,0,-2.7070689877,-0.6140037846,-0.4632445705  
Cl,0,-0.2892845415,-3.3257858407,0.7603474654  
H,0,-1.1143631457,-2.4460550356,0.344662197

### HCl Dimer PCM

MP2/6-31+G\*\*  
EUMP2 = -0.92042455018430D+03

Zero-point correction= 0.015834 (Hartree/Particle)  
Thermal correction to Energy= 0.020926  
Thermal correction to Enthalpy= 0.021870  
Thermal correction to Gibbs Free Energy= -0.011928  
Sum of electronic and ZPE= -920.408716  
Sum of electronic and thermal Energies= -920.403624  
Sum of electronic and thermal Enthalpies= -920.402680  
Sum of electronic and thermal Free Energies= -920.436479

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 13.131 13.200 71.135

H,0,-2.041580278,0.4577644712,-0.2412473748  
Cl,0,-2.6902031624,-0.6141177003,-0.4680085383  
Cl,0,-0.3078017666,-3.3447098615,0.7523475298  
H,0,-1.1023847929,-2.4339369094,0.3448583833

### Chloride anion – gas phase

MP2/6-31+G\*\*  
EUMP2 = -0.45967114538099D+03

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416

Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.015023  
Sum of electronic and zero-point Energies= -459.671145  
Sum of electronic and thermal Energies= -459.669729  
Sum of electronic and thermal Enthalpies= -459.668785  
Sum of electronic and thermal Free Energies= -459.686168

E (Thermal) CV S  
KCal/Mol Cal/Mol-Kelvin Cal/Mol-Kelvin  
Total 0.889 2.981 36.586

### Chloride anion – SMD

MP2/6-31+G\*\*  
EUMP2 = -0.45977535694708D+03

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.015023  
Sum of electronic and ZPE= -459.775357  
Sum of electronic and thermal Energies= -459.773941  
Sum of electronic and thermal Enthalpies= -459.772996  
Sum of electronic and thermal Free Energies= -459.790380

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 0.889 2.981 36.586

### Chloride anion – PCM

MP2/6-31+G\*\*  
EUMP2 = -0.45978025499771D+03

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.015023  
Sum of electronic and ZPE= -459.780255  
Sum of electronic and thermal Energies= -459.778839  
Sum of electronic and thermal Enthalpies= -459.777895  
Sum of electronic and thermal Free Energies= -459.795278

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 0.889 2.981 36.586

### Bichloride anion SMD

MP2/6-31+G\*\*  
EUMP2 = -0.92000006107913D+03

Zero-point correction= 0.008255 (Hartree/Particle)  
Thermal correction to Energy= 0.011498  
Thermal correction to Enthalpy= 0.012442  
Thermal correction to Gibbs Free Energy= -0.015784  
Sum of electronic and ZPE= -919.991806  
Sum of electronic and thermal Energies= -919.988563  
Sum of electronic and thermal Enthalpies= -919.987619  
Sum of electronic and thermal Free Energies= -920.015845

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 7.215 8.601 59.407

Cl,0,-2.6308407661,-1.0085694525,-0.4012935497  
Cl,0,-0.3881788666,-3.1343659994,0.7031350289  
H,0,-1.3009646093,-2.2691456198,0.253621591

### Bichloride anion PCM

MP2/6-31+G\*\*  
EUMP2 = -0.92000214785299D+03

Zero-point correction= 0.006913 (Hartree/Particle)  
Thermal correction to Energy= 0.010546  
Thermal correction to Enthalpy= 0.011491  
Thermal correction to Gibbs Free Energy= -0.012247  
Sum of electronic and ZPE= -919.995235  
Sum of electronic and thermal Energies= -919.991601  
Sum of electronic and thermal Enthalpies= -919.990657  
Sum of electronic and thermal Free Energies= -920.014395

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 6.618	8.842	49.961

Cl,0,-2.6500252448,-0.9911983622,-0.4102938476  
Cl,0,-0.3826060758,-3.1396919337,0.7059033626  
H,0,-1.2873886794,-2.2812197041,0.2598704851

### Pentadienyl cation – gas phase

MP2/6-31+G\*\*  
EUMP2 = -0.1949988809994D+03

Zero-point correction= 0.127013 (Hartree/Particle)  
Thermal correction to Energy= 0.133800  
Thermal correction to Enthalpy= 0.134744  
Thermal correction to Gibbs Free Energy= 0.097091  
Sum of electronic and ZPE= -194.871875  
Sum of electronic and thermal Energies= -194.865088  
Sum of electronic and thermal Enthalpies= -194.864144  
Sum of electronic and thermal Free Energies= -194.901797

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 83.961	22.384	79.248

C,0,1.8922072426,-0.3592629232,-0.3156541599  
H,0,1.9704872805,-0.1696073453,-1.3844503717  
C,0,0.7921813258,0.1617612585,0.3488755183  
H,0,0.6634572611,0.0039675293,1.4126860519  
C,0,-0.1398492157,0.8886460229,-0.3764383141  
H,0,0.0402499333,1.0157547051,-1.4421914459  
C,0,2.9622054018,-1.1472709532,0.3049755035  
H,0,2.8211363827,-1.2982709435,1.3705883157  
H,0,3.0330442831,-2.1114770751,-0.2093841909  
H,0,3.9200266129,-0.6515125108,0.1149611672  
C,0,-1.3521104082,1.5021292415,0.1759167385  
H,0,-1.4691654808,1.3366428992,1.242286995  
H,0,-1.3345185265,2.575115914,-0.0424477519  
H,0,-2.2211320925,1.1148341804,-0.3663840556

### Pentadienyl cation – SMD

MP2/6-31+G\*\*  
EUMP2 = -0.19509504268429D+03

Zero-point correction= 0.126600 (Hartree/Particle)  
Thermal correction to Energy= 0.133453  
Thermal correction to Enthalpy= 0.134397  
Thermal correction to Gibbs Free Energy= 0.096569  
Sum of electronic and ZPE= -194.968443  
Sum of electronic and thermal Energies= -194.961590  
Sum of electronic and thermal Enthalpies= -194.960645  
Sum of electronic and thermal Free Energies= -194.998474

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 83.743	22.572	79.616

C,0,1.8855777759,-0.3554186563,-0.3138988269  
H,0,1.9587723979,-0.1629717222,-1.3808446868  
C,0,0.7913421715,0.1608449452,0.3577561851  
H,0,0.6627246681,0.0032114035,1.4211226818  
C,0,-0.133524327,0.8845053221,-0.3743198572  
H,0,0.0512044424,1.0082367345,-1.4379603146  
C,0,2.9558465366,-1.1431508474,0.3029074732  
H,0,2.8104838746,-1.2917168963,1.3687863733  
H,0,3.0190861659,-2.1047257121,-0.215922096  
H,0,3.9088415292,-0.6408891464,0.109538107  
C,0,-1.3454647418,1.4982843933,0.1742248529  
H,0,-1.4582946283,1.3302577554,1.2411566279  
H,0,-1.3197705079,2.5697917439,-0.0472650745  
H,0,-2.208605357,1.1051906828,-0.3719414451

### Pentadienyl cation – PCM

MP2/6-31+G\*\*  
EUMP2 = -0.19507893460018D+03

Zero-point correction= 0.127046 (Hartree/Particle)  
Thermal correction to Energy= 0.133910  
Thermal correction to Enthalpy= 0.134854  
Thermal correction to Gibbs Free Energy= 0.096970  
Sum of electronic and ZPE= -194.951888  
Sum of electronic and thermal Energies= -194.945025  
Sum of electronic and thermal Enthalpies= -194.944081  
Sum of electronic and thermal Free Energies= -194.981965

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 84.030	22.488	79.734

C,0,1.8876442894,-0.3558291203,-0.3163777163  
H,0,1.9641465504,-0.1646832651,-1.3830496589  
C,0,0.7918846738,0.1614659291,0.3528438278  
H,0,0.6630209482,0.0032563173,1.4155065605  
C,0,-0.1346847067,0.886242671,-0.3767207843  
H,0,0.0472936501,1.0125079017,-1.4402614572  
C,0,2.9574546451,-1.1446310544,0.3039346781  
H,0,2.81081572,-1.2938399124,1.3685099993  
H,0,3.0234211848,-2.1063741031,-0.2125019259  
H,0,3.9112855791,-0.6440261604,0.1149506794

C,0,-1.3475030292,1.4990932933,0.17548495  
H,0,-1.4598750651,1.3299887447,1.2412532945  
H,0,-1.3246045809,2.5705969669,-0.0422700073  
H,0,-2.212079859,1.1076817916,-0.3679624397

### 1,3-pentadiene – gas phase

MP2/6-31+G\*\*

EUMP2 = -0.19466969392284D+03

Zero-point correction= 0.115035 (Hartree/Particle)  
Thermal correction to Energy= 0.121293  
Thermal correction to Enthalpy= 0.122237  
Thermal correction to Gibbs Free Energy= 0.085939  
Sum of electronic and ZPE= -194.554659  
Sum of electronic and thermal Energies= -194.548401  
Sum of electronic and thermal Enthalpies= -194.547457  
Sum of electronic and thermal Free Energies= -194.583755

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 76.112	21.281	76.396

C,0,1.8986175416,-0.3063618261,-0.3530631927  
H,0,2.0545875479,-0.0835808938,-1.4058816623  
C,0,0.844621285,0.2551048761,0.2739797037  
H,0,0.6773123759,0.0404229432,1.3270872652  
C,0,-0.1042572819,1.1477603725,-0.3767771216  
H,0,0.0650305416,1.3606054755,-1.4286168364  
C,0,2.8836892478,-1.2256332597,0.299160429  
H,0,2.6361369662,-1.3812924108,1.3490783945  
H,0,2.9000585455,-2.1983968283,-0.1963343313  
H,0,3.8957366431,-0.8198806311,0.2428044867  
C,0,-1.1576259486,1.709470842,0.2481003164  
H,0,-1.3558506296,1.5189436999,1.2954884082  
H,0,-1.8378868345,2.3671776406,-0.2741558594

### 1,3-pentadiene – SMD

MP2/6-31+G\*\*

EUMP2 = -0.19467474942796D+03

Zero-point correction= 0.114757 (Hartree/Particle)  
Thermal correction to Energy= 0.120991  
Thermal correction to Enthalpy= 0.121935  
Thermal correction to Gibbs Free Energy= 0.085733  
Sum of electronic and ZPE= -194.559992  
Sum of electronic and thermal Energies= -194.553759  
Sum of electronic and thermal Enthalpies= -194.552815  
Sum of electronic and thermal Free Energies= -194.589016

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 75.923	21.287	76.193

C,0,1.8986506177,-0.3068394863,-0.351625699  
H,0,2.0542324707,-0.0836117741,-1.4049379043  
C,0,0.8440547099,0.2542024714,0.278082517  
H,0,0.6757571333,0.0400645379,1.3316978647  
C,0,-0.103605015,1.1473584644,-0.3770015171  
H,0,0.0679136855,1.3588301033,-1.4295386438  
C,0,2.8832163327,-1.2255035634,0.2998315953

H,0,2.637888906,-1.383003695,1.3505698919  
H,0,2.8999091636,-2.1963702869,-0.2005848917  
H,0,3.8950936022,-0.8185722467,0.2382925317  
C,0,-1.1581536098,1.7099159741,0.2478946605  
H,0,-1.3575182837,1.5199021249,1.2962135764  
H,0,-1.8372697131,2.3679673764,-0.2780239816

### 1,3-pentadiene – PCM

MP2/6-31+G\*\*

EUMP2 = -0.19467188131503D+03

Zero-point correction= 0.114872 (Hartree/Particle)  
Thermal correction to Energy= 0.121139  
Thermal correction to Enthalpy= 0.122083  
Thermal correction to Gibbs Free Energy= 0.085748  
Sum of electronic and ZPE= -194.557010  
Sum of electronic and thermal Energies= -194.550742  
Sum of electronic and thermal Enthalpies= -194.549798  
Sum of electronic and thermal Free Energies= -194.586133

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 76.016	21.298	76.473

C,0,1.8987457869,-0.3067875372,-0.3520884305  
H,0,2.0546869952,-0.0839042488,-1.4050086382  
C,0,0.8443065787,0.2544989767,0.276609854  
H,0,0.6764521076,0.0400996601,1.3298921265  
C,0,-0.1041795484,1.147775429,-0.376736048  
H,0,0.0661963138,1.3600299947,-1.4288493043  
C,0,2.8841335986,-1.2262002102,0.299735835  
H,0,2.6377617847,-1.3831025606,1.3497488521  
H,0,2.9008604977,-2.1970934331,-0.1992080587  
H,0,3.895560725,-0.8196140232,0.2400276397  
C,0,-1.1587257348,1.7103701202,0.2478487224  
H,0,-1.3576946048,1.5201979866,1.29547575  
H,0,-1.8379345001,2.368069846,-0.2765783

### (E)-4-chloropent-2-ene – gas phase

Two alternative conformations were located but they were higher in energy by >1.2 kcal/mol.

MP2/6-31+G\*\*

EUMP2 = -0.65491058652331D+03

Zero-point correction= 0.130852 (Hartree/Particle)  
Thermal correction to Energy= 0.138388  
Thermal correction to Enthalpy= 0.139332  
Thermal correction to Gibbs Free Energy= 0.098800  
Sum of electronic and ZPE= -654.779735  
Sum of electronic and thermal Energies= -654.772199  
Sum of electronic and thermal Enthalpies= -654.771254  
Sum of electronic and thermal Free Energies= -654.811787

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 86.840	26.015	85.307

C,0,-3.2925531327,-0.1071523078,-0.0091588398  
H,0,-2.5605937451,-0.0937028347,-0.8186151747  
H,0,-4.2265807461,0.31062227,-0.3834741079  
H,0,-3.4645175151,-1.152555433,0.2532777581



C,0,-2.7966995236,0.6632648295,1.1751779092  
H,0,-1.8676690195,0.3261809732,1.628360819  
C,0,-3.4214341268,1.7261102179,1.7076960031  
H,0,-4.3589435812,2.0790701119,1.2852918924  
C,0,-2.8874755406,2.4931577298,2.8687114528  
H,0,-1.9393669411,2.0607303071,3.1891939089  
C,0,-2.7184178154,3.9735610308,2.5699137514  
H,0,-3.6705072634,4.415299463,2.2767005455  
H,0,-2.3419529373,4.5067953905,3.4415327799  
H,0,-2.0099247095,4.0914538259,1.7488830912  
Cl,0,-4.0036831926,2.3016632958,4.283032291

### (E)-4-chloropent-2-ene – SMD

MP2/6-31+G\*\*

EUMP2 = -0.65491942935983D+03

Zero-point correction= 0.130492 (Hartree/Particle)  
Thermal correction to Energy= 0.138035  
Thermal correction to Enthalpy= 0.138980  
Thermal correction to Gibbs Free Energy= 0.098454  
Sum of electronic and ZPE= -654.788938  
Sum of electronic and thermal Energies= -654.781394  
Sum of electronic and thermal Enthalpies= -654.780450  
Sum of electronic and thermal Free Energies= -654.820975

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 86.619	26.111	85.293

C,0,-3.2958154036,-0.1112620922,-0.0068775017  
H,0,-2.5497911896,-0.1094332105,-0.8043007435  
H,0,-4.2203797265,0.3158539832,-0.395569642  
H,0,-3.4789346601,-1.1550284534,0.2572507902  
C,0,-2.8043555629,0.654939887,1.1803677641  
H,0,-1.8839704289,0.3088699057,1.644993285  
C,0,-3.4192522198,1.7326501455,1.6982006271  
H,0,-4.3427323616,2.104366653,1.2599578159  
C,0,-2.8744162842,2.4960141781,2.8548555887  
H,0,-1.9244836283,2.0677834946,3.1722834743  
C,0,-2.7280402243,3.9792573617,2.5755564114  
H,0,-3.6851322261,4.4156951977,2.2889223744  
H,0,-2.3439440637,4.5074391135,3.447631781  
H,0,-2.0240789492,4.1089862365,1.75185107  
Cl,0,-3.9849928612,2.2783664694,4.2914009854

### (E)-4-chloropent-2-ene – PCM

MP2/6-31+G\*\*

EUMP2 = -0.65491435631652D+03

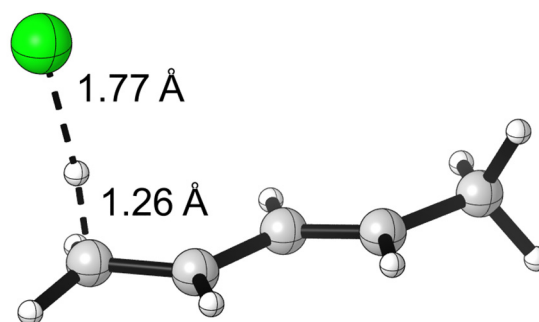
Zero-point correction= 0.130654 (Hartree/Particle)  
Thermal correction to Energy= 0.138205  
Thermal correction to Enthalpy= 0.139149  
Thermal correction to Gibbs Free Energy= 0.098603  
Sum of electronic and ZPE= -654.783702  
Sum of electronic and thermal Energies= -654.776151  
Sum of electronic and thermal Enthalpies= -654.775207  
Sum of electronic and thermal Free Energies= -654.815754

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 86.619	26.111	85.293

Total 86.725 26.098 85.337

C,0,-3.2950014165,-0.1105234363,-0.0081159605  
H,0,-2.554252851,-0.1015271968,-0.8094250695  
H,0,-4.2233971105,0.3126422715,-0.3902797175  
H,0,-3.471788296,-1.1552089504,0.2536881272  
C,0,-2.802403249,0.6565279307,1.1795580916  
H,0,-1.8788937772,0.3136286269,1.6393420352  
C,0,-3.4206615768,1.7294477402,1.7018374183  
H,0,-4.3478275523,2.0953322431,1.2675766272  
C,0,-2.8787365547,2.4952933424,2.8586973003  
H,0,-1.9304828625,2.0654359228,3.1791457347  
C,0,-2.7243065714,3.9783939704,2.5735879207  
H,0,-3.6794441152,4.4162473399,2.2846276642  
H,0,-2.3427682363,4.5071664827,3.4455872317  
H,0,-2.0190619973,4.1039922083,1.7512834774  
Cl,0,-3.9912936231,2.2876503745,4.2894131994

### TS / one HCl SMD



MP2/6-31+G\*\*

EUMP2 = -0.65486742472659D+03

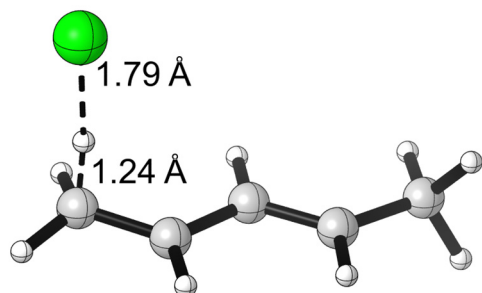
Zero-point correction= 0.122625 (Hartree/Particle)  
Thermal correction to Energy= 0.130529  
Thermal correction to Enthalpy= 0.131473  
Thermal correction to Gibbs Free Energy= 0.088845  
Sum of electronic and ZPE= -654.744800  
Sum of electronic and thermal Energies= -654.736896  
Sum of electronic and thermal Enthalpies= -654.735952  
Sum of electronic and thermal Free Energies= -654.778580

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 81.908	26.505	89.718

C,0,1.906869462,-0.3190801909,-0.3194016219  
H,0,2.0149998658,-0.0892567782,-1.3764309099  
C,0,0.854930977,0.2271148658,0.3490388147  
H,0,0.7001471122,0.029881773,1.404111111  
C,0,-0.0541343529,1.0734417814,-0.3393885819  
H,0,0.1438576185,1.2484760914,-1.3945142704  
C,0,2.9329931043,-1.194995172,0.2931624372  
H,0,2.7352042206,-1.3762003363,1.3477262782  
H,0,2.9698857681,-2.1473097106,-0.2411300043  
H,0,3.9185422011,-0.7362634465,0.1808836563  
C,0,-1.2466169259,1.5512056289,0.1981354329  
H,0,-1.3520199066,1.5426736473,1.2784619132

H,0,-1.7436571403,2.3583884618,-0.3284557787  
 H,0,-1.9043565594,0.5427435719,-0.1577078187  
 Cl,0,-3.0022254444,-0.8007201873,-0.4918106577

**TS / one HCl PCM**



MP2/6-31+G\*\*

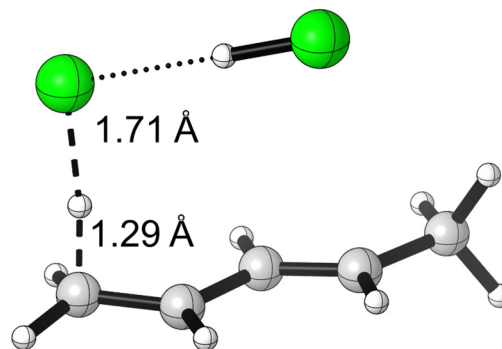
EUMP2 = -0.65485976096748D+03

Zero-point correction= 0.123215 (Hartree/Particle)  
 Thermal correction to Energy= 0.131079  
 Thermal correction to Enthalpy= 0.132023  
 Thermal correction to Gibbs Free Energy= 0.089427  
 Sum of electronic and ZPE= -654.736546  
 Sum of electronic and thermal Energies= -654.728682  
 Sum of electronic and thermal Enthalpies= -654.727737  
 Sum of electronic and thermal Free Energies= -654.770334

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 82.253	26.280	89.653

C,0,1.9053438602,-0.3207654083,-0.3155452003  
 H,0,2.0086385871,-0.0953106519,-1.3735165429  
 C,0,0.854755916,0.2276361288,0.3558172977  
 H,0,0.7050131926,0.0341752085,1.4114256405  
 C,0,-0.0542544822,1.0696033955,-0.3332852798  
 H,0,0.1429490573,1.2417846401,-1.3884855908  
 C,0,2.9366793534,-1.1949735983,0.2920551463  
 H,0,2.7522390318,-1.3696641763,1.3491393074  
 H,0,2.9648689059,-2.1500124074,-0.2363562098  
 H,0,3.9210080199,-0.7396311126,0.1646069372  
 C,0,-1.253462111,1.5493425714,0.1982267781  
 H,0,-1.3575762392,1.5514736059,1.2779981007  
 H,0,-1.736317885,2.3643382112,-0.3281025515  
 H,0,-1.9100175876,0.5578519989,-0.1549120869  
 Cl,0,-3.0054476191,-0.8157484055,-0.516385746

**TS / two HCl conf B SMD**



MP2/6-31+G\*\*

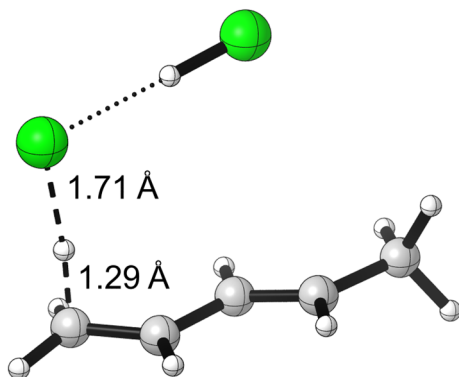
EUMP2 = -0.11150900183123D+04

Zero-point correction= 0.131333 (Hartree/Particle)  
 Thermal correction to Energy= 0.142062  
 Thermal correction to Enthalpy= 0.143007  
 Thermal correction to Gibbs Free Energy= 0.091832  
 Sum of electronic and ZPE= -1114.958685  
 Sum of electronic and thermal Energies= -1114.947956  
 Sum of electronic and thermal Enthalpies= -1114.947012  
 Sum of electronic and thermal Free Energies= -1114.998187

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 89.145	34.972	107.707

C,0,-2.0107804706,-0.9201827246,-0.503670501  
 H,0,-2.0217408152,-1.4310822536,-1.4632457834  
 C,0,-0.9803310121,-1.1763020941,0.3437232003  
 H,0,-0.9164253433,-0.6907380421,1.311513035  
 C,0,0.0439093856,-2.0866585645,-0.0458354138  
 H,0,-0.0669511138,-2.5586604843,-1.019565269  
 C,0,-3.138034121,-0.001551897,-0.2125429905  
 H,0,-3.0332891434,0.4719321184,0.7618407433  
 H,0,-3.1963782109,0.7674959041,-0.9865085978  
 H,0,-4.0807118297,-0.5531313468,-0.2482632639  
 C,0,1.2333506459,-2.2685093537,0.6409269644  
 H,0,1.293541434,-1.9334124397,1.6712970917  
 H,0,1.8695190372,-3.0983022524,0.3558549996  
 H,0,1.7596733093,-1.2762413854,0.0009625348  
 Cl,0,2.6201567556,0.045608343,-0.6565187022  
 Cl,0,0.1388080885,1.3028695631,-2.7145468288  
 H,0,1.0641544037,0.8321489096,-1.9361102185

**TS / two HCl conf C SMD**



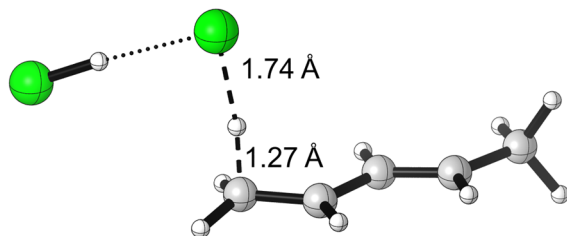
MP2/6-31+G\*\*  
EUMP2 = -0.11150900058283D+04

Zero-point correction= 0.131285 (Hartree/Particle)  
Thermal correction to Energy= 0.142016  
Thermal correction to Enthalpy= 0.142961  
Thermal correction to Gibbs Free Energy= 0.090871  
Sum of electronic and ZPE= -1114.958721  
Sum of electronic and thermal Energies= -1114.947989  
Sum of electronic and thermal Enthalpies= -1114.947045  
Sum of electronic and thermal Free Energies= -1114.999134

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 89.117	34.996	109.631

6	-2.151880	-0.706361	-0.458131
1	-2.156234	-1.020974	-1.498821
6	-1.158560	-1.168524	0.345303
1	-1.105716	-0.881550	1.390098
6	-0.159135	-2.032745	-0.186809
1	-0.252846	-2.303218	-1.236154
6	-3.247419	0.189134	-0.014132
1	-3.143596	0.466749	1.033183
1	-3.261945	1.090816	-0.630842
1	-4.209856	-0.306882	-0.163392
6	0.996981	-2.395374	0.485513
1	1.030767	-2.272626	1.563239
1	1.616369	-3.176092	0.059985
1	1.570567	-1.312903	0.078930
17	2.484218	0.098418	-0.245441
17	0.061035	2.535975	0.149755
1	0.963271	1.615231	-0.000020

### TS / two HCl conf A PCM



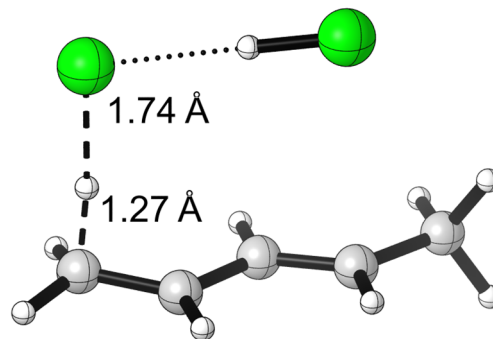
MP2/6-31+G\*\*  
EUMP2 = -0.11150795326429D+04

Zero-point correction= 0.131690 (Hartree/Particle)  
Thermal correction to Energy= 0.142527  
Thermal correction to Enthalpy= 0.143471  
Thermal correction to Gibbs Free Energy= 0.090812  
Sum of electronic and ZPE= -1114.947843  
Sum of electronic and thermal Energies= -1114.937006  
Sum of electronic and thermal Enthalpies= -1114.936062  
Sum of electronic and thermal Free Energies= -1114.988721

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 89.437	34.899	110.830

C,0,-	-2.0704254843	-0.9266551322	-0.4392028426
H,0,-	-2.0731717953	-1.4214147928	-1.4066872948
C,0,-	-0.9699224797	-1.0668206591	0.3477432148
H,0,-	-0.917343687	-0.5940408728	1.3216606471
C,0,0	0.125791589	-1.8531940428	-0.1018670474
H,0,0	0.0280458435	-2.3138599937	-1.0818411384
C,0,-	-3.2849969593	-0.158697425	-0.0698332636
H,0,-	-3.1899241743	0.3060535619	0.9086424106
H,0,-	-3.4767823863	0.6104100916	-0.8205261834
H,0,-	-4.1525646918	-0.8216898345	-0.073102717
C,0,1	1.3552193007	-1.9370393402	0.5417713931
H,0,1	1.4083507595	-1.6395666061	1.583464315
H,0,2	0.0375719539	-2.7177099905	0.2278024326
H,0,1	1.7985932237	-0.916474155	-0.0669252
Cl,0,2	6.183015696	0.4852957599	-0.697382034
Cl,0,5	1.325002674	-0.7013146321	1.3838269065
H,0,4	2.2232671505	-0.2242249367	0.5936984016

### TS / two HCl conf B PCM



MP2/6-31+G\*\*  
EUMP2 = -0.11150810974512D+04

Zero-point correction= 0.131841 (Hartree/Particle)  
Thermal correction to Energy= 0.142559  
Thermal correction to Enthalpy= 0.143503  
Thermal correction to Gibbs Free Energy= 0.092297  
Sum of electronic and ZPE= -1114.949256  
Sum of electronic and thermal Energies= -1114.938538  
Sum of electronic and thermal Enthalpies= -1114.937594  
Sum of electronic and thermal Free Energies= -1114.988801

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K

Total 89.457 34.801 107.773

C,0,1.8347004771,-0.4106001163,-0.2588846025  
H,0,1.7728489307,-0.5147252813,-1.3387413798  
C,0,0.9125641048,0.3723951461,0.3624138479  
H,0,0.9263923216,0.5032740044,1.4384216533  
C,0,-0.1016896971,1.0092154294,-0.4030948287  
H,0,-0.0670038525,0.8611240513,-1.4797457183  
C,0,2.9347102677,-1.131453275,0.42642887  
H,0,2.9062195474,-0.9857877813,1.503729557  
H,0,2.869868969,-2.1977578338,0.2014160585  
H,0,3.8961648783,-0.7871920919,0.0396420068  
C,0,-1.2188453852,1.6372536464,0.1357790105  
H,0,-1.1850425675,1.9408846093,1.1763358222  
H,0,-1.8319719044,2.2383105495,-0.5243055778  
H,0,-1.8420314131,0.5302003845,0.1902241082  
Cl,0,-2.7994861648,-0.903049798,0.4308087554  
Cl,0,-0.4288318945,-3.299221791,-0.4158261412  
H,0,-1.3203676175,-2.4135308524,-0.0957834415

### *M06-2X/6-31+G\*\* structures*

#### **HCl-gas phase**

M062X/6-31+G\*\*

E(RM062X) = -460.762018131

Zero-point correction= 0.006832 (Hartree/Particle)  
Thermal correction to Energy= 0.009192  
Thermal correction to Enthalpy= 0.010136  
Thermal correction to Gibbs Free Energy= -0.011048  
Sum of electronic and ZPE= -460.755187  
Sum of electronic and thermal Energies= -460.752826  
Sum of electronic and thermal Enthalpies= -460.751882  
Sum of electronic and thermal Free Energies= -460.773067

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 5.768	4.968	44.587

H,0,0.,0.,0.  
Cl,0,0.,0.,1.2809

#### **HCl SMD**

M062X/6-31+G\*\*

E(RM062X) = -460.767806264

Zero-point correction= 0.006681 (Hartree/Particle)  
Thermal correction to Energy= 0.009042  
Thermal correction to Enthalpy= 0.009986  
Thermal correction to Gibbs Free Energy= -0.011210  
Sum of electronic and ZPE= -460.761125  
Sum of electronic and thermal Energies= -460.758765  
Sum of electronic and thermal Enthalpies= -460.757820  
Sum of electronic and thermal Free Energies= -460.779017

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K

Total 5.674 4.968 44.612

Cl,0,-0.3810752433,-3.1584008224,0.7161453808  
H,0,-1.2351447567,-2.3023591776,0.2699946192

#### **HCl PCM**

M062X/6-31+G\*\*

E(RM062X) = -460.765738082

Zero-point correction= 0.006771 (Hartree/Particle)  
Thermal correction to Energy= 0.009132  
Thermal correction to Enthalpy= 0.010076  
Thermal correction to Gibbs Free Energy= -0.011113  
Sum of electronic and ZPE= -460.758967  
Sum of electronic and thermal Energies= -460.756606  
Sum of electronic and thermal Enthalpies= -460.755662  
Sum of electronic and thermal Free Energies= -460.776851

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 5.730	4.968	44.595

Cl,0,-0.3828436838,-3.1566282983,0.7152215788  
H,0,-1.2333763162,-2.3041317017,0.2709184212

#### **(HCl)2 dimer-gas phase**

M062X/6-31+G\*\*

E(RM062X) = -921.527330709

Zero-point correction= 0.014886 (Hartree/Particle)  
Thermal correction to Energy= 0.020402  
Thermal correction to Enthalpy= 0.021346  
Thermal correction to Gibbs Free Energy= -0.014841  
Sum of electronic and ZPE= -921.512445  
Sum of electronic and thermal Energies= -921.506929  
Sum of electronic and thermal Enthalpies= -921.505984  
Sum of electronic and thermal Free Energies= -921.542172

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 12.803	13.392	76.163

1 1.902832 1.215626 0.004412  
17 1.868993 -0.066067 -0.000619  
17 -1.939857 0.013197 -0.000735  
1 -0.698142 -0.316830 0.018600

#### **(HCl)2 dimer SMD**

M062X/6-31+G\*\*

E(RM062X) = -921.536203447

Zero-point correction= 0.014564 (Hartree/Particle)  
Thermal correction to Energy= 0.020045  
Thermal correction to Enthalpy= 0.020989  
Thermal correction to Gibbs Free Energy= -0.014453  
Sum of electronic and ZPE= -921.521639  
Sum of electronic and thermal Energies= -921.516158  
Sum of electronic and thermal Enthalpies= -921.515214  
Sum of electronic and thermal Free Energies= -921.550656

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 12.578 13.481 74.594

H,0,-1.9774656865,0.4064149934,-0.2062048138  
Cl,0,-2.7073344093,-0.6191137879,-0.4911642161  
Cl,0,-0.2632137611,-3.2608088049,0.7402692635  
H,0,-1.193955143,-2.4614924006,0.3450507665

### (HCl)<sub>2</sub> dimer PCM

M062X/6-31+G\*\*  
E(RM062X) = -921.533573966

Zero-point correction= 0.014659 (Hartree/Particle)  
Thermal correction to Energy= 0.019228  
Thermal correction to Enthalpy= 0.020172  
Thermal correction to Gibbs Free Energy= -0.012630  
Sum of electronic and ZPE= -921.518915  
Sum of electronic and thermal Energies= -921.514346  
Sum of electronic and thermal Enthalpies= -921.513401  
Sum of electronic and thermal Free Energies= -921.546204

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 12.066 11.444 69.039

H,0,-2.0054861315,0.4129814016,-0.2168371338  
Cl,0,-2.6994177596,-0.6357041248,-0.4772544091  
Cl,0,-0.31361205,-3.3123082894,0.749124104  
H,0,-1.1234540589,-2.3999689874,0.3329174389

### Chloride anion – gas phase

M062X/6-31+G\*\*  
E(RM062X) = -460.235297359

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.015023  
Sum of electronic and zero-point Energies= -460.235297  
Sum of electronic and thermal Energies= -460.233881  
Sum of electronic and thermal Enthalpies= -460.232937  
Sum of electronic and thermal Free Energies= -460.250320

E (Thermal) CV S  
KCal/Mol Cal/Mol-Kelvin Cal/Mol-Kelvin  
Total 0.889 2.981 36.586

### Chloride anion – SMD

M062X/6-31+G\*\*  
E(RM062X) = -460.339779210

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.015023  
Sum of electronic and ZPE= -460.339779  
Sum of electronic and thermal Energies= -460.338363

Sum of electronic and thermal Enthalpies= -460.337419  
Sum of electronic and thermal Free Energies= -460.354802

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 0.889 2.981 36.586

### Chloride anion – PCM

M062X/6-31+G\*\*  
E(RM062X) = -460.344843251

Zero-point correction= 0.000000 (Hartree/Particle)  
Thermal correction to Energy= 0.001416  
Thermal correction to Enthalpy= 0.002360  
Thermal correction to Gibbs Free Energy= -0.015023  
Sum of electronic and ZPE= -460.344843  
Sum of electronic and thermal Energies= -460.343427  
Sum of electronic and thermal Enthalpies= -460.342483  
Sum of electronic and thermal Free Energies= -460.359866

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 0.889 2.981 36.586

### Bichloride anion – SMD

M062X/6-31+G\*\*  
E(RM062X) = -921.124048470

Zero-point correction= 0.002956 (Hartree/Particle)  
Thermal correction to Energy= 0.006865  
Thermal correction to Enthalpy= 0.007810  
Thermal correction to Gibbs Free Energy= -0.017237  
Sum of electronic and ZPE= -921.121093  
Sum of electronic and thermal Energies= -921.117183  
Sum of electronic and thermal Enthalpies= -921.116239  
Sum of electronic and thermal Free Energies= -921.141285

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 4.308 10.094 52.714

Cl,0,-2.5168414281,-1.1345281374,-0.3353119414  
Cl,0,-0.3676479508,-3.1382948219,0.7047063261  
H,0,-1.4355306211,-2.1392870407,0.1860856153

### Bichloride anion – PCM

M062X/6-31+G\*\*  
E(RM062X) = -921.125593733

Zero-point correction= 0.005400 (Hartree/Particle)  
Thermal correction to Energy= 0.008701  
Thermal correction to Enthalpy= 0.009645  
Thermal correction to Gibbs Free Energy= -0.018571  
Sum of electronic and ZPE= -921.120193  
Sum of electronic and thermal Energies= -921.116893  
Sum of electronic and thermal Enthalpies= -921.115949  
Sum of electronic and thermal Free Energies= -921.144165

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 5.460 9.134 59.385

Cl,0,-2.54443073,-1.1054689919,-0.35049718  
Cl,0,-0.3836506949,-3.1243626452,0.6975054644  
H,0,-1.3919414505,-2.1822807238,0.208473096

### Pentadienyl cation – gas phase

M062X/6-31+G\*\*

E(RM062X) = -195.547125325

Zero-point correction= 0.124740 (Hartree/Particle)  
Thermal correction to Energy= 0.131507  
Thermal correction to Enthalpy= 0.132451  
Thermal correction to Gibbs Free Energy= 0.094921  
Sum of electronic and ZPE= -195.422385  
Sum of electronic and thermal Energies= -195.415618  
Sum of electronic and thermal Enthalpies= -195.414674  
Sum of electronic and thermal Free Energies= -195.452204

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 82.522	22.577	78.988

C,0,1.8915383279,-0.358632542,-0.3169984956  
H,0,1.9757194848,-0.1717039753,-1.3896130202  
C,0,0.7926973786,0.1623636768,0.3440068769  
H,0,0.6634850011,0.0039660088,1.4117606751  
C,0,-0.1389191421,0.8883121522,-0.3777310033  
H,0,0.0362503051,1.0193440159,-1.4476266867  
C,0,2.9573891473,-1.1449091423,0.3077394682  
H,0,2.8167029241,-1.2969355972,1.3770206572  
H,0,3.0343284854,-2.1125993527,-0.2093610679  
H,0,3.9215739895,-0.6519583999,0.1150963386  
C,0,-1.3479503874,1.4989817402,0.1789503529  
H,0,-1.4662694187,1.3334433446,1.2489340931  
H,0,-1.3356237132,2.5763011277,-0.0423711696  
H,0,-2.2227023823,1.1154769431,-0.3664670185

### Pentadienyl cation – SMD

M062X/6-31+G\*\*

E(RM062X) = -195.642801576

Zero-point correction= 0.124227 (Hartree/Particle)  
Thermal correction to Energy= 0.131079  
Thermal correction to Enthalpy= 0.132024  
Thermal correction to Gibbs Free Energy= 0.094240  
Sum of electronic and ZPE= -195.518575  
Sum of electronic and thermal Energies= -195.511722  
Sum of electronic and thermal Enthalpies= -195.510778  
Sum of electronic and thermal Free Energies= -195.548562

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 82.254	22.797	79.523

C,0,1.8857342176,-0.3556097727,-0.314578006  
H,0,1.9648443651,-0.1660346004,-1.3852431976  
C,0,0.7914350287,0.1609417811,0.3533074053  
H,0,0.6620684635,0.002673198,1.4207400657

C,0,-0.1337131284,0.8843527075,-0.375513388  
H,0,0.0463708416,1.0117697994,-1.4431578282  
C,0,2.9515212147,-1.1411158729,0.3066547742  
H,0,2.8071590866,-1.2916254783,1.375924924  
H,0,3.0221642489,-2.1048669369,-0.216788163  
H,0,3.9103558257,-0.6415863392,0.1092917045  
C,0,-1.3418295532,1.4955515249,0.1773170704  
H,0,-1.4576495315,1.3271869822,1.2474215751  
H,0,-1.3201758401,2.5710756844,-0.0477236856  
H,0,-2.2100652393,1.108737323,-0.3743132506

### Pentadienyl cation – PCM

M062X/6-31+G\*\*

E(RM062X) = -195.626628369

Zero-point correction= 0.124644 (Hartree/Particle)  
Thermal correction to Energy= 0.131509  
Thermal correction to Enthalpy= 0.132453  
Thermal correction to Gibbs Free Energy= 0.094639  
Sum of electronic and ZPE= -195.501984  
Sum of electronic and thermal Energies= -195.495119  
Sum of electronic and thermal Enthalpies= -195.494175  
Sum of electronic and thermal Free Energies= -195.531989

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 82.523	22.734	79.587

C,0,1.8874873385,-0.355689829,-0.3173545985  
H,0,1.9702339601,-0.1671380279,-1.3876057593  
C,0,0.7920812296,0.1616609781,0.3481104029  
H,0,0.6623878133,0.0025795226,1.4146939015  
C,0,-0.1342879021,0.8861658469,-0.3780365471  
H,0,0.0430297619,1.0165672984,-1.4454581998  
C,0,2.9527200721,-1.142514578,0.3074755711  
H,0,2.8062944213,-1.2934763795,1.3753367406  
H,0,3.0260689927,-2.1065617473,-0.213164418  
H,0,3.9124301986,-0.6444314246,0.1154482236  
C,0,-1.3435680985,1.4961926235,0.1785569407  
H,0,-1.4576912841,1.3271437519,1.2476593829  
H,0,-1.3257287013,2.5715470506,-0.043225677  
H,0,-2.2132378022,1.1094049144,-0.3690959637

### 1,3-pentadiene – gas phase

M062X/6-31+G\*\*

E(RM062X) = -195.218450825

Zero-point correction= 0.114155 (Hartree/Particle)  
Thermal correction to Energy= 0.120270  
Thermal correction to Enthalpy= 0.121214  
Thermal correction to Gibbs Free Energy= 0.085315  
Sum of electronic and ZPE= -195.104296  
Sum of electronic and thermal Energies= -195.098181  
Sum of electronic and thermal Enthalpies= -195.097236  
Sum of electronic and thermal Free Energies= -195.133135

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 75.471	21.056	75.556

C,0,1.8920441373,-0.3038310985,-0.3461098071

H,0,2.0463750967,-0.0787892503,-1.4023143613  
C,0,0.845874336,0.2531205264,0.2773747453  
H,0,0.675475632,0.0396722821,1.3336212811  
C,0,-0.1062881338,1.1484533514,-0.3743436774  
H,0,0.0692879901,1.3577620724,-1.429337583  
C,0,2.8820196052,-1.2244298297,0.2991681633  
H,0,2.6411412391,-1.3861758304,1.3530544546  
H,0,2.8988270397,-2.1979173903,-0.2030427251  
H,0,3.8967713926,-0.8162616565,0.2370981309  
C,0,-1.1530207814,1.7078069548,0.2428802307  
H,0,-1.3529634666,1.5172556349,1.2942365901  
H,0,-1.8353740869,2.3676742338,-0.2814154419

### 1,3-pentadiene – SMD

M062X/6-31+G\*\*

E(RM062X) = -195.224267908

Zero-point correction= 0.113805 (Hartree/Particle)  
Thermal correction to Energy= 0.119911  
Thermal correction to Enthalpy= 0.120855  
Thermal correction to Gibbs Free Energy= 0.084998  
Sum of electronic and ZPE= -195.110463  
Sum of electronic and thermal Energies= -195.104357  
Sum of electronic and thermal Enthalpies= -195.103413  
Sum of electronic and thermal Free Energies= -195.139270

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 75.245	21.088	75.468

C,0,1.8916836388,-0.30485062,-0.3431683221  
H,0,2.0445878668,-0.0795579002,-1.4000664538  
C,0,0.8447817487,0.2519730063,0.2840235993  
H,0,0.6732153543,0.0401274775,1.3410109021  
C,0,-0.105635,1.1473209625,-0.3738801279  
H,0,0.0737602688,1.3531480759,-1.4297296037  
C,0,2.8822579715,-1.2243447162,0.2994516239  
H,0,2.6465641848,-1.3892724789,1.3545315142  
H,0,2.8992310299,-2.1949991154,-0.2092424635  
H,0,3.8962784254,-0.8143819045,0.2293030073  
C,0,-1.1544595666,1.7091821845,0.2418265075  
H,0,-1.3569542747,1.5211041431,1.2943027524  
H,0,-1.8351416561,2.3688908735,-0.2874929395

### 1,3-pentadiene – PCM

M062X/6-31+G\*\*

E(RM062X) = -195.221027859

Zero-point correction= 0.113957 (Hartree/Particle)  
Thermal correction to Energy= 0.120087  
Thermal correction to Enthalpy= 0.121031  
Thermal correction to Gibbs Free Energy= 0.085089  
Sum of electronic and ZPE= -195.107071  
Sum of electronic and thermal Energies= -195.100941  
Sum of electronic and thermal Enthalpies= -195.099997  
Sum of electronic and thermal Free Energies= -195.135938

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 75.355	21.090	75.645

C,0,1.8918510865,-0.3046382317,-0.3440008932  
H,0,2.0456856779,-0.0799405837,-1.4004668143  
C,0,0.8452084093,0.2523834219,0.2816421112  
H,0,0.6740074613,0.040183006,1.3382394255  
C,0,-0.1063220985,1.1479496029,-0.3739260511  
H,0,0.0714914636,1.3549922247,-1.4293287538  
C,0,2.882947602,-1.224952695,0.2995346522  
H,0,2.6456093375,-1.3886625134,1.3538372648  
H,0,2.8997364018,-2.1959172391,-0.2070612694  
H,0,3.8966059736,-0.8155789854,0.2316848205  
C,0,-1.1546682344,1.7092813716,0.2420212202  
H,0,-1.3561681131,1.5205058298,1.2937487044  
H,0,-1.8358149675,2.3687347914,-0.2850544171

### (E)-4-chloropent-2-ene – gas phase

M062X/6-31+G\*\*

E(RM062X) = -656.014200700

Zero-point correction= 0.128769 (Hartree/Particle)  
Thermal correction to Energy= 0.136352  
Thermal correction to Enthalpy= 0.137296  
Thermal correction to Gibbs Free Energy= 0.096680  
Sum of electronic and ZPE= -655.885432  
Sum of electronic and thermal Energies= -655.877848  
Sum of electronic and thermal Enthalpies= -655.876904  
Sum of electronic and thermal Free Energies= -655.917521

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 85.562	26.292	85.485

C,0,-3.2959339927,-0.1068581332,-0.0107816581  
H,0,-2.565320829,-0.0901615549,-0.8261025845  
H,0,-4.2382501887,0.3020389801,-0.3834492793  
H,0,-3.4567059166,-1.1567918395,0.2551316836  
C,0,-2.7980465646,0.668591427,1.171198102  
H,0,-1.8609368187,0.3327158955,1.6176154996  
C,0,-3.4179073148,1.7207029767,1.7064623863  
H,0,-4.3631301162,2.0749601481,1.2930441184  
C,0,-2.8806990104,2.4920472881,2.8680056759  
H,0,-1.938979843,2.0547703763,3.2071366656  
C,0,-2.713592095,3.9739618459,2.569269339  
H,0,-3.6689268333,4.4111634072,2.2660533471  
H,0,-2.3479476626,4.5111529045,3.4469053866  
H,0,-1.9975346428,4.0963848463,1.7509489354  
Cl,0,-4.0164079617,2.3098203017,4.2850864625

### (E)-4-chloropent-2-ene – SMD

M062X/6-31+G\*\*

E(RM062X) = -656.023907117

Zero-point correction= 0.128242 (Hartree/Particle)  
Thermal correction to Energy= 0.135873  
Thermal correction to Enthalpy= 0.136817  
Thermal correction to Gibbs Free Energy= 0.096094  
Sum of electronic and ZPE= -655.895665  
Sum of electronic and thermal Energies= -655.888034  
Sum of electronic and thermal Enthalpies= -655.887090  
Sum of electronic and thermal Free Energies= -655.927814

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 85.261 26.473 85.709

C,0,-3.3007960436,-0.1137179762,-0.0078734143  
H,0,-2.5522603706,-0.1161969454,-0.8078162664  
H,0,-4.2295061055,0.3092242287,-0.4002848091  
H,0,-3.47954401,-1.1604627606,0.2620643973  
C,0,-2.8065775479,0.6574112566,1.1765187533  
H,0,-1.8820377907,0.307938141,1.6391101481  
C,0,-3.412133041,1.7304262094,1.6920489769  
H,0,-4.339481199,2.1080542042,1.2578857957  
C,0,-2.8627272356,2.4966818928,2.8490468938  
H,0,-1.9181826309,2.0648598801,3.1841635077  
C,0,-2.7264419539,3.9831457149,2.577958125  
H,0,-3.6886392519,4.4129941202,2.2843083132  
H,0,-2.3522380648,4.5128348721,3.4572351292  
H,0,-2.0167357828,4.1241848267,1.7563204649  
Cl,0,-3.9930187617,2.2771212053,4.2958380647

### (E)-4-chloropent-2-ene – PCM

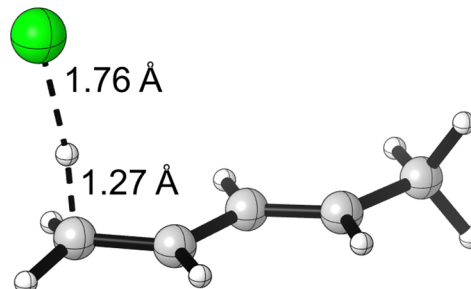
M062X/6-31+G\*\*  
E(RM062X) = -656.018604171

Zero-point correction= 0.128450 (Hartree/Particle)  
Thermal correction to Energy= 0.136080  
Thermal correction to Enthalpy= 0.137025  
Thermal correction to Gibbs Free Energy= 0.096300  
Sum of electronic and ZPE= -655.890154  
Sum of electronic and thermal Energies= -655.882524  
Sum of electronic and thermal Enthalpies= -655.881580  
Sum of electronic and thermal Free Energies= -655.922305

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 85.392 26.443 85.713

C,0,-3.3000333938,-0.1128722242,-0.008982679  
H,0,-2.5569007607,-0.1083847734,-0.81287881  
H,0,-4.2324347921,0.3063800528,-0.3947359367  
H,0,-3.4728772164,-1.1603027005,0.2589517677  
C,0,-2.8045208078,0.659298202,1.1756310623  
H,0,-1.8767012724,0.313029163,1.6330261973  
C,0,-3.4134007094,1.7271695019,1.6957232804  
H,0,-4.34449838,2.099089286,1.2658534282  
C,0,-2.8671397924,2.4957848585,2.85301186  
H,0,-1.9242125187,2.0627035552,3.1910807063  
C,0,-2.7226784438,3.9821697822,2.5758954429  
H,0,-3.6828870754,4.412887982,2.2791073839  
H,0,-2.3521480011,4.5126137881,3.455395329  
H,0,-2.0110925318,4.1188317791,1.756218388  
Cl,0,-3.9987940941,2.2861006175,4.29322666

### TS / one HCl SMD



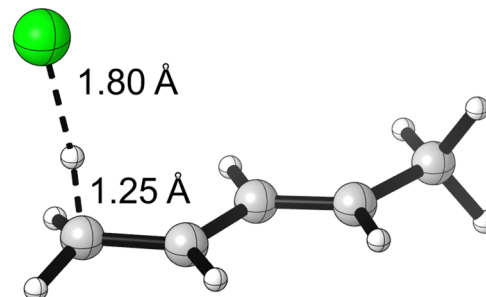
M06-2X/6-31+G\*\*  
E(RM062X) = -655.982854808

Zero-point correction= 0.120261 (Hartree/Particle)  
Thermal correction to Energy= 0.128176  
Thermal correction to Enthalpy= 0.129120  
Thermal correction to Gibbs Free Energy= 0.086619  
Sum of electronic and ZPE= -655.862594  
Sum of electronic and thermal Energies= -655.854679  
Sum of electronic and thermal Enthalpies= -655.853735  
Sum of electronic and thermal Free Energies= -655.896236

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 80.431 26.878 89.451

C,0,1.9285979896,-0.3023708143,-0.3173152528  
H,0,2.0557197106,-0.0562659872,-1.3722841561  
C,0,0.86232593,0.2217621306,0.3368706081  
H,0,0.690893148,0.0085126672,1.3904337167  
C,0,-0.0486351997,1.0662935257,-0.3549853606  
H,0,0.1581031586,1.2526948784,-1.4098584904  
C,0,2.9485875617,-1.1837491249,0.297247169  
H,0,2.7366956379,-1.3889811775,1.3481706756  
H,0,3.0023512321,-2.127539007,-0.2583419309  
H,0,3.9381825569,-0.7195876036,0.2065968361  
C,0,-1.235605934,1.5540294206,0.1856587875  
H,0,-1.3478931911,1.5368231813,1.2693855504  
H,0,-1.7450880253,2.3556932636,-0.3446786149  
H,0,-1.9275058816,0.5392938592,-0.1528576485  
Cl,0,-3.0605106937,-0.779727212,-0.4244208892

### TS / one HCl PCM



M062X/6-31+G\*\*  
E(RM062X) = -655.975241704

Zero-point correction= 0.121448 (Hartree/Particle)



Thermal correction to Energy= 0.129305  
 Thermal correction to Enthalpy= 0.130250  
 Thermal correction to Gibbs Free Energy= 0.087630  
 Sum of electronic and ZPE= -655.853793  
 Sum of electronic and thermal Energies= -655.845936  
 Sum of electronic and thermal Enthalpies= -655.844992  
 Sum of electronic and thermal Free Energies= -655.887611

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 81.140	26.341	89.700

C,0,1.9249228192,-0.3100566217,-0.3133336428  
 H,0,2.0493309999,-0.0676448985,-1.3687636527  
 C,0,0.8586075349,0.2148223063,0.3432283264  
 H,0,0.6913657135,0.0036285111,1.3967343317  
 C,0,-0.051467335,1.0543143798,-0.3480424634  
 H,0,0.1546253121,1.2415876563,-1.4021168815  
 C,0,2.9486983616,-1.1898187748,0.2974166  
 H,0,2.7501703235,-1.3849816173,1.3516344943  
 H,0,2.9899247656,-2.1377344524,-0.250642674  
 H,0,3.9378314123,-0.7309045813,0.1887467851  
 C,0,-1.2483429895,1.5417750381,0.1875513161  
 H,0,-1.3530087135,1.5371308041,1.2713841108  
 H,0,-1.7341494259,2.3608095467,-0.3370312778  
 H,0,-1.9429195897,0.5606284748,-0.1502840613  
 Cl,0,-3.1011691892,-0.7834557714,-0.4638013109

### TS / two HCl conf A SMD

M062X/6-31+G\*\*  
 E(RM062X) = -1116.75854615

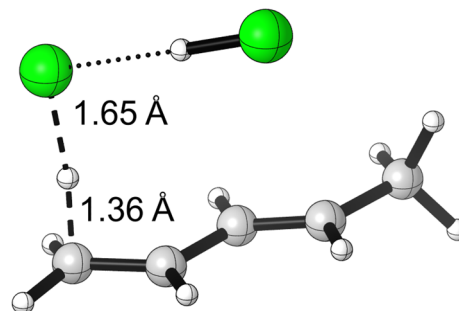
Zero-point correction= 0.128181 (Hartree/Particle)  
 Thermal correction to Energy= 0.139101  
 Thermal correction to Enthalpy= 0.140046  
 Thermal correction to Gibbs Free Energy= 0.087471  
 Sum of electronic and ZPE= -1116.630365  
 Sum of electronic and thermal Energies= -1116.619445  
 Sum of electronic and thermal Enthalpies= -1116.618501  
 Sum of electronic and thermal Free Energies= -1116.671075

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 87.287	35.549	110.652

C,0,-2.0626795417,-0.9421207812,-0.432294246  
 H,0,-2.0697293794,-1.4397281601,-1.402763446  
 C,0,-0.9656004586,-1.075859343,0.3449550053  
 H,0,-0.9091523904,-0.5996998343,1.322506353  
 C,0,0.1486366593,-1.8550939322,-0.1052090592  
 H,0,0.0580674843,-2.3195784194,-1.0878566754  
 C,0,-3.2754660403,-0.1690198473,-0.06233132  
 H,0,-3.1807358058,0.2934126812,0.9221952028  
 H,0,-3.4629006448,0.6082145697,-0.8122875479  
 H,0,-4.1528874776,-0.8260797368,-0.0723728106  
 C,0,1.3516792789,-1.9506703916,0.5594974897  
 H,0,1.4199656787,-1.6073966528,1.5910819514  
 H,0,2.0895073875,-2.6748608546,0.2228945145  
 H,0,1.7876713853,-0.8366008087,-0.0890435725

Cl,0,2.5860651426,0.4963724871,-0.6327872979  
 Cl,0,5.0790687207,-0.7607912943,1.3275756414  
 H,0,4.1510000014,-0.2314426817,0.5574818173

### TS / two HCl conf B SMD



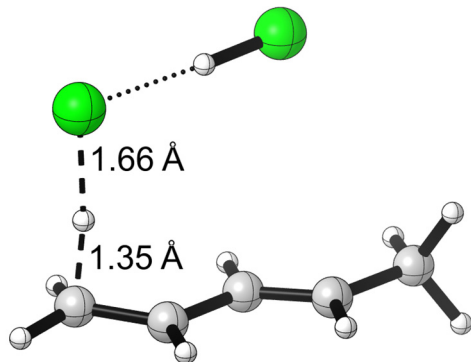
M062X/6-31+G\*\*  
 E(RM062X) = -1116.75924267

Zero-point correction= 0.128037 (Hartree/Particle)  
 Thermal correction to Energy= 0.138933  
 Thermal correction to Enthalpy= 0.139877  
 Thermal correction to Gibbs Free Energy= 0.088699  
 Sum of electronic and ZPE= -1116.631206  
 Sum of electronic and thermal Energies= -1116.620310  
 Sum of electronic and thermal Enthalpies= -1116.619365  
 Sum of electronic and thermal Free Energies= -1116.670544

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 87.182	35.701	107.713

C,0,-2.012893179,-0.9120542401,-0.5051678252  
 H,0,-2.028147455,-1.4010607961,-1.4798161101  
 C,0,-0.9860842965,-1.1855573712,0.3297387772  
 H,0,-0.9224012994,-0.7201364844,1.311943014  
 C,0,0.0573677762,-2.0774933434,-0.0771779253  
 H,0,-0.0408173643,-2.5300625178,-1.064916764  
 C,0,-3.1313443351,0.0152212606,-0.1994956025  
 H,0,-3.0379521035,0.4551094285,0.7953695452  
 H,0,-3.1596986125,0.8155052064,-0.9488598209  
 H,0,-4.0879687176,-0.5143573231,-0.2764694736  
 C,0,1.2244938992,-2.2803818239,0.6268795277  
 H,0,1.2885209243,-1.9451944955,1.6610359797  
 H,0,1.9110066326,-3.0603338275,0.3086050686  
 H,0,1.7504727326,-1.1928649854,0.0045589591  
 Cl,0,2.5638180425,0.1377303004,-0.5395791074  
 Cl,0,0.1328152372,1.0937791412,-2.7557789747  
 H,0,1.0572791183,0.7274538713,-1.8915802677

### TS / two HCl conf C SMD



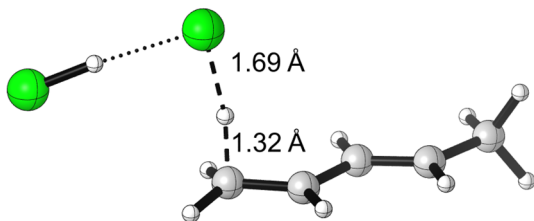
M062X/6-31+G\*\*  
E(RM062X) = -1116.75957665

Zero-point correction= 0.128513 (Hartree/Particle)  
Thermal correction to Energy= 0.139244  
Thermal correction to Enthalpy= 0.140188  
Thermal correction to Gibbs Free Energy= 0.089888  
Sum of electronic and ZPE= -1116.631063  
Sum of electronic and thermal Energies= -1116.620333  
Sum of electronic and thermal Enthalpies= -1116.619388  
Sum of electronic and thermal Free Energies= -1116.669688

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 87.377	35.440	105.865

C,0,1.8867329602,-0.2907435859,-0.329720355  
H,0,1.99969153,-0.0722017062,-1.3921847413  
C,0,0.8644010857,0.290014808,0.336599993  
H,0,0.7068442184,0.0989406985,1.3970547961  
C,0,-0.0548415316,1.1460601215,-0.3500361505  
H,0,0.1318384459,1.3206951753,-1.4103376389  
C,0,2.8761234481,-1.2149857364,0.2786569576  
H,0,2.682789434,-1.3793562081,1.3406533259  
H,0,2.8548461942,-2.1768527045,-0.2472634807  
H,0,3.8885552239,-0.8143871376,0.150013132  
C,0,-1.2231157891,1.6268788305,0.2016967732  
H,0,-1.3626356681,1.5780135142,1.2807297491  
H,0,-1.8138262758,2.3544366733,-0.34812801  
H,0,-1.8129737831,0.4597724578,-0.1484230846  
Cl,0,-2.7046195431,-0.9228122375,-0.3563550463  
Cl,0,-0.3999714082,-3.2306981604,0.698472775  
H,0,-1.2616385416,-2.3234348025,0.2873910054

### TS / two HCl conf A PCM



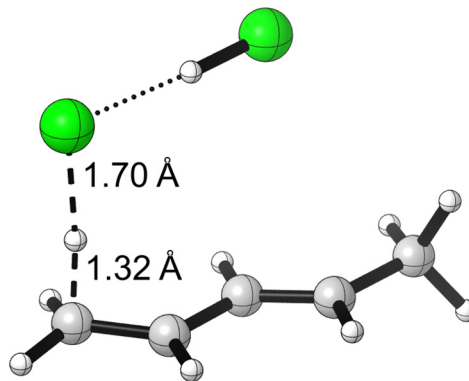
M062X/6-31+G\*\*  
E(RM062X) = -1116.74942001

Zero-point correction= 0.128750 (Hartree/Particle)  
Thermal correction to Energy= 0.139606  
Thermal correction to Enthalpy= 0.140550  
Thermal correction to Gibbs Free Energy= 0.088181  
Sum of electronic and ZPE= -1116.620670  
Sum of electronic and thermal Energies= -1116.609814  
Sum of electronic and thermal Enthalpies= -1116.608870  
Sum of electronic and thermal Free Energies= -1116.661239

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 87.604	35.300	110.221

C,0,-2.0766888111,-0.9395778978,-0.4388491044  
H,0,-2.0837285369,-1.4433434188,-1.4054958038  
C,0,-0.977181058,-1.0642664367,0.3393901887  
H,0,-0.9238759348,-0.5813269655,1.3127164343  
C,0,0.1346544993,-1.842612654,-0.1042683249  
H,0,0.0460346202,-2.3131972593,-1.083687497  
C,0,-3.2929955375,-0.1692540364,-0.0744498102  
H,0,-3.200189741,0.3043007539,0.90381066  
H,0,-3.4861624768,0.5971392163,-0.8328407493  
H,0,-4.1652147141,-0.8320274538,-0.0758788193  
C,0,1.3458076166,-1.9327021658,0.5593084189  
H,0,1.4027058645,-1.6063444591,1.5962503553  
H,0,2.0650138868,-2.6814463611,0.23888501  
H,0,1.8082362223,-0.8592279429,-0.0591040638  
Cl,0,2.6459763509,0.4982142281,-0.6153536192  
Cl,0,5.1358819679,-0.7853851278,1.3292955798  
H,0,4.2142357816,-0.2398850191,0.5615131448

### TS / two HCl conf B PCM



M062X/6-31+G\*\*  
E(RM062X) = -1116.75078734

Zero-point correction= 0.128718 (Hartree/Particle)  
Thermal correction to Energy= 0.139515  
Thermal correction to Enthalpy= 0.140459  
Thermal correction to Gibbs Free Energy= 0.089778  
Sum of electronic and ZPE= -1116.622070  
Sum of electronic and thermal Energies= -1116.611272  
Sum of electronic and thermal Enthalpies= -1116.610328  
Sum of electronic and thermal Free Energies= -1116.661010

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 87.547 35.405 106.669

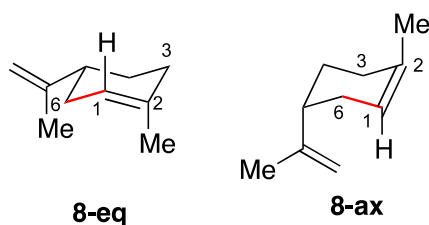
C,0,1.8560461444,-0.3330454932,-0.3608328225  
H,0,1.9312743391,-0.1864159291,-1.4384658752  
C,0,0.8680604278,0.3077498219,0.3049357936  
H,0,0.7497180014,0.1857943047,1.3797917796  
C,0,-0.0655280854,1.1234436544,-0.4015546837  
H,0,0.0836612173,1.2256060137,-1.4766804841  
C,0,2.8509264403,-1.237970573,0.2666219014  
H,0,2.7078068124,-1.3170113727,1.3452504679

H,0,2.7671808258,-2.2351277903,-0.1803922146  
H,0,3.8654827094,-0.8835734674,0.0549984146  
C,0,-1.2195449503,1.6466837487,0.1555860931  
H,0,-1.305151162,1.6946074447,1.2395497298  
H,0,-1.8097130459,2.354123425,-0.4187658877  
H,0,-1.8325365947,0.4970286841,-0.0652757731  
Cl,0,-2.7371934389,-0.9366068102,-0.1197732441  
Cl,0,-0.2514950391,-3.1570322059,0.7075093981  
H,0,-1.2007946016,-2.2989134554,0.3963174069

## Calculated Structures and Complete Energies for Chapter III

### Key to Structures

The intermediate formed when (+)-limonene undergoes cis-trans isomerization is referred to as “trans-limonene.” Trans-limonene exists as two diastereomers, **8-eq** and **8-ax**. Each of these had two low-energy conformations, referred to as “A” and “B”. The intermediates and transition structures derived from **8-eq** are described as being in the “isopropenyl-equatorial series” and the intermediates and transition structures derived from **8-ax** are described as being in the “isopropenyl-axial series.”



Triethylborane conformers are designated as triethylborane-A, triethylborane-B, etc.

“TS1” structures refer to transition structures for attack of the borane on the trans-limonene isomers, and are analogs of **11**<sup>‡</sup> in the main text. There are up to 22 of these in each of the axial and equatorial series, arising from the different conformations of the borane and the differing conformations of the isopropenyl group. These are labeled TS1-eq-A, TS1-eq-B, etc., in the equatorial series and TS1-ax-A, TS1-ax-B, etc., in the axial series.

“Int” structures refer to the shallow local potential energy minima in between TS1 and TS2, and are analogs of **12** in the main text. There are up to 22 of these in each of the axial and equatorial series, arising from the different conformations of the borane and the differing conformations of the isopropenyl group. These are labeled Int-eq-A, Int-eq-B, etc., in the equatorial series and Int-ax-A, Int-ax-B, etc., in the axial series.

“TS2” structures refer to transition structures for the ring contraction, and are analogs of **13**<sup>‡</sup> in the main text. There are up to 22 of these in each of the axial and equatorial series, arising from the different conformations of the borane and the differing conformations of the isopropenyl group. These are labeled TS2-eq-A, TS2-eq-B, etc., in the equatorial series and TS2-ax-A, TS2-ax-B, etc., in the axial series.

We have endeavored to make the lettering consistent, so that “Int-eq-A” is derived from “TS1-eq-A” and leads on to “TS2-eq-A.”

To gauge whether conformational interconversion could be significant in these series, a limited study of the barriers for conformational interconversion at the stage of the intermediate was undertaken. The TSs located are referred to as TSR-A-1, TSR-A-2, etc.

The systems **S6**<sup>‡</sup> and **S7**<sup>‡</sup> that were used to examine the effect of distant substituent groups on the stereochemistry, described in a previous section, are referred to as “Truncated Model Systems.”

### *Complete Table of Energies*

The energies here are not an exact match with those in Figure 2 of the main text. The energies here were obtained with Gaussian 09, default grids, and default optimization parameters. The energies in the main text were based on structures reoptimized in Gaussian 16, with its enlarged default grid. Since most results were only obtained with Gaussian 09, the complete Gaussian 09 set is presented here for consistency.

The free energies reported in the “G (1 atm)” column are the raw Gaussian values in the gas phase based on the harmonic approximation for every frequency. Free energies in the “G (1 M)” column are converted from the raw Gaussian free energies, changing the standard state from 1 atm to 1 M. No corrections for symmetry have been applied.

The listed relative energies (kcal/mol) are versus the lowest-energy reactant structures in the separate **8-ex** and **8-ax** series.

structure name	potential energy	E + ZPE	enthalpy	G (1 atm)	G (1 M)	S (e.u.)	relative energy kcal/mol
trans-limonene-eq-A	-390.341063	-390.107693	-390.096280	-390.142952	-390.141055	98.23	
trans-limonene-eq-B	-390.342558	-390.109418	-390.097855	-390.144960	-390.143063	99.14	
triethylborane-A	-262.356708	-262.157581	-262.146136	-262.193390	-262.191493	99.455	
triethylborane-B	-262.357274	-262.158459	-262.147813	-262.192584	-262.190687	94.228	
triethylborane-C	-262.358680	-262.160151	-262.148630	-262.196194	-262.194297	100.107	
triethylborane-D	-262.355996	-262.156519	-262.145168	-262.191777	-262.189880	98.10	
TS1-eq-A	-652.711243	-652.277583	-652.255100	-652.327024	-652.325127	151.38	7.7
TS1-eq-B	-652.709950	-652.276070	-652.253614	-652.325407	-652.323510	151.10	8.7
TS1-eq-C	-652.709761	-652.276077	-652.253649	-652.325323	-652.323426	150.85	8.7
TS1-eq-D	-652.712249	-652.278502	-652.256284	-652.326957	-652.325060	148.74	7.7
TS1-eq-E	-652.709564	-652.275320	-652.253187	-652.324688	-652.322791	150.49	9.1
TS1-eq-F	-652.710428	-652.276581	-652.254296	-652.325580	-652.323683	150.03	8.6
TS1-eq-G	-652.708794	-652.274883	-652.252496	-652.324004	-652.322107	150.50	9.6
TS1-eq-H	-652.711559	-652.277419	-652.255366	-652.325481	-652.323584	147.57	8.6
TS1-eq-I	-652.711020	-652.276588	-652.254512	-652.325025	-652.323128	148.41	8.9
TS1-eq-J	-652.710834	-652.277041	-652.254665	-652.326437	-652.324540	151.06	8.0
TS1-eq-K	-652.711106	-652.277436	-652.255007	-652.326657	-652.324760	150.80	7.9
TS1-eq-L	-652.710490	-652.276641	-652.254278	-652.325884	-652.323987	150.71	8.4
TS1-eq-M	-652.709164	-652.275423	-652.252949	-652.325144	-652.323247	151.95	8.9

TS1-eq-N	-652.708980	-652.275160	-652.252798	-652.324218	-652.322321	150.32	9.4
TS1-eq-O	-652.711483	-652.277751	-652.255549	-652.326269	-652.324372	148.84	8.1
TS1-eq-P	-652.708638	-652.274098	-652.252036	-652.322596	-652.320699	148.51	10.5
TS1-eq-Q	-652.709721	-652.275479	-652.253429	-652.323986	-652.322089	148.50	9.6
TS1-eq-R	-652.707952	-652.274320	-652.251930	-652.323857	-652.321960	151.38	9.7
TS1-eq-S	-652.710724	-652.276778	-652.254685	-652.325093	-652.323196	148.19	8.9
TS1-eq-T	-652.710299	-652.275876	-652.253787	-652.324712	-652.322815	149.28	9.1
TS1-eq-U	-652.709975	-652.276158	-652.253764	-652.325729	-652.323832	151.46	8.5
TS1-eq-V	-652.710326	-652.276395	-652.254074	-652.325330	-652.323433	149.97	8.7
Int-eq-A	-652.717808	-652.283179	-652.260873	-652.331333	-652.329436	148.30	5.0
Int-eq-B	-652.716199	-652.281531	-652.259157	-652.330014	-652.328117	149.13	5.8
Int-eq-C	-652.716073	-652.281638	-652.259152	-652.330369	-652.328472	149.89	5.6
Int-eq-D	-652.718028	-652.283417	-652.261208	-652.331182	-652.329285	147.27	5.1
Int-eq-E	-652.716880	-652.282608	-652.260211	-652.330954	-652.329057	148.89	5.2
Int-eq-F	-652.716242	-652.281885	-652.259474	-652.330453	-652.328556	149.39	5.5
Int-eq-G	-652.718657	-652.284009	-652.261778	-652.331962	-652.330065	147.72	4.6
Int-eq-H	-652.716616	-652.281965	-652.259740	-652.329908	-652.328011	147.68	5.9
Int-eq-I	-652.715909	-652.280921	-652.258853	-652.328551	-652.326654	146.69	6.7
Int-eq-J	-652.718594	-652.284036	-652.261812	-652.332158	-652.330261	148.06	4.5
Int-eq-K	-652.716958	-652.282369	-652.260166	-652.330109	-652.328212	147.21	5.7
Int-eq-L	-652.717541	-652.282768	-652.260558	-652.330597	-652.328700	147.41	5.4
Int-eq-M	-652.715865	-652.281301	-652.258873	-652.330063	-652.328166	149.83	5.8
Int-eq-N	-652.715801	-652.281110	-652.258793	-652.329330	-652.327433	148.46	6.2
Int-eq-O	-652.717785	-652.283084	-652.260831	-652.331362	-652.329465	148.45	5.0
Int-eq-P	-652.716821	-652.282428	-652.260115	-652.330498	-652.328601	148.13	5.5
Int-eq-Q	-652.715917	-652.281387	-652.259065	-652.329674	-652.327777	148.61	6.0
Int-eq-R	-652.718426	-652.283760	-652.261490	-652.331819	-652.329922	148.02	4.7
Int-eq-S	-652.716325	-652.281333	-652.259306	-652.328545	-652.326648	145.73	6.7
Int-eq-T	-652.715674	-652.280818	-652.258642	-652.329182	-652.327285	148.46	6.3
Int-eq-U	-652.718355	-652.283752	-652.261550	-652.331716	-652.329819	147.68	4.7
Int-eq-V	-652.716698	-652.281934	-652.259806	-652.329476	-652.327579	146.63	6.1
TS2-eq-A	-652.716407	-652.282628	-652.260557	-652.331557	-652.329660	149.43	4.8
TS2-eq-B	-652.714945	-652.280923	-652.258908	-652.329620	-652.327723	148.83	6.0
TS2-eq-C	-652.715171	-652.281250	-652.259155	-652.330030	-652.328133	149.17	5.8
TS2-eq-D	-652.717113	-652.282653	-652.261006	-652.329746	-652.327849	144.68	6.0
TS2-eq-E	-652.715025	-652.281209	-652.259137	-652.329999	-652.328102	149.14	5.8
TS2-eq-F	-652.713643	-652.279434	-652.257504	-652.327688	-652.325791	147.71	7.3
TS2-eq-G	-652.717245	-652.283189	-652.261285	-652.331642	-652.329745	148.08	4.8
TS2-eq-H	-652.714472	-652.279812	-652.258136	-652.327181	-652.325284	145.32	7.6
TS2-eq-I	-652.714094	-652.279654	-652.257889	-652.327746	-652.325849	147.03	7.2
TS2-eq-J	-652.717731	-652.283207	-652.261600	-652.330419	-652.328522	144.84	5.5
TS2-eq-K	-652.715105	-652.281200	-652.259268	-652.329611	-652.327714	148.05	6.1
TS2-eq-L	-652.716478	-652.282247	-652.260423	-652.330320	-652.328423	147.11	5.6
TS2-eq-M	-652.714995	-652.281162	-652.259089	-652.330179	-652.328282	149.62	5.7

TS2-eq-N	-652.715191	-652.281224	-652.259266	-652.329494	-652.327597	147.81	6.1
TS2-eq-O	-652.717149	-652.282945	-652.261249	-652.330225	-652.328328	145.17	5.7
TS2-eq-P	-652.715299	-652.281325	-652.259381	-652.329517	-652.327620	147.61	6.1
TS2-eq-Q	-652.713745	-652.279251	-652.257493	-652.327033	-652.325136	146.36	7.7
TS2-eq-R	-652.717325	-652.283021	-652.261229	-652.330863	-652.328966	146.56	5.3
TS2-eq-S	-652.714548	-652.280149	-652.258426	-652.327544	-652.325647	145.47	7.3
TS2-eq-T	-652.714302	-652.279634	-652.257982	-652.327594	-652.325697	146.51	7.3
TS2-eq-U	-652.717651	-652.283524	-652.261758	-652.331075	-652.329178	145.89	5.1
TS2-eq-V	-652.715235	-652.280898	-652.259219	-652.328355	-652.326458	145.51	6.8
TSR-A-1	-652.709975	-652.275711	-652.254042	-652.323303	-652.321406	145.77	10.0
TSR-A-2	-652.711494	-652.276836	-652.255368	-652.323831	-652.321934	144.09	9.7
TSR-A-3	-652.712527	-652.277995	-652.256383	-652.325291	-652.323394	145.03	8.8
TSR-B-1	-652.709720	-652.275519	-652.253921	-652.322876	-652.320979	145.13	10.3
TSR-B-2	-652.711242	-652.276569	-652.255137	-652.323590	-652.321693	144.07	9.8
TSR-B-3	-652.710307	-652.275779	-652.254188	-652.323128	-652.321231	145.10	10.1
trans-limonene-ax-A	-390.340818	-390.107280	-390.095938	-390.142716	-390.140819	98.45	
trans-limonene-ax-B	-390.338851	-390.105212	-390.093943	-390.140266	-390.138369	97.49	
TS1-ax-A	-652.710988	-652.277196	-652.254833	-652.326467	-652.324570	150.77	6.6
TS1-ax-B	-652.708762	-652.275105	-652.252669	-652.324806	-652.322909	151.83	7.7
TS1-ax-C	-652.709604	-652.275157	-652.253229	-652.323301	-652.321404	147.48	8.6
TS1-ax-D	-652.712064	-652.277601	-652.255898	-652.324939	-652.323042	145.31	7.6
TS1-ax-E	-652.711174	-652.276789	-652.254879	-652.324936	-652.323039	147.45	7.6
TS1-ax-F	-652.708476	-652.274819	-652.253066	-652.324128	-652.322231	149.56	8.1
TS1-ax-G	-652.710559	-652.276232	-652.254197	-652.324202	-652.322305	147.34	8.0
TS1-ax-H	-652.712957	-652.278923	-652.256772	-652.328157	-652.326260	150.24	5.6
TS1-ax-I	-652.710085	-652.275466	-652.253528	-652.323394	-652.321497	147.05	8.5
TS1-ax-J	-652.710763	-652.275834	-652.254169	-652.323215	-652.321318	145.32	8.7
TS1-ax-K	-652.711569	-652.277494	-652.255336	-652.326222	-652.324325	149.19	6.8
TS1-ax-M	-652.708889	-652.274505	-652.252334	-652.323075	-652.321178	148.89	8.7
TS1-ax-N	-652.707243	-652.272291	-652.250560	-652.319713	-652.317816	145.55	10.9
TS1-ax-O	-652.709023	-652.274186	-652.252647	-652.321312	-652.319415	144.52	9.9
TS1-ax-P	-652.709573	-652.274862	-652.252976	-652.322880	-652.320983	147.13	8.9
TS1-ax-Q	-652.708299	-652.274092	-652.252007	-652.322756	-652.320859	148.90	8.9
TS1-ax-R	-652.707919	-652.273511	-652.251517	-652.321523	-652.319626	147.34	9.7
TS1-ax-S	-652.709870	-652.275275	-652.253580	-652.322468	-652.320571	144.99	9.1
TS1-ax-T	-652.707760	-652.272776	-652.251048	-652.320405	-652.318508	145.97	10.4
TS1-ax-U	-652.709044	-652.274172	-652.252455	-652.321513	-652.319616	145.35	9.7
TS1-ax-V	-652.709727	-652.275318	-652.253246	-652.323645	-652.321748	148.17	8.4
Int-ax-A	-652.718934	-652.284254	-652.262089	-652.332376	-652.330479	147.93	2.9
Int-ax-B	-652.718775	-652.284182	-652.261942	-652.333029	-652.331132	149.61	2.5
Int-ax-C	-652.713478	-652.277887	-652.255905	-652.325884	-652.323987	147.28	7.0
Int-ax-D	-652.717263	-652.281898	-652.260036	-652.328474	-652.326577	144.04	5.4
Int-ax-E	-652.717355	-652.281965	-652.260240	-652.328840	-652.326943	144.38	5.1
Int-ax-F	-652.716819	-652.282070	-652.259968	-652.329451	-652.327554	146.24	4.7

Int-ax-G	-652.718682	-652.284008	-652.261959	-652.331299	-652.329402	145.94	3.6
Int-ax-H	-652.719048	-652.283648	-652.261878	-652.330579	-652.328682	144.59	4.0
Int-ax-I	-652.719003	-652.284193	-652.262220	-652.331720	-652.329823	146.28	3.3
Int-ax-J	-652.718452	-652.283246	-652.261458	-652.330167	-652.328270	144.61	4.3
Int-ax-K	-652.720192	-652.285231	-652.263277	-652.332552	-652.330655	145.80	2.8
Int-ax-L	-652.717097	-652.281823	-652.260039	-652.328502	-652.326605	144.09	5.3
Int-ax-M	-652.717238	-652.282499	-652.260430	-652.330334	-652.328437	147.13	4.2
Int-ax-N	-652.710867	-652.275672	-652.253575	-652.323698	-652.321801	147.59	8.4
Int-ax-O	-652.712465	-652.277222	-652.255401	-652.324453	-652.322556	145.33	7.9
Int-ax-P	-652.715403	-652.279991	-652.258312	-652.326730	-652.324833	144.00	6.5
Int-ax-Q	-652.715096	-652.280086	-652.258082	-652.327123	-652.325226	145.31	6.2
Int-ax-R	-652.716227	-652.281000	-652.259164	-652.327724	-652.325827	144.30	5.8
Int-ax-S	-652.716084	-652.280426	-652.258749	-652.327145	-652.325248	143.95	6.2
Int-ax-T	-652.717239	-652.282498	-652.260430	-652.330332	-652.328435	147.12	4.2
Int-ax-U	-652.716771	-652.281595	-652.259717	-652.328685	-652.326788	145.15	5.2
Int-ax-V	-652.717828	-652.282712	-652.260801	-652.329964	-652.328067	145.57	4.4
TS2-ax-A	-652.717871	-652.283090	-652.261612	-652.329728	-652.327831	143.36	4.6
TS2-ax-B	-652.718262	-652.283672	-652.262060	-652.331262	-652.329365	145.65	3.6
TS2-ax-C	-652.714206	-652.279695	-652.258082	-652.326630	-652.324733	144.27	6.5
TS2-ax-D	-652.715267	-652.280325	-652.258870	-652.326751	-652.324854	142.87	6.4
TS2-ax-E	-652.716827	-652.281424	-652.260362	-652.327083	-652.325186	140.43	6.2
TS2-ax-F	-652.716507	-652.282068	-652.260506	-652.329041	-652.327144	144.24	5.0
TS2-ax-G	-652.718550	-652.283898	-652.262504	-652.330256	-652.328359	142.60	4.2
TS2-ax-H	-652.718714	-652.284226	-652.262782	-652.331003	-652.329106	143.58	3.8
TS2-ax-I	-652.717288	-652.282966	-652.261351	-652.330609	-652.328712	145.77	4.0
TS2-ax-J	-652.716130	-652.281080	-652.259726	-652.327709	-652.325812	143.08	5.8
TS2-ax-K	-652.719567	-652.284794	-652.263410	-652.331261	-652.329364	142.81	3.6
TS2-ax-L	-652.715155	-652.280448	-652.259010	-652.327396	-652.325499	143.93	6.0
TS2-ax-M	-652.715630	-652.280952	-652.259413	-652.328240	-652.326343	144.86	5.5
TS2-ax-N	-652.709389	-652.274302	-652.252960	-652.322185	-652.320288	145.70	9.3
TS2-ax-O	-652.710761	-652.275826	-652.254471	-652.322803	-652.320906	143.82	8.9
TS2-ax-P	-652.714360	-652.279146	-652.257959	-652.325157	-652.323260	141.43	7.4
TS2-ax-Q	-652.714481	-652.279665	-652.258222	-652.326204	-652.324307	143.08	6.8
TS2-ax-R	-652.715773	-652.280929	-652.259589	-652.327203	-652.325306	142.31	6.2
TS2-ax-S	-652.715670	-652.280424	-652.259321	-652.326333	-652.324436	141.04	6.7
TS2-ax-T	-652.715096	-652.280755	-652.259102	-652.328287	-652.326390	145.61	5.5
TS2-ax-U	-652.713697	-652.278568	-652.257174	-652.325452	-652.323555	143.70	7.3
TS2-ax-V	-652.716926	-652.281919	-652.260654	-652.328103	-652.326206	141.96	5.6
Truncated Model System <b>S6</b> <sup>†</sup>	-457.511448	-457.196261	-457.180348	-457.236392	-457.234498	117.955	
Truncated Model System <b>S7</b> <sup>†</sup>	-457.512488	-457.197832	-457.181884	-457.237952	-457.236055	118.01	

*Isopropenyl-Equatorial Series, Derived from  
8-eq*

**Reactants**

*trans-limonene-eq-A*

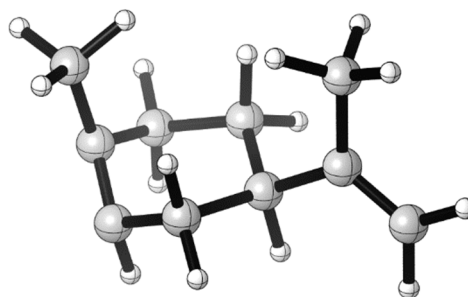
E(RM11) = -390.341063282

Zero-point correction= 0.233370 (Hartree/Particle)  
Thermal correction to Energy= 0.243839  
Thermal correction to Enthalpy= 0.244783  
Thermal correction to Gibbs Free Energy= 0.198112  
Sum of electronic and ZPE= -390.107693  
Sum of electronic and thermal Energies= -390.097224  
Sum of electronic and thermal Enthalpies= -390.096280  
Sum of electronic and thermal Free Energies= -390.142952

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 153.011	41.595	98.228

C,0,-1.8274446076,-2.2125530374,-1.1741229445  
C,0,-2.9038204813,-1.1754802081,-0.6394784225  
H,0,-1.6085687,-2.0051731061,-2.2314541697  
H,0,-2.2109799989,-3.2397027174,-1.0773910144  
C,0,-0.679324202,-1.8402921825,-0.2752028473  
C,0,-0.2524821747,-0.5923198155,-0.5857284475  
C,0,-0.6995543229,-2.3640000102,1.137696518  
C,0,-0.9815587519,0.4633480937,0.1974574918  
H,0,-0.2614391697,-0.3600516443,-1.6604303153  
C,0,-2.4250642879,0.2978202015,-0.4818537506  
H,0,-0.6242640999,1.4940032778,0.0670548736  
H,0,-1.0544078277,0.2438678391,1.2721459178  
C,0,-3.4435631767,1.1938621238,0.2054813198  
H,0,-2.2987382096,0.7059388182,-1.5028021209  
H,0,-3.2561631826,-1.5343556252,0.3392443677  
H,0,-3.7785310474,-1.185207965,-1.3067014963  
H,0,-0.0839308158,-1.7430637107,1.8012410604  
H,0,-1.7156881302,-2.4363199372,1.5560387838  
H,0,-0.2774431263,-3.380590031,1.1525637955  
C,0,-4.6280189117,0.7762710976,0.6624719086  
C,0,-3.039502555,2.6454995318,0.3372349604  
H,0,-5.3155578338,1.4796279062,1.1364543911  
H,0,-4.9622151181,-0.257751565,0.5826587188  
H,0,-2.6389926194,3.0304771341,-0.6130851523  
H,0,-3.8941451092,3.2670615979,0.630766586  
H,0,-2.2522985395,2.771274934,1.0949229879

*trans-limonene-eq-B*



E(RM11) = -390.342557539

Zero-point correction= 0.233139 (Hartree/Particle)  
Thermal correction to Energy= 0.243758  
Thermal correction to Enthalpy= 0.244703  
Thermal correction to Gibbs Free Energy= 0.197597  
Sum of electronic and ZPE= -390.109418  
Sum of electronic and thermal Energies= -390.098799  
Sum of electronic and thermal Enthalpies= -390.097855  
Sum of electronic and thermal Free Energies= -390.144960

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 152.961	41.761	99.141

C,0,-1.8614235917,0.7981417044,-1.0759096588  
C,0,-0.329592407,1.1032577466,-0.7748488568  
H,0,-1.9590036509,0.3728161085,-2.085000603  
H,0,-2.4502740293,1.7261582249,-1.0145919374  
C,0,-2.1151143321,-0.2256662868,-0.004570317  
C,0,-1.4036635847,-1.3468618963,-0.274936416  
C,0,-2.3139067271,0.2826053223,1.4015934905  
C,0,-0.0431114525,-1.3066257602,0.3576185698  
H,0,-1.3470712089,-1.6135520987,-1.3398118111  
C,0,0.5913512389,-0.1377465203,-0.5410015666  
H,0,0.5838305674,-2.2038453856,0.2590146721  
H,0,-0.0657409829,-1.0072707603,1.4140904869  
C,0,1.9406676294,0.2613659302,0.0285621395  
H,0,0.7692126646,-0.6001107789,-1.5257439814  
H,0,-0.2887307875,1.756178642,0.1085369817  
H,0,0.0945555736,1.6867353887,-1.6055884946  
H,0,-2.1959618751,-0.5250960775,2.1350058797  
H,0,-1.6214109983,1.1001388526,1.663370452  
H,0,-3.3325022002,0.6852188349,1.5080605375  
C,0,3.076805398,-0.1718644237,-0.5243915314  
C,0,1.9450981697,1.1277024936,1.2674503487  
H,0,4.049352779,0.0706254727,-0.0911574421  
H,0,3.070405734,-0.7843976331,-1.4285858986  
H,0,1.1697236145,0.813618458,1.9831284303  
H,0,2.917816014,1.0867534382,1.7723968841  
H,0,1.742233565,2.178354994,1.0122912722

*triethylborane-A*

E(RM11) = -262.356707725

Zero-point correction= 0.199127 (Hartree/Particle)  
Thermal correction to Energy= 0.209628



Thermal correction to Enthalpy= 0.210572  
Thermal correction to Gibbs Free Energy= 0.163318  
Sum of electronic and ZPE= -262.157581  
Sum of electronic and thermal Energies= -262.147080  
Sum of electronic and thermal Enthalpies= -262.146136  
Sum of electronic and thermal Free Energies= -262.193390

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 131.543 36.770 99.455

B,0,-1.4613023462,-3.5621435732,-0.1893749645  
C,0,-0.5667609212,-4.0420967294,1.0278621582  
C,0,-0.981230678,-3.8108881332,-1.6722042553  
C,0,-2.8987049389,-2.9809334448,0.1343101062  
H,0,-1.015451037,-5.0076031927,1.3358104722  
H,0,-0.7301578748,-3.3861331177,1.899214765  
C,0,0.9326154838,-4.238020286,0.7701090019  
H,0,-2.7284247391,-2.0403772888,0.6915060982  
H,0,-3.3769745096,-3.6385955182,0.8819276455  
C,0,-3.8485852918,-2.7225608853,-1.0412102718  
C,0,-1.2933951564,-5.3015181694,-1.9634067886  
H,0,0.0987552935,-3.6445673847,-1.8018885663  
H,0,-1.5071770049,-3.1860918259,-2.4083096832  
H,0,1.4605187007,-4.6035255209,1.661775408  
H,0,1.1081604848,-4.9633090321,-0.0379303455  
H,0,1.4106374912,-3.2951981324,0.4667018367  
H,0,-1.0194280131,-5.5765449344,-2.9908051162  
H,0,-0.7415420766,-5.9665659609,-1.2823127633  
H,0,-2.3649538825,-5.5210142644,-1.8394503369  
H,0,-4.8309983591,-2.3622048132,-0.7059627665  
H,0,-3.4376203442,-1.9676081454,-1.7263757809  
H,0,-4.0161122809,-3.6361786473,-1.6308208531

### triethylborane-B

M11/6-31+G\*\*  
E(RM11) = -262.357274078

Zero-point correction= 0.198816 (Hartree/Particle)  
Thermal correction to Energy= 0.208517  
Thermal correction to Enthalpy= 0.209461  
Thermal correction to Gibbs Free Energy= 0.164690  
Sum of electronic and ZPE= -262.158459  
Sum of electronic and thermal Energies= -262.148757  
Sum of electronic and thermal Enthalpies= -262.147813  
Sum of electronic and thermal Free Energies= -262.192584

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 130.846 34.914 94.228

B,0,-1.3793497976,-3.5012738098,-0.2335966265  
C,0,-0.3322336015,-3.7099276145,0.9333843093  
C,0,-1.0117956909,-4.0391800059,-1.67345162  
C,0,-2.7959341198,-2.8657046285,0.0647820137  
H,0,0.4800000584,-2.9886659277,0.7158789108  
H,0,0.1549410614,-4.692534827,0.8036464699  
C,0,-0.8129206706,-3.5318328141,2.3781477284  
H,0,-2.658761305,-1.9815461514,0.7116232995  
H,0,-3.3121835267,-3.5863677588,0.7292772496  
C,0,-3.6876196284,-2.5184700778,-1.1328537109  
C,0,-1.5963190801,-5.4709103,-1.7638142211  
H,0,0.0758698079,-4.0893874954,-1.8364242965  
H,0,-1.4440703245,-3.427913618,-2.480002486  
H,0,-0.0004081845,-3.67289447,3.1042668485  
H,0,-1.2298060205,-2.5278531941,2.5418493476  
H,0,-1.6042015294,-4.2543924176,2.6259406073

H,0,-1.4002855726,-5.9248349924,-2.7445392825  
H,0,-1.1564457285,-6.1309277022,-1.0013659867  
H,0,-2.6861933178,-5.4732417038,-1.6109650412  
H,0,-4.6651889284,-2.1261217869,-0.8201768607  
H,0,-3.2152588582,-1.7567555825,-1.7699121714  
H,0,-3.8717330425,-3.3983621214,-1.7664734812

### triethylborane-C

M11/6-31+G\*\*  
E(RM11) = -262.358679592

Zero-point correction= 0.198528 (Hartree/Particle)  
Thermal correction to Energy= 0.209105  
Thermal correction to Enthalpy= 0.210049  
Thermal correction to Gibbs Free Energy= 0.162485  
Sum of electronic and ZPE= -262.160151  
Sum of electronic and thermal Energies= -262.149575  
Sum of electronic and thermal Enthalpies= -262.148630  
Sum of electronic and thermal Free Energies= -262.196194

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 131.215 37.096 100.107

B,0,-1.4306313363,-3.6137906658,-0.137625269  
C,0,-0.4650406374,-3.9143019917,1.0780876827  
C,0,-1.0495037274,-4.1065836047,-1.591161653  
C,0,-2.7956585858,-2.8525527489,0.105889586  
H,0,0.5461263228,-3.564160686,0.8016908625  
H,0,-0.3462057815,-5.0137459753,1.1195358717  
C,0,-0.8565665903,-3.3744687162,2.4582269343  
H,0,-2.5714909734,-1.9239752532,0.6616797661  
H,0,-3.3624928071,-3.4541750411,0.8417429339  
C,0,-3.6740907403,-2.5455242601,-1.1121963714  
C,0,0.2977495449,-4.8122625155,-1.7820935493  
H,0,-1.8739921258,-4.7630501698,-1.9281510051  
H,0,-1.1278788315,-3.238707819,-2.2711994001  
H,0,-0.1350100362,-3.6648671234,3.2343627981  
H,0,-0.9125941197,-2.2762358828,2.4563544643  
H,0,-1.8433870517,-3.746686489,2.7697174568  
H,0,0.4511599558,-5.1339028349,-2.8215452419  
H,0,1.1360093405,-4.1524387447,-1.5153527909  
H,0,0.3759780272,-5.7057576591,-1.1457729136  
H,0,-4.6083708134,-2.0405445612,-0.8303934806  
H,0,-3.1512831178,-1.8942715905,-1.8275482682  
H,0,-3.9460879158,-3.464144667,-1.6521684134

### triethylborane-D

E(RM11) = -262.355995503

Zero-point correction= 0.199477 (Hartree/Particle)  
Thermal correction to Energy= 0.209883  
Thermal correction to Enthalpy= 0.210827  
Thermal correction to Gibbs Free Energy= 0.164218  
Sum of electronic and ZPE= -262.156519  
Sum of electronic and thermal Energies= -262.146112  
Sum of electronic and thermal Enthalpies= -262.145168  
Sum of electronic and thermal Free Energies= -262.191777

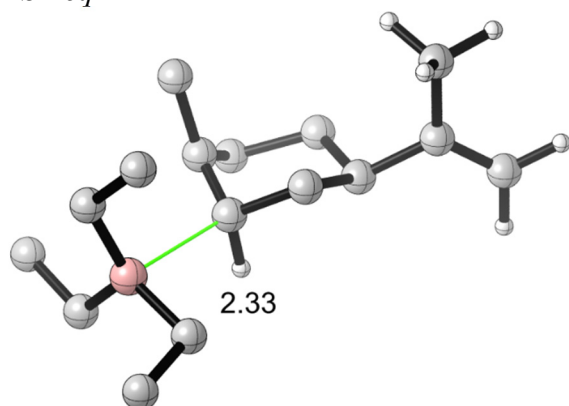
E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 131.704 36.512 98.097

B,0,-0.9442628726,1.9591742958,0.1310099042  
C,0,-1.7157957732,0.5868724282,0.2484331865  
H,0,-2.7676510705,0.6704285294,-0.0665951083

H,0,-1.2521606184,-0.2214447798,-0.3369974471  
 C,0,-1.7637286196,3.3106395796,0.161638005  
 H,0,-1.1698832822,4.1617737621,0.5292055234  
 H,0,-2.6608082776,3.2274020848,0.7962699616  
 C,0,0.6324672414,2.0156333754,0.0466258964  
 H,0,0.9261975963,2.835821055,-0.6318404633  
 H,0,0.9540309695,2.3783562738,1.0430060951  
 C,0,1.3778656415,0.7232683648,-0.3050041034  
 H,0,1.1015394776,0.3666587149,-1.3078290557  
 H,0,2.4685009977,0.8561424267,-0.2906815585  
 H,0,1.1338469173,-0.0834856886,0.4019654588  
 C,0,-1.6709786233,3.5972891678,1.7502101022  
 H,0,-2.1427296356,0.9827140982,2.3732301532  
 H,0,-2.1988712072,-0.7355137106,1.9435623744  
 H,0,-0.6357699787,0.0865485803,2.1034979118  
 C,0,-2.2106718382,3.5972891678,-1.2919558362  
 H,0,-2.8278587412,2.7782451647,-1.6902868967  
 H,0,-2.8042245234,4.5191808522,-1.356487261  
 H,0,-1.3457568997,3.715913814,-1.9617700324

## TS1 Structures

### TS1-eq-A



E(RM11) = -652.711243027

Zero-point correction= 0.433660 (Hartree/Particle)  
 Thermal correction to Energy= 0.455199  
 Thermal correction to Enthalpy= 0.456143  
 Thermal correction to Gibbs Free Energy= 0.384219  
 Sum of electronic and ZPE= -652.277583  
 Sum of electronic and thermal Energies= -652.256044  
 Sum of electronic and thermal Enthalpies= -652.255100  
 Sum of electronic and thermal Free Energies= -652.327024

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.642	81.814	151.377

C,0,-1.1261906902,-2.2345666496,0.0100969838  
 C,0,-2.4275658715,-1.3314514666,0.182930855  
 H,0,-0.9922512178,-2.4848930845,-1.0514075094  
 H,0,-1.2196576847,-3.1545210025,0.6051614747  
 C,0,-0.1254995709,-1.2333772121,0.4812648569  
 C,0,0.0114772063,-0.197175474,-0.4006218392  
 C,0,0.0850520622,-1.0862184381,1.959516995  
 C,0,-0.9919494773,0.8805786017,-0.0348807196  
 H,0,-0.1321171875,-0.4975567345,-1.4489520015  
 C,0,-2.3413085016,0.124547908,-0.3801174085  
 H,0,-0.920230305,1.8093063465,-0.6204723509  
 H,0,-0.9631463223,1.1374242254,1.0331655454  
 C,0,-3.5626442442,0.9150317321,0.0610599942

H,0,-2.3737244306,0.0451601604,-1.4791089332  
 H,0,-2.6688253454,-1.2905129431,1.2561263302  
 H,0,-3.2737619788,-1.8364597998,-0.3036283946  
 B,0,2.2629570962,0.3124503186,-0.7214158584  
 C,0,2.6877781583,-1.0499021576,-1.4456249741  
 C,0,2.8267155934,0.5928334346,0.7475871863  
 C,0,1.942429039,1.5720273024,-1.6561604827  
 H,0,3.6267860061,-0.811166757,-1.982111875  
 H,0,1.9702516,-1.3021024199,-2.2456377355  
 C,0,2.9310922915,-2.2658728354,-0.5471974331  
 H,0,1.3407618229,2.3277962977,-1.1253446852  
 H,0,1.3697086422,1.2815449669,-2.5534562046  
 C,0,3.2707989675,2.2247354657,-2.0952012342  
 C,0,2.3432480048,1.8816154052,1.4239984193  
 H,0,3.9287063758,0.6339671129,0.6337960299  
 H,0,2.6587239308,-0.2763838264,1.4045275234  
 H,0,0.4400862607,-0.0836527491,2.2277388375  
 H,0,-0.8231901872,-1.3255892989,2.533348652  
 H,0,0.8594642528,-1.8054385554,2.2748347378  
 C,0,-4.5649597162,1.1653270826,-0.7846696283  
 C,0,-3.5846490446,1.4101042345,1.4886223707  
 H,0,-5.452250901,1.7177450021,-0.4688852053  
 H,0,-4.5287899737,0.8274265543,-1.8225936336  
 H,0,-3.2336036361,0.6411317528,2.1935321662  
 H,0,-2.9204461553,2.2793930564,1.6063207143  
 H,0,-4.5953027982,1.714858723,1.7857564333  
 H,0,3.2073125732,-3.1649752443,-1.1169044074  
 H,0,3.7357980183,-2.0724823183,0.1773525062  
 H,0,2.0247110293,-2.5099121397,0.0330875599  
 H,0,2.711866348,1.9839161156,2.4552709494  
 H,0,2.6723739462,2.7711145936,0.8666223549  
 H,0,1.2424423184,1.9252997891,1.4546789565  
 H,0,3.1062479006,3.1161440108,-2.7174052311  
 H,0,3.8677827019,2.5358506534,-1.2239320901  
 H,0,3.8877113637,1.5253527906,-2.6785330374

### TS1-eq-B

E(RM11) = -652.709949972

Zero-point correction= 0.433880 (Hartree/Particle)  
 Thermal correction to Energy= 0.455391  
 Thermal correction to Enthalpy= 0.456336  
 Thermal correction to Gibbs Free Energy= 0.384543  
 Sum of electronic and ZPE= -652.276070  
 Sum of electronic and thermal Energies= -652.254559  
 Sum of electronic and thermal Enthalpies= -652.253614  
 Sum of electronic and thermal Free Energies= -652.325407

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.762	81.728	151.101

C,0,-1.1105517918,-2.0698998776,-0.4106340174  
 C,0,-2.4089903129,-1.2290193962,-0.0307887717  
 H,0,-1.0137020698,-2.1123475328,-1.504146658  
 H,0,-1.1781643255,-3.0861401921,0.0031182542  
 C,0,-0.1080936598,-1.1568728584,0.2128620245  
 C,0,-0.0023444134,0.0257421265,-0.46525727  
 C,0,0.162269901,-1.2833431769,1.6802861354  
 C,0,-1.0162600364,1.0068508974,0.0928401428  
 H,0,-0.1578305122,-0.083482559,-1.5484927612  
 C,0,-2.3589390494,0.29763196,-0.3575322492  
 H,0,-0.9646674716,2.0248052067,-0.3224944438  
 H,0,-0.9788330066,1.0749525081,1.1885198072  
 C,0,-3.5847935398,0.9886601517,0.2182105401  
 H,0,-2.4064482274,0.3931291958,-1.4547748131  
 H,0,-2.595635483,-1.3624161753,1.0462776874

H,0,-3.2735049459,-1.664489011,-0.5515191308  
B,0,2.2687555954,0.4843243956,-0.5929414166  
C,0,2.8754085424,-0.9144338391,-1.0924438707  
C,0,2.7036506886,0.9243223663,0.883839939  
C,0,2.010616015,1.635350683,-1.6776074117  
H,0,2.7753691662,-1.6811571709,-0.3044214255  
H,0,3.9661596928,-0.738945614,-1.171690401  
C,0,2.3716050186,-1.4653573829,-2.4312003346  
H,0,1.3723272097,2.4397229386,-1.2764689461  
H,0,1.5036269074,1.2517918398,-2.5779842369  
C,0,3.3741415172,2.2297176657,-2.0887797809  
C,0,2.0912961083,2.2098078777,1.44978742  
H,0,3.8009316594,1.0593945337,0.8061528234  
H,0,2.5924103959,0.09180011,1.5981742104  
H,0,0.3729285621,-0.3120656495,2.1464060978  
H,0,-0.6527056943,-1.7910160241,2.2162037225  
H,0,1.0663455911,-1.9040159267,1.8053547367  
C,0,-4.5984969303,1.3595768649,-0.5675334173  
C,0,-3.5988332223,1.2450911681,1.7073287906  
H,0,-5.488206478,1.843044533,-0.1590008356  
H,0,-4.569383858,1.19490751875,-1.6467638222  
H,0,-3.2433268826,0.3724286694,2.2759565455  
H,0,-2.9353963896,2.0853697577,1.9614624109  
H,0,-4.6082036661,1.494954665,2.0557441395  
H,0,2.8824939809,-2.3950191475,-2.72103322  
H,0,1.2929803647,-1.6860291263,-2.3915718277  
H,0,2.5240665077,-0.7388563693,-3.2436207526  
H,0,2.4736374882,2.4528393942,2.4520108064  
H,0,2.3061201332,3.0701165094,0.798357736  
H,0,0.9957869061,2.133251239,1.5217999846  
H,0,3.2680097535,3.0320241135,-2.8329727962  
H,0,3.9029386934,2.6517471217,-1.2200278065  
H,0,4.0272944878,1.4577542086,-2.5246653375

### TSl-eq-C

E(RM11) = -652.709761369

Zero-point correction= 0.433685 (Hartree/Particle)  
Thermal correction to Energy= 0.455168  
Thermal correction to Enthalpy= 0.456112  
Thermal correction to Gibbs Free Energy= 0.384438  
Sum of electronic and ZPE= -652.276077  
Sum of electronic and thermal Energies= -652.254594  
Sum of electronic and thermal Enthalpies= -652.253649  
Sum of electronic and thermal Free Energies= -652.325323

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.622	81.832	150.850

C,0,-1.1227543684,-2.2380541768,0.1387170002  
C,0,-2.3981816367,-1.2853906188,0.2115438796  
H,0,-0.9526541408,-2.5401025939,-0.9036339808  
H,0,-1.2762067531,-3.1248676323,0.7702272348  
C,0,-0.1122769622,-1.2491530782,0.6107403413  
C,0,0.1088013536,-0.2592745846,-0.3091386446  
C,0,0.0435331954,-1.0534839144,2.0883906807  
C,0,-0.8829888378,0.8615248614,-0.0397237929  
H,0,-0.0069211933,-0.6139000712,-1.3427967649  
C,0,-2.2359916012,0.1344271772,-0.4191699161  
H,0,-0.7490957227,1.760505972,-0.6603469866  
H,0,-0.8942983497,1.1668577612,1.0160211431  
C,0,-3.4497194019,0.9871663885,-0.0869302328  
H,0,-2.2124464734,-0.0009533357,-1.5134967424  
H,0,-2.6826648505,-1.1820699321,1.2700449282  
H,0,-3.2389190995,-1.7887832648,-0.2861692867  
B,0,2.3165721753,0.31470256,-0.5669433466

C,0,2.7871942832,-1.0261874538,-1.3100659864  
C,0,2.8530337817,0.5385858984,0.9243053949  
C,0,2.0481629329,1.6202333774,-1.4556100015  
H,0,2.0916120485,-1.3150379615,-2.1161161328  
H,0,2.8190750398,-1.8753253538,-0.6062655903  
C,0,4.1870332113,-0.8193926122,-1.9233973973  
H,0,3.0559413037,2.0675882123,-1.5784685317  
H,0,1.4837406459,2.3788767546,-0.8885694874  
C,0,1.4198822684,1.4243179349,-2.8407910801  
C,0,2.3810093493,1.8081767152,1.6446821001  
H,0,3.9563185581,0.5735047242,0.834392075  
H,0,2.6611284783,-0.3554186921,1.5405902799  
H,0,0.4025521302,-0.0478598967,2.338123554  
H,0,-0.8868962828,-1.2668442016,2.636044556  
H,0,0.7968879106,-1.7717800859,2.4526196821  
C,0,-4.3869408958,1.2400350634,-1.0034660029  
C,0,-3.5365593147,1.5468333695,1.3139294564  
H,0,-5.2672012736,1.8410704273,-0.7666290296  
H,0,-4.3019468688,0.8573377712,-2.022839548  
H,0,-3.262514794,0.7980166943,2.0725326223  
H,0,-2.8439745419,2.3932002575,1.4345235929  
H,0,-4.5490933653,1.9055522749,1.5345093838  
H,0,4.5573789847,-1.7246100171,-2.4258947175  
H,0,4.1801817161,-0.0080997931,-2.6675734161  
H,0,4.9248866317,-0.5466413376,-1.1537233103  
H,0,2.7117844281,1.849066269,2.6931513838  
H,0,2.7620901151,2.7100650054,1.1441339165  
H,0,1.2816435029,1.8898367423,1.6361339957  
H,0,1.393461805,2.3573309097,-3.4223404067  
H,0,1.9747517363,0.6814073902,-3.4333192681  
H,0,0.3817722515,1.0635221162,-2.7639444203

### TSl-eq-D

E(RM11) = -652.712248606

Zero-point correction= 0.433746 (Hartree/Particle)  
Thermal correction to Energy= 0.455020  
Thermal correction to Enthalpy= 0.455965  
Thermal correction to Gibbs Free Energy= 0.385292  
Sum of electronic and ZPE= -652.278502  
Sum of electronic and thermal Energies= -652.257228  
Sum of electronic and thermal Enthalpies= -652.256284  
Sum of electronic and thermal Free Energies= -652.326957

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.530	81.730	148.743

C,0,-1.0861646209,-2.2432730656,0.0523172883  
C,0,-2.3722751746,-1.3107063221,0.1678283574  
H,0,-0.9291155383,-2.5211252119,-0.9989001958  
H,0,-1.2150190874,-3.1456283838,0.6672106823  
C,0,-0.0792834603,-1.251334865,0.527808781  
C,0,0.1140638576,-0.2392086895,-0.3754702767  
C,0,0.0998163801,-1.0864424974,2.0066686528  
C,0,-0.8903791504,0.8602718711,-0.0682465466  
H,0,-0.0145076554,-0.5748362067,-1.4141063057  
C,0,-2.2400675939,0.1224432116,-0.438201051  
H,0,-0.781189176,1.7724972004,-0.6742502481  
H,0,-0.8875786241,1.1454804429,0.9931813259  
C,0,-3.4607235681,0.9500519699,-0.0699484744  
H,0,-2.2333156946,0.0071759991,-1.5349291856  
H,0,-2.6375110097,-1.230652798,1.2334739902  
H,0,-3.2160262774,-1.8157268724,-0.3229550003  
B,0,2.3169713667,0.368903553,-0.6304172091  
C,0,2.7664161137,-0.9354435173,-1.4452711303  
C,0,2.8673717532,0.5344934551,0.8633570618

C,0,2.0283272794,1.7128043683,-1.4534761497  
 H,0,3.7139083251,-0.6500645076,-1.9443986913  
 H,0,2.0719290671,-1.1458555774,-2.2760269514  
 C,0,2.9993370605,-2.2053849463,-0.6222779351  
 H,0,3.0207086248,2.2012543309,-1.5316980483  
 H,0,1.427350133,2.4190198561,-0.8567982034  
 C,0,1.4335891784,1.5735723688,-2.8597018256  
 C,0,2.423426128,1.7949012611,1.6165196146  
 H,0,3.9714150257,0.543274708,0.7687890382  
 H,0,2.6581615654,-0.3673648021,1.4613216472  
 H,0,0.4356794261,-0.0774583444,2.2740984746  
 H,0,-0.8129394442,-1.3400153793,2.5663158399  
 H,0,0.8818769524,-1.7909834582,2.3370276126  
 C,0,-4.4264203305,1.1884488006,-0.9604311279  
 C,0,-3.5255469894,1.4955556806,1.3377200746  
 H,0,-5.3134946188,1.7678837592,-0.696743574  
 H,0,-4.359471253,0.8135076898,-1.9839719552  
 H,0,-3.2322472544,0.7405298869,2.0831015705  
 H,0,-2.836869813,2.3456869225,1.4543607635  
 H,0,-4.5364706962,1.8442662225,1.5807085457  
 H,0,3.287985736,-3.0661429482,-1.2428012878  
 H,0,3.7897731022,-2.0572926433,0.1281396377  
 H,0,2.0829497682,-2.4870927733,-0.0741654039  
 H,0,2.7669376874,1.8077247174,2.6615033747  
 H,0,2.8101365718,2.702473583,1.1307948294  
 H,0,1.3250327827,1.8909681124,1.6229469367  
 H,0,1.3414518013,2.5428594998,-3.3710525627  
 H,0,2.0534197126,0.9232855955,-3.4941166655  
 H,0,0.4266426914,1.1277841335,-2.8273557341

### TS1-eq-E

E(RM11) = -652.709564341

Zero-point correction= 0.434244 (Hartree/Particle)  
 Thermal correction to Energy= 0.455433  
 Thermal correction to Enthalpy= 0.456377  
 Thermal correction to Gibbs Free Energy= 0.384877  
 Sum of electronic and ZPE= -652.275320  
 Sum of electronic and thermal Energies= -652.254131  
 Sum of electronic and thermal Enthalpies= -652.253187  
 Sum of electronic and thermal Free Energies= -652.324688

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.789	81.472	150.486

C,0,-0.8792124174,-1.6335822703,-1.6543504488  
 C,0,-2.2065504021,-0.9421905719,-1.0993108722  
 H,0,-0.5193096643,-1.0782460769,-2.5308882297  
 H,0,-1.0849493148,-2.6791541501,-1.9241164437  
 C,0,-0.0184093145,-1.4159368449,-0.4592958192  
 C,0,0.3091919631,-0.0933810112,-0.28398443  
 C,0,-0.1780590435,-2.385604208,0.677986779  
 C,0,-0.7777504402,0.4997565855,0.6075446393  
 H,0,0.3577705509,0.4546979593,-1.2351730483  
 C,0,-2.0234652112,0.4237024352,-0.3627533281  
 H,0,-0.6085897379,1.5426982133,0.9101414045  
 H,0,-0.9381348912,-0.099997818,1.5143730501  
 C,0,-3.3176301569,0.7964877962,0.3430360054  
 H,0,-1.8377572335,1.1820576302,-1.1414686326  
 H,0,-2.7071348524,-1.6578569862,-0.4305523404  
 H,0,-2.8907680889,-0.7842724139,-1.9443988587  
 B,0,2.364398054,0.422797647,0.3334903339  
 C,0,3.073280259,0.3001004158,-1.1021528982  
 C,0,2.7375450008,-0.6730275578,1.4456593861  
 C,0,2.0892359136,1.9057068301,0.8870521362  
 H,0,2.5683753962,0.9124473484,-1.8682236188

H,0,3.061261123,-0.7378305476,-1.4739214006  
 C,0,4.5330953326,0.7793052302,-0.9698885798  
 H,0,3.0617490628,2.2276671217,1.3081161863  
 H,0,1.4115968258,1.8865779053,1.7576886355  
 C,0,1.6320514278,2.9577162491,-0.131761538  
 C,0,3.1561132333,-2.0505489698,0.9195018591  
 H,0,1.9246814709,-0.758020205,2.1882632256  
 H,0,3.577361007,-0.2421689583,2.0239702995  
 H,0,0.3694363576,-2.0629350631,1.5699891858  
 H,0,-1.2406050744,-2.5166444604,0.9404942939  
 H,0,0.1944965487,-3.37494429,0.3738959174  
 C,0,-4.143398445,1.7133121116,-0.1664473538  
 C,0,-3.618336274,0.0889484223,1.6436005383  
 H,0,-5.0818122525,1.9715999697,0.3282575747  
 H,0,-3.9054670279,2.2385075763,-1.0939765577  
 H,0,-3.4077213778,-0.9898528569,1.5800507878  
 H,0,-2.9935994505,0.4902198113,2.4554775205  
 H,0,-4.6688892611,0.2170193045,1.9306590809  
 H,0,5.0944452406,0.6735934093,-1.9095326084  
 H,0,4.5751096053,1.8394113042,-0.6760655587  
 H,0,5.0715840187,0.2085824026,-0.1967378758  
 H,0,3.2499590684,-2.8043232888,1.7157067223  
 H,0,2.4369924174,-2.4313027372,0.1769026954  
 H,0,4.1264586514,-1.9923831753,0.4044043102  
 H,0,1.4771275825,3.9461828699,0.324977222  
 H,0,2.3761515817,3.0789200557,-0.9332973284  
 H,0,0.6857956589,2.6722316566,-0.6196824597

### TS1-eq-F

E(RM11) = -652.710428245

Zero-point correction= 0.433848 (Hartree/Particle)  
 Thermal correction to Energy= 0.455188  
 Thermal correction to Enthalpy= 0.456132  
 Thermal correction to Gibbs Free Energy= 0.384848  
 Sum of electronic and ZPE= -652.276581  
 Sum of electronic and thermal Energies= -652.255240  
 Sum of electronic and thermal Enthalpies= -652.254296  
 Sum of electronic and thermal Free Energies= -652.325580

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.635	81.657	150.029

C,0,-0.8185239082,-1.8033440579,1.2877698927  
 C,0,-2.172643291,-1.0873845385,0.8508178055  
 H,0,-0.5836460791,-2.6064032543,0.5760406481  
 H,0,-0.9153081237,-2.2124474265,2.3034587931  
 C,0,0.0837329303,-0.6287132457,1.1264894324  
 C,0,0.2602966489,-0.2802157813,-0.18869237  
 C,0,0.1746077465,0.3553059966,2.2519226  
 C,0,-0.8438356835,0.7053322822,-0.5491141405  
 H,0,0.2068581577,-1.1448438689,-0.8643966851  
 C,0,-2.110067615,-0.2358194929,-0.456232761  
 H,0,-0.7663017214,1.1441420642,-1.555146485  
 H,0,-0.928795136,1.5244842576,0.177749791  
 C,0,-3.4071153745,0.5387314936,-0.6260077292  
 H,0,-2.0320331952,-0.9439989036,-1.2974193735  
 H,0,-2.5011504733,-0.4484437326,1.6851430539  
 H,0,-2.948538347,-1.8555517421,0.7261609251  
 B,0,2.4352047175,0.2250445954,-0.6068097148  
 C,0,2.7061996406,-1.08293669,-1.4995786131  
 C,0,3.1575775212,0.2869476755,0.8229217675  
 C,0,2.2214591201,1.6052048159,-1.3928611349  
 H,0,2.0601479097,-1.1013718794,-2.3938560024  
 H,0,2.4891386284,-2.0066167224,-0.9349749827  
 C,0,4.1811299331,-1.1111393769,-1.949665408

H,0,1.4535780576,1.4915617135,-2.1765538203  
 H,0,3.1637540376,1.767674997,-1.9517880629  
 C,0,1.9386544264,2.8468260894,-0.5401293967  
 C,0,3.3273557246,-1.0467132602,1.5581986618  
 H,0,2.6876360225,1.0340543847,1.4830034525  
 H,0,4.1606322219,0.710581657,0.6146387324  
 H,0,0.4047113937,1.3672126875,1.8952746244  
 H,0,-0.7383872622,0.3688292646,2.8654887779  
 H,0,1.0024806525,0.0461493715,2.9119100753  
 C,0,-4.3319978867,0.1495293258,-1.5066208383  
 C,0,-3.5946427315,1.7682318198,0.231962543  
 H,0,-5.2721457442,0.6926565393,-1.6220597694  
 H,0,-4.1770878454,-0.7236080032,-2.1441324855  
 H,0,-3.2841659466,1.5923225477,1.2731123095  
 H,0,-2.9837728008,2.6007807023,-0.1480222059  
 H,0,-4.6423264757,2.0920328242,0.2348483517  
 H,0,4.4146092292,-2.00453372,-2.5468198934  
 H,0,4.4260802927,-0.2322000183,-2.5641860397  
 H,0,4.8639909481,-1.1030229602,-1.086240652  
 H,0,3.7674894338,-0.928317592,2.559837067  
 H,0,2.3582045301,-1.5625018698,1.6778578664  
 H,0,3.973469671,-1.7344781627,0.9933899912  
 H,0,1.7857819142,3.7513918368,-1.146780099  
 H,0,1.0357181144,2.7084053647,0.0758813368  
 H,0,2.7695667665,3.0495796727,0.1514436161

### TS1-eq-G

E(RM11) = -652.708794120

Zero-point correction= 0.433912 (Hartree/Particle)  
 Thermal correction to Energy= 0.455354  
 Thermal correction to Enthalpy= 0.456298  
 Thermal correction to Gibbs Free Energy= 0.384790  
 Sum of electronic and ZPE= -652.274883  
 Sum of electronic and thermal Energies= -652.253440  
 Sum of electronic and thermal Enthalpies= -652.252496  
 Sum of electronic and thermal Free Energies= -652.324004

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.739	81.731	150.500

C,0,-0.9610379671,-1.7809440816,1.4970764031  
 C,0,-2.2851479439,-1.0748353829,0.9629366167  
 H,0,-0.7369120245,-2.6534269982,0.8687787186  
 H,0,-1.0916651779,-2.0891004932,2.5441016892  
 C,0,-0.0245910741,-0.6497429345,1.2489746165  
 C,0,0.199673971,-0.4297763987,-0.0875829269  
 C,0,0.0813360707,0.4172726992,2.2916960476  
 C,0,-0.8828224338,0.5310972446,-0.5724215272  
 H,0,0.139790888,-1.3578957056,-0.6720791403  
 C,0,-2.1680868002,-0.3713428754,-0.4235951939  
 H,0,-0.7695256747,0.8623330436,-1.6155544167  
 H,0,-0.9648555907,1.4226933066,0.0649140403  
 C,0,-3.4442283547,0.3986727172,-0.7230954203  
 H,0,-2.0743521365,-1.1677570562,-1.1806996383  
 H,0,-2.6052168079,-0.3397237782,1.7177696678  
 H,0,-3.0824097488,-1.8289646083,0.9054325134  
 B,0,2.3429303281,0.1547923762,-0.5843065918  
 C,0,2.5755035523,-1.0993046349,-1.5626064075  
 C,0,3.1173565854,0.1240144355,0.8212741609  
 C,0,2.1309739144,1.5855620851,-1.2768497891  
 H,0,2.357493811,-2.0452139923,-1.0378140953  
 H,0,3.6663600183,-1.1293584767,-1.7493329473  
 C,0,1.8501330853,-1.0543310408,-2.9137136278  
 H,0,1.3571244727,1.5443044354,-2.0606259878  
 H,0,3.0730392784,1.7568890449,-1.8367904337

C,0,1.8803542469,2.7824079401,-0.353369111  
 C,0,4.5934351431,0.5170644152,0.6079214421  
 H,0,3.0704354599,-0.8767917023,1.28454962563  
 H,0,2.6780535339,0.8281434434,1.5465766631  
 H,0,0.3530572655,1.3888710221,1.8607573355  
 H,0,-0.8361936016,0.5078967996,2.8918253622  
 H,0,0.8915865537,0.1321431209,2.983569357  
 C,0,-4.3403471521,-0.0677925814,-1.5959790645  
 C,0,-3.6448917041,1.7123780876,-0.0041627738  
 H,0,-5.2658353547,0.4724579226,-1.8051480694  
 H,0,-4.1752894485,-1.0042227786,-2.1331434752  
 H,0,-3.3998017761,1.6355435256,1.0659979326  
 H,0,-2.9912230979,2.489185598,-0.4282984889  
 H,0,-4.681919276,2.0570446279,-0.0950376953  
 H,0,2.0164050793,-1.961424456,-3.5129504983  
 H,0,0.7612870358,-0.9392215512,-2.7841210906  
 H,0,2.1884684611,-0.1970789567,-3.5136752135  
 H,0,5.1617823465,0.5210482065,1.5493612404  
 H,0,5.0987941861,-0.1791182663,-0.077251624  
 H,0,4.6769322782,1.5228278969,0.167954062  
 H,0,1.815508774,3.7325875745,-0.9033562715  
 H,0,0.9353789331,2.6644402013,0.1998516163  
 H,0,2.679644813,2.8878173497,0.3955483066

### TS1-eq-H

E(RM11) = -652.711559237

Zero-point correction= 0.434140 (Hartree/Particle)  
 Thermal correction to Energy= 0.455249  
 Thermal correction to Enthalpy= 0.456193  
 Thermal correction to Gibbs Free Energy= 0.386078  
 Sum of electronic and ZPE= -652.277419  
 Sum of electronic and thermal Energies= -652.256310  
 Sum of electronic and thermal Enthalpies= -652.255366  
 Sum of electronic and thermal Free Energies= -652.325481

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.673	81.485	147.569

C,0,0.5337601199,-1.9143203378,1.3356288144  
 C,0,1.9318709739,-1.3819956978,0.7922157917  
 H,0,0.3279746905,-1.4689770702,2.3182881874  
 H,0,0.5492837823,-3.0109290913,1.4099695963  
 C,0,-0.3200189701,-1.3331124466,0.2616667703  
 C,0,-0.4086014043,0.0350848431,0.3395409413  
 C,0,-0.4659446579,-2.0975897441,-1.01573383  
 C,0,0.759688772,0.616089216,-0.4495063695  
 H,0,-0.3449498178,0.3908766393,1.3770132886  
 C,0,1.9842573461,0.1288746966,0.4282140674  
 H,0,0.7651633704,1.7136429255,-0.5152443475  
 H,0,0.8315449966,0.2113270944,-1.4691205397  
 C,0,3.2941850448,0.5002884106,-0.2453106738  
 H,0,1.920837413,0.6981761146,1.3703747498  
 H,0,2.1897702614,-1.9784198273,-0.0962962165  
 H,0,2.702760664,-1.5940886783,1.5472678766  
 B,0,-2.4716004691,0.8316129186,-0.1536443554  
 C,0,-2.7101086664,1.4595358411,1.3066009469  
 C,0,-3.330121231,-0.4689202676,-0.5283191247  
 C,0,-2.1315502567,1.8570288999,-1.3382019772  
 H,0,-2.5459335301,0.7017941773,2.0918977853  
 H,0,-3.7950013148,1.6792614303,1.357854197  
 C,0,-1.9271797419,2.7384620427,1.6304900611  
 H,0,-1.2820151322,2.5069983306,-1.0721250409  
 H,0,-3.0001778533,2.5449714612,-1.3687334609  
 C,0,-1.9234150679,1.2648060677,-2.7361303763  
 C,0,-3.6199405734,-1.4495233647,0.6118949453

H,0,-2.9038091356,-1.0015975374,-1.3937985116  
H,0,-4.2919912304,-0.0694250285,-0.9070690696  
H,0,-0.6114893289,-1.435433123,-1.8784747973  
H,0,0.3793665503,-2.7777823519,-1.1947348486  
H,0,-1.3713699237,-2.7228430833,-0.9305813274  
C,0,4.004503664,1.5498221691,0.175029229  
C,0,3.7346114477,-0.3334989647,-1.4264095135  
H,0,4.9216695664,1.8564615513,-0.3317210629  
H,0,3.6880978514,2.1400036534,1.0376349155  
H,0,4.1467486307,-1.2984398882,-1.0949343785  
H,0,2.8942795354,-0.5552001274,-2.1019473766  
H,0,4.5114498507,0.1826715081,-2.0030728903  
H,0,-2.1053813052,3.0947680176,2.6555802637  
H,0,-0.8408505337,2.5844044138,1.5188500026  
H,0,-2.2009925323,3.5538123246,0.9452487937  
H,0,-4.1759598062,-2.3384195149,0.2780933312  
H,0,-2.683200888,-1.7992266302,1.0815154989  
H,0,-4.2084932729,-0.9711760495,1.4080913454  
H,0,-1.7183122273,2.0354837658,-3.4935454831  
H,0,-1.0736161935,0.5638016035,-2.7488797093  
H,0,-2.808265887,0.7020410773,-3.0680225181

### *TSl-eq-I*

E(RM11) = -652.711020047

Zero-point correction= 0.434432 (Hartree/Particle)  
Thermal correction to Energy= 0.455564  
Thermal correction to Enthalpy= 0.456508  
Thermal correction to Gibbs Free Energy= 0.385995  
Sum of electronic and ZPE= -652.276588  
Sum of electronic and thermal Energies= -652.255456  
Sum of electronic and thermal Enthalpies= -652.254512  
Sum of electronic and thermal Free Energies= -652.325025

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.871	81.346	148.407

C,0,-1.0901020899,-1.9514732948,1.2399143559  
C,0,-2.4436334748,-1.2041145807,0.858935846  
H,0,-0.8667166854,-2.7091641788,0.4764323724  
H,0,-1.180835186,-2.4232399734,2.2284942805  
C,0,-0.1843179442,-0.771339338,1.1460626616  
C,0,-0.0128267205,-0.3395174456,-0.1449356665  
C,0,-0.0840072138,0.141565259,2.3281875827  
C,0,-1.1232154357,0.6606524717,-0.4417427799  
H,0,-0.0597100641,-1.1597021201,-0.8754026405  
C,0,-2.3840528383,-0.2902906107,-0.4040342196  
H,0,-1.0477937873,1.1619044402,-1.4186190586  
H,0,-1.2115389672,1.4322790639,0.3350870337  
C,0,-3.6847581707,0.4846065461,-0.5441031817  
H,0,-2.2973237498,-0.9561166328,-1.2785152509  
H,0,-2.7567771802,-0.603962538,1.7272286165  
H,0,-3.2270446777,-1.9590962178,0.7045218699  
B,0,2.1604422471,0.2107385742,-0.5109250627  
C,0,2.5135528252,-1.1408763646,-1.3033895169  
C,0,2.8537355579,0.4118903705,0.9209755024  
C,0,1.9096769843,1.5194090315,-1.4044597337  
H,0,3.5013692966,-0.9515183783,-1.7668005252  
H,0,1.8318187125,-1.2891319496,-2.1578186131  
C,0,2.6031242747,-2.41163540296,-0.4592437902  
H,0,1.1564612739,1.3196411628,-2.1852295714  
H,0,2.8507441024,1.6776672433,-1.9663950853  
C,0,1.5684261435,2.8031690105,-0.6392162021  
C,0,4.3533923509,0.6958146645,0.6968338961  
H,0,2.7514796361,-0.4822173224,1.5587092246  
H,0,2.4178604682,1.2526342189,1.4849085829

H,0,0.1392391021,1.173569777,2.0283814218  
H,0,-0.9886915039,0.1142870034,2.9533495495  
H,0,0.7543922071,-0.2006180551,2.9566678271  
C,0,-4.6028817305,0.1301815118,-1.4462944953  
C,0,-3.8838655983,1.6721332572,0.3683895386  
H,0,-5.5452252254,0.6731206415,-1.5430427701  
H,0,-4.4397146513,-0.7130107928,-2.1210398813  
H,0,-3.5906827027,1.4454138151,1.4047197647  
H,0,-3.2660193283,2.5208672677,0.0385658889  
H,0,-4.9310879372,1.997484793,0.3704222939  
H,0,2.7926650708,-3.3147074502,-1.0645221459  
H,0,3.4116405414,-2.3426611645,0.2834383114  
H,0,1.6699955596,-2.5857741924,0.1050740261  
H,0,4.8909632416,0.8667023162,1.6406854877  
H,0,4.8435487253,-0.1464548325,0.1844314551  
H,0,4.49955172,1.5875423001,0.0671308376  
H,0,1.3293556485,3.6450322614,-1.3054221747  
H,0,0.7040784283,2.650854923,0.0273502261  
H,0,2.4083773654,3.1162978887,-0.0008969776

### *TSl-eq-J*

E(RM11) = -652.710834013

Zero-point correction= 0.433793 (Hartree/Particle)  
Thermal correction to Energy= 0.455224  
Thermal correction to Enthalpy= 0.456169  
Thermal correction to Gibbs Free Energy= 0.384397  
Sum of electronic and ZPE= -652.277041  
Sum of electronic and thermal Energies= -652.255610  
Sum of electronic and thermal Enthalpies= -652.254665  
Sum of electronic and thermal Free Energies= -652.326437

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.658	81.714	151.055

C,0,-1.0656661569,-2.2247873573,0.7466639211  
C,0,-2.3865271905,-1.3642906588,0.517938193  
H,0,-0.8489223348,-2.8105430118,-0.1572262162  
H,0,-1.1948493565,-2.8958822112,1.6081770944  
C,0,-0.114005283,-1.0883365175,0.9224040234  
C,0,0.0815926328,-0.4054056093,-0.2458731762  
C,0,-0.0362694734,-0.4473784696,2.2766442453  
C,0,-0.9540979312,0.6990482512,-0.3336039028  
H,0,0.0263727056,-1.0512860399,-1.1340106655  
C,0,-2.2727439722,-0.1681649765,-0.4829547718  
H,0,-0.8517257506,1.3714185854,-1.198453375  
H,0,-0.9883261565,1.3105519757,0.5788428086  
C,0,-3.5253046731,0.6889702371,-0.3967773127  
H,0,-2.2332237084,-0.6023569118,-1.4958448701  
H,0,-2.7186719342,-0.9871015208,1.4971774934  
H,0,-3.1832923091,-2.0318276389,0.1609971981  
B,0,2.3200445337,0.2677033275,-0.5499829279  
C,0,2.8655876397,-1.1672207533,-0.9961576147  
C,0,2.7573527774,0.830461879,0.8812902656  
C,0,2.0012539333,1.3521416079,-1.6818062951  
H,0,3.838749761,-0.9612496211,-1.4862933469  
H,0,2.2424438185,-1.5951151142,-1.7989355408  
C,0,3.0731566075,-2.1969730388,0.1179221228  
H,0,2.9663019125,1.869003106,-1.8517825875  
H,0,1.3385098825,2.1388608315,-1.283057668  
C,0,1.479437501,0.8414052172,-3.0304515777  
C,0,4.25049128,1.2199687564,0.834362492  
H,0,2.6199071738,0.079640955,1.6760677333  
H,0,2.1646626598,1.7162211645,1.1688423759  
H,0,0.2880104277,0.5979609364,2.2195084725  
H,0,-0.99012365,-0.5126706008,2.8220429992

H,0,0.7108687536,-0.9928710128,2.8768414136  
C,0,-4.4756703691,0.6214771879,-1.332001311  
C,0,-3.6383419141,1.6231643718,0.7856193721  
H,0,-5.3843651221,1.2231330146,-1.2643197397  
H,0,-4.3738705172,-0.0360760817,-2.1980380769  
H,0,-3.3148046637,1.1400513528,1.7202128348  
H,0,-2.9967705162,2.5054013173,0.6422748639  
H,0,-4.669176344,1.9736700643,0.9165809807  
H,0,3.4378200261,-3.1625223082,-0.2613561578  
H,0,3.7975530144,-1.8396750078,0.8651591123  
H,0,2.1265323898,-2.386358023,0.6530235646  
H,0,4.6097121367,1.5949125732,1.8034195475  
H,0,4.8767817229,0.3563897605,0.561715695  
H,0,4.4371598036,2.0057320323,0.0877508679  
H,0,1.3151418325,1.6563736705,-3.7503291164  
H,0,2.1878489532,0.135947706,-3.4887936228  
H,0,0.5227400173,0.306678573,-2.9185132076

### TSI-eq-K

E(RM11) = -652.711106318

Zero-point correction= 0.433670 (Hartree/Particle)  
Thermal correction to Energy= 0.455155  
Thermal correction to Enthalpy= 0.456100  
Thermal correction to Gibbs Free Energy= 0.384449  
Sum of electronic and ZPE= -652.277436  
Sum of electronic and thermal Energies= -652.255951  
Sum of electronic and thermal Enthalpies= -652.255007  
Sum of electronic and thermal Free Energies= -652.326657

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.614	81.795	150.802

C,0,-0.812257427,-1.7433557305,1.5706237897  
C,0,-2.1547605033,-1.0852351633,1.0205735309  
H,0,-0.5964624507,-2.6592398134,1.0035695186  
H,0,-0.9131580114,-1.9777402737,2.6402204375  
C,0,0.1157220861,-0.6294469663,1.2170120066  
C,0,0.2853935074,-0.5109805074,-0.133771451  
C,0,0.2087171225,0.5344367398,2.1573801556  
C,0,-0.7825397233,0.4253381328,-0.6685166983  
H,0,0.2489093631,-1.4746851883,-0.6626250605  
C,0,-2.0769015781,-0.4480176256,-0.4046645024  
H,0,-0.7070884913,0.6650951339,-1.7396085113  
H,0,-0.8230363386,1.369637612,-0.107377986  
C,0,-3.3510686924,0.3321445824,-0.6851088927  
H,0,-2.0301267147,-1.2826540726,-1.1238332945  
H,0,-2.4798485142,-0.3215286907,1.7434391839  
H,0,-2.9425027496,-1.8515694302,1.008887841  
B,0,2.5106440483,0.2050790172,-0.5544638128  
C,0,2.7690608372,-0.9482060095,-1.6340796765  
C,0,3.274005206,0.0841918856,0.8450179941  
C,0,2.1685763732,1.6805211956,-1.0704303051  
H,0,2.5674995496,-1.9398687471,-1.1952571258  
H,0,3.8640200828,-0.9434900056,-1.8078123032  
C,0,2.0443369587,-0.8071836417,-2.9778337502  
H,0,1.7665599251,2.3151664043,-0.2618182175  
H,0,1.4125017462,1.6715266218,-1.8714636683  
C,0,3.457390621,2.3303284107,-1.6189296554  
C,0,3.4031820909,-1.312193351,1.4620837771  
H,0,2.8729238599,0.7973807067,1.5838906832  
H,0,4.2915718537,0.4640476322,0.6257883493  
H,0,0.5493940408,1.4441121314,1.6469774422  
H,0,-0.7430907009,0.7310759753,2.6744598223  
H,0,0.9510596869,0.2905229091,2.935901599  
C,0,-4.30298475,-0.1608536927,-1.4809055892

C,0,-3.4830748534,1.6884608497,-0.0321207394  
H,0,-5.2266433677,0.3893113892,-1.6715836659  
H,0,-4.1870788015,-1.1300151601,-1.9709162575  
H,0,-3.142349912,1.6726060074,1.014502996  
H,0,-2.8650387068,2.4312957364,-0.5582716372  
H,0,-4.5220465998,2.0388136474,-0.0517157648  
H,0,2.2751552697,-1.631181183,-3.6683774277  
H,0,0.9516027941,-0.7886589758,-2.8399128214  
H,0,2.3170881204,0.1320069887,-3.4818748247  
H,0,3.957319277,-1.3032090552,2.4121292479  
H,0,2.4095336822,-1.7487752119,1.6604162875  
H,0,3.925356713,-2.0016405665,0.7829614446  
H,0,3.270387125,3.3315235417,-2.0330352574  
H,0,4.2184861667,2.435592507,-0.8319915754  
H,0,3.8998364092,1.7190501636,-2.4211293349

### TSI-eq-L

E(RM11) = -652.710490338

Zero-point correction= 0.433850 (Hartree/Particle)  
Thermal correction to Energy= 0.455268  
Thermal correction to Enthalpy= 0.456212  
Thermal correction to Gibbs Free Energy= 0.384607  
Sum of electronic and ZPE= -652.276641  
Sum of electronic and thermal Energies= -652.255222  
Sum of electronic and thermal Enthalpies= -652.254278  
Sum of electronic and thermal Free Energies= -652.325884

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.685	81.671	150.707

C,0,-1.1539537168,-2.3291402081,-0.4168036645  
C,0,-2.4651094124,-1.4450802746,-0.2372319092  
H,0,-0.8955483312,-2.3879861893,-1.4833313462  
H,0,-1.3186594977,-3.3388007819,-0.0134183802  
C,0,-0.2127715165,-1.452559489,0.3420153133  
C,0,0.021305126,-0.2769476526,-0.3145834002  
C,0,-0.1706581024,-1.5847688041,1.8355393112  
C,0,-1.0250263753,0.7348002678,0.116965677  
H,0,0.0080949623,-0.3810383494,-1.4095154724  
C,0,-2.310379235,0.0855158951,-0.5270360402  
H,0,-0.8788762444,1.7548752515,-0.2682595726  
H,0,-1.1362458041,0.7832165685,1.209718018  
C,0,-3.6028049567,0.8128969182,-0.1884091781  
H,0,-2.1793186314,0.1812054092,-1.6216440812  
H,0,-2.8277284124,-1.5663294951,0.7962292936  
H,0,-3.2424568171,-1.8598882953,-0.8939668627  
B,0,2.3116437107,0.2688579138,-0.2802173349  
C,0,2.8252534576,-0.9445419432,-1.1861175387  
C,0,2.6911844691,0.2704405676,1.2710381818  
C,0,2.0742279782,1.6766893403,-1.0021092578  
H,0,3.8176702242,-0.6242176985,-1.5596013218  
H,0,2.2059183901,-1.0361062664,-2.0951466708  
C,0,2.9731809272,-2.3071064515,-0.5030782195  
H,0,1.4135598787,2.3301065004,-0.409430481  
H,0,1.5998638039,1.5552199233,-1.9908415786  
C,0,3.4337383139,2.3868277129,-1.1782606286  
C,0,2.1161088018,1.4196312083,2.108021031  
H,0,3.7984393878,0.3169886625,1.3021201629  
H,0,2.4523514204,-0.7019576937,1.7321199414  
H,0,0.1295013102,-0.6493689919,2.3237907427  
H,0,-1.1289631453,-1.9309627068,2.2503001092  
H,0,0.5834250956,-2.34706948,2.0944137828  
C,0,-3.6653812336,1.8334794195,0.6704375266  
C,0,-4.8405224926,0.3259875168,-0.9080820599  
H,0,-4.6140061897,2.3375951035,0.8648012657  
H,0,-2.7913976999,2.209332678,1.2021469456

H,0,-4.6438267391,0.1980256711,-1.9835416666  
H,0,-5.1674252302,-0.6498595303,-0.5190511134  
H,0,-5.6718622197,1.0315984836,-0.7893963998  
H,0,3.321109893,-3.0902759153,-1.1922043488  
H,0,3.6872605908,-2.2596731311,0.3322548425  
H,0,2.0078959863,-2.6408207326,-0.0853245958  
H,0,2.358982318,1.3282076102,3.1768884009  
H,0,2.4992201618,2.3920863957,1.7647680096  
H,0,1.0188659587,1.4675993395,2.015971  
H,0,3.3239493594,3.3771963283,-1.6428271243  
H,0,3.9359353569,2.5308114727,-0.2089364958  
H,0,4.1139069909,1.7993001923,-1.8123646425

### TS1-eq-M

E(RM11) = -652.709163618

Zero-point correction= 0.433740 (Hartree/Particle)  
Thermal correction to Energy= 0.455270  
Thermal correction to Enthalpy= 0.456215  
Thermal correction to Gibbs Free Energy= 0.384020  
Sum of electronic and ZPE= -652.275423  
Sum of electronic and thermal Energies= -652.253893  
Sum of electronic and thermal Enthalpies= -652.252949  
Sum of electronic and thermal Free Energies= -652.325144

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.687	81.714	151.947

C,0,-1.1041054203,2.3195447498,-0.4083926592  
C,0,-2.4262040458,1.4520092226,-0.2317436153  
H,0,-0.7959879732,2.713928429,0.5698770748  
H,0,-1.2816379197,3.1471823957,-1.1099655548  
C,0,-0.2134276357,1.2187541522,-0.8828182469  
C,0,0.0480848912,0.3168512924,0.1095825404  
C,0,-0.2317783057,0.856143455,-2.3356124065  
C,0,-1.0290904592,-0.7516343857,0.1061847012  
H,0,0.1059488151,0.7763760656,1.1070191364  
C,0,-2.2691691378,0.111351156,0.5600275742  
H,0,-0.8644128055,-1.5869004493,0.8035499544  
H,0,-1.2127029236,-1.1615426561,-0.8967660735  
C,0,-3.5835744181,-0.6549295719,0.5573405626  
H,0,-2.0762359416,0.392953841,1.6126424985  
H,0,-2.827060717,1.2182586394,-1.2316156988  
H,0,-3.1748654375,2.0821688552,0.2684246001  
B,0,2.3351107623,-0.169060625,-0.0404169594  
C,0,2.9861179161,1.2951231777,-0.1032238196  
C,0,2.4947169933,-1.0432600765,-1.3701710384  
C,0,2.2915255516,-0.9300596276,1.3676547344  
H,0,2.733000144,1.7880947625,-1.0580080908  
H,0,4.0775607783,1.1157464835,-0.1641527596  
C,0,2.7121524486,2.2436436386,1.0690523413  
H,0,1.6102565114,-1.7961995794,1.3428998573  
H,0,1.9412358834,-0.2770804223,2.1836236865  
C,0,3.718324066,-1.4182620367,1.6968584682  
C,0,1.8123346384,-2.4152965303,-1.4024987624  
H,0,3.5895147618,-1.1894970399,-1.4618816794  
H,0,2.2321206632,-0.4561943214,-2.2654587274  
H,0,-0.0849274306,-0.2201219643,-2.4942038973  
H,0,-1.1484252109,1.1906596048,-2.8420320247  
H,0,0.6140295493,1.3722508247,-2.8221069392  
C,0,-3.7000524156,-1.9075625656,0.1094282996  
C,0,-4.7771730707,0.0818665112,1.1227510615  
H,0,-4.6614925768,-2.4231747101,0.1485010982  
H,0,-2.8592340028,-2.4664958794,-0.3009314922  
H,0,-4.5210707401,0.5722695497,2.074386655  
H,0,-5.1203870558,0.8680040622,0.4337531586

H,0,-5.6171575457,-0.6009304738,1.2997790718  
H,0,3.2517157066,3.196900322,0.9715812931  
H,0,1.6397357293,2.4836830779,1.1451005984  
H,0,3.012454514,1.7912094486,2.0262225437  
H,0,1.9991259492,-2.9566061654,-2.3414465337  
H,0,2.1668234695,-3.0531359777,-0.5789562411  
H,0,0.7219500188,-2.3217585217,-1.2839000275  
H,0,3.7604635039,-1.9572909295,2.6541156115  
H,0,4.0966029997,-2.097707321,0.9171809077  
H,0,4.4210745945,-0.5729098268,1.7616724583

### TS1-eq-N

E(RM11) = -652.708980169

Zero-point correction= 0.433820 (Hartree/Particle)  
Thermal correction to Energy= 0.455238  
Thermal correction to Enthalpy= 0.456182  
Thermal correction to Gibbs Free Energy= 0.384762  
Sum of electronic and ZPE= -652.275160  
Sum of electronic and thermal Energies= -652.253742  
Sum of electronic and thermal Enthalpies= -652.252798  
Sum of electronic and thermal Free Energies= -652.324218

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.666	81.731	150.315

C,0,-1.1253807235,-1.6160610233,-1.8822978879  
C,0,-2.4233349338,-0.991464635,-1.2048654308  
H,0,-0.8024658197,-0.9723432521,-2.7119512827  
H,0,-1.3420266977,-2.6287365865,-2.2516848626  
C,0,-0.2149616816,-1.5174775446,-0.7043362973  
C,0,0.0994638535,-0.218718893,-0.4077963618  
C,0,-0.2624108419,-2.6120446513,0.3174791598  
C,0,-0.9602627124,0.3136717218,0.5460898397  
H,0,0.1450942734,0.4168348762,-1.3031983759  
C,0,-2.2105117348,0.3382766563,-0.4108483013  
H,0,-0.7635558677,1.3201369391,0.945226569  
H,0,-1.1435286196,-0.3680103388,1.3888400994  
C,0,-3.5044487778,0.7496353754,0.2747826792  
H,0,-1.9966621351,1.1201749376,-1.1649096937  
H,0,-2.85426826,-1.7387995479,-0.5189387596  
H,0,-3.1664610168,-0.8260927253,-1.9973565309  
B,0,2.3100518536,0.1541964437,0.1843601701  
C,0,2.9419896446,-0.0584262621,-1.2728071305  
C,0,2.6170959348,-0.9693539313,1.2805887171  
C,0,2.0898271644,1.6526636548,0.7034152129  
H,0,2.3761916293,0.4837715203,-2.0492428392  
H,0,2.925435873,-1.1237444975,-1.5589019302  
C,0,4.3980154172,0.4504651704,-1.282434314  
H,0,3.0789049109,1.9367917012,1.1181068022  
H,0,1.4149123487,1.6788869514,1.5747853931  
C,0,1.6621874423,2.707069084,-0.3250996395  
C,0,1.9928299643,-0.7679724455,2.6671452763  
H,0,3.7195203817,-0.9794922561,1.3864861382  
H,0,2.3756113336,-1.9693439624,0.8837524314  
H,0,0.0097789642,-2.2564826666,1.3186044118  
H,0,-1.2414342488,-3.1123703385,0.3488976762  
H,0,0.4771713542,-3.3781463267,0.0300064494  
C,0,-3.6061590416,0.9405537308,1.5924713626  
C,0,-4.6943118659,0.9569076039,-0.6352285056  
H,0,-4.5527596861,1.2559404758,2.035637642  
H,0,-2.7669458392,0.8019893113,2.2741743083  
H,0,-4.4168344618,1.5611043197,-1.5125024904  
H,0,-5.0784893579,-0.0035638636,-1.0099670683  
H,0,-5.5121985302,1.4645926106,-0.1094682224  
H,0,4.8805839293,0.3082426564,-2.2601456214



H,0,4.4453093222,1.5240180483,-1.0433627916  
H,0,5.0108397196,-0.075356202,-0.5346166797  
H,0,2.1711429758,-1.6194459298,3.3404650052  
H,0,2.3995895841,0.1291682388,3.15593587  
H,0,0.9030472764,-0.6171112167,2.5981968279  
H,0,1.6505517402,3.7220224329,0.0980433561  
H,0,2.3378189236,2.7189456945,-1.19351245  
H,0,0.6493996388,2.5059739314,-0.7092087307

### TS1-eq-O

E(RM11) = -652.711483070

Zero-point correction= 0.433732 (Hartree/Particle)  
Thermal correction to Energy= 0.454989  
Thermal correction to Enthalpy= 0.455934  
Thermal correction to Gibbs Free Energy= 0.385214  
Sum of electronic and ZPE= -652.277751  
Sum of electronic and thermal Energies= -652.256494  
Sum of electronic and thermal Enthalpies= -652.255549  
Sum of electronic and thermal Free Energies= -652.326269

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.510	81.726	148.842

C,0,-0.8644411397,-2.2342603169,-0.9376945966  
C,0,-2.227263755,-1.5107330174,-0.5493544482  
H,0,-0.6111137836,-2.0007029584,-1.9811089545  
H,0,-0.9619452851,-3.3217364456,-0.8072466692  
C,0,0.0241509348,-1.5244756931,0.0290847262  
C,0,0.1847568719,-0.2063250455,-0.303430786  
C,0,0.0953856789,-2.0432592677,1.4331825605  
C,0,-0.9292435785,0.5909504143,0.3560712383  
H,0,0.1609585844,-0.0432705884,-1.3901054334  
C,0,-2.1720324083,0.0487578477,-0.4463471176  
H,0,-0.8492342865,1.6828963551,0.2438285165  
H,0,-1.0361986697,0.3550071206,1.4246147981  
C,0,-3.5065338181,0.5887297453,0.0442500814  
H,0,-2.0471888204,0.4238687417,-1.480625979  
H,0,-2.5710950151,-1.9092431979,0.4189735443  
H,0,-2.9831777839,-1.797894762,-1.2934838708  
B,0,2.3672353342,0.5774602249,-0.0513649622  
C,0,2.9721228178,-0.1995363894,-1.3129440244  
C,0,2.7916532011,0.0765387997,1.4063551745  
C,0,1.9948619919,2.1248925597,-0.2186567857  
H,0,3.9189248555,0.3274921632,-1.5463617805  
H,0,2.3471473552,-0.0483821543,-2.2090672551  
C,0,3.2651346513,-1.6901863787,-1.1210353643  
H,0,2.9364696713,2.6584479839,0.0226532124  
H,0,1.2937613573,2.4480694481,0.5684297682  
C,0,1.4978870929,2.5934592918,-1.5914681404  
C,0,2.1776722015,0.8295758388,2.5931804571  
H,0,3.8940521455,0.1831297226,1.443942923  
H,0,2.6256298142,-1.0081971954,1.5090942041  
H,0,0.2977364775,-1.2478795335,2.1608897989  
H,0,-0.8121459445,-2.5941155583,1.7205745946  
H,0,0.9344179334,-2.7575692159,1.489431865  
C,0,-3.6307345066,1.358850889,1.128102603  
C,0,-4.7133199105,0.2191045517,-0.788817385  
H,0,-4.6086066269,1.7405563405,1.4279945571  
H,0,-2.780756348,1.6446593156,1.7477343809  
H,0,-4.510373674,0.3659796851,-1.8607033503  
H,0,-4.9813391621,-0.8390523869,-0.6505341735  
H,0,-5.5848916973,0.8260720094,-0.5148573891  
H,0,3.6664035153,-2.1629331027,-2.0292488804  
H,0,3.9921295977,-1.8547461921,-0.3122577399  
H,0,2.3454677235,-2.2346248189,-0.8441249417

H,0,2.4446518334,0.3823047197,3.5620483913  
H,0,2.5084032482,1.878169868,2.6118582736  
H,0,1.077459524,0.8517953641,2.5259576335  
H,0,1.3354697462,3.680553927,-1.626811057  
H,0,2.2168602325,2.3414780595,-2.3846068019  
H,0,0.5422296525,2.1142944218,-1.8590597832

### TS1-eq-P

E(RM11) = -652.708637537

Zero-point correction= 0.434540 (Hartree/Particle)  
Thermal correction to Energy= 0.455658  
Thermal correction to Enthalpy= 0.456602  
Thermal correction to Gibbs Free Energy= 0.386041  
Sum of electronic and ZPE= -652.274098  
Sum of electronic and thermal Energies= -652.252980  
Sum of electronic and thermal Enthalpies= -652.252036  
Sum of electronic and thermal Free Energies= -652.322596

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.930	81.392	148.507

C,0,1.0464797105,-1.7219094163,1.7069574819  
C,0,2.3875282376,-1.082873557,1.1298404646  
H,0,0.7072998218,-1.1356692804,2.5718060943  
H,0,1.2254311325,-2.7655679593,2.002464475  
C,0,0.1800756635,-1.5121378564,0.5121038796  
C,0,-0.1014944998,-0.1850583077,0.3050030215  
C,0,0.2947681033,-2.5193461562,-0.5968515429  
C,0,1.0008073738,0.3524656052,-0.6026232189  
H,0,-0.1326471622,0.3872873531,1.2423952819  
C,0,2.2353986108,0.2770257078,0.3710425503  
H,0,0.8567028801,1.3871057246,-0.9436568207  
H,0,1.1528091163,-0.2848824386,-1.48538552  
C,0,3.557093859,0.658109261,-0.2779569167  
H,0,2.0394584815,1.041388784,1.1476402255  
H,0,2.8601639336,-1.8124025078,0.454172374  
H,0,3.0774456968,-0.9466542464,1.9741010628  
B,0,-2.1562801712,0.4257764695,-0.3190220333  
C,0,-2.8706433248,0.2882815214,1.1103438848  
C,0,-2.5443636459,-0.6287003396,-1.4646298016  
C,0,-1.8138620177,1.9077377382,-0.8315942802  
H,0,-2.335821843,0.8456667664,1.8975633492  
H,0,-2.9105608499,-0.7617545409,1.4432618046  
C,0,-4.3049492383,0.8446374496,0.9987727364  
H,0,-2.7766982505,2.282832154,-1.2306399144  
H,0,-1.1496263333,1.88232647,-1.712059517  
C,0,-1.2974578249,2.911370266,0.2073122118  
C,0,-3.0454180538,-1.9956714058,-0.9849665768  
H,0,-1.7081836291,-0.7383777694,-2.1778471453  
H,0,-3.3402230323,-0.1465639547,-2.0642241513  
H,0,-0.215841919,-2.1848574703,-1.5064561916  
H,0,1.3489671736,-2.7324302592,-0.8347778094  
H,0,-0.1536391285,-3.4705991163,-0.2729500001  
C,0,3.6896122632,0.8909468718,-1.5861533803  
C,0,4.7383207675,0.7807656847,0.6578752292  
H,0,4.6567431663,1.1786621315,-2.0029539841  
H,0,2.8569003571,0.8143938348,-2.2851915044  
H,0,4.475448557,1.3760555984,1.5456176684  
H,0,5.0657545691,-0.2073601012,1.014263476  
H,0,5.5907250092,1.2589160732,0.1602472127  
H,0,-4.8741631578,0.7212460794,1.93147698  
H,0,-4.2947614662,1.918475828,0.7565579332  
H,0,-4.8681444296,0.3385807482,0.1985921424  
H,0,-3.1652296548,-2.7194030393,-1.8051527153  
H,0,-2.3602089024,-2.4359307178,-0.2438017286

H,0,-4.0205298349,-1.9004622127,-0.4843852714  
H,0,-1.1357023558,3.9119182932,-0.2196434963  
H,0,-2.0105268735,3.0197395623,1.0384381203  
H,0,-0.340634135,2.5885963571,0.6492138984

### *TS1-eq-Q*

E(RM11) = -652.709720874

Zero-point correction= 0.434242 (Hartree/Particle)  
Thermal correction to Energy= 0.455348  
Thermal correction to Enthalpy= 0.456292  
Thermal correction to Gibbs Free Energy= 0.385734  
Sum of electronic and ZPE= -652.275479  
Sum of electronic and thermal Energies= -652.254373  
Sum of electronic and thermal Enthalpies= -652.253429  
Sum of electronic and thermal Free Energies= -652.323986

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.735	81.425	148.502

C,0,-0.9652723058,-2.3423000767,-0.3343577757  
C,0,-2.3501801048,-1.5664154879,-0.2240112036  
H,0,-0.6759897797,-2.4237369874,-1.3909661272  
H,0,-1.0543216931,-3.3421995547,0.1136120726  
C,0,-0.1266762358,-1.3556168041,0.4037393676  
C,0,0.0444181597,-0.1890187841,-0.2976513469  
C,0,-0.1017666912,-1.4242331216,1.89947436  
C,0,-1.114552567,0.7322058428,0.0656846179  
H,0,0.0515678408,-0.3479219197,-1.3846926216  
C,0,-2.3167436412,-0.0460036504,-0.5860986853  
H,0,-1.0437711579,1.7501163507,-0.3454935716  
H,0,-1.2661236914,0.8069736087,1.1514249014  
C,0,-3.6755020299,0.5822881149,-0.3155830027  
H,0,-2.1599666163,0.0101779081,-1.6800269711  
H,0,-2.7264422266,-1.6687930494,0.8067172985  
H,0,-3.0709443882,-2.080165131,-0.875104832  
B,0,2.1962755938,0.5484735256,-0.1613218695  
C,0,2.5522022895,0.2067501561,-1.6897002735  
C,0,2.8926667572,-0.3544814229,0.964659328  
C,0,1.9066239332,2.0846764639,0.1899479532  
H,0,1.9161686842,0.7745111744,-2.3899989055  
H,0,2.3862167795,-0.8625647157,-1.9084365218  
C,0,4.0299009912,0.5480153578,-1.9702198101  
H,0,1.1586577102,2.5088434337,-0.500923869  
H,0,2.844616649,2.6185589942,-0.0591189688  
C,0,1.5350121753,2.4000983757,1.6429919259  
C,0,3.1427237039,-1.8218415153,0.6004620694  
H,0,2.3570929518,-0.2821454139,1.9249912112  
H,0,3.8660815959,0.1363710173,1.164724839  
H,0,0.0600084933,-0.4382830997,2.3533139299  
H,0,-1.012569305,-1.8839199218,2.3095441914  
H,0,0.7460072438,-2.0634001296,2.1983186837  
C,0,-3.8503346638,1.6226178885,0.5033511293  
C,0,-4.8437692343,-0.0302894134,-1.0550021583  
H,0,-4.8431943646,2.0521617789,0.6503036333  
H,0,-3.0285953024,2.0884068775,-1.0472000113  
H,0,-4.6017679411,-0.175338736,-2.1189494581  
H,0,-5.1016715691,-1.0171326231,-0.6424334825  
H,0,-5.7341378141,0.6064485108,-0.9859209649  
H,0,4.3234427049,0.3001232146,-3.0005563146  
H,0,4.2258013057,1.620353011,-1.8220122402  
H,0,4.7034396581,-0.0005011634,-1.2939029138  
H,0,3.5536233898,-2.4048004398,1.4385355654  
H,0,2.2100287918,-2.3154182003,0.2748293575  
H,0,3.8468591977,-1.9109465306,-0.2397231795  
H,0,1.3307860506,3.4684784371,1.8059258969

H,0,0.6363681943,1.8429240234,1.952078209  
H,0,2.3430743681,2.1097652264,2.3304434552

### *TS1-eq-R*

E(RM11) = -652.707951635

Zero-point correction= 0.433632 (Hartree/Particle)  
Thermal correction to Energy= 0.455077  
Thermal correction to Enthalpy= 0.456022  
Thermal correction to Gibbs Free Energy= 0.384095  
Sum of electronic and ZPE= -652.274320  
Sum of electronic and thermal Energies= -652.252874  
Sum of electronic and thermal Enthalpies= -652.251930  
Sum of electronic and thermal Free Energies= -652.323857

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.565	81.780	151.382

C,0,-1.1806456981,1.8189230667,1.6947865547  
C,0,-2.4553495001,1.2360283275,0.9409334129  
H,0,-1.0169991468,1.2527050024,2.6216500881  
H,0,-1.330045722,2.8841943116,1.9213655687  
C,0,-0.1684118106,1.4974171721,0.6497547825  
C,0,0.0603331351,0.149146904,0.5354619074  
C,0,0.0173761052,2.4668004322,-0.4735669653  
C,0,-0.9604363961,-0.3978642031,-0.4597867823  
H,0,-0.0614091124,-0.3717141216,1.4949455055  
C,0,-2.2955874173,-0.1976599069,0.343020666  
H,0,-0.8224463624,-1.4575866307,-0.7209728826  
H,0,-0.9903377304,0.187457208,-1.3897745619  
C,0,-3.5457913108,-0.5814551415,-0.4342551072  
H,0,-2.2404616843,-0.8904021339,1.2045418377  
H,0,-2.7242275576,1.9251967927,0.1239728949  
H,0,-3.2935122877,1.2454751217,1.6513613175  
B,0,2.2446465223,-0.3951762387,0.1295509802  
C,0,2.391185746,-1.2691418351,1.469754646  
C,0,3.0190667237,1.0096121596,0.1016337341  
C,0,2.1139386543,-1.1965469507,-1.2520907846  
H,0,2.11068816,-0.6701038966,2.3529688421  
H,0,3.4775184564,-1.4467076745,1.5886676435  
C,0,1.671522241,-2.6240824446,1.4885996679  
H,0,1.3315546803,-1.9707214674,-1.1955411178  
H,0,3.0590604896,-1.7731339551,-1.3206981909  
C,0,1.9459018984,-0.3701856944,-2.5316216964  
C,0,4.5161204528,0.7710418071,-0.1836365063  
H,0,2.9126003439,1.5445232157,1.0612552828  
H,0,2.6256363929,1.6806652616,-0.6791754338  
H,0,0.3478055049,1.9702744895,-1.3943743952  
H,0,-0.8859248667,3.0644188373,-0.6641347889  
H,0,0.8146753593,3.1705350088,-0.1811471069  
C,0,-3.5250324944,-0.9468540099,-1.7184544062  
C,0,-4.8415245318,-0.5491312101,0.3448308297  
H,0,-4.4464663899,-1.234859972,-2.2281931539  
H,0,-2.6075836624,-0.9824412102,-2.3059249777  
H,0,-4.7240357183,-1.0396680128,1.3231699882  
H,0,-5.16339555,0.4855188382,0.5361138091  
H,0,-5.6459495415,-1.0556793839,-0.2022943245  
H,0,1.7889652149,-3.150253555,2.4472219594  
H,0,0.5900781617,-2.5117045889,1.3050027913  
H,0,2.05797498,-3.286470248,0.7002852352  
H,0,5.0863170668,1.7108115139,-0.2156972715  
H,0,4.9757082038,0.1346949504,0.587028525  
H,0,4.6608772139,0.2645932181,-1.1504983259  
H,0,1.934547514,-0.9940528815,-3.4372872803  
H,0,1.0014461551,0.1959601426,-2.5174307285  
H,0,2.7577562252,0.3638057352,-2.6457959815

### *TS1-eq-S*

E(RM11) = -652.710723758

Zero-point correction= 0.433946 (Hartree/Particle)  
Thermal correction to Energy= 0.455095  
Thermal correction to Enthalpy= 0.456039  
Thermal correction to Gibbs Free Energy= 0.385631  
Sum of electronic and ZPE= -652.276778  
Sum of electronic and thermal Energies= -652.255629  
Sum of electronic and thermal Enthalpies= -652.254685  
Sum of electronic and thermal Free Energies= -652.325093

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.576	81.568	148.186

C,0,0.8842317405,2.1479954826,-1.1104066664  
C,0,2.2377082075,1.4551528476,-0.6421618957  
H,0,0.6546665186,1.8392193686,-2.1392752605  
H,0,0.9792701547,3.2417022209,-1.0536069346  
C,0,-0.0201334473,1.5073546427,-0.1143944862  
C,0,-0.1964739096,0.1665894992,-0.3513001453  
C,0,-0.1339090994,2.1310744376,1.2403593204  
C,0,0.9244264991,-0.5721107079,0.3747521034  
H,0,-0.1445065941,-0.0702389509,-1.4227824414  
C,0,2.176585732,-0.092815672,-0.4449758652  
H,0,0.8423828418,-1.6688858651,0.3461612699  
H,0,1.0189653215,-0.2593764034,1.4243187887  
C,0,3.5019838405,-0.6047750938,0.097930223  
H,0,2.0641271028,-0.5309268661,-1.4553710311  
H,0,2.5559318192,1.9141346351,0.3080390616  
H,0,3.0099078082,1.6990945587,-1.3848001718  
B,0,-2.3270938313,-0.5580279865,0.0266944791  
C,0,-2.5840488898,-0.9737092614,-1.503406992  
C,0,-3.0946080693,0.7389307342,0.5681920373  
C,0,-2.0549038514,-1.7443383580,1.0689631582  
H,0,-2.3581592893,-0.1320342185,-2.180259644  
H,0,-3.6796431372,-1.1129259591,-1.5932034483  
C,0,-1.879045125,-2.2477163859,-1.9862949835  
H,0,-1.2505055438,-2.4094976095,0.7141708171  
H,0,-2.9669597423,-2.3726135855,1.0199838027  
C,0,-1.8075763189,-1.3455369065,2.5277258981  
C,0,-3.3193505171,1.8708131152,-0.4386086649  
H,0,-2.6260255237,1.1289114488,1.4863098917  
H,0,-4.0795989178,0.362280161,0.9091506504  
H,0,-0.3224621318,1.3866203797,2.0242336978  
H,0,0.7459383838,2.7388455482,1.495899972  
H,0,-1.0038095303,2.8102736869,1.2229293408  
C,0,3.6078336167,-1.2998166051,1.2332787022  
C,0,4.7210373466,-0.2984194829,-0.7428481667  
H,0,4.5795721028,-1.6651352548,-1.5710966642  
H,0,2.7484133879,-1.5387909237,1.8597400851  
H,0,4.5306271045,-0.5165403552,-1.8048460614  
H,0,4.9942076934,0.7651676086,-0.6729008113  
H,0,5.5854528616,-0.889970346,-0.417434614  
H,0,-2.0638343962,-2.4552105855,-3.0503790556  
H,0,-0.7870586553,-2.1799268646,-1.8475656131  
H,0,-2.2144606802,-3.1257049008,-1.4154852271  
H,0,-3.8092379948,2.7483033906,0.0095879788  
H,0,-2.3618958341,2.209141858,-0.8729742412  
H,0,-3.9434902707,1.5373164045,-1.2803898696  
H,0,-1.6441891314,-2.2150005385,3.181117179  
H,0,-0.9196247004,-0.6996509776,2.6172773471  
H,0,-2.6575884411,-0.7799894817,2.9368120222

### *TS1-eq-T*

E(RM11) = -652.710299388

Zero-point correction= 0.434424 (Hartree/Particle)  
Thermal correction to Energy= 0.455568  
Thermal correction to Enthalpy= 0.456513  
Thermal correction to Gibbs Free Energy= 0.385587  
Sum of electronic and ZPE= -652.275876  
Sum of electronic and thermal Energies= -652.254731  
Sum of electronic and thermal Enthalpies= -652.253787  
Sum of electronic and thermal Free Energies= -652.324712

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.874	81.307	149.275

C,0,-1.0171779646,-2.2878691208,0.6569340576  
C,0,-2.3780033403,-1.4703097086,0.5569683286  
H,0,-0.822044973,-2.7864082906,-0.3026940294  
H,0,-1.0791414017,-3.0313120056,1.4643054069  
C,0,-0.1039568856,-1.1308622189,0.8856450952  
C,0,0.018895626,-0.3376749285,-0.2256912541  
C,0,0.0508085954,-0.6091468178,2.2803249623  
C,0,-1.0959974201,0.6993243121,-0.1749773435  
H,0,-0.0533888329,-0.9063182067,-1.164225072  
C,0,-2.3542780449,-0.2216148936,-0.3822009259  
H,0,-1.0474639471,1.471665977,-0.9571795823  
H,0,-1.159310187,1.1980109409,0.8022190895  
C,0,-3.6790226349,0.5218195334,-0.2981259125  
H,0,-2.2812374648,-0.6108545487,-1.4155795838  
H,0,-2.6633862316,-1.1390976954,1.5685345896  
H,0,-3.1597637044,-2.1651152052,0.2201665671  
B,0,2.2010412724,0.3283060215,-0.537940302  
C,0,2.5339551953,-0.7953858218,-1.633167573  
C,0,2.927811146,0.2048756335,0.8834046685  
C,0,1.8813902636,1.7985440718,-1.0907345917  
H,0,3.5024462231,-0.4860039731,-2.0725496178  
H,0,1.822742696,-0.7504079634,-2.4751258104  
C,0,2.6646445508,-2.2310455858,-1.1153766869  
H,0,1.0888231054,1.7607643324,-1.8573204514  
H,0,2.7861333838,2.108616308,-1.6491013883  
C,0,1.5620955637,2.8614111456,-0.0328586163  
C,0,4.4147688885,0.5723487845,0.6952812959  
H,0,2.8618761342,-0.8158239691,1.2951603598  
H,0,2.4905455429,0.8790978434,1.6376958711  
H,0,0.2605420261,0.4683193883,2.2917675298  
H,0,-0.8222020321,-0.8329270834,2.9103807621  
H,0,0.9189131338,-1.1109422677,2.738679345  
C,0,-3.7755283997,1.8086512194,0.0452704579  
C,0,-4.9095038469,-0.2824452625,-0.6528742696  
H,0,-4.7479071943,2.3042990632,0.0707631027  
H,0,-2.908033076,2.4158991691,0.303502341  
H,0,-4.7485408278,-0.8590561379,-1.5765315441  
H,0,-5.1554941051,-1.00311676,0.1414536878  
H,0,-5.7802861515,0.3685207744,-0.7978835932  
H,0,2.8484738408,-2.9580636694,-1.9197597141  
H,0,3.4930183537,-2.3179534705,-0.3963551009  
H,0,1.7495741984,-2.5447806506,-0.5846074486  
H,0,4.9755781011,0.5365910649,1.6403151468  
H,0,4.9070106022,-0.1170292446,-0.0081177501  
H,0,4.524597214,1.5881465717,0.2838349692  
H,0,1.2719115945,3.8263323047,-0.4738218606  
H,0,0.7402625201,2.5342378853,0.6244630228  
H,0,2.4316695744,3.0436263351,0.6163249456

### *TS1-eq-U*

E(RM11) = -652.709975352

Zero-point correction= 0.433818 (Hartree/Particle)  
 Thermal correction to Energy= 0.455267  
 Thermal correction to Enthalpy= 0.456211  
 Thermal correction to Gibbs Free Energy= 0.384247  
 Sum of electronic and ZPE= -652.276158  
 Sum of electronic and thermal Energies= -652.254708  
 Sum of electronic and thermal Enthalpies= -652.253764  
 Sum of electronic and thermal Free Energies= -652.325729

E CV S  
 KCal/Mol Cal/Mol-K Cal/Mol-K  
 Total 285.685 81.695 151.462

C,0,-1.0666420674,-2.1454663304,-1.0542914563  
 C,0,-2.4095872002,-1.4417739287,-0.5712259875  
 H,0,-0.8478955192,-1.8445118533,-2.0882174435  
 H,0,-1.1694081334,-3.2387565737,-0.99459288  
 C,0,-0.1376356713,-1.5086876062,-0.072660601  
 C,0,0.0189052329,-0.1742731477,-0.3232313478  
 C,0,-0.0464229254,-2.1138786105,1.2968726509  
 C,0,-1.0528984936,0.5879893932,0.4336607553  
 H,0,-0.0257954218,0.0691225269,-1.3947487564  
 C,0,-2.3357979128,0.1058815361,-0.3481033749  
 H,0,-0.9726866909,1.6842011749,0.385923259  
 H,0,-1.1096396093,0.286484868,1.4893364676  
 C,0,-3.6419011505,0.6125574342,0.2444524414  
 H,0,-2.2566341661,0.5592471628,-1.3549957872  
 H,0,-2.7310306107,-1.912438407,0.3716945041  
 H,0,-3.1899645983,-1.6617766954,-1.3131656212  
 B,0,2.2531430805,0.5897622914,0.0246937734  
 C,0,2.837797972,-0.0053959272,-1.3384844881  
 C,0,2.6763324871,-0.1064527671,1.3984089976  
 C,0,1.8705332348,-2.1401668089,0.0857684575  
 H,0,3.7913154739,0.5369906268,-1.5007333571  
 H,0,2.2102360851,0.2855640481,-2.1971880296  
 C,0,3.1043195976,-1.5130431884,-1.3660152589  
 H,0,2.8102714678,2.64557732,0.3838860153  
 H,0,1.1809645518,2.3322477021,0.9250228981  
 C,0,1.3509096971,2.7960021735,-1.1991879933  
 C,0,4.1516515931,0.235427004,1.700304312  
 H,0,2.578057495,-1.2025170204,1.3475068594  
 H,0,2.0483693154,0.2361259347,2.2388964873  
 H,0,0.2220514875,-1.3738306702,2.059839746  
 H,0,-0.9733903935,-2.6306210637,1.5863491175  
 H,0,0.7521209129,-2.8746194424,1.2835157863  
 C,0,-3.709247719,1.2964676567,1.3896842939  
 C,0,-4.8890803192,0.3173719313,-0.5580728962  
 H,0,-4.6687629141,1.65893018,1.7637197546  
 H,0,-2.8291809848,1.5286048369,1.9891690959  
 H,0,-4.7378118488,0.5592173815,-1.6212508776  
 H,0,-5.1541130868,-0.7489846783,-0.501732596  
 H,0,-5.7437913162,0.8973379932,-0.1890828102  
 H,0,3.487774041,-1.8573822001,-2.3373177332  
 H,0,3.8361447461,-1.805882037,-0.5983066132  
 H,0,2.1768273505,-2.0732348727,-1.1566885455  
 H,0,4.5038662625,-0.2413264117,2.6261549541  
 H,0,4.8110405751,-0.0999742425,0.884602869  
 H,0,4.2981669547,1.3197786023,1.8123591066  
 H,0,1.1559510142,3.8705800495,-1.0704627439  
 H,0,2.0747557113,2.6880931862,-2.0200492236  
 H,0,0.4111071133,2.3315713415,-1.536976277

*TS1-eq-V*  
 E(RM11) = -652.710326179

Zero-point correction= 0.433931 (Hartree/Particle)  
 Thermal correction to Energy= 0.455308

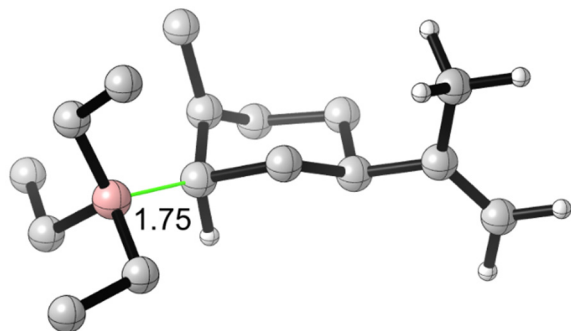
Thermal correction to Enthalpy= 0.456252  
 Thermal correction to Gibbs Free Energy= 0.384996  
 Sum of electronic and ZPE= -652.276395  
 Sum of electronic and thermal Energies= -652.255019  
 Sum of electronic and thermal Enthalpies= -652.254074  
 Sum of electronic and thermal Free Energies= -652.325330

E CV S  
 KCal/Mol Cal/Mol-K Cal/Mol-K  
 Total 285.710 81.625 149.970

C,0,1.2111552502,-2.3204856836,0.6552329623  
 C,0,2.4896712166,-1.4420005027,0.3011442057  
 H,0,1.0153961153,-2.2594784293,1.7347388215  
 H,0,1.3758603502,-3.3672524369,0.3612966306  
 C,0,0.2101608152,-1.553421238,0.1441962059  
 C,0,-0.0241749589,-0.3150317118,0.3827382198  
 C,0,0.0923833801,-1.8578093397,-1.6067669326  
 C,0,0.9774141079,0.6571650023,-0.216098694  
 H,0,0.0318285018,-0.2919951659,1.4811648918  
 C,0,2.3116692574,0.1084318123,0.4187124895  
 H,0,0.8332534118,1.7119442753,0.0609333138  
 H,0,1.0121814113,0.5893580758,-1.3129468191  
 C,0,3.5637942682,0.8152222269,-0.0780959374  
 H,0,2.2389706844,0.3285949299,1.5011200374  
 H,0,2.8036830675,-1.6778353356,-0.7283063677  
 H,0,3.3086598905,-1.7617210324,0.9604302346  
 B,0,-2.3106261512,0.275316711,-0.0107512723  
 C,0,-2.5509092868,0.6874331404,1.5167321668  
 C,0,-3.0087510427,-1.0646163557,-0.5306603554  
 C,0,-2.0497636927,1.4273862721,-1.08942083  
 H,0,-2.2824165723,-0.1460947454,2.1871783581  
 H,0,-3.6501837696,0.7816317356,1.6247836492  
 C,0,-1.8834043445,1.9835437103,1.9911156988  
 H,0,-1.6441241,1.0225213377,-2.0327364702  
 H,0,-1.3251671589,2.174002529,-0.7273834446  
 C,0,-3.3851280416,2.1432287675,-1.3871757909  
 C,0,-3.050241157,-2.2589979207,0.4280869757  
 H,0,-2.6094312513,-1.3701793641,-1.5115661919  
 H,0,-4.0503639865,-0.7542040175,-0.7467491866  
 H,0,-0.2879007043,-0.9971290454,-2.1714532797  
 H,0,1.0420370491,-2.2020916399,-2.0427043882  
 H,0,-0.6329721666,-2.6803072235,-1.727087082  
 C,0,3.5512554818,1.7253879498,-1.0554324653  
 C,0,4.852831286,0.4413994625,0.6187225301  
 H,0,4.4745083853,2.2190741907,-1.3649513996  
 H,0,2.6394288763,2.0183772327,-1.5755392061  
 H,0,4.722355369,0.4411432046,1.7117683496  
 H,0,5.1812991265,-0.5682835654,0.3302553182  
 H,0,5.6576145541,1.1425287722,0.3660175006  
 H,0,-2.0966644945,2.2042256072,3.046976959  
 H,0,-0.7888982232,1.9296152155,1.8795844047  
 H,0,-2.2214593104,2.8466199775,1.3983110405  
 H,0,-3.5628883044,-3.129850154,-0.0061296043  
 H,0,-2.0308317907,-2.5766636022,0.7052829454  
 H,0,-3.5707765636,-2.0026437475,1.362134668  
 H,0,-3.256677642,2.9809191569,-2.0875450654  
 H,0,-4.1190716766,1.453461865,-1.8289695734  
 H,0,-3.8318583061,2.5486454366,-0.465759479

## Intermediate Structures

*Int-eq-A*



E(RM11) = -652.717807795

Zero-point correction= 0.434629 (Hartree/Particle)  
 Thermal correction to Energy= 0.455990  
 Thermal correction to Enthalpy= 0.456934  
 Thermal correction to Gibbs Free Energy= 0.386475  
 Sum of electronic and ZPE= -652.283179  
 Sum of electronic and thermal Energies= -652.261818  
 Sum of electronic and thermal Enthalpies= -652.260873  
 Sum of electronic and thermal Free Energies= -652.331333

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.138	82.656	148.295

C,0,-0.8618243508,-2.1545744118,0.1298530971  
 C,0,-2.0743489387,-1.1722713325,0.3789923056  
 H,0,-0.8470287634,-2.4571386914,-0.9247059753  
 H,0,-0.9510752406,-3.0281760229,0.7884742394  
 C,0,0.2572593293,-1.2492039344,0.4613259186  
 C,0,0.6049055344,-0.2551495947,-0.4872365562  
 C,0,0.7054587852,-1.2021319872,1.8755399749  
 C,0,-0.5242556955,0.7918739628,-0.0687776353  
 H,0,0.2991831714,-0.5942027631,-1.492774808  
 C,0,-1.9057760826,0.1666025663,-0.3659505152  
 H,0,-0.3523399271,1.6929839549,-0.6723624877  
 H,0,-0.4427597999,1.0792880931,0.9896411202  
 C,0,-3.053209087,1.1094898736,-0.0369723129  
 H,0,-1.94453703,-0.0467754919,-1.446816604  
 H,0,-2.1601094723,-0.9901725877,1.4624959183  
 H,0,-2.9951434775,-1.6798167294,0.062466535  
 B,0,2.2240285191,0.3701731503,-0.6745837214  
 C,0,2.9771308742,-0.8777469769,-1.4451976443  
 C,0,3.0151554829,0.7629522585,0.7099790728  
 C,0,2.0592712122,1.6631363734,-1.6698178221  
 H,0,4.0288183424,-0.5782910351,-1.6022056226  
 H,0,2.55818197,-1.0184698049,-2.46016163  
 C,0,2.9748407175,-2.2234350853,-0.7137736275  
 H,0,1.5079801137,2.4879117513,-1.1801540358  
 H,0,1.4514995594,1.3864124566,-2.5545540714  
 C,0,3.4017580571,2.2299746539,-2.1572402192  
 C,0,2.507624544,1.996597201,1.4724145143  
 H,0,4.0568554282,0.968110477,0.4010210488  
 H,0,3.1169807269,-0.0866529512,1.409288591  
 H,0,1.0368214898,-0.2015072824,2.1721169959  
 H,0,-0.0494610836,-1.6044709007,2.5640972249  
 H,0,1.5924772415,-1.8576194199,1.9262438857  
 C,0,-4.0307645831,1.3280516186,-0.918812596  
 C,0,-3.0300603785,1.786516694,1.3131128775  
 H,0,-4.8666749686,1.9912171865,-0.6881005886  
 H,0,-4.0234526222,0.8570115204,-1.9040723231  
 H,0,-2.8169967625,1.0751926829,2.1255813493  
 H,0,-2.2463019265,2.5579611259,1.3470328514  
 H,0,-3.9904601966,2.2705169461,1.5261913749

H,0,3.5161874763,-3.0152750516,-1.253555821  
 H,0,3.4335862894,-2.1357111616,0.2844366556  
 H,0,1.9455146909,-2.6085866481,-0.5699550661  
 H,0,3.1023133852,2.2233480159,2.3710081028  
 H,0,2.5332512509,2.888881032,0.8288191874  
 H,0,1.4590322982,1.8876178946,1.8003522235  
 H,0,3.2797359929,3.0983154356,-2.8229084498  
 H,0,4.0234296419,2.5540329907,-1.3076787555  
 H,0,3.9782013318,1.4719124189,-2.7083362273

### Int-eq-B

E(RM11) = -652.716199312

Zero-point correction= 0.434669 (Hartree/Particle)  
 Thermal correction to Energy= 0.456098  
 Thermal correction to Enthalpy= 0.457043  
 Thermal correction to Gibbs Free Energy= 0.386185  
 Sum of electronic and ZPE= -652.281531  
 Sum of electronic and thermal Energies= -652.260101  
 Sum of electronic and thermal Enthalpies= -652.259157  
 Sum of electronic and thermal Free Energies= -652.330014

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.206	82.686	149.132

C,0,-1.1575479902,-2.1054852628,-0.2188274148  
 C,0,-2.3516433397,-1.1557609602,0.208527163  
 H,0,-1.1666276996,-2.2274306253,-1.3091757519  
 H,0,-1.2520539957,-3.0726832383,0.2910465712  
 C,0,-0.0349852574,-1.2703466178,0.2375230298  
 C,0,0.3030797621,-0.1352529745,-0.5408317113  
 C,0,0.4875816762,-1.4598289821,1.6078397117  
 C,0,-0.8091426979,0.8511226315,0.0222644034  
 H,0,-0.0015330918,-0.3112323347,-1.5859444293  
 C,0,-2.195701195,0.2755983949,-0.3441356926  
 H,0,-0.6320510712,1.82901559,-0.4477171079  
 H,0,-0.7199214222,0.9825940458,1.1095480545  
 C,0,-3.3380348373,1.159103896,0.1341291506  
 H,0,-2.253047349,0.2166970528,-1.4434336633  
 H,0,-2.4012330393,-1.1308434061,1.3093682887  
 H,0,-3.2844860679,-1.6120875123,-0.1479661353  
 B,0,1.9324291119,0.4759301176,-0.5766987297  
 C,0,2.8371853813,-0.7853632189,-1.128928143  
 C,0,2.5600246218,0.980481242,0.8569192599  
 C,0,1.8459205726,1.7066553257,-1.6670535534  
 H,0,2.9083700396,-1.5809860738,-0.3591098151  
 H,0,3.8753588413,-0.4234736933,-1.2402884641  
 C,0,2.3926415357,-1.4205410912,-2.454513679  
 H,0,1.3742355457,2.600145271,-1.2160164973  
 H,0,1.1913509743,1.437532911,-2.5194899689  
 C,0,3.213405411,2.1233603931,-2.2310253536  
 C,0,1.8181745789,2.0497479723,1.6760040135  
 H,0,3.5460896171,1.3983908421,0.5829570408  
 H,0,2.8178901051,0.1313168428,1.5181360696  
 H,0,0.7513949999,-0.5057142092,2.078776592  
 H,0,-0.1688691902,-2.0694799978,2.2410379664  
 H,0,1.4441704461,-1.9985544269,1.47161321  
 C,0,-4.3195674061,1.5131536592,-0.6980340576  
 C,0,-3.3053114289,1.6225322813,1.5712793806  
 H,0,-5.1504323059,2.1370198018,-0.3631406195  
 H,0,-4.3200435426,1.1980453928,-1.743639899  
 H,0,-3.1094469856,0.7922719533,2.2666437594  
 H,0,-2.5068339334,2.3641329802,1.7226489535  
 H,0,-4.2569489975,2.0872975302,1.8549811877  
 H,0,3.112126096,-2.1581906208,-2.8416798524  
 H,0,1.4280140765,-1.9487953092,-2.3512574095

H,0,2.2531373895,-0.6543907414,-3.2343000492  
H,0,2.4644142547,2.53302201,2.4245130266  
H,0,1.4176043314,2.8458924936,1.0285858919  
H,0,0.9612102188,1.6361761851,2.2349814352  
H,0,3.1492150876,3.0010846544,-2.8923839088  
H,0,3.9191224189,2.3726486076,-1.4233906491  
H,0,3.6681882502,1.3066145486,-2.8123126647

### Int-eq-C

E(RM11) = -652.716073215

Zero-point correction= 0.434435 (Hartree/Particle)  
Thermal correction to Energy= 0.455977  
Thermal correction to Enthalpy= 0.456921  
Thermal correction to Gibbs Free Energy= 0.385704  
Sum of electronic and ZPE= -652.281638  
Sum of electronic and thermal Energies= -652.260096  
Sum of electronic and thermal Enthalpies= -652.259152  
Sum of electronic and thermal Free Energies= -652.330369

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.130	82.796	149.889

C,0,-1.5687747009,-2.2728016264,0.080880715  
C,0,-2.7289640989,-1.2454548502,0.386751847  
H,0,-1.5748734066,-2.5147924143,-0.9890784249  
H,0,-1.7024263509,-3.1757971176,0.690303151  
C,0,-0.399917905,-1.4529788221,0.4543834808  
C,0,0.0042213747,-0.4256451627,-0.4353914025  
C,0,0.1113518976,-1.5457931663,1.8393109367  
C,0,-1.0900879953,0.6459900422,0.0292410548  
H,0,-0.3068413809,-0.7011866775,-1.4564712943  
C,0,-2.4952022381,0.1088149629,-0.308977866  
H,0,-0.8528183824,1.5661741,-0.5239068991  
H,0,-1.0053587307,0.8729801734,1.1014931757  
C,0,-3.5971878491,1.0946773565,0.0488660801  
H,0,-2.5347565883,-0.0608513114,-1.3979612108  
H,0,-2.7903095361,-1.1003151231,1.4776634117  
H,0,-3.67721677,-1.6952210672,0.0644915857  
B,0,1.6233366123,0.1699626506,-0.5236342185  
C,0,2.4352801051,-1.1454980441,-1.1079937463  
C,0,2.302189739,0.6784764256,0.8877786148  
C,0,1.5902694984,1.4088734716,-1.6039241552  
H,0,1.8787604851,-1.6153741256,-1.9422270889  
H,0,2.4853497982,-1.9240911056,-0.3183115741  
C,0,3.8617913924,-0.8491915662,-1.5915627443  
H,0,2.6406755883,1.7126665386,-1.7636816362  
H,0,1.110769085,2.3130265423,-1.1832040458  
C,0,0.955773234,1.1096362334,-2.9708258854  
C,0,1.6164945211,1.8033409232,1.6828039321  
H,0,3.2952042592,1.059193712,0.5872568195  
H,0,2.537676268,-0.1612517608,1.5698304959  
H,0,0.4625657076,-0.5776359431,2.2111998106  
H,0,-0.5945682385,-2.0269964231,2.5279815174  
H,0,1.0127686783,-2.1824302221,1.7631803596  
C,0,-4.5508787249,1.3991199913,-0.8336198947  
C,0,-3.5580949589,1.71286074,1.4263986873  
H,0,-5.3542336593,2.0947466162,-0.5839387725  
H,0,-4.5545123328,0.9703394416,-1.8379732685  
H,0,-3.4137370166,0.9564475644,2.2127178476  
H,0,-2.7249639839,2.4266685656,1.5087898967  
H,0,-4.4883224823,2.2525262404,1.6397616965  
H,0,4.4021652345,-1.7550340938,-1.907915978  
H,0,3.8478299469,-0.1598143161,-2.4498132112  
H,0,4.4588753337,-0.368753736,-0.8015414445  
H,0,2.2797303642,2.2531442875,2.4373845076

H,0,1.2825688574,2.6145752332,1.0174405866  
H,0,0.7214320518,1.4593615841,2.2299866845  
H,0,1.1078504658,1.9200307348,-3.699996738  
H,0,1.3742552976,0.1891700528,-3.4098564361  
H,0,-0.1355913757,0.960625451,-2.8928435194

### Int-eq-D

E(RM11) = -652.718027928

Zero-point correction= 0.434611 (Hartree/Particle)  
Thermal correction to Energy= 0.455876  
Thermal correction to Enthalpy= 0.456820  
Thermal correction to Gibbs Free Energy= 0.386846  
Sum of electronic and ZPE= -652.283417  
Sum of electronic and thermal Energies= -652.262152  
Sum of electronic and thermal Enthalpies= -652.261208  
Sum of electronic and thermal Free Energies= -652.331182

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.066	82.728	147.273

C,0,-0.8004852239,-2.1184240113,0.0023403401  
C,0,-1.9953877248,-1.1161586397,0.2516647224  
H,0,-0.7637635314,-2.3843917023,-1.0615466991  
H,0,-0.9314870692,-3.0124208402,0.6258900802  
C,0,0.3387587366,-1.2629221315,0.3953616079  
C,0,0.7317904583,-0.2422367735,-0.5065974484  
C,0,0.767061071,-1.2986721037,1.816011014  
C,0,-0.3806700887,0.8127395766,-0.0512055968  
H,0,0.435002659,-0.5360529645,-1.528023049  
C,0,-1.7677048262,0.2497743744,-0.4263641428  
H,0,-0.1535992601,1.7472913298,-0.5831346962  
H,0,-0.321895274,1.0269204583,1.025714831  
C,0,-2.897114669,1.2114133239,-0.0902361727  
H,0,-1.775159873,0.0896518791,-1.517649635  
H,0,-2.1130506531,-0.977394452,1.3386105022  
H,0,-2.9175395068,-1.5845911295,-0.1164796859  
B,0,2.3326162379,0.4027545776,-0.6169799546  
C,0,3.1717257803,-0.8238570599,-1.3342343416  
C,0,3.0475494348,0.8300672107,0.8017582172  
C,0,2.2382353989,1.7002983828,-1.6228519597  
H,0,4.2193624055,-0.4822503428,-1.4226127372  
H,0,2.8306477837,-0.9860108572,-2.3730295398  
C,0,3.1622381699,-2.1746331239,-0.6122481314  
H,0,3.2813132063,1.9747694814,-1.8669476451  
H,0,1.8335694881,2.5925046029,-1.1092585829  
C,0,1.4684682327,1.5140745461,-2.9406899943  
C,0,2.4206838899,1.9580285938,1.6392053072  
H,0,4.0559363966,1.1712960826,0.5019598279  
H,0,3.2468859346,-0.038100637,1.4578366153  
H,0,1.1745691333,-0.3401535625,2.1495731279  
H,0,-0.0297225947,-1.6600275227,2.4802619276  
H,0,1.5934167641,-2.0292974195,1.8579568484  
C,0,-3.8334643015,1.504936639,-0.9948566942  
C,0,-2.9055281694,1.81858642,1.2928314907  
H,0,-4.6566998181,2.1825599855,-0.7607497217  
H,0,-3.8024444712,1.0845571522,-2.0022992066  
H,0,-2.763796916,1.0582567103,2.0757881115  
H,0,-2.0900803153,2.5492142693,1.4017020104  
H,0,-3.852034612,2.3365270141,1.4876066284  
H,0,3.7755648231,-2.9390463179,-1.1132744738  
H,0,3.5336889985,-2.083713158,0.4212717672  
H,0,2.1392807253,-2.5981635639,-0.5601433228  
H,0,3.0740878853,2.2848698919,2.4628447143  
H,0,2.210954529,2.8434522275,1.020959434  
H,0,1.4610030784,1.6697856174,2.1015040814

H,0,1.5764959975,2.3740412729,-3.6189915224  
H,0,1.8148004686,0.623546735,-3.4875538113  
H,0,0.3847507115,1.3834329683,-2.7734224617

### Int-eq-E

E(RM11) = -652.716880140

Zero-point correction= 0.434272 (Hartree/Particle)  
Thermal correction to Energy= 0.455725  
Thermal correction to Enthalpy= 0.456669  
Thermal correction to Gibbs Free Energy= 0.385926  
Sum of electronic and ZPE= -652.282608  
Sum of electronic and thermal Energies= -652.261155  
Sum of electronic and thermal Enthalpies= -652.260211  
Sum of electronic and thermal Free Energies= -652.330954

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.972	82.784	148.891

C,0,-1.1781121491,-1.8430985013,1.4926524174  
C,0,-2.4214572486,-0.984978167,1.0362735054  
H,0,-1.1019144018,-2.7366403296,0.8602114796  
H,0,-1.2821395453,-2.1177652145,2.5503043251  
C,0,-0.091336269,-0.8825592149,1.2198866297  
C,0,0.3047957049,-0.6716782905,-0.1256530338  
C,0,0.3325322372,0.022327249,2.3102391016  
C,0,-0.8890835219,0.3121742459,-0.5080739383  
H,0,0.1084317434,-1.5878374905,-0.7097369601  
C,0,-2.2367428573,-0.4273975786,-0.3875508028  
H,0,-0.6903162683,0.6309040514,-1.5411217516  
H,0,-0.8666186181,1.2129355491,0.1252215354  
C,0,-3.4156141389,0.450292255,-0.7797667147  
H,0,-2.2082644768,-1.2847851573,-1.0800109507  
H,0,-2.5597246601,-0.1559970954,1.7494673003  
H,0,-3.163337277,-1.6181593157,1.0969722726  
B,0,1.8569999795,-0.0223133033,-0.5362017151  
C,0,2.0377115042,-0.5340470746,-2.0910851519  
C,0,2.9529375022,-0.7277213932,0.4752570098  
C,0,2.0171119918,1.6171580809,-0.4261446758  
H,0,1.1686959428,-0.2275495063,-2.7079077521  
H,0,2.0332444518,-1.6403027549,-2.1267268071  
C,0,3.3174528699,-0.0306193373,-2.7752917664  
H,0,3.104226399,1.7766057023,-0.5530133744  
H,0,1.824044648,2.0054355832,0.5926545111  
C,0,1.2988903943,2.5297391197,-1.4393515677  
C,0,2.761980297,-2.2232743767,0.756508121  
H,0,3.0222335494,-0.1823204751,1.4371448595  
H,0,3.9491534824,-0.5875812939,0.019233206  
H,0,0.722511984,0.9705666598,1.9267901787  
H,0,-0.4442719302,0.1633384087,3.0733754558  
H,0,1.1821140362,-0.5003278421,2.7882910521  
C,0,-4.3551074935,-0.0023653214,-1.6124198468  
C,0,-3.467256559,1.8431208252,-0.1977770167  
H,0,-5.213357859,0.6127643254,-1.889529268  
H,0,-4.2929951806,-1.0004842392,-2.0513633482  
H,0,-3.2888584842,1.8407964281,0.8883375614  
H,0,-2.6933831614,2.4821518499,-0.6497933593  
H,0,-4.4419501439,2.3096796055,-0.3829657274  
H,0,3.4352024158,-0.4250386616,-3.7964264828  
H,0,3.3321339739,1.0678241916,-2.8442489622  
H,0,4.2121690586,-0.3264476669,-2.2061048155  
H,0,3.5787159079,-2.6642559303,1.348143775  
H,0,1.8303221769,-2.427337955,1.3211302811  
H,0,2.6848298144,-2.796952937,-0.1805124617  
H,0,1.7706339584,3.5219718999,-1.510375975  
H,0,1.3074245941,2.0935728764,-2.4508372484

H,0,0.2446834568,2.7084413671,-1.1777823237

### Int-eq-F

E(RM11) = -652.716242044

Zero-point correction= 0.434357 (Hartree/Particle)  
Thermal correction to Energy= 0.455824  
Thermal correction to Enthalpy= 0.456768  
Thermal correction to Gibbs Free Energy= 0.385789  
Sum of electronic and ZPE= -652.281885  
Sum of electronic and thermal Energies= -652.260418  
Sum of electronic and thermal Enthalpies= -652.259474  
Sum of electronic and thermal Free Energies= -652.330453

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.034	82.801	149.387

C,0,-0.790590145,-1.4243429628,1.7551619525  
C,0,-2.047605504,-0.7046212287,1.1229887174  
H,0,-0.6472405461,-2.3964556315,1.2669922835  
H,0,-0.9346418713,-1.5442959357,2.83671304  
C,0,0.2574670268,-0.4557401121,1.3797230081  
C,0,0.6879641131,-0.4367559821,0.0300379415  
C,0,0.5806914129,0.6239877372,2.3350671277  
C,0,-0.5142494425,0.4187681262,-0.5627433615  
H,0,0.5400467463,-1.4419444097,-0.3996588039  
C,0,-1.8334239487,-0.3583509602,-0.3630858368  
H,0,-0.2887475081,0.5664207077,-1.6282875291  
H,0,-0.5588163313,1.4131952953,-0.0934289027  
C,0,-3.0386833577,0.3890942298,-0.9139341126  
H,0,-1.7439494789,-1.3083020207,-0.9154867336  
H,0,-2.253189421,0.2133227354,1.69743083  
H,0,-2.9158525623,-1.3652160559,1.2471259212  
B,0,2.2523006327,0.1946327184,-0.4673342937  
C,0,2.5642144628,-0.7949116456,-1.7511425612  
C,0,3.3294963868,-0.0288429668,0.7515907778  
C,0,2.2199115984,1.7570443404,-0.9795841972  
H,0,1.8035686983,-0.6255697081,-2.5401012251  
H,0,2.4469846458,-1.8561855583,-1.4604477851  
C,0,3.9597818007,-0.6278905758,-2.3694362982  
H,0,1.530003186,1.8789923677,-1.8363532702  
H,0,3.2204984457,1.9255364528,-1.4162255948  
C,0,1.9773874424,2.9055913196,0.013952473  
C,0,3.4002216215,-1.4552817821,1.3103961776  
H,0,3.1834829199,0.6813978463,1.5861710529  
H,0,4.3243288696,0.2378486168,0.3510638905  
H,0,0.9443313579,1.5256017993,1.8322591084  
H,0,-0.2414241755,0.8318001729,3.0330213994  
H,0,1.427528165,0.2273369407,2.9261591378  
C,0,-3.9236732455,-0.2289416722,-1.6987176959  
C,0,-3.1819086679,1.8458761029,-0.541458245  
H,0,-4.8014723888,0.2919611785,-2.0857453182  
H,0,-3.7959071281,-1.2748221278,-1.9860081987  
H,0,-3.0323386408,2.0108055006,0.5364991209  
H,0,-2.4325915365,2.4565088229,-1.0669164036  
H,0,-4.1754490697,2.2237144202,-0.8101530578  
H,0,4.1193046773,-1.290302879,-3.2343298387  
H,0,4.1301891151,0.4031464747,-2.7128537311  
H,0,4.7460342507,-0.8583161339,-1.6334507073  
H,0,4.1298283796,-1.5710813743,2.1269394571  
H,0,2.4232726648,-1.7930396712,1.7101589488  
H,0,3.6700470123,-2.1738521187,0.5215157514  
H,0,2.205136416,3.8900185823,-0.4230190174  
H,0,0.9276685098,2.9605593834,0.3504307399  
H,0,2.6081803013,2.8020219012,0.9118591818

### Int-eq-G

E(RM11) = -652.718657371

Zero-point correction= 0.434649 (Hartree/Particle)  
Thermal correction to Energy= 0.455935  
Thermal correction to Enthalpy= 0.456880  
Thermal correction to Gibbs Free Energy= 0.386695  
Sum of electronic and ZPE= -652.284009  
Sum of electronic and thermal Energies= -652.262722  
Sum of electronic and thermal Enthalpies= -652.261778  
Sum of electronic and thermal Free Energies= -652.331962

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.104	82.607	147.716

C,0,-1.6356389779,-2.1959669721,-0.3106899963  
C,0,-2.7676046444,-1.1818722205,0.1167221219  
H,0,-1.6307807077,-2.2978925491,-1.4032385006  
H,0,-1.8036757078,-3.1668208067,0.1734532425  
C,0,-0.4462657983,-1.4707827134,0.1773057685  
C,0,0.0122791375,-0.3519291561,-0.5619311061  
C,0,0.0147189381,-1.7403977921,1.559646134  
C,0,-1.0476229812,0.6817726423,0.0471763998  
H,0,-0.2839645596,-0.4672270381,-1.6190845664  
C,0,-2.4711255724,0.2517993616,-0.3626320432  
H,0,-0.7854577845,1.664862827,-0.3644607434  
H,0,-0.942697614,0.75191377,1.140963724  
C,0,-3.5367010302,1.2134305846,0.1415244694  
H,0,-2.5105766397,0.2514165501,-1.4647690699  
H,0,-2.856815058,-1.1983648553,1.2148364603  
H,0,-3.7216550789,-1.5409209145,-0.2910460818  
B,0,1.664815909,0.1945744076,-0.4371226137  
C,0,2.6254134542,-1.1261603397,-0.202657818  
C,0,1.8513855219,1.2939695128,0.772422814  
C,0,1.9700273693,0.8433564051,-1.9172480636  
H,0,2.6686697901,-1.4306682717,0.8612453682  
H,0,3.6577392067,-0.8094881765,-0.4353696149  
C,0,2.3128846449,-2.3520617983,-1.0709474883  
H,0,1.8533320503,0.0753696372,-2.7051597036  
H,0,3.0401715013,1.1171722142,-1.9470515351  
C,0,1.1369215887,2.072107658,-2.311801563  
C,0,3.2551959321,1.9213633725,0.7883193397  
H,0,1.6765567616,0.8386299517,1.7679755726  
H,0,1.1191199919,2.1198423124,0.7032586441  
H,0,0.5508933274,-0.886741316,1.9866618886  
H,0,-0.7986419725,-2.0904618518,2.2098921633  
H,0,0.7424145023,-2.5665719049,1.4664119958  
C,0,-4.4839022412,1.6729199564,-0.6787095493  
C,0,-3.4695207858,1.6242724036,1.5932040056  
H,0,-5.2626981012,2.3503860619,-0.3234857001  
H,0,-4.5069815884,1.3934929299,-1.734235455  
H,0,-3.3371608501,0.7583752837,2.2596521622  
H,0,-2.6162992098,2.2967274068,1.7666249213  
H,0,-4.3827508985,2.1506339955,1.8949484912  
H,0,3.0258582452,-3.1792534224,-0.9315924667  
H,0,1.3093129375,-2.7738300733,-0.8628091068  
H,0,2.3154234853,-2.0904999086,-2.1398255333  
H,0,3.4056906609,2.6041520475,1.6387249823  
H,0,4.0364408795,1.1478776626,0.8438140468  
H,0,3.4369535463,2.4984168689,-0.1312394599  
H,0,1.4642445535,2.5240284469,-3.2607977418  
H,0,0.0708166649,1.8157446043,-2.4402426861  
H,0,1.1928173819,2.857196316,-1.5397687191

### Int-eq-H

E(RM11) = -652.716616260

Zero-point correction= 0.434652 (Hartree/Particle)  
Thermal correction to Energy= 0.455932  
Thermal correction to Enthalpy= 0.456876  
Thermal correction to Gibbs Free Energy= 0.386709  
Sum of electronic and ZPE= -652.281965  
Sum of electronic and thermal Energies= -652.260684  
Sum of electronic and thermal Enthalpies= -652.259740  
Sum of electronic and thermal Free Energies= -652.329908

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.102	82.657	147.680

C,0,-0.6142382048,-1.4319180032,1.7177316263  
C,0,-1.9004627651,-0.7520553842,1.1018469551  
H,0,-0.4514788468,-2.4036151521,1.2348457572  
H,0,-0.7386444625,-1.5479484095,2.8022080491  
C,0,0.4059271634,-0.4415140089,1.3208319549  
C,0,0.8139013228,-0.4200210981,-0.0359292468  
C,0,0.7103044756,0.6602476961,2.2601959704  
C,0,-0.418090539,0.4290020301,-0.5878731048  
H,0,0.6709581644,-1.4270611693,-0.4633289823  
C,0,-1.7138959603,-0.3840881259,-0.3833818429  
H,0,-0.2180007454,0.6143275859,-1.6515688353  
H,0,-0.4754876237,1.4092001087,-0.0903047912  
C,0,-2.9421600735,0.3369482462,-0.9171613814  
H,0,-1.6038828179,-1.324375232,-0.9495158244  
H,0,-2.1313490951,0.1532356214,1.6861782847  
H,0,-2.7444812307,-1.442799404,1.2280939939  
B,0,2.3658552303,0.2213203263,-0.5363021608  
C,0,2.7640797356,-0.7717769871,-1.7916273612  
C,0,3.4417113082,0.0277612969,0.6925974541  
C,0,2.3194248295,1.777470698,-1.0692753907  
H,0,2.8893082073,-1.812344478,-1.4377417131  
H,0,3.7655512261,-0.4628696907,-2.1442976716  
C,0,1.8082502299,-0.7889632927,-2.9943414745  
H,0,1.6062126581,1.9005138056,-1.9048391838  
H,0,3.3093912616,1.9325510581,-1.5372508972  
C,0,2.0978925154,2.9358523093,-0.0820125312  
C,0,3.487035935,-1.3634635356,1.339488723  
H,0,3.3257561097,0.7870417452,1.4878959219  
H,0,4.4388455892,0.237641004,0.2638377738  
H,0,1.0633777831,1.5573493648,1.7417719054  
H,0,-0.1240766909,0.8715951498,2.9428512428  
H,0,1.5541538559,0.2918985438,2.8721063743  
C,0,-3.8032597277,-0.2888232753,-1.7222903054  
C,0,-3.1350115478,1.7783889819,-0.5088908858  
H,0,-4.6949725953,0.2143657414,-2.100909277  
H,0,-3.6399024683,-1.3217696869,-2.0368843275  
H,0,-3.0061476472,1.9192290248,0.5749603932  
H,0,-2.3982482545,2.4257761623,-1.0074746785  
H,0,-4.1359180646,2.13262215,-0.7823728463  
H,0,2.1749783974,-1.4210800058,-3.8176531224  
H,0,0.8131552256,-1.1813682018,-2.7203892833  
H,0,1.6570976421,0.2214768085,-3.4049858112  
H,0,4.222116269,-1.4396979028,2.1557154349  
H,0,2.50974551,-1.6574002758,1.7719779957  
H,0,3.7348414848,-2.138928145,0.6004675643  
H,0,2.3304410138,3.9147405729,-0.528614767  
H,0,1.0503039827,3.0014978039,0.2590873343  
H,0,2.7321250343,2.8348711293,0.8134441887

### Int-eq-I

E(RM11) = -652.715909276

Zero-point correction= 0.434989 (Hartree/Particle)



Thermal correction to Energy= 0.456112  
Thermal correction to Enthalpy= 0.457056  
Thermal correction to Gibbs Free Energy= 0.387358  
Sum of electronic and ZPE= -652.280921  
Sum of electronic and thermal Energies= -652.259797  
Sum of electronic and thermal Enthalpies= -652.258853  
Sum of electronic and thermal Free Energies= -652.328551

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 286.215 82.464 146.692

C,0,-1.4343509236,-2.2490679633,0.7665832584  
C,0,-2.6739510582,-1.2682479436,0.6812797674  
H,0,-1.3397798408,-2.8034304431,-0.1752590864  
H,0,-1.5611827513,-2.9312914917,1.6171185559  
C,0,-0.3690291021,-1.2433065807,0.9343297781  
C,0,0.0339097768,-0.5151271522,-0.2131213105  
C,0,-0.0571112633,-0.8103673056,2.3202353862  
C,0,-1.1263065174,0.5695977663,-0.1917354969  
H,0,-0.176164486,-1.1192478858,-1.1131442838  
C,0,-2.4798024873,-0.1588786444,-0.3712162048  
H,0,-0.9389029474,1.2458551276,-1.0352164085  
H,0,-1.1036748207,1.1677065601,0.732398086  
C,0,-3.663635527,0.7964665338,-0.3572891778  
H,0,-2.4533656638,-0.6459280604,-1.3601552788  
H,0,-2.8361766304,-0.821426021,1.675201544  
H,0,-3.5637817423,-1.8678243541,0.4483107743  
B,0,1.6707002575,0.0983575081,-0.4259320226  
C,0,2.4653532174,-1.2700479622,-0.8757315021  
C,0,2.325655589,0.7788388786,0.9153811823  
C,0,1.595777176,1.1576032572,-1.6822834  
H,0,3.5010951165,-0.9827642521,-1.1304453929  
H,0,2.0426948084,-1.6725505578,-1.815844274  
C,0,2.5117712642,-2.3824916383,0.1749062364  
H,0,0.840071122,0.8223996578,-2.4209876185  
H,0,2.5517858603,1.0929087727,-2.2336020852  
C,0,1.3529120571,2.6381333218,-1.3382555065  
C,0,3.7936653288,1.1768005851,0.6738250781  
H,0,2.3218155552,0.1064725521,1.7901212573  
H,0,1.7568686507,1.6772665697,1.2266967214  
H,0,0.2122914315,0.2491840346,2.3747033611  
H,0,-0.8597192337,-1.0658753414,3.0245263501  
H,0,0.8429993839,-1.3794350496,2.6133629899  
C,0,-4.5960843139,0.7410638958,-1.3105187131  
C,0,-3.7329858947,1.8001697151,0.769317314  
H,0,-5.4593723203,1.4091632562,-1.3006582836  
H,0,-4.5225218531,0.0308846366,-2.1369269869  
H,0,-3.5394396179,1.3331837337,1.7470040949  
H,0,-2.977973533,2.5889465298,0.6341482674  
H,0,-4.7184908896,2.2791466609,0.8085338806  
H,0,3.0639437119,-3.2762883474,-0.1532001962  
H,0,2.9810873985,-2.027940536,1.1075694795  
H,0,1.4938972213,-2.7355523309,0.4369443907  
H,0,4.2131292181,1.7771587839,1.4957481526  
H,0,4.4236705716,0.2801306142,0.5693425971  
H,0,3.9106792887,1.75477475,-0.2555054839  
H,0,1.2241688344,3.2663293498,-2.2334548087  
H,0,0.4642610071,2.7866291991,-0.7039838904  
H,0,2.198326851,3.0523418328,-0.7692557014

### Int-eq-J

E(RM11) = -652.718594172

Zero-point correction= 0.434558 (Hartree/Particle)  
Thermal correction to Energy= 0.455838  
Thermal correction to Enthalpy= 0.456782

Thermal correction to Gibbs Free Energy= 0.386436  
Sum of electronic and ZPE= -652.284036  
Sum of electronic and thermal Energies= -652.262757  
Sum of electronic and thermal Enthalpies= -652.261812  
Sum of electronic and thermal Free Energies= -652.332158

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 286.042 82.630 148.055

C,0,-0.7854902737,-2.1363065802,0.5593091695  
C,0,-1.9853209709,-1.1096497074,0.5025190158  
H,0,-0.7018214842,-2.654464331,-0.4040532505  
H,0,-0.9508055037,-2.8504680285,1.3765810809  
C,0,0.3366652002,-1.2010942839,0.7842123616  
C,0,0.784043961,-0.4412095274,-0.3251972385  
C,0,0.6717735497,-0.8708315738,2.1942074497  
C,0,-0.3387556195,0.6922144071,-0.1966644101  
H,0,0.5369473664,-0.9845289022,-1.2529075678  
C,0,-1.7169190669,0.0545056538,-0.4715733565  
H,0,-0.0831962642,1.457013599,-0.9429958692  
H,0,-0.3097968435,1.1757900245,0.7912029956  
C,0,-2.8503396998,1.067770745,-0.4173473118  
H,0,-1.6860318875,-0.3624036879,-1.4922650941  
H,0,-2.1559150962,-0.7167428168,1.5177042427  
H,0,-2.8908166959,-1.6582812774,0.2121311251  
B,0,2.3750060768,0.2121300151,-0.5102292271  
C,0,3.3068455432,-1.1137050095,-0.8087893151  
C,0,2.8825935774,1.0556519464,0.8077323844  
C,0,2.316047593,1.1854116609,-1.8357459288  
H,0,4.3513837426,-0.7629563744,-0.8974982928  
H,0,3.0671769463,-1.5487481367,-1.7964886656  
C,0,3.2604069791,-2.2321519046,0.2360797881  
H,0,3.3636701638,1.3837937421,-2.1255205087  
H,0,1.9076637609,2.1845465166,-1.5841808848  
C,0,1.5808730644,0.6442961719,-3.0728522694  
C,0,4.145214821,1.8879087518,0.5272278364  
H,0,3.1056978083,0.3878668623,1.6610453801  
H,0,2.0954528466,1.7514075641,1.1650583779  
H,0,1.0545782999,0.147495979,2.3037652637  
H,0,-0.1684509349,-1.0666333222,2.87413987  
H,0,1.4914923844,-1.5549317531,2.4736849235  
C,0,-3.7585704844,1.127991207,-1.3932338929  
C,0,-2.8956325989,1.995715759,0.773578833  
H,0,-4.5848979723,1.8403498118,-1.3566521506  
H,0,-3.7002377947,0.4732462778,-2.2653574036  
H,0,-2.7639760477,1.4533391019,1.7221606159  
H,0,-2.0894144612,2.7420831812,0.7150422808  
H,0,-3.8506857794,2.5323728476,0.8168836951  
H,0,3.9355895719,-3.0706205111,0.0067228793  
H,0,3.5322716707,-1.8583407961,1.2367065343  
H,0,2.2464851991,-2.6730929994,0.3119169232  
H,0,4.5395194762,2.3770058413,1.431302958  
H,0,4.949923177,1.2584833847,0.1162109442  
H,0,3.944465938,2.6759964049,-0.2127579435  
H,0,1.7315815511,1.272780222,-3.9635993197  
H,0,1.924357247,-0.370338381,-3.3295477031  
H,0,0.4895346937,0.5807038954,-2.9179440545

### Int-eq-K

E(RM11) = -652.716958287

Zero-point correction= 0.434589 (Hartree/Particle)  
Thermal correction to Energy= 0.455848  
Thermal correction to Enthalpy= 0.456792  
Thermal correction to Gibbs Free Energy= 0.386850  
Sum of electronic and ZPE= -652.282369

Sum of electronic and thermal Energies= -652.261110  
Sum of electronic and thermal Enthalpies= -652.260166  
Sum of electronic and thermal Free Energies= -652.330109

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 286.049 82.606 147.207

C,0,-1.1004922143,-2.1698043939,-0.2793519761  
C,0,-2.2169503723,-1.1197979593,0.0954088481  
H,0,-1.1139274188,-2.3409265546,-1.3633406144  
H,0,-1.2698658942,-3.1065860709,0.267375148  
C,0,0.1071267737,-1.431685869,0.1414692412  
C,0,0.5587088333,-0.3602407014,-0.6686089066  
C,0,0.6221420837,-1.6517987349,1.5113036632  
C,0,-0.4927937343,0.7171167312,-0.1341802783  
H,0,0.2575220219,-0.5419137439,-1.7150404511  
C,0,-1.9212541175,0.2687145368,-0.5027542234  
H,0,-0.2163907581,1.6638875296,-0.6210532109  
H,0,-0.389797363,0.8642551168,0.9517097414  
C,0,-2.9766436103,1.2765529483,-0.0730634382  
H,0,-1.9703884792,0.1772999428,-1.6002184711  
H,0,-2.2791135394,-1.0493846096,1.1936135549  
H,0,-3.1822033928,-1.5031110855,-0.2605987729  
B,0,2.1879133488,0.2314319952,-0.5886991801  
C,0,3.1788047662,-1.0777745092,-0.4352102315  
C,0,2.3890312117,1.3305556284,0.6324426175  
C,0,2.3364410321,0.9469667662,-2.0652062972  
H,0,3.2611224779,-1.4186343731,0.6151379439  
H,0,4.2022949116,-0.7464645358,-0.6878122426  
C,0,2.8340692235,-2.2819817024,-1.3206488147  
H,0,1.480345852,1.6318327569,-2.2345894114  
H,0,2.2588525706,0.1882542635,-2.8674722656  
C,0,3.6270394394,1.7514723104,-2.2745752892  
C,0,3.8379506592,1.452430901,1.13765468  
H,0,1.7604090326,1.1237586571,1.5206333975  
H,0,2.0515208474,2.3281465891,0.2888923092  
H,0,1.197270789,-0.7961119244,1.878607661  
H,0,-0.1632633725,-1.9663712322,2.212053127  
H,0,1.3295187318,-2.495926761,1.408432214  
C,0,-3.9161568914,1.685026617,-0.9284190688  
C,0,-2.9078822158,1.7944045514,1.3440233205  
H,0,-4.6870452051,2.3971044968,-0.6278129935  
H,0,-3.9405174924,1.3271775836,-1.9599212746  
H,0,-2.7910790199,0.9790796503,2.0739797326  
H,0,-2.0455325306,2.4656746315,1.4711285355  
H,0,-3.8141130811,2.3553234642,1.6011170532  
H,0,3.5762737404,-3.0927042115,-1.2612418537  
H,0,1.8606503493,-2.7355645142,-1.0474071098  
H,0,2.7489039436,-1.9884127164,-2.3781949303  
H,0,3.9592968611,2.2551576133,1.8816256829  
H,0,4.1695719911,0.5147837548,1.6093331737  
H,0,4.5392590253,1.6549690326,0.3156680179  
H,0,3.7079628835,2.1618043913,-3.2931879478  
H,0,3.6812412635,2.6000286482,-1.5757539867  
H,0,4.5190773888,1.1288766552,-2.1012011231

### Int-eq-L

E(RM11) = -652.717541389

Zero-point correction= 0.434774 (Hartree/Particle)  
Thermal correction to Energy= 0.456039  
Thermal correction to Enthalpy= 0.456983  
Thermal correction to Gibbs Free Energy= 0.386944  
Sum of electronic and ZPE= -652.282768  
Sum of electronic and thermal Energies= -652.261502  
Sum of electronic and thermal Enthalpies= -652.260558  
Sum of electronic and thermal Free Energies= -652.330597

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 286.169 82.530 147.410

C,0,-1.1752746954,-2.3609172221,-0.3783262252  
C,0,-2.4393969203,-1.4564549181,-0.1095311932  
H,0,-1.0083900527,-2.4464248277,-1.4595404156  
H,0,-1.324322777,-3.3496757331,0.0745573813  
C,0,-0.1335758054,-1.5410961154,0.2760380416  
C,0,0.3076029664,-0.3753890893,-0.3969785067  
C,0,0.1287794242,-1.7873681723,1.7156706965  
C,0,-0.9014440039,0.5548993186,0.0789990014  
H,0,0.1421249341,-0.4997652433,-1.4817448738  
C,0,-2.210868527,0.0133093651,-0.522907099  
H,0,-0.6722334371,1.5621591415,-0.2927336978  
H,0,-0.9711199081,0.6103075777,1.175266498  
C,0,-3.4365621396,0.854407038,-0.2011142588  
H,0,-2.0932593003,0.0281622608,-1.6226893995  
H,0,-2.6863261471,-1.4920820986,0.9643752349  
H,0,-3.2829202644,-1.9021541525,-0.6527650139  
B,0,1.9125502443,0.2840504245,-0.2371121831  
C,0,2.7998647165,-0.775065205,-1.1377232319  
C,0,2.5080468405,0.3908327186,1.2895771754  
C,0,1.8336272117,1.7513649005,-0.9653554282  
H,0,3.8534504675,-0.4473238558,-1.0841094342  
H,0,2.5242503137,-0.7023384463,-2.2074708464  
C,0,2.7405161513,-2.2434879553,-0.7059822047  
H,0,1.2075784536,2.4598210337,-0.3907116557  
H,0,1.3407075478,1.6570019894,-1.9538031093  
C,0,3.2083335602,2.40753888,-1.1665501218  
C,0,1.8644206073,1.4349630542,2.2151343543  
H,0,3.5720073618,0.6663641991,1.1679540419  
H,0,2.5519442886,-0.5845525442,1.8074784389  
H,0,0.4103239594,-0.8732148925,2.2479970878  
H,0,-0.7052841713,-2.3064214426,2.2062896861  
H,0,1.0066560765,-2.4565240687,1.7441588588  
C,0,-3.4010900974,1.9157156044,0.6080534813  
C,0,-4.7198381922,0.4226732901,-0.8731852418  
H,0,-4.3039756079,2.49988416,0.7955571275  
H,0,-2.4884270463,2.2501099956,1.1017115153  
H,0,-4.5567168526,0.2247490866,-1.9435198768  
H,0,-5.1134303302,-0.5028572833,-0.4262898752  
H,0,-5.4936812513,1.1938948568,-0.7793582296  
H,0,3.3751565851,-2.9045370763,-1.3157273537  
H,0,3.0562024907,-2.3636472369,0.3430616485  
H,0,1.7139429424,-2.6532992081,-0.7896878645  
H,0,2.339215931,1.4821695874,3.2075011964  
H,0,1.9313739967,2.440025545,1.7719704126  
H,0,0.7895419248,1.2463093918,2.3829699236  
H,0,3.1420299408,3.3897868813,-1.6593792718  
H,0,3.7174737758,2.5602861992,-0.20172409  
H,0,3.8655467646,1.7749630376,-1.7818041

### Int-eq-M

E(RM11) = -652.715865314

Zero-point correction= 0.434565 (Hartree/Particle)  
Thermal correction to Energy= 0.456048  
Thermal correction to Enthalpy= 0.456992  
Thermal correction to Gibbs Free Energy= 0.385802  
Sum of electronic and ZPE= -652.281301  
Sum of electronic and thermal Energies= -652.259817  
Sum of electronic and thermal Enthalpies= -652.258873  
Sum of electronic and thermal Free Energies= -652.330063

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 286.175 82.684 149.833

C,0,-1.134798444,2.415432689,-0.1898495136  
C,0,-2.4076029412,1.4768190448,-0.180445347  
H,0,-0.9045277238,2.7223595316,0.8382266844  
H,0,-1.3209634919,3.2858747676,-0.8317394946  
C,0,-0.1445569475,1.4603634892,-0.7161025893  
C,0,0.3369449285,0.4578680156,0.161366741  
C,0,0.0821226807,1.3949100838,-2.1756620342  
C,0,-0.8897056,-0.5453672808,0.0106303061  
H,0,0.2606119662,0.820099322,1.2000895438  
C,0,-2.1567223347,0.1408859001,0.5525735041  
H,0,-0.6257723227,-1.4414725018,0.589652295  
H,0,-1.0379889976,-0.8527284694,-1.0337620148  
C,0,-3.4032401003,-0.7298307898,0.5048334428  
H,0,-1.972857085,0.3809695369,1.6165563568  
H,0,-2.7070928168,1.265842893,-1.2204906723  
H,0,-3.2226213064,2.0465751133,0.2845868173  
B,0,1.9193621852,-0.2324301092,-0.0296067862  
C,0,2.9470284743,1.0496907239,0.0962714755  
C,0,2.2212216843,-1.0059915977,-1.4493337952  
C,0,2.039601086,-1.2568190673,1.2544284321  
H,0,2.8707605951,1.6987757744,-0.8002026546  
H,0,3.9776732997,0.6529404808,0.0559648305  
C,0,2.8043543201,1.9229813633,1.3512383782  
H,0,1.4655800105,-2.1851882607,1.0728939972  
H,0,1.5841312294,-0.8125756343,2.1616229287  
C,0,3.4858515974,-1.6506368001,1.5933993461  
C,0,1.3020477892,-2.1536300724,-1.8994977047  
H,0,3.2339325966,-1.4274725295,-1.3125838742  
H,0,2.3523379706,-0.2960715144,-2.2881998683  
H,0,0.2401557423,0.3657210242,-2.5178054337  
H,0,-0.6898867944,1.9132192783,-2.7577520478  
H,0,1.0473341453,1.9127302297,-2.3315106886  
C,0,-3.4216322315,-1.9459951826,-0.045873138  
C,0,-4.6399481693,-0.1377440506,1.1412518116  
H,0,-4.3365693978,-2.5414609268,-0.0429945373  
H,0,-2.5433780628,-2.398716681,-0.5069152291  
H,0,-4.4096273616,0.2818198595,2.1323919878  
H,0,-5.0541618773,0.6779999442,0.5294636421  
H,0,-5.4235282298,-0.8952820231,1.2611165289  
H,0,3.6049110148,2.6722246071,1.448557352  
H,0,1.8514794941,2.4818161552,1.3542760846  
H,0,2.8144627245,1.3079636522,2.265653496  
H,0,1.7656940151,-2.7893244161,-2.6691786369  
H,0,1.0340879764,-2.8085877425,-1.0551199308  
H,0,0.3537191195,-1.7924811899,-2.3331068567  
H,0,3.5435007681,-2.3998913458,2.3979354566  
H,0,4.0006376306,-2.0718868948,0.715913401  
H,0,4.0698229219,-0.7754823492,1.9172911276

### Int-eq-N

E(RM11) = -652.715801041

Zero-point correction= 0.434691 (Hartree/Particle)  
Thermal correction to Energy= 0.456064  
Thermal correction to Enthalpy= 0.457008  
Thermal correction to Gibbs Free Energy= 0.386471  
Sum of electronic and ZPE= -652.281110  
Sum of electronic and thermal Energies= -652.259737  
Sum of electronic and thermal Enthalpies= -652.258793  
Sum of electronic and thermal Free Energies= -652.329330

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 286.185 82.585 148.459

C,0,-1.0824822617,-1.9733135111,-1.5065202384  
C,0,-2.3712580514,-1.327609054,-0.8675003454  
H,0,-0.8841322267,-1.5004360993,-2.4765163381  
H,0,-1.2275206923,-3.0553546918,-1.6197611625  
C,0,-0.0714213436,-1.5991064075,-0.4971859956  
C,0,0.3751759161,-0.2549396263,-0.4700678879  
C,0,0.215356057,-2.5528648356,0.5971279086  
C,0,-0.8813363853,0.3105224296,0.3497741011  
H,0,0.2561358783,0.1785577192,-1.476429277  
C,0,-2.1548788529,0.15351346,-0.4954343243  
H,0,-0.6397923973,1.3650798268,0.5461164059  
H,0,-0.9941254367,-0.1907584898,1.3216245589  
C,0,-3.4052508949,0.7267137136,0.1539829627  
H,0,-1.9958281056,0.7112088851,-1.4379543227  
H,0,-2.6444082525,-1.8894460715,0.0412393073  
H,0,-3.190629085,-1.4518699178,-1.587422964  
B,0,1.9168566622,0.2280160501,0.1310913119  
C,0,2.9372220993,-0.4525474559,-0.9766648766  
C,0,2.3094031511,-0.2707122054,1.6503439589  
C,0,1.9322459415,1.8710127608,0.0665438126  
H,0,2.5714475441,-0.2813925022,-2.007948129  
H,0,2.9328400799,-1.5551413137,-0.8466410977  
C,0,4.3880418787,0.0424970442,-0.8969045947  
H,0,2.9596177551,2.1854937704,0.3249789241  
H,0,1.3076341312,2.3203276097,0.8617205245  
C,0,1.5492656167,2.5121554037,-1.2762180037  
C,0,1.3965471232,0.1226212259,2.8252726344  
H,0,3.2935331673,0.1946934106,1.8402684898  
H,0,2.5187702984,-1.3569276676,1.6967281379  
H,0,0.4251910033,-2.0423022273,1.5427520971  
H,0,-0.5538693621,-3.3281496219,0.7039115963  
H,0,1.1625456227,-3.0415893386,0.3010688758  
C,0,-3.416496494,1.2405384854,1.3861460673  
C,0,-4.6553397898,0.6921638225,-0.6948968417  
H,0,-4.3357164037,1.6534406892,1.8057817355  
H,0,-2.5276663262,1.2813276567,2.0163569407  
H,0,-4.45126045,1.065053839,-1.7101206852  
H,0,-5.0421456207,-0.3332396233,-0.7952688078  
H,0,-5.4494584473,1.3069081329,-0.2547256362  
H,0,5.0555146629,-0.4774400519,-1.6017283274  
H,0,4.4463465257,1.1182220694,-1.1237312799  
H,0,4.803090248,-0.0976015361,0.1128868882  
H,0,1.886668606,-0.0043208725,3.8026275395  
H,0,1.0841621181,1.1760526574,2.7520682734  
H,0,0.4702286295,-0.4759548222,2.8689163435  
H,0,1.7363996962,3.5965539493,-1.3015433396  
H,0,2.115243366,2.0612276197,-2.1077412069  
H,0,0.4777299409,2.3753295119,-1.5056975936

### Int-eq-O

E(RM11) = -652.717785441

Zero-point correction= 0.434701 (Hartree/Particle)  
Thermal correction to Energy= 0.456010  
Thermal correction to Enthalpy= 0.456954  
Thermal correction to Gibbs Free Energy= 0.386423  
Sum of electronic and ZPE= -652.283084  
Sum of electronic and thermal Energies= -652.261775  
Sum of electronic and thermal Enthalpies= -652.260831  
Sum of electronic and thermal Free Energies= -652.331362

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 286.151 82.574 148.445

C,0,-0.7481134205,-2.3048125703,-0.8594437192

C,0,-2.1076412593,-1.6417258693,-0.4139735091  
H,0,-0.5820307227,-2.1167278293,-1.9277516672  
H,0,-0.7778602011,-3.3825797729,-0.6526558605  
C,0,0.206274492,-1.5506303721,-0.0175371548  
C,0,0.4917927719,-0.2155072816,-0.3935787255  
C,0,0.5360258463,-2.1090083959,1.3177131477  
C,0,-0.8107753835,0.413626229,0.2943480414  
H,0,0.3136613455,-0.1059146126,-1.476638487  
C,0,-2.0556643395,-0.0987793287,-0.4493980505  
H,0,-0.6937826332,1.5031732186,0.2118531753  
H,0,-0.8710081922,0.1687676695,1.3645491626  
C,0,-3.3654518768,0.488046631,0.054265925  
H,0,-1.9519006063,0.2057623743,-1.5082157644  
H,0,-2.3456540258,-1.9653323942,0.612776172  
H,0,-2.8954810622,-2.0343724984,-1.0699971337  
B,0,1.9650175236,0.6129205274,-0.0466047422  
C,0,3.0371984566,-0.1055258357,-1.0754140908  
C,0,2.5075703827,0.5168774759,1.5026277488  
C,0,1.7218148494,2.1819809613,-0.4772095602  
H,0,4.01678866,0.3756646962,-0.8999485154  
H,0,2.788187118,0.1181932215,-2.1288514242  
C,0,3.2103633188,-1.6212059156,-0.9367693405  
H,0,2.718382601,2.6609759202,-0.4686054184  
H,0,1.145062349,2.7357675901,0.2870577306  
C,0,1.073015962,2.4414773224,-1.8472906807  
C,0,1.6528283853,1.1308947464,2.6245966195  
H,0,3.4684473408,1.0642833593,1.4882803025  
H,0,2.7928593831,-0.512778222,1.7895381182  
H,0,0.7622736511,-1.3286235085,2.0500672586  
H,0,-0.2386203187,-2.798604929,1.6797444319  
H,0,1.4623869972,-2.6922346864,1.1740128472  
C,0,-3.4407036086,1.3024357275,1.1095021493  
C,0,-4.5987923815,0.0990345761,-0.7279062523  
H,0,-4.401841662,1.7112476646,1.4266096083  
H,0,-2.5653972271,1.601186824,1.6868545422  
H,0,-4.4313971,0.2159039093,-1.809459427  
H,0,-4.8689148722,-0.9531269909,-0.551104637  
H,0,-5.458469447,0.7172791268,-0.4431010927  
H,0,3.9653197862,-2.0362308711,-1.6219441364  
H,0,3.5084481026,-1.9021889085,0.0862947722  
H,0,2.2690370363,-2.1594617811,-1.1669896104  
H,0,2.1894409236,1.1817005126,3.584561238  
H,0,1.3414434193,2.1554130037,2.3723504071  
H,0,0.7257884574,0.5647548593,2.8183473166  
H,0,1.0836507847,3.506149451,-2.1259150926  
H,0,1.5883003557,1.8902264925,-2.649230342  
H,0,0.0156087003,2.1238135319,-1.8704579906

### Int-*eq-P*

E(RM11) = -652.716821262

Zero-point correction= 0.434394 (Hartree/Particle)  
Thermal correction to Energy= 0.455762  
Thermal correction to Enthalpy= 0.456706  
Thermal correction to Gibbs Free Energy= 0.386324  
Sum of electronic and ZPE= -652.282428  
Sum of electronic and thermal Energies= -652.261059  
Sum of electronic and thermal Enthalpies= -652.260115  
Sum of electronic and thermal Free Energies= -652.330498

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.995	82.662	148.133

C,0,-1.16732342,-2.4533161682,-0.2307259482  
C,0,-2.4262438253,-1.5300214805,-0.0209105864  
H,0,-0.9915932211,-2.591905357,-1.3051969403

H,0,-1.3254833136,-3.4183482216,0.2679210414  
C,0,-0.1196896305,-1.6175198123,0.3900282031  
C,0,0.3549944856,-0.4883828561,-0.3231174392  
C,0,0.181195262,-1.8204754658,1.8235548819  
C,0,-0.868831598,0.4652894288,0.0503248007  
H,0,0.2455970356,-0.6702533444,-1.4066779916  
C,0,-2.1776564295,-0.0946621293,-0.5281569783  
H,0,-0.6147039112,1.4406775188,-0.3873587555  
H,0,-0.9411541173,0.6004040616,1.1409815202  
C,0,-3.3903718114,0.7858053178,-0.267074255  
H,0,-2.0528179372,-0.1529577558,-1.6257789174  
H,0,-2.675053839,-1.494374256,1.0526878204  
H,0,-3.2720249613,-2.003308258,-0.536426457  
B,0,1.8881193723,0.2360601359,0.0133633698  
C,0,2.2024555427,1.0389057075,-1.3900337187  
C,0,2.9537860898,-0.9989514054,0.2645852503  
C,0,1.9481128795,1.2583405751,1.3083496943  
H,0,1.3569178567,1.7034248842,-1.6608427902  
H,0,2.2742485533,0.3182171198,-2.2270816864  
C,0,3.4875177842,1.879665822,-1.3599497889  
H,0,3.0298440036,1.4558924303,1.4276859288  
H,0,1.6755950745,0.7681720021,2.2629544446  
C,0,1.2375781402,2.6245902373,1.2417836139  
C,0,2.8251042168,-2.2117422282,-0.6653350763  
H,0,2.9305384498,-1.3436485675,1.3172748956  
H,0,3.9686748579,-0.5797016743,0.1450539772  
H,0,0.550949028,-0.9054186921,2.2969342142  
H,0,-0.654139426,-2.2727157509,2.3743447831  
H,0,1.0188663102,-2.542930512,1.8293346692  
C,0,-3.3333731349,1.908285767,0.4536534965  
C,0,-4.6839253004,0.3200079494,-0.8948285286  
H,0,-4.2265932087,2.5183921853,0.6002629459  
H,0,-2.4119337586,2.2693230272,0.9121124793  
H,0,-4.5331019488,0.0472867732,-1.9505291799  
H,0,-5.0802962991,-0.5692793277,-0.3816546553  
H,0,-5.4504963761,1.1026271667,-0.8472173706  
H,0,3.7030439748,2.3602263638,-2.3267791981  
H,0,3.4287654023,2.6767253816,-0.6032384719  
H,0,4.3595567112,1.2590063191,-1.1021496104  
H,0,3.6271517334,-2.9533332665,-0.5298671764  
H,0,1.8737804263,-2.7591266622,-0.511015632  
H,0,2.8339444755,-1.9037542308,-1.7227471655  
H,0,1.6638166858,3.3492655823,1.9525631172  
H,0,1.315245621,3.0709585076,0.2376025892  
H,0,0.1645416149,2.5572662582,1.4789448609

### Int-*eq-Q*

E(RM11) = -652.715916950

Zero-point correction= 0.434530 (Hartree/Particle)  
Thermal correction to Energy= 0.455908  
Thermal correction to Enthalpy= 0.456852  
Thermal correction to Gibbs Free Energy= 0.386243  
Sum of electronic and ZPE= -652.281387  
Sum of electronic and thermal Energies= -652.260009  
Sum of electronic and thermal Enthalpies= -652.259065  
Sum of electronic and thermal Free Energies= -652.329674

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.087	82.684	148.609

C,0,-1.1182609659,-2.3706631532,-0.46347615  
C,0,-2.4068547914,-1.506299068,-0.1778786904  
H,0,-0.9443243881,-2.4154698871,-1.5460511871  
H,0,-1.2445852868,-3.3772900275,-0.0444708257  
C,0,-0.1036741286,-1.546210344,0.2236326657

C,0,0.3090701834,-0.3460068131,-0.4041935026  
 C,0,0.2057101014,-1.8552584825,1.6343869221  
 C,0,-0.9318022818,0.5471816029,0.0403782475  
 H,0,0.1814026998,-0.457700527,-1.4942196485  
 C,0,-2.2195371448,-0.0272730384,-0.5752269619  
 H,0,-0.718731963,1.5583111457,-0.3331088346  
 H,0,-1.0065847169,0.6067261937,1.1369145276  
 C,0,-3.4719134081,0.7747578448,-0.2555732147  
 H,0,-2.0949562278,0.0001543757,-1.6741377997  
 H,0,-2.6497128716,-1.5630547638,0.8961867496  
 H,0,-3.2385066866,-1.9693497216,-0.7248477799  
 B,0,1.8397610128,0.4420311579,-0.0649912498  
 C,0,2.1513422193,1.1073291453,-1.5434914133  
 C,0,2.9486692124,-0.700931313,0.3373135299  
 C,0,1.7563091752,1.6374483203,1.0617492947  
 H,0,1.3596185058,1.8435705863,-1.7907772037  
 H,0,2.0853328745,0.3366689123,-2.3349052037  
 C,0,3.5180058449,1.7959341893,-1.668031305  
 H,0,1.0521483085,2.4313000695,0.7464106768  
 H,0,2.7461017331,2.1256659877,1.0188162172  
 C,0,1.4952363175,1.3388986835,2.5413277292  
 C,0,3.0702305061,-1.8720080482,-0.6455452211  
 H,0,2.8004106562,-1.0984381315,1.3583412219  
 H,0,3.9276373483,-0.1912915892,0.3938277739  
 H,0,0.5454985179,-0.9729192688,2.1855697647  
 H,0,-0.6137297764,-2.3809856893,2.1424651125  
 H,0,1.0665424368,-2.5483726766,1.5824358367  
 C,0,-3.4705714461,1.8383022149,0.5514084134  
 C,0,-4.7398712048,0.3026368194,-0.9297477811  
 H,0,-4.39167253,2.3941802966,0.7362685342  
 H,0,-2.5698752237,2.2013087828,1.0469030114  
 H,0,-4.5675980053,0.1054274368,-1.9988179728  
 H,0,-5.1075025047,-0.6323292109,-0.4803873445  
 H,0,-5.536549911,1.0509003086,-0.841372743  
 H,0,3.6836380673,2.2246534859,-2.6685831716  
 H,0,3.6272243937,2.6141676774,-0.9409502349  
 H,0,4.3361892196,1.0830904777,-1.479608277  
 H,0,3.819459524,-2.6209425899,-0.3451460058  
 H,0,2.1114259681,-2.4151069238,-0.763779046  
 H,0,3.3438020713,-1.5153452541,-1.6501920303  
 H,0,1.6929375199,2.1680465302,3.2006078859  
 H,0,0.4484542699,1.0168044647,2.7328047173  
 H,0,2.1388415957,0.4851864019,2.8906846962

### Int-eq-R

E(RM11) = -652.718426373

Zero-point correction= 0.434667 (Hartree/Particle)  
 Thermal correction to Energy= 0.455992  
 Thermal correction to Enthalpy= 0.456936  
 Thermal correction to Gibbs Free Energy= 0.386608  
 Sum of electronic and ZPE= -652.283760  
 Sum of electronic and thermal Energies= -652.262434  
 Sum of electronic and thermal Enthalpies= -652.261490  
 Sum of electronic and thermal Free Energies= -652.331819

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.139	82.596	148.018

C,0,-1.1406340736,-2.3868147516,-0.4593679728  
 C,0,-2.4000552021,-1.5243580116,-0.0668799053  
 H,0,-1.0241976348,-2.3884535691,-1.5505954532  
 H,0,-1.2561798346,-3.4091878477,-0.0765726698  
 C,0,-0.0733264679,-1.6088563796,0.2017929664  
 C,0,0.340352221,-0.3913819794,-0.3922541856  
 C,0,0.2899820264,-1.9679185053,1.5925784291

C,0,-0.8681062984,0.4767619594,0.2040489252  
 H,0,0.1484307896,-0.4305195988,-1.4786107591  
 C,0,-2.1996402607,-0.0261621431,-0.3757364411  
 H,0,-0.6606487458,1.5129911258,-0.0908953293  
 H,0,-0.8701356226,0.4474998028,1.3047473688  
 C,0,-3.4123220807,0.7754121882,0.0721115911  
 H,0,-2.1343557255,0.0760765905,-1.4756431476  
 H,0,-2.5983120677,-1.6443245089,1.0108772479  
 H,0,-3.2626703653,-1.9377451612,-0.6054298462  
 B,0,1.9106081479,0.2868806232,-0.0615824159  
 C,0,2.9719673578,-0.9597513811,0.1470238293  
 C,0,1.8828943285,1.2766975797,1.2525838576  
 C,0,2.2813277143,1.1009597466,-1.4417865035  
 H,0,2.9511643279,-1.3610274196,1.1790394273  
 H,0,3.9852401372,-0.532379955,0.0431855034  
 C,0,2.8567593339,-2.1193580137,-0.8514858584  
 H,0,2.3120150115,0.4056036193,-2.3020196567  
 H,0,3.3171628731,1.4726039344,-1.3423430472  
 C,0,1.3687047098,2.2818432777,-1.8054858513  
 C,0,3.2104087531,2.0253255251,1.4556603232  
 H,0,1.6695299315,0.7131152185,2.1829765858  
 H,0,1.0801818596,2.0347799418,1.1876491072  
 H,0,0.710452351,-1.1172053221,2.1381301421  
 H,0,-0.5424553233,-2.4397211381,2.1323689816  
 H,0,1.0919306496,-2.7217385952,1.4957979958  
 C,0,-3.341598299,1.7671714656,0.9630608345  
 C,0,-4.7252395637,0.3856064107,-0.5671626694  
 H,0,-4.2375632408,2.3235547808,1.2446570305  
 H,0,-2.4070727938,2.0699663451,1.4358817864  
 H,0,-4.6179956214,0.2870569414,-1.6581882091  
 H,0,-5.0842361731,-0.5823739757,-0.1858437925  
 H,0,-5.5010281511,1.1331406613,-0.3631700555  
 H,0,3.6327641642,-2.8888619463,-0.7182476631  
 H,0,1.8854823572,-2.6482789717,-0.7777093381  
 H,0,2.9261429085,-1.7566891136,-1.8881802759  
 H,0,3.2202794461,2.6311942436,2.3748404019  
 H,0,4.0578447588,1.3250739535,1.5128353757  
 H,0,3.4097341462,2.7050188828,0.6131449974  
 H,0,1.7289019355,2.8479870169,-2.6782822631  
 H,0,0.3468990382,1.944768061,-2.0529613552  
 H,0,1.2831846079,2.9931951727,-0.9675251833

### Int-eq-S

E(RM11) = -652.716324911

Zero-point correction= 0.434992 (Hartree/Particle)  
 Thermal correction to Energy= 0.456074  
 Thermal correction to Enthalpy= 0.457019  
 Thermal correction to Gibbs Free Energy= 0.387780  
 Sum of electronic and ZPE= -652.281333  
 Sum of electronic and thermal Energies= -652.260251  
 Sum of electronic and thermal Enthalpies= -652.259306  
 Sum of electronic and thermal Free Energies= -652.328545

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.191	82.452	145.725

C,0,0.8013278318,-2.3205418181,0.8670661457  
 C,0,2.14161923,-1.6484365187,0.3767351952  
 H,0,0.6783825148,-2.1453994514,1.9433434276  
 H,0,0.8225314111,-3.395284921,0.6445955497  
 C,0,-0.1757317415,-1.5511438227,0.0704650609  
 C,0,-0.4557914233,-0.2224352235,0.4718946248  
 C,0,-0.5686339311,-2.0823381171,-1.2528734499  
 C,0,0.8257094714,0.4419942487,-0.2085103095  
 H,0,-0.2727522926,-0.1346952353,1.556410276

C,0,2.0968213753,-0.1077205695,0.461420176  
H,0,0.7234761386,1.5247709575,-0.0590954504  
H,0,0.8363236998,0.2593054474,-1.2937868966  
C,0,3.3880343865,0.4912783695,-0.0760919342  
H,0,2.040050954,0.1607830587,1.533616136  
H,0,2.3316086722,-1.9437997798,-0.6682916946  
H,0,2.9563332357,-2.0621272291,0.9852693458  
B,0,-1.9503241667,0.5885343507,0.0505921164  
C,0,-2.2367936301,1.502883551,1.3923243282  
C,0,-3.1383603114,-0.535552453,-0.1257394909  
C,0,-1.8429492278,1.5703900373,-1.2659006091  
H,0,-2.3843480015,0.856371795,2.277649219  
H,0,-3.2062374766,2.0124027792,1.2394496265  
C,0,-1.1801953024,2.5609859463,1.7465692021  
H,0,-1.0507595101,2.3318358274,-1.1452521057  
H,0,-2.7809879474,2.1561661341,-1.2435876852  
C,0,-1.7146973126,0.9726721464,-2.67719463  
C,0,-3.2615399917,-1.5718099246,1.0000092507  
H,0,-3.0893892136,-1.0647062512,-1.0952263945  
H,0,-4.0877782398,0.0286168751,-0.1755900145  
H,0,-0.8650644029,-1.2875856067,-1.9447512398  
H,0,0.1918747149,-2.7494767043,-1.6806044376  
H,0,-1.4726143091,-2.6879925537,-1.056854631  
C,0,3.4233924788,1.3440571612,-1.1027689621  
C,0,4.6514492073,0.0697165557,0.6383649823  
H,0,4.3729140004,1.7600168606,-1.444719435  
H,0,2.5267835341,1.6674476533,-1.6319130588  
H,0,4.5316287842,0.1505921102,1.7295303105  
H,0,4.9074164466,-0.9770194052,0.4146941823  
H,0,5.5019584939,0.6931278353,0.3377512267  
H,0,-1.4666702986,3.1717092265,2.6165125727  
H,0,-0.2086042734,2.0997045493,1.9967783393  
H,0,-1.0039592672,3.2532655436,0.9087349733  
H,0,-4.0645452078,-2.3058263528,0.8296032231  
H,0,-2.3295023113,-2.155920522,1.1374765674  
H,0,-3.4590168213,-1.0880528435,1.9674482822  
H,0,-1.8869116461,1.7226452325,-3.4643771189  
H,0,-0.7092687157,0.5598313767,-2.8687216772  
H,0,-2.4420574978,0.1621481564,-2.8444072245

### Int-eq-T

E(RM11) = -652.715673892

Zero-point correction= 0.434856 (Hartree/Particle)  
Thermal correction to Energy= 0.456088  
Thermal correction to Enthalpy= 0.457032  
Thermal correction to Gibbs Free Energy= 0.386492  
Sum of electronic and ZPE= -652.280818  
Sum of electronic and thermal Energies= -652.259586  
Sum of electronic and thermal Enthalpies= -652.258642  
Sum of electronic and thermal Free Energies= -652.329182

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.199	82.492	148.464

C,0,-1.1187632565,-2.4332559877,-0.150980695  
C,0,-2.3995496689,-1.5595177464,0.1533044947  
H,0,-1.0268188547,-2.5865599719,-1.2334157025  
H,0,-1.1918281111,-3.3918881282,0.3787301431  
C,0,-0.0851474349,-1.5189375802,0.3725945722  
C,0,0.2590654227,-0.3935709429,-0.4163916762  
C,0,0.2562629421,-1.6366691736,1.8126853613  
C,0,-0.9481609564,0.5374117083,0.0390804489  
H,0,0.0432993477,-0.6167159436,-1.4760980142  
C,0,-2.2761247393,-0.1196051741,-0.3871175669  
H,0,-0.8045908537,1.4913738463,-0.4827747236

H,0,-0.9242735816,0.7352078261,1.1220677475  
C,0,-3.5108696233,0.6944604584,-0.0301978016  
H,0,-2.2532917348,-0.1930256595,-1.491135377  
H,0,-2.5629956735,-1.5256765796,1.2429478478  
H,0,-3.2593107046,-2.080345073,-0.2880553193  
B,0,1.8523505224,0.3438713518,-0.3980192215  
C,0,2.6912597543,-0.6951321289,-1.3598667932  
C,0,2.527465323,0.4816112934,1.0911605014  
C,0,1.6879571788,1.8042941106,-1.1376382524  
H,0,3.7045081005,-0.2765434805,-1.4952492221  
H,0,2.2551236224,-0.7198693555,-2.3765853291  
C,0,2.8200217807,-2.1255998801,-0.8296697684  
H,0,0.9260454645,1.7433777973,-1.9409023974  
H,0,2.628055798,2.0137759686,-1.6802325053  
C,0,1.3873148366,3.0174597167,-0.2387924216  
C,0,3.9656666313,1.0247127276,1.0015801184  
H,0,2.5870082601,-0.4795683304,1.6296447306  
H,0,1.9311485357,1.1521054452,1.7412229203  
H,0,0.5033435609,-0.6703780977,2.2632206655  
H,0,-0.5198510546,-2.1667804519,2.3801758692  
H,0,1.1763786,-2.2469756163,1.8479516414  
C,0,-3.4543540403,1.8528372894,0.6310612423  
C,0,-4.8301491207,0.1207905173,-0.4944968029  
H,0,-4.3664606001,2.4130206941,0.845183564  
H,0,-2.5165606663,2.2933446978,0.9705654317  
H,0,-4.7714214975,-0.1982766023,-1.5464698829  
H,0,-5.1136928021,-0.7615756392,0.0989438812  
H,0,-5.6361609001,0.8584935014,-0.4025332925  
H,0,3.392975724,-2.7917590342,-1.4926224242  
H,0,3.3109400013,-2.1403491996,0.1574213256  
H,0,1.8271659829,-2.603222102,-0.7053366501  
H,0,4.3877708385,1.2769104234,1.9865826749  
H,0,4.6316119949,0.2781692071,0.5422559199  
H,0,4.0218615986,1.9268601127,0.3734745622  
H,0,1.2032570492,3.937566383,-0.8150848377  
H,0,0.5118671001,2.8592845576,0.4119251705  
H,0,2.2291663739,3.2213647505,0.4392509229

### Int-eq-U

E(RM11) = -652.718355113

Zero-point correction= 0.434604 (Hartree/Particle)  
Thermal correction to Energy= 0.455861  
Thermal correction to Enthalpy= 0.456805  
Thermal correction to Gibbs Free Energy= 0.386639  
Sum of electronic and ZPE= -652.283752  
Sum of electronic and thermal Energies= -652.262494  
Sum of electronic and thermal Enthalpies= -652.261550  
Sum of electronic and thermal Free Energies= -652.331716

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.057	82.540	147.677

C,0,-1.0537503769,-2.2797002283,-0.7813011481  
C,0,-2.3406799186,-1.5249437791,-0.2685791799  
H,0,-0.930560155,-2.1054281337,-1.857565619  
H,0,-1.1458087137,-3.3522533037,-0.5659786312  
C,0,-0.015474197,-1.5867275829,0.011216586  
C,0,0.350853632,-0.2806407964,-0.3976752247  
C,0,0.3093572502,-2.1525387393,1.3463223046  
C,0,-0.8704202691,0.4503261154,0.338158914  
H,0,0.1404765986,-0.1715453442,-1.4749980031  
C,0,-2.1870909687,0.0098587414,-0.3235885705  
H,0,-0.6860310011,1.5259851925,0.2141335408  
H,0,-0.8774292314,0.2397807415,1.418175691  
C,0,-3.4259419386,0.6874154009,0.2414447794

H,0,-2.1227359854,0.2960298503,-1.3908189724  
H,0,-2.5433978339,-1.8270529329,0.7720457989  
H,0,-3.1866046134,-1.8681625385,-0.8782688944  
B,0,1.8702375113,0.4734358292,-0.0825082336  
C,0,2.9145416825,-0.3230453214,-1.0784161825  
C,0,2.3178334211,0.3866808952,1.4993375177  
C,0,1.7109525434,2.0420724,-0.5534057292  
H,0,3.9223213889,0.0894207119,-0.8886901152  
H,0,2.704234052,-0.0869844217,-2.1378245233  
C,0,2.9801965134,-1.8458962384,-0.9280383146  
H,0,2.7339125886,2.4548385506,-0.6163610552  
H,0,1.2185233551,2.6505839463,0.2312831133  
C,0,1.0124597032,2.304825284,-1.8976629272  
C,0,3.5003973553,1.3119988513,1.8324754688  
H,0,2.607058516,-0.6407762576,1.7899860828  
H,0,1.4765977321,0.6645557769,2.1674514965  
H,0,0.5966377935,-1.3827119094,2.0678110431  
H,0,-0.4977117973,-2.7909019314,1.7303476636  
H,0,1.1951951089,-2.7921034836,1.1893471946  
C,0,-3.3868325579,1.5311174865,1.2752707383  
C,0,-4.7264286591,0.356000484,-0.4537521919  
H,0,-4.3001676255,2.0062998481,1.6379544766  
H,0,-2.4613096612,1.7895471649,1.7898888839  
H,0,-4.6176064665,0.4278180215,-1.5467029976  
H,0,-5.0516696878,-0.6701657706,-0.2247638163  
H,0,-5.5265226011,1.0375828094,-0.1412686069  
H,0,3.724635241,-2.3161258347,-1.5885762306  
H,0,3.2304080221,-2.1384024151,0.104818008  
H,0,2.0109446672,-2.3208113023,-1.180476062  
H,0,3.8632666147,1.1801335756,2.8634658715  
H,0,4.3505012148,1.1253267209,1.157776777  
H,0,3.2223717323,2.3691288805,1.713951564  
H,0,1.0945921079,3.3538887282,-2.2198269323  
H,0,1.4422660952,1.6837502094,-2.6994291461  
H,0,-0.066663502,2.074173019,-1.8608640967

### Int-*eq-V*

E(RM11) = -652.716697891

Zero-point correction= 0.434764 (Hartree/Particle)  
Thermal correction to Energy= 0.455948  
Thermal correction to Enthalpy= 0.456892  
Thermal correction to Gibbs Free Energy= 0.387222  
Sum of electronic and ZPE= -652.281934  
Sum of electronic and thermal Energies= -652.260750  
Sum of electronic and thermal Enthalpies= -652.259806  
Sum of electronic and thermal Free Energies= -652.329476

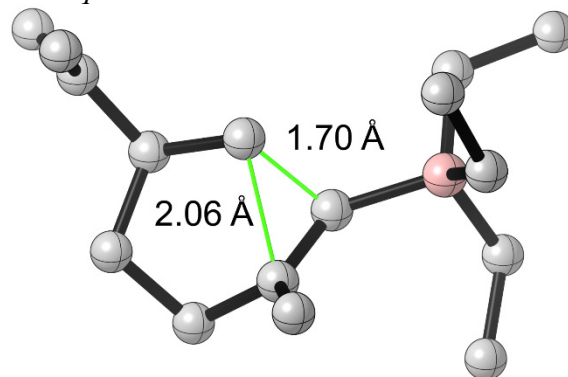
E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.111	82.461	146.632

C,0,1.3575016293,-2.3454232325,0.3017698555  
C,0,2.5775988541,-1.4004914554,-0.0135478824  
H,0,1.246368781,-2.4446041422,1.389281008  
H,0,1.5145997728,-3.326194907,-0.1656918258  
C,0,0.2494392614,-1.5655682619,-0.2876967427  
C,0,-0.204504754,-0.4147534958,0.4017835788  
C,0,-0.1476425835,-1.8536680677,-1.6835606239  
C,0,0.9695095089,0.5482430235,-0.1003248447  
H,0,-0.0160322048,-0.5374740234,1.4825644432  
C,0,2.3186090665,0.0509353129,0.4410602778  
H,0,0.7069206305,1.5434385279,0.2867525288  
H,0,0.9872271292,0.6159417774,-1.1987638583  
C,0,3.4976272501,0.9425084741,0.0815437471  
H,0,2.2487729673,0.0417453793,1.5448705217  
H,0,2.7696532875,-1.4068842822,-1.0993325635

H,0,3.4613601903,-1.8289485471,0.4767692739  
B,0,-1.7701829136,0.2696826336,0.1202229637  
C,0,-2.8305999604,-0.9843241566,-0.0374288653  
C,0,-1.7794869604,1.2834585286,-1.1879520249  
C,0,-2.009881885,1.1047118106,1.5199990146  
H,0,-2.8406354883,-1.3977284052,-1.0647567538  
H,0,-3.848258803,-0.5740028235,0.0936030239  
C,0,-2.6491372488,-2.1380139669,0.9576399279  
H,0,-1.1280816771,1.7456027101,1.7262977462  
H,0,-2.0632247839,0.4065939534,2.3774739822  
C,0,-3.255449542,2.0020554358,1.5411522824  
C,0,-3.1608797798,1.4502816214,-1.8461124757  
H,0,-1.0804687294,0.9771484407,-1.9905449876  
H,0,-1.4145972608,2.2827792317,-0.8792164641  
H,0,-0.6302902037,-0.9952813297,-2.16080735  
H,0,0.6780147843,-2.2622857407,-2.2819225249  
H,0,-0.9139444915,-2.6462746221,-1.5927927872  
C,0,3.3872778831,2.0142402502,-0.7068259083  
C,0,4.8235480955,0.5475951019,0.6900682526  
H,0,4.2588960309,2.6346506746,-0.9235930544  
H,0,2.4421657867,2.322005711,-1.1547265142  
H,0,4.7160330377,0.3358819825,1.7648233862  
H,0,5.2260785259,-0.3609635606,0.2171297863  
H,0,5.5667821039,1.3445390967,0.5685279949  
H,0,-3.4395425475,-2.9010280408,0.8884894481  
H,0,-1.6911090392,-2.6741560958,0.8057849534  
H,0,-2.6335755184,-1.7710640796,1.9955053504  
H,0,-3.1581144186,2.2054191679,-2.6476078839  
H,0,-3.5021301434,0.5024490976,-2.2899456449  
H,0,-3.9261061474,1.7471138208,-1.1146138288  
H,0,-3.4031716977,2.4962420613,2.5140195861  
H,0,-3.1852112447,2.7941587276,0.7800858099  
H,0,-4.1681981902,1.4238955834,1.3263922458

### TS2 Structures

#### TS2-*eq-A*



E(RM11) = -652.716406599

Zero-point correction= 0.433779 (Hartree/Particle)  
Thermal correction to Energy= 0.454906  
Thermal correction to Enthalpy= 0.455850  
Thermal correction to Gibbs Free Energy= 0.384850  
Sum of electronic and ZPE= -652.282628  
Sum of electronic and thermal Energies= -652.261501  
Sum of electronic and thermal Enthalpies= -652.260557  
Sum of electronic and thermal Free Energies= -652.331557

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.458	81.149	149.432

C,0,-0.8933765188,-2.1206634512,0.1346473236  
C,0,-2.1030222184,-1.1753933092,0.3678656645  
H,0,-0.8913720786,-2.477501944,-0.904100436  
H,0,-0.9344840984,-2.9800586213,0.8172806737  
C,0,0.3136861906,-1.2692680467,0.3986978851  
C,0,0.8109782606,-0.4191405952,-0.6043066859  
C,0,0.843546653,-1.2899327164,1.794860845  
C,0,-0.4115888566,0.6083015476,-0.0173973568  
H,0,0.400782314,-0.6971680819,-1.5904096045  
C,0,-1.8262088643,0.1391722793,-0.3765493405  
H,0,-0.0947359019,1.4951582764,-0.584133725  
H,0,-0.3171771922,0.8575897647,1.0475616235  
C,0,-2.871534095,1.202508441,-0.0780103212  
H,0,-1.8504681954,-0.065573633,-1.4589877404  
H,0,-2.2042979474,-0.9787204586,1.4477830834  
H,0,-3.0356479533,-1.6463591119,0.0310862512  
B,0,2.3390378799,0.2513084981,-0.8143331178  
C,0,3.1457029567,-1.0020902571,-1.5358753635  
C,0,3.1432343901,0.7435965314,0.5324776089  
C,0,2.1389929937,1.4863357089,-1.884384019  
H,0,4.1915667104,-0.6791213116,-1.682069511  
H,0,2.7512229196,-1.1853762551,-2.5539977662  
C,0,3.159389192,-2.3287054119,-0.7640273032  
H,0,1.5066067438,2.2995359809,-1.4741697821  
H,0,1.5953356273,1.1184772125,-2.7775916384  
C,0,3.4556450485,2.128047907,-2.3465207962  
C,0,2.5705172548,1.956874862,1.2827475123  
H,0,4.1551724802,1.0178715656,0.18314498  
H,0,3.3294492458,-0.0796465066,1.246431602  
H,0,1.4275962169,-0.3962752179,2.0297864699  
H,0,0.0411847316,-1.4476963873,2.5299350134  
H,0,1.5225022668,-2.1570169804,1.8493001906  
C,0,-3.7819863955,1.5344665421,-0.9951887542  
C,0,-2.8301626072,1.8585804421,1.2817775278  
H,0,-4.5500331076,2.2818094756,-0.7876590926  
H,0,-3.7854585503,1.075600363,-1.9860291984  
H,0,-2.7598364271,1.1183303188,2.0930238268  
H,0,-1.9556016294,2.5206167501,1.3699054349  
H,0,-3.7280465813,2.464323634,1.4509722028  
H,0,3.7862193422,-3.0987522482,-1.2392131902  
H,0,3.5378894247,-2.1881728352,0.2616001872  
H,0,2.1460877503,-2.7652850179,-0.6832448081  
H,0,3.2214722115,2.3043050222,2.1000372998  
H,0,2.4257684669,2.8063477065,0.596939607  
H,0,1.5836563432,1.7509771439,1.7334762163  
H,0,3.3049407949,2.909329598,-3.1073525686  
H,0,3.9852927631,2.5940079594,-1.5009153931  
H,0,4.1335193261,1.3754070881,-2.7769169468

### TS2-eq-B

E(RM11) = -652.714945092

Zero-point correction= 0.434022 (Hartree/Particle)  
Thermal correction to Energy= 0.455092  
Thermal correction to Enthalpy= 0.456037  
Thermal correction to Gibbs Free Energy= 0.385325  
Sum of electronic and ZPE= -652.280923  
Sum of electronic and thermal Energies= -652.259853  
Sum of electronic and thermal Enthalpies= -652.258908  
Sum of electronic and thermal Free Energies= -652.329620

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.575	81.070	148.825

C,0,-0.8760119137,-2.0310540593,-0.1093947853

C,0,-2.0644404443,-1.0932588776,0.2421455387  
H,0,-0.9017213722,-2.2788371063,-1.1791373965  
H,0,-0.9219140171,-2.9538449945,0.4843758003  
C,0,0.3479394647,-1.2291870052,0.2122100612  
C,0,0.8336801045,-0.2788325887,-0.7019777331  
C,0,0.9338458566,-1.4026233929,1.5714820503  
C,0,-0.3635554372,0.7009806448,-0.0131721256  
H,0,0.4133847453,-0.4507473677,-1.7060293311  
C,0,-1.7890354487,0.280723889,-0.3873163341  
H,0,-0.0438104684,1.6365750141,-0.49416604  
H,0,-0.2522804111,0.8423482763,1.0692231969  
C,0,-2.8183218687,1.3180748545,0.0336324658  
H,0,-1.8395804039,0.1760176894,-1.4831303445  
H,0,-2.1330626123,-0.9939795476,1.3380022976  
H,0,-3.0119907354,-1.5214874851,-0.1095149912  
B,0,2.3641329864,0.4152611271,-0.8114197048  
C,0,3.3039099102,-0.8270621323,-1.3620818888  
C,0,3.0481169638,0.9906766337,0.5739062304  
C,0,2.1964509306,1.6096132583,-1.936687194  
H,0,3.3538161884,-1.6248484522,-0.5934003045  
H,0,4.3399551457,-0.4507386654,-1.4406266179  
C,0,2.9051466572,-1.4539666622,-2.7057334087  
H,0,1.6143488888,2.4655598313,-1.5397281239  
H,0,1.6074182667,1.2435223304,-2.8012268579  
C,0,3.5285405261,2.1606532236,-2.4665226385  
C,0,2.3244422889,2.0882048935,1.3729891101  
H,0,4.0164997214,1.4078985219,0.2450618875  
H,0,3.3450127463,0.1737568909,1.2588294642  
H,0,1.5060707651,-0.5254070806,1.8860237386  
H,0,0.1778137852,-1.6837894513,2.3178366422  
H,0,1.6472646783,-2.2397770555,1.480794552  
C,0,-3.7628343906,1.7206126629,-0.8186435282  
C,0,-2.7246387248,1.8627290086,1.4393775633  
H,0,-4.52199059,2.4467099886,-0.5221862887  
H,0,-3.8047071039,1.3426987929,-1.8422937019  
H,0,-2.6131119446,1.0600615278,2.1840445861  
H,0,-1.8522192925,2.5254110227,1.5443968722  
H,0,-3.6197943573,2.4417808654,1.6947286851  
H,0,3.6225249687,-2.2127576772,-3.0545758242  
H,0,1.9218717557,-1.9525627037,-2.6505308377  
H,0,2.8297996253,-0.6873503492,-3.4930565215  
H,0,2.9861967123,2.5946863128,2.0921933158  
H,0,1.9172401373,2.8652063075,0.705751188  
H,0,1.4760413693,1.6979203286,1.9616227934  
H,0,3.3929502163,2.9585669796,-3.2128894488  
H,0,4.1394503673,2.577346248,-1.6510609479  
H,0,4.1244588743,1.3646935503,-2.9396573303

### TS2-eq-C

E(RM11) = -652.715170864

Zero-point correction= 0.433920 (Hartree/Particle)  
Thermal correction to Energy= 0.455072  
Thermal correction to Enthalpy= 0.456016  
Thermal correction to Gibbs Free Energy= 0.385141  
Sum of electronic and ZPE= -652.281250  
Sum of electronic and thermal Energies= -652.260099  
Sum of electronic and thermal Enthalpies= -652.259155  
Sum of electronic and thermal Free Energies= -652.330030

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.562	81.144	149.170

C,0,-1.5655532006,-2.2026695578,0.1571978373  
C,0,-2.733651853,-1.2078974648,0.4003983843  
H,0,-1.5825225124,-2.5456912693,-0.8858909306



H,0,-1.6463286729,-3.0670980241,0.8298605818  
 C,0,-0.3212853345,-1.4103776727,0.4267034995  
 C,0,0.2025317012,-0.5587121357,-0.5611039015  
 C,0,0.2409518957,-1.4933614707,1.8043703367  
 C,0,-0.9773780088,0.5087240324,0.0241262526  
 H,0,-0.2090969366,-0.8183344291,-1.5491617979  
 C,0,-2.407194865,0.0975730077,-0.3402784488  
 H,0,-0.6225219591,-1.3868448839,-0.5362346987  
 H,0,-0.8723727214,0.7454248591,1.0909094017  
 C,0,-3.4128491353,1.1971249632,-0.0372969322  
 H,0,-2.4379985985,-0.1013315604,-1.4241288313  
 H,0,-2.8207036095,-1.0109216701,1.4815510864  
 H,0,-3.6861452242,-1.64005343,0.0670575337  
 B,0,1.738834108,0.101610794,-0.7204007338  
 C,0,2.5830171536,-1.202145308,-1.2949744072  
 C,0,2.4683469731,0.686605156,0.63804745  
 C,0,1.6257255965,1.3054909831,-1.8408384837  
 H,0,2.0163605414,-1.7309766722,-2.0860922939  
 H,0,2.6952745087,-1.9421154012,-0.4763744021  
 C,0,3.9734672625,-0.8641943048,-1.8502239704  
 H,0,2.6558897028,1.6447905687,-2.049620076  
 H,0,1.1287716207,2.2079138053,-1.4326146864  
 C,0,0.9509399452,0.9413650288,-3.1724741359  
 C,0,1.7789170035,1.8132788846,1.4290433948  
 H,0,3.4313755669,1.0930909812,0.2805978238  
 H,0,2.7658028619,-0.1215440157,1.3338519054  
 H,0,0.8724465126,-0.6343903535,2.0439461127  
 H,0,-0.5402302916,-1.6487175985,2.5618487895  
 H,0,0.8889819729,-2.3866177716,1.8042955534  
 C,0,-4.3129377106,1.5617822331,-0.9523571865  
 C,0,-3.3453482061,1.8493509888,1.3233620244  
 H,0,-5.0546268338,2.334563063,-0.7422191022  
 H,0,-4.333955879,1.104486129,-1.9437078877  
 H,0,-3.2996413941,1.105924217,-2.1335324821  
 H,0,-2.4473726244,2.4795438858,1.4107393526  
 H,0,-4.2212766934,2.4857543774,1.4952183693  
 H,0,4.5424200331,-1.7590111136,-2.1472168047  
 H,0,3.8939638569,-0.217437223,-2.7378134566  
 H,0,4.5786258812,-0.3209501732,-1.1084828021  
 H,0,2.4563778789,2.3032663905,2.1450526515  
 H,0,1.3980734842,2.5976242192,0.7559000379  
 H,0,0.9163530327,1.4585694377,2.0195680658  
 H,0,1.0607993145,1.7249639428,-3.9375581388  
 H,0,1.3731525955,0.0123426553,-3.5894045162  
 H,0,-0.1347239793,0.7758732926,-3.0527114419

### TS2-eq-D

E(RM11) = -652.717112933

Zero-point correction= 0.434460 (Hartree/Particle)  
 Thermal correction to Energy= 0.455163  
 Thermal correction to Enthalpy= 0.456107  
 Thermal correction to Gibbs Free Energy= 0.387367  
 Sum of electronic and ZPE= -652.282653  
 Sum of electronic and thermal Energies= -652.261950  
 Sum of electronic and thermal Enthalpies= -652.261006  
 Sum of electronic and thermal Free Energies= -652.329746

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.619	80.896	144.675

C,0,-0.8137312219,-2.097419935,0.047580687  
 C,0,-1.9873919897,-1.1077130783,0.2727710651  
 H,0,-0.8178367511,-2.449445627,-0.9929252053  
 H,0,-0.8966858179,-2.9588355586,0.7238382679  
 C,0,0.4332677053,-1.3050632127,0.3237852004

C,0,0.9707941976,-0.4698578085,-0.670095016  
 C,0,0.9750148176,-1.3908109892,1.712504985  
 C,0,-0.2158928149,0.5953269835,-0.0653333624  
 H,0,0.5528969736,-0.7255175774,-1.6574710235  
 C,0,-1.6441181206,0.2017431921,-0.4525550091  
 H,0,0.1560936445,1.4782867539,-0.606246369  
 H,0,-0.1186878356,0.8183171346,1.0051189655  
 C,0,-2.6421073567,1.3083945651,-0.1515044361  
 H,0,-1.6617351652,0.0135970401,-1.5386923116  
 H,0,-2.0963331635,-0.916392186,1.3529683234  
 H,0,-2.9336280753,-1.5362873891,-0.0820249873  
 B,0,2.4845364926,0.2200629299,-0.8346219029  
 C,0,3.3772290462,-1.0077132227,-1.4916506352  
 C,0,3.2290822156,0.7827793776,0.5255574282  
 C,0,2.3372491299,1.4548334732,-1.9212001099  
 H,0,4.4135365668,-0.635028465,-1.5830335591  
 H,0,3.0548201137,-1.2273818236,-2.526448099  
 C,0,3.3951829732,-2.3225896242,-0.7000761573  
 H,0,3.3633224885,1.6984123133,-2.2511824383  
 H,0,1.9786248561,2.3872941582,-1.442472905  
 C,0,1.4761908106,1.1963812515,-3.1686264667  
 C,0,2.5391659672,1.8754969225,1.3629140612  
 H,0,4.1748913443,1.2132096223,0.148156839  
 H,0,3.5600761252,-0.0302860288,1.1990755027  
 H,0,1.6905704833,-0.593711021,1.9275294306  
 H,0,0.1690742072,-1.4224731066,2.46066293  
 H,0,1.5117845614,-2.3520988728,1.766222139  
 C,0,-3.5271262059,1.6915308205,-1.0736571577  
 C,0,-2.5844531601,1.9462470776,1.2163969165  
 H,0,-4.2625168689,2.4706315134,-0.8648766009  
 H,0,-3.541093506,1.2440254779,-2.0696005545  
 H,0,-2.5502535284,1.1941384119,2.0189837405  
 H,0,-1.6843483865,2.5710803545,1.318733281  
 H,0,-3.4586603482,2.5854157867,1.3866110539  
 H,0,4.0829897738,-3.0717694921,-1.1212475984  
 H,0,3.6976195082,-2.1556385028,0.3468480724  
 H,0,2.3962143741,-2.7965428757,-0.681424467  
 H,0,3.2281356307,2.3616829669,2.0703767985  
 H,0,2.1231810411,2.6691736546,0.7226619112  
 H,0,1.7021501765,1.4892467345,1.9696986633  
 H,0,1.5795338722,1.9858835819,-3.9282113712  
 H,0,1.744459981,0.2429528958,-3.6514769749  
 H,0,0.3993128786,1.1408474131,-2.9263863136

### TS2-eq-E

E(RM11) = -652.715025333

Zero-point correction= 0.433816 (Hartree/Particle)  
 Thermal correction to Energy= 0.454945  
 Thermal correction to Enthalpy= 0.455889  
 Thermal correction to Gibbs Free Energy= 0.385026  
 Sum of electronic and ZPE= -652.281209  
 Sum of electronic and thermal Energies= -652.260081  
 Sum of electronic and thermal Enthalpies= -652.259137  
 Sum of electronic and thermal Free Energies= -652.329999

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.482	81.265	149.142

C,0,-1.2412470154,-1.8990073833,1.4425507541  
 C,0,-2.4913839385,-1.0908973197,1.0232788022  
 H,0,-1.1657994859,-2.8140378959,0.8390045108  
 H,0,-1.279214492,-2.1689432637,2.5064540158  
 C,0,-0.0744786922,-0.9903004573,1.1639122458  
 C,0,0.5348911991,-0.9396035,-0.0970159143  
 C,0,0.3747521512,-0.1253816055,2.2965929571

C,0,-0.8015251191,0.1199169654,-0.3370503017  
H,0,0.2426766858,-1.797285344,-0.7259331477  
C,0,-2.1913574372,-0.5229530402,-0.3708878181  
H,0,-0.4474343653,0.4026194541,-1.338726858  
H,0,-0.7479877864,1.0254966783,0.2817423214  
C,0,-3.2546440935,0.4542563113,-0.8470077307  
H,0,-2.1562145442,-1.3635397081,-1.0828872065  
H,0,-2.654096556,-0.2670875468,1.7376374351  
H,0,-3.3947046453,-1.7145893686,1.0274045703  
B,0,2.0056553896,-0.2468425765,-0.5198132386  
C,0,2.2242325693,-0.7394486866,-2.0777985564  
C,0,3.1207448822,-0.9078635575,0.503847278  
C,0,2.1190467704,1.4040739117,-0.4149920069  
H,0,1.3592697788,-0.4380817154,-2.706105422  
H,0,2.2287551454,-1.8456302508,-2.1227151552  
C,0,3.5075104458,-0.2211481922,-2.7407932646  
H,0,3.2029215248,1.5867014974,-0.5316269966  
H,0,1.9054141908,1.8026932202,0.5953574786  
C,0,1.3967915616,2.2930085705,-1.4472432413  
C,0,3.019040255,-2.4227840455,0.7356683727  
H,0,3.1048650784,-0.3932198266,1.4844540287  
H,0,4.1216847445,-0.6827624779,0.0946946105  
H,0,0.9836794616,0.7144415951,1.9516257623  
H,0,-0.4659357777,0.2131072242,2.918796106  
H,0,1.0188289715,-0.7685731405,2.9196744374  
C,0,-4.152101045,0.0850183215,-1.7626209852  
C,0,-3.2505033139,1.8373931419,-0.2403582194  
H,0,-4.9381682077,0.7661208156,-2.0936710058  
H,0,-4.128106764,-0.9086048494,-2.2149962731  
H,0,-3.1608521505,1.8040484318,0.8561573528  
H,0,-2.4008006752,2.4272534167,-0.6174160689  
H,0,-4.1709967747,2.3773683936,-0.4910257281  
H,0,3.6444218411,-0.6046473049,-3.7636467257  
H,0,3.5160170101,0.8782382671,-2.7991896841  
H,0,4.3948618328,-0.5159171275,-2.1596627207  
H,0,3.8420632362,-2.8232269354,1.3473270926  
H,0,2.0816106597,-2.6987140616,1.2534066426  
H,0,3.0240538557,-2.9718446236,-0.2191901808  
H,0,1.8538805064,3.2915599657,-1.5244115701  
H,0,1.4249307731,1.8473185968,-2.4542081256  
H,0,0.336505419,2.4645281863,-1.201223629

### TS2-eq-F

E(RM11) = -652.713642664

Zero-point correction= 0.434209 (Hartree/Particle)  
Thermal correction to Energy= 0.455194  
Thermal correction to Enthalpy= 0.456138  
Thermal correction to Gibbs Free Energy= 0.385955  
Sum of electronic and ZPE= -652.279434  
Sum of electronic and thermal Energies= -652.258448  
Sum of electronic and thermal Enthalpies= -652.257504  
Sum of electronic and thermal Free Energies= -652.327688

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.639	81.048	147.714

C,0,-1.4491586634,-1.6614431842,1.754189577  
C,0,-2.7184076714,-0.9875416563,1.1853537652  
H,0,-1.3236042769,-2.6591176188,1.3115827174  
H,0,-1.5036386897,-1.7570252468,2.846928631  
C,0,-0.3027454006,-0.7656295005,1.3550145467  
C,0,0.3335871732,-0.9049884618,0.1137712985  
C,0,0.1017046951,0.268281578,2.3575488547  
C,0,-1.0356267,0.0911230829,-0.2750262332  
H,0,0.0351232082,-1.8439046157,-0.3813286595

C,0,-2.3939914133,-0.6150067206,-0.2677518154  
H,0,-0.6521880563,0.2731059784,-1.2885692863  
H,0,-1.0482962775,1.0649916521,0.2301824538  
C,0,-3.4777923868,0.2292284607,-0.9184061198  
H,0,-2.2931024572,-1.5465831513,-0.8476866974  
H,0,-2.941166439,-0.077061074,1.7654651285  
H,0,-3.5928904771,-1.6471569143,1.2566187227  
B,0,1.8270097736,-0.3059031684,-0.4184572497  
C,0,2.1648157118,-1.3094562391,-1.6895189466  
C,0,2.9142923308,-0.5014464615,0.8036822755  
C,0,1.8020670167,1.2482273154,-0.9737674889  
H,0,1.4479701286,-1.1097090897,-2.5129806791  
H,0,1.9868168069,-2.3654408272,-1.4063206285  
C,0,3.5925651484,-1.2086155264,-2.2426756426  
H,0,1.08691371,1.3594056079,-1.8135020188  
H,0,2.7875504183,1.3880884515,-1.4510673278  
C,0,1.6122260513,2.4288607747,-0.006545862  
C,0,3.0085477935,-1.9311855652,1.3557518768  
H,0,2.737400039,0.1930739628,1.6449880243  
H,0,3.9055276003,-0.2080414222,0.4131725623  
H,0,0.6963776992,1.0676946371,1.9079245778  
H,0,-0.7656738166,0.6734455289,2.898723462  
H,0,0.7411337501,-0.2550733515,3.0878172254  
C,0,-4.2850824323,-0.2997410152,-1.8397049242  
C,0,-3.5984571081,1.6691493486,-0.4786569478  
H,0,-5.0837058325,0.2862765579,-2.2981718619  
H,0,-4.1714185961,-1.3344121812,-2.1696936338  
H,0,-3.6012663943,1.7640961619,0.6176399319  
H,0,-2.7536477216,2.2660754743,-0.8543048893  
H,0,-4.5222779125,2.1182785666,-0.8613899189  
H,0,3.7544460745,-1.8525956479,-3.1209156339  
H,0,3.8392878274,-0.1792764913,-2.543424528  
H,0,4.3294920455,-1.5055309807,-1.4799752614  
H,0,3.7487716983,-2.0389453335,2.1638136082  
H,0,2.0392451977,-2.2756420705,1.762319189  
H,0,3.2823045968,-2.6424321046,0.5612667436  
H,0,1.8422023531,3.3960796824,-0.4794130041  
H,0,0.5779969532,2.5131547659,0.3688125304  
H,0,2.2728621819,2.3364225222,0.8704863664

### TS2-eq-G

E(RM11) = -652.717244750

Zero-point correction= 0.434056 (Hartree/Particle)  
Thermal correction to Energy= 0.455016  
Thermal correction to Enthalpy= 0.455960  
Thermal correction to Gibbs Free Energy= 0.385602  
Sum of electronic and ZPE= -652.283189  
Sum of electronic and thermal Energies= -652.262229  
Sum of electronic and thermal Enthalpies= -652.261285  
Sum of electronic and thermal Free Energies= -652.331642

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.527	81.041	148.080

C,0,-1.024717067,-2.0760468043,-0.281133279  
C,0,-2.170386705,-1.1138172013,0.1204289247  
H,0,-1.0344854578,-2.2382790305,-1.3675318487  
H,0,-1.122874224,-3.0418631511,0.2326027355  
C,0,0.2374830938,-1.3729205353,0.130320795  
C,0,0.8506619191,-0.4265890393,-0.7046946748  
C,0,0.7566289049,-1.6813554351,1.496520727  
C,0,-0.3385616964,0.5670706733,0.0364641665  
H,0,0.4657088793,-0.4915058502,-1.7364613621  
C,0,-1.7834969391,0.2832836727,-0.3847977109  
H,0,0.0520866353,1.4941304505,-0.4033616535

H,0,-0.2095073522,0.6606166372,1.1230829285  
C,0,-2.7394601864,1.3600835602,0.104021607  
H,0,-1.8152795889,0.2730284065,-1.4868593559  
H,0,-2.267405949,-1.1008976739,1.2182677635  
H,0,-3.1317622508,-1.4474681661,-0.2911356023  
B,0,2.4263704676,0.175151032,-0.576817132  
C,0,3.4231196946,-1.1178074569,-0.316338078  
C,0,2.5836604099,1.2941354693,0.6278775316  
C,0,2.7410359848,0.8363903399,-2.05209798  
H,0,3.4619592196,-1.4035010667,0.7531105669  
H,0,4.448959747,-0.781807032,-0.5498921809  
C,0,3.1388113233,-2.3706710029,-1.15951114  
H,0,2.6449103974,0.0664071086,-2.8416575343  
H,0,3.8011155058,1.143903434,-2.0856716322  
C,0,1.8667071402,2.0389093363,-2.4403738558  
C,0,3.9917047722,1.9078405894,0.6778019494  
H,0,2.3713355093,0.8650991917,1.6277448754  
H,0,1.8642646852,2.1286948359,0.52135507  
H,0,1.4509494909,-0.9144348214,1.8514078919  
H,0,-0.0566163106,-1.8558225747,2.2155791863  
H,0,1.3240636957,-2.621664906,1.3949639731  
C,0,-3.6265809898,1.9080341737,-0.7285029571  
C,0,-2.6421687514,1.7714843688,1.5539423618  
H,0,-4.3350860581,2.6637905145,-0.384563054  
H,0,-3.6695047702,1.6246090323,-1.7822096501  
H,0,-2.5991632922,0.9010536529,2.2259567715  
H,0,-1.7317515293,2.3633486743,1.73177738  
H,0,-3.5031286424,2.384343752,1.8453679329  
H,0,3.8911221094,-3.1628808606,-1.0237997657  
H,0,2.1602995928,-2.8258161246,-0.9175196663  
H,0,3.110875409,-2.1269048712,-2.2328669547  
H,0,4.1164419647,2.6195176691,1.5085148015  
H,0,4.7602369943,1.1284588375,0.7918507271  
H,0,4.2156987924,2.448316034,-0.2543148835  
H,0,2.1380994619,2.4750902651,-3.4140388926  
H,0,0.7994854306,1.7600171974,-2.5140455486  
H,0,1.9407944596,2.8447516948,-1.6916846641

### TS2-eq-H

E(RM11) = -652.714472341

Zero-point correction= 0.434660 (Hartree/Particle)  
Thermal correction to Energy= 0.455392  
Thermal correction to Enthalpy= 0.456336  
Thermal correction to Gibbs Free Energy= 0.387291  
Sum of electronic and ZPE= -652.279812  
Sum of electronic and thermal Energies= -652.259081  
Sum of electronic and thermal Enthalpies= -652.258136  
Sum of electronic and thermal Free Energies= -652.327181

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.763	80.854	145.317

C,0,-0.6176275295,-1.5162272211,1.6334016507  
C,0,-1.9084196366,-0.8764367601,1.0697307073  
H,0,-0.4691267839,-2.51121183,1.1919949163  
H,0,-0.6668477513,-1.6103208716,2.7265624244  
C,0,0.5019588165,-0.5943970893,1.2248082316  
C,0,1.1129680753,-0.7105058063,-0.0317534927  
C,0,0.8965691939,0.451847503,2.2163776702  
C,0,-0.273182374,0.2522188095,-0.4111107447  
H,0,0.8387622119,-1.6622591532,-0.5162743037  
C,0,-1.6113466477,-0.4910818153,-0.3863437513  
H,0,0.0824751358,0.4554729672,-1.4301246669  
H,0,-0.3040962628,1.2205176118,0.1052980393  
C,0,-2.7273373022,0.3248119957,-1.0185419942

H,0,-1.492437173,-1.4170731021,-0.9728617438  
H,0,-2.1523281104,0.02658133,1.6528736373  
H,0,-2.7626907184,-1.5611427348,1.1487886481  
B,0,2.5841398011,-0.0717823348,-0.5699476246  
C,0,2.9734505421,-1.041947581,-1.8490682156  
C,0,3.6922696337,-0.2576988124,0.6372979402  
C,0,2.5291539533,1.4911092323,-1.1055197049  
H,0,3.0780821597,-2.0932595125,-1.5192732516  
H,0,3.9755518341,-0.7511237188,-2.2128605496  
C,0,1.9947311089,-1.0074628495,-3.033972813  
H,0,1.7907055576,1.6177308989,-1.9202272229  
H,0,3.5024454577,1.6346645238,-1.6098147114  
C,0,2.3527198668,2.6621249533,-0.1236032336  
C,0,3.7424041208,-1.6470442826,1.2921197409  
H,0,3.5836460565,0.5002037503,1.4350130987  
H,0,4.6819386659,-0.0489610205,0.1914515707  
H,0,1.4766072779,1.2547106674,1.754200282  
H,0,0.0280595321,0.8474354803,2.7627725879  
H,0,1.5498691915,-0.0568603204,2.9447935556  
C,0,-3.5282473089,-0.2204872636,-1.9358961021  
C,0,-2.8859293551,1.757654287,-0.567729897  
H,0,-4.3477514583,0.3459444955,-2.3818920764  
H,0,-3.3874840035,-1.2485721717,-2.2758650055  
H,0,-2.8729062103,1.8466747626,0.5289065432  
H,0,-2.0673584337,2.3831741922,-0.9545819125  
H,0,-3.8302523603,2.1790482332,-0.9315964561  
H,0,2.2912842201,-1.6772668203,-3.8557982451  
H,0,0.9761625467,-1.3181949598,-2.7355454414  
H,0,1.9111899096,0.005255346,-3.4572710544  
H,0,4.5302981894,-1.7355532365,2.0561456621  
H,0,2.7894884872,-1.9029215249,1.7918251003  
H,0,3.9224293151,-2.4336195197,0.5443370008  
H,0,2.5728356549,3.6333749161,-0.5927156778  
H,0,1.3223321853,2.7398959029,0.2639701299  
H,0,3.0238729888,2.5679529064,0.7449647056

### TS2-eq-I

E(RM11) = -652.714093723

Zero-point correction= 0.434440 (Hartree/Particle)  
Thermal correction to Energy= 0.455261  
Thermal correction to Enthalpy= 0.456205  
Thermal correction to Gibbs Free Energy= 0.386348  
Sum of electronic and ZPE= -652.279654  
Sum of electronic and thermal Energies= -652.258833  
Sum of electronic and thermal Enthalpies= -652.257889  
Sum of electronic and thermal Free Energies= -652.327746

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.680	80.813	147.026

C,0,-0.768385971,-2.1237906397,0.7551466293  
C,0,-1.9947242483,-1.1784784511,0.6574573028  
H,0,-0.6931231288,-2.7387134928,-0.1516107787  
H,0,-0.8458319832,-2.775886819,1.6356480604  
C,0,0.4064698916,-1.1964196363,0.8674173139  
C,0,1.0071541938,-0.6581188835,-0.2823759708  
C,0,0.7876983581,-0.8019395466,2.2583481335  
C,0,-0.2750392442,0.458671452,-0.12846943  
H,0,0.6897546458,-1.2077238575,-1.1852974225  
C,0,-1.6688115684,-0.1198330254,-0.4055413874  
H,0,0.0657989457,1.094277639,-0.9559331728  
H,0,-0.2259899959,1.0584007193,0.789948249  
C,0,-2.7299825924,0.9663675985,-0.4843629877  
H,0,-1.6267287029,-0.6242049635,-1.384776194  
H,0,-2.1602072404,-0.6936415676,1.6334447259

H,0,-2.9057341469,-1.7386580343,0.4100857413  
B,0,2.5486700189,-0.0150643454,-0.5288965964  
C,0,3.3616570394,-1.3673704386,-1.0229606682  
C,0,3.2582241894,0.6559498451,0.7942296018  
C,0,2.4441150262,1.0568507684,-1.7817285733  
H,0,4.3761847148,-1.0583324093,-1.3300600495  
H,0,2.9013820381,-1.7798476229,-1.9416037195  
C,0,3.4797297139,-2.4804145651,0.0261115325  
H,0,1.6622593167,0.7322266357,-2.5002228026  
H,0,3.379310077,0.9963042151,-2.3665722287  
C,0,2.2185117847,2.5377396341,-1.4220157924  
C,0,4.7184112274,1.0503577849,0.5113074729  
H,0,3.2747805808,-0.0311661521,1.6584186295  
H,0,2.7056690786,1.5542707436,1.1370900172  
H,0,1.2872064766,0.1693836646,2.2956703185  
H,0,-0.0754564005,-0.8322445266,2.938090718  
H,0,1.5152693252,-1.5577845715,2.599395017  
C,0,-3.5899595594,1.0011870482,-1.503912364  
C,0,-2.7662378213,1.9865165848,0.6289158491  
H,0,-4.3720262734,1.7605286174,-1.5611942253  
H,0,-3.5370752242,0.2752965659,-2.3179624642  
H,0,-2.7012424786,1.5136286199,1.620508851  
H,0,-1.9198118316,2.6850760947,0.546559593  
H,0,-3.6907565357,2.5743874028,0.5915539052  
H,0,4.0442896699,-3.3565935439,-0.328096083  
H,0,3.9815547961,-2.1123110875,0.9357955479  
H,0,2.4857381303,-2.8547017332,0.3361583712  
H,0,5.1667880994,1.643797631,1.3230487714  
H,0,5.3408675572,0.1518915877,0.3807230636  
H,0,4.8091157992,1.6333115326,-0.4181310484  
H,0,2.0790499787,3.1747261053,-2.3092713454  
H,0,1.3433280526,2.695194694,-0.7694262816  
H,0,3.0775182911,2.9387837088,-0.8643179396

### TS2-eq-J

E(RM11) = -652.717731458

Zero-point correction= 0.434524 (Hartree/Particle)  
Thermal correction to Energy= 0.455187  
Thermal correction to Enthalpy= 0.456131  
Thermal correction to Gibbs Free Energy= 0.387313  
Sum of electronic and ZPE= -652.283207  
Sum of electronic and thermal Energies= -652.262544  
Sum of electronic and thermal Enthalpies= -652.261600  
Sum of electronic and thermal Free Energies= -652.330419

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.634	80.766	144.841

C,0,-0.7774546448,-2.2079134618,0.5628366813  
C,0,-1.9571054462,-1.1999759904,0.5075915425  
H,0,-0.7180741653,-2.7657064052,-0.3813422949  
H,0,-0.9072305158,-2.9114267222,1.3962867549  
C,0,0.4466088217,-1.3582873446,0.7492865306  
C,0,1.0547007561,-0.7532828922,-0.3641109972  
C,0,0.8665532825,-1.1175237632,2.1627615411  
C,0,-0.1588969758,0.4102102608,-0.0914856472  
H,0,0.7077161459,-1.2291816083,-1.295788385  
C,0,-1.5671322731,-0.0700692993,-0.4569158603  
H,0,0.2448486664,1.1440897561,-0.8043711081  
H,0,-0.1137620715,0.8745839227,0.9029334189  
C,0,-2.5784596888,1.0650872447,-0.4531915906  
H,0,-1.5258425858,-0.48486125,-1.4776555712  
H,0,-2.1269754858,-0.7882208112,1.5158455312  
H,0,-2.8833073527,-1.7005666793,0.1970197929  
B,0,2.5668462914,-0.0601497225,-0.573705535

C,0,3.5493451786,-1.3543279816,-0.8685245593  
C,0,3.0928141908,0.8296462461,0.7120302019  
C,0,2.4633112032,0.8971042438,-1.9167956603  
H,0,4.5809494821,-0.9709770859,-0.9666137887  
H,0,3.3194471823,-1.8096775714,-1.8498707665  
C,0,3.5351461986,-2.4591133041,0.1965080841  
H,0,3.4982656156,1.0941250096,-2.2475046056  
H,0,2.0634252232,1.9018276595,-1.6675328134  
C,0,1.6777156585,0.3410643618,-3.11601019  
C,0,4.3059598682,1.7105051047,0.3701150081  
H,0,3.3832831562,0.1843994042,1.5623876463  
H,0,2.2944923955,1.4971384247,1.1001119443  
H,0,1.5056899727,-0.2370148585,2.2617642887  
H,0,0.0003398536,-1.0618313104,2.8379883856  
H,0,1.4590866382,-1.9998882112,2.4555616281  
C,0,-3.4099788231,1.2345117809,-1.4828599032  
C,0,-2.5968658126,1.978660241,0.7494242725  
H,0,-4.1563117098,2.0310584223,-1.4847582545  
H,0,-3.3675467182,0.5863890431,-2.3606749205  
H,0,-2.5928266345,1.4143108913,1.6940411186  
H,0,-1.711150391,2.6315840722,0.7572838889  
H,0,-3.4861548636,2.6196577274,0.739801878  
H,0,4.2741295671,-3.2528413583,0.0076639176  
H,0,3.7460081599,-2.0502355037,1.198446621  
H,0,2.5499647455,-2.9584183645,0.2465767052  
H,0,4.719717701,2.2223623161,1.2526267705  
H,0,5.1160639087,1.1097423882,-0.0718283377  
H,0,4.0427746748,2.4839230924,-0.3657632572  
H,0,1.8193838448,0.9367114374,-4.0303157294  
H,0,1.9829132365,-0.6917892161,-3.3498480642  
H,0,0.5887496688,0.3183045647,-2.9290597831

### TS2-eq-K

E(RM11) = -652.715104640

Zero-point correction= 0.433905 (Hartree/Particle)  
Thermal correction to Energy= 0.454892  
Thermal correction to Enthalpy= 0.455836  
Thermal correction to Gibbs Free Energy= 0.385494  
Sum of electronic and ZPE= -652.281200  
Sum of electronic and thermal Energies= -652.260213  
Sum of electronic and thermal Enthalpies= -652.259268  
Sum of electronic and thermal Free Energies= -652.329611

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.449	81.120	148.048

C,0,-1.0574035794,-2.2482421305,-0.1632910364  
C,0,-2.1898836715,-1.2479413056,0.1684509989  
H,0,-1.0858036563,-2.5048929664,-1.2313793391  
H,0,-1.1531953054,-3.1669368181,0.4307845937  
C,0,0.2278844894,-1.5333216852,0.1605409902  
C,0,0.8339803867,-0.6697410151,-0.7621030853  
C,0,0.8125245029,-1.785192451,1.5130294243  
C,0,-0.3381186018,0.37756058,-0.0519951465  
H,0,0.4164180082,-0.792939226,-1.7753437457  
C,0,-1.7890343939,0.0977423828,-0.4525801522  
H,0,0.087748386,1.2669458788,-0.539949764  
H,0,-0.2148471936,0.5285326057,1.0284189026  
C,0,-2.7212141647,1.2296278327,-0.0513863229  
H,0,-1.827472226,-0.0019564146,-1.5493310891  
H,0,-2.275861042,-1.1435906397,1.262522175  
H,0,-3.1588248558,-1.6021260946,-0.2065221692  
B,0,2.3922479288,-0.038540312,-0.7213848288  
C,0,3.4032328333,-1.337441843,-0.581291204  
C,0,2.6036074107,1.0725310571,0.497237551

C,0,2.52658189,0.6979836348,-2.1906980594  
H,0,3.4606762925,-1.698444955,0.4637470935  
H,0,4.4290746858,-0.9967667272,-0.8084572242  
C,0,3.0753704621,-2.5316766055,-1.490247156  
H,0,1.6753915462,1.3993646944,-2.3284134319  
H,0,2.4155956888,-0.0456205684,-3.0036783167  
C,0,3.8235478677,1.4845756045,-2.4192759247  
C,0,4.0490430793,1.1704446666,1.0143543087  
H,0,1.9600577067,0.9032117439,1.3827561995  
H,0,2.2962483171,2.0724179783,0.1302117386  
H,0,1.5645798024,-1.0377264318,1.7816600366  
H,0,0.0382187512,-1.8792067124,2.2879119395  
H,0,1.3259289829,-2.758242399,1.4311653664  
C,0,-3.5953496278,1.7287810186,-0.9272340428  
C,0,-2.6158298087,1.7534553719,1.3611867444  
H,0,-4.2877776999,2.5244782457,-0.6465850609  
H,0,-3.6448874043,1.3620613479,-1.9545764434  
H,0,-2.6096688677,0.9394180145,2.101624232  
H,0,-1.685296837,2.3244743117,1.4986348606  
H,0,-3.4551460936,2.4189118478,1.5945444775  
H,0,3.8281682196,-3.2304511587,1.4377650302  
H,0,2.1063637685,-2.9942857791,-1.2258835943  
H,0,2.9992305064,-2.222697773,-2.5443346934  
H,0,4.1816237525,1.9786412425,1.7504459428  
H,0,4.3574921511,0.2304511587,1.4971542802  
H,0,4.7593555729,1.3488875421,0.1944351782  
H,0,3.8884339811,1.9134581059,-3.4313461984  
H,0,3.9110971858,2.3181429821,-1.7056894325  
H,0,4.707510623,0.8423602468,-2.2788303125

### TS2-eq-L

E(RM11) = -652.716478163

Zero-point correction= 0.434231 (Hartree/Particle)  
Thermal correction to Energy= 0.455111  
Thermal correction to Enthalpy= 0.456055  
Thermal correction to Gibbs Free Energy= 0.386158  
Sum of electronic and ZPE= -652.282247  
Sum of electronic and thermal Energies= -652.261367  
Sum of electronic and thermal Enthalpies= -652.260423  
Sum of electronic and thermal Free Energies= -652.330320

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.586	80.908	147.111

C,0,-1.2403582987,-2.3420292205,-0.3553698813  
C,0,-2.5304240109,-1.5121781511,-0.1175787072  
H,0,-1.0611590603,-2.4570968433,-1.4329201929  
H,0,-1.3273959423,-3.3326993912,0.110540469  
C,0,-0.1465203709,-1.5316712641,0.273143385  
C,0,0.4193953964,-0.4534013818,-0.4293130206  
C,0,0.1779695334,-1.8477260777,1.6950609927  
C,0,-0.9297170525,0.3763994366,0.1690848417  
H,0,0.1766767697,-0.5196129897,-1.5039900976  
C,0,-2.2434093879,-0.0468251908,-0.4884457268  
H,0,-0.598832182,1.3779511336,-0.138393954  
H,0,-1.0068166391,0.3830761442,1.2644182291  
C,0,-3.4157704526,0.8583209772,-0.1463996244  
H,0,-2.1021172896,0.0035390413,-1.5838730851  
H,0,-2.8119298415,-1.561533511,0.9476448834  
H,0,-3.3593301149,-1.9378374394,-0.6980750517  
B,0,1.9191528529,0.2936855162,-0.2520524313  
C,0,2.8944161935,-0.7300589736,-1.1140276314  
C,0,2.4972838097,0.474845526,1.2762935334  
C,0,1.7902611206,1.7401780871,-1.0257313702  
H,0,3.9287395833,-0.354099123,-1.0225728673

H,0,2.6580950729,-0.6765298754,-2.1943986212  
C,0,2.8810656771,-2.2011080525,-0.6763443923  
H,0,1.0635215429,2.4169547707,-0.5327664013  
H,0,1.3915783272,1.5799962386,-2.0475734921  
C,0,3.1169886785,2.5061546833,-1.1356367963  
C,0,1.7587338614,1.4678785367,2.1882505071  
H,0,3.5325211587,0.8426601169,1.1557201406  
H,0,2.6242589151,-0.4884592966,1.8035623034  
H,0,0.6527890639,-1.0078176537,2.2088589465  
H,0,-0.7059219845,-2.2049295224,2.2424236409  
H,0,0.9079752737,-2.6737760982,1.6607177128  
C,0,-3.319777301,1.9053323088,0.6762357246  
C,0,-4.72238581,0.4945461408,-0.8118366331  
H,0,-4.1909163241,2.5302319583,0.880873762  
H,0,-2.3880454363,2.189598553,1.1662168602  
H,0,-4.5817565576,0.3272406034,-1.8905457449  
H,0,-5.1385829044,-0.4324482396,-0.3895343334  
H,0,-5.4671519529,1.2882513039,-0.6798796953  
H,0,3.609977384,-2.8210970166,-1.2203954924  
H,0,3.108400792,-2.2985592447,0.3977739165  
H,0,1.8932008972,-2.6692483459,-0.8463204709  
H,0,2.2625658544,1.6210691659,3.1552704577  
H,0,1.6755023524,2.4533634557,1.7037966759  
H,0,0.7272044333,1.1480594808,2.4185884791  
H,0,3.0216331384,3.4439430035,-1.7043919594  
H,0,3.5055049587,2.7676176915,-0.1388394518  
H,0,3.8867982429,1.8964139287,-1.6324717751

### TS2-eq-M

E(RM11) = -652.714994801

Zero-point correction= 0.433833 (Hartree/Particle)  
Thermal correction to Energy= 0.454962  
Thermal correction to Enthalpy= 0.455906  
Thermal correction to Gibbs Free Energy= 0.384816  
Sum of electronic and ZPE= -652.281162  
Sum of electronic and thermal Energies= -652.260033  
Sum of electronic and thermal Enthalpies= -652.259089  
Sum of electronic and thermal Free Energies= -652.330179

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.493	81.134	149.622

C,0,-1.2793838607,2.3947906279,0.0097484168  
C,0,-2.5491184576,1.499042626,0.0110450847  
H,0,-1.0191983868,2.6722903693,1.0402562437  
H,0,-1.448355869,3.30183254,-0.5859064578  
C,0,-0.2101456926,1.5316598103,-0.5843325352  
C,0,0.4473126522,0.5769977997,0.2105214154  
C,0,0.0177460947,1.6422421052,-2.0516331219  
C,0,-0.9087528608,-0.3696881375,-0.1087516998  
H,0,0.310387933,0.7992882964,1.2811693591  
C,0,-2.1771875828,0.1216241034,0.5863902524  
H,0,-0.5137367759,-1.3010697003,0.3209245197  
H,0,-1.079231798,-0.552547627,-1.1771688595  
C,0,-3.3373546631,-0.8565330565,0.4899887217  
H,0,-1.9471410218,0.2522761635,1.6599183379  
H,0,-2.9101304809,1.3678011064,-1.0228574074  
H,0,-3.3478511868,1.9918782304,0.5804282476  
B,0,1.9256143263,-0.19101198,-0.0496050447  
C,0,3.0289719885,1.0134715676,0.1900034023  
C,0,2.2012148911,-0.8467742677,-1.5378722544  
C,0,2.0024050562,-1.3461218462,1.1271683441  
H,0,2.9326258409,1.7731342616,-0.6121051178  
H,0,4.0344418498,0.5789662114,0.0439161199  
C,0,2.9900916878,1.720154467,1.5528067535

H,0,1.3404453394,-2.204131397,0.8939296169  
H,0,1.6225287769,-0.9484600786,2.0897267485  
C,0,3.4146674509,-1.900324576,1.3677362452  
C,0,1.2328721958,-1.9061600708,-2.0936245891  
H,0,3.1916053001,-1.3263727637,-1.4417087175  
H,0,2.3707146935,-0.0685873511,-2.3063013722  
H,0,0.4574061025,0.7315002181,-2.467899719  
H,0,-0.8895089802,1.941841925,-2.594117318  
H,0,0.7647377271,2.4463022952,-2.1710530303  
C,0,-3.2655793313,-2.0162735662,-0.1674483099  
C,0,-4.5992997828,-0.4281634254,1.2015286945  
H,0,-4.1252359908,-2.6879262192,-0.2001387915  
H,0,-2.3647480244,-2.3486144233,-0.6850285154  
H,0,-4.3786280517,-0.0987063219,2.2282315104  
H,0,-5.0807071612,0.415751628,0.6848243491  
H,0,-5.3238843575,-1.2495406934,1.25071631  
H,0,3.8208809195,2.4286465286,1.693652958  
H,0,2.0587685459,2.2972449908,1.6883291999  
H,0,3.0360768768,0.9915179484,2.3779542496  
H,0,1.6706360745,-2.4871671765,-2.9196178634  
H,0,0.9361845888,-2.6272319671,-1.314340347  
H,0,0.3022682734,-1.4661181783,-2.4915623296  
H,0,3.4356093275,-2.6984551163,2.12582768  
H,0,3.8421844894,-2.3174354104,0.4430696922  
H,0,4.0983280841,-1.1065484899,1.7063871282

### TS2-eq-N

E(RM11) = -652.715191348

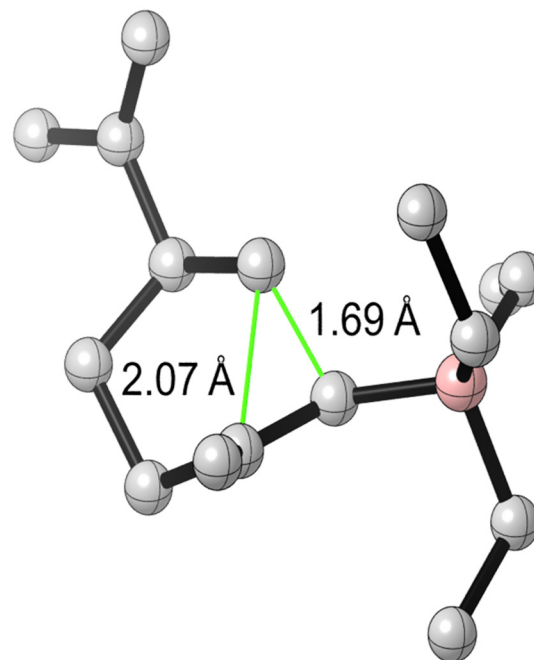
Zero-point correction= 0.433967 (Hartree/Particle)  
Thermal correction to Energy= 0.454982  
Thermal correction to Enthalpy= 0.455926  
Thermal correction to Gibbs Free Energy= 0.385698  
Sum of electronic and ZPE= -652.281224  
Sum of electronic and thermal Energies= -652.260210  
Sum of electronic and thermal Enthalpies= -652.259266  
Sum of electronic and thermal Free Energies= -652.329494

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.505	81.056	147.807

C,0,-1.1908641745,-1.9050805204,-1.5347057832  
C,0,-2.4851289294,-1.2780286986,-0.948189368  
H,0,-0.9627214132,-1.4442540002,-2.5050780743  
H,0,-1.3116091395,-2.9893863522,-1.6603483247  
C,0,-0.121887611,-1.5780718959,-0.5374925705  
C,0,0.4691386503,-0.3024037875,-0.5370867116  
C,0,0.1738034573,-2.6076280335,0.4967572311  
C,0,-0.8989286403,0.1422660114,0.3394644102  
H,0,0.2917313588,0.200819039,-1.5006874314  
C,0,-2.1751187727,0.1609377309,-0.4993996433  
H,0,-0.5458028293,1.145946095,0.6186590311  
H,0,-1.0352196216,-0.4215341606,1.2716521323  
C,0,-3.3618770405,0.7919212319,0.2105983146  
H,0,-1.976009835,0.7648532569,-1.4045167303  
H,0,-2.8138594334,-1.8604755458,-0.071123485  
H,0,-3.2887761984,-1.3220372887,-1.6947202823  
B,0,1.9305244299,0.2041833559,0.1222252799  
C,0,3.0031514471,-0.4059984611,-0.981751622  
C,0,2.3165166196,-0.3300426496,1.6341178142  
C,0,1.9090528571,1.8521292902,0.1190078757  
H,0,2.6605385583,-0.2201504824,-2.0185231563  
H,0,3.0296210542,-1.5101574784,-0.879277852  
C,0,4.4324175194,0.1370454088,-0.8477777514  
H,0,2.9202481354,2.1829516823,0.4160206478  
H,0,1.2541629345,2.2609616604,0.9139601737

C,0,1.5419721647,2.532802374,-1.2088393547  
C,0,1.3675748387,-0.0150947249,2.8051789373  
H,0,3.2769927283,0.165739514,1.8622226374  
H,0,2.5666337534,-1.4086494243,1.6453302717  
H,0,0.6189892932,-2.1747258548,1.3961150695  
H,0,-0.7042942515,-3.2243805442,0.7334832469  
H,0,0.9350356429,-3.2655045569,0.0422868669  
C,0,-3.3056307364,1.2598485264,1.4596405463  
C,0,-4.633108738,0.8617725577,-0.602763002  
H,0,-4.1850847652,1.7124429649,1.9210908075  
H,0,-2.3991500734,1.2231008683,2.065239825  
H,0,-4.4368683539,1.2726997194,-1.6047365536  
H,0,-5.0721119093,-0.1378346428,-0.7408710456  
H,0,-5.3829511036,1.4931341909,-0.1116387915  
H,0,5.1370334492,-0.339998811,-1.5467911255  
H,0,4.4590456646,1.2200228104,-1.0442258528  
H,0,4.8241995936,-0.0162584244,0.1693375418  
H,0,1.8421400256,-0.1683680004,3.7864906671  
H,0,1.0266652846,1.0318122782,2.7720362223  
H,0,0.4596633584,-0.6425547885,2.8049501944  
H,0,1.713751001,3.6198691054,-1.1956433702  
H,0,2.1295955686,2.1165751813,-2.0434837145  
H,0,0.4764145115,2.3910612738,-1.4638360278

### TS2-eq-O



E(RM11) = -652.717149211

Zero-point correction= 0.434204 (Hartree/Particle)  
Thermal correction to Energy= 0.454956  
Thermal correction to Enthalpy= 0.455900  
Thermal correction to Gibbs Free Energy= 0.386924  
Sum of electronic and ZPE= -652.282945  
Sum of electronic and thermal Energies= -652.262194  
Sum of electronic and thermal Enthalpies= -652.261249  
Sum of electronic and thermal Free Energies= -652.330225

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.489	80.945	145.172

C,0,-0.826114165,-2.2616875093,-0.9279374307  
 C,0,-2.1965320875,-1.6535916523,-0.5239027182  
 H,0,-0.6363579318,-2.0768536965,-1.9939945254  
 H,0,-0.8146050455,-3.342987556,-0.736187106  
 C,0,0.188777907,-1.5412737087,-0.0893263721  
 C,0,0.6171324741,-0.2572228652,-0.4690756222  
 C,0,0.5867306004,-2.2025131368,1.186529099  
 C,0,-0.8038492064,0.2296974566,0.3072975712  
 H,0,0.3724386977,-0.0711145682,-1.5275246532  
 C,0,-2.0650819731,-0.1212559309,-0.4777427922  
 H,0,-0.5749405738,1.3053807364,0.3138539542  
 H,0,-0.8773640908,-0.0857862892,1.356605078  
 C,0,-3.3242180915,0.5290754646,0.0719778588  
 H,0,-1.9321092489,0.2443288813,-1.5132364566  
 H,0,-2.4797630996,-2.0147361792,0.4789232946  
 H,0,-2.9718080821,-1.9877186746,-1.2256796809  
 B,0,1.9672381274,0.630768908,-0.0240788068  
 C,0,3.1596627871,-0.0014455952,-0.978829673  
 C,0,2.433640149,0.5851247887,1.5575108798  
 C,0,1.6705690346,2.1978266531,-0.4545571472  
 H,0,4.0997121987,0.5049065228,-0.6941104077  
 H,0,3.000234988,0.2572593563,-2.0421240729  
 C,0,3.3672262728,-1.5184291135,-0.8750182348  
 H,0,2.6511262259,2.7071247923,-0.4563350701  
 H,0,1.0869183831,2.7364537679,0.3177781134  
 C,0,0.998027814,2.4370624099,-1.8165718671  
 C,0,1.4382147048,1.0239192188,2.6473981884  
 H,0,3.2888074489,1.284555869,1.5989343882  
 H,0,2.8752218009,-0.3878950926,1.8456201238  
 H,0,1.1109753296,-1.5201890968,1.8598444942  
 H,0,-0.2729745639,-2.6790729379,1.6806679522  
 H,0,1.2861151194,-3.0058263631,0.9018643909  
 C,0,-3.3338606386,1.3033130621,1.1595896276  
 C,0,-4.5874923215,0.2401366173,-0.7042151247  
 H,0,-4.2642946896,1.752973182,1.5107520114  
 H,0,-2.4341116273,1.5283160206,1.7334749232  
 H,0,-4.4341626415,0.4082131001,-1.7810837521  
 H,0,-4.9003011991,-0.807495958,-0.5790232344  
 H,0,-5.4124255797,0.8797526098,-0.3688517056  
 H,0,4.2413473469,-1.8759452923,-1.4405156369  
 H,0,3.5062443326,-1.8323118458,0.1725601584  
 H,0,2.4962837282,-2.0731284305,-1.2711612053  
 H,0,1.9300675308,1.2218968142,3.6120067066  
 H,0,0.9099827343,1.9473774086,2.3610118055  
 H,0,0.6627027197,0.265876594,2.8505138071  
 H,0,1.0016118415,3.496596675,-2.1137824518  
 H,0,1.5014915761,1.8719582892,-2.6176053567  
 H,0,-0.060385266,2.1194669839,-1.8170181822

### TS2-eq-P

E(RM11) = -652.715299294

Zero-point correction= 0.433974 (Hartree/Particle)  
 Thermal correction to Energy= 0.454974  
 Thermal correction to Enthalpy= 0.455918  
 Thermal correction to Gibbs Free Energy= 0.385782  
 Sum of electronic and ZPE= -652.281325  
 Sum of electronic and thermal Energies= -652.260325  
 Sum of electronic and thermal Enthalpies= -652.259381  
 Sum of electronic and thermal Free Energies= -652.329517

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.500	81.129	147.613

C,0,-1.2649029081,-2.4026657632,-0.2684163882

C,0,-2.5560956277,-1.5682843529,-0.1012266947  
 H,0,-1.0581231183,-2.5647267143,-1.3353025541  
 H,0,-1.3543418799,-3.3740814776,0.2359771698  
 C,0,-0.1773374866,-1.571964732,0.3532044051  
 C,0,0.4839364481,-0.5730246567,-0.3745777408  
 C,0,0.122497765,-1.8351610076,1.7914488577  
 C,0,-0.9148783318,0.2914269877,0.100032106  
 H,0,0.3161708969,-0.6830457154,-1.4591848591  
 C,0,-2.2279440074,-0.1363064002,-0.5533377825  
 H,0,-0.5335261562,1.2387850457,-0.3067583831  
 H,0,-0.9940142309,0.4234538244,1.1878261343  
 C,0,-3.3731547283,0.828192546,-0.2917514183  
 H,0,-2.0636308943,-0.1591608154,-1.6468340604  
 H,0,-2.8579686999,-1.5509983928,0.9594113484  
 H,0,-3.3794883805,-2.0150875613,-0.6736833883  
 B,0,1.9133383702,0.2214757812,0.0150791664  
 C,0,2.2608019464,1.0706517135,-1.3550649784  
 C,0,3.0221615723,-0.968243021,0.3057691177  
 C,0,1.8819149194,1.2333669376,1.3270207085  
 H,0,1.4011533519,1.7105042383,-1.6474364336  
 H,0,2.3879619017,0.3714785836,-2.2039795753  
 C,0,3.511196261,1.9556581535,-1.2609605165  
 H,0,2.9502127353,1.4697044404,1.4831843847  
 H,0,1.5960568505,0.7310341643,2.2707897871  
 C,0,1.1255669452,2.5745294489,1.2439370857  
 C,0,3.0231267332,-2.1554940646,-0.6687361693  
 H,0,2.9199893598,-1.3536738426,1.3390868698  
 H,0,4.0226956241,-0.5005789288,0.2875741293  
 H,0,0.6625253961,-1.0048795405,2.2544343579  
 H,0,-0.7778189882,-2.1029102774,2.3620381206  
 H,0,0.7959785625,-2.7092073244,1.791533388  
 C,0,-3.2398469023,1.9520852863,0.4164507265  
 C,0,-4.6951823358,0.4335330443,-0.9065829388  
 H,0,-4.0927851014,2.6167592261,0.5642126703  
 H,0,-2.295052026,2.2626271089,0.8645332027  
 H,0,-4.5725950368,0.1731732052,-1.9690686437  
 H,0,-5.1209760293,-0.4469346383,-0.4024073179  
 H,0,-5.4238170642,1.2494547135,-0.833289964  
 H,0,3.7512906942,2.458061936,-2.210695827  
 H,0,3.3936498585,2.7393464861,-0.4967091139  
 H,0,4.3919266868,1.3605930444,-0.9738470843  
 H,0,3.8453886908,-2.8642814737,-0.486265114  
 H,0,2.0867862593,-2.7408876034,-0.6066208639  
 H,0,3.111392273,-1.8135230925,-1.7121186816  
 H,0,1.5188516537,3.317840469,1.9542529103  
 H,0,1.1990847799,3.019314079,0.2384607626  
 H,0,0.0530704282,2.4746819126,1.4750288321

### TS2-eq-Q

E(RM11) = -652.713745079

Zero-point correction= 0.434494 (Hartree/Particle)  
 Thermal correction to Energy= 0.455308  
 Thermal correction to Enthalpy= 0.456252  
 Thermal correction to Gibbs Free Energy= 0.386712  
 Sum of electronic and ZPE= -652.279251  
 Sum of electronic and thermal Energies= -652.258437  
 Sum of electronic and thermal Enthalpies= -652.257493  
 Sum of electronic and thermal Free Energies= -652.327033

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.710	80.915	146.360

C,0,-1.2360842573,-2.2932365184,-0.5241826223  
 C,0,-2.5628873808,-1.5330539904,-0.2982843311  
 H,0,-1.0181530615,-2.3553916255,-1.5992225055

H,0,-1.2857245157,-3.3077217016,-0.1065697874  
C,0,-0.1802649842,-1.4761803665,0.1736680399  
C,0,0.4384461804,-0.39395365,-0.4681756009  
C,0,0.1359217106,-1.8682665275,1.5797647928  
C,0,-1.0017700346,0.3493162996,0.1174494525  
H,0,0.230485501,-0.4071610909,-1.5508930366  
C,0,-2.2886345443,-0.0508146913,-0.5994849448  
H,0,-0.6516658396,1.3533867005,-0.1575445815  
H,0,-1.104585773,0.3421013237,1.210189394  
C,0,-3.4740504746,0.8355454826,-0.2555987483  
H,0,-2.1118580055,0.046151803,-1.6866979724  
H,0,-2.8790839624,-1.6329779984,0.7535912457  
H,0,-3.3596708621,-1.9529729538,-0.9260394193  
B,0,1.8685591935,0.4286421445,-0.0688093174  
C,0,2.2780284226,1.115449613,-1.5167780701  
C,0,2.9854582877,-0.6873061431,0.4006256795  
C,0,1.6995460735,1.6290558637,1.0511976117  
H,0,1.5285824713,1.8905401334,-1.7802997327  
H,0,2.2111522205,0.3653893315,-2.3290336626  
C,0,3.6772863508,1.7427257182,-1.5726005481  
H,0,0.9753146589,2.3954023285,0.7085363615  
H,0,2.6671252829,2.1601951512,1.0353936842  
C,0,1.4063105841,1.3001279886,2.5250267793  
C,0,3.2210963388,-1.8241581824,-0.6039724213  
H,0,2.7577793127,-1.1275235417,1.388442631  
H,0,3.9395137691,-0.1518681355,0.5567185991  
H,0,0.6502828681,-1.0713618316,2.1225708426  
H,0,-0.7575993611,-2.211076767,2.120827689  
H,0,0.8312735,-2.7209776799,1.5003522885  
C,0,-3.4016493467,1.8655769642,0.5906659532  
C,0,-4.7649668341,0.4724380015,-0.950818463  
H,0,-4.2824619078,2.4769315842,0.7944815836  
H,0,-2.4812343949,2.1486071761,1.1026617535  
H,0,-4.6055052125,0.3356056239,-2.0312125551  
H,0,-5.1740849295,-0.4712131153,-0.5596825069  
H,0,-5.5224838681,1.2523389405,-0.8097222724  
H,0,3.8916313045,2.2174285054,-2.5427074413  
H,0,3.8079741015,2.5129879831,-0.7976607438  
H,0,4.4545515383,0.9809364988,-1.4033537114  
H,0,3.977171652,-2.5517201758,-0.2700580711  
H,0,2.2938333427,-2.3946772637,-0.8001641907  
H,0,3.5524657604,-1.4275264927,-1.5760532446  
H,0,1.5414201522,2.173584649,3.1814422979  
H,0,0.3716179455,0.9539186294,2.6904518334  
H,0,2.0794324667,0.5122983951,2.8998580199

### TS2-eq-R

E(RM11) = -652.717325291

Zero-point correction= 0.434304 (Hartree/Particle)  
Thermal correction to Energy= 0.455152  
Thermal correction to Enthalpy= 0.456096  
Thermal correction to Gibbs Free Energy= 0.386462  
Sum of electronic and ZPE= -652.283021  
Sum of electronic and thermal Energies= -652.262173  
Sum of electronic and thermal Enthalpies= -652.261229  
Sum of electronic and thermal Free Energies= -652.330863

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.612	80.928	146.557

C,0,-1.2210754575,-2.3450073675,-0.4742370386  
C,0,-2.5114782473,-1.5655446352,-0.1177634532  
H,0,-1.0863895348,-2.3679986672,-1.5642811745  
H,0,-1.2648260536,-3.3726623655,-0.0892650762  
C,0,-0.1102178206,-1.56969505,0.1713252152

C,0,0.4559610956,-0.4523636553,-0.4620457379  
C,0,0.2884273704,-1.9902181426,1.5462542736  
C,0,-0.9060289789,0.3086354004,0.2280973756  
H,0,0.2029396697,-0.4301945001,-1.5355365076  
C,0,-2.2470083836,-0.0762697886,-0.3937518978  
H,0,-0.5920446664,1.3230044402,-0.0497568891  
H,0,-0.9152560966,0.2725464301,1.3261547515  
C,0,-3.4013299316,0.79983406,0.0647076046  
H,0,-2.153822662,0.0527679579,-1.4886224572  
H,0,-2.7434512518,-1.6962274873,0.9524226903  
H,0,-3.3615734642,-1.9572517763,-0.691428699  
B,0,1.9294260398,0.2896538251,-0.075895178  
C,0,3.038976263,-0.9161293209,0.1449205267  
C,0,1.8251049049,1.250713273,1.2629351357  
C,0,2.3160372091,1.1664628829,-1.4148441873  
H,0,2.9931468491,-1.3409642209,1.1666467569  
H,0,4.0375403689,-0.4482773273,0.0849633534  
C,0,2.9993932937,-2.0628963637,-0.8770170173  
H,0,2.3895143796,0.5019074246,-2.2970822475  
H,0,3.3322914471,1.5792373004,-1.287180988  
C,0,1.3555098144,2.3167803152,-1.75472329  
C,0,3.1258503326,2.0227421372,1.5360745719  
H,0,1.5858338262,0.6685072805,2.1753166347  
H,0,1.0106029827,1.9965204795,1.1834150044  
H,0,0.8271550361,-1.1983298909,2.0741770352  
H,0,-0.5675674743,-2.3581489502,2.1294708136  
H,0,0.9886671447,-2.8313090505,1.4065707145  
C,0,-3.2623208012,1.8027992829,0.934767317  
C,0,-4.7427099344,0.460636075,-0.5416604771  
H,0,-4.1233937748,2.4081607911,1.2234442798  
H,0,-2.3051487213,2.0693745834,1.3841987382  
H,0,-4.6647902096,0.3515906244,-1.6341203831  
H,0,-5.1284526294,-0.4908982431,-0.1457720316  
H,0,-5.4825617491,1.2399544792,-0.3242516703  
H,0,3.8170587448,-2.7882198007,-0.745432501  
H,0,2.0583079375,-2.6414901579,-0.822044418  
H,0,3.0664497884,-1.6772880817,-1.9060531482  
H,0,3.082458969,2.6136483351,2.4639921795  
H,0,3.9833269106,1.3379788255,1.620128706  
H,0,3.3485180995,2.7194596118,0.7135923472  
H,0,1.6769740359,2.9053586385,-2.6277774265  
H,0,0.341509792,1.9448308782,-1.9901047963  
H,0,1.2563384653,3.017271981,-0.9091670953

### TS2-eq-S

E(RM11) = -652.714547565

Zero-point correction= 0.434398 (Hartree/Particle)  
Thermal correction to Energy= 0.455177  
Thermal correction to Enthalpy= 0.456121  
Thermal correction to Gibbs Free Energy= 0.387004  
Sum of electronic and ZPE= -652.280149  
Sum of electronic and thermal Energies= -652.259370  
Sum of electronic and thermal Enthalpies= -652.258426  
Sum of electronic and thermal Free Energies= -652.327544

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.628	80.978	145.470

C,0,0.9275978138,-2.2536397102,0.9072092355  
C,0,2.2924018668,-1.6559046749,0.4906525282  
H,0,0.7596918338,-2.09275084,1.9809344763  
H,0,0.8882177728,-3.3298584347,0.6918404949  
C,0,-0.101162661,-1.5048322208,0.1037692191  
C,0,-0.592115112,-0.266237896,0.5415063892  
C,0,-0.5221071061,-2.1269591292,-1.1864377749



C,0,0.8564920293,0.2333835527,-0.2379137574  
H,0,-0.330810113,-0.0945839271,1.5988145714  
C,0,2.1457849545,-0.1251467958,0.4952912647  
H,0,0.6021453383,1.2988870317,-0.1636604848  
H,0,0.8978846071,-0.0037012874,-1.3092990631  
C,0,3.375882108,0.5653901501,-0.0701844975  
H,0,2.0374347155,0.2047199668,1.5456416201  
H,0,2.5501100551,-1.9864141644,-0.5294842018  
H,0,3.0855003442,-2.0075344083,1.1633843059  
B,0,-1.9795220739,0.5700343562,0.0420982736  
C,0,-2.3085453849,1.5553495558,1.3257155348  
C,0,-3.1953228822,-0.5275240427,-0.1523969114  
C,0,-1.795584962,1.5105911681,-1.30383218  
H,0,-2.4818347585,0.9549457045,2.2391383459  
H,0,-3.266955959,2.0700953057,1.1309148785  
C,0,-1.2418101391,2.6150107356,1.6469151865  
H,0,-0.9815069181,2.2503594085,-1.1801670765  
H,0,-2.7108270636,2.130444257,-1.3250926677  
C,0,-1.647447885,0.874842122,-2.6967065967  
C,0,-3.3937509898,-1.5171490465,1.0061829368  
H,0,-3.1018646752,-1.1036133782,-1.0913490185  
H,0,-4.1281404853,0.0525358861,-0.2757693047  
H,0,-1.0051417384,-1.4044299095,-1.8491394656  
H,0,0.3125481778,-2.6377302415,-1.6877749649  
H,0,-1.2728365373,-2.8896537346,-0.9186400611  
C,0,3.3357833347,1.4046712873,-1.1077966855  
C,0,4.6725991166,0.2373391865,0.631556236  
H,0,4.2491548247,1.8794048148,-1.4704935867  
H,0,2.4123647193,1.6599635939,-1.6287237634  
H,0,4.5676825014,0.343909121,1.7220171648  
H,0,4.9796313369,-0.8006480827,0.4335063366  
H,0,5.4811661665,0.8975529212,0.2963287249  
H,0,-1.5003880297,3.2332312439,2.520348939  
H,0,-0.2614433509,2.1562688937,1.8738013393  
H,0,-1.0870307822,3.3015895539,0.8005224417  
H,0,-4.234333214,-2.2094331019,0.8430346618  
H,0,-2.497563778,-2.1435584551,1.1728776801  
H,0,-3.583990476,-0.9900183972,1.9527230911  
H,0,-1.7697458352,1.6125388803,-3.5046094402  
H,0,-0.6550737902,0.4175598257,-2.8516403509  
H,0,-2.4007108163,0.0888648155,-2.8653819235

### TS2-eq-T

E(RM11) = -652.714301950

Zero-point correction= 0.434668 (Hartree/Particle)  
Thermal correction to Energy= 0.455376  
Thermal correction to Enthalpy= 0.456320  
Thermal correction to Gibbs Free Energy= 0.386708  
Sum of electronic and ZPE= -652.279634  
Sum of electronic and thermal Energies= -652.258926  
Sum of electronic and thermal Enthalpies= -652.257982  
Sum of electronic and thermal Free Energies= -652.327594

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.753	80.663	146.511

C,0,-1.2171746691,-2.4034581051,-0.1480070623  
C,0,-2.5225061321,-1.610909108,0.1260064013  
H,0,-1.1049852763,-2.5841403021,-1.2254462881  
H,0,-1.2246294108,-3.3623031634,0.3875986083  
C,0,-0.1292898864,-1.5030688637,0.3560490033  
C,0,0.3848988169,-0.4815448767,-0.4600496813  
C,0,0.2417534327,-1.6761320579,1.7926427273  
C,0,-0.9750359943,0.3599572671,0.1052088714  
H,0,0.106134166,-0.6462868912,-1.5152563436

C,0,-2.3175968047,-0.1781245113,-0.3926476816  
H,0,-0.7157988899,1.3031709644,-0.3915349011  
H,0,-0.9599929518,0.5397769172,1.1886974754  
C,0,-3.4918808795,0.7267504771,-0.0558190678  
H,0,-2.2581112582,-0.2316059374,-1.4960572426  
H,0,-2.7194719814,-1.5788941754,1.2106223331  
H,0,-3.3749232048,-2.1128220377,-0.3500042356  
B,0,1.8602211678,0.3419540448,-0.3940486357  
C,0,2.7823459513,-0.6120203369,-1.3797700088  
C,0,2.5317502945,0.477365004,1.1012113454  
C,0,1.6350496262,1.8175087628,-1.1014065139  
H,0,3.7637666028,-0.121602021,-1.5030940863  
H,0,2.3513710226,-0.6442606498,-2.3991330831  
C,0,3.00505921,-2.0454404334,-0.8805957775  
H,0,0.877720149,1.743779614,-1.9100621167  
H,0,2.5634499497,2.0883886672,-1.6353863314  
C,0,1.2747731124,2.9947831089,-0.1749906484  
C,0,3.9412808297,1.0914517011,1.0342978116  
H,0,2.6335940212,-0.4981727278,1.6083322786  
H,0,1.9038235466,1.0987741147,1.7715660107  
H,0,0.6429965172,-0.7604580025,2.2339679428  
H,0,-0.5966492379,-2.0701499629,2.3835821014  
H,0,1.05002367,-2.4271831943,1.8058379849  
C,0,-3.3618266311,1.8883661673,0.58926671794  
C,0,-4.8403297828,0.2298705091,-0.521997807  
H,0,-4.2359195083,2.5100531061,0.7909173396  
H,0,-2.3993438812,2.2732277375,0.9284905675  
H,0,-4.7997568524,-0.0858299352,-1.5757743714  
H,0,-5.169431783,-0.6399454021,0.0662958466  
H,0,-5.6038654744,1.0105961781,-0.4247635709  
H,0,3.6492228255,-2.6440760496,-1.5427830921  
H,0,3.4701666673,-2.0460496238,0.1188369019  
H,0,2.0507234163,-2.5987519429,-0.7924482197  
H,0,4.3481860725,1.3371357783,2.0274072997  
H,0,4.6438909735,0.391026626,0.5574007555  
H,0,3.9564064587,2.0118631716,0.4305026378  
H,0,1.0633732399,3.9227411665,-0.7287313562  
H,0,0.3972527826,2.791250515,0.4621619527  
H,0,2.0989394816,3.2104584035,0.5206706466

### TS2-eq-U

E(RM11) = -652.717651113

Zero-point correction= 0.434128 (Hartree/Particle)  
Thermal correction to Energy= 0.454949  
Thermal correction to Enthalpy= 0.455893  
Thermal correction to Gibbs Free Energy= 0.386576  
Sum of electronic and ZPE= -652.283524  
Sum of electronic and thermal Energies= -652.262703  
Sum of electronic and thermal Enthalpies= -652.261758  
Sum of electronic and thermal Free Energies= -652.331075

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.485	80.978	145.890

C,0,-1.1388642523,-2.2608838937,-0.7687462211  
C,0,-2.4436728589,-1.5569708599,-0.3078640256  
H,0,-0.9976180169,-2.1168653838,-1.8482954524  
H,0,-1.1808227675,-3.3350388397,-0.5434312351  
C,0,-0.0467023497,-1.5777536771,-0.0004688828  
C,0,0.4616160441,-0.3504690854,-0.460998818  
C,0,0.3261679732,-2.2038440899,1.3026622757  
C,0,-0.8863201428,0.2735153968,0.3522991341  
H,0,0.1877151208,-0.1963780826,-1.5176107461  
C,0,-2.2141162468,-0.0359713315,-0.3379318073  
H,0,-0.5910849434,1.3287383051,0.2636317387  
H,0,-0.9076219964,0.0358179422,1.4246656232

C,0,-3.3979488172,0.7204341546,0.2414768191  
H,0,-2.1172614282,0.2714658619,-1.3963320816  
H,0,-2.6845502364,-1.8613345587,0.724429919  
H,0,-3.2799970838,-1.8678902688,-0.9473305242  
B,0,1.8772336935,0.4728313334,-0.0920801772  
C,0,3.008356953,-0.2614297398,-1.0454705941  
C,0,2.292588638,0.4231430358,1.5033173761  
C,0,1.652344582,2.0375944683,-0.5702067656  
H,0,3.9844365242,0.2044251672,-0.8199496694  
H,0,2.8269988997,-0.0415394874,-2.1141113315  
C,0,3.1399216846,-1.7811787591,-0.8776726962  
H,0,2.6536132121,2.4994025862,-0.6287146867  
H,0,1.1278334315,2.6272653305,0.2099801695  
C,0,0.9429351781,2.263208538,-1.9157803771  
C,0,3.3957500508,1.4316389851,1.8644814642  
H,0,2.6523110235,-0.5805470878,1.7978816497  
H,0,1.4198150529,0.6343791326,2.1566487296  
H,0,0.819170505,-1.5010622567,1.9784487372  
H,0,-0.5401062575,-2.6806039319,1.7835145451  
H,0,1.0491158936,-2.999414071,1.0572342851  
C,0,-3.29725544,1.5688086652,1.2673076754  
C,0,-4.7224106035,0.4524393351,-0.4340466926  
H,0,-4.1784876591,2.0946834508,1.6389907594  
H,0,-2.3527555272,1.782750631,1.7682760486  
H,0,-4.6283867042,0.5299511325,-1.5279561062  
H,0,-5.085390867,-0.5617863215,-0.2091384938  
H,0,-5.4868298441,1.1648306025,-0.1019593161  
H,0,3.9641561915,-2.2123720111,-1.4662457555  
H,0,3.3156601957,-2.0532983175,0.1760934427  
H,0,2.2214534488,-2.3043714894,-1.2027461334  
H,0,3.7429849271,1.3251291813,2.9037724711  
H,0,4.2725752099,1.3071938138,1.2100010262  
H,0,3.0460679478,2.4664950884,1.7384238828  
H,0,0.9936325294,3.3091386357,-2.2537917318  
H,0,1.3865741738,1.641834706,-2.7104050425  
H,0,-0.1305926318,2.005135745,-1.8706979588

### TS2-eq-V

E(RM11) = -652.715234910

Zero-point correction= 0.434337 (Hartree/Particle)  
Thermal correction to Energy= 0.455072  
Thermal correction to Enthalpy= 0.456016  
Thermal correction to Gibbs Free Energy= 0.386880  
Sum of electronic and ZPE= -652.280898  
Sum of electronic and thermal Energies= -652.260163  
Sum of electronic and thermal Enthalpies= -652.259219  
Sum of electronic and thermal Free Energies= -652.328355

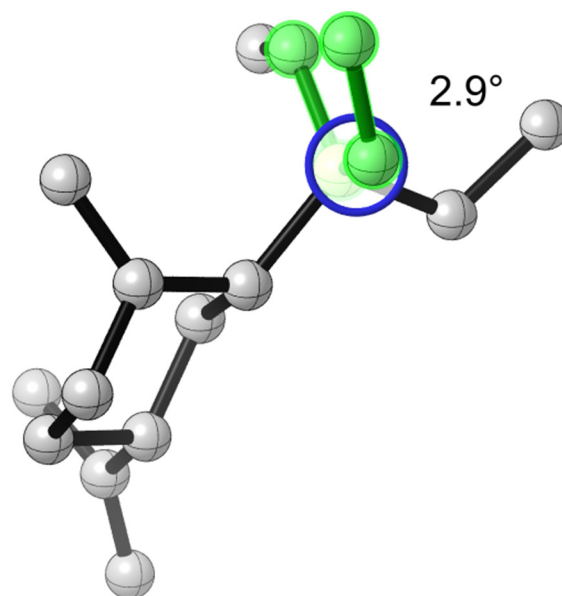
E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.562	80.852	145.509

C,0,1.4558751534,-2.2916145035,0.3183372929  
C,0,2.7129241715,-1.4270695664,0.0641222934  
H,0,1.3083772594,-2.4292299079,1.3985604671  
H,0,1.5511073118,-3.274726161,-0.16169424  
C,0,0.3054924694,-1.5166393844,-0.2636714144  
C,0,-0.3227940554,-0.4970023825,0.4645756256  
C,0,-0.1076554913,-1.868291624,-1.6548673692  
C,0,1.0191316842,0.3690928555,-0.1593683952  
H,0,-0.0686565358,-0.5447465914,1.5366737138  
C,0,2.3667821776,0.0163304083,0.4650864367  
H,0,0.6240386694,1.3397215239,0.1744717171  
H,0,1.0609261299,0.4090891709,-1.2559638233  
C,0,3.4776263558,0.9894922651,0.1067579465  
H,0,2.2490709991,0.044632706,1.5641049842

H,0,2.9707622762,-1.4474826766,-1.0079860366  
H,0,3.5710612526,-1.8270183433,0.6198562714  
B,0,-1.7940690203,0.2511614241,0.1322098122  
C,0,-2.8995003562,-0.9676499962,-0.0181032666  
C,0,-1.7286567857,1.2269479486,-1.2117462456  
C,0,-2.0520457145,1.160867576,1.4829272697  
H,0,-2.8550661776,-1.4370060524,-1.0199031271  
H,0,-3.9086569381,-0.5209818403,0.0287424924  
C,0,-2.8094100938,-2.0752775865,1.0425461081  
H,0,-1.161287228,1.7981727216,1.6720749509  
H,0,-2.128834117,0.5088410868,2.3745843438  
C,0,-3.2819256799,2.0767024576,1.4373885067  
C,0,-3.0759380791,1.3885019362,-1.9369076759  
H,0,-0.9953380776,0.900694717,-1.9749866052  
H,0,-1.3721113174,2.2326184402,-0.9106394877  
H,0,-0.7346765508,-1.0938639747,-2.1058428541  
H,0,0.752079924,-2.1192057759,-2.2923246504  
H,0,-0.7254506994,-2.7766674693,-1.5503066202  
C,0,3.298500116,2.0531709429,-0.6799771535  
C,0,4.823696042,0.6731653013,0.7147201703  
H,0,4.1298216729,2.7259620672,-0.8978674433  
H,0,2.3364085883,2.304342676,-1.127741464  
H,0,4.7320981149,0.4809962198,1.7946146075  
H,0,5.2628446275,-0.2272333555,0.2596370511  
H,0,5.5272668678,1.5014171986,0.5698911585  
H,0,-3.6224989832,-2.8133903642,0.9658281677  
H,0,-1.8632700743,-2.6427876667,0.9648905367  
H,0,-2.8421380983,-1.656867346,2.0605487175  
H,0,-3.0283155461,2.1169894235,-2.7613338546  
H,0,-3.4091566564,0.4298222285,-2.3632880919  
H,0,-3.8681143258,1.7171186695,-1.2489401389  
H,0,-3.4419166632,2.6220914709,2.3804619888  
H,0,-3.1859550718,2.8281022224,0.6386759174  
H,0,-4.1982673365,1.5004269807,1.2330444497

### Conformational Interconversion Transition Structures

#### TSR-A-1



E(RM11) = -652.709975042

Zero-point correction= 0.434264 (Hartree/Particle)  
Thermal correction to Energy= 0.454989  
Thermal correction to Enthalpy= 0.455933

Thermal correction to Gibbs Free Energy= 0.386672  
 Sum of electronic and ZPE= -652.275711  
 Sum of electronic and thermal Energies= -652.254986  
 Sum of electronic and thermal Enthalpies= -652.254042  
 Sum of electronic and thermal Free Energies= -652.323303

E CV S  
 KCal/Mol Cal/Mol-K Cal/Mol-K  
 Total 285.510 80.806 145.772

C,0,-1.2456648559,-2.2805503493,-0.6817165496  
 C,0,-2.485643963,-1.3891660097,-0.2712581078  
 H,0,-1.1161004481,-2.2381549679,-1.7703087121  
 H,0,-1.4006404193,-3.3120905683,-0.340635689  
 C,0,-0.1790550981,-1.5548598421,0.029928498  
 C,0,0.27890752,-0.3249597744,-0.5106480153  
 C,0,0.1777985411,-1.9781210234,1.4008960238  
 C,0,-0.9177871846,0.5654701198,0.0658100427  
 H,0,0.1109096517,-0.3253060396,-1.6019570853  
 C,0,-2.2451777181,0.1030161875,-0.5697211618  
 H,0,-0.6749252287,-1.6049945387,-0.1942479337  
 H,0,-0.9759784794,0.5054638309,1.1614672489  
 C,0,-3.4320542863,0.9367357175,-0.1103619136  
 H,0,-2.1539865508,0.2166592407,-1.6623693575  
 H,0,-2.6780385603,-1.5307176283,0.804852318  
 H,0,-3.3653414927,-1.763227208,-0.8112922279  
 B,0,1.9005305005,0.2336639335,-0.2490002664  
 C,0,2.8506087116,-0.9338976266,-0.9857871356  
 C,0,2.3402562942,0.4936140688,1.3137433422  
 C,0,1.9682954198,1.6302549219,-1.1189452265  
 H,0,3.3750063208,-0.4689158206,-1.8404162502  
 H,0,2.2286900713,-1.7225740647,-1.4559496987  
 C,0,3.9136723434,-1.6277946545,-0.1174655157  
 H,0,1.186468033,2.3614085702,-0.8371694351  
 H,0,1.7791277608,1.3966221908,-2.1845935772  
 C,0,3.3297635544,2.3328750529,-1.0039321504  
 C,0,1.5428281796,1.5352454535,2.1146249098  
 H,0,3.3834645063,0.8514043566,1.2521026774  
 H,0,2.4272650428,-0.4326732745,1.9096888988  
 H,0,0.373096017,-1.1194097028,2.0539169909  
 H,0,-0.5417978771,-2.6797208786,1.8404305656  
 H,0,1.1515826916,-2.4916349627,1.2866372416  
 C,0,-4.3040581766,1.4261235559,-0.9942233999  
 C,0,-3.5715904765,1.1892417649,1.3721809166  
 H,0,-5.1673507421,2.0128884603,-0.6747308603  
 H,0,-4.1790859831,1.2631995615,-2.0668206168  
 H,0,-3.4639896492,0.2639161414,1.9584462009  
 H,0,-2.7940129084,1.8843821943,1.722496559  
 H,0,-4.5487146485,1.6285798244,1.6051154288  
 H,0,4.5137531417,-2.3539078091,-0.6880365066  
 H,0,4.6104472411,-0.8951622227,0.3166346309  
 H,0,3.4689424584,-2.1713426341,0.7325277476  
 H,0,2.0670172928,1.8627378971,3.0255947052  
 H,0,1.3426510113,2.434188153,1.5094392539  
 H,0,0.5625046212,1.15138304,2.4446784927  
 H,0,3.4527858887,3.1508991881,-1.7301782494  
 H,0,3.4674758321,2.7637624636,-0.0002129004  
 H,0,4.1565074199,1.6206400239,-1.1629581006

### TSR-A-2

E(RM11) = -652.711494427

Zero-point correction= 0.434659 (Hartree/Particle)  
 Thermal correction to Energy= 0.455182  
 Thermal correction to Enthalpy= 0.456126  
 Thermal correction to Gibbs Free Energy= 0.387664  
 Sum of electronic and ZPE= -652.276836  
 Sum of electronic and thermal Energies= -652.256312

Sum of electronic and thermal Enthalpies= -652.255368  
 Sum of electronic and thermal Free Energies= -652.323831

E CV S  
 KCal/Mol Cal/Mol-K Cal/Mol-K  
 Total 285.631 80.661 144.091

C,0,-1.1694568791,-2.3070747428,-0.6143285319  
 C,0,-2.435280932,-1.4131659308,-0.3243753467  
 H,0,-0.9747350296,-2.3286589464,-1.6940133595  
 H,0,-1.3369307635,-3.3216602623,-0.2293565042  
 C,0,-0.1237000473,-1.5522765258,0.1127284988  
 C,0,0.3537011952,-0.3521124024,-0.4697845275  
 C,0,0.095519551,-1.9029964674,1.541741996  
 C,0,-0.8669996995,0.5325419678,0.087401041  
 H,0,0.1942177093,-0.3844295855,-1.5621518412  
 C,0,-2.1703495264,0.0790270572,-0.602405832  
 H,0,-0.6121830868,1.5743411033,-0.1536891968  
 H,0,-0.9591813195,0.4633362292,1.180368479  
 C,0,-3.3688020234,0.9186628338,-0.1853100622  
 H,0,-2.0331613647,0.2015982535,-1.689163082  
 H,0,-2.7232401612,-1.5486402248,0.7304037117  
 H,0,-3.2690316762,-1.7817796604,-0.9361204838  
 B,0,1.9422805626,0.301403438,-0.2226938548  
 C,0,2.904925844,-0.8076738802,-0.9767972746  
 C,0,2.4048560002,0.4890507005,1.3447888054  
 C,0,1.9483691243,1.7724632959,-0.998448794  
 H,0,3.9488587615,-0.4705582689,-0.8414004453  
 H,0,2.7418217891,-0.8021505479,-2.0692357142  
 C,0,2.8052705157,-2.2555872956,-0.4896558634  
 H,0,2.2578513038,2.5571526237,-0.2845072625  
 H,0,0.9352410055,2.0839479012,-1.3192093111  
 C,0,2.8550433618,1.8910500789,-2.2357508871  
 C,0,1.5585979101,1.4111286214,2.2394128966  
 H,0,3.4118636983,0.9394626993,1.266204461  
 H,0,2.5802116433,-0.4679616773,1.8714573344  
 H,0,0.559494649,-1.0863920006,2.1007510093  
 H,0,-0.8363232217,-2.2423408652,2.0174167868  
 H,0,0.7898133712,-2.7588595785,1.5507020374  
 C,0,-4.2110275194,1.4064734983,-1.0983168105  
 C,0,-3.5571497691,1.1746238184,1.2913997535  
 H,0,-5.0837648312,1.9947471079,-0.808678834  
 H,0,-4.0514860903,1.2407205177,-2.1659328412  
 H,0,-3.4679165497,0.2507236937,1.8830180493  
 H,0,-2.7927447554,1.8717077872,1.6662046801  
 H,0,-4.5421970067,1.6128838069,1.4906637222  
 H,0,3.525548534,-2.9257484588,-0.9832273198  
 H,0,2.9745703213,-2.3339006974,0.5962805495  
 H,0,1.8061228149,-2.6866327057,-0.7022391091  
 H,0,2.087553961,1.720318507,3.1538071998  
 H,0,1.2709215016,2.3292676069,1.7025963448  
 H,0,0.6199711782,0.9366956193,2.5725861424  
 H,0,2.8574218737,2.9109007397,-2.6509903715  
 H,0,3.8972218146,1.6314352295,-1.9968537952  
 H,0,2.5347894878,1.2128178485,-3.0415468828

### TSR-A-3

E(RM11) = -652.712527016

Zero-point correction= 0.434532 (Hartree/Particle)  
 Thermal correction to Energy= 0.455200  
 Thermal correction to Enthalpy= 0.456144  
 Thermal correction to Gibbs Free Energy= 0.387236  
 Sum of electronic and ZPE= -652.277995  
 Sum of electronic and thermal Energies= -652.257327  
 Sum of electronic and thermal Enthalpies= -652.256383  
 Sum of electronic and thermal Free Energies= -652.325291

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.642 80.707 145.029

C,0,-1.1541271293,-2.334476391,-0.593950135  
C,0,-2.4347622598,-1.4584266251,-0.2941805017  
H,0,-0.959497765,-2.3419602299,-1.6736199608  
H,0,-1.3064509232,-3.3530535541,-0.2137869524  
C,0,-0.1464373883,-1.5500319454,0.1474716947  
C,0,0.3102113469,-0.3434354854,-0.4416409528  
C,0,0.0447888049,-1.884040267,1.5832067303  
C,0,-0.9166432188,0.557498254,0.0406447395  
H,0,0.1952049195,-0.4103371231,-1.5379770186  
C,0,-2.2123455468,0.0323642113,-0.6166260368  
H,0,-0.6879569169,1.5805191005,-0.2870177552  
H,0,-0.9961178625,0.5694267563,1.1382154658  
C,0,-3.4362383091,0.8478115121,-0.2275450311  
H,0,-2.0826818499,0.1195203048,-1.7079495045  
H,0,-2.700006664,-1.5772676493,0.7685411759  
H,0,-3.2696372226,-1.8617342248,-0.882199307  
B,0,1.8662993251,0.37546408,-0.1405624127  
C,0,2.8959192403,-0.6318883524,-0.9408894506  
C,0,2.2068766792,0.4991631164,1.4625909206  
C,0,1.7732985268,1.8504590097,-0.872367034  
H,0,3.9274442584,-0.2960789026,-0.7330516736  
H,0,2.7726722621,-0.5171841049,-2.0347926769  
C,0,2.8155520157,-2.1188355617,-0.583719961  
H,0,1.260181115,2.5699873094,-0.206221289  
H,0,1.1193719066,1.7702799859,-1.7629158629  
C,0,3.1171410869,2.4777306365,-1.3277305684  
C,0,3.4206161865,1.3994321829,1.7463811113  
H,0,2.4081249371,-0.4880968673,1.919767865  
H,0,1.3434051643,0.9208557869,2.0173317137  
H,0,0.3019411159,-1.0086550128,2.1858283974  
H,0,-0.8153386874,-2.4268817135,1.9975629676  
H,0,0.9141906274,-2.5629324769,1.617699909  
C,0,-4.289620329,1.2832702067,-1.1567121237  
C,0,-3.6360443814,1.1426644598,1.2399994095  
H,0,-5.1800775793,1.8543093077,-0.8870482962  
H,0,-4.1210566883,1.0909854249,-2.2185061552  
H,0,-3.5061084007,0.2435099634,1.8614180976  
H,0,-2.902236707,1.8839848897,1.5895765189  
H,0,-4.6386896943,1.5450529911,1.4269055506  
H,0,3.5522239378,-2.7347086094,-1.1216307082  
H,0,2.98282398,-2.2791313551,0.4939396088  
H,0,1.8247782382,-2.5485452726,-0.8326111574  
H,0,3.6810232509,1.4322634075,2.8156967729  
H,0,4.3116994872,1.0494036101,1.2022854201  
H,0,3.2311060302,2.4325840881,1.4202398728  
H,0,3.1286901935,2.6878424767,-2.407129186  
H,0,3.3239739031,3.4303500128,-0.8186815837  
H,0,3.9752921244,1.8214545693,-1.1259865666

### TSR-B-1

E(RM11) = -652.709720315

Zero-point correction= 0.434201 (Hartree/Particle)  
Thermal correction to Energy= 0.454855  
Thermal correction to Enthalpy= 0.455799  
Thermal correction to Gibbs Free Energy= 0.386845  
Sum of electronic and ZPE= -652.275519  
Sum of electronic and thermal Energies= -652.254866  
Sum of electronic and thermal Enthalpies= -652.253921  
Sum of electronic and thermal Free Energies= -652.322876

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.426 80.732 145.126

C,0,0.8999763958,2.2753600748,-0.7006736335  
C,0,2.1979439492,1.5410799817,-0.1939980445  
H,0,0.8098628337,2.1389802037,-1.7858533156  
H,0,0.9505152344,3.3409020893,-0.4425453954  
C,0,-0.1425900701,1.5262831611,0.0295335725  
C,0,-0.4701014162,0.2216474055,-0.4210471313  
C,0,-0.626176013,2.0507456762,1.3226209013  
C,0,0.7874416382,-0.4955012774,0.2710775828  
H,0,-0.2530259216,0.1563774952,-1.5002558354  
C,0,2.0927348263,0.0110393443,-0.3581939847  
H,0,0.6229848907,-1.5684618147,0.0944415616  
H,0,0.7996618637,-0.3386930688,1.358786113  
C,0,3.3427331523,-0.6693734597,0.179619184  
H,0,2.0466957944,-0.2051974862,-1.4424792989  
H,0,2.3544974642,1.7768758339,0.8719376429  
H,0,3.0488836092,1.9562272606,-0.7495769149  
B,0,-1.9904869509,-0.5172600462,-0.1288656137  
C,0,-3.0532454503,0.410754741,-1.0362352351  
C,0,-2.4625410101,-0.6430925018,1.4481344407  
C,0,-1.8758061496,-2.0335314128,-0.76632748656  
H,0,-3.4114925114,-0.1941058872,-1.8892484758  
H,0,-2.5416152695,1.270267895,-1.5155029593  
C,0,-4.2928532677,0.9587741095,-0.3091985291  
H,0,-2.9117273151,-2.4184229004,-0.8052742906  
H,0,-1.3443860579,-2.7357383387,-0.0961242046  
C,0,-1.264522633,-2.1456712882,-2.1718660531  
C,0,-1.5333474636,-1.3447932792,2.4554345004  
H,0,-3.3920424984,-1.2393511704,1.397664452  
H,0,-2.7937373059,0.3161323796,1.8860250092  
H,0,-0.8178164357,1.2473193552,2.0422956753  
H,0,0.0077021725,2.843792124,1.7377028263  
H,0,-1.6207281282,2.4766596078,1.0846674274  
C,0,3.314149254,-1.5710421632,1.1637192537  
C,0,4.641028172,-0.2675021083,-0.4815617886  
H,0,4.2352599565,-2.0446432778,1.5083452204  
H,0,2.3901974902,-1.8799453818,1.6534031868  
H,0,4.5456500277,-0.2830459713,-1.5779911901  
H,0,4.9374388745,0.7527161716,-0.1941272495  
H,0,5.4553006338,-0.9442662194,-0.1965972125  
H,0,-4.9687566418,1.5028210003,-0.9875680485  
H,0,-4.8757905846,0.1491021918,0.154253424  
H,0,-4.021589507,1.6521008405,0.5035977658  
H,0,-2.0685097467,-1.6729549244,3.3595026135  
H,0,-1.057219384,-2.2367414136,2.0189929822  
H,0,-0.7162071274,-0.6921778646,2.8091522923  
H,0,-1.4211390227,-3.1342634828,-2.62936108  
H,0,-1.6969447741,-1.3962012023,-2.8554480151  
H,0,-0.1731112066,-1.9776882418,-2.1606268925

### TSR-B-2

E(RM11) = -652.711242029

Zero-point correction= 0.434674 (Hartree/Particle)  
Thermal correction to Energy= 0.455161  
Thermal correction to Enthalpy= 0.456105  
Thermal correction to Gibbs Free Energy= 0.387652  
Sum of electronic and ZPE= -652.276569  
Sum of electronic and thermal Energies= -652.256081  
Sum of electronic and thermal Enthalpies= -652.255137  
Sum of electronic and thermal Free Energies= -652.323590

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.618 80.602 144.071

C,0,0.8314519266,2.2963376268,-0.6744973299  
C,0,2.1619731867,1.5743137077,-0.2483754855

H,0,0.6876683376,2.1941231595,-1.7577919033  
H,0,0.877783556,3.3558165091,-0.389787122  
C,0,-0.1815786578,1.5190132241,0.0789595818  
C,0,-0.5130399984,0.2273367494,-0.3967316738  
C,0,-0.5271958814,1.9969558556,1.4446220042  
C,0,0.7641185024,-0.4510318419,0.3205269115  
H,0,-0.2855742682,0.1611885385,-1.4754174697  
C,0,2.0513874211,0.039523202,-0.3599425863  
H,0,0.6101712267,-1.5318925015,0.1965530929  
H,0,0.7953768598,-0.2459349388,1.4000361248  
C,0,3.3170826696,-0.6230655747,0.162078613  
H,0,1.9742947781,-0.2117641631,-1.4339957447  
H,0,2.3958172361,1.8380453165,0.7961900735  
H,0,2.9734410609,1.9694617305,-0.8732199473  
B,0,-2.0251444861,-0.5733542738,-0.1572388768  
C,0,-3.0608941537,0.3399084321,-1.063527468  
C,0,-2.5560478298,-0.6623741079,1.3978987053  
C,0,-1.8272319996,-2.1047662752,-0.7758687943  
H,0,-4.0686010026,-0.0967032218,-0.9387143682  
H,0,-2.839630101,0.2460783841,-2.1417299665  
C,0,-3.1417647232,-1.8313023645,-0.7255750807  
H,0,-2.093551782,-2.8456790096,-0.000400129  
H,0,-0.7687618065,-2.3302630579,-1.0125623772  
C,0,-2.6398481081,-2.4433410479,-2.0374905373  
C,0,-1.6656684918,-1.3878770055,2.4215022752  
H,0,-3.4998690247,-1.2331957647,1.317942691  
H,0,-2.8688070057,0.313671235,1.8146170105  
H,0,-0.9675972004,1.2077044724,2.0596817323  
H,0,0.3412960314,2.4577477564,1.9377648021  
H,0,-1.2807992596,2.7905732466,1.3149865661  
C,0,3.3230924075,-1.4756616806,1.1894289674  
C,0,4.5899904475,-0.2605099736,-0.5671310051  
H,0,4.2555402329,-1.9346313476,1.5230648591  
H,0,2.4174310515,-1.7567550919,1.7276382301  
H,0,4.457872323,-0.3505903311,-1.6561011526  
H,0,4.8877555217,0.7784654184,-0.3596248071  
H,0,5.4181458138,-0.9125632573,-0.2649585628  
H,0,-3.9067970339,2.3636072605,-1.3112922017  
H,0,-3.3694986005,1.9978978522,0.3395525063  
H,0,-2.1862585721,2.3482949397,-0.946298644  
H,0,-2.2132451883,-1.6829014359,3.3295895247  
H,0,-1.2311595152,-2.3042640513,1.9902831751  
H,0,-0.8182618185,-0.7690787477,2.7620141964  
H,0,-2.5078374258,-3.49181311,-2.3471342028  
H,0,-3.7161887491,-2.2806843505,-1.8773122514  
H,0,-2.3462494768,-1.8128693698,-2.8907444955

### TSR-B-3

E(RM11) = -652.710307300

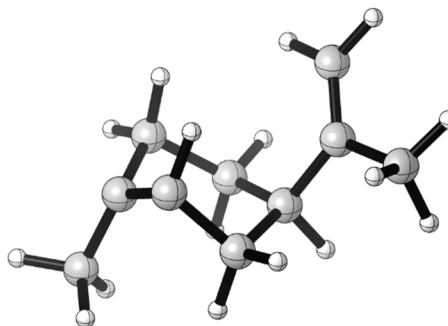
Zero-point correction= 0.434529 (Hartree/Particle)  
Thermal correction to Energy= 0.455176  
Thermal correction to Enthalpy= 0.456120  
Thermal correction to Gibbs Free Energy= 0.387179  
Sum of electronic and ZPE= -652.275779  
Sum of electronic and thermal Energies= -652.255132  
Sum of electronic and thermal Enthalpies= -652.254188  
Sum of electronic and thermal Free Energies= -652.323128

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	285.627	80.769 145.097

C,0,0.896991121,2.2615083846,-0.8472022648  
C,0,2.1543308335,1.4936275317,-0.299293783  
H,0,0.8034933714,2.0845646491,-1.9264141422  
H,0,1.0020967313,3.3349855061,-0.6416349974  
C,0,-0.2074480319,1.614802055,-0.0941779776

C,0,-0.6044223513,0.3209527674,-0.5100767747  
C,0,-0.5660114285,2.2546616038,1.2025270939  
C,0,0.5964978358,-0.4159964055,0.284004083  
H,0,-0.3426145351,0.204917347,-1.5734175452  
C,0,1.9511510829,-0.0333710617,-0.3286785415  
H,0,0.3752047134,-1.484368349,0.1494858428  
H,0,0.554247252,-0.2009191337,1.3630897361  
C,0,3.1360820758,-0.7449681841,0.3066333275  
H,0,1.9221641001,-0.34158647,-1.3910628143  
H,0,2.3486956154,1.8106392816,0.7382440496  
H,0,3.021981847,1.7975512291,-0.8993400855  
B,0,-2.0728146272,-0.5232732269,-0.2032873038  
C,0,-3.2348500981,0.3532364948,-0.9749576179  
C,0,-2.4141905622,-0.7042168839,1.4178217057  
C,0,-1.9027216534,-1.9838474718,-0.9556538797  
H,0,-4.1915824254,-0.1625547345,-0.773072678  
H,0,-3.108128363,0.3144062936,-2.0726467194  
C,0,-3.3706404392,1.8184975416,-0.5531652268  
H,0,-2.9202159932,-2.4123856336,-1.0144917834  
H,0,-1.3388687416,-2.7126559743,-0.34601892  
C,0,-1.295270494,-1.9861390321,-2.3681346642  
C,0,-2.303389339,-2.1266405259,1.9957832701  
H,0,-3.4464673052,-0.3485711499,1.5938945595  
H,0,-1.7952632052,-0.0682289579,2.0740751039  
H,0,-1.2782425549,1.6698489936,1.7855504097  
H,0,0.3403663376,2.4695710899,1.7900552669  
H,0,-1.01576354,3.2305901163,0.960833874  
C,0,3.017218525,-1.5730907005,1.3472186465  
C,0,4.4793199365,-0.4653534888,-0.3267857059  
H,0,3.8957853253,-2.0713990064,1.7611429163  
H,0,2.0596005588,-1.7962963756,1.8183324414  
H,0,4.4258340437,-0.5649301004,-1.421690438  
H,0,4.8185923928,0.5585896079,-0.108482641  
H,0,5.2435422332,-1.1579235665,0.0455397677  
H,0,-4.240663295,2.3222770584,-1.0016254687  
H,0,-3.4623255088,1.9151726793,0.5419806432  
H,0,-2.4860076393,2.4056642873,-0.8643794163  
H,0,-2.6055409497,-2.1688695206,3.0538373784  
H,0,-2.9335365049,-2.8386280328,1.4436961798  
H,0,-1.2702334447,-2.507310846,1.9376632374  
H,0,-1.4382168279,-2.9456372033,-2.8876805301  
H,0,-1.7349288244,-1.2012938186,-3.0045948827  
H,0,-0.2054203692,-1.8085240138,-2.3415426471

### Isopropenyl-Axial Series, Derived from 8-ax Reactants *trans*-limonene-ax-A



E(RM11) = -390.340818265

Zero-point correction= 0.233539 (Hartree/Particle)  
Thermal correction to Energy= 0.243936

Thermal correction to Enthalpy= 0.244881  
Thermal correction to Gibbs Free Energy= 0.198102  
Sum of electronic and ZPE= -390.107280  
Sum of electronic and thermal Energies= -390.096882  
Sum of electronic and thermal Enthalpies= -390.095938  
Sum of electronic and thermal Free Energies= -390.142716

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 153.072	41.398	98.454

C,0,1.5658186062,-1.8757425086,-1.3394987973  
C,0,2.6222922722,-1.647483468,-0.1672935959  
H,0,1.6851718232,-1.0991804893,-2.1077120248  
H,0,1.7158358258,-2.8666562652,-1.7950605937  
C,0,0.3009778265,-1.6917385915,-0.5478394354  
C,0,0.2166233176,-0.4046040605,-0.1282191386  
C,0,-0.1838727888,-2.8556602753,0.2774813562  
C,0,0.8735877413,-0.2139634872,1.2094514664  
H,0,0.575514622,0.3377371763,-0.8541764986  
C,0,2.402396974,-0.4031169131,0.7448739509  
H,0,0.74031992,0.7557429488,1.7065312778  
H,0,0.6215506279,-1.0080126166,1.9243806306  
C,0,2.9460128892,0.8962633154,0.1644217105  
H,0,2.9800369197,-0.5817067651,1.6693302506  
H,0,2.5920862473,-2.5395159725,0.4756631373  
H,0,3.6393731345,-1.6096925039,-0.5831493589  
H,0,-0.8077239813,-2.5200927245,1.116379265  
H,0,0.6353963891,-3.481870571,0.6646833092  
H,0,-0.8078151905,-3.5084341844,-0.3522969146  
C,0,3.450250037,1.0147161667,-1.0669502088  
C,0,2.9017345657,2.0927991536,1.0895871269  
H,0,3.846148839,1.9702860791,-1.4161787415  
H,0,3.4942461952,0.1816927927,-1.7687638586  
H,0,3.1949599762,1.8126359732,2.1126457365  
H,0,1.8883426,2.5165530384,1.1468198688  
H,0,3.5741576112,2.8856247525,0.7400170802

### *trans-limonene-ax-B*

E(RM11) = -390.338851321

Zero-point correction= 0.233639 (Hartree/Particle)  
Thermal correction to Energy= 0.243964  
Thermal correction to Enthalpy= 0.244908  
Thermal correction to Gibbs Free Energy= 0.198586  
Sum of electronic and ZPE= -390.105212  
Sum of electronic and thermal Energies= -390.094887  
Sum of electronic and thermal Enthalpies= -390.093943  
Sum of electronic and thermal Free Energies= -390.140266

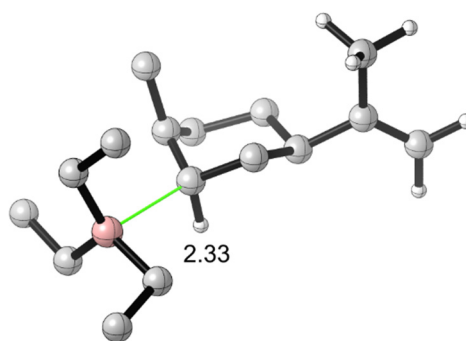
E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 153.090	41.313	97.494

C,0,1.3748898259,1.2978181862,-0.4353971543  
C,0,0.4665751382,1.0424968086,0.8436756072  
H,0,0.7429157167,1.6393446161,-1.2685480914  
H,0,2.1360755967,2.0621760773,-0.2148136816  
C,0,1.8703314614,-0.1098484333,-0.6364173148  
C,0,0.8307477487,-0.8971917725,-1.0105850607  
C,0,2.9923132735,-0.5941964652,0.2451130492  
C,0,0.1129386643,-1.4811031943,0.180705271  
H,0,0.1293694086,-0.4122931318,-1.6986224504  
C,0,-0.548980674,-0.1463142163,0.7419908441  
H,0,-0.6564513216,-2.2425939217,-0.0048433716  
H,0,0.8073428447,-1.871924895,0.9365458307  
C,0,-1.8295128675,0.2574736509,0.0118207548  
H,0,-0.8647906555,-0.3541484428,1.7805880929

H,0,1.1369695906,0.834856317,1.6906169987  
H,0,-0.0670851733,1.966117511,1.1055602579  
H,0,2.9553208545,-1.6837755248,0.3771971832  
H,0,3.0109734094,-0.1103639444,1.234014025  
H,0,3.9533996557,-0.3594058064,-0.2380200543  
C,0,-2.3898590536,-0.4420028965,-0.9787018864  
C,0,-2.5008343834,1.5159434181,0.5187598394  
H,0,-3.3349236339,-0.1175734268,-1.4185167848  
H,0,-1.9427136964,-1.3448482964,-1.3950933367  
H,0,-1.9741641231,2.4169903929,0.1702339443  
H,0,-2.5078630916,1.5487412486,1.6188921272  
H,0,-3.5365326049,1.5776776794,0.1632771415

## TS1 Structures

### *TS1-ax-A*



E(RM11) = -652.710988151

Zero-point correction= 0.433792 (Hartree/Particle)  
Thermal correction to Energy= 0.455211  
Thermal correction to Enthalpy= 0.456155  
Thermal correction to Gibbs Free Energy= 0.384521  
Sum of electronic and ZPE= -652.277196  
Sum of electronic and thermal Energies= -652.255777  
Sum of electronic and thermal Enthalpies= -652.254833  
Sum of electronic and thermal Free Energies= -652.326467

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.649	81.683	150.766

C,0,-1.2224635161,2.1909781073,-0.8317178185  
C,0,-2.3754268,1.7615110733,0.1875173201  
H,0,-1.3680660897,1.6906413667,-1.7982322786  
H,0,-1.2286322214,3.2823979737,-0.9675730674  
C,0,-0.0672083463,1.622036654,-0.077260604  
C,0,-0.0998172497,0.2564284799,-0.0683852234  
C,0,0.5435677633,2.4380266363,1.0215236227  
C,0,-0.904904965,-0.2058753847,1.1289916675  
H,0,-0.5169858684,-0.171553781,-0.9905674591  
C,0,-2.3593571189,0.2911070634,0.696615331  
H,0,-0.8995336219,-1.2880542709,1.3159436504  
H,0,-0.6033839605,0.297962868,2.0577380468  
C,0,-2.9976329175,-0.7117839355,-0.2560473761  
H,0,-2.9782523026,0.2709963198,1.6113089123  
H,0,-2.2883113535,2.4201940724,1.0646119804  
H,0,-3.3539832866,1.9791880719,-0.2633396077  
B,0,2.1457507864,-0.6176683155,-0.1253374798  
C,0,1.8132637275,-1.5746375102,-1.3626712607  
C,0,3.0692363917,0.656964729,-0.3942147407  
C,0,2.1674158475,-1.2379044385,1.347698718  
H,0,1.4217507618,-0.9864020286,-2.2093072795  
H,0,2.7963612382,-1.9452814323,-1.7167306306

C,0,0.8932906323,-2.7682036904,-1.0810534458  
H,0,2.1446967977,-0.4523868941,2.1228508647  
H,0,1.2993935135,-1.8905623991,1.5319884479  
C,0,3.4530996378,-2.0763754045,1.5157423518  
C,0,2.8934961278,1.3858269382,-1.7303940239  
H,0,4.1022354002,0.2590224129,-0.3443433926  
H,0,3.0138757201,1.3695326369,0.4450849637  
H,0,1.0137404803,1.8045966804,1.7851868987  
H,0,-0.178790141,3.1213561846,1.4924750345  
H,0,1.3367083482,3.0656267913,0.5809162228  
C,0,-3.3944431875,-0.4168725571,-1.4968947233  
C,0,-3.1882179932,-2.1061988987,0.2992822237  
H,0,-3.8646951908,-1.1746964751,-2.1261446506  
H,0,-3.2781246224,0.575999456,-1.93233293  
H,0,-3.5832750955,-2.069884784,1.3257774923  
H,0,-2.2390151247,-2.6603896627,0.3372662896  
H,0,-3.8843182719,-2.6836853764,-0.320798319  
H,0,0.7236867898,-3.3878306974,-1.9734276989  
H,0,-0.0927823274,-2.4275908862,-0.7263660462  
H,0,1.3104409606,-3.4204661318,-0.2990043928  
H,0,3.5680905869,2.2487363432,-1.8309517089  
H,0,1.8598905056,1.7541789473,-1.8435671048  
H,0,3.0886758626,0.7147570327,-2.5793454104  
H,0,3.5020127434,-2.5645516599,2.4996191137  
H,0,4.3542128899,-1.4545325551,1.4107721294  
H,0,3.5121421796,-2.8673517295,0.751578301

### TS1-ax-B

E(RM11) = -652.708762371

Zero-point correction= 0.433657 (Hartree/Particle)  
Thermal correction to Energy= 0.455150  
Thermal correction to Enthalpy= 0.456094  
Thermal correction to Gibbs Free Energy= 0.383957  
Sum of electronic and ZPE= -652.275105  
Sum of electronic and thermal Energies= -652.253613  
Sum of electronic and thermal Enthalpies= -652.252669  
Sum of electronic and thermal Free Energies= -652.324806

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.611	81.654	151.825

C,0,-1.771980247,0.9885895564,-1.6236380029  
C,0,-2.6295104275,1.5577442745,-0.4051870977  
H,0,-2.0661355147,-0.0504898807,-1.8282009083  
H,0,-1.9270141072,1.6058963823,-2.5211627837  
C,0,-0.4217309861,1.0768884188,-0.9790202259  
C,0,-0.322115815,0.1886402286,0.0479020196  
C,0,0.285367305,2.4026584403,-0.9959852921  
C,0,-0.8123897226,0.8125655097,1.3322293069  
H,0,-0.8365437763,-0.7656548911,-0.1373381486  
C,0,-2.3694427386,0.8932808761,0.9756821869  
H,0,-0.6554483422,0.2422894344,2.2560978406  
H,0,-0.4227185753,1.828911757,1.4840640778  
C,0,-3.0295859787,-0.4752098951,1.1292375555  
H,0,-2.8319039783,1.5418708133,1.7416786583  
H,0,-2.3991645602,2.6295312689,-0.3108413584  
H,0,-3.7000482562,1.4992693479,-0.6464358429  
B,0,2.2016723862,-0.7602073766,0.0046090801  
C,0,2.610294022,-0.426444967,-1.4955884889  
C,0,2.8145485704,0.1658010628,1.1480634679  
C,0,1.6042041755,-2.1868509674,0.3574470978  
H,0,2.6122554949,0.6648915798,-1.6563061025  
H,0,3.6790437689,-0.7125032654,-1.5635432352  
C,0,1.8306588584,-1.1374322954,-2.6072129672  
H,0,1.0941286837,-2.1950787702,1.3348774668

H,0,0.875166267,-2.5294955915,-0.3930921141  
C,0,2.792774682,-3.1757699951,0.3895062076  
C,0,2.5277109569,-0.2245293316,2.601999845  
H,0,2.5047829481,1.2091011883,0.9655350935  
H,0,3.908086817,0.1802257036,0.9783431413  
H,0,0.9704553804,2.5103539372,-0.1447679625  
H,0,-0.4052544092,3.2590764844,-1.0201633655  
H,0,0.8933005516,2.4614439972,-1.913882166  
C,0,-3.8439264768,-1.0192001194,0.2207225098  
C,0,-2.7222015831,-1.2166321529,2.4109115491  
H,0,-4.3106450386,-1.988652843,0.4049850078  
H,0,-4.0804841424,-0.5375736193,-0.7280490165  
H,0,-2.7459770204,-0.5414899485,3.2797685517  
H,0,-1.716713813,-1.6642612891,2.3726666749  
H,0,-3.4426115737,-2.026242842,2.5783593489  
H,0,2.1781906722,-0.8512220253,-3.610281206  
H,0,0.756998226,-0.8996851,-2.5436903396  
H,0,1.9271575366,-2.2305068999,-2.5250497394  
H,0,3.009189823,0.4556716919,3.3191082324  
H,0,2.885143052,-1.2418893218,2.8206974309  
H,0,1.4481823786,-0.2145539585,2.8089544153  
H,0,2.4742113416,-4.1914544699,0.6623489071  
H,0,3.558362446,-2.8630729998,1.1166325008  
H,0,3.2838542135,-3.235218347,-0.594000696

### TS1-ax-C

E(RM11) = -652.709603992

Zero-point correction= 0.434447 (Hartree/Particle)  
Thermal correction to Energy= 0.455431  
Thermal correction to Enthalpy= 0.456375  
Thermal correction to Gibbs Free Energy= 0.386303  
Sum of electronic and ZPE= -652.275157  
Sum of electronic and thermal Energies= -652.254173  
Sum of electronic and thermal Enthalpies= -652.253229  
Sum of electronic and thermal Free Energies= -652.323301

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.787	81.223	147.480

C,0,-1.0560600508,1.8429179807,-1.0434627344  
C,0,-2.1672211135,1.6172290783,0.0821744734  
H,0,-1.2234989831,1.1385036068,-1.8691383129  
H,0,-1.0921852397,2.8796561977,-1.4070978987  
C,0,0.1269459176,1.4683813653,-0.2193893924  
C,0,0.1486684735,0.1287478282,0.0828015689  
C,0,0.7686761288,2.5114208241,0.6404163496  
C,0,-0.6553801648,-0.0520637804,1.3671711093  
H,0,-0.3152726045,-0.4751000051,-0.706394867  
C,0,-2.1129917331,0.2570777118,0.8262762346  
H,0,-0.5891912202,-1.0471263791,1.8270391492  
H,0,-0.3999391892,0.6900094388,2.136026051  
C,0,-2.6547640194,-0.9186724237,0.018563174  
H,0,-2.7686378842,0.3484369979,1.7113905167  
H,0,-2.0444068601,2.4159940314,0.8298215954  
H,0,-3.160071565,1.7655656101,-0.3644852422  
B,0,2.1843933249,-0.8275125183,-0.1729437166  
C,0,1.899466206,-1.4634597045,-1.6214010103  
C,0,3.2438083447,0.3761174892,-0.1261531838  
C,0,2.1067350816,-1.7969293685,1.1016391946  
H,0,1.5438740288,-0.6835267969,-2.317276107  
H,0,2.8941777574,-1.7509212657,-2.012902247  
C,0,0.9818715484,-2.6916643712,-1.6851640151  
H,0,1.150088885,-2.3484972201,1.1176414582  
H,0,2.8686730644,-2.5823963152,0.9245676046  
C,0,2.3697725452,-1.1368299742,2.4599354235

C,0,4.6772364332,-0.1911185367,-0.1835046802  
H,0,3.1451066085,0.973866955,0.7949957606  
H,0,3.0988547665,1.0713205658,-0.9715747875  
H,0,1.1866838345,2.0815287371,1.5604807275  
H,0,0.0858040692,3.3391244824,0.8808311598  
H,0,1.6136969036,2.9406785301,0.0765960596  
C,0,-3.2225122982,-0.8013759287,-1.1849317367  
C,0,-2.5234947583,-2.2750306458,0.6726623052  
H,0,-3.6156640379,-1.6793352745,-1.7006242851  
H,0,-3.3223488538,0.1529702431,-1.7028228478  
H,0,-2.8069549068,-2.2343286348,1.7353925264  
H,0,-1.4830193492,-2.6341412282,0.6274280409  
H,0,-3.1556028741,-3.0165058864,0.1697350252  
H,0,0.8821807111,-3.0862648484,-2.70692421  
H,0,-0.0353051909,-2.4615269324,-1.3282323279  
H,0,1.3671674471,-3.5056877507,-1.0532918508  
H,0,5.4386868307,0.6009154007,-0.1360514531  
H,0,4.8479752545,-0.7551029535,-1.1124248769  
H,0,4.8667004489,-0.8811956475,0.6531650479  
H,0,2.2305077831,-1.8282154566,3.3040465891  
H,0,1.6987912921,-0.2770198694,2.6187171034  
H,0,3.397013247,-0.7475100279,2.5185125346

### TSI-ax-D

E(RM11) = -652.712064034

Zero-point correction= 0.434463 (Hartree/Particle)  
Thermal correction to Energy= 0.455222  
Thermal correction to Enthalpy= 0.456166  
Thermal correction to Gibbs Free Energy= 0.387125  
Sum of electronic and ZPE= -652.277601  
Sum of electronic and thermal Energies= -652.256843  
Sum of electronic and thermal Enthalpies= -652.255898  
Sum of electronic and thermal Free Energies= -652.324939

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.656	81.152	145.308

C,0,-1.4349822937,-0.1310757707,-0.4699121729  
C,0,-0.5897624439,1.1795124549,-0.1205267575  
H,0,-1.8335208991,-0.5725184693,0.4531622771  
H,0,-2.2528045602,0.1225879866,-1.1593173439  
C,0,-0.3181575906,-0.9365256048,-1.0363424064  
C,0,0.59493333,-1.3121609226,-0.0792460078  
C,0,0.0344902662,-0.7621266152,-2.4807985182  
C,0,1.6184694097,-0.1828965981,0.0145239044  
H,0,0.1250953468,-1.4405581358,0.9034488154  
C,0,0.7296822176,0.9576410422,0.664822546  
H,0,2.5058332473,-0.4052558637,0.6217037206  
H,0,1.9650176057,0.1570907177,-0.9707754854  
C,0,0.5409912858,0.7116885282,2.1576865211  
H,0,1.3088733747,1.8952674564,0.5834453565  
H,0,-0.3361498358,1.6666059702,-1.0744933909  
H,0,-1.2364864266,1.8831349408,0.4217617236  
B,0,1.2942918591,-3.4369409902,-0.2445360359  
C,0,0.4552399292,-3.9938987986,1.0087957166  
C,0,0.8087833845,-3.9124251644,-1.6967884566  
C,0,2.8644643672,-3.1959131911,-0.0310856469  
H,0,-0.6128309889,-3.7331247816,0.9094479811  
H,0,0.4805952085,-5.0969938974,0.9066557087  
C,0,0.9599725938,-3.6154773127,2.4068115624  
H,0,3.0492733562,-2.5513798606,0.8458958465  
H,0,3.2740602671,-4.1815478342,0.2669013112  
C,0,3.6412062351,-2.6804970367,-1.2473712122  
C,0,-0.6958454689,-4.1537921677,-1.85793536  
H,0,1.3441089603,-4.863892808,-1.8860638782  
H,0,1.177822187,-3.2358759386,-2.4848316506

H,0,1.1079805189,-0.9057854974,-2.6604437207  
H,0,-0.2914845699,0.2100682045,-2.8778366903  
H,0,-0.4949806754,-1.5409195577,-3.055374214  
C,0,-0.6463681847,0.6946884067,2.769297215  
C,0,1.8135328697,0.49434837,2.9447011411  
H,0,-0.7144907196,0.5377356382,3.8472927357  
H,0,-1.5873778897,0.8356567453,2.2368039389  
H,0,2.5898494648,1.2163731132,2.6488311256  
H,0,2.2227913176,-0.5124893552,2.7679396623  
H,0,1.6326445998,0.5968070087,4.0213411313  
H,0,0.3471185313,-4.0558080221,3.2068567038  
H,0,0.9507773598,-2.5233039734,2.5568594825  
H,0,1.9958842716,-3.9520722638,2.5605883619  
H,0,-0.9805619893,-4.3966142949,-2.8929826977  
H,0,-1.2772137407,-3.2664265046,-1.5501797062  
H,0,-1.0353615066,-4.9819924418,-1.2192707822  
H,0,4.7033344247,-2.4974136917,-1.0276090159  
H,0,3.2130409991,-1.7356227806,-1.6191847892  
H,0,3.594497995,-3.3985154382,-2.0793710448

### TSI-ax-E

E(RM11) = -652.711174491

Zero-point correction= 0.434385 (Hartree/Particle)  
Thermal correction to Energy= 0.455351  
Thermal correction to Enthalpy= 0.456295  
Thermal correction to Gibbs Free Energy= 0.386239  
Sum of electronic and ZPE= -652.276789  
Sum of electronic and thermal Energies= -652.255823  
Sum of electronic and thermal Enthalpies= -652.254879  
Sum of electronic and thermal Free Energies= -652.324936

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.737	81.155	147.446

C,0,1.4824595128,-1.7466284523,-1.4536019924  
C,0,2.5449267279,-1.6749513073,-0.2648395489  
H,0,1.6370743103,-0.8965573909,-2.1324259839  
H,0,1.5853891244,-2.6953207446,-1.9996903251  
C,0,0.252139743,-1.5903263779,-0.620922713  
C,0,0.1570572889,-0.3362182218,-0.0787476639  
C,0,-0.3336247978,-2.8044056536,0.0336894597  
C,0,0.9140778293,-0.3319513766,1.2402172427  
H,0,0.5662993441,0.4434125884,-0.7367462871  
C,0,2.3972417989,-0.4600691736,0.6885371247  
H,0,0.7833061129,0.5606895855,1.8666148102  
H,0,0.6920648251,-1.2125781609,1.8583355244  
C,0,2.87622486,0.8575316433,0.0814350132  
H,0,3.0464976955,-0.6506351145,1.562402653  
H,0,2.4359713525,-2.5913626022,0.3352865419  
H,0,3.5590933837,-1.7061502459,-0.6860339918  
B,0,-2.0621169209,0.5105739597,-0.1540607191  
C,0,-1.7834074866,1.4398340506,-1.4261522926  
C,0,-2.9865166067,-0.7770245325,-0.3465135151  
C,0,-2.0307027224,1.2214077391,1.2788736662  
H,0,-2.6628961914,2.1110402123,-1.4848762083  
H,0,-0.9328983233,2.117381685,-1.2376874029  
C,0,-1.6149488678,0.7266350419,-2.7716569289  
H,0,-1.1089153683,1.8183078787,1.3927507631  
H,0,-2.840553059,1.9764267088,1.2522876473  
C,0,-2.239258729,0.3095772765,2.4930472064  
C,0,-4.4500829118,-0.3014321559,-0.4675303491  
H,0,-2.7164137127,-1.3453062367,-1.2515743788  
H,0,-2.9092129074,-1.4756025449,0.5022684941  
H,0,-0.8047945243,-2.5593516798,0.9953202561  
H,0,0.4011058234,-3.6121816181,0.1651205971  
H,0,-1.1311155919,-3.1948461581,-0.6198469519



C,0,3.5586703725,0.9474308619,-1.0634071014  
C,0,2.5447768549,2.1050439082,0.8681429329  
H,0,3.9030946191,1.9168296798,-1.4279758644  
H,0,3.8020794921,0.0817856024,-1.6798664103  
H,0,2.7523008605,1.9696697948,1.9404728592  
H,0,1.4753754368,2.3531817474,0.7719097621  
H,0,3.1237054732,2.9629238584,0.5060516656  
H,0,-1.3944807728,1.4222008208,-3.5941156413  
H,0,-2.5265376464,0.1730561852,-3.042467536  
H,0,-0.795770475,-0.0104495307,-2.728483204  
H,0,-5.1509366682,-1.1403082167,-0.5846248128  
H,0,-4.5809050823,0.3627443979,-1.3359785048  
H,0,-4.7594145705,0.2656460377,0.4245611889  
H,0,-2.1440647504,0.846259422,3.4482628651  
H,0,-1.5088776058,-0.5152248984,2.4992530144  
H,0,-3.238043609,-0.1517451525,2.4719127293

### TSI-ax-F

E(RM11) = -652.708476056

Zero-point correction= 0.433657 (Hartree/Particle)  
Thermal correction to Energy= 0.454466  
Thermal correction to Enthalpy= 0.455410  
Thermal correction to Gibbs Free Energy= 0.384348  
Sum of electronic and ZPE= -652.274819  
Sum of electronic and thermal Energies= -652.254010  
Sum of electronic and thermal Enthalpies= -652.253066  
Sum of electronic and thermal Free Energies= -652.324128

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.182	79.642	149.563

C,0,-1.4781663863,1.804052576,-1.3304997358  
C,0,-2.5421072232,1.7465508611,-0.1404400793  
H,0,-1.6485049443,0.9815456739,-2.0381505419  
H,0,-1.556593999,2.7676648694,-1.8558049862  
C,0,-0.2396697774,1.5966353231,-0.5107090601  
C,0,-0.2458667329,0.3298128542,-0.0133153227  
C,0,0.323043508,2.7923117862,0.2172109022  
C,0,-0.9125074147,0.2503934593,1.3319267781  
H,0,-0.6919994287,-0.402606377,-0.7017438692  
C,0,-2.4230363959,0.5689832267,0.8778535866  
H,0,-0.8629557828,-0.723525607,1.8358880622  
H,0,-0.5631237636,1.0131179284,2.0372919447  
C,0,-3.1014863848,-0.7198501637,0.4341838488  
H,0,-2.9546495787,0.8930465383,1.7893956026  
H,0,-2.4308420738,2.6868417102,0.422010364  
H,0,-3.5601247581,1.7544792771,-0.556732331  
B,0,2.0670345298,-0.90305659,-0.172793102  
C,0,1.8603956565,-1.3316590038,-1.6887120828  
C,0,3.0396299782,0.3034468089,0.1768067363  
C,0,1.6613313733,-1.9119588233,0.9895656993  
H,0,2.5922404789,-2.1497403212,-1.8505719457  
H,0,0.8806838462,-1.8188158037,-1.8222697959  
C,0,2.0658072855,-0.2445641752,-2.748268437  
H,0,2.6017360437,-2.4284442191,1.2662836625  
H,0,1.3901646075,-1.3448254223,1.8955922569  
C,0,0.5919198558,-2.9618749937,0.6617094121  
C,0,4.4992670441,-0.1928441387,0.0766182038  
H,0,2.8544261582,0.697008165,1.1904513226  
H,0,2.9037280256,1.1392357555,-0.5277821289  
H,0,1.4205337368,2.7473717861,0.2139570264  
H,0,0.0121657021,2.8440027135,1.2719278635  
H,0,0.0173158843,3.7291943755,-0.2672252996  
C,0,-3.5036019049,-0.9567049048,-0.8176176751  
C,0,-3.3182778325,-1.7506328396,1.519900024  
H,0,-3.9926549257,-1.896893104,-1.0791381831

H,0,-3.3741994607,-0.231512739,-1.6213298489  
H,0,-3.7887499474,-1.2929233688,2.4033841186  
H,0,-2.370402299,-2.1982259429,1.8530143914  
H,0,-3.9633612187,-2.5640723991,1.1663639111  
H,0,1.9052808776,-0.6195288315,-3.769186879  
H,0,3.0834660055,0.1715809593,-2.7046342267  
H,0,1.3670414321,0.5912661828,-2.5814914175  
H,0,5.2210232971,0.6087541598,0.287142381  
H,0,4.7178992749,-0.5775228437,-0.9317473289  
H,0,4.6966637393,-1.0087823761,0.7875726783  
H,0,0.9296844211,-3.6332820665,-0.1410174967  
H,0,-0.3395850633,-2.4906295741,0.3077846774  
H,0,0.3401503544,-3.5877855818,1.5307570693

### TSI-ax-G

E(RM11) = -652.710559340

Zero-point correction= 0.434327 (Hartree/Particle)  
Thermal correction to Energy= 0.455419  
Thermal correction to Enthalpy= 0.456363  
Thermal correction to Gibbs Free Energy= 0.386358  
Sum of electronic and ZPE= -652.276232  
Sum of electronic and thermal Energies= -652.255141  
Sum of electronic and thermal Enthalpies= -652.254197  
Sum of electronic and thermal Free Energies= -652.324202

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.779	81.407	147.338

C,0,-1.4183186729,1.6764511942,-1.3168669031  
C,0,-2.4264463342,1.5687006897,-0.0802029314  
H,0,-1.5873959037,0.8462253638,-2.0147703909  
H,0,-1.5606404805,2.6380017829,-1.8310317086  
C,0,-0.1486732284,1.5129449924,-0.5545443063  
C,0,-0.0242815835,0.2463403394,-0.0507435426  
C,0,0.4673908504,2.7230424044,0.0786652876  
C,0,-0.6656713015,0.215135876,1.324346937  
H,0,-0.5004523821,-0.5060002108,-0.6931539523  
C,0,-2.2007365253,0.4063019789,0.9296618207  
H,0,-0.5134853289,-0.7152068329,1.8890174955  
H,0,-0.350967034,1.0551386115,1.9589113273  
C,0,-2.8066658185,-0.926079549,0.5103826007  
H,0,-2.7251624723,0.6968682032,1.8570511245  
H,0,-2.3475219307,2.5147394298,0.4766536657  
H,0,-3.4551710527,1.5214134757,-0.4647256847  
B,0,2.0763140708,-0.6877827445,-0.2533921438  
C,0,2.068033728,-0.8587376366,-1.8466450089  
C,0,3.0544210602,0.4224947695,0.3541941248  
C,0,1.7627340423,-1.975305711,0.6462324604  
H,0,1.1283449166,-1.3142471737,-2.2026325511  
H,0,2.1534885616,0.1193250338,-2.3496761829  
C,0,3.244147948,-1.758454831,-2.2783987645  
H,0,2.7454484055,-2.4801768256,0.746371995  
H,0,1.5049994258,-1.6856460149,1.6786345629  
C,0,0.7397233479,-2.9826347226,0.1058076081  
C,0,3.0275039688,0.6070612184,1.8766050657  
H,0,2.9038488268,1.3870123241,-0.1587263991  
H,0,4.0736998967,0.1105992115,0.05352398  
H,0,1.0462642006,2.4697869339,0.9754071758  
H,0,-0.2783656611,3.496212221,0.3160663409  
H,0,1.1676307991,3.1698357701,-0.6468266056  
C,0,-3.288858991,-1.1762794185,-0.7100775088  
C,0,-2.8496201873,-1.9863324278,1.5881465492  
H,0,-3.7225101981,-2.1487418815,-0.9502540267  
H,0,-3.2805388368,-0.4346037557,-1.5094992015  
H,0,-3.2497239117,-1.5735560592,2.5266375031

H,0,-1.8470351342,-2.3814003435,1.808595088  
H,0,-3.479538339,-2.8307391008,1.2835831054  
H,0,3.2834403529,-1.8936483724,-3.3689255276  
H,0,3.1688578872,-2.7585551929,-1.8244198257  
H,0,4.2094941338,-1.3324229586,-1.965680999  
H,0,3.6702438213,1.4331751332,2.215080499  
H,0,3.3654256277,-0.3045620721,2.3907084816  
H,0,2.0056414784,0.8082763381,2.2377494385  
H,0,0.6345058818,-3.8622352957,0.7583837328  
H,0,1.0264626413,-3.3456951779,-0.8923973552  
H,0,-0.2595046952,-2.5301660165,0.0014874499

### *TS1-ax-H*

E(RM11) = -652.712956784

Zero-point correction= 0.434034 (Hartree/Particle)  
Thermal correction to Energy= 0.455240  
Thermal correction to Enthalpy= 0.456185  
Thermal correction to Gibbs Free Energy= 0.384799  
Sum of electronic and ZPE= -652.278923  
Sum of electronic and thermal Energies= -652.257716  
Sum of electronic and thermal Enthalpies= -652.256772  
Sum of electronic and thermal Free Energies= -652.328157

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.668	81.570	150.243

C,0,-1.3234408021,1.5846923488,-1.3475745702  
C,0,-2.3212973039,1.5110462665,-0.1006550187  
H,0,-1.5136741218,0.7506925948,-2.0358380235  
H,0,-1.4512765162,2.5431676605,-1.8713574434  
C,0,-0.047227071,1.4047206136,-0.5978436658  
C,0,0.054025134,0.1414423804,-0.0798747335  
C,0,0.6001593148,2.6097489134,0.0138180127  
C,0,-0.5715785419,0.1382071645,1.3016379116  
H,0,-0.4457031395,-0.6078089839,-0.7078956971  
C,0,-2.106465423,0.358431497,0.9235993893  
H,0,-0.4367009815,-0.7913683866,1.8710407407  
H,0,-0.2283523505,0.9746870302,1.9257151568  
C,0,-2.7448670427,-0.9671537382,0.5315151057  
H,0,-2.6125996263,0.6731513824,1.8532403424  
H,0,-2.218882127,2.4625346927,0.4428991452  
H,0,-3.3546511565,1.4779460392,-0.4740643166  
B,0,2.1533898171,-0.8287772134,-0.275769635  
C,0,2.0809234272,-1.0759811321,-1.8555567301  
C,0,3.150936952,0.3017763737,0.2574446776  
C,0,1.8451558452,-2.0622980894,0.6969156031  
H,0,2.8511066508,-1.8458674363,-2.0621776081  
H,0,1.1295857757,-1.5577667338,-2.1370623462  
C,0,2.3395132915,0.1408678367,-2.7485038877  
H,0,2.8251699607,-2.5659922678,0.8205327781  
H,0,1.5958057509,-1.7100107729,1.7117113572  
C,0,0.813126161,-3.0941197557,0.2243341601  
C,0,3.1808854855,0.5258155414,1.7744080512  
H,0,2.9759372452,1.253721363,-0.270080148  
H,0,4.1588628322,-0.0112264214,-0.0803304938  
H,0,1.1707557333,2.3587645289,0.9166224971  
H,0,-0.1250459048,3.4068857098,0.2348432223  
H,0,1.3142197378,3.0237032549,-0.7182198603  
C,0,-3.2360545797,-1.2288887422,-0.6828457159  
C,0,-2.8111827494,-2.005497562,1.6293211795  
H,0,-3.6920546566,-2.1955609926,-0.9043774189  
H,0,-3.213178646,-0.502078389,-1.4955067341  
H,0,-3.444772984,-2.8502986789,1.3335505686  
H,0,-3.2203293143,-1.5704795221,2.5536977747  
H,0,-1.8154094837,-2.4049969991,1.8714172281

H,0,2.2582112254,-0.0951529648,-3.8195223793  
H,0,3.3422064194,0.5585793776,-2.575513329  
H,0,1.6132206128,0.9433842065,-2.5312099516  
H,0,3.8240776903,1.3695643453,2.0650727643  
H,0,3.5504036594,-0.3666842014,2.3000322831  
H,0,2.1705027633,0.7231417941,2.1691359689  
H,0,0.6854660786,-3.9167291025,0.9439202008  
H,0,1.1082616811,-3.5412170285,-0.7361601123  
H,0,-0.1773438373,-2.6356946111,0.0697965603

### *TS1-ax-I*

E(RM11) = -652.710085384

Zero-point correction= 0.434619 (Hartree/Particle)  
Thermal correction to Energy= 0.455613  
Thermal correction to Enthalpy= 0.456557  
Thermal correction to Gibbs Free Energy= 0.386691  
Sum of electronic and ZPE= -652.275466  
Sum of electronic and thermal Energies= -652.254472  
Sum of electronic and thermal Enthalpies= -652.253528  
Sum of electronic and thermal Free Energies= -652.323394

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.902	81.293	147.046

C,0,-1.3222958463,1.7309787687,-1.32867977733  
C,0,-2.3771233449,1.5663923484,-0.1347782518  
H,0,-1.4925582485,0.960190975,-2.0913065077  
H,0,-1.423239355,2.7313632635,-1.7736059042  
C,0,-0.0803143168,1.4799594909,-0.5498606952  
C,0,0.0083470593,0.174419668,-0.1352281323  
C,0,0.4999527075,2.6387676194,0.2107007477  
C,0,-0.6462513303,0.1061519121,1.2362033758  
H,0,-0.4931518041,-0.5193713035,-0.8227141471  
C,0,-2.1741856957,0.3829096166,0.8589982779  
H,0,-0.5424696892,-0.8608801071,1.7446085744  
H,0,-0.2790467855,0.8871592148,1.91598216  
C,0,-2.8293083341,-0.9204295416,0.4226838508  
H,0,-2.6765921468,0.6780293622,1.7963630046  
H,0,-2.3527353808,2.5032132589,0.4400440977  
H,0,-3.3836388561,1.4979289463,-0.5707466342  
B,0,1.9662878176,-0.8633193159,-0.2618283969  
C,0,1.9221911692,-1.2223906493,-1.8253307021  
C,0,3.0307157122,0.2333471152,0.2277137404  
C,0,1.6669256146,-2.0562621774,0.7702634493  
H,0,1.0021479514,-1.766158932,-2.0979826033  
H,0,1.9469969158,-0.3155230622,-2.4518440734  
C,0,3.1385783626,-2.1092243016,-2.1613532656  
H,0,2.6283539621,-2.5997192996,0.85297718  
H,0,1.491840143,-1.6662953566,1.7877473423  
C,0,0.5745952454,-3.0594692219,0.3746630604  
C,0,3.4292663743,1.2917558216,-0.8064169018  
H,0,3.9339904498,-0.3332197877,0.5252891708  
H,0,2.6911275782,0.7018104394,1.1680262274  
H,0,1.2876228327,2.3206454496,0.9025567573  
H,0,-0.27844898,3.1772236546,0.7745216409  
H,0,0.9291459384,3.3621557794,-0.4984804279  
C,0,-3.1895439546,-1.185673975,-0.8357149712  
C,0,-3.0597696406,-1.9283190646,1.5248126427  
H,0,-3.6473939068,-2.1409467797,-1.0982770325  
H,0,-3.0497786545,-0.4701981999,-1.6470498475  
H,0,-3.6787297623,-1.4908060666,2.3230099314  
H,0,-2.1152273445,-2.2504271859,1.9874097884  
H,0,-3.5674399256,-2.8224625163,1.1434719455  
H,0,3.1935864062,-2.3537514305,-3.2320899181  
H,0,3.1007399366,-3.0595835112,-1.606693332

H,0,4.0828696238,-1.6129446065,-1.8866978328  
H,0,4.0407979741,2.1007302701,-0.3791782788  
H,0,2.5421125838,1.7487933009,-1.2726536407  
H,0,4.0074307976,0.8384805737,-1.6253701995  
H,0,0.4071821851,-3.8256105349,1.1468535071  
H,0,0.8439575424,-3.5846679104,-0.5539581379  
H,0,-0.3919395406,-2.5646032615,0.1835972256

### *TS1-ax-J*

E(RM11) = -652.710763285

Zero-point correction= 0.434929 (Hartree/Particle)  
Thermal correction to Energy= 0.455650  
Thermal correction to Enthalpy= 0.456594  
Thermal correction to Gibbs Free Energy= 0.387548  
Sum of electronic and ZPE= -652.275834  
Sum of electronic and thermal Energies= -652.255114  
Sum of electronic and thermal Enthalpies= -652.254169  
Sum of electronic and thermal Free Energies= -652.323215

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.924	80.927	145.319

C,0,-1.084350319,1.9493721766,-1.0199653214  
C,0,-2.2028710855,1.7507609422,0.1022528634  
H,0,-1.295172047,1.283218496,-1.8673751493  
H,0,-1.0618261568,2.9972605701,-1.3517547633  
C,0,0.0811533028,1.485868906,-0.2116947476  
C,0,0.0268298143,0.1404872312,0.0530106929  
C,0,0.7648043523,2.4667999696,0.6914415482  
C,0,-0.7905131952,-0.0400780766,1.327281949  
H,0,-0.445823183,-0.4273753545,-0.7595128089  
C,0,-2.2247102823,0.3568201061,0.7817120284  
H,0,-0.779186072,-1.0471457927,1.7647285874  
H,0,-0.5067470604,0.6701576194,2.115711813  
C,0,-2.8047473569,-0.747942321,-0.0999940025  
H,0,-2.8909234144,0.4330822157,1.6603137996  
H,0,-2.0280531618,2.5059145194,0.8841803294  
H,0,-3.1866411555,-1.9809985606,-0.3286647716  
B,0,2.0771871994,-0.9431999777,-0.1470452038  
C,0,1.6901221084,-1.6966201589,-1.5075833565  
C,0,3.1414761047,0.2476916419,-0.2322197375  
C,0,2.000018637,-1.79623182,1.2038575115  
H,0,0.8261739039,-2.368897611,-1.365279012  
H,0,1.4050674436,-0.9803640866,-2.2970410899  
C,0,2.8943293749,-2.5274968836,-1.9965708283  
H,0,1.0293043833,-2.3176645649,1.2738953827  
H,0,2.7391434775,-2.6114013089,1.078011674  
C,0,2.306655224,-1.0466572779,2.5047715948  
C,0,3.1507573157,1.0566190133,-1.5334927036  
H,0,4.1305648284,-0.2353384878,-0.1003427042  
H,0,3.0539013705,0.9182530651,0.6383329757  
H,0,1.150145816,1.9857493318,1.600355229  
H,0,0.1198349435,3.3170163203,0.9565688438  
H,0,1.6359636352,2.8763927946,0.1527100879  
C,0,-3.4491039987,-0.5250644979,-1.2487083892  
C,0,-2.6256935373,-2.1598225106,0.4088849568  
H,0,-3.8702803905,-1.3564398721,-1.8167129387  
H,0,-3.5864973915,0.4706450513,-1.6709522152  
H,0,-2.8738584748,-2.2345658507,1.4786011884  
H,0,-1.5791297455,-2.4856124125,0.2937868811  
H,0,-3.2600371035,-2.8607497675,-0.1464767144  
H,0,2.6824479723,-3.0444469283,-2.943545136  
H,0,3.1747484367,-3.2941327178,-1.2590490757  
H,0,3.7796124459,-1.8932472365,-2.1573077033  
H,0,3.8516759348,1.9043080826,-1.50231235

H,0,2.1468008212,1.4574407589,-1.7548551113  
H,0,3.4300393373,0.4294063229,-2.3928291356  
H,0,2.1941455985,-1.6798546635,3.3969668825  
H,0,1.6380522606,-0.1795438702,2.6266798268  
H,0,3.3355525788,-0.6579795059,2.5026058036

### *TS1-ax-K*

E(RM11) = -652.711568726

Zero-point correction= 0.434075 (Hartree/Particle)  
Thermal correction to Energy= 0.455289  
Thermal correction to Enthalpy= 0.456233  
Thermal correction to Gibbs Free Energy= 0.385346  
Sum of electronic and ZPE= -652.277494  
Sum of electronic and thermal Energies= -652.256280  
Sum of electronic and thermal Enthalpies= -652.255336  
Sum of electronic and thermal Free Energies= -652.326222

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.698	81.446	149.194

C,0,-1.4475925542,1.5744511447,-1.4130989469  
C,0,-2.4218575498,1.6706999057,-0.1514109003  
H,0,-1.6852509752,0.6729755453,-1.9942643685  
H,0,-1.55057772,2.470865034,-2.041785612  
C,0,-0.165522399,1.4362475046,-0.6580209594  
C,0,-0.0955569,0.2379227875,-0.0031498253  
C,0,0.5119995559,2.680948989,-0.1625969449  
C,0,-0.7314217131,0.3951112355,1.3656157902  
H,0,-0.5875144213,-0.5821325698,-0.546209547  
C,0,-2.2510188365,0.5622474621,0.9225633222  
H,0,-0.6020951896,-0.4457287033,2.0596578743  
H,0,-0.4116875396,1.3131454762,1.8776351991  
C,0,-2.8559289106,-0.7812949719,0.5238503712  
H,0,-2.8063070807,0.8926792697,1.8192488129  
H,0,-2.2378905194,2.64128794,0.3338294362  
H,0,-3.4637392808,1.698133642,-0.4991288384  
B,0,2.0572809985,-0.8025686104,-0.2208089978  
C,0,2.0246617102,-1.0156395321,-1.8209052558  
C,0,3.0412586704,0.2950278919,0.3872348144  
C,0,1.6270377561,-2.0407954242,0.694355394  
H,0,2.7695211044,-1.811843575,-1.9999158268  
H,0,1.0615823538,-1.4595118349,-2.1083326841  
C,0,2.3532101039,0.1968623542,-2.6783014629  
H,0,1.3012890095,-1.7143043876,1.6959174527  
H,0,0.7876313136,-2.600911494,0.2477511502  
C,0,2.8350910998,-2.9885390924,0.8565200186  
C,0,2.9481761284,0.5287825043,1.8997213852  
H,0,2.9395746806,1.2479708059,-0.1578731978  
H,0,4.0629382966,-0.0530081485,0.1333915859  
H,0,1.0673872729,2.5031127116,0.7676288457  
H,0,-0.1878433498,3.5187122839,-0.0267611527  
H,0,1.2464425027,2.9997786791,-0.9212984055  
C,0,-3.5897751369,-0.9743797122,-0.5755205477  
C,0,-2.5920103044,-1.9266631025,1.4746289941  
H,0,-4.0230690098,-1.9535343965,-0.7875875718  
H,0,-3.7915805302,-0.1858985628,-1.3007959199  
H,0,-2.7256349411,-1.6143360427,2.5215933803  
H,0,-1.5569260975,-2.2887922911,1.3731857421  
H,0,-3.2651332392,-2.7683906926,1.2727789859  
H,0,2.3218412381,-0.037850569,-3.7521508013  
H,0,3.3548362926,0.5924719157,-2.4544275322  
H,0,1.6327230948,1.0118472143,-2.497544873  
H,0,3.6234976638,1.3242919902,2.2471993702  
H,0,3.1973167863,-0.3840745234,2.461004945  
H,0,1.9231413388,0.8066594043,2.1928698903

H,0,2.6002417951,-3.8492464857,1.4988862487  
H,0,3.6938289201,-2.4658186405,1.3054640026  
H,0,3.1666657519,-3.3837406887,-0.1150014101

## TS1-ax-L – Not found

### TS1-ax-M

E(RM11) = -652.708888915

Zero-point correction= 0.434383 (Hartree/Particle)  
Thermal correction to Energy= 0.455610  
Thermal correction to Enthalpy= 0.456555  
Thermal correction to Gibbs Free Energy= 0.385813  
Sum of electronic and ZPE= -652.274505  
Sum of electronic and thermal Energies= -652.253279  
Sum of electronic and thermal Enthalpies= -652.252334  
Sum of electronic and thermal Free Energies= -652.323075

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.900	81.352	148.887

C,0,-1.7119810965,1.3139345959,-1.4388192  
C,0,-2.7336722283,1.1910745791,-0.2233342168  
H,0,-1.7217664323,0.3784009747,-2.0168462918  
H,0,-1.9837987903,2.1619001702,-2.0840082899  
C,0,-0.4727011966,1.4617904148,-0.6138185667  
C,0,-0.1689706157,0.2952660162,0.02928472  
C,0,-0.1100123723,2.8129018373,-0.0769430402  
C,0,-0.900010745,0.2369471818,1.360366987  
H,0,-0.4227318408,-0.5899755784,-0.5648920884  
C,0,-2.389794929,0.1064684508,0.8475019846  
H,0,-0.6292579655,-0.5946070377,2.0261395132  
H,0,-0.8085155328,1.1714793902,1.9309425585  
C,0,-2.7661952425,-1.3005222097,0.3846290567  
H,0,-3.0539534588,0.3193415569,1.7050645762  
H,0,-2.7620127977,2.1669327561,0.2853293847  
H,0,-3.7438449849,1.026016037,-0.6210837408  
B,0,2.178275231,-0.0257883384,-0.1491017622  
C,0,2.4276452735,0.2518197721,-1.7059622523  
C,0,2.805007081,1.0509372779,0.8515060306  
C,0,2.0152215059,-1.5364159644,0.3513960848  
H,0,2.2526099531,1.316727684,-1.9368873182  
H,0,3.5180211248,0.1136018493,-1.8462083859  
C,0,1.6878690014,-0.6364299379,-2.7123438765  
H,0,1.575638748,-1.5862539287,1.3620333667  
H,0,1.3581622928,-2.1239331623,-0.3108297005  
C,0,3.4135975021,-2.1892266216,0.3754344437  
C,0,2.5063994138,0.8894851477,2.3457342799  
H,0,2.5737232449,2.0762380168,0.5178567823  
H,0,3.8984912449,0.9613730154,0.6943538963  
H,0,0.3111518421,2.7510104894,0.9360437187  
H,0,-0.951403272,3.5202443265,-0.0939622095  
H,0,0.6793872691,3.2332934542,-0.7237436127  
C,0,-1.9657728273,-2.3648539245,0.4894459709  
C,0,-4.1642754231,-1.4540032586,-0.1732312686  
H,0,-2.3177014971,-3.3527283237,0.1861001899  
H,0,-0.9421556748,-2.3053660864,0.8624898175  
H,0,-4.2357164454,-1.0358989373,-1.1889973042  
H,0,-4.9034096794,-0.9261736822,0.4488232851  
H,0,-4.44977858,-2.5113567129,-0.2282767996  
H,0,1.9605701951,-0.405934381,-3.7524227718  
H,0,0.5968819072,-0.5122673433,-2.6257086533  
H,0,1.908080983,-1.7011089217,-2.5425517818  
H,0,3.0055358963,1.6539198606,2.9589721261  
H,0,2.8368431084,-0.0938546219,2.7128779711

H,0,1.4261701358,0.9570479165,2.5449320074  
H,0,3.3771800201,-3.2325670718,0.7199688583  
H,0,4.0971085958,-1.6426433598,1.0437571492  
H,0,3.8673886981,-2.187385767,-0.6278659077

### TS1-ax-N

E(RM11) = -652.707242610

Zero-point correction= 0.434951 (Hartree/Particle)  
Thermal correction to Energy= 0.455739  
Thermal correction to Enthalpy= 0.456683  
Thermal correction to Gibbs Free Energy= 0.387530  
Sum of electronic and ZPE= -652.272291  
Sum of electronic and thermal Energies= -652.251504  
Sum of electronic and thermal Enthalpies= -652.250560  
Sum of electronic and thermal Free Energies= -652.319713

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.980	80.950	145.545

C,0,-1.5568012807,1.6906440949,-1.4305223257  
C,0,-2.5831312012,1.6228048561,-0.2117999204  
H,0,-1.7084367619,0.8173967505,-2.0808271299  
H,0,-1.7002708627,2.6234242819,-1.9942726598  
C,0,-0.3161290214,1.5821667879,-0.6138301759  
C,0,-0.1496170416,0.326574889,-0.0803290824  
C,0,0.2449719917,2.820593258,0.0099774598  
C,0,-0.9005666348,0.3011493046,1.2541203479  
H,0,-0.5689837916,-0.4477235097,-0.7312332883  
C,0,-2.393013299,0.4245193058,0.7671931157  
H,0,-0.7424150692,-0.6002839816,1.8619596099  
H,0,-0.6656747314,1.1702510165,1.8841795156  
C,0,-2.9771105587,-0.8762504425,0.2163148571  
H,0,-3.0110891211,0.6686540689,1.650620195  
H,0,-2.47397388,2.5532571409,0.3654983837  
H,0,-3.6034952648,1.6321754235,-0.6169875376  
B,0,1.9537799792,-0.395550038,-0.2646071021  
C,0,1.7814272155,-1.1808546913,-1.6591861797  
C,0,2.8979723377,0.9028945042,-0.3156716715  
C,0,1.9757019407,-1.2615811493,1.0879352726  
H,0,1.3296103021,-0.5174355623,-2.417536329  
H,0,2.8114673577,-1.3561554224,-2.0241123597  
C,0,1.047479775,-2.5277639954,-1.6280047795  
H,0,1.0759476892,-1.8979131432,1.1641445282  
H,0,2.8073968488,-1.9842466347,0.9663273408  
C,0,2.1854489081,-0.4682284871,2.3833211407  
C,0,4.3785369364,0.469346043,-0.3150466631  
H,0,2.7334829418,1.5681943202,0.5481486369  
H,0,2.7055996232,1.5046898159,-1.2213459749  
H,0,0.6988605529,2.6146739691,0.9882592392  
H,0,-0.497492103,3.6267647793,0.092954668  
H,0,1.0541795957,3.1885151676,-0.6423318575  
C,0,-2.3571976693,-2.0574568228,0.2795509646  
C,0,-4.369218757,-0.7784504411,-0.3677062574  
H,0,-2.8495581888,-2.9620829003,-0.082314122  
H,0,-1.3475444109,-2.1774626909,0.6751555766  
H,0,-4.3549290304,-0.2970424583,-1.3576437996  
H,0,-5.0313078353,-0.1797769479,0.2766533049  
H,0,-4.8128779178,-1.7738570598,-0.4885022217  
H,0,1.0300543742,-3.0166523412,-2.6132540852  
H,0,0.0008426492,-2.4181156598,-1.303416085  
H,0,1.5291658028,-3.2227570568,-0.9240919641  
H,0,5.0625242049,1.3303190393,-0.3339948947  
H,0,4.6133563779,-0.1553438772,-1.1893644018  
H,0,4.620175406,-0.1242191243,0.5799299852  
H,0,2.0953175893,-1.0921959096,3.2847933321

H,0,1.45507312,0.3521172466,2.4706484582  
H,0,3.1813897624,-0.0015265464,2.4042118456

### *TS1-ax-O*

E(RM11) = -652.709023088

Zero-point correction= 0.434837 (Hartree/Particle)  
Thermal correction to Energy= 0.455432  
Thermal correction to Enthalpy= 0.456376  
Thermal correction to Gibbs Free Energy= 0.387712  
Sum of electronic and ZPE= -652.274186  
Sum of electronic and thermal Energies= -652.253591  
Sum of electronic and thermal Enthalpies= -652.252647  
Sum of electronic and thermal Free Energies= -652.321312

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.788	80.889	144.517

C,0,-1.1866556629,1.9997347974,-1.0677728005  
C,0,-2.295474399,1.8031513225,0.0617684246  
H,0,-1.3798717297,1.3009085062,-1.8937770394  
H,0,-1.1946711533,3.0384764498,-1.4268108848  
C,0,-0.0229256317,1.5883783754,-0.2373416037  
C,0,-0.0078468843,0.2354028538,0.0296734339  
C,0,0.6068959164,2.6087012171,0.659938066  
C,0,-0.8525772494,0.0496351273,1.3003340341  
H,0,-0.4737583809,-0.3384130742,-0.7793796356  
C,0,-2.2900417873,0.4229014761,0.7837761472  
H,0,-0.8184172875,-0.9577085635,1.7357875181  
H,0,-0.5745471006,0.7565064059,2.0937639207  
C,0,-2.9600393414,-0.6765596692,-0.0408652705  
H,0,-2.9372691136,0.5563762226,1.6701863616  
H,0,-2.1362904892,2.5833529287,0.8210470112  
H,0,-3.2786403364,2.0053359646,-0.3820997648  
B,0,1.9677816829,-0.6537163744,-0.1456953055  
C,0,1.7902659666,-1.3443282481,-1.591964597  
C,0,3.0197209469,0.5618265151,-0.1056201139  
H,0,1.9251874209,-1.6203041891,1.1378111309  
H,0,1.4353247576,-0.6100353216,-2.3368044578  
H,0,2.8211780474,-1.5889352443,-1.916472168  
C,0,0.9398504126,-2.6175879032,-1.6686155944  
H,0,0.984691398,-2.1986989604,1.1696571252  
H,0,2.7080273051,-2.3842403336,0.9618366522  
C,0,2.1850999647,-0.9444273596,2.4889439978  
C,0,3.099525563,1.4122764541,-1.3791301064  
H,0,4.0059128979,0.0857040227,0.0616662196  
H,0,2.8785046206,1.2010104043,0.780611323  
H,0,0.9668855422,2.1642100415,1.5967419836  
H,0,-0.065531611,3.4519452061,0.8707942207  
H,0,1.4889211398,3.018605928,0.1411000773  
C,0,-2.4982566303,-1.9268215068,-0.1202938284  
C,0,-4.253691039,-0.2989116789,-0.7273676273  
H,0,-3.0479566096,-2.687807546,-0.6774803145  
H,0,-1.5653007609,-2.2451536221,0.3468359676  
H,0,-4.0713849947,0.3525148284,-1.5960669408  
H,0,-4.9229746135,-0.2476638603,-0.044935677  
H,0,-4.780718218,-1.1914187042,-1.0849158444  
H,0,0.9428500555,-3.0617702484,-2.6751022275  
H,0,-0.11091195,-2.4190048556,-1.4077059607  
H,0,1.3068376355,-3.3834157582,-0.9691092967  
H,0,3.7395395783,2.3005751273,-1.2630675235  
H,0,2.0989875366,1.7587473517,-1.6946898588  
H,0,3.4974773803,0.8271947891,-2.2205749049  
H,0,2.0744588161,-1.6328505922,3.3398693973  
H,0,1.4933143967,-0.1019154049,2.6524508718  
H,0,3.2025339826,-0.5283990673,2.5305301224

### *TS1-ax-P*

E(RM11) = -652.709572637

Zero-point correction= 0.434710 (Hartree/Particle)  
Thermal correction to Energy= 0.455652  
Thermal correction to Enthalpy= 0.456596  
Thermal correction to Gibbs Free Energy= 0.386692  
Sum of electronic and ZPE= -652.274862  
Sum of electronic and thermal Energies= -652.253921  
Sum of electronic and thermal Enthalpies= -652.252976  
Sum of electronic and thermal Free Energies= -652.322880

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.926	81.100	147.125

C,0,1.5131995952,2.084192684,0.4604437812  
C,0,2.6099229528,1.4563548349,-0.5080775254  
H,0,1.6340211118,1.6592251122,1.4674844366  
H,0,1.6156526406,3.1784743729,0.493267413  
C,0,0.3117295328,1.5415956085,-0.2438066797  
C,0,0.2152115468,0.1834857206,-0.0952642877  
C,0,-0.2243629154,2.2765025456,-1.4334659866  
C,0,1.0241391951,-0.4842417616,-1.2015829024  
H,0,0.5877861649,-0.149667082,0.8790318976  
C,0,2.4863540448,-0.0776488105,-0.7697433035  
H,0,0.9155617513,-1.5748334104,-1.2850127707  
H,0,0.8178812437,-0.0507095824,-2.189965575  
C,0,3.0459241893,-0.9095239565,0.3838575366  
H,0,3.15308055,-0.2843305544,-1.6267516783  
H,0,2.5305900494,1.9714730265,-1.4774787399  
H,0,3.6068096212,1.697563991,-0.1156757104  
B,0,-1.9848043821,-0.4967787719,0.3135680446  
C,0,-1.7718676489,-0.6513154341,1.8934774259  
C,0,-2.9085181501,0.7005164863,-0.2042886003  
C,0,-1.9330994872,-1.8418219312,-0.5547330867  
H,0,-2.6678414102,-1.195837397,2.2509245027  
H,0,-0.9301509136,-1.3311800771,2.1113614076  
C,0,-1.6324454558,0.6489918953,2.6917260756  
H,0,-1.0235238172,-2.4213233889,-0.3185737766  
H,0,-2.7616153736,-2.4711930375,-0.1751919387  
C,0,-2.088977012,-1.672784998,-2.0702536483  
C,0,-4.3794367972,0.3271212937,0.0757111039  
H,0,-2.6753181895,1.6495521749,0.3059943222  
H,0,-2.7875634374,0.8835214099,-1.2844167141  
H,0,-0.6446168778,1.587714541,-2.1791214613  
H,0,0.5240457545,2.9326717466,-1.9007432069  
H,0,-1.0528162122,2.9195129947,-1.09357277  
C,0,2.409170377,-1.9434272723,0.9407399533  
C,0,4.4339278474,-0.5295596012,0.8507318873  
H,0,2.8876838412,-2.5301880429,1.7270901513  
H,0,1.3990452097,-2.24167845,0.6549880439  
H,0,4.4136204523,0.3896676078,1.4560347424  
H,0,5.1048127343,-0.3427839579,-0.0017482252  
H,0,4.8710698619,-1.3237186804,1.4676838131  
H,0,-1.4402596318,0.4720325835,3.759812575  
H,0,-2.5453578584,1.2587055525,2.6169673516  
H,0,-0.805597314,1.2653640379,2.3001583228  
H,0,-5.0790364528,1.1000641084,-0.2734712518  
H,0,-4.553341114,0.1856791522,1.1537826741  
H,0,-4.6519139281,-0.6159665727,-0.4235731233  
H,0,-1.9710413821,-2.6191969962,-2.6179024635  
H,0,-1.3467132955,-0.9619639173,-2.4674014863  
H,0,-3.0808835838,-1.2677798367,-2.3210929598

### *TS1-ax-Q*

E(RM11) = -652.708299288

Zero-point correction= 0.434207 (Hartree/Particle)  
Thermal correction to Energy= 0.455348  
Thermal correction to Enthalpy= 0.456292  
Thermal correction to Gibbs Free Energy= 0.385543  
Sum of electronic and ZPE= -652.274092  
Sum of electronic and thermal Energies= -652.252952  
Sum of electronic and thermal Enthalpies= -652.252007  
Sum of electronic and thermal Free Energies= -652.322756

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.735	81.423	148.903

C,0,-1.4270888222,-1.9186285381,1.1727005592  
C,0,-2.4968920209,-1.7591810756,0.0014378197  
H,0,-1.6087450946,-1.1520775281,1.9393449198  
H,0,-1.4948833026,-2.9238577771,1.6133967599  
C,0,-0.2160676424,-1.6246375072,0.3470877855  
C,0,-0.170809445,-0.3052061344,-0.018609286  
C,0,0.3601865814,-2.7389328411,-0.4799903205  
C,0,-0.940711694,-0.1445543708,-1.3231675043  
H,0,-0.5903176451,0.3570024419,0.7484520663  
C,0,-2.4110592298,-0.4383561676,-0.8267524757  
H,0,-0.8720238751,0.8388760072,-1.8069871081  
H,0,-0.6578530426,-0.9008208964,-2.0678443422  
C,0,-3.0655688764,0.7409449492,-0.1069438336  
H,0,-3.0344676989,-0.6140719826,-1.722703738  
H,0,-2.3550926446,-2.6010037508,-0.6926535082  
H,0,-3.5031734546,-1.8807594204,0.4231695245  
B,0,1.9636771992,0.6515093343,-0.0043431546  
C,0,2.4000433117,0.3710338747,1.5071387183  
C,0,2.6547498455,-0.1876109641,-1.1766582673  
C,0,1.4622108768,2.1340097175,-0.3513036192  
H,0,3.2467347321,1.0657251463,1.6837859022  
H,0,1.6177404025,0.7163249252,2.2040103004  
C,0,2.8332865854,-1.0505804262,1.8716856689  
H,0,2.3519079646,2.6520346681,-0.7585981387  
H,0,0.7566289234,2.1189376278,-1.1993000412  
C,0,0.9003723146,2.9696063754,0.8073084697  
C,0,4.1144959395,0.2827745091,-1.3500117223  
H,0,2.1155998943,-0.0691194766,-2.1329678798  
H,0,2.6668464636,-1.2645425563,-0.9454143878  
H,0,0.7367377465,-2.3858451777,-1.4477312097  
H,0,-0.3534617253,-3.5605984948,-0.6344861683  
H,0,1.2220721749,-3.1616032439,0.0621435181  
C,0,-2.5289106711,1.9616525834,-0.0311489092  
C,0,-4.4317937412,0.4754186811,0.4865312094  
H,0,-3.0725872046,2.7765615825,0.4508772201  
H,0,-1.541311352,2.2036524947,-0.4258438292  
H,0,-4.9372884355,1.4150426061,0.7396891918  
H,0,-4.3582290443,-0.1227855252,1.4076636254  
H,0,-5.0700715476,-0.0838551677,-0.2147552574  
H,0,3.1934594555,-1.1268297351,-2.9079409447  
H,0,3.638470432,-1.4117462629,1.2136623343  
H,0,1.9878326973,-1.7492375316,1.7687537215  
H,0,4.6434844688,-0.2888569471,-2.1260769142  
H,0,4.679897835,0.1677611525,-0.4119883884  
H,0,4.1646356681,1.34478667,-1.631681645  
H,0,0.5371330048,3.9537263436,0.4753160955  
H,0,1.668319175,3.1440035427,1.5748630465  
H,0,0.0614435778,2.4612802363,1.3079751875

### *TS1-ax-R*

E(RM11) = -652.707919125

Zero-point correction= 0.434409 (Hartree/Particle)  
Thermal correction to Energy= 0.455457  
Thermal correction to Enthalpy= 0.456402  
Thermal correction to Gibbs Free Energy= 0.386397  
Sum of electronic and ZPE= -652.273511  
Sum of electronic and thermal Energies= -652.252462  
Sum of electronic and thermal Enthalpies= -652.251517  
Sum of electronic and thermal Free Energies= -652.321523

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.804	81.315	147.338

C,0,1.4768252173,1.3740952208,1.7058469644  
C,0,2.6105043171,1.4586832695,0.5881570335  
H,0,1.527772864,0.3947053899,2.2029628282  
H,0,1.604219498,2.1830375528,2.4397259763  
C,0,0.3110491082,1.4802733069,0.7788976084  
C,0,0.1735199111,0.3528034443,0.0159587421  
C,0,-0.1428409256,2.8361840977,0.3329009151  
C,0,1.0244140208,0.5003928763,-1.2376823585  
H,0,0.4769016848,-0.5505663171,0.5573751879  
C,0,2.4701556216,0.4581289816,-0.6029841209  
H,0,0.8943528423,-0.2778686444,-2.0029802374  
H,0,0.8863708668,1.4755762802,-1.7249225659  
C,0,2.9450545843,-0.9482326308,-0.2384637745  
H,0,3.1802056391,0.8159856465,-1.3709816466  
H,0,2.590699586,2.4786351892,0.1746151607  
H,0,3.5908888135,1.3446288419,1.0692494626  
B,0,-2.0798298674,-0.2575932441,-0.0326182812  
C,0,-2.3952703824,-0.2179918785,1.5373336893  
C,0,-2.7575800809,0.8727373046,-0.9358453319  
C,0,-1.780983429,-1.6789415645,-0.7164427297  
H,0,-1.6592492825,-0.8085239749,2.1096130637  
H,0,-2.3464389905,0.8125607091,1.929103229  
C,0,-3.8067513643,-0.7834481146,1.7976173506  
H,0,-2.7398256561,-1.9895632063,-1.1776851226  
H,0,-1.1011125187,-1.5559156979,-1.5782179001  
C,0,-1.2830614278,-2.8058026241,0.1992095805  
C,0,-2.3372823678,0.9424233536,-2.4080715205  
H,0,-2.6716438959,1.8633860303,-0.4588948855  
H,0,-3.840468742,0.6412794115,-0.8890269449  
H,0,-0.4973854237,2.8288486128,-0.7067024318  
H,0,0.6268452855,3.6097896188,0.4660861114  
H,0,-1.0030189886,3.1252355767,0.9611255177  
C,0,2.2811174602,-2.0650528152,-0.5482794688  
C,0,4.2817902438,-1.0288179318,0.46547688  
H,0,2.6996940901,-3.0436882552,-0.3054699697  
H,0,1.3052983458,-2.0614835911,-1.0362779061  
H,0,4.1973602639,-0.7176754336,1.5180175395  
H,0,5.0240113338,-0.3695974189,-0.0104099684  
H,0,4.6706352698,-2.0540748479,0.4514128078  
H,0,-4.0387134798,-0.8409016708,2.8708830282  
H,0,-3.9188164613,-1.7968472883,1.3818499289  
H,0,-4.5778326971,-0.1549433148,1.3279568115  
H,0,-2.8861473697,1.7144940806,-2.96701556  
H,0,-2.5109901452,-0.0176611474,-2.9160800256  
H,0,-1.2634184074,1.1633783099,-2.5044369362  
H,0,-1.0908083959,-3.7374119741,-0.3536389552  
H,0,-2.0186260642,-3.0345479565,0.9841163598  
H,0,-0.3487168442,-2.5325920131,0.7132339349

### *TS1-ax-S*

E(RM11) = -652.709870412

Zero-point correction= 0.434595 (Hartree/Particle)  
Thermal correction to Energy= 0.455347

Thermal correction to Enthalpy= 0.456291  
Thermal correction to Gibbs Free Energy= 0.387402  
Sum of electronic and ZPE= -652.275275  
Sum of electronic and thermal Energies= -652.254524  
Sum of electronic and thermal Enthalpies= -652.253580  
Sum of electronic and thermal Free Energies= -652.322468

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.734 81.174 144.988

C,0,-1.1244810783,-2.0154785577,1.0718818657  
C,0,-2.2383025969,-1.8758164631,-0.0600189226  
H,0,-1.3361824743,-1.3044180457,1.8832505767  
H,0,-1.1031850316,-3.0444499543,1.4588780101  
C,0,0.0330805965,-1.5886863774,0.23323831  
C,0,-0.0196814549,-0.2512344827,-0.0678839494  
C,0,0.6921560918,-2.605713041,-0.6508194136  
C,0,-0.8440404516,-0.0982917986,-1.344355217  
H,0,-0.4836004847,0.3369151713,0.7331967992  
C,0,-2.2734761708,-0.5131322415,-0.820570472  
H,0,-0.8507527634,0.9045300826,-1.7929318985  
H,0,-0.5402392142,-0.8093943442,-2.1248289399  
C,0,-2.9831078772,0.5830594689,-0.0256207702  
H,0,-2.9122078323,-0.6899926472,-1.7054312821  
H,0,-2.0573714272,-2.6693584073,-0.8004947877  
H,0,-3.2187416171,-2.0925346912,0.3835248987  
B,0,2.0075514843,0.7408048807,0.178460116  
C,0,2.2659981817,0.4410598748,1.7317689767  
C,0,2.9318346742,-0.0078213348,-0.8916762474  
C,0,1.4937599533,2.2189583853,-0.1933797264  
H,0,3.0396228754,1.1750257096,2.0341518488  
H,0,1.3822627015,0.7139224269,2.3341715783  
C,0,2.7412972241,-0.9627307288,-2.1135383477  
H,0,2.3978862162,2.7700206541,-0.5192608825  
H,0,0.856307208,2.2014643384,-1.0946002699  
C,0,0.8146271825,3.0125662161,0.9315616189  
C,0,2.6280897535,0.2675427319,-2.3690177474  
H,0,2.9650072706,-1.0931535212,-0.702890255  
H,0,3.9609939085,0.3374832395,-0.6665586651  
H,0,1.0673846086,-2.1591649493,-1.5806304786  
H,0,0.0338968787,-3.4563542571,-0.8785027015  
H,0,1.5660341452,-3.0116125122,-0.114375106  
C,0,-2.5428070745,1.8407138773,0.063169931  
C,0,-4.2901251535,0.1881962155,0.6256350157  
H,0,-3.1221809561,2.5944168059,0.599983714  
H,0,-1.6004445345,2.1731871076,-0.374028251  
H,0,-4.8487204832,1.0745795035,0.9492220553  
H,0,-4.1212640585,-0.4426267075,1.511862588  
H,0,-4.9239353273,-0.386629673,-0.0672370362  
H,0,2.9480405459,-1.0586342374,3.1895324541  
H,0,3.658675521,-1.2398281632,1.5733452879  
H,0,1.9751110838,-1.7155459338,1.8638254155  
H,0,3.3028025856,-0.2740188354,-3.0483544228  
H,0,2.7178625344,1.3391626284,-2.600086529  
H,0,1.5964824999,-0.0228228452,-2.6237491171  
H,0,0.4400810727,3.9888758564,0.5887687601  
H,0,1.5156063012,3.2005307001,1.7579034047  
H,0,-0.0387906068,2.4652303155,1.3614645383

### *TS1-ax-T*

E(RM11) = -652.707760095

Zero-point correction= 0.434984 (Hartree/Particle)  
Thermal correction to Energy= 0.455767  
Thermal correction to Enthalpy= 0.456712  
Thermal correction to Gibbs Free Energy= 0.387355

Sum of electronic and ZPE= -652.272776  
Sum of electronic and thermal Energies= -652.251993  
Sum of electronic and thermal Enthalpies= -652.251048  
Sum of electronic and thermal Free Energies= -652.320405

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.998 81.033 145.974

C,0,1.1595401713,2.1828900336,0.9237218589  
C,0,2.4874421791,1.7618340165,0.1506067985  
H,0,1.1161022987,1.6512986589,1.8846222238  
H,0,1.1435095919,3.2703291816,1.086193855  
C,0,0.1900272761,1.6372686183,-0.0712220923  
C,0,0.183559426,0.2664659666,-0.0795497303  
C,0,-0.1421055219,2.4675940074,-1.2741680109  
C,0,1.2617776585,-0.1961414024,-1.0574489792  
H,0,0.3729955024,-0.1555602689,0.9126022777  
C,0,2.5658082988,0.2700349802,-0.3024953475  
H,0,1.2936231947,-1.2716490502,-1.2722295108  
H,0,1.1970548625,0.3326836665,-2.0185511339  
C,0,2.9824510105,-0.6543560903,0.8410408227  
H,0,3.3990778267,0.2263109385,-1.0274043898  
H,0,2.5653121615,2.394244465,-0.7461784266  
H,0,3.3529666192,2.014989159,0.7771665819  
B,0,-1.992897524,-0.4912780578,-0.3616107516  
C,0,-2.0511609743,-1.1696119648,1.0883645953  
C,0,-2.9005906176,0.8078029958,-0.5902321122  
C,0,-1.760896536,-1.4264939642,-1.6483706511  
H,0,-1.2780370493,-1.9462312089,1.2137440342  
H,0,-1.8859288122,-0.4302519578,1.8899989767  
C,0,-3.4449128088,-1.8067660702,1.2714347696  
H,0,-2.752798726,-1.5611350775,-2.1202188635  
H,0,-1.1709486736,-0.884066632,-2.4082994806  
C,0,-1.1487176399,-2.8078027478,-1.3835530181  
C,0,-3.0491514398,1.7702680203,0.5931625877  
H,0,-3.9000384432,0.3972248383,-0.8342232385  
H,0,-2.6088036817,1.3501197126,-1.5045324566  
H,0,-0.3767408016,1.8438786354,-2.1466427345  
H,0,0.6524831101,3.1845143701,-1.5263117519  
H,0,-1.0453768529,3.0571202847,-1.0437319825  
C,0,2.3536146569,-1.7887748398,1.1603418802  
C,0,4.2274338795,-0.2396183597,1.5948889272  
H,0,2.7381025445,-2.4287634776,1.9567283885  
H,0,1.4412250962,-2.1247085331,0.6648109931  
H,0,4.017801065,0.5886322494,2.28883459  
H,0,5.0150349327,0.103528331,0.9066637305  
H,0,4.6233615706,-1.0743883727,2.1856164372  
H,0,-3.5368358067,-2.3369948435,2.2302551518  
H,0,-3.6622380776,-2.5311734106,0.4707069413  
H,0,-4.2371311397,-1.043142754,1.2374420856  
H,0,-3.6414198901,2.6632218555,0.3431459189  
H,0,-2.0658699567,2.1114243334,0.9595244109  
H,0,-3.5419035718,1.2770922141,1.4441209068  
H,0,-0.9678321025,-3.3749876965,-2.3083817767  
H,0,-1.808382955,-3.415497953,-0.746503867  
H,0,-0.1899413305,-2.7305141112,-0.8491973069

### *TS1-ax-U*

E(RM11) = -652.709044447

Zero-point correction= 0.434872 (Hartree/Particle)  
Thermal correction to Energy= 0.455646  
Thermal correction to Enthalpy= 0.456590  
Thermal correction to Gibbs Free Energy= 0.387531  
Sum of electronic and ZPE= -652.274172  
Sum of electronic and thermal Energies= -652.253399

Sum of electronic and thermal Enthalpies= -652.252455  
Sum of electronic and thermal Free Energies= -652.321513

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.922 80.988 145.346

C,0,-1.5090206649,1.7616476429,-1.2110334133  
C,0,-2.6780261112,1.4127853116,-0.1861010865  
H,0,-1.5126913444,1.0277899709,-2.029551691  
H,0,-1.6426371054,2.7785173459,-1.6072235605  
C,0,-0.3700932918,1.5519460495,-0.2687518199  
C,0,-0.2098512383,0.2261611163,0.0458285243  
C,0,0.0245485478,2.6682366919,0.6483468608  
C,0,-1.1088133,-0.0826740249,1.2417748109  
H,0,-0.4885571552,-0.4246551541,-0.7883098442  
C,0,-2.5309208323,0.0603363879,0.5792483194  
H,0,-0.9728735166,-1.0718505187,1.7004108352  
H,0,-1.0165136232,0.6688138476,2.0380623281  
C,0,-2.9406506175,-1.1406819893,-0.2729229066  
H,0,-3.2742623565,0.1040927874,1.3962504008  
H,0,-2.7141962311,2.2199220705,0.5613170049  
H,0,-3.6363111023,1.4492501847,-0.7208818561  
B,0,1.9822441111,-0.4504816266,0.0715533391  
C,0,1.8819648212,-1.285517472,-1.2949285015  
C,0,2.8266611444,0.9099075636,0.0446459246  
C,0,1.9471263137,-1.2877022199,1.435459918  
H,0,1.146119249,-2.1045947635,-1.2152449854  
H,0,1.5507227756,-0.6469953065,-2.1319240772  
C,0,3.2604387956,-1.8853876087,-1.639715716  
H,0,1.0885947668,-1.9817520341,1.4416562291  
H,0,2.8332444426,-1.9507683362,1.3937247026  
C,0,1.9981934988,-0.4788957428,2.7361563375  
C,0,2.8196819287,1.6838107554,-1.2776711658  
H,0,3.8677190873,0.6117487096,0.2815417157  
H,0,2.5419043402,1.5703610441,0.8801732811  
H,0,0.3851416068,2.2930625673,1.6156127186  
H,0,-0.7848150946,3.39633009,0.8016635222  
H,0,0.8644374913,2.108010373,0.1825008511  
C,0,-2.2222841604,-2.2618905728,-0.3792635838  
C,0,-4.2756345931,-1.0221513328,-0.9744102903  
H,0,-2.5960710394,-3.1056210122,-0.9622865247  
H,0,-1.2438631783,-2.3866501787,0.0879594103  
H,0,-4.21012598,-0.3522779851,-1.8455140758  
H,0,-5.0443286832,-0.6092324648,-0.3032467593  
H,0,-4.6182938392,-2.0002280394,-1.3327054938  
H,0,3.24210323,-2.4462886536,-2.5853267715  
H,0,3.601965399,-2.5763713513,-0.8547026199  
H,0,4.0263588434,-1.1004695761,-1.7360514898  
H,0,3.3480400231,2.6467935596,-1.2104887217  
H,0,1.7874815981,1.8887906872,-1.6107137702  
H,0,3.2935783019,1.1033100294,-2.0826732319  
H,0,1.9290240791,-1.1114578987,3.6331837763  
H,0,1.174155511,0.2509896383,2.7814323161  
H,0,2.9345995827,0.093743434,2.8065946903

*TS1-ax-V*

E(RM11) = -652.709727170

Zero-point correction= 0.434409 (Hartree/Particle)  
Thermal correction to Energy= 0.455537  
Thermal correction to Enthalpy= 0.456481  
Thermal correction to Gibbs Free Energy= 0.386082  
Sum of electronic and ZPE= -652.275318  
Sum of electronic and thermal Energies= -652.254190  
Sum of electronic and thermal Enthalpies= -652.253246  
Sum of electronic and thermal Free Energies= -652.323645

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.854 81.316 148.167

C,0,1.6824826652,1.8860195696,0.8266942931  
C,0,2.7382556198,1.3047144422,-0.2151202084  
H,0,1.7314659007,1.3050729343,1.7589877776  
H,0,1.8905307676,2.9470111228,1.0282746869  
C,0,0.4539459094,1.579923944,0.0312845745  
C,0,0.2276422754,0.2326581343,-0.029187148  
C,0,0.0413677824,2.5365417232,-1.0489149157  
C,0,0.9838524301,-0.344441147,-1.216644534  
H,0,0.5289492199,-0.2881925191,0.8873965764  
C,0,2.4719857848,-0.1500387604,-0.7196364157  
H,0,0.7774509459,-1.3961235597,-1.4586106402  
H,0,0.8405278688,0.2477155831,-2.1312495313  
C,0,2.9323206152,-1.2034627293,0.2872331998  
H,0,3.131675807,-0.2808277539,-1.5968826885  
H,0,2.737527664,1.9698318124,-1.0918081736  
H,0,3.7437572778,1.3782611255,0.2198107063  
B,0,-2.0637836842,-0.2602883685,0.3237005051  
C,0,-2.1841010835,0.2932849908,1.8180383149  
C,0,-2.7957711294,0.5340814123,-0.8506426808  
C,0,-1.8349569624,-1.8350148403,0.1528359506  
H,0,-3.0802087685,-0.206006269,2.2364308444  
H,0,-1.3482049888,-0.0838854948,2.4323126412  
C,0,-2.3338791761,1.8065332765,1.9983169956  
H,0,-1.3729349832,-2.0795238827,-0.8182992458  
H,0,-1.1693526598,-2.2323462456,0.9380740171  
C,0,-3.1986039844,-2.5536150445,0.2423616551  
C,0,-2.5644712688,0.0097312591,-2.2728748183  
H,0,-2.5664100147,1.6107109643,-0.7940633236  
H,0,-3.8770131164,0.4761462726,-0.6119214574  
H,0,-0.4352032596,2.0216996512,-1.8934726341  
H,0,0.875824021,3.1554624213,-1.4092784268  
H,0,-0.7093578166,3.2269672781,-0.6289113608  
C,0,2.2025355402,-2.2598700216,0.6556807357  
C,0,4.333965078,-1.0237124687,0.8285138214  
H,0,2.6146937176,-3.0040336698,1.3399196567  
H,0,1.1810878679,-2.4267614744,0.3109299189  
H,0,4.3731607627,-0.216503438,1.575912336  
H,0,5.0412007231,-0.7600777529,0.0272214237  
H,0,4.6865812383,-1.9420845065,1.3130686188  
H,0,-2.4364702783,2.0969437768,3.0540122473  
H,0,-3.2152925107,2.1884392932,1.4623097633  
H,0,-1.4533585013,2.3355281491,-1.5968288203  
H,0,-3.0684846212,0.6202444135,-3.0364141942  
H,0,-2.9292676934,-1.022353414,-2.3818703386  
H,0,-1.4902112825,-0.0117097263,-2.5160246365  
H,0,-3.1004851701,-3.6410804288,0.1142068383  
H,0,-3.8921626048,-2.190308863,-0.5315238404  
H,0,-3.6789768037,-2.3793615315,1.2165964558

**Axial Intermediate Structures**

*Int-ax-A*

E(RM11) = -652.718934077

Zero-point correction= 0.434680 (Hartree/Particle)  
Thermal correction to Energy= 0.455901  
Thermal correction to Enthalpy= 0.456845  
Thermal correction to Gibbs Free Energy= 0.386558  
Sum of electronic and ZPE= -652.284254  
Sum of electronic and thermal Energies= -652.263034  
Sum of electronic and thermal Enthalpies= -652.262089



Sum of electronic and thermal Free Energies= -652.332376

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 286.082 82.570 147.932

C,0,-1.4757217821,2.3527177818,-0.5022804836  
C,0,-2.6007745285,1.794445547,0.4640105422  
H,0,-1.649778499,2.0080812166,-1.5277991676  
H,0,-1.4687691397,3.4495581106,-0.4520377936  
C,0,-0.284138105,1.7108291311,0.0802820041  
C,0,-0.0988152939,0.3284885733,-0.1579631422  
C,0,0.4735800494,2.4497294715,1.1189586205  
C,0,-1.0776523819,-0.1643820049,1.0085556057  
H,0,-0.6098931312,0.0503397956,-1.0953168075  
C,0,-2.5346746598,0.276572378,0.7054599952  
H,0,-0.9684005798,-1.2545256254,1.0487072427  
H,0,-0.7505887207,0.2199160271,1.9855902495  
C,0,-3.1715912704,-0.5871783314,-0.3744884755  
H,0,-3.1155340053,0.0805914947,1.624420462  
H,0,-2.4834459302,2.30273041788,1.4309903529  
H,0,-3.5771951876,2.0917577709,0.0579911735  
B,0,1.4846474788,-0.398308187,-0.0560260566  
C,0,1.4126196348,-1.63693206,-1.1370502912  
C,0,2.5945190162,0.7122449987,-0.5586658347  
C,0,1.811015973,-0.9272058192,1.4681867611  
H,0,1.3320011358,-1.2393948931,-2.1662208088  
H,0,2.3851919796,-2.1605278445,-1.1120909827  
C,0,0.2916396112,-2.66753403,-0.9376172423  
H,0,1.6929995589,-0.1233638806,2.2223795856  
H,0,1.1019300098,-1.7154307698,1.784260214  
C,0,3.2349176796,-1.4878936962,1.6141309476  
C,0,2.2260262046,1.5249922214,-1.8070944129  
H,0,3.5154829456,0.1470221143,-0.7896688556  
H,0,2.8967395591,1.4029674067,0.25307168  
H,0,1.0222719235,1.7781968793,1.7864561894  
H,0,-0.1621632054,3.1557326009,1.6712375308  
H,0,1.2223421538,3.0455107609,0.5672916917  
C,0,-3.5487335161,-0.1310433912,-1.5713762085  
C,0,-3.4104152373,-2.0260330847,0.0208489661  
H,0,-4.0140687033,-0.7966972502,-2.3000542272  
H,0,-3.4274242766,0.9098018453,-1.8733298845  
H,0,-4.0726639518,-2.0732946015,0.8991091635  
H,0,-2.4774561177,-2.5410070503,0.2896665602  
H,0,-3.8796811926,-2.5873543841,-0.7957081709  
H,0,0.3739239537,-3.5258274248,-1.6220874704  
H,0,-0.6999327569,-2.2179989894,-1.1185522586  
H,0,0.2923365753,-3.0715172392,0.0890624972  
H,0,3.0362002834,2.1865078655,-2.1506138526  
H,0,1.3450645944,2.1778101015,-1.6461385841  
H,0,1.9623619213,0.8634136495,-2.6460694798  
H,0,3.4378813629,-1.8707437226,2.6262832988  
H,0,3.9890951739,-0.716413997,1.3971344078  
H,0,3.4084136539,-2.3158987642,0.9102738793

### Int-ax-B

E(RM11) = -652.718775369

Zero-point correction= 0.434593 (Hartree/Particle)  
Thermal correction to Energy= 0.455889  
Thermal correction to Enthalpy= 0.456833  
Thermal correction to Gibbs Free Energy= 0.385747  
Sum of electronic and ZPE= -652.284182  
Sum of electronic and thermal Energies= -652.262886  
Sum of electronic and thermal Enthalpies= -652.261942  
Sum of electronic and thermal Free Energies= -652.333029

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 286.075 82.465 149.614

C,0,-1.8147439889,1.4588875179,-1.3437645066  
C,0,-2.6478103704,1.730372652,-0.0224148558  
H,0,-2.1669976387,0.528361798,-1.8057219063  
H,0,-1.9191436862,2.3114847575,-2.0267646527  
C,0,-0.468487309,1.3072836606,-0.7650021266  
C,0,-0.1668892218,0.1085334438,-0.0671281893  
C,0,0.4126774077,2.4929476159,-0.6783958187  
C,0,-0.8881655097,0.5359732761,1.2975823355  
H,0,-0.8035321249,-0.7038767857,-0.4584681644  
C,0,-2.4084724474,0.6495577702,1.0395832646  
H,0,-0.6247403886,-0.2326195515,2.0352150088  
H,0,-0.5093887758,1.4919940182,1.6838775969  
C,0,-3.0489071742,-0.6997015855,0.7275722466  
H,0,-2.869371585,1.0006304915,1.9807056874  
H,0,-2.3399468275,2.706000443,0.3851418502  
H,0,-3.7058206785,1.8212684778,-0.299529981  
B,0,1.4482096901,-0.5016750686,0.05557923451  
C,0,1.9421003165,-0.6955164568,-1.5076989366  
C,0,2.5486412365,0.4355053193,0.8364798851  
C,0,1.2439617001,-1.9496470978,0.8182761416  
H,0,2.2707721223,0.2751661936,-1.931073348  
H,0,2.8627279953,-1.3060318876,-1.4887741303  
C,0,0.947905627,-1.3418109355,-2.4833524166  
H,0,0.7122700598,-1.8336003193,1.7838268064  
H,0,0.5915686129,-2.6062632465,0.2095620469  
C,0,2.5552959532,-2.6953400659,1.1087675026  
C,0,2.2960571723,0.7795079314,2.3125374026  
H,0,2.7885892238,1.3603538403,0.2797387039  
H,0,3.4880390724,-0.1444796343,0.7801913829  
H,0,0.9849376395,2.5025514862,0.2566541409  
H,0,-0.1136579047,3.4392490397,-0.8546478232  
H,0,1.1589646085,2.3481022602,-1.4819379861  
C,0,-3.9471803924,-0.8860274165,-0.242811824  
C,0,-2.6253815154,-1.839612444,1.6222676373  
H,0,-4.4017145457,-1.8660009437,-0.3963279799  
H,0,-4.2721986413,-0.0904090713,-0.9146191175  
H,0,-2.6526996576,-1.5420878021,2.6819073062  
H,0,-1.5935837125,-2.1515659327,1.3978845267  
H,0,-3.2801435194,-2.708475067,1.4880224177  
H,0,1.3968663475,-1.5791240015,-3.4598269612  
H,0,0.087229203,-0.679722599,-2.689765681  
H,0,0.5362795945,-2.2784493843,-2.0744931568  
H,0,3.1941567749,1.1609019026,2.8224515328  
H,0,1.9524154892,-0.1056186833,2.872807395  
H,0,1.5188189747,1.5527197825,2.4341325834  
H,0,2.3878575613,-3.7067889687,1.5099688653  
H,0,3.1653168479,-2.1487305916,1.8442377725  
H,0,3.1659070047,-2.7988608675,0.1984290246

### Int-ax-C

E(RM11) = -652.713478164

Zero-point correction= 0.435591 (Hartree/Particle)  
Thermal correction to Energy= 0.456629  
Thermal correction to Enthalpy= 0.457573  
Thermal correction to Gibbs Free Energy= 0.387594  
Sum of electronic and ZPE= -652.277887  
Sum of electronic and thermal Energies= -652.256849  
Sum of electronic and thermal Enthalpies= -652.255905  
Sum of electronic and thermal Free Energies= -652.325884

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K

Total 286.539 82.198 147.284

C,0,-1.627698281,2.0486686377,-0.8993730715  
C,0,-2.6660320799,1.8049064814,0.2601524867  
H,0,-1.8649561848,1.3962100838,-1.7485850628  
H,0,-1.6537592167,3.1049066948,-1.1985046181  
C,0,-0.3494337126,1.6518796718,-0.2589143393  
C,0,-0.0788995478,0.2740065339,-0.0941050152  
C,0,0.428607619,2.7253236238,0.4137422869  
C,0,-0.9948924017,0.2448768155,1.2642996243  
H,0,-0.7040657264,-0.2900455676,-0.8017578237  
C,0,-2.4798641407,0.4206857561,0.889314976  
H,0,-0.7704052372,-0.7346712101,1.7016098599  
H,0,-0.6960820985,0.9994364966,2.0049073041  
C,0,-2.9939476858,-0.7477346735,0.0546348271  
H,0,-3.0494523714,0.399361985,1.8362315981  
H,0,-2.501840783,2.5708351189,1.0340817793  
H,0,-3.6803556031,1.9585234683,-0.1296992579  
B,0,1.4885145402,-0.5009143121,-0.0283612544  
C,0,1.5320894101,-1.2893180885,-1.4793031911  
C,0,2.718481027,0.589318586,0.061809568  
C,0,1.538286645,-1.567916393,1.2184085679  
H,0,1.4224918522,-0.5715870781,-2.3164353895  
H,0,2.5453638292,-1.7120010885,-1.5926738413  
C,0,0.5336790044,-2.4425863709,-1.6699487525  
H,0,0.6095941621,-2.1686852639,1.2859473895  
H,0,2.3146522134,-2.320025978,0.984472925  
C,0,1.8553658854,-0.959069536,2.5940115488  
C,0,4.1077357734,-0.0617397657,-0.0566986093  
H,0,2.7062684773,1.1513342841,1.0136256394  
H,0,2.6325556004,1.3509308366,-0.7385081075  
H,0,1.0461628023,2.3379018132,1.2293880988  
H,0,-0.2181263952,3.5491717709,0.7469673818  
H,0,1.1157164725,3.1306271739,-0.3485183798  
C,0,-3.712878905,-0.603035372,-1.0611031713  
C,0,-2.653282491,-2.118089857,0.589803616  
H,0,-4.0796515718,-1.4774563956,-1.6009521749  
H,0,-3.9706138139,0.3704076337,-1.4808664188  
H,0,-2.8592313464,-2.1837859506,1.6693564531  
H,0,-1.584684212,-2.3426741838,0.4452958357  
H,0,-3.2310778119,-2.8953553069,0.0762710042  
H,0,0.6777907361,-2.9724444458,-2.6242702026  
H,0,-0.5165487837,-2.1024811734,-1.6609049136  
H,0,0.6375249315,-3.1875808424,-0.8653242651  
H,0,4.9249440443,0.655504356,0.1172106047  
H,0,4.2641072362,-0.4972785427,-1.0534985437  
H,0,4.225709317,-0.878943879,0.672485562  
H,0,1.7487094565,-1.6758724113,3.4232034944  
H,0,1.2077620433,-0.0945726729,2.8220903311  
H,0,2.8873172231,-0.5785963327,2.6218199614

### Int-ax-D

E(RM11) = -652.717262783

Zero-point correction= 0.435365 (Hartree/Particle)  
Thermal correction to Energy= 0.456282  
Thermal correction to Enthalpy= 0.457227  
Thermal correction to Gibbs Free Energy= 0.388789  
Sum of electronic and ZPE= -652.281898  
Sum of electronic and thermal Energies= -652.260980  
Sum of electronic and thermal Enthalpies= -652.260036  
Sum of electronic and thermal Free Energies= -652.328474

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.321	82.352	144.040

C,0,-1.3847143795,2.232365406,-0.5768033646  
C,0,-2.5155483977,1.7171555982,0.4081553617  
H,0,-1.555888035,1.8442604175,-1.5872312929  
H,0,-1.3771573909,3.3302770248,-0.5740676956  
C,0,-0.1973303707,1.6131168148,0.0394537105  
C,0,-0.0292676579,0.2189014976,-0.1344883604  
C,0,0.5652490514,2.3966654351,1.0374478512  
C,0,-1.0072497977,-0.2273554144,1.0437034214  
H,0,-0.549444736,-0.086742294,-1.0574122246  
C,0,-2.4602717395,0.2094816195,0.7109425929  
H,0,-0.9037622616,-1.31576035,1.1316773622  
H,0,-0.6912290836,0.1995587389,2.0063608519  
C,0,-3.0941582554,-0.6922849057,-0.3392789464  
H,0,-3.0496620835,0.0540472895,1.6323084439  
H,0,-2.3989115474,2.268320834,1.3539674057  
H,0,-3.4891474121,2.0027076438,-0.0125693767  
B,0,1.5471151285,-0.5470448342,-0.0510768475  
C,0,1.4254873889,-1.7284804831,-1.1949367704  
C,0,2.6922957939,0.5482564646,-0.4942673278  
C,0,1.8951606963,-1.235006781,1.4025273661  
H,0,1.3296216579,-1.285917019,-2.2037388623  
H,0,2.3896284196,-2.2696724791,-1.2043054736  
C,0,0.2895963515,-2.7470768894,-1.0173779106  
H,0,1.140975185,-1.9921065234,1.6869796316  
H,0,2.8085231172,-1.828044389,1.2096789276  
C,0,2.1773374969,-0.3569282504,2.633129076  
C,0,2.4160141247,1.335506012,-1.7825573813  
H,0,3.6257712787,-0.0262045187,-0.6394302731  
H,0,2.9379573121,1.2615305549,0.314008275  
H,0,1.09296498,1.7566078366,1.7515103425  
H,0,-0.0564645956,3.1533306222,1.535791281  
H,0,1.336048477,2.934427576,0.4561081931  
C,0,-3.4691331157,-0.2786905346,-1.5521385997  
C,0,-3.3322554504,-2.1171216449,0.1043517345  
H,0,-3.932006246,-0.9699489258,-2.2581499678  
H,0,-3.3472039894,0.7509489135,-1.8901698931  
H,0,-3.9915203387,-2.1358545997,0.9858769241  
H,0,-2.3982022014,-2.6233063028,0.3854554263  
H,0,-3.8038666155,-2.7042033823,-0.6924976195  
H,0,0.3361748444,-3.5674447679,-1.7501163884  
H,0,-0.6973989263,-2.2708581597,-1.1454715474  
H,0,0.3092017895,-3.2070401935,-0.0156078467  
H,0,3.2092379817,2.0586510818,-2.0284816622  
H,0,1.4728756435,1.914797823,-1.7268824781  
H,0,2.3053248185,0.6633655236,-2.6456158966  
H,0,2.609949073,-0.9325157106,3.4658409342  
H,0,1.2625003583,0.1124189627,3.0333658478  
H,0,2.8890213789,0.4513758724,2.4002519558

### Int-ax-E

E(RM11) = -652.717355069

Zero-point correction= 0.435390 (Hartree/Particle)  
Thermal correction to Energy= 0.456170  
Thermal correction to Enthalpy= 0.457115  
Thermal correction to Gibbs Free Energy= 0.388515  
Sum of electronic and ZPE= -652.281965  
Sum of electronic and thermal Energies= -652.261185  
Sum of electronic and thermal Enthalpies= -652.260240  
Sum of electronic and thermal Free Energies= -652.328840

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.251	82.080	144.379

C,0,-0.9891727686,1.4137673929,-1.3742166308  
C,0,-1.8847843344,1.4816668058,-0.0684337786

H,0,-1.3054595076,0.5665198038,-1.993730117  
H,0,-1.0667906176,2.3626223148,-1.9207323575  
C,0,0.3227293031,1.1826417633,-0.7418042865  
C,0,0.6027346834,-0.117327068,-0.2463305092  
C,0,1.1065890738,2.3841220441,-0.3568390383  
C,0,-0.1906472939,0.0431123384,1.131681885  
H,0,0.0002340162,-0.8524209228,-0.8099837171  
C,0,-1.6969995176,0.2521852491,0.8288452468  
H,0,-0.0101730989,-0.8806395865,1.6919388196  
H,0,0.2028450395,0.8736223383,1.7369563623  
C,0,-2.3582509427,-1.0180473035,0.3008325934  
H,0,-2.1876676543,0.4692681512,1.79506841  
H,0,-1.602417265,2.3832644647,0.4966358994  
H,0,-2.9302389571,1.6147014017,-0.3748457997  
B,0,2.2183461035,-0.7767425395,-0.1478406654  
C,0,2.4739181413,-1.2190872446,-1.7133820717  
C,0,3.3669139821,0.2644268095,0.3943186472  
C,0,2.1204532445,-2.1165271673,0.8053311818  
H,0,3.4467783704,-1.7402464066,-1.7598096683  
H,0,1.7297713492,-1.9769986235,-2.0239265539  
C,0,2.4833335365,-0.0758086402,-2.7316749418  
H,0,1.1470735873,-2.6239962488,0.6505947463  
H,0,2.8586028351,-2.8492053719,0.4309780237  
C,0,2.3693785013,-1.9353282795,2.3137546657  
C,0,4.7688081786,-0.3698878928,0.3308330123  
H,0,3.1607902581,0.5756419945,1.4379489208  
H,0,3.4212436973,1.199093331,-0.1893853276  
H,0,1.6696909004,2.2344287905,0.5698738385  
H,0,0.4845292146,3.2879025591,-0.3164207143  
H,0,1.8516123981,2.5222865259,-1.1600830068  
C,0,-3.1775775834,-1.0473261707,-0.7534587136  
C,0,-2.0651654584,-2.2770822095,1.0819043672  
H,0,-3.6545781164,-1.9802932249,-1.0577796577  
H,0,-3.41516512,-0.1657373555,-1.3502266903  
H,0,-2.1333530623,-2.0978577106,2.1657528389  
H,0,-1.0469900559,-2.6399109899,0.8763330061  
H,0,-2.7678195647,-3.0755373474,0.8163917409  
H,0,2.669646002,-0.4082694838,-3.7643186525  
H,0,3.2539843929,0.6725503931,-2.4827906941  
H,0,1.5102558458,0.4547799789,-2.7564571645  
H,0,5.5342146224,0.2373192355,0.8382613062  
H,0,5.0893247371,-0.4908767555,-0.7153025655  
H,0,4.7841402423,-1.3729479053,0.7835812812  
H,0,2.1879179633,-2.8572973706,2.8882075385  
H,0,1.7446732506,-1.1442397856,2.7586109292  
H,0,3.4099615079,-1.6343965415,2.5050184416

### Int-ax-F

E(RM11) = -652.716819085

Zero-point correction= 0.434749 (Hartree/Particle)  
Thermal correction to Energy= 0.455907  
Thermal correction to Enthalpy= 0.456851  
Thermal correction to Gibbs Free Energy= 0.387368  
Sum of electronic and ZPE= -652.282070  
Sum of electronic and thermal Energies= -652.260912  
Sum of electronic and thermal Enthalpies= -652.259968  
Sum of electronic and thermal Free Energies= -652.329451

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.086	82.610	146.239

C,0,-1.5586211665,2.3203037224,-0.2025634671  
C,0,-2.6585588522,1.6352200729,0.689863768  
H,0,-1.7500034519,2.080444312,-1.2557512778  
H,0,-1.5702695533,3.4058589987,-0.037927887

C,0,-0.3182870527,1.6723887756,0.2820915278  
C,0,-0.0406069541,0.3384628711,-0.1100832504  
C,0,0.4472058046,2.3792300734,1.3358982205  
C,0,-1.0893837018,-0.2842113966,0.9653922766  
H,0,-0.532761517,0.1404933179,-1.0760174731  
C,0,-2.536796972,0.1101936418,0.6165359879  
H,0,-0.9031702091,-1.3617918612,0.8793821788  
H,0,-0.8346454815,0.0042108528,1.9962072665  
C,0,-2.9940353535,-0.5028107084,-0.7051024367  
H,0,-3.1838617011,-0.3228219707,1.4008161719  
H,0,-2.5122030319,1.9560343762,1.7330630433  
H,0,-3.6468019294,1.9988232341,0.3807512719  
B,0,1.4897038941,-0.4199634755,0.0068764532  
C,0,1.3634431318,-1.7637262397,-0.937486757  
C,0,2.5745184278,0.6574737225,-0.6198892358  
C,0,1.9131582094,-0.8369227597,1.5615228965  
H,0,2.3106499165,-2.3254574802,-0.8390982647  
H,0,0.5984129071,-2.4614811124,-0.5398112685  
C,0,1.0971468196,-1.531142162,-2.4330902597  
H,0,3.0105456557,-0.7291402785,1.6332503562  
H,0,1.5312694725,-0.1289174241,2.3221183939  
C,0,1.5700821195,-2.2559381541,2.0515215015  
C,0,3.9343371007,0.0350315025,-0.9703957729  
H,0,2.7570400015,1.4804431093,0.0988705449  
H,0,2.1672665858,1.1446917091,-1.5286214204  
H,0,1.1087382227,1.7111928045,1.893161223  
H,0,-0.2015671168,2.9739582163,1.9942936997  
H,0,1.0877200551,3.0906924696,0.7837588285  
C,0,-3.6794156052,0.1702029352,-1.6327631082  
C,0,-2.6494983084,-1.9598594096,-0.903240614  
H,0,-4.0150687009,-0.3279303018,-2.5436314297  
H,0,-3.9413551589,1.2243420022,-1.5314337293  
H,0,-2.8804336982,-2.5492687366,-0.0025495009  
H,0,-1.5752171881,-2.0877025678,-1.1098298937  
H,0,-3.2072390334,-2.3825163975,-1.7469383142  
H,0,1.1290630888,-2.4623231581,-3.0199745029  
H,0,1.840639406,-0.8444901339,-2.8662586434  
H,0,0.1082306841,-1.0785498436,-2.6199476319  
H,0,4.6744123722,0.7810821071,-1.2993914924  
H,0,3.8364204726,-0.7082731057,-1.7759200849  
H,0,4.3632928002,-0.4924978287,-0.1041233186  
H,0,1.9482767043,-2.4477046358,3.0679308012  
H,0,2.0069712226,-3.0185566002,1.3913574509  
H,0,0.4849991425,-2.4465963852,2.0758090928

### Int-ax-G

E(RM11) = -652.718682096

Zero-point correction= 0.434674 (Hartree/Particle)  
Thermal correction to Energy= 0.455779  
Thermal correction to Enthalpy= 0.456724  
Thermal correction to Gibbs Free Energy= 0.387383  
Sum of electronic and ZPE= -652.284008  
Sum of electronic and thermal Energies= -652.262903  
Sum of electronic and thermal Enthalpies= -652.261959  
Sum of electronic and thermal Free Energies= -652.331299

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.006	82.494	145.939

C,0,-1.1180040497,1.2932763711,-1.3253901867  
C,0,-1.9470801941,1.4310938883,0.0102515727  
H,0,-1.4696180964,0.4156124956,-1.8811089039  
H,0,-1.2263880053,2.208784827,-1.9213078879  
C,0,0.2477674638,1.0830682075,-0.8018563678  
C,0,0.5705381949,-0.1812389672,-0.249372439

C,0,1.1322196574,2.2606073996,-0.6368608995  
 C,0,-0.1297230835,0.1684921868,1.1697281993  
 H,0,-0.0972568367,-0.9433969819,-0.6840759374  
 C,0,-1.6578708828,0.278638048,0.980385198  
 H,0,0.1776159153,-0.6491050949,1.8347458614  
 H,0,0.2551752545,1.0973911014,1.6110150297  
 C,0,-2.2877590958,-1.0585184187,0.6081458255  
 H,0,-2.0807639194,0.5560179741,1.9631370471  
 H,0,-1.6628871328,2.3791114172,0.49329697  
 H,0,-3.0117695048,1.5095268641,-0.2445940731  
 B,0,2.163055491,-0.8185956338,-0.1911412176  
 C,0,2.5617422486,-0.9271645172,-1.788511651  
 C,0,3.2916418943,0.0643207547,0.6197067129  
 C,0,2.0067753761,-2.3097161237,0.4980362222  
 H,0,1.7796982478,-1.4799040831,-2.3442023511  
 H,0,2.5859222688,0.083086675,-2.2475023957  
 C,0,3.9184480655,-1.5991928058,-2.0450310636  
 H,0,3.0217519722,-2.6868365468,0.7212435807  
 H,0,1.5239821514,-2.250168041,1.494831183  
 C,0,1.2795739931,-3.3721352487,-0.3435509915  
 C,0,3.0296470262,0.4255250574,-2.0916196791  
 H,0,3.5941696038,0.9755415214,0.067113098  
 H,0,4.1975756237,-0.5675950426,0.5992984215  
 H,0,1.8094108144,2.145499404,0.2162366324  
 H,0,0.578964136,3.2083510484,-0.6043993923  
 H,0,1.7716375868,2.2673857892,-1.5384318116  
 C,0,-3.1671775762,-1.2146429188,-0.384366378  
 C,0,-1.8710375722,-2.224782786,1.4720614437  
 H,0,-3.6109656131,-2.1912659113,-0.5836909249  
 H,0,-3.4881052453,-0.3951275946,-1.0292810635  
 H,0,-1.9285056483,-1.9636158456,2.5401405068  
 H,0,-0.8312885892,-2.5202068968,1.2636967296  
 H,0,-2.5113060636,-3.096156567,1.2917719838  
 H,0,4.134497698,-1.7335358111,-3.1165049266  
 H,0,3.9632294276,-2.5935242909,-1.5728575455  
 H,0,4.7397656911,-1.0053275194,-1.6168263606  
 H,0,3.9403316857,0.7530625289,2.6161567021  
 H,0,2.6278430692,-0.4377188465,2.6461600493  
 H,0,2.2991954669,1.2446841186,2.2046277238  
 H,0,1.1221642592,-4.3162754002,0.2018302591  
 H,0,1.8522461583,-3.6119969013,-1.2519686897  
 H,0,0.2877222377,-3.0311593536,-0.6880844732

### Int-ax-H

E(RM11) = -652.719047977

Zero-point correction= 0.435400 (Hartree/Particle)  
 Thermal correction to Energy= 0.456226  
 Thermal correction to Enthalpy= 0.457170  
 Thermal correction to Gibbs Free Energy= 0.388469  
 Sum of electronic and ZPE= -652.283648  
 Sum of electronic and thermal Energies= -652.262822  
 Sum of electronic and thermal Enthalpies= -652.261878  
 Sum of electronic and thermal Free Energies= -652.330579

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.286	82.157	144.594

C,0,-1.719439499,1.6130479642,-1.3029697906  
 C,0,-2.6183909791,1.6938265121,-0.0041971839  
 H,0,-2.0154243173,0.7448113261,-1.9038582235  
 H,0,-1.8222384765,2.5442513704,-1.8754603973  
 C,0,-0.3816891815,1.4208611787,-0.7030568561  
 C,0,-0.081520262,0.1437086716,-0.1676465946  
 C,0,0.4211113711,2.6363724368,-0.4020068876  
 C,0,-0.822397857,0.4456618406,1.2316704162

H,0,-0.7262778786,-0.6069235604,-0.6553088523  
 C,0,-2.3457710844,0.5467150309,0.9789231297  
 H,0,-0.5463675119,-0.381246728,1.8970667144  
 H,0,-0.4639134153,1.3680353665,1.7079864174  
 C,0,-2.9461957316,-0.7995238741,0.5937459325  
 H,0,-2.8100004714,0.8232520482,1.942913403  
 H,0,-2.3973102857,2.6475303929,0.4997481534  
 H,0,-3.6716165979,1.7329881708,-0.3114387418  
 B,0,1.5081055748,-0.5334558419,-0.0871437974  
 C,0,1.8418329914,-0.8451671243,-1.6717268128  
 C,0,2.6618802649,0.4239542106,0.583143771  
 C,0,1.3689116943,-1.9388776904,0.7611778547  
 H,0,2.8280478869,-1.3453707059,-1.7006363313  
 H,0,1.1300532004,-1.582635197,-2.0846355578  
 C,0,1.8745670933,0.3588626306,-2.6181441572  
 H,0,2.3924357598,-2.2766884406,1.0087939313  
 H,0,0.9000444637,-1.7793925863,1.7522342195  
 C,0,0.6437631274,-3.0953951481,0.0514692044  
 C,0,2.5074839665,0.7705773521,2.0731064002  
 H,0,2.8482225079,1.3511265538,0.0103186465  
 H,0,3.5999291146,-0.1509841267,0.4719508978  
 H,0,1.0761157647,2.4948908581,0.4631215586  
 H,0,-0.2115431557,3.5278646488,-0.2909363017  
 H,0,1.0726691587,2.7967659192,-1.2772931913  
 C,0,-3.7220779186,-0.9901121829,-0.4761211216  
 C,0,-2.6264229177,-1.9330660827,1.5390998626  
 H,0,-4.147674524,-1.972741316,-0.68579568  
 H,0,-3.9711812856,-0.1933270155,-1.1785855141  
 H,0,-2.7941775707,-1.6303070531,2.584324687  
 H,0,-1.5727172593,-2.2383401134,1.452739858  
 H,0,-3.2482224712,-2.8105182184,1.3262634816  
 H,0,2.1620438599,0.0917283993,-3.6465257106  
 H,0,2.5776566152,1.1327334989,-2.2705813128  
 H,0,0.8750439149,0.8307722437,-2.7009938895  
 H,0,3.4017103343,1.2547689699,2.4951687736  
 H,0,2.3141857301,-0.134961135,2.6686577073  
 H,0,1.6629889871,1.4552336413,2.262927745  
 H,0,0.4416184426,-3.9472772372,0.7202821088  
 H,0,1.2424267429,-3.4770130527,-0.7881443507  
 H,0,-0.3241680154,-2.7815551556,-0.377651818

### Int-ax-I

E(RM11) = -652.719003177

Zero-point correction= 0.434811 (Hartree/Particle)  
 Thermal correction to Energy= 0.455839  
 Thermal correction to Enthalpy= 0.456783  
 Thermal correction to Gibbs Free Energy= 0.387283  
 Sum of electronic and ZPE= -652.284193  
 Sum of electronic and thermal Energies= -652.263164  
 Sum of electronic and thermal Enthalpies= -652.262220  
 Sum of electronic and thermal Free Energies= -652.331720

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.043	82.297	146.275

C,0,-0.7405854218,1.9299076004,-0.404354504  
 C,0,-1.8208491795,1.3141419893,0.5716420367  
 H,0,-0.9892821537,1.6550505153,-1.436536523  
 H,0,-0.7055085335,3.0198005069,-0.2782028085  
 C,0,0.4703729704,1.2342489551,0.0693385249  
 C,0,0.6465820461,-0.1343126347,-0.2689156165  
 C,0,1.3076541303,1.8994238821,1.0904986867  
 C,0,-0.3621359964,-0.7067841679,0.8340551846  
 H,0,0.1346859739,-0.3345907739,-1.2273614271  
 C,0,-1.7985301301,-0.2183738734,0.5398342016

H,0,-0.2573404852,-1.7981277253,0.7790478728  
H,0,-0.0536431868,-0.4066757201,1.8472981583  
C,0,-2.3693349996,-0.8323433607,-0.7357636985  
H,0,-2.4351689618,-0.5799716352,1.3676967864  
H,0,-1.5989241525,1.6540427295,1.5953461725  
H,0,-2.8024191942,1.7271698044,0.3060605024  
B,0,2.1914187309,-0.898996675,-0.2369362274  
C,0,1.9443847756,-2.22482629986,-1.1861396908  
C,0,3.2553943993,0.1582685636,-0.9252745127  
C,0,2.7734708804,-1.3449918618,1.2434121869  
H,0,1.1113783803,-2.8379813232,-0.7857629961  
H,0,1.6118235306,-1.9167776071,-2.1964755333  
C,0,3.1727198308,-3.13528495,-1.3320825501  
H,0,3.821743675,-1.6290865079,1.0338150923  
H,0,2.8806465493,-0.4963553995,1.945938966  
C,0,2.123531807,-2.5202088319,1.9974271989  
C,0,2.7565366179,0.9237587655,-2.1575735176  
H,0,4.1479816022,-0.4226388224,-1.2173477953  
H,0,3.6431082341,0.8814901491,-0.180580767  
H,0,1.832017528,1.1755529572,1.7220801525  
H,0,0.7565500276,2.6498258862,1.6725792822  
H,0,2.0834837129,2.4297399177,0.5070598385  
C,0,-3.05427765,-0.1389112616,-1.6487527717  
C,0,-2.1443818192,-2.3160877695,-0.9026869932  
H,0,-3.4749013504,-0.6386942479,-2.5227197251  
H,0,-3.2329882064,0.9343449607,-1.5718967473  
H,0,-2.3599212767,-2.8588092805,0.0303926043  
H,0,-1.0969214459,-2.5260274594,-1.1686675306  
H,0,-2.7824821336,-2.7220442746,-1.6962765268  
H,0,2.9856982156,-3.9991710682,-1.9885630797  
H,0,3.4973771651,-3.5278138631,-0.3562771819  
H,0,4.026474683,-2.5835273281,-1.7541924399  
H,0,3.542018962,1.5162375156,-2.6511163579  
H,0,1.9461964567,1.6369449834,-1.9073640873  
H,0,2.3386185015,0.2352358231,-2.9090570768  
H,0,2.7844675983,-2.9291704276,2.7773078022  
H,0,1.8785850207,-3.3485388093,1.3139967546  
H,0,1.188826112,-2.2352613369,2.5034340906

### Int-ax-J

E(RM11) = -652.718451550

Zero-point correction= 0.435205 (Hartree/Particle)  
Thermal correction to Energy= 0.456050  
Thermal correction to Enthalpy= 0.456994  
Thermal correction to Gibbs Free Energy= 0.388284  
Sum of electronic and ZPE= -652.283246  
Sum of electronic and thermal Energies= -652.262402  
Sum of electronic and thermal Enthalpies= -652.261458  
Sum of electronic and thermal Free Energies= -652.330167

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.175	82.107	144.611

C,0,-0.7266714208,1.9234638822,-0.5500633131  
C,0,-1.8018236416,1.4154084093,0.4934521427  
H,0,-0.9778092882,1.5323297899,-1.543585294  
H,0,-0.6993467495,3.0207761515,-0.54876237  
C,0,0.4896860764,1.2922191428,-0.0023763736  
C,0,0.657778915,-0.1059413042,-0.1817375836  
C,0,1.324708114,2.0807526526,0.9265026804  
C,0,-0.3383943405,-0.5610756812,0.9836196293  
H,0,0.1286929908,-0.4021110704,-1.104090508  
C,0,-1.7751405029,-0.110527543,0.6374252352  
H,0,-0.2344255483,-1.651533586,1.0485878115  
H,0,-0.0275386645,-0.152593432,1.9569995335

C,0,-2.3442164029,-0.8663951142,-0.5609792401  
H,0,-2.4117678508,-0.3765011111,1.5008921271  
H,0,-1.5800051062,1.871515682,1.4709792142  
H,0,-2.7855972604,1.7914508062,0.1850335077  
B,0,2.1942274135,-0.9193402072,-0.0694695924  
C,0,1.9449376815,-2.2083378523,-1.0772361629  
C,0,3.3637874007,0.0816047744,-0.6416461028  
C,0,2.5606407566,-1.5071810883,1.4261153404  
H,0,1.2496044041,-2.921104324,-0.5884387331  
H,0,1.4363057931,-1.8979736266,-2.0104127252  
C,0,3.2204939883,-2.968384946,-1.4704749582  
H,0,1.7859744746,-2.2194223183,1.7693624734  
H,0,3.4489569114,-2.1424056633,1.259601031  
C,0,2.9044876946,-0.5660792349,2.5926959271  
C,0,3.0743301737,0.6890749556,-2.020195394  
H,0,4.2938335782,-0.5114978175,-0.707302264  
H,0,3.6170190645,0.8932833962,0.0654396835  
H,0,1.8692755428,1.4454692165,1.6312340223  
H,0,0.763545501,2.8828381146,1.4245302967  
H,0,2.084875307,2.5570959004,0.2788856677  
C,0,-3.0414380191,-0.2840680849,-1.5399730046  
C,0,-2.100379568,-2.3565902229,-0.5695103763  
H,0,-3.4582655554,-0.8804701789,-2.353070554  
H,0,-3.2335407037,0.7890215415,-1.5795025082  
H,0,-2.308528535,-2.7994011881,0.416567563  
H,0,-1.0503923979,-2.580590747,-0.8138790085  
H,0,-2.7340754892,-2.852606202,-1.3139383753  
H,0,3.0087839179,-3.8770928623,-2.0549840293  
H,0,3.7977764153,-3.2750670723,-0.585067732  
H,0,3.8815677976,-2.3342258352,-2.0814700523  
H,0,3.8917723343,1.319499809,-2.4032379141  
H,0,2.1660184184,1.3227281263,-2.0093036882  
H,0,2.8863807814,-0.1000374942,-2.7650271405  
H,0,3.3578779453,-1.1017583425,3.4408091568  
H,0,2.0140788363,-0.0561819816,2.9997676246  
H,0,3.6228979866,0.2121150727,2.2868370719

### Int-ax-K

E(RM11) = -652.720191681

Zero-point correction= 0.434961 (Hartree/Particle)  
Thermal correction to Energy= 0.455971  
Thermal correction to Enthalpy= 0.456915  
Thermal correction to Gibbs Free Energy= 0.387640  
Sum of electronic and ZPE= -652.285231  
Sum of electronic and thermal Energies= -652.264221  
Sum of electronic and thermal Enthalpies= -652.263277  
Sum of electronic and thermal Free Energies= -652.332552

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.126	82.290	145.801

C,0,-1.6767852397,1.6956921747,-1.2970669082  
C,0,-2.5748910597,1.7981193182,0.0006475881  
H,0,-2.0010800633,0.8390137588,-1.900208354  
H,0,-1.7460191132,2.6319284469,-1.8661947074  
C,0,-0.3519335623,1.4610080718,-0.6857124266  
C,0,-0.0847165073,0.1718704301,-0.1566291325  
C,0,0.4766350762,2.6518289645,-0.3637651044  
C,0,-0.8522301444,0.4484310043,1.2300657548  
H,0,-0.7233824433,-0.5677996153,-0.6716524432  
C,0,-2.364556568,0.6065552025,0.9440086344  
H,0,-0.6230847481,-0.4078206226,1.8756299007  
H,0,-0.4752003394,1.3435827071,1.7434101724  
C,0,-2.999915136,-0.6987983515,0.4763782508  
H,0,-2.8470555088,0.8548129066,1.9068250686

H,0,-2.3049086192,2.7236956393,0.5326726957  
H,0,-3.6221925949,1.9045495364,-0.3097477748  
B,0,1.4959528531,-0.5272598308,-0.06137614  
C,0,1.8078535973,-0.8893981432,-1.6407320611  
C,0,2.6763793598,0.4236957049,0.5674337957  
C,0,1.3033337875,-1.9140133862,0.8003269613  
H,0,2.8154469197,-1.3406248964,-1.6802914633  
H,0,1.1194642823,-1.6792912972,-1.997535631  
C,0,1.775951392,0.2760350247,-2.6343917154  
H,0,0.9262099442,-1.730610536,1.8255288784  
H,0,0.5359540167,-2.5441411041,0.3082774481  
C,0,2.5937490698,-2.7392532705,0.9295314792  
C,0,2.5623258476,0.7662860929,2.0611386799  
H,0,2.8433358018,1.3488370708,-0.0141316378  
H,0,3.6141303172,-0.1443658418,0.4259683631  
H,0,1.086633746,2.5005923955,0.5324588766  
H,0,-0.1258424828,3.5677724382,-0.2969681082  
H,0,1.1762182772,2.7691209686,-1.2090365408  
C,0,-3.8347356399,-0.788622402,-0.5618903122  
C,0,-2.6492021526,-1.9161705498,1.2977671159  
H,0,-4.2881899701,-1.7450044628,-0.8269885733  
H,0,-4.10679801,0.0654114085,-1.1836733396  
H,0,-2.7428317519,-1.7060643008,2.3744467744  
H,0,-1.608824607,-2.2270967641,1.1169392025  
H,0,-3.3040058315,-2.7596744183,1.0497337265  
H,0,2.0319354898,-0.0228738697,-3.6623100276  
H,0,2.4791715408,1.0722798316,-2.3410277284  
H,0,0.767827589,0.7322020151,-2.6981316601  
H,0,3.4416593807,1.3032696597,2.4495240501  
H,0,2.4452680998,-0.1496904948,2.661028778  
H,0,1.6827983137,1.3944924255,2.2857988271  
H,0,2.4347621896,-3.6979308135,1.4469571185  
H,0,3.3612509617,-2.1867447591,1.493671407  
H,0,3.0208980997,-2.9659478266,-0.0590611879

### Int-ax-L

E(RM11) = -652.717096891

Zero-point correction= 0.435274 (Hartree/Particle)  
Thermal correction to Energy= 0.456113  
Thermal correction to Enthalpy= 0.457057  
Thermal correction to Gibbs Free Energy= 0.388595  
Sum of electronic and ZPE= -652.281823  
Sum of electronic and thermal Energies= -652.260984  
Sum of electronic and thermal Enthalpies= -652.260039  
Sum of electronic and thermal Free Energies= -652.328502

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.215	82.126	144.091

C,0,1.4823463954,2.2133117522,0.3576695765  
C,0,2.4317495007,1.6182222041,-0.7546228292  
H,0,1.7776308572,1.8112387676,1.3362630075  
H,0,1.5342189663,3.3097101929,0.3437806487  
C,0,0.1954592793,1.6608446694,-0.1075484666  
C,0,-0.0833767128,0.2923830268,0.1530650509  
C,0,-0.6015682019,2.4682560151,-1.0572326014  
C,0,0.8379262752,-0.3044427835,-1.0199833722  
H,0,0.4353030972,0.0101103162,1.0805883429  
C,0,2.3139872715,0.084514921,-0.8188875142  
H,0,0.682227556,-1.3895731183,-1.0006687169  
H,0,0.4796115419,0.0461587318,-1.999814456  
C,0,3.0146456621,-0.5938197205,0.3562028021  
H,0,2.8659146565,-0.2338508818,-1.7222146397  
H,0,2.1476469478,2.0464023198,-1.7282785596  
H,0,3.454981142,1.9542838189,-0.5458999939  
B,0,-1.7020226454,-0.3278821051,0.1224844926

C,0,-1.6656967718,-1.6535046297,1.1188511619  
C,0,-2.682463559,0.8231569298,0.7841314107  
C,0,-2.1870232643,-0.7382941793,-1.3942812758  
H,0,-1.0371300301,-1.4561501107,2.009313735  
H,0,-2.6832755056,-1.7906317753,1.5299819093  
C,0,-1.2372033284,-2.9969156344,0.5031366235  
H,0,-2.0973639888,0.0924870382,-2.1218999395  
H,0,-1.5528215831,-1.5449581856,-1.8079378104  
C,0,-3.6500384638,-1.2118347135,-1.4173714888  
C,0,-2.1541459388,1.4831760841,2.0649226603  
H,0,-3.6359353653,0.3239771891,1.030873958  
H,0,-2.9693672155,1.6076482362,0.0562839857  
H,0,-1.2072262306,1.8416369633,-1.7194532483  
H,0,0.0041469572,3.2013882922,-1.6060786631  
H,0,-1.3091655491,3.0281419024,-0.4182645136  
C,0,2.4715311478,-1.5725809022,1.0837089269  
C,0,4.4265172707,-0.1244163059,0.6293601831  
H,0,3.0465992525,-2.0534816382,1.877326168  
H,0,1.4522148569,-1.9318146752,0.9355500675  
H,0,4.4357218311,0.8639940098,1.1151375196  
H,0,5.0057873918,-0.0349237536,-0.3026392347  
H,0,4.9487694734,-0.822731963,1.2938524553  
H,0,-1.2344144043,-3.8161692457,1.2390912038  
H,0,-0.2269683429,-2.9643719862,0.0634273155  
H,0,-1.9148458035,-3.292195455,-0.3118609527  
H,0,-2.8738081496,2.1730111529,2.5321088364  
H,0,-1.2331809189,2.0728245472,1.8847300609  
H,0,-1.8874834288,0.722545594,2.8154350541  
H,0,-3.9614713783,-1.5963413665,-2.4009915558  
H,0,-4.3320251136,-0.3894225593,-1.1537702145  
H,0,-3.8178538663,-2.0118800665,-0.6791781927

### Int-ax-M

E(RM11) = -652.717238470

Zero-point correction= 0.434739 (Hartree/Particle)  
Thermal correction to Energy= 0.455864  
Thermal correction to Enthalpy= 0.456808  
Thermal correction to Gibbs Free Energy= 0.386904  
Sum of electronic and ZPE= -652.282499  
Sum of electronic and thermal Energies= -652.261375  
Sum of electronic and thermal Enthalpies= -652.260430  
Sum of electronic and thermal Free Energies= -652.330334

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.059	82.314	147.125

C,0,1.9792908247,1.4662869393,1.0843706719  
C,0,2.7368527584,1.2333958034,-0.2819989054  
H,0,2.1693552707,0.61297761,1.749100041  
H,0,2.3096415266,2.4093434752,1.5385783873  
C,0,0.59188574,1.4851915723,0.5848448969  
C,0,-0.0212474012,0.2459021824,0.2568609915  
C,0,0.0043710348,2.7823314178,0.1888482452  
C,0,0.7140878362,0.0294129031,-1.1494290578  
H,0,0.4071811033,-0.5300785195,0.9101815703  
C,0,2.2415886206,-0.0490180313,-0.9745060529  
H,0,0.2849454429,-0.8924854902,-1.5642153151  
H,0,0.4537192939,0.8437753051,-1.8430765005  
C,0,2.7559023636,-1.3113893495,-0.2868032783  
H,0,2.6910678267,-0.0519591766,-1.9844747961  
H,0,2.5524959531,2.0962665397,-0.9408670951  
H,0,3.8144835953,1.2147354973,-0.0763334753  
B,0,-1.7310650379,0.057992546,0.1467696757  
C,0,-2.383709962,0.8777669195,1.421523714  
C,0,-2.4439280546,0.5928296406,-1.2452089416

C,0,-1.9132982136,-1.5732387608,0.3117699788  
H,0,-2.517931417,1.9517734996,1.1842568672  
H,0,-3.4160271215,0.5079231508,1.5510131357  
C,0,-1.6528847562,0.743466227,2.7634431365  
H,0,-1.3579502432,-2.1082483629,-0.4857502357  
H,0,-1.4562314469,-1.9198915736,1.2591631829  
C,0,-3.3733312113,-2.0492922951,0.2733947767  
C,0,-2.2710650907,-0.2113133479,-2.5472269586  
H,0,-2.2272544445,1.6569549163,-1.4617518393  
H,0,-3.5237153337,0.6002800322,-1.0054280196  
H,0,-0.6982489439,2.6718589217,-0.644017055  
H,0,0.7563995242,3.5606452135,0.0069657114  
H,0,-0.6010415099,3.0868175077,1.0632887879  
C,0,1.9904249872,-2.3689167046,-0.0081814549  
C,0,4.2368296601,-1.3282160767,0.0200912623  
H,0,2.429071988,-3.2643926943,0.4362264463  
H,0,0.9162220083,-2.393779776,-0.1971917457  
H,0,4.4775341584,-0.6832045216,0.8798313893  
H,0,4.8262918436,-0.9637570563,-0.8354635154  
H,0,4.5743650167,-2.3422635964,0.2641656773  
H,0,-2.1901132613,1.2101612848,3.6032571646  
H,0,-0.6490545202,1.2125552817,2.7416594109  
H,0,-1.4906463819,-0.3154302173,3.0201093352  
H,0,-3.0161031506,0.067523974,-3.3086345257  
H,0,-2.3805712469,-1.2920700961,-2.3674897507  
H,0,-1.2844471222,-0.0641982321,-3.01123348  
H,0,-3.4666868584,-3.1428556948,0.3609654354  
H,0,-3.867029941,-1.7495246534,-0.6637195843  
H,0,-3.9544827069,-1.6057501338,1.0959766906

### Int-ax-N

E(RM11) = -652.710866545

Zero-point correction= 0.435195 (Hartree/Particle)  
Thermal correction to Energy= 0.456348  
Thermal correction to Enthalpy= 0.457292  
Thermal correction to Gibbs Free Energy= 0.387169  
Sum of electronic and ZPE= -652.275672  
Sum of electronic and thermal Energies= -652.254519  
Sum of electronic and thermal Enthalpies= -652.253575  
Sum of electronic and thermal Free Energies= -652.323698

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.363	82.383	147.587

C,0,-1.8144513917,1.5739844759,-1.3401678538  
C,0,-2.6446923268,1.6067052022,-0.0002722805  
H,0,-2.075132267,0.670906277,-1.9079854636  
H,0,-2.0181745319,2.4820066344,-1.9228605558  
C,0,-0.4430685478,1.5096464972,-0.7869434541  
C,0,0.0321992157,0.2619457057,-0.3143179567  
C,0,0.2158225492,2.8070230154,-0.492986734  
C,0,-0.7523478538,0.3811371053,1.1042265526  
H,0,-0.5279375411,-0.5296942895,-0.8275780978  
C,0,-2.2764864943,0.4111098152,0.8941190378  
H,0,-0.4292473553,-0.503857358,1.6649107187  
H,0,-0.4248624544,1.2632807899,-1.6742851202  
C,0,-2.888958548,-0.897267323,0.3969256945  
H,0,-2.7389563849,0.6012493012,1.880066411  
H,0,-2.4156934731,2.5423044282,0.5328047975  
H,0,-3.7121446565,1.6363079899,-0.2513587663  
B,0,1.7036691446,-0.2432473896,-0.2363431348  
C,0,1.8952695555,-0.9912962181,-1.6973143453  
C,0,2.7629614255,1.004006628,-0.0721931307  
C,0,1.8673787892,-1.3243279579,0.99483481  
H,0,1.6391600636,-0.2995480355,-2.5253041484  
H,0,2.9711759011,-1.2047339358,-1.8235494003

C,0,1.1410740005,-2.3165673658,-1.8923822768  
H,0,0.9950741899,-2.0060495676,1.0553120375  
H,0,2.7027508061,-2.0002080841,0.731945151  
C,0,2.1542932682,-0.7426765244,2.3906453913  
C,0,4.2316454356,0.54261918,-0.1007752094  
H,0,2.5966762339,1.5486985379,0.8783099278  
H,0,2.6440937542,1.753998907,-0.876222283  
H,0,0.9025130846,2.7438295981,0.3562526139  
H,0,-0.5082071662,3.6245527094,-0.3777052691  
H,0,0.8328296612,3.031884314,-1.3807187546  
C,0,-2.2239150003,-2.0528591024,0.3291965577  
C,0,-4.3556935708,-0.8314128046,0.0331873789  
H,0,-2.7353853999,-2.9657493613,0.0184530946  
H,0,-1.1626325785,-2.1468127667,0.5655129054  
H,0,-4.5099591439,-0.3192438061,-0.9295802147  
H,0,-4.9320382914,-0.2795684319,0.7919548306  
H,0,-4.7804242467,-1.8379884956,-0.0569788977  
H,0,1.3428075035,-2.7791858794,-2.8710054981  
H,0,0.046309943,-2.1989512416,-1.8212728574  
H,0,1.4307302101,-3.0468601023,-1.1213152716  
H,0,4.932620785,1.3502791672,0.1613882338  
H,0,4.5125327167,0.1817188595,-1.1002880899  
H,0,4.408420324,-0.2890382855,0.5980953233  
H,0,2.1617908169,-1.5098506339,3.1806916748  
H,0,1.421616065,0.0249938485,2.6875382408  
H,0,3.1343441415,-0.2441001662,2.4119385809

### Int-ax-O

E(RM11) = -652.712464539

Zero-point correction= 0.435243 (Hartree/Particle)  
Thermal correction to Energy= 0.456119  
Thermal correction to Enthalpy= 0.457064  
Thermal correction to Gibbs Free Energy= 0.388011  
Sum of electronic and ZPE= -652.277222  
Sum of electronic and thermal Energies= -652.256345  
Sum of electronic and thermal Enthalpies= -652.255401  
Sum of electronic and thermal Free Energies= -652.324453

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.219	82.245	145.333

C,0,-1.1184153802,2.1767851018,-0.7247679329  
C,0,-2.0709006532,1.9124873015,0.5102726677  
H,0,-1.510291826,1.661858945,-1.6110494469  
H,0,-1.0296981489,3.2573928704,-0.896454831  
C,0,0.0998201599,1.5350438773,-0.2020551995  
C,0,0.1772105731,0.1191989941,-0.2313037124  
C,0,1.0160023686,2.3664292637,0.6125308578  
C,0,-0.7230753346,-0.1460128444,1.068712046  
H,0,-0.43959997,-0.2596851988,-1.0643326408  
C,0,-2.1519816126,0.4206485196,0.8767415305  
H,0,-0.7094012016,-1.2319282704,1.2195053817  
H,0,-0.2561950912,0.3007489181,1.9586422002  
C,0,-3.0395484918,-0.3904051498,-0.0753125981  
H,0,-2.6501244185,0.3777471373,1.8620422715  
H,0,-1.6796138562,2.4719678564,1.3733940648  
H,0,-3.0533437312,2.340733203,0.2772595256  
B,0,1.7394480092,-0.6860079076,-0.1769582887  
C,0,1.5468912084,-1.9731898316,-1.1874632892  
C,0,2.8946367669,0.3043100595,-0.8105196176  
C,0,2.1613392523,-1.2325562539,1.3188368238  
H,0,1.3503756584,-1.6329467887,-2.2211015715  
H,0,2.5263938965,-2.4847599027,-1.231494289  
C,0,0.4692836535,-3.0005401787,-0.8171341051  
H,0,1.3824254327,-1.889307541,1.7483077185

H,0,3.0104332053,-1.9152116454,1.1284187269  
 C,0,2.6106090674,-0.2494871687,2.4132607377  
 C,0,2.5633598153,0.9482275422,-2.1647287764  
 H,0,3.788477932,-0.3312461322,-0.9489549116  
 H,0,3.2345613278,1.0897171135,-0.1122194763  
 H,0,1.5518404505,1.7729074361,1.3602381877  
 H,0,0.5124131606,3.2375775415,1.0520756532  
 H,0,1.7748879786,2.7426523778,-0.0962888355  
 C,0,-2.9513827326,-1.7187145832,-0.1672469297  
 C,0,-4.1295788038,0.3471587619,-0.8207276402  
 H,0,-3.6355580067,-2.2796405177,-0.8062945324  
 H,0,-2.217470948,-2.302680472,0.3872554442  
 H,0,-3.7279567826,1.0927488655,-1.5233119918  
 H,0,-4.7915952474,0.8831859213,-0.1224683185  
 H,0,-4.7444380709,-0.3558057426,-1.3944686832  
 H,0,0.5024103933,-3.8991586433,-1.4525776118  
 H,0,-0.5375782556,-2.571656535,-0.9348291434  
 H,0,0.5686687172,-3.3382170263,0.2273133915  
 H,0,3.354248158,1.6210598815,-2.5318403727  
 H,0,1.6320590332,1.5485422808,-2.1315906446  
 H,0,2.3983557557,0.1844861321,-2.9378120962  
 H,0,3.0777893443,-0.7629684256,3.2676625405  
 H,0,1.7702750068,0.3298515263,2.8333381987  
 H,0,3.3502154781,0.4726488115,2.0315636389

### Int-ax-P

E(RM11) = -652.715402976

Zero-point correction= 0.435412 (Hartree/Particle)  
 Thermal correction to Energy= 0.456147  
 Thermal correction to Enthalpy= 0.457091  
 Thermal correction to Gibbs Free Energy= 0.388673  
 Sum of electronic and ZPE= -652.279991  
 Sum of electronic and thermal Energies= -652.259256  
 Sum of electronic and thermal Enthalpies= -652.258312  
 Sum of electronic and thermal Free Energies= -652.326730

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.236	81.991	143.998

C,0,1.6691973923,2.0386778114,0.1771288797  
 C,0,2.5662628774,1.2755543011,-0.8786598317  
 H,0,1.9352992537,1.7053120971,1.1887442166  
 H,0,1.803039502,3.1219275293,0.0614124199  
 C,0,0.3550820617,1.5317607957,-0.2604516666  
 C,0,-0.0166390312,0.219869752,0.1372511784  
 C,0,-0.3235030356,2.272682634,-1.3533980074  
 C,0,0.8500417972,-0.5735972441,-0.9521469171  
 H,0,0.4889935111,-0.0064661778,1.0893812567  
 C,0,2.3511498285,-0.2466159575,-0.7991696397  
 H,0,0.6472209949,-1.6366756422,-0.7785954585  
 H,0,0.5086393944,-0.3407792249,-1.9725008769  
 C,0,3.0273239979,-0.8528581556,0.4292855006  
 H,0,2.8732157595,-0.6808301278,-1.671390686  
 H,0,2.3017049766,1.62783243,-1.8873546005  
 H,0,3.6113295897,1.562109944,-0.707631291  
 B,0,-1.6746807796,-0.2949700721,0.3176128218  
 C,0,-2.0418355007,0.3340588492,1.7952782392  
 C,0,-2.7071227392,0.2292922891,-0.8493380073  
 C,0,-1.6558654436,-1.9409560802,0.4003437727  
 H,0,-3.0572897965,-0.0076548933,2.0641757476  
 H,0,-1.3810840071,-0.0997510073,2.5700460899  
 C,0,-1.9976852129,1.8611950115,1.8949100374  
 H,0,-0.7457341521,-2.2916178725,0.9274708322  
 H,0,-2.4784839614,-2.2512961649,1.07030689  
 C,0,-1.8124562884,-2.7181751053,-0.9194215347

C,0,-4.1585965778,-0.1802674479,-0.5372254188  
 H,0,-2.4267888977,-0.1770829825,-1.8418331306  
 H,0,-2.7143283178,1.3258935895,-0.9696077054  
 H,0,-0.8320264131,1.5992133069,-2.0514593771  
 H,0,0.3504479641,2.9674657093,-1.8706558389  
 H,0,-1.1153008031,2.864566184,-0.8619178756  
 C,0,2.4477964576,-1.7451292875,1.2350741464  
 C,0,4.459437491,-0.4246138754,0.6623399154  
 H,0,3.0049378426,-2.1814580484,2.0662511525  
 H,0,1.4156145758,-2.0741068633,1.1123742937  
 H,0,4.5142783214,0.5991673468,1.0644706544  
 H,0,5.0382355268,-0.4385960485,-0.2741962464  
 H,0,4.9531469434,-1.0882669656,1.3818058597  
 H,0,-2.2564221947,2.2445962708,2.8937756047  
 H,0,-2.6903231888,2.3275273536,1.1744841872  
 H,0,-0.9846421742,2.2538894116,1.6739932936  
 H,0,-4.8455926395,0.0161345237,-1.3748739651  
 H,0,-4.5372245076,0.3780705742,0.3325981757  
 H,0,-4.2372662678,-1.2486556343,-0.2852245483  
 H,0,-1.697768,-3.8056188892,-0.7885468827  
 H,0,-1.089446113,-2.4033135741,-1.6887042089  
 H,0,-2.8068246763,-2.5476268624,-1.3575366113

### Int-ax-Q

E(RM11) = -652.715096162

Zero-point correction= 0.435010 (Hartree/Particle)  
 Thermal correction to Energy= 0.456070  
 Thermal correction to Enthalpy= 0.457014  
 Thermal correction to Gibbs Free Energy= 0.387973  
 Sum of electronic and ZPE= -652.280086  
 Sum of electronic and thermal Energies= -652.259027  
 Sum of electronic and thermal Enthalpies= -652.258082  
 Sum of electronic and thermal Free Energies= -652.327123

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.188	82.441	145.309

C,0,-1.8375022944,-1.7489253066,1.0620545829  
 C,0,-2.7312730977,-1.4347628344,-0.1933669058  
 H,0,-2.0260279289,-0.9913778901,1.8351519361  
 H,0,-2.0591620763,-2.7571712647,1.4358963035  
 C,0,-0.4816482717,-1.6175366781,0.4812751381  
 C,0,0.0454031155,-0.319063542,0.2662048586  
 C,0,0.1463603894,-2.8438876431,-0.0612971134  
 C,0,-0.8437696037,-0.0515479022,-1.0685156168  
 H,0,-0.4010553901,0.3615208701,1.0044664433  
 C,0,-2.3514265286,-0.0664360071,-0.7815598963  
 H,0,-0.4860387858,0.9282702568,-1.4085269326  
 H,0,-0.5872782173,-0.7767744757,-1.8553925661  
 C,0,-2.8606433788,1.0962348505,0.0678132586  
 H,0,-2.8716412415,0.0172343859,-1.753468431  
 H,0,-2.5647750585,-2.2150822077,-0.9522883005  
 H,0,-3.7863962948,-1.4952178486,0.1009756364  
 B,0,1.6964899598,0.0360876674,-0.0270538303  
 C,0,1.8180244625,1.6600229777,0.2244904971  
 C,0,2.556645902,-0.8109076384,1.1012136143  
 C,0,2.204660588,-0.3584715402,-1.5613866409  
 H,0,2.8473608222,1.9607358508,-0.0451137832  
 H,0,1.1818908191,2.2260422162,-0.4872437367  
 C,0,1.5326906496,2.1580824099,1.6504473443  
 H,0,3.268980826,-0.6432738386,-1.4796732341  
 H,0,1.7209967374,-1.2719408175,-1.9587881211  
 C,0,2.1143975532,0.7197446258,-2.6572415304  
 C,0,4.0107377052,-0.3390468831,1.2537664706  
 H,0,2.5810021416,-1.8871179967,0.8398090127



H,0,2.0651797893,-0.7579502632,2.0937656225  
H,0,0.9017569687,-2.6233344867,-0.8205132236  
H,0,-0.5917973604,-3.5828362366,-0.4018236395  
H,0,0.6778350512,-3.2842174549,0.8022422062  
C,0,-2.1279980158,2.1718830143,0.3660205621  
C,0,-4.3011125258,0.994239665,0.5168103643  
H,0,-2.5646706364,2.9971854176,0.9315453031  
H,0,-1.0820592092,2.2825745342,0.073813141  
H,0,-4.4205037867,0.2551693328,1.3248325656  
H,0,-4.9560514069,0.6802430848,-0.3107356181  
H,0,-4.6615208366,1.9581486296,0.8944952746  
H,0,1.7005628711,3.2406421219,1.762880308  
H,0,2.1750419414,1.6490849833,2.3851398735  
H,0,0.491746788,1.9685828442,1.9619843479  
H,0,4.5917187975,-0.9630249547,1.9507464303  
H,0,4.0580081392,0.6967187585,1.6221214506  
H,0,4.5358241985,-0.3540353775,0.2860815228  
H,0,2.5391185779,0.3766196882,-3.6137128286  
H,0,2.6620425857,1.6267264821,-2.3642320811  
H,0,1.0783870759,1.0318076008,-2.864136319

### Int-ax-R

E(RM11) = -652.716226750

Zero-point correction= 0.435227 (Hartree/Particle)  
Thermal correction to Energy= 0.456119  
Thermal correction to Enthalpy= 0.457063  
Thermal correction to Gibbs Free Energy= 0.388503  
Sum of electronic and ZPE= -652.281000  
Sum of electronic and thermal Energies= -652.260108  
Sum of electronic and thermal Enthalpies= -652.259164  
Sum of electronic and thermal Free Energies= -652.327724

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.219	82.203	144.297

C,0,1.6587151756,1.5360176653,1.4521169088  
C,0,2.6394424857,1.5094538224,0.2152144021  
H,0,1.8351228521,0.6460588434,2.0708405462  
H,0,1.8124682192,2.4587623009,2.0263507285  
C,0,0.3664248753,1.471459327,0.7426068055  
C,0,-0.0591841361,0.2192679709,0.2310524685  
C,0,-0.2877347237,2.739507608,0.3459432224  
C,0,0.8866043544,0.2794647456,-1.0785412291  
H,0,0.3884679782,-0.5792142094,0.8414150129  
C,0,2.3731195454,0.2850887598,-0.6795286642  
H,0,0.6001425502,-0.5921783032,-1.6810146329  
H,0,0.6705908472,1.1671931328,-1.6868561901  
C,0,2.8874559121,-1.0192676119,-0.0747261488  
H,0,2.961430767,0.442240961,-1.6022454054  
H,0,2.4827975439,2.4260348735,-0.3746928347  
H,0,3.6688970039,1.5441991934,0.5931213575  
B,0,-1.7193695286,-0.157728374,-0.0380438978  
C,0,-2.3744515071,-0.0201621451,1.4706770612  
C,0,-2.5405172033,0.7975413207,-1.099303816  
C,0,-1.7231371848,-1.7243558154,-0.5572944706  
H,0,-1.8077959592,-0.6401288435,2.1917872665  
H,0,-2.2793742311,1.0204244895,1.8444782123  
C,0,-3.8579523837,-0.4120257391,1.5388177364  
H,0,-2.7276781454,-1.9474355982,-0.9614818997  
H,0,-1.053227397,-1.8668058696,-1.42946811  
C,0,-1.3894944357,-2.7874319636,0.5031981022  
C,0,-2.0090863838,0.9470713123,-2.534871968  
H,0,-2.7603079383,1.8007287073,-0.6841571492  
H,0,-3.5348207607,0.3217762302,-1.1721182429  
H,0,-0.7490099771,2.6597819288,-0.6454262546

H,0,0.372045079,3.6123151086,0.4278707825  
H,0,-1.127843876,2.8628904721,1.0533250351  
C,0,2.2145154228,-2.1700920269,-0.1416648471  
C,0,4.2622295988,-0.9601093162,0.5513451471  
H,0,2.6492397973,-3.090451662,0.2528714898  
H,0,1.2164257667,-2.2502360206,-0.5759890091  
H,0,4.2477659485,-0.4149258658,1.5083305914  
H,0,4.9785994368,-0.4436203181,-0.1065604975  
H,0,4.643729181,-1.9683577496,0.7502867312  
H,0,-4.2540191736,-0.4148255391,2.566386472  
H,0,-4.0213274586,-1.4173773741,1.1191227353  
H,0,-4.476458697,0.2824773919,0.9509427657  
H,0,-2.7706262267,1.3324859725,-3.230110798  
H,0,-1.6639459728,-0.0204592375,-2.9337179586  
H,0,-1.1552446695,1.6426180987,-2.6017320548  
H,0,-1.2922657486,-3.799256366,0.0787583139  
H,0,-2.1729215414,-2.8313346072,1.2744704714  
H,0,-0.448337793,-2.5682029604,1.0351995828

### Int-ax-S

E(RM11) = -652.716084304

Zero-point correction= 0.435658 (Hartree/Particle)  
Thermal correction to Energy= 0.456391  
Thermal correction to Enthalpy= 0.457335  
Thermal correction to Gibbs Free Energy= 0.388939  
Sum of electronic and ZPE= -652.280426  
Sum of electronic and thermal Energies= -652.259693  
Sum of electronic and thermal Enthalpies= -652.258749  
Sum of electronic and thermal Free Energies= -652.327145

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.390	82.013	143.952

C,0,-1.2984031104,-2.0115428824,0.9150974928  
C,0,-2.2888031884,-1.7953417241,-0.2958931785  
H,0,-1.5949634945,-1.3649524775,1.7520085475  
H,0,-1.3036082949,-3.0692596012,1.2091554548  
C,0,-0.0375643421,-1.5619259464,0.2873395686  
C,0,0.1738468993,-0.1662843518,0.1550673351  
C,0,0.751674777,-2.5739332443,-0.465244212  
C,0,-0.7307173694,-0.0371292633,-1.178066531  
H,0,-0.4102817595,0.356254021,0.9287416821  
C,0,-2.0222369,-0.3629969489,-0.8556516676  
H,0,-0.5845444764,0.9883770547,-1.5384126894  
H,0,-0.3745931234,-0.7023393786,-1.9758691463  
C,0,-2.9130511582,0.6674582119,0.0197196179  
H,0,-2.7547340344,-0.3736948896,-1.8131372702  
H,0,-2.0213409021,-2.5066476732,-1.0923178664  
H,0,-3.3008225423,-2.0574400179,0.0365651825  
B,0,1.7445830087,0.5646097432,0.1070689306  
C,0,2.2896162639,0.3606698022,1.6507240161  
C,0,2.8030137952,-0.0723657062,-0.9770040205  
C,0,1.507223128,-2.1662267336,-0.2096477614  
H,0,3.271771726,0.8661676915,1.7126527882  
H,0,1.6430872737,0.8967653324,2.3684119178  
C,0,2.4494728198,-1.0786827937,2.1485592874  
H,0,2.4784873411,2.587561145,-0.5292067051  
H,0,0.8543992957,2.3255418585,-1.0905508672  
C,0,0.9817864868,3.0210351937,0.957023325  
C,0,2.4558413581,0.0677787865,-2.4682660465  
H,0,3.0777378443,-1.1219209647,-0.764211261  
H,0,3.7399423585,0.4879418504,-0.801579755  
H,0,1.257551979,-2.1344534931,-1.3307796343  
H,0,0.1472594444,-3.4468019395,-0.7458877596  
H,0,1.5428631016,-2.9180275202,0.221047809

C,0,-2.4355936827,1.8953533445,0.2334157462  
 C,0,-4.2542435171,0.2506321586,0.5785604636  
 H,0,-3.0079285309,2.6198742528,0.8158962973  
 H,0,-1.4684322317,2.2303172515,-0.1445009065  
 H,0,-4.1431963143,-0.4957859005,1.3806902146  
 H,0,-4.8887197738,-0.2005247987,-0.2003554897  
 H,0,-4.7864447263,1.112159597,0.9984057784  
 H,0,2.8717636347,-1.1382043701,3.1633545988  
 H,0,3.1016183592,-1.6712992796,1.4868319754  
 H,0,1.4706580481,-1.5957445734,2.2024658855  
 H,0,3.3043198388,-0.1678918766,-3.1290909825  
 H,0,2.1337797652,1.094447416,-2.7018135298  
 H,0,1.6302907658,-0.5967821505,-2.7754998477  
 H,0,0.6803817208,4.032923917,0.642576338  
 H,0,1.7515226745,3.1374836023,1.7336003581  
 H,0,0.1114127243,2.559544482,1.4536780266

### Int-ax-T

E(RM11) = -652.717238500

Zero-point correction= 0.434740 (Hartree/Particle)  
 Thermal correction to Energy= 0.455864  
 Thermal correction to Enthalpy= 0.456809  
 Thermal correction to Gibbs Free Energy= 0.386906  
 Sum of electronic and ZPE= -652.282498  
 Sum of electronic and thermal Energies= -652.261374  
 Sum of electronic and thermal Enthalpies= -652.260430  
 Sum of electronic and thermal Free Energies= -652.330332

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.059	82.314	147.122

C,0,1.9353280318,1.8155569828,0.4257655779  
 C,0,2.7479768644,1.0254227812,-0.6744820769  
 H,0,2.0938678878,1.3362383628,1.4010810184  
 H,0,2.2507008741,2.8668050774,0.4399361944  
 C,0,0.5700371102,1.5971354416,-0.087041096  
 C,0,-0.0343204996,0.3294014737,0.1294348584  
 C,0,0.0051638005,2.587092664,-1.0280734343  
 C,0,0.7577766433,-0.4636215352,-1.0146399026  
 H,0,0.3630933055,-0.0817571829,1.0704589466  
 C,0,2.2763557621,-0.437160162,-0.7630618304  
 H,0,0.3422702739,-1.4801828186,-1.006261875  
 H,0,0.5300298435,-0.0330785791,-2.0019996029  
 C,0,2.7561097928,-1.270775594,0.4226368312  
 H,0,2.767407921,-0.8701391282,-1.6538355679  
 H,0,2.5949249072,1.5159591645,-1.6484341031  
 H,0,3.8160334579,1.1126598292,-0.4387206342  
 B,0,-1.7389503213,0.0883415519,0.0442407554  
 C,0,-1.9349611862,-1.3134765652,0.8914590728  
 C,0,-2.4404238294,1.3695399532,0.8119927258  
 C,0,-2.3910390982,-0.0413777988,-1.4689634231  
 H,0,-1.3490532859,-2.1328502841,0.4266710233  
 H,0,-1.5194660013,-1.209721135,1.9128463712  
 C,0,-3.3941541113,-1.7799824806,1.0050360045  
 H,0,-3.4798116166,0.053604908,-1.2985558447  
 H,0,-2.1611153698,0.827598506,-2.1156515242  
 C,0,-2.1675027522,-1.3267798931,-2.2871786118  
 C,0,-1.7665642682,1.8393669014,2.107387079  
 H,0,-3.4787906146,1.0775286797,1.048129669  
 H,0,-2.5601245393,2.2331685047,0.1281615152  
 H,0,-0.6621566834,2.1173317953,-1.7585339858  
 H,0,0.7674727756,3.2210212283,-1.4986326655  
 H,0,-0.6353033953,3.2308683417,-0.3962496243  
 C,0,1.9750918028,-2.1146370167,1.1007625606  
 C,0,4.2228813999,-1.1324115998,0.7647489749

H,0,2.3909346355,-2.7237495513,1.9056506386  
 H,0,0.9095991129,-2.2339084802,0.8988664323  
 H,0,4.4304133757,-0.1757291257,1.2695438075  
 H,0,4.8490742273,-1.1655465313,-0.1402696594  
 H,0,4.5454857479,-1.9363362171,1.4366316691  
 H,0,-3.4958725959,-2.7291460011,1.5536801719  
 H,0,-3.8467623628,-1.9223863065,0.0117313064  
 H,0,-4.0074057393,-1.0324734024,1.5306441659  
 H,0,-2.3362862654,2.6157405802,2.6406365088  
 H,0,-0.7607528983,2.2670694403,1.9240983427  
 H,0,-1.6195391367,0.9981423772,2.8032220943  
 H,0,-2.8792250589,-1.4153243103,-3.1227523628  
 H,0,-2.2885909736,-2.2250344037,-1.6620301365  
 H,0,-1.1619262399,-1.3805469521,-2.7302249948

### Int-ax-U

E(RM11) = -652.716771356

Zero-point correction= 0.435177 (Hartree/Particle)  
 Thermal correction to Energy= 0.456110  
 Thermal correction to Enthalpy= 0.457054  
 Thermal correction to Gibbs Free Energy= 0.388087  
 Sum of electronic and ZPE= -652.281595  
 Sum of electronic and thermal Energies= -652.260662  
 Sum of electronic and thermal Enthalpies= -652.259717  
 Sum of electronic and thermal Free Energies= -652.328685

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.213	82.136	145.153

C,0,-1.7264953014,1.5635672369,-1.1978550761  
 C,0,-2.6310853993,1.3990265768,0.0880010332  
 H,0,-1.939000554,0.7387678779,-1.8910967469  
 H,0,-1.9154012488,2.5389026486,-1.664334375  
 C,0,-0.4014195157,1.434523321,-0.5618637885  
 C,0,0.0317666701,0.1319509086,-0.1991165664  
 C,0,0.2683798764,2.6634563442,-0.0912741923  
 C,0,-0.848542323,-0.0368094484,1.1249154055  
 H,0,-0.4219745956,-0.5755099375,-0.909104818  
 C,0,-2.3506828293,0.062446452,0.800058119  
 H,0,-0.5704546663,-1.011753878,1.5471995644  
 H,0,-0.5698301795,0.7238557618,1.8693991822  
 C,0,-2.933252593,-1.1267272614,0.0401376437  
 H,0,-2.8959279052,0.1017724581,1.7608817058  
 H,0,-2.4183469108,2.2297429368,0.7788315674  
 H,0,-3.67958079,1.5012869728,-0.2185204316  
 B,0,1.6996538633,-0.2870187177,0.0882505851  
 C,0,1.695105836,-1.8824523675,-0.3515504259  
 C,0,2.6547395462,0.6113169969,-0.9011371781  
 C,0,2.1748598356,-0.1809859068,1.661324886  
 H,0,1.1246287417,-2.4669611874,0.3994163453  
 H,0,1.1560171513,-2.0317142814,-1.307009764  
 C,0,3.0891062412,-2.5101657295,-0.4973075511  
 H,0,1.5556530685,-0.833297416,2.3062518185  
 H,0,3.1725416346,-0.6547711979,1.682495708  
 C,0,2.3229077464,1.18618578,2.3497558389  
 C,0,2.2523360344,0.5937602989,-2.3814770593  
 H,0,3.6801056453,0.208893065,-0.8127687815  
 H,0,2.7544304414,1.6598550578,-0.5637329782  
 H,0,0.8843422806,2.4817232303,0.7957454174  
 H,0,-0.4225226393,3.5065618878,0.038621567  
 H,0,0.9707337156,2.9215109796,-0.9063643657  
 C,0,-2.2626451536,-2.2551695592,-0.2028270824  
 C,0,-4.3765918661,-0.9803697193,-0.3883796646  
 H,0,-2.7539420009,-3.0903025329,-0.7057701164  
 H,0,-1.2166994255,-2.3994211533,0.0722443458

H,0,-4.4751040733,-0.3017827396,-1.2503389225  
H,0,-4.9946053743,-0.5668792318,0.423687226  
H,0,-4.7970910788,-1.9493207773,-0.682055615  
H,0,3.0470185018,-3.5889680221,-0.7134990717  
H,0,3.6884650954,-2.3824850154,0.4166988927  
H,0,3.6481151217,-2.034588115,-1.3181993586  
H,0,2.9257356406,1.1784207895,-3.0274410718  
H,0,1.2335396338,-0.9996261441,-2.5384350715  
H,0,2.2315343479,-0.4363806381,-2.7701425871  
H,0,2.8722233127,1.1180416859,3.3013171987  
H,0,1.3484238163,1.6421021369,2.5968606236  
H,0,2.8721033452,1.9001720356,1.7145547761

### Int-ax-V

E(RM11) = -652.717827902

Zero-point correction= 0.435116 (Hartree/Particle)  
Thermal correction to Energy= 0.456083  
Thermal correction to Enthalpy= 0.457027  
Thermal correction to Gibbs Free Energy= 0.387864  
Sum of electronic and ZPE= -652.282712  
Sum of electronic and thermal Energies= -652.261745  
Sum of electronic and thermal Enthalpies= -652.260801  
Sum of electronic and thermal Free Energies= -652.329964

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 286.196	82.223	145.565

C,0,1.8004623445,1.8239092122,0.6295593025  
C,0,2.6779527338,1.2248210987,-0.540034724  
H,0,1.9978226366,1.2671781367,1.5554127277  
H,0,2.0252918088,2.8916107931,0.7495251921  
C,0,0.4573915784,1.5394981974,0.0841260366  
C,0,-0.0231170848,0.207980899,0.1775345194  
C,0,-0.1464967338,2.5534006514,-0.8184563951  
C,0,0.7920888108,-0.3433395909,-1.0944623278  
H,0,0.45967585,-0.2786472251,1.0393521011  
C,0,2.3089326388,-0.2413591941,-0.8363840005  
H,0,0.4574264403,-1.3761318106,-1.2491249109  
H,0,0.5354848179,0.2124429601,-2.0067093283  
C,0,2.854043339,-1.2102547941,0.2110469851  
H,0,2.8227262608,-0.5033103709,-1.7794730451  
H,0,2.5085902149,1.827730391,-1.44560765  
H,0,3.734554614,1.346826391,-0.2710832648  
B,0,-1.7086100519,-0.1953033089,0.2668933156  
C,0,-2.0926738555,0.2735910236,1.8025933774  
C,0,-2.6926489287,0.5259267503,-0.8312341601  
C,0,-1.7676537496,-1.834728984,0.1551123159  
H,0,-3.1645243988,0.0535118625,1.9553477335  
H,0,-1.5573070721,-0.355117251,2.5396226372  
C,0,-1.8600436412,1.7462214564,2.1521513676  
H,0,-1.3463719374,-2.2127655088,-0.7964674824  
H,0,-1.1425790777,-2.277996507,0.9554410128  
C,0,-3.1888821931,-2.4067020224,0.2827757705  
C,0,-2.5143979012,0.1109361283,-2.3000850838  
H,0,-2.6941322139,1.6286543031,-0.7565549632  
H,0,-3.7175816079,0.2440996874,-0.527201063  
H,0,-0.7177405329,2.0896923359,-1.6299571925  
H,0,0.5936770723,3.2698809344,-1.1980542077  
H,0,-0.8746512236,3.1085123843,-0.2030700018  
C,0,2.1506344294,-2.2309231374,0.7063642659  
C,0,4.2948802883,-0.9963794081,0.6168159698  
H,0,2.6104740984,-2.9295380146,1.4079576521  
H,0,1.1057936397,-2.4118729583,0.4498344404  
H,0,4.4047655639,-0.112898516,1.2651766618  
H,0,4.938606048,-0.8373118417,-0.2623573956

H,0,4.6769975298,-1.8620530479,1.1703572379  
H,0,-2.1591208941,2.0008639264,3.1803981224  
H,0,-2.4181307542,2.4132693323,1.4751071686  
H,0,-0.7882336344,2.0190840406,2.0765967942  
H,0,-3.291879722,0.5232048708,-2.9619694331  
H,0,-2.5443139806,-0.9851805071,-2.4010925042  
H,0,-1.5436219201,0.4314691636,-2.7165277888  
H,0,-3.2044212515,-3.5075035369,0.2878053476  
H,0,-3.8246460966,-2.0745723746,-0.5526322206  
H,0,-3.672369961,-2.0663887702,1.2109666275

### Axial TS2 Structures

#### TS2-ax-A

E(RM11) = -652.717871169

Zero-point correction= 0.434781 (Hartree/Particle)  
Thermal correction to Energy= 0.455315  
Thermal correction to Enthalpy= 0.456260  
Thermal correction to Gibbs Free Energy= 0.388143  
Sum of electronic and ZPE= -652.283090  
Sum of electronic and thermal Energies= -652.262556  
Sum of electronic and thermal Enthalpies= -652.261612  
Sum of electronic and thermal Free Energies= -652.329728

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.715	80.701	143.363

H,0,-0.5514654825,-0.0209138118,-1.2146193992  
C,0,-2.5040724726,0.1716495424,0.7045032798  
H,0,-0.8068982802,-1.2407804727,0.8982904254  
H,0,-0.6694716557,0.1724228559,1.9276168221  
C,0,-3.106590499,-0.6806741836,-0.4035207609  
H,0,-3.0311189269,-0.1196779518,1.6301746508  
H,0,-2.5416375628,2.1595709693,1.5337287403  
H,0,-3.620617257,1.980158563,0.1418623031  
B,0,1.545549852,-0.5349055569,-0.2169360449  
C,0,1.4678136449,-1.7738160008,-1.3016272558  
C,0,2.6956845955,0.5518672689,-0.6954534577  
C,0,1.8550080216,-1.1047316146,1.3035627427  
H,0,1.4350000346,-1.3744103359,-2.3331515556  
H,0,2.4109554108,-2.3461716744,-1.2496714936  
C,0,0.2908255952,-2.7471940656,-1.1332659789  
H,0,1.6904277319,-0.345729144,2.0949322685  
H,0,1.1666118843,-1.9319527718,1.5661727347  
C,0,3.2932245496,-1.6228343858,1.4610308005  
C,0,2.3474230337,1.402796453,-1.9261576546  
H,0,3.6028373207,-0.0323435413,-0.9332565901  
H,0,3.0077581746,1.2226478414,0.129056203  
H,0,1.2599300878,1.5831707767,1.6504514064  
H,0,-0.0343164315,2.8437253672,1.8217156719  
H,0,1.1987545542,2.9677142208,0.5463461823  
C,0,-3.5103482251,-0.1956660874,-1.5794654816  
C,0,-3.2784717363,-2.1404779594,-0.054575602  
H,0,-3.9458159322,-0.8541034882,-2.3327320336  
H,0,-3.4414471714,0.8617134969,-1.8377938674  
H,0,-4.0113637885,-2.247881807,0.7601033509  
H,0,-2.3404243014,-2.597879002,0.2903293488  
H,0,-3.6338608359,-2.7162273779,-0.9172457533  
H,0,0.3367824269,-3.6024472527,-1.8250926564  
H,0,-0.6754271978,-2.2472551428,-1.3231345238  
H,0,0.254107337,-3.1646882288,-0.112051128  
H,0,3.1871365244,2.024324293,-2.2734542867  
H,0,1.5067692141,2.095138292,-1.7336555578  
H,0,2.0382199852,0.7681474138,-2.771116062  
H,0,3.4765143013,-2.0773350289,2.4469591485

H,0,4.0221167232,-0.808584757,1.3326101685  
H,0,3.5244681291,-2.3832075507,0.6999979533

### TS2-ax-B

E(RM11) = -652.718262148

Zero-point correction= 0.434591 (Hartree/Particle)  
Thermal correction to Energy= 0.455258  
Thermal correction to Enthalpy= 0.456202  
Thermal correction to Gibbs Free Energy= 0.387000  
Sum of electronic and ZPE= -652.283672  
Sum of electronic and thermal Energies= -652.263005  
Sum of electronic and thermal Enthalpies= -652.262060  
Sum of electronic and thermal Free Energies= -652.331262

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	285.678	80.691 145.647

C,0,-1.8519905221,1.631911342,-1.2071472941  
C,0,-2.7121188001,1.7968795423,0.0812964155  
H,0,-2.2008681632,0.7637787429,-1.7806003313  
H,0,-1.9119266741,2.5383851446,-1.8241838038  
C,0,-0.4605560391,1.4007679607,-0.7071142139  
C,0,-0.0690198676,0.1234275357,-0.2668183886  
C,0,0.4262954057,2.5940974845,-0.5891915018  
C,0,-0.8417131433,0.6087912439,1.1662271195  
H,0,-0.7733545161,-0.6447174271,-0.6270223597  
C,0,-2.371965852,0.6543572012,1.0432316361  
H,0,-0.4557676812,-0.2040005921,1.7964345491  
H,0,-0.4573449286,1.5426418765,1.5943580173  
C,0,-2.9717289359,-0.701359402,0.6899425419  
H,0,-2.7549906529,0.9107208595,2.0474743471  
H,0,-2.4471693335,2.7526755604,0.560205563  
H,0,-3.7793873162,1.8477903856,-0.1686851945  
B,0,1.484502151,-0.5095956739,-0.1065341601  
C,0,1.9706643253,-0.7191761151,-1.6732056306  
C,0,2.616651239,0.4143542722,0.6528256108  
C,0,1.2723224139,-1.9507365929,0.6664287692  
H,0,1.9933843212,0.2631597266,-2.187968347  
H,0,3.0260372186,-1.0471239294,-1.6577188389  
C,0,1.1670062047,-1.7115307197,-2.5254811281  
H,0,0.8664313263,-1.8178095059,1.6910131857  
H,0,0.5105293893,-2.5525329119,0.1322018147  
C,0,2.5529885917,-2.7894013915,0.7839428758  
C,0,2.3837608736,0.8023854912,2.121771414  
H,0,2.8825922555,1.3153565456,0.0686500351  
H,0,3.5388532963,-0.1922304944,0.6128004659  
H,0,1.186382776,2.4644949053,0.1866957231  
H,0,-0.1436521731,3.522155576,-0.4437057339  
H,0,0.95943313,2.6689211078,-1.5523703102  
C,0,-3.8770220919,-0.8781546419,-0.2749640453  
C,0,-2.4941242029,-1.8556432173,1.537366425  
H,0,-4.3015927682,-1.8657031325,-0.4620048214  
H,0,-4.2351585081,-0.0663416977,-0.9095960217  
H,0,-2.5108635908,-1.5938507653,2.6067806424  
H,0,-1.4585606928,-2.1304638534,1.2849567817  
H,0,-3.1233620554,-2.7406382613,1.3873736992  
H,0,1.548762374,-1.7976735589,-3.5546346662  
H,0,0.1042089277,-1.4243973863,-2.6030559479  
H,0,1.1916438359,-2.719354144,-2.0828430567  
H,0,3.288351038,1.1998862139,2.6072875248  
H,0,2.054829992,-0.0686706966,2.7121024173  
H,0,1.6059267748,1.5763623076,2.2382512813  
H,0,2.375495583,-3.7823601879,1.2251545797  
H,0,3.3013680547,-2.2821999461,1.4119756833  
H,0,3.0146111011,-2.944583721,-0.2042457428

### TS2-ax-C

E(RM11) = -652.714206390

Zero-point correction= 0.434511 (Hartree/Particle)  
Thermal correction to Energy= 0.455180  
Thermal correction to Enthalpy= 0.456124  
Thermal correction to Gibbs Free Energy= 0.387577  
Sum of electronic and ZPE= -652.279695  
Sum of electronic and thermal Energies= -652.259026  
Sum of electronic and thermal Enthalpies= -652.258082  
Sum of electronic and thermal Free Energies= -652.326630

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	285.630	80.944 144.270

C,0,1.2184203215,-2.1651027114,-0.7570986602  
C,0,2.3367197091,-1.8763157398,0.2841436404  
H,0,1.4448107738,-1.6887641493,-1.7185650376  
H,0,1.111180797,-3.2485268051,-0.9033383986  
C,0,-0.0282872039,-1.5708627554,-0.173429962  
C,0,-0.2936302889,-0.2003731398,-0.3245963601  
C,0,-0.8842875818,-2.4917178326,0.6300474152  
C,0,0.7385677078,-0.112268514,1.037437777  
H,0,0.3488211032,0.2305296498,-1.1097206062  
C,0,2.2227521992,-0.4297699012,0.7805614552  
H,0,0.5484333308,0.9544904372,1.2109201955  
H,0,0.3404679202,-0.6401928582,1.9132347809  
C,0,2.8878818329,0.631386118,-0.0849453711  
H,0,2.7158673107,-0.367668112,1.7667058971  
H,0,2.1894946415,-2.5540166325,1.1394274727  
H,0,3.3279406786,-2.0938249659,-0.1355496022  
B,0,-1.758549305,0.6405809539,-0.1193062608  
C,0,-1.5450507968,2.0132383316,-1.0126970009  
C,0,-2.9373857771,-0.2945319617,-0.7956949042  
C,0,-2.1210946673,1.0801520137,1.4326296574  
H,0,-1.4735245749,1.7587317684,-2.0885148426  
H,0,-2.4528243393,2.6346439846,-0.9201707429  
C,0,-0.3334222336,2.8816020522,-0.6374058583  
H,0,-1.3055245367,1.6606926001,1.9059112393  
H,0,-2.9324612693,1.8218755302,1.3227753896  
C,0,-2.6063234557,0.0240934576,2.4397452425  
C,0,-4.3066524539,0.398959426,-0.8614131231  
H,0,-3.0759339904,-1.2512266601,-0.2586893003  
H,0,-2.6367864752,-0.5783736408,-1.8238140048  
H,0,-1.6046005188,-1.9524432222,1.2502819409  
H,0,-0.2794526157,-3.1895989586,1.2279153486  
H,0,-1.450967412,-3.0904685361,-0.1017425809  
C,0,3.3308313776,0.4098682644,-1.3241590269  
C,0,3.0730094014,1.9708860493,0.5884276603  
H,0,3.8107040081,1.2065969452,-1.8946047153  
H,0,3.2506389252,-0.560574036,-1.8155692669  
H,0,3.7681606963,1.8722847349,1.4365908975  
H,0,2.1287496997,2.3692079329,0.9862990047  
H,0,3.4804838948,2.7127582315,-0.1084822492  
H,0,-0.2873800234,3.822892698,-1.2067862285  
H,0,0.6190623111,2.3576092427,-0.829874422  
H,0,-0.351280949,3.1555080617,0.431391509  
H,0,-5.0832179794,-0.2336878514,-1.3191025499  
H,0,-4.253806025,1.3287170017,-1.4466411371  
H,0,-4.6577632328,0.6714374141,0.1466142314  
H,0,-3.0673331824,0.475701103,3.331675302  
H,0,-1.7868452069,-0.6140501667,2.8130650545  
H,0,-3.3610418949,-0.6413511419,1.9883061313

### TS2-ax-D

E(RM11) = -652.715266714

Zero-point correction= 0.434941 (Hartree/Particle)  
Thermal correction to Energy= 0.455453  
Thermal correction to Enthalpy= 0.456397  
Thermal correction to Gibbs Free Energy= 0.388516  
Sum of electronic and ZPE= -652.280325  
Sum of electronic and thermal Energies= -652.259814  
Sum of electronic and thermal Enthalpies= -652.258870  
Sum of electronic and thermal Free Energies= -652.326751

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.801 80.759 142.868

C,0,-1.4073371151,2.1072408853,-0.4825797132  
C,0,-2.5785461361,1.6524502875,0.4289901424  
H,0,-1.5740047525,1.7984712012,-1.5219856603  
H,0,-1.2978428888,3.1995282333,-0.4452381941  
C,0,-0.1796368807,1.4273006678,0.0561871685  
C,0,0.1240502386,0.1111273711,-0.3178641395  
C,0,0.6580198322,2.2137189826,1.0117466192  
C,0,-0.9767881236,-0.1630823321,0.9864771293  
H,0,-0.4939142285,-0.2017343703,-1.1749372255  
C,0,-2.455395905,0.1473515694,0.6981517647  
H,0,-0.7506973209,-1.2367373746,1.018679683  
H,0,-0.6428651676,0.2436640861,1.9484956682  
C,0,-3.0358779682,-0.7784130712,-0.3616576483  
H,0,-2.9975349404,-0.0823714119,1.6322731892  
H,0,-2.4936065149,2.1864324004,1.3884033569  
H,0,-3.5496925503,1.9215763676,-0.007166222  
B,0,1.597113418,-0.7169052672,-0.1878001562  
C,0,1.4810802572,-1.9028022128,-1.3313667724  
C,0,2.8079887543,0.3298764561,-0.589222687  
C,0,1.8853149343,-1.4360576657,1.2725943969  
H,0,1.4209364132,-1.4634239399,-2.3449538999  
H,0,2.4232253558,-2.4801967827,-1.3199308364  
C,0,0.3028081728,-2.8758659273,-1.1698395903  
H,0,1.0898995073,-2.1597486066,1.5376801893  
H,0,2.7678342662,-2.0751420301,1.0866725409  
C,0,2.194860751,-0.5944046217,2.5224912122  
C,0,2.5887291424,1.1536107867,-1.8676983818  
H,0,3.7177781175,-0.2829506681,-0.7264662599  
H,0,3.0636737973,1.0226266274,0.2336130679  
H,0,1.3383960076,1.5754648434,1.581228571  
H,0,0.0428458422,2.83671448,1.6774404878  
H,0,1.2706413788,2.8895844679,0.3922167289  
C,0,-3.4360562981,-0.368535435,-1.5669084099  
C,0,-3.1864765346,-2.2180124241,0.0702328309  
H,0,-3.8553375067,-1.0755692389,-2.2845343595  
H,0,-3.3766780768,0.6725749007,-1.8866754289  
H,0,-3.9023485938,-2.2888316426,0.9037341936  
H,0,-2.2367425944,-2.6477195559,0.4194982407  
H,0,-3.5509833705,-2.8433775042,-0.7531920515  
H,0,0.3129035902,-3.6901267594,-1.9108597044  
H,0,-0.6652147044,-2.3590021304,-1.2927976363  
H,0,0.3006233656,-3.3485993057,-0.1736380363  
H,0,3.4441939801,1.8013922532,-2.1149548143  
H,0,1.7063190337,1.8150662879,-1.7886547576  
H,0,2.4106356886,0.5025308133,-2.7363320681  
H,0,2.5759041331,-1.2089027973,3.3526525413  
H,0,1.3065024074,-0.0707746201,2.9153235338  
H,0,2.9603900268,0.1702187166,2.3148752767

### TS2-ax-E

E(RM11) = -652.716826622

Zero-point correction= 0.435403 (Hartree/Particle)  
Thermal correction to Energy= 0.455521  
Thermal correction to Enthalpy= 0.456465  
Thermal correction to Gibbs Free Energy= 0.389744  
Sum of electronic and ZPE= -652.281424  
Sum of electronic and thermal Energies= -652.261306  
Sum of electronic and thermal Enthalpies= -652.260362  
Sum of electronic and thermal Free Energies= -652.327083

H,0,0.4483864797,-0.4605852281,1.1881873577  
C,0,1.9904977155,-0.0133299878,-0.9560269461  
H,0,0.0218995345,-1.0079204668,-1.1981487969  
H,0,0.0503352029,0.6719971511,-1.7143141986  
C,0,2.5719090786,-1.1583517515,-0.1332062499  
H,0,2.3127026142,-0.1870333768,-1.9985499722  
H,0,2.170574116,2.1037102781,-1.3186143777  
H,0,3.5238490553,1.4651133165,-0.3803019008  
B,0,-1.8142905218,-0.4088301928,0.7196304356  
C,0,-2.1210872606,-0.1493458766,2.3242115383  
C,0,-2.9123577551,0.3536990703,-0.2456214463  
C,0,-1.8384498643,-2.0435879414,0.075094977  
H,0,-3.1531393434,-0.4898420273,2.5232478743  
H,0,-1.4814123253,-0.8088237241,2.9416545734  
C,0,-1.977773932,1.2907629929,2.8316196302  
H,0,-1.0404432629,-2.5405619799,1.0575324821  
H,0,-2.7697238929,-2.3866209529,0.9554198282  
C,0,-1.8373886465,-2.6015148603,-0.9713326239  
C,0,-4.2949071125,-0.3201830248,-0.2250878735  
H,0,-3.0615215841,1.4021431363,0.0713025456  
H,0,-2.5711226871,0.4090741848,-1.3009749055  
H,0,-1.3829944045,2.2453620836,-0.7293456829  
H,0,0.0995087742,3.2822840524,-0.6927024948  
H,0,-0.9558140101,3.1537196263,0.7300799679  
C,0,3.5612125513,-1.0051432099,0.749990336  
C,0,1.9713044057,-2.5170159929,-0.4018420014  
H,0,3.9659193934,-1.8671368167,1.2826981247  
H,0,4.0097556312,-0.0378547758,0.9798609725  
H,0,1.8665895312,-2.6999162482,-1.4827426311  
H,0,0.9662603316,-2.5961892901,0.0411515361  
H,0,2.5919089012,-3.3128390981,0.0260629644  
H,0,-2.2711254985,1.4085004047,3.8859691801  
H,0,-2.5989401355,1.9851321481,2.2421804076  
H,0,-0.9321051565,1.6445751997,2.7632610083  
H,0,-5.0447514861,0.235234499,-0.8093668982  
H,0,-4.6745551574,-0.3987292153,0.8052645105  
H,0,-4.2552850469,-1.3429413155,-0.6275699623  
H,0,-2.3664850839,-3.5638638254,-1.0462486601  
H,0,-0.8249903594,-2.7935368451,-1.3637069466  
H,0,-2.3266153659,-1.9100027095,-1.6761823982

### TS2-ax-F

E(RM11) = -652.716506596

Zero-point correction= 0.434438 (Hartree/Particle)  
Thermal correction to Energy= 0.455056  
Thermal correction to Enthalpy= 0.456000  
Thermal correction to Gibbs Free Energy= 0.387466  
Sum of electronic and ZPE= -652.282068  
Sum of electronic and thermal Energies= -652.261451  
Sum of electronic and thermal Enthalpies= -652.260506  
Sum of electronic and thermal Free Energies= -652.329041

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.552 80.860 144.243

C,0,-1.4972321312,2.2083085422,-0.2260167217

C,0,-2.6592383255,1.5740742497,0.5899145857  
H,0,-1.650840713,2.0243045672,-1.296948404  
H,0,-1.4430699911,3.289059786,-0.0383550367  
C,0,-0.2543376762,1.5145192548,0.2472947938  
C,0,0.0872238865,0.2414042739,-0.2446011368  
C,0,0.522834505,2.2111984209,1.3131990277  
C,0,-1.0519912396,-0.2669351757,0.9108002704  
H,0,-0.4549078888,0.0317544356,-1.1798424055  
C,0,-2.5037024409,0.0525016325,0.533390848  
H,0,-0.7939085091,-1.3312521975,0.8396452112  
H,0,-0.8116542666,0.0404471369,1.9374685728  
C,0,-2.9087307759,-0.5970079181,-0.7862927649  
H,0,-3.1381560926,-0.403560262,1.3143569988  
H,0,-2.574903236,1.9009854957,1.6383512897  
H,0,-3.6321766461,1.9236603496,0.2223355093  
B,0,1.5558617944,-0.57037208,-0.0928749826  
C,0,1.4262503048,-1.9083801667,-1.0469930739  
C,0,2.6854856584,0.4820770861,-0.6844437527  
C,0,1.9212206335,-1.0125285369,1.4729256352  
H,0,2.3641815852,-2.4844412144,-0.9471822515  
H,0,0.6488170122,-2.6000075573,-0.6625841996  
C,0,1.1729770188,-1.657535194,-2.5416119603  
H,0,3.0144121771,-0.9069064888,1.5929403677  
H,0,1.5072123266,-0.3227096128,2.2332383621  
C,0,1.5568973037,-2.4416915422,1.9158503185  
C,0,4.0376549478,-0.174720579,-0.9976702848  
H,0,2.8612189545,1.2996160131,0.0420216939  
H,0,2.3189620878,0.9825856557,-1.6026732975  
H,0,1.2510696164,1.5557384171,1.7968037953  
H,0,-0.1351423838,2.7006248187,2.0462059425  
H,0,1.0812062442,3.0072876683,0.7927951299  
C,0,-3.5510017756,0.0523185327,-1.7599622356  
C,0,-2.5571356171,-2.0591629684,-0.9247680632  
H,0,-3.8492227489,-0.4694328353,-2.6706199902  
H,0,-3.8091006203,1.1103623318,-1.6989910297  
H,0,-2.8110748735,-2.6180666786,-0.0108189462  
H,0,-1.4779006428,-2.1920405338,-1.100339631  
H,0,-3.0909204009,-2.5125533763,-1.7679353562  
H,0,1.1967024761,-2.5822924676,-3.1388719463  
H,0,1.928008914,-0.9753421074,-2.9620047793  
H,0,0.1903267159,-1.1911783578,-2.7296748212  
H,0,4.8089141888,0.5533176942,-1.2935928797  
H,0,3.9443298693,-0.9050970899,-1.8157122909  
H,0,4.422767655,-0.7250639272,-0.1247263174  
H,0,1.8601484558,-2.6467058122,2.9544544659  
H,0,2.0461343796,-3.1905851318,1.2773941505  
H,0,0.4741473043,-2.6445600309,1.8565377101

H,0,-1.1337012864,2.1864934218,-1.8458677665  
C,0,0.3100582257,0.9734028983,-0.79547688  
C,0,0.6530862764,-0.3242820235,-0.3671518792  
C,0,1.2376371042,2.1292992167,-0.6566991698  
C,0,-0.0671618893,0.120079006,1.0829757079  
H,0,-0.070939186,-1.055355558,-0.7619252475  
C,0,-1.5974471541,0.2095510692,0.9717166418  
H,0,0.2984484177,-0.7087055355,1.7040009585  
H,0,0.3404751158,1.0394130103,1.5216285626  
C,0,-2.2281948723,-1.1273227934,0.6038760232  
H,0,-1.9686688302,0.4589168626,1.9821470875  
H,0,-1.6461433007,2.319018232,0.540529119  
H,0,-2.9906374022,1.4477582971,-0.2060308087  
B,0,2.1932572933,-1.0070467512,-0.2732525447  
C,0,2.6032317024,-1.1248619254,-1.8692902766  
C,0,3.3558322038,-0.1724544173,0.5454442153  
C,0,1.9893921743,-2.4953262254,0.4133852716  
H,0,1.808091775,-1.644641602,-2.4380332822  
H,0,2.6661170268,-0.111060508,-2.3157187623  
C,0,3.9367288308,-1.8442146513,-2.1172946238  
H,0,2.990485892,-2.9110517029,0.6291395742  
H,0,1.5172527234,-2.4216741397,1.4158126612  
C,0,1.2169517904,-3.5276011486,-0.4253115082  
C,0,3.1010455077,0.2049921889,2.0147656131  
H,0,3.7035090656,0.722359137,-0.0072238872  
H,0,4.2328815999,-0.8436532762,0.5343136579  
H,0,2.0217705699,1.9368190219,0.0817567146  
H,0,0.7064124469,3.0694665312,-0.453412348  
H,0,1.7353294216,2.2279264908,-1.6369328402  
C,0,-3.1141664918,-1.2816943743,-0.382536185  
C,0,-1.7997055531,-2.2918518653,1.4640536388  
H,0,-3.5573378649,-2.2585050808,-0.5824376969  
H,0,-3.4389632172,-0.4599381661,-1.0225277271  
H,0,-1.8519837994,-2.0310476769,2.5325282259  
H,0,-0.7603295448,-2.5834236019,1.2488683126  
H,0,-2.4360558341,-3.1669645708,1.2880056534  
H,0,4.1607834809,-1.9735997043,-3.1877442506  
H,0,3.9375443787,-2.8452412333,-1.6572291822  
H,0,4.7744703988,-1.2871194896,-1.6718961546  
H,0,4.0207214198,0.5034093835,2.5409956483  
H,0,2.6699188294,-0.6419063143,2.5729791107  
H,0,2.3989861558,1.0494918796,2.1216504114  
H,0,1.0336667247,-4.4697197449,0.1155360739  
H,0,1.7718553355,-3.7797652328,-1.3414237088  
H,0,0.2327971568,-3.1526672351,-0.757110063

*TS2-ax-H*

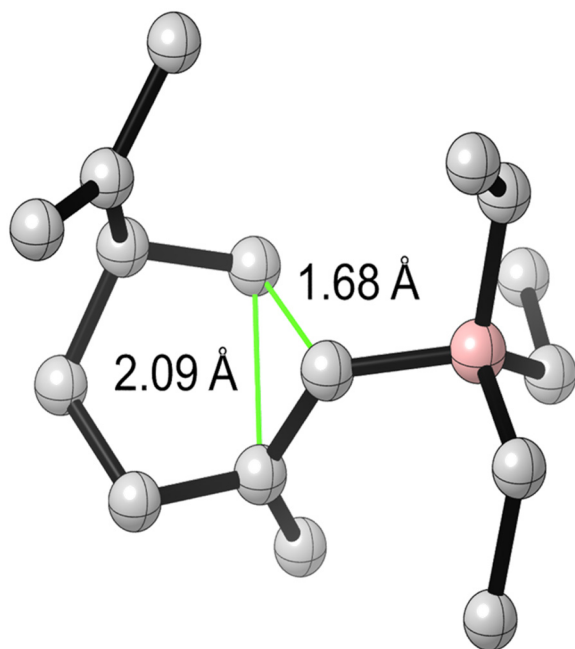
*TS2-ax-G*

E(RM11) = -652.718549727

Zero-point correction= 0.434652 (Hartree/Particle)  
Thermal correction to Energy= 0.455101  
Thermal correction to Enthalpy= 0.456045  
Thermal correction to Gibbs Free Energy= 0.388294  
Sum of electronic and ZPE= -652.283898  
Sum of electronic and thermal Energies= -652.263448  
Sum of electronic and thermal Enthalpies= -652.262504  
Sum of electronic and thermal Free Energies= -652.330256

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	285.580	80.649 142.596

C,0,-1.0778082378,1.2532206661,-1.2698265618  
C,0,-1.9226467437,1.37918763,0.0373111254  
H,0,-1.4486953459,0.4146695957,-1.872410664



E(RM11) = -652.718714242

Zero-point correction= 0.434488 (Hartree/Particle)  
 Thermal correction to Energy= 0.454988  
 Thermal correction to Enthalpy= 0.455932  
 Thermal correction to Gibbs Free Energy= 0.387712  
 Sum of electronic and ZPE= -652.284226  
 Sum of electronic and thermal Energies= -652.263726  
 Sum of electronic and thermal Enthalpies= -652.262782  
 Sum of electronic and thermal Free Energies= -652.331003

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.509	80.707	143.582

H,0,-0.7201321703,-0.7733057797,-0.7224105517  
 C,0,-2.2731001707,0.4679625421,1.0025601909  
 H,0,-0.3808260443,-0.4338577186,1.7581607647  
 H,0,-0.3481266435,1.314089314,1.5821765537  
 C,0,-2.8858544455,-0.8792091281,0.6439938096  
 H,0,-2.6580378505,0.7228471028,2.0063952175  
 H,0,-2.3613705299,2.5731411242,0.5622129512  
 H,0,-3.6658128007,1.6672178961,-0.2122486331  
 B,0,1.527410913,-0.7607926673,-0.186169138  
 C,0,1.9045518476,-1.073382607,-1.7645174333  
 C,0,2.7169587585,0.1271160986,0.526979721  
 C,0,1.3244421593,-2.1744179276,0.6438062529  
 H,0,2.8732337891,-1.607167312,-1.7653345954  
 H,0,1.1825871493,-1.7811568345,-2.2108863724  
 C,0,2.008580397,0.1430243608,-2.6930254693  
 H,0,2.3292126455,-2.5568269484,0.9010744114  
 H,0,0.8502250437,-2.0099849978,1.6338219957  
 C,0,0.562506496,-3.2939944091,-0.0862148243  
 C,0,2.5289337588,0.5112372477,2.0044766062  
 H,0,2.9985406493,1.0290429385,-0.0472901113  
 H,0,3.6139437994,-0.5159925385,0.4649643218  
 H,0,1.3520863348,2.2350529592,0.1837013162  
 H,0,-0.0432285683,3.3254749809,-0.2036383314  
 H,0,0.9845465129,2.6729338611,-1.4948904338  
 C,0,-3.7215278237,-1.0639029859,-0.3802910805  
 C,0,-2.5025084609,-2.0148457684,1.5617360167  
 H,0,-4.154683543,-2.0465588264,-0.5733735407

H,0,-4.0134884484,-0.2610746034,-1.0588402518  
 H,0,-2.6234815986,-1.7234064186,-2.6166388113  
 H,0,-1.4502104182,-2.3031596952,1.4199132188  
 H,0,-3.1199162735,-2.9005895001,1.3719545513  
 H,0,2.3664358894,-0.1158355848,-3.7013634813  
 H,0,2.6920725526,0.9069959019,-2.2890372838  
 H,0,1.0222817061,0.6233267228,-2.8343615958  
 H,0,3.448363911,0.9069968324,2.4628694309  
 H,0,2.2166701514,-0.3593482045,2.6026976399  
 H,0,1.7552487717,1.2854457881,2.1445387201  
 H,0,0.3255633031,-4.1479115727,0.5686330131  
 H,0,1.1535685936,-3.683855733,-0.9272077413  
 H,0,-0.3918419058,-2.9420967226,-0.5169567187

### TS2-ax-I

E(RM11) = -652.717287584

Zero-point correction= 0.434322 (Hartree/Particle)  
 Thermal correction to Energy= 0.454992  
 Thermal correction to Enthalpy= 0.455936  
 Thermal correction to Gibbs Free Energy= 0.386679  
 Sum of electronic and ZPE= -652.282966  
 Sum of electronic and thermal Energies= -652.262295  
 Sum of electronic and thermal Enthalpies= -652.261351  
 Sum of electronic and thermal Free Energies= -652.330609

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.512	80.845	145.766

C,0,-0.746627506,1.8194064866,-0.3625747107  
 C,0,-1.8853351241,1.2997171921,0.5556862143  
 H,0,-0.9758533772,1.5951421102,-1.4122840192  
 H,0,-0.6103445448,2.9020014781,-0.2377778728  
 C,0,0.4833651318,1.0734395206,0.0723130463  
 C,0,0.7624395788,-0.2156807079,-0.4097417354  
 C,0,1.3517683949,1.7625179861,1.0732999484  
 C,0,-0.3467197499,-0.6039486458,0.8413080507  
 H,0,0.1572906486,-0.4454465541,-1.3028154038  
 C,0,-1.8064913542,-0.2284260355,0.5571317496  
 H,0,-0.1491653565,-1.6795925145,0.7648755987  
 H,0,-0.0149312124,-0.3034173983,1.8436134066  
 C,0,-2.3374183579,-0.9107395721,-0.7000443575  
 H,0,-2.399090424,-0.6243658232,1.4011335709  
 H,0,-1.7117732026,1.6659276182,1.5798097833  
 H,0,-2.8623286563,1.684800998,0.2383192544  
 B,0,2.2113663014,-1.0716910052,-0.3080962813  
 C,0,1.990288631,-2.3602532361,-1.3120443134  
 C,0,3.3790386928,-0.0528783807,-0.8723842432  
 C,0,2.6217888538,-1.5794452083,1.2219068796  
 H,0,1.2528761448,-3.0635961373,-0.8740768992  
 H,0,1.5450453123,-2.0418589064,-2.2750794612  
 C,0,3.2842000424,-3.131615891,-1.6114963809  
 H,0,3.7250290335,-1.649577889,1.2308973845  
 H,0,2.4046883191,-0.8259342014,2.0042144497  
 C,0,2.0849353145,-2.9350777016,1.7173758219  
 C,0,3.0819217606,0.6060774912,-2.2265299914  
 H,0,4.314068242,-0.6340970163,-0.958538299  
 H,0,3.6171482811,0.7336422535,-0.1306283542  
 H,0,2.0370499388,1.0729331918,1.573078288  
 H,0,0.7629373827,2.3447781295,1.796564538  
 H,0,1.9617066407,2.4732627966,0.4903176124  
 C,0,-3.020697977,-0.2710679361,-1.6515318226  
 C,0,-2.0677159899,-2.3938914945,-0.7963941557  
 H,0,-3.4116129461,-0.8143116286,-2.5133178612  
 H,0,-3.222242326,0.8004605862,-1.6199555781  
 H,0,-2.2753501635,-2.8994915867,0.1592957245

H,0,-1.0138295539,-2.5905654275,-1.049244774  
H,0,-2.6881582239,-2.855128688,-1.5734894765  
H,0,3.1105377406,-4.0767746759,-2.14891165  
H,0,3.8308816604,-3.3704072849,-0.6848301464  
H,0,3.9631968693,-2.5237671396,-2.2290133448  
H,0,3.9080046224,1.2320908314,-2.5979752723  
H,0,2.1884883904,1.2557902114,-2.1778652452  
H,0,2.8739825429,-0.15514828,-2.9954208427  
H,0,2.4690475538,-3.1934664399,2.7165001458  
H,0,2.3733122412,-3.7485576838,1.0361836326  
H,0,0.9849670863,-2.9687341414,1.7894972124

### TS2-ax-J

E(RM11) = -652.716130262

Zero-point correction= 0.435051 (Hartree/Particle)  
Thermal correction to Energy= 0.455460  
Thermal correction to Enthalpy= 0.456404  
Thermal correction to Gibbs Free Energy= 0.388421  
Sum of electronic and ZPE= -652.281080  
Sum of electronic and thermal Energies= -652.260670  
Sum of electronic and thermal Enthalpies= -652.259726  
Sum of electronic and thermal Free Energies= -652.327709

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.806	80.556	143.083

C,0,-0.7152210814,1.7909202777,-0.5298371942  
C,0,-1.8637862564,1.3949097999,0.435295892  
H,0,-0.9409924254,1.4467508836,-1.547507539  
H,0,-0.5680833097,2.8791759629,-0.5354742444  
C,0,0.5131921269,1.091454944,-0.0076435357  
C,0,0.7869412373,-0.2421444848,-0.3487817653  
C,0,1.3981898244,1.8925335292,0.8931883078  
C,0,-0.314909865,-0.4298951041,0.9766338784  
H,0,0.1413534353,-0.5717654233,-1.1799729488  
C,0,-1.7781267938,-0.1188941765,0.6414159245  
H,0,-0.0864237588,-1.498269408,1.0782445141  
H,0,-0.0000048764,0.0342448848,1.9193005499  
C,0,-2.3022487939,-0.971844311,-0.5083388069  
H,0,-2.3669513878,-0.401386677,1.532405991  
H,0,-1.7021918877,1.8938529108,1.4039277656  
H,0,-2.8390214111,1.729737519,0.0604956497  
B,0,2.2339945799,-1.1193446441,-0.2160331541  
C,0,2.0226551045,-2.3314858085,-1.3242301349  
C,0,3.4757373562,-0.129899461,-0.6533067932  
C,0,2.4944233202,-1.8127280268,1.258825163  
H,0,1.2751211599,-3.0538742185,-0.9360798277  
H,0,1.5820924674,-1.9368602768,-2.2607949466  
C,0,3.2962601261,-3.1057510754,-1.6917259345  
H,0,1.6663463086,-2.5000087342,1.5275799125  
H,0,3.3520678224,-2.4906696599,1.103908526  
C,0,2.832727833,-0.94487992,2.4821053772  
C,0,3.3102422789,0.5328642491,-2.0287856841  
H,0,4.3946957182,-0.7434281893,-0.6661718684  
H,0,3.6847358924,0.654524848,0.0962722328  
H,0,2.0640462213,1.2582998144,1.4839984155  
H,0,0.8188308093,2.5717776293,1.5351852299  
H,0,2.0259741828,2.5096983894,0.2291762339  
C,0,-2.9822106014,-0.4735502552,-1.5430311255  
C,0,-2.0278598983,-2.4520948533,-0.3899677021  
H,0,-3.3690846897,-1.1327494093,-2.3216894654  
H,0,-3.1838328272,0.5917448641,-1.6622242754  
H,0,-2.2539516508,-2.8179168656,0.6234633912  
H,0,-0.9682440296,-2.6749163177,-0.5915578179  
H,0,-2.6302151474,-3.0219655496,-1.1067353288

H,0,3.0984711279,-3.9555011069,-2.3633725189  
H,0,3.797419373,-3.5060657027,-0.7972091394  
H,0,4.0218697497,-2.450759507,-2.1986400627  
H,0,4.1657106949,1.1644690109,-2.3148162384  
H,0,2.411584342,1.1761701292,-2.0664487462  
H,0,3.1808296173,-0.2247739507,-2.8172906623  
H,0,3.1842775755,-1.5439944763,3.3361128767  
H,0,1.9669305297,-0.3684401681,2.8503421927  
H,0,3.6309044965,-0.2225379545,2.2474982165

### TS2-ax-K

E(RM11) = -652.719566888

Zero-point correction= 0.434773 (Hartree/Particle)  
Thermal correction to Energy= 0.455213  
Thermal correction to Enthalpy= 0.456157  
Thermal correction to Gibbs Free Energy= 0.388306  
Sum of electronic and ZPE= -652.284794  
Sum of electronic and thermal Energies= -652.264354  
Sum of electronic and thermal Enthalpies= -652.263410  
Sum of electronic and thermal Free Energies= -652.331261

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.650	80.596	142.805

C,0,-1.6726552803,1.6348957488,-1.2098076443  
C,0,-2.5683101973,1.7512636393,0.0598492461  
H,0,-2.0338087611,0.82305136,-1.8536527579  
H,0,-1.6754949017,2.5821135947,-1.7656761254  
C,0,-0.3073883928,1.3148224197,-0.6821940233  
C,0,0.0143989128,-0.0067871403,-0.3202287248  
C,0,0.5972895521,2.4790873957,-0.4404068344  
C,0,-0.7702757154,0.4323598669,1.1227493298  
H,0,-0.7152149572,-0.7136872059,-0.7526561627  
C,0,-2.294741808,0.5477785569,0.966125947  
H,0,-0.4383166273,-0.43053087,1.7146536482  
H,0,-0.3577638808,1.3221828136,1.6139859302  
C,0,-2.9359722912,-0.7636374745,0.5289519026  
H,0,-2.6936109482,0.7654519956,1.9732684077  
H,0,-2.2915832771,2.6700423377,0.6004967217  
H,0,-3.6254330367,1.8493291136,-0.2174186339  
B,0,1.5171874469,-0.7525741228,-0.1837646616  
C,0,1.8642889828,-1.0999800919,-1.7646222774  
C,0,2.7376525675,0.1174222467,0.4916163743  
C,0,1.2533295021,-2.1552519912,0.6423936114  
H,0,2.8576787477,-1.5825524312,-1.7850369  
H,0,1.1621041449,-1.8596345289,-2.1582959315  
C,0,1.8917395189,0.0918861995,-2.7305922152  
H,0,0.8172875971,-1.9863621018,1.6494251468  
H,0,0.5022422678,-2.7599912091,0.0959012269  
C,0,2.5138666096,-3.0114165283,0.8367935659  
C,0,2.5915403387,0.4790481586,1.9786674502  
H,0,2.9951031296,1.0240759107,-0.0863354497  
H,0,3.6357895896,-0.5178706787,0.3892164172  
H,0,1.3819875808,2.25075854,0.2855077238  
H,0,0.0310198269,3.3754308285,-0.1485476351  
H,0,1.0859487218,2.6933544709,-1.4048199981  
C,0,-3.8101264062,-0.8600804131,-0.4752260994  
C,0,-2.5377532978,-1.9725420236,1.3405834072  
H,0,-4.2661928898,-1.8200747525,-0.7223037425  
H,0,-4.1109312435,-0.0078284413,-1.0861521434  
H,0,-2.5885619696,-1.7574900202,2.419277254  
H,0,-1.5035878516,-2.2760618159,1.1172831538  
H,0,-3.1934905386,-2.8242907167,1.1254116553  
H,0,2.2091461448,-0.184162897,-3.7477791252  
H,0,2.5795581844,0.8765755158,-2.3759103111



H,0,0.8916877148,0.5527272194,-2.835633415  
H,0,3.5119599296,0.8992975891,2.4128651035  
H,0,2.3259468605,-0.4100069563,2.573116267  
H,0,1.7948461664,1.2219721525,2.1573647183  
H,0,2.2986280577,-3.9886915137,1.2956897742  
H,0,3.2430732246,-2.5002120594,1.4841274527  
H,0,3.0145465518,-3.2013858801,-0.1247937944

### TS2-ax-L

E(RM11) = -652.715155123

Zero-point correction= 0.434707 (Hartree/Particle)  
Thermal correction to Energy= 0.455201  
Thermal correction to Enthalpy= 0.456145  
Thermal correction to Gibbs Free Energy= 0.387759  
Sum of electronic and ZPE= -652.280448  
Sum of electronic and thermal Energies= -652.259954  
Sum of electronic and thermal Enthalpies= -652.259010  
Sum of electronic and thermal Free Energies= -652.327396

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.643	80.701	143.931

C,0,1.5828501497,2.1280361429,0.3955629064  
C,0,2.59323349,1.6543679571,-0.6752722058  
H,0,1.8527200001,1.7096624817,1.3758630718  
H,0,1.5509813174,3.2241859076,0.457538186  
C,0,0.2629052418,1.5806522761,-0.0737119756  
C,0,-0.1896258321,0.311933677,0.315084902  
C,0,-0.5137279248,2.4614548763,-0.9993350161  
C,0,0.8839228815,-0.0958252132,-0.9997328894  
H,0,0.3782668634,-0.0594882666,1.1800180982  
C,0,2.3846536201,0.1368256538,-0.8065576308  
H,0,0.5950195035,-1.1539231524,-0.9628739065  
H,0,0.5229273766,0.2812072088,-1.9646873097  
C,0,3.0365350107,-0.6444355199,0.3314142589  
H,0,2.8791603584,-0.2038822754,-1.7338680061  
H,0,2.3595800108,2.1376397958,-1.6368215455  
H,0,3.6206632542,1.9351327286,-0.4143476579  
B,0,-1.7464546939,-0.3154170032,0.1441170847  
C,0,-1.7966399966,-1.6790645193,1.0841584735  
C,0,-2.7667097456,0.8259542633,0.7681564916  
C,0,-2.1321605734,-0.6785769043,-1.4186874604  
H,0,-1.242710544,-1.5157300184,2.0296100637  
H,0,-2.8411468617,-1.8482357671,1.4044835748  
C,0,-1.2936429731,-2.9827673012,0.439721053  
H,0,-1.9940169428,0.1662141465,-2.1217523655  
H,0,-1.477222321,-1.4798687809,-1.8124574775  
C,0,-3.5906904011,-1.1466223639,-1.5509028937  
C,0,-2.3382377253,1.4258908538,2.1162003168  
H,0,-3.7480081283,0.3394458741,0.9070688371  
H,0,-2.961906652,1.647604987,0.0515056559  
H,0,-1.2635367593,1.9039935055,-1.5663883124  
H,0,0.1391443279,3.0479415566,-1.6608032482  
H,0,-1.0529458288,3.1669989611,-0.3451574967  
C,0,2.4434612018,-1.6374903187,0.9972819293  
C,0,4.4673808063,-0.2609231587,0.6358604598  
H,0,2.9907278627,-2.1896758093,1.7634088608  
H,0,1.4124565407,-1.9462726915,0.8236761528  
H,0,4.5190346574,0.6927395355,1.1835531553  
H,0,5.0537239509,-0.1387541708,-0.2878236521  
H,0,4.9527187819,-1.0249345245,1.2541633158  
H,0,-1.2702849317,-3.8278220197,1.1452747943  
H,0,-0.2745650845,-2.8890419569,0.0259447733  
H,0,-1.9344270203,-3.2788271712,-0.4043292851  
H,0,-3.0922489352,2.1003230543,2.5505947348  
H,0,-1.4046967499,2.0123818803,2.0305451899

H,0,-2.1431402522,0.6318712062,2.854288693  
H,0,-3.8375937616,-1.4985962733,-2.5645525262  
H,0,-4.2870080269,-0.330630242,-1.306572168  
H,0,-3.8075199519,-1.9689061273,-0.8510667441

### TS2-ax-M

E(RM11) = -652.715630164

Zero-point correction= 0.434678 (Hartree/Particle)  
Thermal correction to Energy= 0.455273  
Thermal correction to Enthalpy= 0.456217  
Thermal correction to Gibbs Free Energy= 0.387390  
Sum of electronic and ZPE= -652.280952  
Sum of electronic and thermal Energies= -652.260357  
Sum of electronic and thermal Enthalpies= -652.259413  
Sum of electronic and thermal Free Energies= -652.328240

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.688	80.589	144.859

C,0,2.0286340254,1.3843868464,1.156200486  
C,0,2.9201879491,1.1626372352,-0.0976248705  
H,0,2.1341320221,0.531962374,1.8422169092  
H,0,2.3048228704,2.3154085062,1.6692503826  
C,0,0.6392546593,1.4530573408,0.6014471559  
C,0,-0.0895186674,0.2758072956,0.3629455184  
C,0,0.1357014195,2.8011974971,0.2087345925  
C,0,0.8455117646,0.2424858039,-1.0678613744  
H,0,0.3476386157,-0.5667965782,0.9175657882  
C,0,2.3385939794,-0.031802366,-0.87116564  
H,0,0.2917766137,-0.5778196418,-1.5440966228  
H,0,0.6942506005,1.1243284993,-1.7012045759  
C,0,2.6855101779,-1.3823939829,-0.2495628476  
H,0,2.7966153909,-0.0336211565,-1.876834879  
H,0,2.8722615258,2.0604560128,-0.7337309906  
H,0,3.9695189765,1.026799973,0.1911193991  
B,0,-1.7468671834,0.0715692744,0.1573830081  
C,0,-2.3430752065,0.2997778204,1.6845237041  
C,0,-2.5368878843,1.1103423966,-0.8479283418  
C,0,-1.9232764543,-1.4939203239,-0.332530431  
H,0,-2.0808237446,1.3182327845,2.0367212666  
H,0,-3.4462539082,0.306281367,1.6183576675  
C,0,-1.9277923321,-0.7222673902,2.7524236299  
H,0,-1.4498272821,-1.6832246797,-1.3187448371  
H,0,-1.3954919985,-2.1655831311,0.3727852863  
C,0,-3.3857960066,-1.9515659307,-0.4300097514  
C,0,-2.1354256353,1.1568880823,-2.3312878558  
H,0,-2.5717299496,2.1379395185,-0.4395278397  
H,0,-3.5912239421,0.7848336296,-0.8008723307  
H,0,-0.6005579721,2.7419637211,-0.5982106872  
H,0,0.9497453197,3.4964122473,-0.037285296  
H,0,-0.3924550601,3.1929000056,1.0948097635  
C,0,1.8229880181,-2.3976264472,-0.1660695166  
C,0,4.1181085056,-1.5431617359,0.2053366033  
H,0,2.1443960096,-3.3619884859,0.2316005429  
H,0,0.7788501962,-2.3231214342,-0.4749383128  
H,0,4.3154563841,-0.9721204562,1.126014527  
H,0,4.8227222512,-1.1807622417,-0.5592327305  
H,0,4.344981102,-2.5954649176,0.4121317471  
H,0,-2.3538425417,-0.5023675406,3.7436536294  
H,0,-0.8324372791,-0.7672591376,2.8787984093  
H,0,-2.2557993205,-1.7357942305,2.4741798693  
H,0,-2.8894092264,1.6525180867,-2.9620113569  
H,0,-1.9922100206,0.1406124125,-2.7340126469  
H,0,-1.1903258652,1.7013255704,-2.4996306173  
H,0,-3.4844498701,-3.0243049927,-0.6569792627

H,0,-3.9208210969,-1.4004131367,-1.2183544612  
H,0,-3.9202325296,-1.7617401034,0.5145661038

### *TS2-ax-N*

E(RM11) = -652.709389258

Zero-point correction= 0.435088 (Hartree/Particle)  
Thermal correction to Energy= 0.455485  
Thermal correction to Enthalpy= 0.456429  
Thermal correction to Gibbs Free Energy= 0.387204  
Sum of electronic and ZPE= -652.274302  
Sum of electronic and thermal Energies= -652.253904  
Sum of electronic and thermal Enthalpies= -652.252960  
Sum of electronic and thermal Free Energies= -652.322185

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	285.821	80.488 145.697

C,0,1.576741064,-1.8552820623,-1.1434300811  
C,0,2.5135942777,-1.8278868032,0.093887299  
H,0,1.9123148492,-1.1202442527,-1.8882243424  
H,0,1.5514599135,-2.8585029077,-1.5900795515  
C,0,0.2467150106,-1.4747125277,-0.5743365678  
C,0,-0.1335439129,-0.1270446462,-0.4524176056  
C,0,-0.5630232192,-2.597963766,-0.019463457  
C,0,0.8357849373,-0.2140882708,0.9611940428  
H,0,0.4916057715,0.5141384467,-1.0948460913  
C,0,2.3411637357,-0.4595908705,0.7691736281  
H,0,0.5949909364,0.7993981657,1.3028621482  
H,0,0.4039151338,-0.8979947583,1.7019322744  
C,0,3.0926484867,0.6714839171,0.0593250061  
H,0,2.7757659055,-0.5287546477,1.7821722419  
H,0,2.2037916542,-2.6175107473,0.7953986775  
H,0,3.549348447,-2.0442444692,-0.19330104  
B,0,-1.7166390597,0.4715089796,-0.1894875235  
C,0,-1.7327388454,1.9532811176,-0.9152671516  
C,0,-2.7717759618,-0.5212550033,-0.9879779846  
C,0,-2.1279477395,0.6625761012,1.4013647807  
H,0,-1.6603605916,1.8442099262,-2.0155050631  
H,0,-2.7283142767,2.3941461429,-0.7344314983  
C,0,-0.6746569984,2.9662299894,-0.4554381227  
H,0,-1.3787541973,1.2592982775,1.9567625955  
H,0,-3.0180454927,1.316945637,1.3868695618  
C,0,-2.49085015,-0.568553399,2.2493197529  
C,0,-4.1832815589,0.0725205239,-1.1233046744  
H,0,-2.8864076932,-1.5062524894,-0.5028498243  
H,0,-2.3871722707,-0.7384059935,-2.0055795055  
H,0,-1.2844043631,-2.2544483238,0.7270163816  
H,0,0.0682966732,-3.4075113908,0.3722714314  
H,0,-1.1383080796,-3.0004116625,-0.8695536699  
C,0,2.7309785901,1.9501772639,0.175760019  
C,0,4.351939927,0.2990133823,-0.6894642236  
H,0,3.321114562,2.7408038027,-0.2908853564  
H,0,1.8520289649,2.2703516464,0.7346621051  
H,0,4.1428670179,-0.3415693769,-1.5596482232  
H,0,5.0494111273,-0.2532758319,-0.0404996987  
H,0,4.8643086374,1.1983198602,-1.0500055983  
H,0,-0.8643227394,3.9827669834,-0.8335445808  
H,0,0.3308495773,2.6883712642,-0.8076158598  
H,0,-0.6346379087,3.036163462,0.6454787337  
H,0,-4.8926795908,-0.6270824116,-1.5924720757  
H,0,-4.17666518,0.9890054664,-1.7301355289  
H,0,-4.5919467792,0.3412415478,-0.135635073  
H,0,-2.9552774658,-0.2944670807,3.20910527  
H,0,-1.6131964607,-1.1876891226,2.5034602237  
H,0,-3.2059996948,-1.2188674881,1.7197007199

### *TS2-ax-O*

E(RM11) = -652.710761295

Zero-point correction= 0.434936 (Hartree/Particle)  
Thermal correction to Energy= 0.455346  
Thermal correction to Enthalpy= 0.456290  
Thermal correction to Gibbs Free Energy= 0.387958  
Sum of electronic and ZPE= -652.275826  
Sum of electronic and thermal Energies= -652.255416  
Sum of electronic and thermal Enthalpies= -652.254471  
Sum of electronic and thermal Free Energies= -652.322803

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	285.734	80.644 143.816

C,0,1.2881720065,-2.0637971439,-0.790699272  
C,0,2.2966697634,-1.9128148936,0.3760767784  
H,0,1.631022246,-1.4970178528,-1.667334408  
H,0,1.154728662,-3.1200534399,-1.0611066395  
C,0,0.0194004765,-1.4790008666,-0.2474144674  
C,0,-0.2622474462,-0.1094157335,-0.3611951007  
C,0,-0.8697814877,-2.4223443399,0.4955782082  
C,0,0.7656775596,-0.0772100529,1.032171607  
H,0,0.3912664611,0.3725833433,-1.1070970175  
C,0,2.2435781048,-0.4483390442,0.8333242864  
H,0,0.5968307158,0.9930672932,1.2013735891  
H,0,0.3213578837,-0.5975033676,1.8890594734  
C,0,3.024379699,0.5137572184,-0.0704451155  
H,0,2.7143803829,-0.387968275,1.8302108624  
H,0,1.9797219475,-2.5603109543,1.2083008726  
H,0,3.3002118218,-2.2404251683,0.0788099173  
B,0,-1.7754682372,0.6385365933,-0.1418894249  
C,0,-1.7105779291,1.9984853392,-1.0743995842  
C,0,-2.9491789266,-0.3533877064,-0.7497947409  
C,0,-2.1148414772,1.0892892792,1.4128252497  
H,0,-1.547145084,1.7372544805,-2.1369435194  
H,0,-2.7114942815,2.4666509935,-1.0420854202  
C,0,-0.6620983789,3.0485612904,-0.6813872032  
H,0,-1.3131257816,1.7200669294,1.8428944386  
H,0,-2.9689724832,1.7839770339,1.3123777718  
C,0,-2.5111727435,0.0418009209,2.4679891019  
C,0,-2.6974683289,-0.9041987646,-2.1623002078  
H,0,-3.8737809917,0.251980655,-0.7788328921  
H,0,-3.1997871167,-1.1982652342,-0.0839626271  
H,0,-1.5475177688,-1.8984159659,1.1744410574  
H,0,-0.2979455025,-3.2004795453,1.020334486  
H,0,-1.4897500586,-2.9174471355,-0.2702777263  
C,0,2.7991807316,1.8287193824,-0.0585098914  
C,0,4.1571642499,-0.0589468003,-0.8907714713  
H,0,3.4026529133,2.5044694753,-0.6668433196  
H,0,2.0258845954,2.2917685713,0.5552246448  
H,0,3.8072511693,-0.796368044,-1.6282067202  
H,0,4.8915988355,-0.5677197716,-0.2471265908  
H,0,4.6782969365,0.7381419982,-1.43320527  
H,0,-0.7333369707,3.9702223275,-1.2797026966  
H,0,0.3591068817,2.6616121916,-0.8284464924  
H,0,-0.7569805485,3.3420912944,0.3766599839  
H,0,-3.5178964149,-1.54086937,-2.5287995969  
H,0,-1.7766707718,-1.5148377113,-2.2137369085  
H,0,-2.5668678954,-0.0900103211,-2.8898187268  
H,0,-2.9300723254,0.5043704744,3.3749182874  
H,0,-1.6568470259,-0.5686026815,2.807510766  
H,0,-3.2745852172,-0.6517156411,2.081039469

### *TS2-ax-P*

E(RM11) = -652.714360466

Zero-point correction= 0.435215 (Hartree/Particle)  
Thermal correction to Energy= 0.455457  
Thermal correction to Enthalpy= 0.456401  
Thermal correction to Gibbs Free Energy= 0.389203  
Sum of electronic and ZPE= -652.279146  
Sum of electronic and thermal Energies= -652.258903  
Sum of electronic and thermal Enthalpies= -652.257959  
Sum of electronic and thermal Free Energies= -652.325157

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.804 80.387 141.430

C,0,1.7983114065,1.9805361705,0.2751864212  
C,0,2.707787208,1.2850473043,-0.7809349001  
H,0,2.0373356547,1.6027188916,1.279009446  
H,0,1.9331735405,3.0699767,0.2378168008  
C,0,0.4205000809,1.5746259112,-0.1398639721  
C,0,-0.0948836954,0.332253273,0.2797827891  
C,0,-0.2431263123,2.4515516945,-1.1503629643  
C,0,0.8063795645,-0.2960691844,-1.0082312084  
H,0,0.4621678916,-0.0270738925,1.1580399483  
C,0,2.3257877055,-0.203430048,-0.8358250062  
H,0,0.4238089842,-1.320690115,-0.9644366278  
H,0,0.4901413481,0.1130936364,-1.9765385655  
C,0,2.8979356045,-1.0112892947,0.3269457808  
H,0,2.7791840121,-0.6285898318,-1.7496063246  
H,0,2.5231453995,1.7407092427,-1.7660751018  
H,0,3.7654707916,1.4518835652,-0.5434074973  
B,0,-1.6906305483,-0.2040893303,0.3381633983  
C,0,-2.2756106812,0.5450293405,1.6917994752  
C,0,-2.5849652547,0.1537961994,-0.9998903144  
C,0,-1.694825007,-1.829469294,0.6475275969  
H,0,-3.3346739873,0.2495655838,1.8017000477  
H,0,-1.7739326472,0.1382504858,2.5906883472  
C,0,-2.1906917341,2.0753461015,1.733944279  
H,0,-1.0362855569,-2.061789821,1.5076620567  
H,0,-2.7093162348,-2.0361795849,1.0322760558  
C,0,-1.4191910523,-2.8365627784,-0.4928517568  
C,0,-3.9509189469,-0.5532625864,-1.0123561171  
H,0,-2.7836267966,1.2397071841,-1.0646663753  
H,0,-2.0538531584,-0.1064354916,-1.9397254967  
H,0,-0.9793675147,1.9101262423,-1.7500315801  
H,0,0.4885462367,2.9687188672,-1.7865885795  
H,0,-0.7869042901,3.2190709918,-0.5759780657  
C,0,2.2081225524,-1.9383085192,0.9953113778  
C,0,4.352896531,-0.7510751513,0.645155582  
H,0,2.6913752122,-2.5268916325,1.7773487472  
H,0,1.1536942324,-2.1496270808,0.8099338771  
H,0,4.4845707136,0.2132715772,1.1601776277  
H,0,4.962640144,-0.7171031737,-0.270945841  
H,0,4.7555159722,-1.5338070489,1.2985181236  
H,0,-2.6652780112,2.509463181,2.6272561053  
H,0,-2.6786368947,2.5276765576,0.8548548237  
H,0,-1.14071144,2.4231182994,1.7452198487  
H,0,-4.5819283389,-0.2412252084,-1.8588719358  
H,0,-4.5095936564,-0.336568522,-0.0887786746  
H,0,-3.8417639959,-1.6463520058,-1.0682518968  
H,0,-1.9552021274,-3.7870285907,-0.34850891  
H,0,-0.3549018213,-3.1127115296,-0.582369818  
H,0,-1.7294139127,-2.4385283849,-1.4729708863

### TS2-ax-Q

E(RM11) = -652.714481409

Zero-point correction= 0.434816 (Hartree/Particle)  
Thermal correction to Energy= 0.455315  
Thermal correction to Enthalpy= 0.456259  
Thermal correction to Gibbs Free Energy= 0.388278  
Sum of electronic and ZPE= -652.279665  
Sum of electronic and thermal Energies= -652.259167  
Sum of electronic and thermal Enthalpies= -652.258222  
Sum of electronic and thermal Free Energies= -652.326204

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.714 80.722 143.079

C,0,-1.9067743469,-1.6885611949,1.0447262022  
C,0,-2.8648371561,-1.3904753462,-0.1374571374  
H,0,-2.0531971979,-0.9407184417,1.8374228951  
H,0,-2.0818957237,-2.6952956134,1.4473057021  
C,0,-0.5311485201,-1.5711144832,0.4525009347  
C,0,0.111004884,-0.3253639435,0.3655423256  
C,0,0.0544401625,-2.83149461,-0.0937022564  
C,0,-0.9003022047,-0.1859369375,-1.0164425466  
H,0,-0.3591770282,0.3954278035,1.0480334772  
C,0,-2.4017024134,-0.0634962435,-0.7571880488  
H,0,-0.4328881496,0.7499582354,-1.3490212815  
H,0,-0.6696702805,-0.9350148738,-1.7854385852  
C,0,-2.8223809933,1.1577246011,0.0586599581  
H,0,-2.8897909839,0.0429437061,-1.7427935875  
H,0,-2.7731711853,-2.1912630089,-0.8879585042  
H,0,-3.9101461558,-1.3771776902,0.1946148007  
B,0,1.7144891677,0.0156890017,-0.0068639465  
C,0,1.8773258301,1.6436286558,0.198251765  
C,0,2.5907034103,-0.8245901093,1.1155331212  
C,0,2.1686658284,-0.4140665045,-1.5517489771  
H,0,2.9057460088,1.9211112198,-0.0970856194  
H,0,1.2372780675,2.2038215439,-0.5156555324  
C,0,1.6221396559,2.1792680938,1.6157910899  
H,0,3.2325149622,-0.7058889854,-1.4978508766  
H,0,1.6679937098,-1.3280758656,-1.9244913494  
C,0,2.0558504892,0.6491699489,-2.6604344126  
C,0,4.0593934157,-0.3866725559,1.2104825866  
H,0,2.5679058864,-1.9075252437,0.8822574677  
H,0,2.1339237048,-0.7334781013,2.1209511512  
H,0,0.9083484599,-2.6434712557,-0.7487478598  
H,0,-0.7013249946,-3.4623954949,-0.5831688928  
H,0,0.4250521718,-3.3843600662,0.7854331842  
C,0,-2.0291134806,2.2068963645,0.287974252  
C,0,-4.2515426878,1.1477031743,0.5511868182  
H,0,-2.408027863,3.0747221905,0.8308788475  
H,0,-0.9885116113,2.2578044325,-0.0376619778  
H,0,-4.3831281287,0.4422248184,1.3864295456  
H,0,-4.9463743883,0.8414372764,-0.2460002384  
H,0,-4.5490897471,2.1415006477,0.9051109245  
H,0,1.8090026115,3.2610222285,1.7022060934  
H,0,2.2663342372,1.6750075016,2.3523128196  
H,0,0.5821213382,2.014624738,1.9455951335  
H,0,4.6457009042,-1.0045777235,1.9083427783  
H,0,4.1410862462,0.657695861,1.5477554072  
H,0,4.5556581022,-0.4412386837,0.2290763029  
H,0,2.4291645525,0.2804930412,-3.6287208281  
H,0,2.6359358431,1.5477171892,-2.4075683032  
H,0,1.0194522305,0.9850140027,-2.8307208325

### TS2-ax-R

E(RM11) = -652.715772610

Zero-point correction= 0.434844 (Hartree/Particle)  
Thermal correction to Energy= 0.455240

Thermal correction to Enthalpy= 0.456184  
Thermal correction to Gibbs Free Energy= 0.388569  
Sum of electronic and ZPE= -652.280929  
Sum of electronic and thermal Energies= -652.260533  
Sum of electronic and thermal Enthalpies= -652.259589  
Sum of electronic and thermal Free Energies= -652.327203

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.667 80.533 142.307

C,0,1.7530042998,1.5124978788,1.3981993554  
C,0,2.7684560667,1.468067455,0.2209205092  
H,0,1.8975727774,0.6361583291,2.0456842006  
H,0,1.8781416357,2.4356854142,1.9799941814  
C,0,0.4203994268,1.4586847237,0.7214299041  
C,0,-0.1246609347,0.2225099958,0.3313821948  
C,0,-0.2122133313,2.7583867413,0.3600607476  
C,0,0.9155787175,0.3870663805,-1.0015380271  
H,0,0.3557015993,-0.5962673157,0.8864505013  
C,0,2.4065598853,0.2697486891,-0.6724354599  
H,0,0.5098496563,-0.4480571064,-1.5879886138  
H,0,0.7236424721,1.2948991867,-1.5851365797  
C,0,2.8473047555,-1.074971091,-0.098469684  
H,0,2.9544877043,0.3894472196,-1.624665044  
H,0,2.6726790188,2.394303256,-0.367194716  
H,0,3.7965945833,1.4325149144,0.6010314719  
B,0,-1.7310396255,-0.1416346046,-0.0204144697  
C,0,-2.4338412343,-0.0197738803,1.4710813922  
C,0,-2.5314141788,0.8253756277,-1.0906220676  
C,0,-1.7329145836,-1.7013630359,-0.5676723359  
H,0,-1.896168067,-0.649010323,2.2062755923  
H,0,-2.3376342543,1.018514751,1.8498988841  
C,0,-3.9211957768,-0.4010554483,1.4877575868  
H,0,-2.7274377428,-1.9156913422,-0.9992285959  
H,0,-1.0447848636,-1.8345739345,-1.4296993489  
C,0,-1.4257725548,-2.7821274259,0.482668969  
C,0,-1.9600585285,1.0060113509,-2.5075986212  
H,0,-2.7740798682,1.8180905374,-0.6635336108  
H,0,-3.5178978657,0.3418611978,-1.2024532536  
H,0,-0.8811119181,2.6595054186,-0.5003702122  
H,0,0.5258652106,3.5586188756,0.2122603536  
H,0,-0.8416439529,3.0319684376,1.22418191  
C,0,2.1140329863,-2.1858254387,-0.1970071381  
C,0,4.2221278589,-1.1050398078,0.5283602233  
H,0,2.4972828046,-3.1379933385,0.1745444732  
H,0,1.1146709127,-2.2038917713,-0.6353048331  
H,0,4.2371053561,-0.5729195367,1.4923432692  
H,0,4.9680329514,-0.6217925894,-0.1217633673  
H,0,4.5433190492,-2.1367675477,0.7127237608  
H,0,-4.3492384402,-0.4108208735,2.5023614591  
H,0,-4.0777758671,-1.4010629573,1.0528108532  
H,0,-4.5158731747,0.3038636477,0.8879743881  
H,0,-2.7031009904,1.4030480249,-3.2161204883  
H,0,-1.6021809027,0.047299802,-2.9173623939  
H,0,-1.1073171418,1.7053495287,-2.5365304222  
H,0,-1.3194807939,-3.7878792125,0.0459833497  
H,0,-2.2286526122,-2.8350121321,1.2329538805  
H,0,-0.4977510046,-2.5735606809,1.0420278551

*TS2-ax-S*  
E(RM11) = -652.715669500

Zero-point correction= 0.435246 (Hartree/Particle)  
Thermal correction to Energy= 0.455405  
Thermal correction to Enthalpy= 0.456349  
Thermal correction to Gibbs Free Energy= 0.389336

Sum of electronic and ZPE= -652.280424  
Sum of electronic and thermal Energies= -652.260265  
Sum of electronic and thermal Enthalpies= -652.259321  
Sum of electronic and thermal Free Energies= -652.326333

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.771 80.339 141.040

C,0,-1.3983458384,-1.9587133687,0.9180215737  
C,0,-2.4185553902,-1.7713010618,-0.2441191722  
H,0,-1.6669612079,-1.305570081,1.7603352474  
H,0,-1.3798289702,-3.0072378095,1.244590898  
C,0,-0.0976839059,-1.5396663633,0.3105821045  
C,0,0.2382739589,-0.1733214155,0.2539220106  
C,0,0.6878577831,-2.6065779974,-0.3780567625  
C,0,-0.7551385583,-0.1598504244,-1.1187922539  
H,0,-0.3669218772,0.3957190192,0.9765456212  
C,0,-2.2456158444,-0.3563058414,-0.819536771  
H,0,-0.4951366037,0.8431956857,-1.4811776281  
H,0,-0.4259329613,-0.8612524173,-1.18948368849  
C,0,-2.8885033431,0.7348789643,0.0338611688  
H,0,-2.7721021794,-0.3307062824,-1.7909428614  
H,0,-2.1968404844,-2.5074819338,-1.032402407  
H,0,-3.4374998812,-1.9750142863,0.1065140192  
B,0,1.7597177692,0.5410041862,0.0781858501  
C,0,2.4184600061,0.3620788951,1.5841856849  
C,0,2.7667209586,-0.0926953766,-1.0613339059  
C,0,1.502396929,2.1420633022,-0.2454705306  
H,0,3.4041534396,0.8634969497,1.5652822432  
H,0,1.8290418955,0.9092478352,2.3418289186  
C,0,2.6055250792,-1.076206264,2.0826334794  
H,0,2.4518864642,2.5661621805,-0.6201581477  
H,0,0.8042061249,2.2901211105,-1.0958207465  
C,0,1.0291859835,3.0089783168,0.934418591  
C,0,2.3185152132,-0.0191616061,-2.531030173  
H,0,3.0986630929,-1.1226939424,-0.8344926633  
H,0,3.6896405648,0.5082715867,-0.9679389376  
H,0,1.3599098733,-2.1954045581,-1.1365545442  
H,0,0.0367631647,-3.3860930052,-0.798446152  
H,0,1.3136064148,-3.0773503725,0.3971112321  
C,0,-2.3444853362,1.9416954187,0.2028414903  
C,0,-4.2420649876,0.4048920466,0.6193473182  
H,0,-2.8695678863,2.7124997088,0.7700569491  
H,0,-1.3676616148,2.2167435546,-0.1985022953  
H,0,-4.1599858721,-0.3287220741,1.4364344196  
H,0,-4.910550262,-0.0284031778,-0.1408724243  
H,0,-4.7202261304,1.3038442622,1.0253591968  
H,0,3.1359617244,-1.1301519781,3.045802298  
H,0,3.1728053625,-1.6880485937,1.3627754048  
H,0,1.6302433666,-1.5722292093,2.2442822264  
H,0,3.138616112,-0.2173547576,-3.2381950902  
H,0,1.9148433786,0.9773187871,-2.7710598944  
H,0,1.5250259148,-0.7480884288,-2.7685816771  
H,0,0.7060972757,4.0153577602,0.6233246861  
H,0,1.836293693,3.1389007564,1.669618417  
H,0,0.1866952217,2.5501266758,1.4800219641

*TS2-ax-T*  
E(RM11) = -652.715095644

Zero-point correction= 0.434341 (Hartree/Particle)  
Thermal correction to Energy= 0.455049  
Thermal correction to Enthalpy= 0.455994  
Thermal correction to Gibbs Free Energy= 0.386808  
Sum of electronic and ZPE= -652.280755  
Sum of electronic and thermal Energies= -652.260046

Sum of electronic and thermal Enthalpies= -652.259102  
Sum of electronic and thermal Free Energies= -652.328287

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.548 80.866 145.613

C,0,2.0406376647,1.7423252334,0.4226769131  
C,0,2.9696981831,0.9785177129,-0.5499054673  
H,0,2.1248434049,1.3165215407,1.4329185908  
H,0,2.2869736095,2.8122803492,0.4512730923  
C,0,0.6587776815,1.5247515718,-0.1312934018  
C,0,-0.1158419347,0.420719347,0.2501485095  
C,0,0.1852958272,2.5359937049,-1.1258507917  
C,0,0.8958909588,-0.289659834,-0.9686339221  
H,0,0.2854532513,-0.0454187546,1.1617954245  
C,0,2.3878305999,-0.4392600758,-0.6668759663  
H,0,0.3469794961,-1.2382388352,-0.9131115433  
H,0,0.6987028109,0.118359259,-1.968253813  
C,0,2.7208363996,-1.3223121974,0.5344950982  
H,0,2.8440458069,-0.9315329807,-1.5443022675  
H,0,2.9387402924,1.4638911912,-1.5377494531  
H,0,4.0124917971,0.9981498501,-0.2113292385  
B,0,-1.7479788552,0.1236152819,-0.0170377984  
C,0,-2.0449763393,-1.2537195686,0.83886294  
C,0,-2.5362676899,1.4266992956,0.6162935827  
C,0,-2.2083191555,-0.0668760941,-1.6037681107  
H,0,-1.5238747662,-2.1167547482,0.3737965641  
H,0,-1.6207794799,-1.181436906,1.8595161966  
C,0,-3.5370176169,-1.5941706758,0.9612226718  
H,0,-3.2870313747,0.1742689515,-1.6186912883  
H,0,-1.7695734485,0.6853974042,-2.2873249435  
C,0,-2.0535132046,-1.4492599684,-2.2648290149  
C,0,-2.1575083828,1.7941992016,2.0579633246  
H,0,-3.6199971972,1.2174060251,0.5758782625  
H,0,-2.4048921897,2.3160825657,-0.0304817328  
H,0,-0.6573916155,2.1691263769,-1.7174348348  
H,0,0.9985963055,2.9026202342,-1.7679848166  
H,0,-0.1777684218,3.3875661063,-0.5264463265  
C,0,1.8471956978,-2.1402248302,1.1264855068  
C,0,4.1608240961,-1.2714916341,0.9924827888  
H,0,2.1691514612,-2.7868177417,1.9448662777  
H,0,0.7951721539,-2.2097437303,0.8446975051  
H,0,4.3796015244,-0.3322845031,1.5238236135  
H,0,4.8539944198,-1.3321833268,0.1393366613  
H,0,4.3817040551,-2.0993847999,1.6760359149  
H,0,-3.7197088029,-2.5744956902,1.4279843747  
H,0,-4.0299222881,-1.5987414791,-0.0242682904  
H,0,-4.0569757749,-0.8390521065,1.5707085344  
H,0,-2.7465571654,2.6317631643,2.462580334  
H,0,-1.0941804728,2.0851999399,2.1391284534  
H,0,-2.3013496662,0.9347936787,2.7320832458  
H,0,-2.5066349261,-1.4802735277,-3.2680273543  
H,0,-2.5386044008,-2.2333664558,-1.6652848709  
H,0,-1.0026772983,-1.7560603217,-2.3915393744

### TS2-ax-U

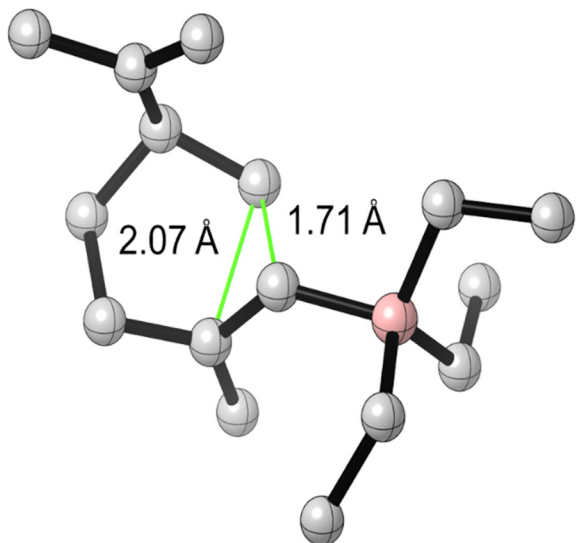
E(RM11) = -652.713697022

Zero-point correction= 0.435129 (Hartree/Particle)  
Thermal correction to Energy= 0.455578  
Thermal correction to Enthalpy= 0.456523  
Thermal correction to Gibbs Free Energy= 0.388245  
Sum of electronic and ZPE= -652.278568  
Sum of electronic and thermal Energies= -652.258119  
Sum of electronic and thermal Enthalpies= -652.257174  
Sum of electronic and thermal Free Energies= -652.325452

E CV S  
KCal/Mol Cal/Mol-K Cal/Mol-K  
Total 285.880 80.555 143.702

C,0,-1.8427327198,1.5014850563,-1.1457107316  
C,0,-2.8881474492,1.2997594712,-0.0276618104  
H,0,-1.9556682045,0.7203424851,-1.911677607  
H,0,-1.9434601098,2.4891686153,-1.6154796731  
C,0,-0.5070601123,1.3734927618,-0.4545748001  
C,0,0.1385403463,0.1363078304,-0.3440143217  
C,0,0.0854473112,2.6438442901,0.0704639538  
C,0,-0.9843954854,0.1390030562,1.0087512197  
H,0,-0.3399880287,-0.6087383711,-0.9953208862  
C,0,-2.4768444483,0.0095325023,0.7024147417  
H,0,-0.527070476,-0.7815378064,1.3939035339  
H,0,-0.7741459956,0.9105211383,1.7589454288  
C,0,-2.8833970624,-1.2607946786,-0.0418195534  
H,0,-3.0005485859,-0.0250455166,1.67430955  
H,0,-2.8344004816,2.1444279492,0.6770527971  
H,0,-3.910595122,1.273160229,-0.4232301101  
B,0,1.7278059369,-0.2408125734,0.0834938426  
C,0,1.8710549647,-1.8122178409,-0.4218280398  
C,0,2.7172487154,0.7609374194,-0.7693816908  
C,0,2.0629131442,-0.204179558,1.7014799661  
H,0,1.293818472,-2.4701894393,0.2616461624  
H,0,1.4024027239,-1.9514954292,-1.4159901531  
C,0,3.3083047075,-2.3448553399,-0.5025256004  
H,0,1.3996397914,-0.8954899418,2.2593241647  
H,0,3.056652674,-0.6785590421,1.7815024359  
C,0,2.1472139567,1.1223553057,2.4755098728  
C,0,2.4703568926,0.7659278487,-2.2854417669  
H,0,3.7579328409,0.4411221607,-0.5801975495  
H,0,2.6796521197,1.8026745028,-0.4010422798  
H,0,0.8715357621,2.4551962916,0.8055763044  
H,0,-0.6801270943,3.3235607491,0.4712382959  
H,0,0.5533854472,3.1362210797,-0.7979597493  
C,0,-2.0984958962,-2.3326539048,-0.1737218458  
C,0,-4.2967164225,-1.2691645839,-0.5782189489  
H,0,-2.4739756348,-3.2308171263,-0.6672625175  
H,0,-1.0686920101,-2.3760080333,0.1842704283  
H,0,-4.3918074273,-0.6243434565,-1.4653773567  
H,0,-5.0107348579,-0.8971281231,0.1726873293  
H,0,-4.5974596494,-2.2823682746,-0.8687162776  
H,0,3.3515483224,-3.4109514084,-0.7743434443  
H,0,3.8373569715,-2.2312503476,0.4559516109  
H,0,3.8892108922,-1.7913389382,-1.2566443136  
H,0,3.1718055795,1.4093405168,-2.8390315618  
H,0,1.4519068669,1.1201356776,-2.530203142  
H,0,2.5555001108,-0.2498980861,-2.7024835852  
H,0,2.6202566542,0.9983059587,3.4617511799  
H,0,1.1570826435,1.5691898312,2.6685589552  
H,0,2.7430627563,1.869346333,1.9265861381

### TS2-ax-V



E(RM11) = -652.716925702

Zero-point correction= 0.435007 (Hartree/Particle)  
 Thermal correction to Energy= 0.455327  
 Thermal correction to Enthalpy= 0.456272  
 Thermal correction to Gibbs Free Energy= 0.388822  
 Sum of electronic and ZPE= -652.281919  
 Sum of electronic and thermal Energies= -652.261598  
 Sum of electronic and thermal Enthalpies= -652.260654  
 Sum of electronic and thermal Free Energies= -652.328103

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 285.722	80.465	141.959

```

C,0,1.9012378505,1.7626943502,0.5900505708
C,0,2.8201701759,1.1848626294,-0.5220013234
H,0,2.0748619934,1.2280133993,1.5347342585
H,0,2.0881103681,2.8363125099,0.7272522334
C,0,0.5158186756,1.5058656031,0.0796681102
C,0,-0.0965455778,0.2601218699,0.3020552589
C,0,-0.0794922876,2.5740711453,-0.7789800875
C,0,0.8371101305,-0.1894078271,-1.0593109091
H,0,0.4197144079,-0.281847475,1.1093095579
C,0,2.3489728545,-0.2482498964,-0.8194368065
H,0,0.3652374861,-1.1695127936,-1.2069332068
H,0,0.608083098,0.400315417,-1.9548534774
C,0,2.8093788508,-1.2674706582,0.2201017925
H,0,2.8107214648,-0.5599861156,-1.7738270433
H,0,2.7072235402,1.7950233482,-1.4318881513
H,0,3.8741359508,1.2437596075,-0.2245825349
B,0,-1.7214620337,-0.1702102855,0.2741833699
C,0,-2.2291421181,0.3358012375,1.7677520706
C,0,-2.6682377076,0.4857514525,-0.8996275621
C,0,-1.7511891579,-1.8191963938,0.2188285563
H,0,-3.3079977262,0.1107767274,1.8431944175
H,0,-1.7489170036,-0.2641919394,2.5643094779
C,0,-2.0265513634,1.8235624644,2.0831856886
H,0,-1.2275652281,-2.2325946698,-0.6689207381
H,0,-1.2025314079,-2.2187054553,1.09468652
C,0,-3.1662791066,-2.4169128241,0.2225683682
C,0,-2.3678977451,0.0748517686,-2.3505600274
H,0,-2.7402556319,1.587212442,-0.8347183965
H,0,-3.6923744433,0.1454903081,-0.6626584394
H,0,-0.8484228764,2.1826649864,-1.4506275182
  
```

```

H,0,0.690373636,3.1284966437,-1.3340368706
H,0,-0.5713842008,3.2802430492,-0.0904147986
C,0,2.0416920595,-2.2658287389,0.6624910887
C,0,4.2446103749,-1.1342543438,0.6751920519
H,0,2.444856196,-3.0032404187,1.3591242005
H,0,0.9987990453,-2.3948884124,0.3682648681
H,0,4.3780366933,-0.2620108781,1.3338444529
H,0,4.9248914492,-1.0028632082,-0.1806552842
H,0,4.5602757328,-2.0238038656,1.2325718266
H,0,-2.4553631084,2.1222968275,3.0520253882
H,0,-2.4882912166,2.4609592673,1.3117496055
H,0,-0.9529727943,2.0856775741,2.1284324339
H,0,-3.1600058204,0.372281763,-3.05508752
H,0,-2.2508946424,-1.0179184934,-2.4318581643
H,0,-1.4315467355,0.517657956,-2.7318239982
H,0,-3.1649350384,-3.5151706216,0.2983705227
H,0,-3.7090221504,-2.1532945191,-0.6982432893
H,0,-3.7565212017,-2.0283676339,1.0664342067
  
```

### Additional Structures

#### Truncated Model System 18‡

E(RM11) = -457.511448151

Zero-point correction= 0.315187 (Hartree/Particle)  
 Thermal correction to Energy= 0.330156  
 Thermal correction to Enthalpy= 0.331100  
 Thermal correction to Gibbs Free Energy= 0.275056  
 Sum of electronic and ZPE= -457.196261  
 Sum of electronic and thermal Energies= -457.181292  
 Sum of electronic and thermal Enthalpies= -457.180348  
 Sum of electronic and thermal Free Energies= -457.236392

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total 207.176	58.698	117.955

```

6 1.544403 1.577812 -0.859211
6 2.637922 0.638144 -0.286977
1 1.434621 1.406883 -1.938638
1 1.798482 2.630971 -0.679046
6 0.288667 1.187733 -0.135684
6 -0.484160 0.097288 -0.563957
6 -0.031952 1.949609 1.105252
6 0.686419 -0.775087 0.311392
1 -0.242286 -0.185121 -1.601744
6 2.086917 -0.789568 -0.301048
1 0.163575 -1.737599 0.211967
1 0.695021 -0.533083 1.383949
6 2.996414 -1.768083 0.448152
1 1.991880 -1.118904 -1.349425
1 2.862091 0.928691 0.753714
1 3.570091 0.733323 -0.860497
5 -2.047528 -0.338580 -0.095701
6 -3.004097 0.939251 -0.479634
6 -2.197800 -0.751375 1.492198
6 -2.393035 -1.650269 -1.020875
1 -4.064399 0.682352 -0.318835
1 -2.911712 1.243405 -1.537726
1 -2.807384 1.836987 0.135619
1 -1.720028 -2.511552 -0.838915
1 -2.352875 -1.435310 -2.103846
1 -3.411318 -2.015777 -0.808917
1 -1.537353 -1.577972 1.813233
1 -3.225078 -1.126063 1.634884
1 -2.083324 0.059230 2.233953
1 -0.755292 1.419267 1.730345
1 0.870927 2.224867 1.668821
  
```

1 -0.507107 2.883949 0.762747  
1 2.594760 -2.789448 0.417600  
1 4.002483 -1.785537 0.007729  
1 3.093680 -1.473397 1.503884

### Truncated Model System 19‡

E(RM11) = -457.512487894

Zero-point correction= 0.314656 (Hartree/Particle)  
Thermal correction to Energy= 0.329660  
Thermal correction to Enthalpy= 0.330604  
Thermal correction to Gibbs Free Energy= 0.274536  
Sum of electronic and ZPE= -457.197832  
Sum of electronic and thermal Energies= -457.182828  
Sum of electronic and thermal Enthalpies= -457.181884  
Sum of electronic and thermal Free Energies= -457.237952

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	206.865	58.793 118.005

C,0,-1.3072518239,-2.2354228747,-0.807681127  
C,0,-2.5562244587,-1.5093797225,-0.2299722635  
H,0,-1.2754547241,-2.0828401789,-1.8965918987  
H,0,-1.3543686209,-3.3120394828,-0.5911542246  
C,0,-0.1212440139,-1.5966062859,-0.1478476339  
C,0,0.4383327294,-0.4117401676,-0.6495285368

C,0,0.3756468336,-2.2406554936,1.1039736572  
C,0,-0.8580455237,0.2643134308,0.2469871068  
H,0,0.1109414353,-0.2158490641,-1.683842978  
C,0,-2.2455369405,-0.0141962754,-0.3157626428  
H,0,-0.5145367277,1.2943339112,0.0768793636  
H,0,-0.7744375573,0.079349373,1.3257099851  
H,0,-2.2878640244,0.3126041732,-1.367841017  
H,0,-2.6403781253,-1.7841950624,0.8360804115  
H,0,4.067589591,-0.3346863691,-0.4778572799  
H,0,3.0101824057,-1.1721163439,-1.6214748938  
B,0,1.904986817,0.3183710132,-0.248505245  
C,0,3.0686903785,-0.7891565382,-0.5867807794  
C,0,2.0026472427,0.84356343,1.3099955553  
C,0,1.9979601373,1.6151807391,-1.2508646081  
H,0,1.1765772581,2.3450437499,-1.1069869887  
H,0,1.9928303417,1.3338898792,-2.3192529277  
H,0,2.9631635851,1.3754696491,1.4130665077  
H,0,2.0146436947,0.0734988213,2.10195664613  
H,0,1.0209001885,-1.5684541757,1.6756680415  
H,0,-0.4435552831,-2.6392374705,1.7193504553  
H,0,0.9900635039,-3.0948076389,0.7747812114  
C,0,-3.836758345,-1.9145687634,-0.9545157353  
H,0,-4.0132068542,-2.9964304636,-0.8817817582  
H,0,-4.7081546443,-1.3997411078,-0.5275329695  
H,0,-3.775791389,-1.650266178,-2.0206480489  
H,0,-2.9939898459,0.5738339965,0.2365189778  
H,0,2.9312415381,2.1753972931,-1.0757781192  
H,0,3.0541305765,-1.6665420864,0.086208518  
H,0,1.2279658146,1.5810141736,1.5907919035

## Calculated Structures and Complete Energies for Chapter IV

*Cyclopentadiene Dimerization*

**freqinHP with isotope label**  
 B3LYP/6-31G\*  
 E(RB3LYP) = -388.171193361

Zero-point correction= 0.188274 (Hartree/Particle)  
 Thermal correction to Energy= 0.196349  
 Thermal correction to Enthalpy= 0.197293  
 Thermal correction to Gibbs Free Energy= 0.156170  
 Sum of electronic and ZPE= -387.982919  
 Sum of electronic and thermal Energies= -  
 387.974845  
 Sum of electronic and thermal Enthalpies= -  
 387.973900  
 Sum of electronic and thermal Free Energies= -  
 388.015024

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	123.211	33.304 86.551

6 0.273732 1.536339 0.112209

*Acetone Cation Radical Dissociation*

**freqinHP**  
 B2PLYP/6-31+G\*\*  
 E(UB2PLYP) = -192.357786728

Zero-point correction= 0.078219 (Hartree/Particle)  
 Thermal correction to Energy= 0.083094  
 Thermal correction to Enthalpy= 0.084038  
 Thermal correction to Gibbs Free Energy= 0.050419  
 Sum of electronic and ZPE= -192.476207  
 Sum of electronic and thermal Energies= -  
 192.471332  
 Sum of electronic and thermal Enthalpies= -  
 192.470387  
 Sum of electronic and thermal Free Energies= -  
 192.504006

E	CV	S
KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	52.142	16.065 70.757

6 0.000000 0.080121 0.000000  
 8 -1.195552 -0.365113 0.000000  
 6 0.375858 1.489939 0.000000  
 1 1.005336 1.683619 0.876526  
 1 -0.499147 2.137346 0.000000  
 6 0.703303 -1.215268 0.000000  
 1 -0.652741 -1.563852 0.000000  
 1 1.115334 -1.574287 -0.942119

6 -0.273732 0.941295 -1.052909  
 6 -1.773217 0.811969 -0.799895  
 6 -1.822414 0.838772 0.704324  
 6 -0.665160 1.401353 1.172886  
 1 -2.247205 -0.056996 -1.266613  
 1 -2.276701 1.708834 -1.200371  
 6 0.273732 -0.941295 -1.052909  
 6 1.773217 -0.811969 -0.799895  
 6 1.822414 -0.838772 0.704324  
 6 0.665160 -1.401353 1.172886  
 6 -0.273732 -1.536339 0.112209  
 1 2.247205 0.056996 -1.266613  
 1 2.276701 -1.708834 -1.200371  
 1 -2.705815 0.607988 1.289153  
 1 -0.462081 1.650739 2.209966  
 1 1.246338 2.005685 0.190054  
 1 0.082429 1.223429 -2.041875  
 1 -0.082429 -1.223429 -2.041875  
 1 -1.246338 -2.005685 0.190054  
 1 0.462081 -1.650739 2.209966  
 1 2.705815 -0.607988 1.289153

1 1.005336 1.683619 -0.876526  
 1 1.115334 -1.574287 0.942119

### acetone cation radical enol form

1 2  
 C,0,-2.9916327026,1.3697827519,0.6811602966  
 O,0,-1.9710271686,0.7500268364,1.1701034018  
 C,0,-2.7046190617,2.3406161821,-0.3956129994  
 H,0,-3.2938979158,2.0870210159,-1.2856692103  
 H,0,-1.6419999539,2.3518194523,-0.6363930167  
 C,0,-4.3070104591,1.1216316802,1.166373254  
 H,0,-2.1663265291,0.1105778115,1.8858618425  
 H,0,-5.1445397908,1.6580911456,0.7350931251  
 H,0,-3.0280308285,3.3403209626,-0.0768255041  
 H,0,-4.4972997399,0.4060371417,1.9609915505

### TS1 – main TS

1 2  
 C,0,-2.9165568456,1.4280804665,0.5844469399  
 O,0,-2.0856822624,0.6483042564,1.1294260281  
 C,0,-2.5898741602,2.4523249724,-0.4025868241  
 H,0,-3.1758477697,2.259664651,-1.311879955  
 H,0,-1.5217826646,2.4704960417,-0.6232592931  
 C,0,-4.1327034422,0.937966714,1.2594438751  
 H,0,-3.0868080966,0.1321142636,1.7868390363  
 H,0,-4.5209720562,1.5192891484,2.0978215573



H,0,-2.9289068386,3.4252037245,-0.0206694968  
H,0,-4.7872500762,0.2624807477,0.705500881

#### acetone cation radical keto form

1 2

C,0,-2.9518299922,1.3894509996,0.6387868288  
O,0,-2.1013878877,0.6922340723,1.1313619533  
C,0,-2.5595706465,2.4095718017,-0.4221173603  
H,0,-2.9527612658,2.01750053,-1.368564567  
H,0,-1.4782779771,2.5305154057,-0.4701440568  
C,0,-4.3986368856,1.2338661702,1.0887973871  
H,0,-4.5292291481,0.3336404753,1.6876816375  
H,0,-4.6232393839,2.1324011244,1.6772529543  
H,0,-3.0694540833,3.3450906505,-0.1733257732  
H,0,-5.0170704699,1.2232137701,0.1862948664

#### ion neutral complex

1 2

C,0,-2.3144576346,1.046125416,0.1826172966  
O,0,-1.5722733867,0.3172932121,-0.2288692014  
C,0,-3.2757787027,1.9480224652,0.7351946295  
H,0,-3.9682307486,2.2505183251,-0.0606310584  
H,0,-2.7442947715,2.816149099,1.1453696546  
C,0,-5.041448761,0.5917649422,3.1703760906  
H,0,-5.7358845173,1.4228345671,3.2028173405  
H,0,-5.3592531904,-0.3254964724,2.6890308921  
H,0,-3.8297727269,1.412531084,1.5488197651  
H,0,-4.2673495603,0.5381213616,3.9266135907

#### TS3 – methyl abstraction

1 2

C,0,-1.8112256032,1.5428869751,-0.4510496357  
O,0,-1.2977438842,0.6760485643,-0.9582485901  
C,0,-2.5160081327,2.5307450063,0.2413139681  
H,0,-3.1344633435,3.1364820461,-0.426944806  
H,0,-1.865156311,3.1112428187,0.9011484911  
C,0,-4.3342226014,1.5114570556,1.9595757811  
H,0,-3.7254624032,0.9240251286,2.6441471552  
H,0,-4.7093516579,2.4587424513,2.3415619487  
H,0,-3.3683995959,1.9459337011,1.0447804278  
H,0,-5.005616237,0.955853093,1.3077837399

#### Ketene Methane Complex

1 2

C,0,-1.934584115,1.176920488,-0.2622377128  
O,0,-1.3861028829,0.334867268,-0.7707930597  
C,0,-2.6047088739,2.2242001709,0.3548643207  
H,0,-3.5940301085,2.4917884719,-0.0105954447  
H,0,-2.1009824884,2.758840898,1.1575704196  
C,0,-3.5278443457,-0.1053538322,2.0667420643  
H,0,-2.4419347602,-0.1782092156,2.1785841218  
H,0,-3.9817203323,-0.7767711685,2.8001084937

H,0,-3.8821785182,0.9073792749,2.2885276769  
H,0,-3.8536816649,-0.4302438556,1.0741220701

#### Methyl radical

0 2

C,0,-1.4234899186,4.4848375139,-0.219118297  
H,0,-0.9138114235,3.5848337074,0.0935873902  
H,0,-0.9137916822,5.2056409226,-0.8421865282  
H,0,-2.4419100428,4.6653907235,0.0935874048

#### Methane

0 1

C,0,-1.334033679,4.611344426,0.  
H,0,-0.9699673309,3.5815696016,-0.0000008957  
H,0,-0.9699478894,5.126224706,0.891807339  
H,0,-0.9699493521,5.1262257403,-0.891807339  
H,0,-2.4262701436,4.6113576561,0.0000008957

#### acylium cation

1 1

C,0,-1.7784789796,1.4578760224,-0.189485578  
O,0,-1.0319962744,0.6970978364,-0.520447513  
C,0,-2.7414088558,2.4398063046,0.2374824506  
H,0,-3.3300373612,2.7442087515,-0.638155433  
H,0,-3.3846427505,1.9792390302,0.9989856909  
H,0,-2.1943619282,3.2954785048,0.6550722133

#### ketene

1 2

C,0,-1.7116365614,1.4629013797,-0.2995454789  
O,0,-1.0402025565,0.6037259827,-0.5797244835  
C,0,-2.5403553744,2.5233403953,0.0462660386  
H,0,-3.4256949962,2.7091769548,-0.5601325837  
H,0,-2.2739643094,3.1295181934,0.9109423015

#### TS2 endo isomerization

1 2

C,0,-0.0530664468,-0.5482294613,0.1246566749  
O,0,-0.0297600184,-1.8287972881,0.0663513251  
C,0,0.1108567881,0.416836029,1.2008912056  
H,0,1.010813727,0.4517307734,1.817271109  
H,0,-0.8197939471,0.7014519064,1.6933399627  
C,0,-0.2760875011,0.3750291849,-0.9699250806  
H,0,-1.1717941602,0.3258538906,-1.5906595801  
H,0,-0.1132826027,1.2712557798,0.1038805494  
H,0,0.6373092269,0.7060722504,-1.4659178964  
H,0,0.0934642443,-2.2676852251,0.9312587204

#### TS2 exo isomerization

1 2

C,0,-0.1035102939,-0.1145375533,-0.0120189762  
O,0,0.3542389569,-1.3544881976,0.0710908437  
C,0,-0.2220167626,0.5959628216,1.2222888039  
H,0,0.1562215514,0.1392351339,2.1277949461  
H,0,-0.7088435236,1.5625731673,1.2511872006  
C,0,-0.2655628689,0.5952643802,-1.2432277173  
H,0,-0.771610929,1.5528766166,-1.249985676  
H,0,0.7259099893,0.9131914959,-0.0307720191  
H,0,0.0885869038,0.1750337221,-2.1765146546  
H,0,0.4634417966,-1.7904228167,-0.7896016312

**protonated ketene**

1 1  
C,0,0.9440677024,-1.2426816049,-0.2586515849  
O,0,1.8348384851,-2.0962884699,-0.2453161828  
C,0,-0.0689467907,-0.4591186505,-0.3418894322  
H,0,-0.18303858,0.1887586496,-1.2103329777  
H,0,-0.7937342192,-0.4222015606,0.4706880261  
H,0,2.6923934024,-1.8276283637,0.1638521515

## APPENDIX C

### PROGRAMS FOR CALCULATIONS AND SAMPLE INPUT FILES

#### Calculations and Sample Input Files for Chapter II

##### *Program Suite PROGDYN*

PROGDYN was used for trajectories in the gas phase or in implicit solvent. A full listing of the subprograms of PROGDYN can be found as a permanent public dataverse set at <https://dataverse.harvard.edu/dataset.xhtml?persistentId=doi:10.7910/DVN/TQZR7E>. To allow the reader to understand or make use of PROGDYN, we describe here the overall structure of the program.

The master control program for PROGDYN, in the form of a Unix Shell Script, is called *progdynstarterHP*. For a user to start to use *progdynstarterHP*, some early lines in it that assign the scratch space and the location of the program files and input files would have to be modified for the local environment. These lines are between lines 49 and 56 and should be apparent. The location of the scratch space is usually passed to *progdynstarterHP* as a parameter. The other system-specific modification is that the component program *proggenHP* calls some python 3.x programs. The system must be set up to run python 3 and the location of the python programs *toxyz.py* and *tozmat.py* must be specified. The location of these lines can be found by searching for “python” in *proggenHP*.

*progdynstarterHP* takes as input files:

*freqinHP* - This is the standard output from a Gaussian 09 or 16 frequency calculation using *freq=hpmodes*. For isotopically labeled compounds, use *freq=(hpmodes,readisotopes)*.

*progdyn.conf* – This is a file giving a variety of configuration options, called on by many of the subprograms. *progdyn.conf* examples are listed below and contains explanations of the program options.

*isomernumber* - A number in file *isomernumber* provides a start for numbering runs. The default is 1.

*detour* – A signal file that, by existing, signals the program to do a side calculation.

*nogo* – A signal file that, by existing, signals the program to stop between points

*bypassproggen* - A signal file that, by existing, signals the program to use a supplied input file *geoPlusVel* instead of generating one for itself. This pathway for initialization is important here because it is used when the program *progdynsam*, described later, is used to generate the *geoPlusVel* file.

*methodfile* – A file that contains lines to be added to the end of each *g09.com* or *g16.com* input file, such as lines that call for an NMR calculation. This is only used when the calculations require numerous special keywords.

*cannontraj* – A file containing a vector for each atom, used to fire an initial geometry in a particular direction. This is not used for ordinary trajectories.

*progdynstarterHP* calls the following programs:

*proggenHP* - An awk program that starts a trajectory, giving each mode its zero point energy (if a quasiclassical calculation) plus random additional excitations depending on the temperature.

*prog1stpoint* - Awk program that creates the first Gaussian input file for each run

*prog2ndpoint* - Awk program that creates the second Gaussian input file for each run. *prog2ndpoint* also checks the energy of the first point to see if it fits with the desired energy, and aborts the run if it does not by creating appropriate output in file *Echeck*

*progdynb* - Creates subsequent Gaussian input files until run is completed, written in awk

*proganal* - A program to analyze the latest point and see if a run is done. This program must be redone for each new system. Elaborate changes are sometimes programmed into *proganal*, such as the automatic changing of configuration variables. *proganal* creates the output to *dynfollowfile* and *NMRlist* or *NMRlistdis*

*randgen* - A program that generates random numbers between 0 and 1. These are generated all at once and stored in a file for use by *proggenHP*.

*tozmat.py* and *toxyz.py* - These programs convert specified geometries from internal coordinates to Cartesian coordinates and back, as a part of initiations that displace structures in internal coordinates. They are called by *proggenHP* by a system call to python. The system must be set to run python 3.x and the correct location of *tozmat.py* and *toxyz.py* must be specified in *proggenHP*.

*progdynstarterHP* and its called programs have the following output files:

*isomernumber* - A running tab of the trajectory number

*runpointnumber* - a running tab of the point in the trajectory

*Echeck* - output form where *prog2ndpoint* checks the energy of the trajectory to see if it fits with the desired energy

*geoRecord* - A record of all of the *geoPlusVel* files.

*geoPlusVel* - Created by *proggen*, this gives the starting positions, velocities, isotopic masses, excitations of the normal modes, and initial displacements of the normal modes for current run.

*g09.com* - Created by *prog1stpoint*, *prog2ndpoint*, and *progdynb*, this is the latest input file for Gaussian 09 for current run and latest point.

*olddynrun*, *olddynrun2*, *olddynrun3* - files containing the last three outputs from Gaussian, for creation of the next point

*traj*, *traj1*, *traj2*, *traj3*, etc. - files containing the geometries and energies for each trajectory, numbered by the *isomernumber*, in a format suitable for reading by Molden.

*dynfollowfile* - A point-by-point record of the trajectory runs including point times and selected distances, along with the trajectory results. The data desired for *dynfollowfile* must be programmed into the script *proganal* as needed for each system studied.

*NMRlist* or *NMRlistdis* - output of NMR predictions at each point in a trajectory, when desired

*skipstart* - A signal file that, by existing, tells *progdynstarterHP* that we are in the middle of a run. For trajectories that are propagated forward and backward in time, *skipstart* keeps track of whether one is in the forward or reverse part.

*diagnostics* - optional output that follows which subprograms are running and configuration variables, decided by variable in *progdyn.conf*

*vellist* - optional output that lists the velocities of each atom, decided by variable in *progdyn.conf*, or lists the total kinetic energy in the system and the classical temperature, often also keeps track of the density

*dzdmlist* – A list of the displacements in internal coordinates per displacement of vibrational modes in Cartesian coordinates.

*zOrig* – The original starting geometry specified in internal coordinates.

A number of files starting with '*temp*' are created then later erased.

For ordinary trajectory runs, a directory containing progdynstarterHP, proggenHP, prog1stpoint, prog2ndpoint, proggenHP, proganal, and a freqinHP file is created, and we typically name this directory *binall*. Separate directories containing progdyn.conf are created for however many trajectories are desired. A central directory containing randgen, tozmat.py, and toxyz.py is also established, typically ~/bin for us. A queue job submission file then goes to the directory containing progdyn.conf then calls progdynstarterHP and passes along the location of the scratch directory.

### *Program Suite ProgdynONIOM*

ProgdynONIOM was used for trajectories in explicit solvent. A full listing of the subprograms of ProgdynONIOM can be found as a permanent public dataverse set at <https://dataverse.harvard.edu/dataset.xhtml?persistentId=doi:10.7910/DVN/TQZR7E>. To allow the reader to understand or make use of ProgdynONIOM, we describe here the overall structure of the program.

ProgdynONIOM is adapted from PROGDYN but designed to combine forces from Gaussian 09 and MOPAC2016 in ONIOM calculations. Its ONIOM capabilities are currently limited to systems where there is no covalent bond between the model (small) system and the real (full) system. The combination of the two programs extends the practical size of the QM/QM calculation, aside from allowing the extended semi-empirical methods in MOPAC2016.

PROGDYN and ProgdynONIOM are similar, and some of the description below is identical to that above, but there are differences to note. In particular, ProgdynONIOM runs three separate QM calculations for each trajectory point, with a separate input and output file for each.

ProgdynONIOM includes the ability to include additional empirical dispersion using Grimme's D2 model.<sup>183</sup> The specific parameters defining this dispersion, given in progdyn.conf, were empiricaldispersion 2.0, radiusmultiplier 1.5, empiricaldispersionb -0.3, radiusmultiplierb 0.8. The PM6-DH+ method already includes dispersion, but these additional corrections bring the solution toward an accurate density and heat of vaporization.

The master control program for dynamics, in the form of a Unix Shell Script, is called progdynONIOM. For a user to start to use progdynONIOM, some early lines in it that assign the scratch space and the location of the program files and input files would have to be modified for the local environment. These lines are between lines 27 and 41 and should be apparent. The location of the scratch space is usually passed to progdynONIOM as a parameter.

progdynONIOM takes as input files:

*freqinHP* - This is the standard output from a Gaussian 98, 03, or 09 frequency calculation using freq=hpmodes. For isotopically labeled compounds, use freq=(hpmodes,readisotopes).

*progdyn.conf* – This is a file giving a variety of configuration options, called on by many of the subprograms. *progdyn.conf* examples are listed below and contains explanations of the program options.

*isomernumber* – A number in file *isomernumber* provides a start for numbering runs. The default is 1.

*detour* – A signal file that, by existing, signals the program to do a side calculation.

*nogo* – A signal file that, by existing, signals the program to stop between points

*bypassprogen* – A signal file that, by existing, signals the program to use a supplied input file *geoPlusVel* instead of generating one for itself. This pathway for initialization is important here because it is used when the program *progdynsam*, described later, is used to generate the *geoPlusVel* file.

*methodfile* – A file that contains lines to be added to the end of each *g09.com* input file, such as lines that call for an NMR calculation

*cannontraj* – A file containing a vector for each atom, used to fire an initial geometry in a particular direction.

*progdynONIOM* calls the following programs:

*progenHP* – An awk program that starts a trajectory, giving each mode its zero point energy (if a quasiclassical calculation) plus random additional excitations depending on the temperature.

*prog1stpoint* – Awk program that creates the first Gaussian input file for each run

*prog2ndpoint* – Awk program that creates the second Gaussian input file for each run.

*prog2ndpoint* also checks the energy of the first point to see if it fits with the desired energy, and aborts the run if it does not by creating appropriate output in file *Echeck*

*progdynb* – Creates subsequent Gaussian input files until run is completed, written in awk

*proganal* – A program to analyze the latest point and see if a run is done. This program must be redone for each new system. Elaborate changes are sometimes programmed into *proganal*, such as the automatic changing of configuration variables. *proganal* creates the output to *dynfollowfile* and *NMRlist* or *NMRlistdis*

*randgen* – A program that generates random numbers between 0 and 1. These are generated all at once and stored in a file for use by *progenHP*.

*progdynONIOM* has the following output files:

*isomernumber* – A running tab of the trajectory number

*runpointnumber* – a running tab of the point in the trajectory

*Echeck* – output form where *prog2ndpoint* checks the energy of the trajectory to see if it fits with the desired energy

*geoRecord* – A record of all of the *geoPlusVel* files.

*geoPlusVel* – Created by *progen*, this gives the starting positions, velocities, isotopic masses, excitations of the normal modes, and initial displacements of the normal modes for current run.

*g09.com* – Created by *prog1stpoint*, *prog2ndpoint*, and *progdynb*, this is the latest input file for Gaussian 09 for current run and latest point.

*model.mop* - Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest input file for the model system for MOPAC2016, for current run and latest point.

*real.mop* - Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest input file for the real (full) system for MOPAC2016, for current run and latest point.

*g09.log, real.out, model.out* – These are the output files for the latest Gaussian 09 and MOPAC 2016 calculations, used for extracting forces in the creation of the next point.

*olddynrun, olddynrun2, olddynrun3* – files containing the last three outputs from MOPAC2016, for creation of the next point

*traj, traj1, traj2, traj3, etc.* – files containing the geometries and energies for each trajectory, numbered by the isomernumber, in a format suitable for reading by Molden.

*dynfollowfile* – A short record of the runs and their results. The data desired for *dynfollowfile* must be programed into the script *proganal* as needed for each system studied.

*skipstart* - A signal file that, by existing, tells progdynstarterHP that we are in the middle of a run. For trajectories that are propagated forward and backward in time, skipstart keeps track of whether one is in the forward or reverse part.

*diagnostics* – optional output that follows which subprograms are running and configuration variables, decided by variable in progdyn.conf

*vellist* – optional output that lists the velocities of each atom, decided by variable in progdyn.conf, or lists the total kinetic energy in the system and the classical temperature, often also keeps track of the density

A number of files starting with '*temp*' are created then later erased.

A number of helper programs used for starting and organization of ProgDynONIOM trajectories are described in a later section.

### **progdyn.conf options used for a typical umbrella slice for PMF**

```
method MP2/6-31+G**
lowmethod PM6-DH+
nonstandard 0
rotationmode 0
method2 read
charge 0
multiplicity 1
onionchargemult 0 1
processors 4
memory 7gb
killcheck 0
checkpoint g09.chk
diagnostics 4
title HClpentadiene 120MeNO2 ONIOM Eq
initialdis 0
timestep 1E-15
scaling 1.0
temperature 298.15
thermostat 1
```

thermostatmult 0.995  
method4 iop(2/9=2000)  
methodfile 0  
numimag 0  
searchdir positive  
classical 2  
keepevery 999999  
highlevel 17  
applyforce 2 0.40 1.32  
afatoms 1 14  
applyforceB 2 0.40 1.6  
afatomsB 14 15  
applyforceC 4 0.00 2.10 0.00 1.0  
afatomsC 15 16  
applyforceD 4 0.00 1.30 0.00 1.0  
afatomsD 16 17  
zeroatom 2  
sphereon 1  
spheresize 14.75  
sphereforce .1  
empiricaldispersion 2.0  
radiusmultiplier 1.5  
empiricaldispersionb -.3  
radiusmultiplierb 0.8  
etolerance 9999999  
damping 1.000  
reversetrajectory true

### **progdyn.conf options used for feeder trajectories**

method MP2/6-31+G\*\*  
lowmethod PM6-DH+  
nonstandard 0  
rotationmode 0  
method2 read  
charge 0  
multiplicity 1  
onionchargemult 0 1  
processors 4  
memory 7gb  
killcheck 0  
checkpoint g09.chk  
diagnostics 4  
title HClpentadiene 120MeNO2 ONIOM Eq  
initialdis 0



timestep 1E-15  
scaling 1.0  
temperature 298.15  
thermostat 1  
thermostatmult 0.995  
method4 iop(2/9=2000)  
methodfile 0  
numimag 0  
searchdir positive  
classical 2  
keepevery 999999  
highlevel 17  
applyforce 4 0.90 1.28 0.00 40.0  
afatoms 1 14  
applyforceB 4 0.60 1.68 0.00 1.0  
afatomsB 14 15  
applyforceC 4 0.00 2.20 0.00 1.0  
afatomsC 15 16  
applyforceD 4 0.00 1.30 0.00 1.0  
afatomsD 16 17  
zeroatom 3  
sphereon 1  
spheresize 14.75  
sphereforce .1  
empiricaldispersion 2.0  
radiusmultiplier 1.5  
empiricaldispersionb -.3  
radiusmultiplierb 0.8  
etolerance 9999999  
damping 1.000  
reversetraj true

### **progdyn.conf options used for spawned MP2 trajectories**

method MP2/6-31+G\*\*  
lowmethod PM6-DH+  
nonstandard 0  
rotationmode 0  
method2 read  
charge 0  
multiplicity 1  
oniomchargemult 0 1  
processors 4  
memory 7gb  
killcheck 0  
checkpoint g09.chk

diagnostics 4  
title HClpentadiene 120MeNO2 ONIOM MP2real  
initialdis 0  
timestep 1E-15  
scaling 1.0  
temperature 298.15  
thermostat 1  
thermostatmult 0.995  
method4 iop(2/9=2000)  
methodfile 0  
numimag 0  
searchdir positive  
classical 2  
keepevery 999999  
highlevel 17  
zeroatom 3  
sphereon 1  
spheresize 14.75  
sphereforce .1  
empiricaldispersion 2.0  
radiusmultiplier 1.5  
empiricaldispersionb -.3  
radiusmultiplierb 0.8  
etolerance 9999999  
reversetraj true

## Helper and Data-Analysis Programs

Terminology and some general explanations of program usage

See the discussion of *MD trajectories*, *feeder trajectories*, and *spawned trajectories* in a previous section. Each trajectory of each type is run in a separate directory.

A *trajectory directory* is one that contains a single completed trajectory.

A *container directory* is one that contains the collection of completed trajectory directories.

Typically, dozens or hundreds of spawned trajectories are set up to run simultaneously. When they are complete, they stop, and at some point the program *progmove* is run to rename the directories for each trajectory in a logical way and move the *trajectory directory* into a *container directory*.

Each spawned trajectory consists of two *legs*, resulting from their integration forward versus backward in time from their initialization. There is no meaning as to which direction is integrated first when the trajectories are ran, but analysis requires keeping track of which leg is of interest for the analysis at hand.

A *traj* file is a file in each *trajectory directory* that contains the geometries of each point in the trajectory for each of the two legs. Usually, only one of these legs is interesting so the analysis has to pick out which leg is of interest and collect this into a *traj-leg* file. For proton transfers from HCl to 1,3-pentadiene, the interesting leg is the one in which the H initially moves closer to C<sub>1</sub> of the diene, and in the main text this is described as “forward in time.”

Several of the programs below function to generate temporary programs that themselves are run to apply analysis to each of a series of trajectory directories. The temporary programs consist of repeated actions on hundreds or thousands of trajectories, and they are not saved. Additional temporary programs were generated by simple shell commands. Their generation and usage is described in a section below, though the programs themselves were not saved.

A *dynf-leg* file is trimmed portion of a *dynfollowfile* (see descriptions under PROGDYN and ProgdynONIOM) containing only the portion for a leg of interest. As with *traj-leg* files, the interesting leg of the *dynf-leg* files is the one that goes “forward in time,” defined by the H initially moving closer to C<sub>1</sub> of the diene.

The programs can be found as a permanent public dataverse set at <https://dataverse.harvard.edu/dataset.xhtml?persistentId=doi:10.7910/DVN/TQZR7E>.

### **Program progdynsam**

This is an awk program that aids in extracting the starting points for spawned trajectories from feeder trajectories. *progdynsam* generates a geoPlusVel file based on input from a *traj* file in the feeder trajectories. If fixed atoms are used as constraints (not a normal practice now), *progdynsam* must be modified for the desired temperature. *progdynsam* takes as input the variable *pt* to decide which points in the *traj* file are used to define the geoPlusVel. For previously fully fixed atoms, *progdynsam* gives the atoms a Boltzmann-random velocity and direction of motion appropriate for the desired temperature. Normally now, constraints in the feeder trajectories are harmonic, in which case no adjustment is made to the motions of the constrained atoms other than to remove the constraints. The program is invoked with `awk -v pt=## -f progdynsam traj` where *##* is the trajectory point used to start a new geoPlusVel, and *traj* is the output file containing the list of trajectory points.

### **Program proglookstart**

This is a bash script that examines a series of directories containing feeder trajectories and creates a temporary program, *progtmp2*, that will set up directories containing spawned trajectories using *progdynsam*. The temporary programs are not saved.

### **Program progmove**

This is a bash script that checks the spawned trajectories for completion. If a trajectory is complete, the trajectory directory is renamed in a meaningful way and moved to a container directory. The program then stops all of the running incomplete trajectories, renames their directories to create a new ordered list, and outputs commands for the user to copy to start the trajectories running again. This directory renaming is done to set up the directories so that *proglookstart* can be run with a specified starting point.

### **Program progci**

This is a bash script that does an initial analysis of the trajectories in the container directory, counts trajectory outcomes, outputs these outcomes along with information on trajectory times, and creates a series of files that contain lists that aid in further analysis.

Output files from *progci* include:

*returnreturn* – includes trajectory directory and final point information for trajectories that recross from reactants to reactants

*tempSMSM* – similar to *returnreturn*, except that it distinguishes between trajectories where

the first step was aimed at products versus those aimed at reactants.

*temp12first*, *temp12second*, *tempmPside1*, *tempmPside2*, *tempm1*, *tempm2*, *tempdiss1*, *tempdiss2* – these are files that collect trajectory directory and final point information for trajectories in various categories. “12first” and “12second” refers to trajectories that go from reactants to the 1,2-product, either in their first leg or their second.

*shortlist* – includes the shortest C-H distance in recrossing trajectories and trajectory directory information

*1212* - includes trajectory directory and final point information for trajectories that recross from 1,2-product to 1,2-product

*1214*- includes trajectory directory and final point information for trajectories that recross from 1,2-product to 1,4-product

*addtimelist12*, *addtimelistT2*, *addtimelist14*, *addtimelistT4* – collect the trajectory times for trajectories that afford the addition products from reactants

*manyswitcheslist* – keeps track of the number of times that trajectories switch from having a C1 atom closer to C2 versus closer to C4.

### **Program progprocessSMSM**

This is a bash script that generates two new programs, *progmsm* and *progmsmcharge*, based on *tempSMSM*. Running *progmsm* collects the interesting leg of the *traj* file (in recrossing trajectories on the reactant side, this is the leg that starts out in the direction of product) in each trajectory directory into a *traj-leg* file named *tempSMSMintraj*. Running *progmsmcharge* runs *progcharge* on the *tempSMSMintraj* in each trajectory directory, placing the output in *tempelectrostaticSMSMin*.

### **Program progcharge**

This is an awk program that takes as input specified *traj-leg* files point by point and calculates the “incipient ion-pair stabilization parameter”  $E_{ip}$  for each point, as described in the main text.

### **Program progaverage**

This is an awk program that takes as input a set of specified output files generated by *progcharge*, averages energies time-by-time, and outputs the average energies.

### **Program progdistanceaverage**

This is an awk program that takes as input a set of specified *dynf-leg* files, averages distances time-by-time, and outputs the average distances.

The input files for *progdistanceaverage* were generated making use of the output files from *progci* and creating a temporary program that created the files directory by directory. For example:  
sed 's/\// /' tempm1 | sed 's/fileHCl/file HCl/' | awk '{print "head -n",\$7,\$1"/dynfollowfile >",\$1"/dynfmanySM"}' > progtemp  
./progtemp

### **Generation and usage of additional temporary programs**

The programs *progml* and *progml2* were generated by these commands:  
sed 's/\// /' tempm1 | awk '{print "head -n 2578718",\$1"/traj1 >",\$1"/tempmanySM"}' > progml

sed 's// /' tempm2 | awk '{print "tail -n 2578718",\$1"/traj\* >",\$1"/tempmanySM"}' > prog2  
These programs collect the interesting long leg of the *traj* file for trajectories that survive 3000 fs after crossing from reactants in each trajectory directory into a *traj-leg* file named *tempmanySM*.

The programs *prog1charge* and *prog2charge* were generated by these commands:

```
sed 's// /' tempm1 | awk '{print "awk -f progcharge",$1"/tempmanySM >",$1"/tempelectrostaticManySM"}' > prog1charge
sed 's// /' tempm2 | awk '{print "awk -f progcharge",$1"/tempmanySM >",$1"/tempelectrostaticManySM"}' > prog2charge
```

These programs run *progcharge* on the *tempmanySM* *traj-leg* files and store the results in files named *tempelectrostaticManySM*.

The programs *prog12first* and *prog12second* were generated by these commands:

```
sed 's// /' temp12first | awk '{print "head -n",($6+1)*859,$1"/traj* >",$1"/temp12fromSM"}' > prog12first
sed 's// /' temp12second | awk '{print "tail -n",($6+1)*859,$1"/traj* >",$1"/temp12fromSM"}' > prog12second
```

These programs collect the interesting product-forming leg of the *traj* file for trajectories that form the 1,2-product after crossing from reactants in each trajectory directory into a *traj-leg* file named *temp12fromSM*.

The programs *prog12firstcharge* and *prog12secondcharge* were generated by these commands:

```
sed 's// /' temp12first | awk '{print "awk -f progcharge",$1"/temp12fromSM >",$1"/tempelectrostatic12fromSM"}' > prog12firstcharge
sed 's// /' temp12second | awk '{print "awk -f progcharge",$1"/temp12fromSM >",$1"/tempelectrostatic12fromSM"}' > prog12secondcharge
```

These programs run *progcharge* on the *temp12fromSM* *traj-leg* files and store the results in files named *tempelectrostatic12fromSM*.

The programs *progMP1* and *progMP2* were generated by these commands:

```
sed 's// /' tempmPside1 | awk '{print "head -n 2578718",$1"/traj* >",$1"/tempmanyPside"}' > progMP1
sed 's// /' tempmPside2 | awk '{print "tail -n 2578718",$1"/traj* >",$1"/tempmanyPside"}' > progMP2
```

These programs collect the interesting long leg of the *traj* file for trajectories that recross on the product side and have a leg that survives 3000 fs in each trajectory directory into a *traj-leg* file named *tempmanyPside*.

The programs *progMP1charge* and *progMP2charge* were generated by these commands:

```
sed 's// /' tempmPside1 | awk '{print "awk -f progcharge",$1"/tempmanyPside >",$1"/tempelectrostaticManyP"}' > progMP1charge
sed 's// /' tempmPside2 | awk '{print "awk -f progcharge",$1"/tempmanyPside >",$1"/tempelectrostaticManyP"}' > progMP2charge
```

These programs run *progcharge* on the *tempmanyPside* *traj-leg* files and store the results in files named *tempelectrostaticManyP*.

The programs *progdiss1* and *progdiss2* were generated by these commands:

```
sed 's// /' tempdiss1 | awk '{print "head -n",($6+1)*859,$1"/traj* >",$1"/tempdissSM"}' > progDiss1
sed 's// /' tempdiss2 | awk '{print "tail -n",($6+1)*859,$1"/traj* >",$1"/tempdissSM"}' > progDiss2
```

These programs collect the interesting ion-dissociating leg of the *traj* file for trajectories that cross from reactants in each trajectory directory into a *traj-leg* file named tempdissSM.

```
sed 's/\// /' tempdiss1 | awk '{print "awk -f progcharge",$1"/tempdissSM
>",$1"/tempelectrostaticdissSM"}' > progdiss1charge
sed 's/\// /' tempdiss2 | awk '{print "awk -f progcharge",$1"/tempdissSM
>",$1"/tempelectrostaticdissSM"}' > progdiss2charge
```

These programs run progcharge on the tempdissSM traj-leg files and store the results in files named tempelectrostaticdissSM.

## Calculations and Sample Input Files for Chapter III

### *Program Suite PROGDYN*

A full listing of the subprograms of PROGDYN is given below. To allow the reader to understand or make use of PROGDYN, we describe here first the overall structure of the program. We also list and describe in this section some helper programs that were used to analyze the data from the trajectory calculations.

The master control program for dynamics, in the form of a Unix Shell Script, is called *progdynstarterHP*. For a user to start to use *progdynstarterHP*, some early lines in it that assign the scratch space and the location of the program files and input files would have to be modified for the local environment. These lines are between lines 45 and 60 and should be apparent. The location of the scratch space is usually passed to *progdynstarterHP* as a parameter.

*progdynstarterHP* takes as input files:

*freqinHP* - This is the standard output from a Gaussian 98, 03, 09, or 16 frequency calculation using freq=hpmodes. For isotopically labeled compounds, use freq=(hpmodes,readisotopes).

*progdyn.conf* - This is a file giving a variety of configuration options, called on by many of the subprograms. *progdyn.conf* examples are listed below and contains explanations of the program options.

*detour* - A signal file that, by existing, signals the program to do a side calculations. This is usually omitted.

*nogo* - A signal file that, by existing, signals the program to stop between points This is usually omitted.

*bypassprogen* - A signal file that, by existing, signals the program to use a supplied input file *geoPlusVel* instead of generating one for itself. This is most often used when running dynamics in solution, and was not employed here.

*methodfile* - A file that contains lines to be added to the end of each g09.com input file, such as lines that call for an NMR calculation. This is usually omitted.

*ZMAT* - An input file for the CFOUR (<http://www.cfour.de>) suite of programs. When ZMAT is supplied, *progdynstarterHP* will automatically run call CFOUR (which must be set up independently by the user) by making use of the script *progefour*. This is usually omitted.

*cannontraj* – A file containing a vector for each atom, used to fire an initial geometry in a particular direction. This is usually omitted.

*progdynstarterHP* calls the following programs:

*proggenHP* – An awk program that starts a trajectory, giving each mode its zero point energy (if a quasiclassical calculation) plus random additional excitations depending on the temperature. Because *proggenHP* calls two python 3 programs, the local environment has to be set up in whatever way will get the python calls to work.

*prog1stpoint* – Awk program that creates the first Gaussian input file for each run

*prog2ndpoint* – Awk program that creates the second Gaussian input file for each run.

*prog2ndpoint* also checks the energy of the first point to see if it fits with the desired energy, and aborts the run if it does not by creating appropriate output in file *Echeck*

*progdynb* – Creates subsequent Gaussian input files until run is completed, written in awk

*proganal* – A program to analyze the latest point and see if a run is done. This program must be redone for each new system. Elaborate changes are sometimes programmed into *proganal*, such as the automatic changing of configuration variables. *proganal* creates the output to *dynfollowfile* and *NMRlist* or *NMRlistdis*

*progcfour* – A control script to run CFOUR calculations (not needed for most kinds of runs, not used or listed here).

*proggenHP* calls three python 3 programs:

*randgen.py* – A python program that generates random numbers between 0 and 1. These are generated all at once and stored in a temporary file for use by *proggenHP*.

*tozmat.py* – a python 3 program that takes a temporary geometry file in cartesian format and converts it to another temporary geometry file in internal coordinates.

*toxyz.py* – a python 3 program that takes a temporary geometry file in internal coordinates format and converts it to another temporary geometry file in cartesian coordinates.

*progdynstarterHP* has the following output files:

*isomernumber* – A running tab of the trajectory number

*runpointnumber* – a running tab of the point in the trajectory

*Echeck* – output from where *prog2ndpoint* checks the energy of the trajectory to see if it fits with the desired energy

*geoRecord* – A record of all of the *geoPlusVel* files.

*geoPlusVel* – Created by *proggen*, this gives the starting positions, velocities, isotopic masses, excitations of the normal modes, and initial displacements of the normal modes for current run.

*g09.com* or *g16.com* – Created by *prog1stpoint*, *prog2ndpoint*, and *progdynb*, this is the latest input file for Gaussian09 or Gaussian 16 for current run and latest point.

*olddynrun*, *olddynrun2*, *olddynrun3* – files containing the last three outputs from Gaussian, for creation of the next point

*traj*, *traj1*, *traj2*, *traj3*, etc. – files containing the geometries and energies for each trajectory, numbered by the *isomernumber*, in a format suitable for reading by Molden. The energies listed in these files are for the previous point.

*dynfollowfile* – A short record of the runs and their results. The data desired for *dynfollowfile* must be programmed into the script *proganal* as needed for each system studied.

*NMRlist* or *NMRlistdis* – output of NMR predictions at each point in a trajectory, when desired. Usually not used.

*skipstart* - A signal file that, by existing, tells progdynstarterHP that we are in the middle of a run. For trajectories that are propagated forward and backward in time, skipstart keeps track of whether one is in the forward or reverse part.

*diagnostics* – optional output that follows which subprograms are running and configuration variables, decided by variable in progdyn.conf.

*vellist* – optional output that lists the velocities of each atom, decided by variable in progdyn.conf, or lists the total kinetic energy in the system and the classical temperature, often also keeps track of the density

A number of files starting with '*temp*' are created then later erased.

The following helper programs were used for the current study.

prograjdynfconall – an awk program that reanalyzes all of the traj files, pulling out desired distances, angles, and dihedral angles. The program is invoked with `awk -f prograjdynfconall pathToAllTrajFiles`

progcount - a bash program that gathers results and counts the occurrence for each result in a set of trajectories.

## progdynstarterHP

```
#!/bin/bash
#progdynstarterHP, made to use high-precision modes from
Gaussian output with freq=hpmodes
#updated to create a random number file temp811 that is used by
proggenHP
#version September 16, 2005, made for workstations
#version August 2007 to allow periodic copying of g09.log to dyn
putting it under control of progdynb
#version Feb 2008 moves variables like the scratch directory and
location of randgen to the beginning
#version March 2008 added proganal reporting to points 1 and 2
#version Jan 2009 fixed bug generator of having proganal run
twice in checking for complete runs
#version May 2009 Echeck catches bad energies after only one
point, other lines written simpler, triple while loop, revised
comments
#version Aug 2010 isomernumber adds words to ease parsing,
increased elements up to bromine, runpointnumber checked for
more appropriate restarts
#version Aug 2011 runpointnumber starts better, restart better if
died during first few points, awk bug fix
#version Aug 2012 freqinHP reads with only 3 freqs, goingwell
and other temp files moved to $scratchdir
#version Aug 2013 adds ability to automatically run a CFOUR
program if the file ZMAT exists
#version Nov 2013 adds ability to bypass generation of geoPlusVel
using the signal file bypassproggen
#version Nov 2015 makes using guess=read easier, improves
ability to restart after disk write failures, partially allows for MM
runs in Gaussian
#version Aug 2017 - modified for Gaussian 16
#LIMITATIONS - standard version only handles elements up to
bromine, must change program to do higher atomic numbers
# only handles up to 4000th excited state for modes - this could
start to affect the initialization of classical modes or transition
vectors at
```

```
# extremely high temperatures
# The routine that checks whether the actual energy
approximately equals the desired energy checks for lines
containing "SCF Done" or "EUMP2 =" or " Energy="
# This should handle ordinary calculations HF, DFT, ONIOM,
and MP2 calculatons but the routine in prog2ndpoint would have
to be changed for other calcs.
#
#                               OUTLINE
# A. initialize to perform Gaussian jobs, set the scratch, program,
and other directories, remove errant control files
# start outermost loop L1L1L1L1L1L1L1L1
# start loop 2 L2L2L2L2L2L2L2L2L2L2
# B. branch on whether there is a file named "skipstart"
# if there is, skip B1, B2, B3 entirely
# if no file named "skipstart" then generate a new isomer.
Instructions: Get rid of skipstart to start new isomer.
# the B loop generates geoPlusVel, adds it to geoRecord,
generates and runs first and second points, and sets up for
continuous loop
# B1. generates geoPlusVel, isomernumber, runpointnumber=1,
then makes g09.com for point 1
# B2. checks for success of B1 or exits, then sets geoRecord then
runs g09.com. Checks for its success or exits.
# B3. runpointnumber=2, kills run if XXXX in dynfollowfile due
to bad energy probably, makes g09.com for point 2, runs it
# checks for its success or exits
# runpointnumber=3, uses progdynb to make g09.com for point
3
# sets skipstart=forward
# B4. Only runs if skipstart=ireverserestart, performs
reverserestart, ends with runpointnumber=3
# sets skipstart=reverse
# C. loop over propagation steps
#
#
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
```





```

cd $Scratchdir
cp $origdir/g16.com $Scratchdir/g16.com
$g16root/g16/g16 $Scratchdir/g16.com $Scratchdir/g16.log
cd $origdir
grep 'Normal termination' $Scratchdir/g16.log >
$Scratchdir/goingwell
if (test -s $Scratchdir/goingwell) then
  cp $Scratchdir/g16.log $origdir
  cp $Scratchdir/g16.log olddynrun2
else
  cp $Scratchdir/g16.log $origdir/g16.log
  break
fi
else
  break
fi
#
B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3
B3B3B3B3B3B3B3B3B3 if B2 worked then you are here. create
2nd point, run it, and set up for propagation loop
rm g16.com
echo 2 > runpointnumber
awk -f $programpdir/prog2ndpoint $Scratchdir/g16.log >
g16.com
# before we decide to run this, check the energy
awk -f $programpdir/proganal $Scratchdir/g16.log >>
dynfollowfile
rm -f $Scratchdir/tempdone
tail -1 dynfollowfile | awk '/XXXX/ {print}' >
$Scratchdir/tempdone
if (test -s $Scratchdir/tempdone) then
  rm -f dyn
  rm -f traj
  echo 0 > runpointnumber
  break
fi
if (test -s g16.com) then
  rm -f $Scratchdir/goingwell
  cd $Scratchdir
  cp $origdir/g16.com $Scratchdir/g16.com
  $g16root/g16/g16 $Scratchdir/g16.com $Scratchdir/g16.log
  cd $origdir
  grep 'Normal termination' $Scratchdir/g16.log >
$Scratchdir/goingwell
if (test -s $Scratchdir/goingwell) then
  cp $Scratchdir/g16.log olddynrun
  awk -f $programpdir/proganal $Scratchdir/g16.log >>
dynfollowfile
  awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' olddynrun | awk '{if (($2>.5)
&& ($2<100)) print}' > old
  awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' olddynrun2 | awk '{if (($2>.5)
&& ($2<100)) print}' > older
  echo 3 > runpointnumber
  if (test -f bypassprogen) then
    cat bypassprogen > runpointnumber
  echo 3 > bypassprogen
  fi
  awk -f $programpdir/progdynb olddynrun > g16.com
  rm -f old older
else
  cp $Scratchdir/g16.log $origdir/g16.log
  break
fi
else
  break
fi
# we've just completed a start, so lets skipstart until instructed
otherwise

```

```

echo "forward" > skipstart
fi
#
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
# Reverse trajectories starter routine
if [ `cat skipstart` = "reverserestart" ]; then
  cd $origdir
  rm g16.com
  echo 1 > runpointnumber
  awk -f $programpdir/prog1stpoint isomernumber > g16.com
  if (test -s g16.com) then
    rm -f $Scratchdir/goingwell
    cd $Scratchdir
    cp $origdir/g16.com $Scratchdir/g16.com
    $g16root/g16/g16 $Scratchdir/g16.com $Scratchdir/g16.log
    cp $Scratchdir/g16.log $origdir
    cd $origdir
    grep 'Normal termination' $Scratchdir/g16.log >
$Scratchdir/goingwell
if (test -s $Scratchdir/goingwell) then
  cp $Scratchdir/g16.log olddynrun2
else
  cp $Scratchdir/g16.log $origdir/g16.log
  break
fi
else
  break
fi
rm g16.com
echo 2 > runpointnumber
awk -f $programpdir/prog2ndpoint $Scratchdir/g16.log >
g16.com
awk -f $programpdir/proganal $Scratchdir/g16.log >>
dynfollowfile
rm -f $Scratchdir/tempdone
if (test -s g16.com) then
  rm -f $Scratchdir/goingwell
  cd $Scratchdir
  cp $origdir/g16.com $Scratchdir/g16.com
  $g16root/g16/g16 $Scratchdir/g16.com $Scratchdir/g16.log
  cp $Scratchdir/g16.log $origdir
  cd $origdir
  grep 'Normal termination' $Scratchdir/g16.log >
$Scratchdir/goingwell
if (test -s $Scratchdir/goingwell) then
  cp $Scratchdir/g16.log olddynrun
  awk -f $programpdir/proganal $Scratchdir/g16.log >>
dynfollowfile
  awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' olddynrun | awk '{if (($2>.5)
&& ($2<100)) print}' > old
  awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' olddynrun2 | awk '{if (($2>.5)
&& ($2<100)) print}' > older
  echo 3 > runpointnumber
  if (test -f bypassprogen) then
    cat bypassprogen > runpointnumber
  echo 3 > bypassprogen
  fi
  awk -f $programpdir/progdynb olddynrun > g16.com
  rm -f old older
else
  cp $Scratchdir/g16.log $origdir/g16.log
  break
fi
else
  break
fi

```

```

# we've just completed a reversestart, so lets skipstart until
instructed otherwise
    echo "reverse" > skipstart
fi

#
END_of_B__END_of_B__END_of_B__END_of_B__END_
of_B__END_of_B__END_of_B__END_of_B__
#
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
propagation loop
while (true)
do
    rm -f $scratchdir/goingwell
    cd $scratchdir
    cp $origdir/g16.com $scratchdir/g16.com
    $g16root/g16/g16 $scratchdir/g16.com $scratchdir/g16.log
    cd $origdir
    grep 'Normal termination' $scratchdir/g16.log >
$scratchdir/goingwell
    if (test -s $scratchdir/goingwell) then
        awk -f $programdir/proganal $scratchdir/g16.log >>
$origdir/dynfollowfile
        mv olddynrun2 olddynrun3
        mv olddynrun olddynrun2
        awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' $scratchdir/g16.log | awk '{if
(($2>.5) && ($2<100)) print}' > old
        cp $scratchdir/g16.log olddynrun
        awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' olddynrun2 | awk '{if (($2>.5)
&& ($2<100)) print}' > older
        #increment runpointnumber
        cp runpointnumber $scratchdir/temp533
        awk 'BEGIN {getline;i=$1+1;print i}' $scratchdir/temp533 >
runpointnumber
        rm $scratchdir/temp533
        awk -f $programdir/progdynb $scratchdir/g16.log >
g16.com
        rm -f old older
    else
        cp $scratchdir/g16.log $origdir/g16.log
        break
    fi
# kludge to do a side calculation of NMR using progcfour. If
ZMAT is there then it gets ran and renamed.
# creation of ZMAT is under the control of progdynb, which is
controlled by keyword NMRec in progdyn.conf
# decisions to be made: erase ZMAT at beginning? what to do if
cfour calc dies?
    if (test -f ZMAT) then
        cp ZMAT $scratchdir
        cd $scratchdir
        $scratchdir/progcfour $origdir $scratchdir
        cd $origdir
        mv ZMAT temp.ZMAT
        echo "generic one two three" `cat runpointnumber`
"runisomer" `cat isomernumber` >> NMRlistcc
        awk '/Nuclear Magnetic Resonance/,/HF-SCF/ {if ($2=="C")
print $1,$2,"Isotropic =", $3; if ($2=="H") print $1,$2,"Isotropic
=", $3}' x.log >> NMRlistcc
    fi

# here is a cool link that lets you interrupt the dynamics with a short
job, then
# it automatically goes back to the dynamics just make the file
'detour' and it
# will delete detour, run run.com, then go back to dynamics
    if (test -f detour) then

```

```

    rm detour
    date >> $logfile
    cat run.com >> $logfile
    cp run.log temp.log
    cd $scratchdir
    $g16root/g16/g16 $origdir/run.com $origdir/run.log
    cd $origdir
fi

#stop it all nicely by creating a nogo file
    if (test -f nogo) then
        break
    fi

#figure out if this isomer is done - change in april 2013 is to move
proganal call up from here
    rm -f $scratchdir/tempdone
    tail -2 dynfollowfile | awk '/XXXX/ {print}' >
$scratchdir/tempdone
    if (test -s $scratchdir/tempdone) then
        if [ `awk /reversetraj/ {if ($1=="reversetraj") print $2}`
progdyn.conf = "true" ]; then
            if [ `cat skipstart` = "reverse" ]; then
                rm -f skipstart
                rm -f geoPlusVel
                rm -f olddynrun
                rm -f olddynrun2
                rm -f olddynrun3
                a=`awk '{print $1}' isomernumber`
                mv traj traj$a
            fi
            if [ `cat skipstart` = "forward" ]; then
                echo reverserestart > skipstart
            fi
        else
            rm -f skipstart
            rm -f geoPlusVel
            rm -f olddynrun
            rm -f olddynrun2
            rm -f olddynrun3
            a=`awk '{print $1}' isomernumber`
            mv traj traj$a
        fi
    break
fi
done
#
END_of_C_Loop__END_of_C_Loop__END_of_C_Loop__
END_of_C_Loop__END_of_C_Loop__END_of_C_Loop__
_____

# We've got to break a second time to get out of this loop
# if we really want to quit. Otherwise, it will start over
# at the top
    if (test -f nogo) then
        break
    fi
    if (test -s $scratchdir/goingwell) then
        echo "starting a new point or a new direction"
    else
        break
    fi
done

    if (test -f nogo) then
        break
    fi
    if (test -s $scratchdir/goingwell) then
        echo "starting a new point or a new direction2"
    else

```

```

    break
  fi
done
exit 0

```

## progenHP

```

BEGIN {
# July 2018 - modified many aspects of the initialization so that
displacements are done in internal coordinates and so that full
quantum distributions of displacements can be done
# June 2018 organized into functions partially
# 2014 - avoids bug with a box on, so that starts without modes use
input geometry, not standard orientation
# aug 2013 summary of changes
#includes molecular rotation, ability to do multiple NMR
calculations, ONIOM with link atoms,
#nonstandard routes, handling of linear molecules using geometry
linear, fixed but with atoms over 99 but
#bug varies with version of Gaussian, randomization based on
PROCINFO (solved many problems), added initialDiss 3 for
random
#phase of normal modes
# Aut 2010 changes classicalSpacing to 2 and upped possible
excited states to 4000
# Jan 2009 - a number of little changes to improve reporting,
precision, etc, specification of displacement on particular modes
# Jan 2009 cannonball trajectories. adds desired energy to initial
velocities based on file cannontraj, so one can shoot toward a ts
# updated Nov 2008 to incorporate running DRPs
# updated Nov 2008 to allow for start without an initial freq calc
using classical = 2
# updated Aug 2008 added to atom list to handle a large number of
atoms without changes needed
# updated June 2008 to incorporate new method for choosing
displacements with initialdis 2
# updated Jan 17 2008 - bug fix for > 99 atoms, 300 excitations of
low modes possible
# version August 2007 - incorporates classical trajectory
calculation option
#also allows listing of number of imaginary frequencies
# version Sept 16, 2005 - incorporates searchdir but not yet
rotation
# now reads random numbers from temp811, starting at a random
place
# The input files are generated before this and are tempfreqs,
tempredmass,
# tempfrc, tempmodes, and tempstangeos.
# It will count the number of atoms.

```

```

initializeparameters()
initializeconstants()
readprogdynconf()
if (diag>=1) diagnosticsA()
getstangeos() #defines numAtoms, atNum[], geoArr[1-
numAtoms,1-3], geoArrOrig[1-numAtoms,1-3](same as geoArr
initially), zeros velArr
print numAtoms #output the number of atoms, used in many
routines
getatomsAndWeights() # put in atomic symbols and atomic
weights - assigns a default mass but then reads it from tempmasses
when possible
getFreqs() # defines numFreq, freq[] (scaled and adjusted in ways),
redMass[], frc[]
if (classical!=2) getModes() # defines mode[freqNum, atom, 1-3]
startRandom() # defines starting point on file temp811, randArr[1-
numFreq], randArrB[1-numfreq], randArrC[1-numfreq],
randArrR[1-6], randArrD[1-numfreq],randArrE[3*numAtoms]
setModeEnergies() # defines zpe[], zpeK[], vibn[], modeEn[],

```

```

modeEnK[] for each mode and desiredModeEnK desired total
energy desired for molecule
setQMrandom() # defines randArrQM[i], a random position based
on the QM psi**2 to use for a QM displacement choice
setModeShifts() #defines shift[i] for each mode, defines
potentialEn[], potentialEnK[]
getVelocities() # defines velArr[], kinEn[i]
if (anharmonic==1) setAnharmonicShifts()
calcdzdm()
if (classical!=2) shiftStructure() # moves the initial geometry by
shift[i], changes geoArr[]
calcEinModes() # defines KEinitmodes, just the kinetic E in the
vibrational modes, and PEinitmodes
if (rotationmode>0) addMolecularRotation() # changes velArr
using a thermal random rotation
if (cannonball>0) {
  readCannonBall() # defines cannArr[1-numAtoms,1-3]
  doCannonBall()
}
# output the geometry and weights
for (j=1;j<=numAtoms;j++) {
  printf("%2s % .7f % .7f % .7f %9.5f
\n",atSym[j],geoArr[j,1],geoArr[j,2],geoArr[j,3],atWeight[j])
}
#output the velocities and calculate the total kinetic energy overall
KEinittotal=0
for (j=1;j<=numAtoms;j++) {
  KEinittotal=KEinittotal + 0.5*atWeight[j]*(velArr[j,1]^2 +
velArr[j,2]^2 + velArr[j,3]^2)/((timestep^2)*conver1)
  printf("% .8f % .8f % .8f\n",velArr[j,1],velArr[j,2],velArr[j,3])
}

#additional info added to file will not affect the trajectories but will
keep a record and be good for analysis
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    if (initialDis==0) printf("% .6f % .6f %4i % 1.4e % .6f
%1i\n", randArr[i], randArrB[i], vibN[i], vel[i], shift[i],
disMode[i])
    if (initialDis==1) printf("% .6f % .6f %4i % 1.4e % .6f
%1i\n", randArr[i], randArrC[i], vibN[i], vel[i], shift[i],
disMode[i])
    if (initialDis==2) printf("% .6f % .6f %4i % 1.4e % .6f
%1i\n", randArr[i], randArrD[i], vibN[i], vel[i], shift[i],
disMode[i])
    if (initialDis==3) printf("% .6f % .6f %4i % 1.4e % .6f
%1i % .6f\n", randArr[i], randArrC[i], vibN[i], vel[i], shift[i],
disMode[i], sin(randArrC[i]*3.141592*2))
    if (initialDis==4) printf("% .6f % .6f %4i % 1.4e % .6f
%1i\n", randArr[i], randArrQM[i], vibN[i], vel[i], shift[i],
disMode[i])
  }
}
print "temp ",temp
print "initialDis",initialDis
print "classical",classical
print "timestep",timestep
print "numimag",numimag
OFMT = "% .3f"
print "Total mode energy desired=",desiredModeEnK," potential
Energy desired", PEinitmodes
print "KE initial from modes=",KEinitmodes," KE initial
total=",KEinittotal," Rotational Energy desired=",rotEdesired
if (cannonball>0) print "cannonball",cannonball," cannon
Energy=",KEinittotal-KEinitmodes
if (boxon>0) print "boxsize",boxsize
if (DRP>0) print "DRP",DRP," maxAtomMove",maxAtomMove
if (DRP>0) print maxAtomMove > "maxMove"
} #####
***** End of BEGIN

```

```

*****

/Zero-point correction/ {zpeGauss=$3}
/zero-point Energies/ {zpePlusE=$7}
END {
zpeGaussK=zpeGauss*627.509
potentialE=zpePlusE - zpeGauss
OFMT = "%.6f"
print "Gaussian zpe=",zpeGauss,"or",zpeGaussK,"kcal/mol E +
zpe=",zpePlusE," potential E=",potentialE
print "" #will use blank line to mark end of geoPlusVel file
}

# default parameters, including quassiclassical, no displacements,
transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the
parameters
function initializeparameters() {
  initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
  classical=0; numimag=1; DRP=0; cannonball=0
  memory=20000000
  diag=1; checkpoint="g16.chk"; searchdir="positive"; boxon=0
  boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
  title3="a"; title4="progdyn.conf"; processors=1;
highlevel=99999; linkatoms=0
  damping=1;nonstandard=0;geometry="nonlinear";nonstandard=0
  nmrtype=0;nmrevery=9999999;nmrcc=0;nmrrand=0;nmrdo=0
  thermostat=0;thermostatmult=1.00
  oniomcharge=0; oniommult=0
  applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
  sphereon=0; spheresize=999; sphereforceK=0.01
  empiricdispersion=0; radiusmultiplier=1.25
  conver1=4.184E26 #dividing by this converts amu ang^2 /s^2 to
kcal/mol
  geometry="nonlinear";rotationmode=0
}

function initializeconstants() {
  for (i=1;i<=10000;i++) {disMode[i]=1}
  i=1;j=1;k=1
  c=29979245800; h=6.626075E-34; avNum=6.0221415E23
  RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
  numAtoms=0; atomnumber=0; classicalSpacing=2
  zpeGauss=0; zpeGaussK=0; zpePlusE=0; potentialE=0
  conver1=4.184E26 #dividing by this converts amu ang^2 /s^2 to
kcal/mol
  OFS=" "
}

# read progdyn.conf for configuration info
function readprogdynconf() {
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="method2") meth2=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity") multiplicity=$2
    if ($1=="oniomchargemult") {
      oniomcharge=$2
      oniommult=$3
    }
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
    if ($1=="checkpoint") checkpoint=$2
    if ($1=="timestep") timestep=$2
    if ($1=="diagnostics") diag=$2
    if ($1=="initialdis") initialDis=$2
    if ($1=="scaling") scaling=$2
    if ($1=="searchdir") searchdir=$2

    if ($1=="temperature") temp=$2
    if ($1=="thermostat") thermostat=$2
    if ($1=="thermostatmult") thermostatmult=$2
    if (thermostatmult>1) thermostatmult=1/thermostatmult
    if ($1=="classical") classical=$2
    if ($1=="numimag") numimag=$2
    if ($1=="geometry") geometry=$2
    if ($1=="cannonball") cannonball=$2
    if ($1=="displacements") disMode[$2]=$3
    if ($1=="anharmonicmode") {
      anharmonic=1
      anharmonicmode[$2]=1
      anharmk2[$2]=$3
      anharmk3[$2]=$4
    }
    if ($1=="controlphase") controlPhase[$2]=$3
    if ($1=="rotationmode") rotationmode=$2
    if ($1=="method3") meth3=$2
    if ($1=="method4") meth4=$2
    if ($1=="method5") meth5=$2
    if ($1=="method6") meth6=$2
    if ($1=="method7") meth7=$2
    if ($1=="highlevel") highlevel=$2
    if ($1=="linkatoms") linkatoms=$2
    if ($1=="fixedatom1") fixedatom1=$2
    if ($1=="fixedatom2") fixedatom2=$2
    if ($1=="fixedatom3") fixedatom3=$2
    if ($1=="fixedatom4") fixedatom4=$2
    if ($1=="boxon") boxon=$2
    if ($1=="boxsize") boxsize=$2
    if ($1=="sphereon") sphereon=$2
    if ($1=="spheresize") spheresize=$2
    if ($1=="sphereforce") sphereforceK=$2
    if ($1=="DRP") DRP=$2; if (DRP==1) classical=2 #this lets
one start a DRP from a point that is not a freq calc
    if ($1=="maxAtomMove") maxAtomMove=$2
    if ($1=="methodfile") methodfilelines=$2
    if ($1=="killcheck") killcheck=$2
    if ($1=="empiricdispersion") empiricdispersion=$2
    if ($1=="radiusmultiplier") radiusmultiplier=$2
    if ($1=="damping") damping=$2
    if ($1=="NMRmethod") nmrmeth=$2
    if ($1=="NMRmethod2") nmrmeth2=$2
    if ($1=="NMRmethod3") nmrmeth3=$2
    if ($1=="NMRTYPE") nmrtype=$2
    if ($1=="NMRrevery") nmrevery=$2
    if ($1=="NMRrand") nmrrand=$2
    if ($1=="loadlimit") loadlimit=$2
    if ($1=="NMRcc") nmrcc=$2
    if ($1=="nonstandard") nonstandard=$2
    if ($1=="applyforce") {
      applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5;
apforce3=$6
    }
    if ($1=="applyforceB") {
      applyforceB=$2; apforceB=$3; apforceX0B=$4;
apforce2B=$5; apforce3B=$6
    }
    if ($1=="applyforceC") {
      applyforceC=$2; apforceC=$3; apforceX0C=$4;
apforce2C=$5; apforce3C=$6
    }
    if ($1=="afatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatom[i]=$ (i+1)
      }
    }
    if ($1=="afatomsB") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatomB[i]=$ (i+1)
      }
    }
  }
}

```

```

    }
}
if ($1=="afatomsC") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatomC[i]=$ (i+1)
  }
}
if ($1=="applyforceplane") {
  applyforceplane=$2; apforceplane=$3; apforceplaneX0=$4
}
if ($1=="afplaneatoms") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afplaneatoms[i]=$ (i+1)
  }
}
if ($1=="zeroatom") {
  zeroatomon=1
  zeroatom=$2
}
if ($1=="title") {
  title1=$2
  title2=$3
  title3=$4
  title4=$5
}
blankLineTester=length($0)
}

function diagnosticsA() {
  print "***** starting proggen
*****" >> "diagnostics"
  print "method,charge,multiplicity,memory" >> "diagnostics"
  print method,charge,multiplicity,memory >> "diagnostics"
  print
  "processors,checkpoint,title,initialdis,timestep,scaling,temperature"
  >> "diagnostics"
  print
  processors,checkpoint,title1,title2,title3,title4,initialDis,timestep,sc
  aling,temp >> "diagnostics"
  print
  "classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,
  cannonball" >> "diagnostics"
  print
  classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,c
  annonball >> "diagnostics"
}

function getstangeos() {
  # note that this picks out the last geometry in a file, assuming
  # that if there is an optimization followed by a freq, nothing else
  follows
  # kludgy - repeats last line twice - must be a better way
  do {
    getline < "tempstangeos"
    if (oldline==$0) $0=""
    oldline=$0
    atom = $1
    if (atom>numAtoms) numAtoms=atom
    atNum[atom]=$2
    geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
    geoArrOrig[atom,1]=$4; geoArrOrig[atom,2]=$5;
  }
  geoArrOrig[atom,3]=$6
  velArr[atom,1]=0; velArr[atom,2]=0; velArr[atom,3]=0
}
while (length($0) > 0)
}

function getatomsAndWeights() {
  # put in atomic symbols and atomic weights - assigns a default

```

```

mass but then reads it from tempmasses when possible
for (i=1;i<=numAtoms;i++) {
  getline < "tempmasses"
  if (atNum[i]==1) {atSym[i]="H";atWeight[i]=1.00783}
  if (atNum[i]==2) {atSym[i]="He";atWeight[i]=4.0026}
  if (atNum[i]==3) {atSym[i]="Li";atWeight[i]=6.941}
  if (atNum[i]==4) {atSym[i]="Be";atWeight[i]=9.012}
  if (atNum[i]==5) {atSym[i]="B";atWeight[i]=10.811}
  if (atNum[i]==6) {atSym[i]="C";atWeight[i]=12.}
  if (atNum[i]==7) {atSym[i]="N";atWeight[i]=14.007}
  if (atNum[i]==8) {atSym[i]="O";atWeight[i]=15.9994}
  if (atNum[i]==9) {atSym[i]="F";atWeight[i]=18.9984}
  if (atNum[i]==10) {atSym[i]="Ne";atWeight[i]=20.1797}
  if (atNum[i]==11) {atSym[i]="Na";atWeight[i]=22.989}
  if (atNum[i]==12) {atSym[i]="Mg";atWeight[i]=24.305}
  if (atNum[i]==13) {atSym[i]="Al";atWeight[i]=26.98154}
  if (atNum[i]==14) {atSym[i]="Si";atWeight[i]=28.0855}
  if (atNum[i]==15) {atSym[i]="P";atWeight[i]=30.9738}
  if (atNum[i]==16) {atSym[i]="S";atWeight[i]=32.066}
  if (atNum[i]==17) {atSym[i]="Cl";atWeight[i]=35.4527}
  if (atNum[i]==18) {atSym[i]="Ar";atWeight[i]=39.948}
  if (atNum[i]==19) {atSym[i]="K";atWeight[i]=39.0983}
  if (atNum[i]==20) {atSym[i]="Ca";atWeight[i]=40.078}
  if (atNum[i]==21) {atSym[i]="Sc";atWeight[i]=44.96}
  if (atNum[i]==22) {atSym[i]="Ti";atWeight[i]=47.867}
  if (atNum[i]==23) {atSym[i]="V";atWeight[i]=50.94}
  if (atNum[i]==24) {atSym[i]="Cr";atWeight[i]=51.9961}
  if (atNum[i]==25) {atSym[i]="Mn";atWeight[i]=54.938}
  if (atNum[i]==26) {atSym[i]="Fe";atWeight[i]=55.845}
  if (atNum[i]==27) {atSym[i]="Co";atWeight[i]=58.933}
  if (atNum[i]==28) {atSym[i]="Ni";atWeight[i]=58.693}
  if (atNum[i]==29) {atSym[i]="Cu";atWeight[i]=63.546}
  if (atNum[i]==30) {atSym[i]="Zn";atWeight[i]=65.38}
  if (atNum[i]==31) {atSym[i]="Ga";atWeight[i]=69.723}
  if (atNum[i]==32) {atSym[i]="Ge";atWeight[i]=72.64}
  if (atNum[i]==33) {atSym[i]="As";atWeight[i]=74.9216}
  if (atNum[i]==34) {atSym[i]="Se";atWeight[i]=78.96}
  if (atNum[i]==35) {atSym[i]="Br";atWeight[i]=79.904}
  if (atNum[i]==46) {atSym[i]="Pd";atWeight[i]=106.42}
  if (atNum[i]==53) {atSym[i]="I";atWeight[i]=126.90447}
  # gets actual weight from freqinHP when possible so a prior calc
  with readisotopes gets you isotopic substitution
  if ((i<100) && ($9>0)) atWeight[i]=$9
  # if ((i>99) && ($8>0)) atWeight[i]=$8

  if ((diag>1) && (i==1)) print
  "atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3]
  ]" >> "diagnostics"
  if (diag>1) print
  atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3]
  >> "diagnostics"
}
}

function getFreqs() {
  # read in frequencies, scale them, read in Reduced masses, read in
  force
  #constants, replace negative frequencies by 2 wavenumbers
  numFreq=3*numAtoms-6
  if (geometry=="linear") numFreq=3*numAtoms-5
  for (i=1;i<=numFreq;i++) {
    $0=""
    getline < "tempfreqs"
    freq[i]=$0*scaling
    if (freq[i]<classicalSpacing) freq[i]=classicalSpacing #replace
    negative freqs and <classicalSpacing by classicalSpacing
    wavenumbers, defaulted at 2 wavenumbers
  }
  for (i=1;i<=numFreq;i++) {
    $0=""

```

```

    getline < "tempredmass"
    redMass[i]=$0
    if (redMass[i]== "") redMass[i]=1.
  }
  for (i=1;i<=numFreq;i++) {
    $0=""
    getline < "tempfrf"
    frf[i]=$0
    if (frf[i]== "") frf[i]=0.0001
    if (frf[i]==0) frf[i]=0.0001
    if ((diag>1) && (i==1)) print "freq[i],redMass[i],frf[i]" >>
"diagnostics"
    if (diag>1) print freq[i],redMass[i],frf[i] >> "diagnostics"
  }
}

function getModes() {
# read in the modes - note that trajectories always need a freq calc
with freq=hp modes unless classical=2
  if (classical!=2) {
    for (i=1;i<=numFreq;i+=5) {
      for (j=1;j<=(3*numAtoms;j++) {
        getline < "tempmodes"
        mode[i,$2,$1]=$4; mode[i+1,$2,$1]=$5;
mode[i+2,$2,$1]=$6; mode[i+3,$2,$1]=$7; mode[i+4,$2,$1]=$8
      }
    }
  }
  if (diag>2) {for (i=1;i<=numFreq;i++) {print
mode[i,1,1],mode[i,1,2],mode[i,1,3] >> "modesread"}}
}

function readCannonBall() {
# if doing a cannonball trajectory, read in the vector
if (cannonball>0) {
  for (i=1;i<=numAtoms;i++) {
    getline < "cannontraj"
    cannonArr[i,1]=$1; cannonArr[i,2]=$2; cannonArr[i,3]=$3
  }
}

function startRandom() {
# collect a series of random numbers from file temp811, generated
from an outside random number generator called by
prodynstarterHP
# read from temp811, starting at a random place
srand(PROCINFO["pid"]); tester=rand()*1000
for (i=1;i<=tester;i++) getline < "temp811"
for (i=1;i<=numFreq;i++) {
  getline < "temp811"; randArr[i]=$1
  getline < "temp811"; randArrB[i]=$1
  getline < "temp811"; randArrC[i]=$1
}
for (i=1;i<=6;i++) {
  getline < "temp811"; randArrR[i]=$1
}
# for a QM-like distribution for a harmonic oscillator in its ground
state, we want to generate a set of random numbers
# between -1 and 1 weighted such that numbers toward the center
are properly more common
i=1
while (i<=numFreq) {
  if ((initialDis==2) || (disMode[i]==2)) {
    getline < "temp811"
    tempNum=2*(($1-.5)
    prob=exp(-(tempNum^2))
    getline < "temp811"
    if ($1<prob) {
      randArrD[i]=tempNum
    }
  }
  i++
}
}

# to start without normal modes or frequencies we need to just
pick a random direction for the motion of each atom, requiring 3N
random numbers
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
    getline < "temp811"
    if ($1>0.5) randArrE[i,j]=1
    if ($1<.5) randArrE[i,j]=-1
  }
}

function setModeEnergies() {
# determine energy in each normal mode
desiredModeEnK=0
for (i=1;i<=numFreq;i++) {
  zpeJ[i]=0.5*h*c*freq[i] #units J per molecule, # the zpe is
not used when classical but the spacing can be used
  zpeK[i]=zpeJ[i]*avNum/4184 #units kcal/mol
  if ((classical==1) || (freq[i]<=classicalSpacing)) { # treat all
modes <=classicalSpacing cm-1 as classical
    modeEnK[i]=-Rgask*temp*log(randArr[i]) # gives a
classical distribution of energies averaging RT
    vibN[i]=modeEnK[i]/(2*zpeK[i]) # the vibN is not an integer
for classical vibrations
    modeEn[i]=zpeJ[i]*1E18*2*vibN[i] # units here are mDyne
Ansgroms for compatability with Gaussian force constants
  }
  if ((classical!=1) && (freq[i]>classicalSpacing)) {
    if (temp<10) vibN[i]=0 # not right at temp<10, which will act
like 0 K
    if (temp>=10) {
      zpeRat[i]=exp((-2*zpeK[i])/(Rgask*temp))
      if (zpeRat[i]==1) zpeRat[i]=.9999999999
      Q[i]=1/(1-zpeRat[i])
      newRand=randArr[i]
      vibN[i]=0
      tester=1/Q[i]
    }
    # get up to 1750 excitations of modes >2 cm-1. This should
be plenty for ordinary temperatures, with a ceiling of about 10
kcal/mol
    for (j=1;j<=(1750*zpeRat[i]+2);j++) {
      if (newRand>tester) vibN[i]++
      tester=tester+((zpeRat[i]^j)/Q[i])
    }
    modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i]+1) # units here are
mDyne Ansgroms for compatability with Gaussian force constants
    modeEnK[i]=zpeK[i]*(2*vibN[i]+1)
  }
  if ((classical==4) && (i>1)) {
    modeEnK[i]=0 #this lets you turn off the
energy in modes outside of 1 for single-trajectory study
    modeEn[i]=0
    vibN[i]=0
  }
  desiredModeEnK=desiredModeEnK + modeEnK[i]
  #print zpeK[i], zpeJ[i], modeEnK[i], modeEn[i], vibN[i]
}
}

function setQMrandom() {
i=1
while (i<=numFreq) {
  getline < "temp811"
}
}

```

```

tempNum=2*($1-.5)
prob=psi2(vibN[i],tempNum)
getline < "temp811"
# print
"i",i,"vibN[i]",vibN[i],"tempNum",tempNum,"newrand", $1,"prob"
,prob
if ($1<prob) {
  randArrQM[i]=tempNum
  i++
}
}
# print randArrQM[i]
}

function psi2(n,myrand) { # n is the vibrational state, myrand is
my trial displacement
if (n>50) n=50 # by this point the distribution is approaching
classical, and anyway running into problems of numerical stability
n = int(n)
thepsi2=(2^(-n))*(pi^0.5)
r=myrand*(2*n+1)^0.5
thepsi2=thepsi2*exp((-r^2))
thei=int((n/2))
if (n==0) Her=1
if (n>0) {
  Her=0
  for (m=0;m<=thei;m++) {
    thez=((2*r)^(n-2*m))/factorial(m)/factorial(n-2*m)
    Her = Her + thez*(-1)^m
  }
}
Her=Her*Her
#thepsi2=Her*thepsi2*factorial(n)*1.75*(2*n+1)^0.2 # scaled
value that wastes fewer random numbers
thepsi2=Her*thepsi2*factorial(n)
return thepsi2
}

function factorial(input) {
myindex=1; fact=1
for (myindex=1;myindex<=input;myindex++) {
  fact=fact*myindex
}
return fact
}

function setModeShifts() {
# figure out maximum classical shift and then actual shift
for (i=1;i<=numFreq;i++) {
  maxShift[i]=(2*modeEn[i]/frc[i])^0.5
  if (initialDis==4) shift[i]=maxShift[i]*randArrQM[i] # a QM-
correct distribution bounded by the classical limits of the
wavefunction
  if (initialDis==3)
shift[i]=maxShift[i]*sin(randArrC[i]*3.141592*2) # initialDis 3
means random phase of normal mode
  if (initialDis==2) shift[i]=maxShift[i]*randArrD[i] # a
Gaussian shift that resembles ground-state harmonic oscillator QM
  if (initialDis==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
#purely random displacement, linearly distributed among
displacements
  if (initialDis==0) shift[i]=0
# lines below allow for setting of displacement mode for individual
modes when set by inputting disMode
  if (disMode[i]==4) shift[i]=maxShift[i]*randArrQM[i]
  if (disMode[i]==3)
shift[i]=maxShift[i]*sin(randArrC[i]*3.141592*2)
  if (disMode[i]==2) shift[i]=maxShift[i]*randArrD[i]
  if (disMode[i]==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
}
}

```

```

if (disMode[i]==10) shift[i]=0 #kept for backward
compatibility
if (disMode[i]==0) shift[i]=0
# no displacements along imaginary frequencies and very low ones
- employing a shift can give you initial weird geometries
if (freq[i]<10) shift[i]=0
if (numimag==1) shift[1]=0
if (numimag==2) shift[2]=0
#diagnostics
if ((diag>1) && (i==1)) print
"zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift
[i]" >> "diagnostics"
if (diag>1) print
zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[
i] >> "diagnostics"
potentialEn[i]=0.5*frc[i]*shift[i]^2 # same units as modeEn
potentialEnK[i]=potentialEn[i]*avNum/(4184*1E18)
}
}

function getVelocities() {
for (i=1;i<=numFreq;i++) {
  kinEn[i]=100000*(modeEn[i]-potentialEn[i]) # the 100000
converts to g angstrom^2 s^2
  vel[i]=(2*kinEn[i]/(redMass[i]/avNum))^0.5 # in angstrom
/s
#use searchdir in progdyn.conf to control the direction for
trajectories started from a saddle point
if (numimag>1) numimag=1 #only the first freq can be sent in
the searchdir direction, the rest go in a random direction
if (i>numimag) {
  if (randArrB[i]<0.5) vel[i]=-vel[i]
}
if (i==numimag) {
  if (searchdir=="negative") vel[i]=-vel[i]
}
if ((diag>1) && (i==1)) print "vel[i]" >> "diagnostics"
if (diag>1) print vel[i] >> "diagnostics"
}
# if controlphase is being used, set the velocity on particular modes
as positive or negative as requested
for (i=1;i<=numFreq;i++) {
  if ((controlPhase[i]=="positive") && (vel[i]<0)) vel[i]=-vel[i]
  if ((controlPhase[i]=="negative") && (vel[i]>0)) vel[i]=-vel[i]
}
# multiply each of the modes by its velocity and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        velMode[i,j,k]=mode[i,j,k]*vel[i]*timestep
        velArr[j,k]=velArr[j,k]+velMode[i,j,k]
      }
    }
  }
}
# to start without normal modes or frequencies we figure out the
energy per atom based on 1/2RT in degree of freedom
if (classical==2) {
# to avoid a bug with a box on, starts without modes should use the
input geometry, not the standard
do {
  getline < "tempinputgeos"
  if (oldline==$0) $0=""
  oldline=$0
  atom = $1
  geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
  geoArrOrig[atom,1]=$4; geoArrOrig[atom,2]=$5;
  geoArrOrig[atom,3]=$6
}
}
}

```



```

    }
    while (length($0) > 0)
    degFreedomEnK=temp*RgasK
    degFreedomEnJ=degFreedomEnK/(avNum/4184)
    cartEn=degFreedomEnJ*1E18
    kinEnCart=100000*cartEn
#print degFreedomEnK, degFreedomEnJ, cartEn, kinEnCart
    for (i=1;i<=numAtoms;i++) {
        for (j=1;j<=3;j++) {
            }
            while (length($0) > 0)
            degFreedomEnK=temp*RgasK
            degFreedomEnJ=degFreedomEnK/(avNum/4184)
            cartEn=degFreedomEnJ*1E18
            kinEnCart=100000*cartEn
#print degFreedomEnK, degFreedomEnJ, cartEn, kinEnCart
            for (i=1;i<=numAtoms;i++) {
                for (j=1;j<=3;j++) {
                    }
                    close("temp394.xyz")
                    system("python ~/bin/tozmat.py temp394.xyz >
temp394.gzmat")
                    for (j=1; j<=numCoord; j+=3) {
                        getline < "temp394.gzmat"
                        zGeoPerturbed[j] = $2; zGeoPerturbed[j+1] = $3;
                        zGeoPerturbed[j+2] = $4
                    }
                    close("temp394.gzmat")
                    for (j=1; j<=numCoord; j++) {
                        dzdm[i,j]=(zGeoPerturbed[j] - zGeoOrig[j])/epsilon
                    }
                }
            }
        }
    }
}

function setAnharmonicShifts() {
    for (i=1;i<=numFreq;i++) {
        if (anharmonicmode[i]==1) {
            PEanarm=anharmk2[i]*shift[i]^2 + anharmk3[i]*shift[i]^3
#            print i, PEanarm, potentialEnK[i],"
difference",PEanarm-potentialEnK[i]
            while (PEanarm < potentialEnK[i]) {
                shift[i]=1.01*shift[i]
                oldPEanarm=PEanarm
                PEanarm=anharmk2[i]*shift[i]^2 +
anharmk3[i]*shift[i]^3
                if (PEanarm<oldPEanarm) break
            }
            while (PEanarm > potentialEnK[i]) {
                shift[i]=0.99*shift[i]
                PEanarm=anharmk2[i]*shift[i]^2 +
anharmk3[i]*shift[i]^3
            }
#            print i, PEanarm, potentialEnK[i]
        }
    }
}

function calcdzdm() {
    numCoord=numFreq+15
#take the parent structure and get a zmat geometry
    print "He 0. 0. 0." > "temp394.xyz"
    print "He 1. 0. 0." >> "temp394.xyz"
    print "He 1. 0. 1." >> "temp394.xyz"
    for (i=1;i<=numAtoms;i++) {
        print atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >>
"temp394.xyz"
    }
    close("temp394.xyz")
    system("python ~/bin/tozmat.py temp394.xyz >
temp394.gzmat")
    for (j=1; j<=numCoord; j+=3) {
        getline < "temp394.gzmat"
        zAtSym[j] = $1; zGeoOrig[j] = $2; zGeoOrig[j+1] = $3;
zGeoOrig[j+2] = $4; zConAtom[j] = $5; zAngAtom[j] = $6;
zDihAtom[j] = $7
    }
    close("temp394.gzmat")
    epsilon=0.001
    for (i=1;i<=numFreq;i++) {
        print "He 0. 0. 0." > "temp394.xyz"
        print "He 1. 0. 0." >> "temp394.xyz"
        print "He 1. 0. 1." >> "temp394.xyz"
        for (j=1;j<=numAtoms;j++) {
            print
atSym[j],geoArr[j,1]+epsilon*mode[i,j,1],geoArr[j,2]+epsilon*mo
de[i,j,2],geoArr[j,3]+epsilon*mode[i,j,3] >> "temp394.xyz"
        }
    }
}

function shiftStructure() {
    for (j=1;j<=numCoord;j++) {
        zGeo[j]=zGeoOrig[j]
        for (i=1;i<=numFreq;i++) {
            zGeo[j]=zGeoOrig[j]+shift[i]*dzdm[i,j]
        }
    }
    for (j=1;j<=numCoord;j+=3) {
        i = (j+2)/3
        print zAtSym[j], zGeo[j], zGeo[j+1], zGeo[j+2], zConAtom[j],
zAngAtom[j], zDihAtom[j] > "temp394.gzmat"
    }
    close("temp394.gzmat")
    system("python ~/bin/toxyz.py temp394.gzmat > temp394.xyz")
    getline < "temp394.xyz"; getline < "temp394.xyz"; getline <
"temp394.xyz"
    for (j=1;j<=numAtoms;j++) {
        getline < "temp394.xyz"
        geoArr[j,1]=$2; geoArr[j,2]=$3; geoArr[j,3]=$4
    }
    close("temp394.xyz")
}

function calcEinModes() {
    KEinitmodes=0
    for (j=1;j<=numAtoms;j++) {
        KEinitmodes=KEinitmodes + 0.5*atWeight[j]*(velArr[j,1]^2 +
velArr[j,2]^2 + velArr[j,3]^2)/((timestep^2)*conver1)
    }
    PEinitmodes=0
    for (i=1;i<=numFreq;i++) {
        PEinitmodes = PEinitmodes + potentialEnK[i]
    }
}

function addMolecularRotation() {
    for (j=1;j<=numAtoms;j++) {
        rotateX[j,1]=0
        rotateX[j,2]=-geoArrOrig[j,3]
        rotateX[j,3]=geoArrOrig[j,2]
        rotateY[j,1]=-geoArrOrig[j,3]
        rotateY[j,2]=0
        rotateY[j,3]=geoArrOrig[j,1]
        rotateZ[j,1]=-geoArrOrig[j,2]
        rotateZ[j,2]=geoArrOrig[j,1]
        rotateZ[j,3]=0
    }
#figure out how much energy is in the raw vectors
    eRotX=0;eRotY=0;eRotZ=0
    for (j=1;j<=numAtoms;j++) {
        for (k=1;k<=3;k++) {
            eRotX=eRotX +
0.5*atWeight[j]*(rotateX[j,k]^2)/((timestep^2)*conver1)
            eRotY=eRotY +

```

```

0.5*atWeight[j]*(rotateY[j,k]^2)/((timestep^2)*conver1)
eRotZ=eRotZ +
0.5*atWeight[j]*(rotateZ[j,k]^2)/((timestep^2)*conver1)
}
}
# print "rotation energies if raw vector used",eRotX,eRotY,eRotZ
#now deciee how much energy we want in each rotation
keRx=-0.5*0.001987*temp*log(1-randArrR[1])
keRy=-0.5*0.001987*temp*log(1-randArrR[2])
keRz=-0.5*0.001987*temp*log(1-randArrR[3])
if (eRotX<1) keRx=0;if (eRotY<1) keRy=0;if (eRotZ<1)
keRz=0
rotEdesired=keRx+keRy+keRz
signX=1;signY=1;signZ=1
if (randArrR[4]<.5) signX=-1
if (randArrR[5]<.5) signY=-1
if (randArrR[6]<.5) signZ=-1

# print "desired energies",keRx,keRy,keRz,"and random
numbers",randArrR[1],randArrR[2],randArrR[3]
#protect against zero rotations
if (eRotX<1) eRotX=1;if (eRotY<1) eRotY=1;if (eRotZ<1)
eRotZ=1
#now scale the rotational vectors
scaleX=(keRx/eRotX)^.5
scaleY=(keRy/eRotY)^.5
scaleZ=(keRz/eRotZ)^.5
# print "scaling factors" scaleX,scaleY,scaleZ
for (j=1;j<=numAtoms;j++) {
for (k=1;k<=3;k++) {
rotateX[j,k]=rotateX[j,k]*scaleX*signX
rotateY[j,k]=rotateY[j,k]*scaleY*signY
rotateZ[j,k]=rotateZ[j,k]*scaleZ*signZ
}
}
for (j=1;j<=numAtoms;j++) {
# print rotateX[j,1]," ",rotateX[j,2]," ",rotateX[j,3]
}
# print ""
for (j=1;j<=numAtoms;j++) {
# print rotateY[j,1]," ",rotateY[j,2]," ",rotateY[j,3]
}
# print ""
for (j=1;j<=numAtoms;j++) {
# print rotateZ[j,1]," ",rotateZ[j,2]," ",rotateZ[j,3]
}
# now add the rotational vectors to velArr
for (j=1;j<=numAtoms;j++) {
for (k=1;k<=3;k++) {
velArr[j,k]=velArr[j,k]+rotateX[j,k]+rotateY[j,k]+rotateZ[j,k]
}
}
}

function doCannonBall() {
# strategy is adjust multiplier until extra energy is correct
multiplier=1; tester=0; tolerance=.1
while (tester==0) {
KEinittotal=0
for (j=1;j<=numAtoms;j++) {
cannonvelArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
cannonvelArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
cannonvelArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
KEinittotal=KEinittotal +
0.5*atWeight[j]*(cannonvelArr[j,1]^2 + cannonvelArr[j,2]^2 +
cannonvelArr[j,3]^2)/((timestep^2)*conver1)
}
if (KEinittotal>(KEinitmodes+cannonball+tolerance))
multiplier=multiplier*0.98901364

```

```

if (KEinittotal<(KEinitmodes+cannonball-tolerance))
multiplier=multiplier*1.01
if ((KEinittotal<(KEinitmodes+cannonball+tolerance)) &&
(KEinittotal>(KEinitmodes+cannonball-tolerance))) tester=1
}
for (j=1;j<=numAtoms;j++) {
velArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
velArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
velArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
}
}

```

## prog1stpoint

```

BEGIN {
# Nov 2016 organized by functions
# 2014 added ONIOMcharge, more reliable convergence
commands
# 2013 added multiple NMR calculations, molecular rotations
# 2012 added NMR calculations
# 2011 added linkatoms in ONIOM
# aug 2010 changed so that it is more careful in reading in from
geoPlusVel
# removed some default parameters that should always be
defined
# Jan 2009 - a number of little changes to improve reporting,
precision, etc
# aug 2008 added to atom list so handles H to Cl without change
needed
# version Feb 2008 incorporates methodfile, boxon and boxsize,
though this point unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 2005 - incorportates meth3, meth4, meth5, meth6,
but not yet rotation
# this program creates the first input file for g16
# the title should be changed as appropriate
# the isomer number comes from a file isomernumber

initializeparameters()
initializeconstants()
readprogdynconf()

getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1

if (diag>=1) diagnosticsA()
readgeoPlusVel() #this is different from prog2ndpoint and
progdynb because we are just getting the geometry, no velocities
or old geos

writecomfile()
}

END {
}

#####
##### FUNCTIONS
#####
function Distance(Atom1,Atom2) {
return sqrt((oldarr[Atom1,1]-
oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
}

# default parameters, including quassiclassical, no displacements,
transition state, not a DRP

```

```

# do not change these - rather, change progdyn.conf to set the
parameters
function initializeparameters() {
  initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
  classical=0; numimag=1; DRP=0; cannonball=0
  memory=20000000
  diag=1; checkpoint="g16.chk"; searchdir="positive"; boxon=0
  boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
  title3="a"; title4="progdyn.conf"; processors=1;
highlevel=99999; linkatoms=0
  damping=1;nonstandard=0;geometry="nonlinear";nonstandard=0
  nmrtype=0;nmrevery=9999999;nmrcc=0;nmrrand=0;nmrdo=0
  thermostat=0;thermostatmult=1.00
  oniomcharge=0; oniommult=0
  applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
  sphereon=0; spheresize=999; sphereforceK=0.01
  empiricaldispersion=0; radiusmultiplier=1.25
}

function initializeconstants() {
  srand(PROCINFO["pid"])
  i=1;j=1;k=1
  c=29979245800; h=6.626075E-34; avNum=6.0221415E23
  RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
  numAtoms=0; atomnumber=0
  converl=4.184E26 #dividing by this converts amu ang^2 /s^2 to
kcal/mol
  OFS=" "
}

# read progdyn.conf for configuration info
function readprogdynconf() {
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="method2") meth2=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity") multiplicity=$2
    if ($1=="oniomchargemult") {
      oniomcharge=$2
      oniommult=$3
    }
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
    if ($1=="checkpoint") checkpoint=$2
    if ($1=="timestep") timestep=$2
    if ($1=="diagnostics") diag=$2
    if ($1=="temperature") temp=$2
    if ($1=="thermostat") thermostat=$2
    if ($1=="thermostatmult") thermostatmult=$2
    if (thermostatmult>1) thermostatmult=1/thermostatmult
    if ($1=="method3") meth3=$2
    if ($1=="method4") meth4=$2
    if ($1=="method5") meth5=$2
    if ($1=="method6") meth6=$2
    if ($1=="method7") meth7=$2
    if ($1=="highlevel") highlevel=$2
    if ($1=="linkatoms") linkatoms=$2
    if ($1=="fixedatom1") fixedatom1=$2
    if ($1=="fixedatom2") fixedatom2=$2
    if ($1=="fixedatom3") fixedatom3=$2
    if ($1=="fixedatom4") fixedatom4=$2
    if ($1=="boxon") boxon=$2
    if ($1=="boxsize") boxsize=$2
    if ($1=="sphereon") sphereon=$2
    if ($1=="spheresize") spheresize=$2
    if ($1=="sphereforce") sphereforceK=$2
    if ($1=="DRP") DRP=$2
    if ($1=="maxAtomMove") maxAtomMove=$2

```

```

    if ($1=="methodfile") methodfilelines=$2
    if ($1=="killcheck") killcheck=$2
    if ($1=="empiricaldispersion") empiricaldispersion=$2
    if ($1=="radiusmultiplier") radiusmultiplier=$2
    if ($1=="damping") damping=$2
    if ($1=="NMRmethod") nmrmethod=$2
    if ($1=="NMRmethod2") nmrmeth2=$2
    if ($1=="NMRmethod3") nmrmethod3=$2
    if ($1=="NMRtype") nmrtype=$2
    if ($1=="NMRrevery") nmrevery=$2
    if ($1=="NMRrand") nmrrand=$2
    if ($1=="loadlimit") loadlimit=$2
    if ($1=="NMRcc") nmrcc=$2
    if ($1=="nonstandard") nonstandard=$2
    if ($1=="applyforce") {
      applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5;
apforce3=$6
    }
    if ($1=="applyforceB") {
      applyforceB=$2; apforceB=$3; apforceX0B=$4;
apforce2B=$5; apforce3B=$6
    }
    if ($1=="applyforceC") {
      applyforceC=$2; apforceC=$3; apforceX0C=$4;
apforce2C=$5; apforce3C=$6
    }
    if ($1=="afatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatom[i]=$ (i+1)
      }
    }
    if ($1=="afatomsB") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatomB[i]=$ (i+1)
      }
    }
    if ($1=="afatomsC") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatomC[i]=$ (i+1)
      }
    }
    if ($1=="applyforceplane") {
      applyforceplane=$2; apforceplane=$3; apforceplaneX0=$4
    }
    if ($1=="afplaneatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afplaneatoms[i]=$ (i+1)
      }
    }
    if ($1=="zeroatom") {
      zeroatomon=1
      zeroatom=$2
    }
    if ($1=="title") {
      title1=$2
      title2=$3
      title3=$4
      title4=$5
    }
    blankLineTester=length($0)
  }
}

function diagnosticsA() {
  print "***** starting progdyn
*****" >> "diagnostics"
  print "method,charge,multiplicity,memory" >> "diagnostics"
  print method,charge,multiplicity,memory >> "diagnostics"
  print "processors,checkpoint,title" >> "diagnostics"
  print processors,checkpoint,title1,title2,title3,title4 >>

```

```

"diagnostics"
}

function readgeoPlusVel() {
#this is different from prog2ndpoint and progdynb because we are
just getting the geometry, no velocities or old geos
#read in number of atoms, geometry, masses from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1
# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$1+j
  }
}
blankLineTester=10
while (blankLineTester>1) {
  getline < "geoPlusVel"
  if ($1=="potential") potentialE=$13
  blankLineTester=length($0)
}
}

function writecomfile () {
  print "%nproc=" processors
  print "%mem=" memory
  if (killcheck!=1) print "%chk=" checkpoint
  if (nonstandard==0) {
    print "#p method force
scf=(xqc,maxconven=155,fulllinear,nosym) "
    if (meth2=="unrestricted") print "guess=mix" #for unrestricted
calculations
    if (length(meth3)>2) print meth3
    if (length(meth4)>2) print meth4
  }
  if (nonstandard==1) {
    print "# "
    print "nonstd"
    system("cat nonstandard")
  }
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  if (DRP==1) {
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove >>
"movelist"
  }
  print ""
  if (oniomult==0) print charge,multiplicity
  if (oniomult>0) print
charge,multiplicity,oniomcharge,oniomult
  for (i=1;i<=numAtoms;i++) {
    printf("%s %.7f %.7f
%.7f",atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3])
    if ((i>highlevel) && (i<=highlevel+linkatoms)) printf("
%s", "M H")
    if (i>(highlevel+linkatoms)) printf(" %s", "M")
    print ""
  }
  print ""
  if (length(meth5)>2) print meth5
  if (length(meth6)>2) print meth6
  if (methodfilelines>=1) {

```

```

for (i=1;i<=methodfilelines;i++) {
  getline < "methodfile"
  print $0
}
}
print ""
if ((nmrtype>0) && ((runpointnum % nmrevery)==0)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# nmrmethod " nmr=giao geom=check"
  if (nmrmeth==method) print "guess=tcheck"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
}
print ""
if ((nmrtype>1) && ((runpointnum % nmrevery)==0)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# nmrmethod2 " nmr=giao geom=check"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
}
print ""
if ((nmrtype>2) && ((runpointnum % nmrevery)==0)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# nmrmethod3 " nmr=giao geom=check"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
}
}
print ""
}
}

```

## prog2ndpoint

```

BEGIN {
# Nov 2016 organized into functions
# 2014 added ONIOMcharge, more reliable convergence
commands
# aug 2013 includes molecular rotation, ability to do multiple
NMR calculations, ONIOM with link atoms,
#nonstandard routes, checks more kinds of energies at point 2
#Aug 2010 added etolerance to make it controllable from
progdyn.conf, made it so that DRP does not check energy
# aug 2008 added to atom list so handles 1 to 17 without change
needed
# version Feb 2008 incorporates methodfile, boxon and boxsize,
though this point unaffected by box

```

```

# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 9, 2005 - incorporates meth3, meth4, meth5,
meth6, but not yet rotation
# read progdyn.conf for configuration info

initializeparameters()
initializeconstants()
readprogdynconf()

getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1

if (diag>=1) diagnosticsA()

#get forward or reverse from skipstart if it exists
getline < "skipstart"
trajdirection = $1

readgeoPlusVel()
putPoint1Traj()
addVelocities()
} # end of BEGIN

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ || /ONIOM:/ {
if (($1=="Energy=") && ($3=="NIter=")) newPotentialE=$2
if ($1=="SCF") newPotentialE=$5 #This was subject to a bug at
one time - grep Samae in old files
if ($2=="extrapolated") newPotentialE=$5
if ($1=="E2") {
tempstring=$6
split(tempstring, arr10, "D")
newPotentialE=arr10[1]*(10^arr10[2])
}
newPotEK=(newPotentialE-potentialE)*627.509
newPotentialEK=(newPotentialE-potentialE)*627.509
}

# now we go ahead and collect the forces from the point 1 file
(/ 1 /||/ 2 /||/ 3 /||/ 4 /||/ 5 /||/
6 /||/ 7 /||/ 8 /||/ 9 /||/ 10 /||/ 11
/||/ 12 /||/ 13 /||/ 14 /||/ 15 /||/ 16 /||/
/ 17 /||/ 18 /||/ 19 /||/ 20 /||/ 21 /||/
22 /||/ 23 /||/ 24 /||/ 25 /||/ 26 /||/
27 /||/ 28 /||/ 29 /||/ 30 /||/ 31 /||/
32 /||/ 33 /||/ 34 /||/ 35 /) && length($3) > 9 {
i=$1
for (j=1;j<=3;j++) {
forceArr[i,j]=$2+j) #the raw units of the forces are
Hartree/Bohr
}
if ((diag>1) && (i==1)) print
"i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
if (diag>1) print
i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >>
"diagnostics"
}

END {
if (DRP==0) doEcheck()
addForceEffect()
writecomfile()
writetraj()
}

#####
##### FUNCTIONS

```

```

#####
function Distance(Atom1,Atom2) {
return sqrt((oldarr[Atom1,1]-
oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
}

# default parameters, including quassiclassical, no displacements,
transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the
parameters
function initializeparameters() {
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=2000000
diag=1; checkpoint="g16.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1;
highlevel=99999; linkatoms=0
damping=1;nonstandard=0;geometry="nonlinear";nonstandard=0
nmrtype=0;nmrevery=9999999;nmrcc=0;nmrnd=0;nmrdo=0
thermostat=0;thermostatmult=1.00
oniomcharge=0; oniommult=0
applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
sphereon=0; spheresize=999; sphereforceK=0.01
empiricaldispersion=0; radiusmultiplier=1.25
etolerance=1
}

function initializeconstants() {
srand(PROCINFO["pid"])
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
numAtoms=0; atomnumber=0
conver1=4.184E26 #dividing by this converts amu ang^2 /s^2 to
kcal/mol
OFS=" "
}

# read progdyn.conf for configuration info
function readprogdynconf() {
blankLineTester=10
while (blankLineTester>1) {
getline < "progdyn.conf"
if ($1=="method") method=$2
if ($1=="method2") meth2=$2
if ($1=="charge") charge=$2
if ($1=="multiplicity") multiplicity=$2
if ($1=="oniomchargemult") {
oniomcharge=$2
oniommult=$3
}
if ($1=="memory") memory=$2
if ($1=="processors") processors=$2
if ($1=="checkpoint") checkpoint=$2
if ($1=="timestep") timestep=$2
if ($1=="diagnostics") diag=$2
if ($1=="temperature") temp=$2
if ($1=="thermostat") thermostat=$2
if ($1=="thermostatmult") thermostatmult=$2
if (thermostatmult>1) thermostatmult=1/thermostatmult
if ($1=="method3") meth3=$2
if ($1=="method4") meth4=$2
if ($1=="method5") meth5=$2
if ($1=="method6") meth6=$2
if ($1=="method7") meth7=$2
if ($1=="highlevel") highlevel=$2
if ($1=="linkatoms") linkatoms=$2
if ($1=="fixedatom1") fixedatom1=$2
}
}

```

```

if ($1=="fixedatom2") fixedatom2=$2
if ($1=="fixedatom3") fixedatom3=$2
if ($1=="fixedatom4") fixedatom4=$2
if ($1=="boxon") boxon=$2
if ($1=="boxsize") boxsize=$2
if ($1=="sphereon") sphereon=$2
if ($1=="spheresize") spheresize=$2
if ($1=="sphereforce") sphereforceK=$2
if ($1=="DRP") DRP=$2
if ($1=="maxAtomMove") maxAtomMove=$2
if ($1=="methodfile") methodfilelines=$2
if ($1=="killcheck") killcheck=$2
if ($1=="etolerance") etolerance=$2
if ($1=="reversetraj") reversetraj=$2
if ($1=="empiricaldispersion") empiricaldispersion=$2
if ($1=="radiusmultiplier") radiusmultiplier=$2
if ($1=="damping") damping=$2
if ($1=="NMRmethod") nmrmethod=$2
if ($1=="NMRmethod2") nmrmethod2=$2
if ($1=="NMRmethod3") nmrmethod3=$2
if ($1=="NMRtype") nmrtype=$2
if ($1=="NMRevery") nmrevery=$2
if ($1=="NMRrand") nmrrand=$2
if ($1=="loadlimit") loadlimit=$2
if ($1=="NMRcc") nmrrcc=$2
if ($1=="nonstandard") nonstandard=$2
if ($1=="applyforce") {
    applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5;
apforce3=$6
}
if ($1=="applyforceB") {
    applyforceB=$2; apforceB=$3; apforceX0B=$4;
apforce2B=$5; apforce3B=$6
}
if ($1=="applyforceC") {
    applyforceC=$2; apforceC=$3; apforceX0C=$4;
apforce2C=$5; apforce3C=$6
}
if ($1=="afatoms") {
    for (i=1;i<8;i++) {
        if ($i>0) afatom[i]=$i
    }
}
if ($1=="afatomsB") {
    for (i=1;i<8;i++) {
        if ($i>0) afatomB[i]=$i
    }
}
if ($1=="afatomsC") {
    for (i=1;i<8;i++) {
        if ($i>0) afatomC[i]=$i
    }
}
if ($1=="applyforceplane") {
    applyforceplane=$2; apforceplane=$3; apforceplaneX0=$4
}
if ($1=="afplaneatoms") {
    for (i=1;i<8;i++) {
        if ($i>0) afplaneatoms[i]=$i
    }
}
if ($1=="zeroatom") {
    zeroatomon=1
    zeroatom=$2
}
if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
}

```

```

}
blankLineTester=length($0)
}
}
function diagnosticsA() {
    print "***** starting progdynb
*****" >> "diagnostics"
    print "method,charge,multiplicity,memory" >> "diagnostics"
    print method,charge,multiplicity,memory >> "diagnostics"
    print "processors,checkpoint,title" >> "diagnostics"
    print processors,checkpoint,title1,title2,title3,title4 >>
"diagnostics"
}
function readgeoPlusVel() {
#this is different from prog1stpoint and progdynb because we are
just getting velocities
#read in number of atoms, geometry, masses from geoPlusVel
    getline < "geoPlusVel"
    numAtoms=$1
# geometry
    for (i=1;i<=numAtoms;i++) {
        getline < "geoPlusVel"
        weight[i]=$5
        atSym[i]=$1
        for (j=1;j<=3;j++) {
            geoArr[i,j]=$i+j
        }
    }
#velocities
    for (i=1;i<=numAtoms;i++) {
        getline < "geoPlusVel"
        for (j=1;j<=3;j++) {
            velArr[i,j]=$j
        }
    }
#pull out other information useful for testing whether total energy
is right or bad
    blankLineTester=10
    while (blankLineTester>1) {
        getline < "geoPlusVel"
        if ($4=="desired=") desiredModeEnK=$5
        if ($4=="modes=") {
            KEinitmodes=$5
            KEinittotal=$9
        }
        if ($11=="potential") potentialE=$13
        blankLineTester=length($0)
    }
}
function addVelocities() {
# ok, now we have to figure the second point. this should be
# x(t) = x + v*t + 1/2*F*t^2/m
#now we go ahead and add the velocities
    for (i=1;i<=numAtoms;i++) {
        for (j=1;j<=3;j++) {
            arr[i,j]=velArr[i,j]+geoArr[i,j]
            if (trajdirection=="reverserestart") arr[i,j]=geoArr[i,j]-
velArr[i,j]
        }
        if ((diag>1) && (i==1)) print "geometry after adding
velocities" >> "diagnostics"
        if (diag>1) print arr[i,1],arr[i,2],arr[i,3] >> "diagnostics"
    }
}
function putPoint1Traj() {
#get initial geometry into file traj
}

```

```

print numAtoms >> "traj"
print potentialE,title1,title2,title3,title4,"runpoint 1 ", "runisomer
",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
    print atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >> "traj"
}

function doEcheck() {
    print "trajectory #",isomernum >> "Echeck"
    print "point 1 potential E=",newPotentialEK," point 1 kinetic
E=",KEinitmodes," Total=",newPotentialEK+KEinitmodes >>
"Echeck"
    print "desired total energy=", desiredModeEnK >> "Echeck"
    if
((newPotentialEK+KEinitmodes)>(desiredModeEnK+etolerance))
print "XXXX bad total Energy" >> "Echeck"
    if ((newPotentialEK+KEinitmodes)<(desiredModeEnK-
etolerance)) print "XXXX bad total Energy" >> "Echeck"
}

function addForceEffect() {
# x(t) = x + v*t + 1/2*F*t^2/m
# turn the forces into motion
    for (i=1;i<=numAtoms;i++) {
        for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg
angstroms / s^2, then mult time (s^s) and divide by weight in kg to
get angstroms

forceArr[i,j]=0.5*1E20*forceArr[i,j]*627.509*(4184/(0.529177*a
vNum))*(timestep^2)/(weight[i]/(avNum*1000))
# for simplicity, DRPs will throw away the forces at the second
pont. This means that if we are not at a saddlepoint, point 2 =
point 1 but this is a minor waste
        if (DRP==1) forceArr[i,j]=0
        arr[i,j]=arr[i,j]+forceArr[i,j]
# if atoms are fixed, replace calcd new position by original position
        if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) ||
(i==fixedatom4)) arr[i,j]=geoArr[i,j]
        }
        if ((diag>1) && (i==1)) print
",i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
        if (diag>1) print
i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >>
"diagnostics"
        }
    }

function writecomfile() {
    print "%nproc=" processors
    print "%mem=" memory
    if (killcheck!=1) print "%chk=" checkpoint
    if (nonstandard==0) {
        print "# " method " force
scf=(xqc,maxconven=55,fulllinear,nosym) "
        if (meth2=="unrestricted") print "guess=mix" #for unrestricted
calculations
        if (meth2=="read") print "guess=tcheck" #for reading orbitals
from check, sometimes faster, sometimes not
        if (length(meth3)>2) print meth3
        if (length(meth4)>2) print meth4
        }
    if (nonstandard==1) {
        print "# "
        print "nonstd"
        system("cat nonstandard")
    }
    print ""
}

```

```

print title1,title2,title3,title4
print "runpoint ",runpointnum
print "runisomer ", isomernum
print ""
if (oniomult==0) print charge,multiplicity
if (oniomult>0) print
charge,multiplicity,oniomcharge,oniomult
for (i=1;i<=numAtoms;i++) {
    printf("%s %.7f %.7f %.7f",atSym[i],arr[i,1],arr[i,2],arr[i,3])
    if ((i>highlevel) && (i<=highlevel+linkatoms)) printf("
%s", "M H")
    if (i>(highlevel+linkatoms)) printf(" %s", "M")
    print ""
}
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
    for (i=1;i<=methodfilelines;i++) {
        getline < "methodfile"
        print $0
    }
}
if ((nmrtype>0) && ((runpointnum % nmrevery)==0)) {
    print "--link 1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmethod " nmr=giao geom=check"
    if (nmrmethod==method) print "guess=tcheck"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
}
print ""
if ((nmrtype>1) && ((runpointnum % nmrevery)==0)) {
    print "--link 1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmethod2 " nmr=giao geom=check"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
}
print ""
if ((nmrtype>2) && ((runpointnum % nmrevery)==0)) {
    print "--link 1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmethod3 " nmr=giao geom=check"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
}
print ""
}
}

```

```

function writetraj() {
#get second geometry into file traj
  print numAtoms >> "traj"
  print newPotentialE,title1,title2,title3,title4,"runpoint
",runpointnum,"runisomer","isomernum >> "traj"
  for (i=1;i<=numAtoms;++) {
    print atSym[i],arr[i,1],arr[i,2],arr[i,3] >> "traj"
  }
}

```

## progdynb

```

BEGIN { #this is the main routine for generating new .com files by
the Verlet algorithm
# Nov 2016 organized into functions, added empirical dispersion
# Oct 2015 added sanity check, eliminated dyn files and keepevery
# May 2015 added ability to force solvent into a sphere
# Feb 2015 added zeroatom ability to make solute centered in
solvent
# Jan 2015 added applyforce to apply forces on motion of atoms
and allow PMF calculations
# Dec 2014 added oniom charge specifications
# 2013 added multiple NMR calculations, molecular rotations,
thermostat commands
# 2012 added NMR calculations
# 2011 added linkatoms in ONIOM
# Aug 2010 increased elements handled automatically but only up
to bromine!
# Jan 2009 - a number of little changes to improve reporting,
precision, etc
# Nov 2008 added ability to handle DRPs
# Aug 2008 added long list of atoms to handle 1-17 without change
# May 2008 added option to put out velocities in vellist - make
diag=3
# version Feb 2008 incorporates methodfile, boxon and boxsize
# version Jan 2008 incorporates fixed atoms, oniom, and velocity
damping
# version August 2007 incorporates keepevery to decrease size of
dyn file
# version Sept 11, 2005 - incorporates meth3, meth4, meth5,
meth6, but not yet rotation

initializeparameters()
initializeconstants()
readprogdynconf()

getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1

if (diag>=1) diagnosticsA()
readgeoPlusVelAndoldAndolder()
#readgeoPlusVelAndoldAndolder sets numAtoms, weight[i],
atSym[i], potentialE, oldarr[at,1to3], olderarr[at,1to3]
# also sets apparentTemp, KEold, does sanitycheck
if (DRP==1) readoldAdjForcesAndmaxMove() #for DRPs read in
oldForce[at,123] and maxAtomMove
nmrstuffA() # sets nmrdo to 0 or 1, controls where NMR calcs are
done
}
##### END OF BEGIN
#####

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ || /ONIOM:/ {
if (($1=="Energy=") && ($3=="NIter=")) newPotentialE=$2
if ($1=="SCF") newPotentialE=$5

```

```

if ($2=="extrapolated") newPotentialE=$5
if ($1=="E2") {
  tempstring=$6
  split(tempstring, arr10, "D")
  newPotentialE=arr10[1]*(10^arr10[2])
}
newPotEK=(newPotentialE-potentialE)*627.509
}

#must adjust next line for weird atoms
(/ 1 /||/ 2 /||/ 3 /||/ 4 /||/ 5 /||/
6 /||/ 7 /||/ 8 /||/ 9 /||/ 10 /||/ 11
/||/ 12 /||/ 13 /||/ 14 /||/ 15 /||/ 16 /||
/ 17 /||/ 18 /||/ 19 /||/ 20 /||/ 21 /||/
22 /||/ 23 /||/ 24 /||/ 25 /||/ 26 /||/
27 /||/ 28 /||/ 29 /||/ 30 /||/ 31 /||/
32 /||/ 33 /||/ 34 /||/ 35 /) && length($3) > 9 {
i=$1
for (j=1;j<=3;j++) {
  forceArr[i,j]=$(2+j) #the raw units of the forces are
Hartree/Bohr
}
#if ((diag>1) && (i==1)) print
"i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
#if (diag>1) print
i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >>
"diagnostics"
}

END {
if (sphereon==1) applysphereforce() # apply a force to bring atoms
within a sphere. This also figures out the density at
0.9*spheresize
# routines to apply forces between atoms, used for umbrella
sampling
if (applyforceplane>0) doapplyforceplane() #used to apply a force
on an atom versus its distance from a plane
setinterlockingsphereatom() #apply force to one of a series of
atoms, whichever is closest to atom1[1]
if (applyforce>0) doapplyforce()
if (applyforceB>0) doapplyforceB()
if (applyforceC>0) doapplyforceC()
if (empiricaldispersion>0) doempiricaldispersion()
if (zeroatomon==1) dozeroatom() #routine to slowly move an atom
toward the origin
if (thermostat==1) dothermostat()
if (DRP==1) doDRP() #routine for steepest descent path in mass
weighted coordinates
if (DRP==0) doVerlet() #normal routine for Verlet
writetraj()
writecomfile()
}

#####
##### FUNCTIONS
#####
function Distance(Atom1,Atom2) {
  return sqrt((oldarr[Atom1,1]-
oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
}

# default parameters, including quassiclassical, no displacements,
transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the
parameters
function initializeparameters() {
  initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
  classical=0; numimag=1; DRP=0; cannonball=0

```



```

memory=2000000
diag=1; checkpoint="g16.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1;
highlevel=99999; linkatoms=0
damping=1;nonstandard=0;geometry="nonlinear";nonstandard=0
nmrtype=0;nmrevery=999999;nmrcc=0;nmrrand=0;nmrdo=0
thermostat=0;thermostatmult=1.00
oniumcharge=0; oniommult=0
applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
sphereon=0; sphereseize=999; sphereforceK=0.01
empiricaldispersion=0; radiusmultiplier=1.25
}

function initializeconstants() {
  srand(PROCINFO["pid"])
  i=1;j=1;k=1
  c=29979245800; h=6.626075E-34; avNum=6.0221415E23
  RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
  numAtoms=0; atomnumber=0
  conver1=4.184E26 #dividing by this converts amu ang^2 /s^2 to
kcal/mol
  OFS=" "
}

# read progdyn.conf for configuration info
function readprogdynconf() {
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="method2") meth2=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity") multiplicity=$2
    if ($1=="oniumchargemult") {
      oniomcharge=$2
      oniommult=$3
    }
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
    if ($1=="checkpoint") checkpoint=$2
    if ($1=="timestep") timestep=$2
    if ($1=="diagnostics") diag=$2
    if ($1=="temperature") temp=$2
    if ($1=="thermostat") thermostat=$2
    if ($1=="thermostatmult") thermostatmult=$2
    if (thermostatmult>1) thermostatmult=1/thermostatmult
    if ($1=="method3") meth3=$2
    if ($1=="method4") meth4=$2
    if ($1=="method5") meth5=$2
    if ($1=="method6") meth6=$2
    if ($1=="method7") meth7=$2
    if ($1=="highlevel") highlevel=$2
    if ($1=="linkatoms") linkatoms=$2
    if ($1=="fixedatom1") fixedatom1=$2
    if ($1=="fixedatom2") fixedatom2=$2
    if ($1=="fixedatom3") fixedatom3=$2
    if ($1=="fixedatom4") fixedatom4=$2
    if ($1=="boxon") boxon=$2
    if ($1=="boxsize") boxsize=$2
    if ($1=="sphereon") sphereon=$2
    if ($1=="sphereseize") sphereseize=$2
    if ($1=="sphereforce") sphereforceK=$2
    if ($1=="DRP") DRP=$2
    if ($1=="maxAtomMove") maxAtomMove=$2
    if ($1=="methodfile") methodfilelines=$2
    if ($1=="killcheck") killcheck=$2
    if ($1=="empiricaldispersion") empiricaldispersion=$2
    if ($1=="radiusmultiplier") radiusmultiplier=$2
    if ($1=="damping") damping=$2

    if ($1=="NMRmethod") nmrmeth=$2
    if ($1=="NMRmethod2") nmrmeth2=$2
    if ($1=="NMRmethod3") nmrmeth3=$2
    if ($1=="NMRtype") nmrtype=$2
    if ($1=="NMRevery") nmrevery=$2
    if ($1=="NMRrand") nmrrand=$2
    if ($1=="loadlimit") loadlimit=$2
    if ($1=="NMRcc") nmrcc=$2
    if ($1=="nonstandard") nonstandard=$2
    if ($1=="applyforce") {
      applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5;
      apforce3=$6
    }
    if ($1=="applyforceB") {
      applyforceB=$2; apforceB=$3; apforceX0B=$4;
      apforce2B=$5; apforce3B=$6
    }
    if ($1=="applyforceC") {
      applyforceC=$2; apforceC=$3; apforceX0C=$4;
      apforce2C=$5; apforce3C=$6
    }
    if ($1=="afatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatom[i]=$i+1
      }
    }
    if ($1=="afatomsB") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatomB[i]=$i+1
      }
    }
    if ($1=="afatomsC") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatomC[i]=$i+1
      }
    }
    if ($1=="applyforceplane") {
      applyforceplane=$2; apforceplane=$3; apforceplaneX0=$4
    }
    if ($1=="afplaneatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afplaneatoms[i]=$i+1
      }
    }
    if ($1=="zeroatom") {
      zeroatomon=1
      zeroatom=$2
    }
    if ($1=="title") {
      title1=$2
      title2=$3
      title3=$4
      title4=$5
    }
    blankLineTester=length($0)
  }
}

function diagnosticsA() {
  print "***** starting progdyn"
  print "*****" >> "diagnostics"
  print "method,charge,multiplicity,memory" >> "diagnostics"
  print "method,charge,multiplicity,memory" >> "diagnostics"
  print "processors,checkpoint,title" >> "diagnostics"
  print "processors,checkpoint,title1,title2,title3,title4" >>
"diagnostics"
}

function readgeoPlusVelAndoldAndolder() {
# get number of atoms and weights from geoPlusVel, and previous

```

```

geometries from old and older
getline < "geoPlusVel"
numAtoms=$1
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5; atSym[i]=$1
}
blankLineTester=10
while (blankLineTester>1) {
  getline < "geoPlusVel"
  if ($1=="potential") potentialE=$13
  blankLineTester=length($0)
}

for (at=1;at<=numAtoms;at++) {
  getline < "old"
  oldarr[at,1]=$4; oldarr[at,2]=$5; oldarr[at,3]=$6
}

for (at=1;at<=numAtoms;at++) {
  getline < "older"
  olderarr[at,1]=$4; olderarr[at,2]=$5; olderarr[at,3]=$6
  atomVel=((oldarr[at,1]-olderarr[at,1])^2 + (oldarr[at,2]-
  olderarr[at,2])^2 +(oldarr[at,3]-olderarr[at,3])^2)^.5

KEold=KEold+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver
1)
# sanity check - avoids trajectory blow up
  if (atomVel>1) exit
}
  apparentTemp=KEold*2/(3*RgasK*numAtoms) # this is not the
  temperature at the previous point but rather 1.5 points back.
# sanity check - avoids trajectory blow up
  for (at=1;at<=numAtoms;at++) {
    if (((oldarr[at,1]-olderarr[at,1])^2)>1) exit
  }
}

function readoldAdjForcesAndmaxMove() {
#for DRPs read in oldAdjForces and maxAtomMove
  for (at=1;at<=numAtoms;at++) {
    getline < "oldAdjForces"
    oldForce[at,1]=$1; oldForce[at,2]=$2; oldForce[at,3]=$3
  }
  getline < "maxMove"
  if (($1<maxAtomMove) && ($1>0)) maxAtomMove=$1
  if (maxAtomMove<0.000001) maxAtomMove=0.000001
}

function nmrstuffA() {
# sets nmrd to 0 or 1, controls where NMR calcs are done
  if ((nmrrand==0) && ((runpointnum % nmrevery)==0))
nmrdo=1
  if ((nmrrand==1) && (rand()<(1/nmrevery))) nmrdo=1
  getline < "uptimelist"
  x=1.0001*substr($10,1,3);if (x<8) x=8
# turn of nmrs if load is too high - this is under control of loadlimit
parameter in progdyn.conf and requires proganal to make
uptimelist
  if ((nmrrand==1) && (x>loadlimit)) nmrdo=0
}

function applysphereforce() {
# apply a force to bring atoms within a sphere. This also figures
out the density at 0.9*spheresize
# We are going through the loop twice, the first time figure outs
the total pressure, then scales the forces to limit the pressure to
maxpressure
# the second time actually applies the pressure
  maxpressure=1000 #atmospheres. Later we may parameterize

```

```

this.
  sphereforcetotal=0
  for (i=1;i<=numAtoms;i++) {
    distToOrig=((oldarr[i,1]^2+oldarr[i,2]^2+oldarr[i,3]^2)^.5)
    if (distToOrig>spheresize) {
      sphereforce=sphereforceK*(distToOrig-spheresize)
      if (sphereforce>0.01) sphereforce=0.01 #important limit on
force for atoms far outside of the sphere, not sure if value chosen is
best
      sphereforcetotal=sphereforcetotal+sphereforce
    }
  }

  sphereforcetotalNewtons=sphereforcetotal*627.509*4184*1E10/(0
.529177*avNum)
  surfaceareaSqMeters=4*pi*spheresize^2/1E20
  pressurePascal=sphereforcetotalNewtons/surfaceareaSqMeters
  pressureAtm=pressurePascal/101325
  if (pressureAtm>maxpressure)
sphereforceK=sphereforceK*maxpressure/pressureAtm
# go through the loop again
  sphereforcetotal=0; totalweight=0
  for (i=1;i<=numAtoms;i++) {
    distToOrig=((oldarr[i,1]^2+oldarr[i,2]^2+oldarr[i,3]^2)^.5)
    if (distToOrig>spheresize) {
      sphereforce=sphereforceK*(distToOrig-spheresize)
      if (sphereforce>0.01) sphereforce=0.01 #important limit on
force for atoms far outside of the sphere, not sure if value chosen is
best
      sphereforcetotal=sphereforcetotal+sphereforce
    }
  }
  unitX=sphereforce*oldarr[i,1]/distToOrig;unitY=sphereforce*olda
rr[i,2]/distToOrig;unitZ=sphereforce*oldarr[i,3]/distToOrig
  forceArr[i,1]=forceArr[i,1]-
unitX;forceArr[i,2]=forceArr[i,2]-
unitY;forceArr[i,3]=forceArr[i,3]-unitZ
}
# calculate the density at 0.9*spheresize
  if (distToOrig<0.9*spheresize) {
    totalweight=totalweight+weight[i]
  }
}
#recalculate pressure

  sphereforcetotalNewtons=sphereforcetotal*627.509*4184*1E10/(0
.529177*avNum)
  surfaceareaSqMeters=4*pi*spheresize^2/1E20
  pressurePascal=sphereforcetotalNewtons/surfaceareaSqMeters
  pressureAtm=pressurePascal/101325
  density=(totalweight/avNum)/((4/3)*pi*(0.9*spheresize*1E-
8)^3)
}

function doapplyforceplane() {
#used to apply a force on an atom versus its distance from a plane
  if (afplaneatoms[4]<.5) {
    print "you need more atoms to define a plane"
    exit
  }
  for (i=2;i<8;i++) {
    if (afplaneatoms[i]>.5) {
      k=afplaneatoms[i]

```

```

A[1,1]=A[1,1]+oldarr[k,1]^2;A[1,2]=A[1,2]+oldarr[k,1]*oldarr[k,
2];A[1,3]=A[1,3]+oldarr[k,1]

```

```

A[2,1]=A[2,1]+oldarr[k,1]*oldarr[k,2];A[2,2]=A[2,2]+oldarr[k,2]^
2;A[2,3]=A[2,3]+oldarr[k,2]

```

```

A[3,1]=A[3,1]+oldarr[k,1];A[3,2]=A[3,2]+oldarr[k,2];A[3,3]++

```

```

b[1]=b[1]+oldarr[k,1]*oldarr[k,3];b[2]=b[2]+oldarr[k,2]*oldarr[k,3];b[3]=b[3]+oldarr[k,3]
# find center of mass assuming all atoms same weight

```

```

cmass[1]=cmass[1]+oldarr[k,1];cmass[2]=cmass[2]+oldarr[k,2];cmass[3]=cmass[3]+oldarr[k,3];
}
}
numplaneatoms=A[3,3]

```

```

cmass[1]=cmass[1]/A[3,3];cmass[2]=cmass[2]/A[3,3];cmass[3]=cmass[3]/A[3,3]
# print "matrix A"
# for (i=1;i<=3;i++) {
#   print A[i,1],A[i,2],A[i,3]
# }
# print "matrix b"
# print b[1],b[2],b[3]

```

```

Det=A[1,1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*A[3,2]-A[1,3]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*A[3,2]

```

```

E=(b[1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*b[3]+A[1,3]*b[2]*A[3,2]-A[1,3]*A[2,2]*b[3]-A[1,2]*b[2]*A[3,3]-b[1]*A[2,3]*A[3,2])/Det

```

```

F=(A[1,1]*b[2]*A[3,3]+b[1]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*b[3]-A[1,3]*b[2]*A[3,1]-b[1]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*b[3])/Det

```

```

G=(A[1,1]*A[2,2]*b[3]+A[1,2]*b[2]*A[3,1]+b[1]*A[2,1]*A[3,2]-b[1]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*b[3]-A[1,1]*b[2]*A[3,2])/Det
# E, F, and G are the coefficients in the plane z=Ex+Fy+G"

```

```

# make a function that tests the fit
for (i=2;i<8;i++) {
  if (afplaneatoms[i]>.5) {
    k=afplaneatoms[i]
    distplane=(-oldarr[k,1]*E-oldarr[k,2]*F+oldarr[k,3]-G)/(E^2+F^2+1)^.5;if (distplane<0) distplane=-distplane
    aberror=aberror+distplane
  }
}

```

```

# if the fit is bad, as can happen, decrease to 3 atoms in plane, using only the first three atoms in list after the conatom
if (aberror>2) {
  print "original aberror",aberror >> "diagnostics"
}

```

```

A[1,1]=0;A[1,2]=0;A[1,3]=0;A[2,1]=0;A[2,2]=0;A[2,3]=0;A[3,1]=0;A[3,2]=0;A[3,3]=0
for (i=2;i<5;i++) {
  k=afplaneatoms[i]
}

```

```

A[1,1]=A[1,1]+oldarr[k,1]^2;A[1,2]=A[1,2]+oldarr[k,1]*oldarr[k,2];A[1,3]=A[1,3]+oldarr[k,1]*oldarr[k,3]

```

```

A[2,1]=A[2,1]+oldarr[k,1]*oldarr[k,2];A[2,2]=A[2,2]+oldarr[k,2]^2;A[2,3]=A[2,3]+oldarr[k,2]*oldarr[k,3]

```

```

A[3,1]=A[3,1]+oldarr[k,1]*oldarr[k,3];A[3,2]=A[3,2]+oldarr[k,2]*oldarr[k,3];A[3,3]=A[3,3]+oldarr[k,3]^2

```

```

b[1]=b[1]+oldarr[k,1]*oldarr[k,3];b[2]=b[2]+oldarr[k,2]*oldarr[k,3];b[3]=b[3]+oldarr[k,3]*oldarr[k,3]
}
}

```

```

Det=A[1,1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*A[3,2]-A[1,3]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*A[3,2]

```

```

E=(b[1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*b[3]+A[1,3]*b[2]*A[3,2]-A[1,3]*A[2,2]*b[3]-A[1,2]*b[2]*A[3,3]-b[1]*A[2,3]*A[3,2])/Det

```

```

F=(A[1,1]*b[2]*A[3,3]+b[1]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*b[3]-A[1,3]*b[2]*A[3,1]-b[1]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*b[3])/Det

```

```

G=(A[1,1]*A[2,2]*b[3]+A[1,2]*b[2]*A[3,1]+b[1]*A[2,1]*A[3,2]-b[1]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*b[3]-A[1,1]*b[2]*A[3,2])/Det
aberror=0

```

```

for (i=2;i<5;i++) {
  k=afplaneatoms[i]
  distplane=(-oldarr[k,1]*E-oldarr[k,2]*F+oldarr[k,3]-G)/(E^2+F^2+1)^.5;if (distplane<0) distplane=-distplane
  aberror=aberror+distplane
}
}

```

```

conatom=afplaneatoms[1]
distplane=(-oldarr[conatom,1]*E-oldarr[conatom,2]*F+oldarr[conatom,3]-G)/(E^2+F^2+1)^.5
if (distplane<0) distplane=-distplane
t=(oldarr[conatom,1]*E+oldarr[conatom,2]*F-oldarr[conatom,3]+G)/(E^2+F^2+1)
planepoint[1]=oldarr[conatom,1]-t*E;planepoint[2]=oldarr[conatom,2]-t*F;planepoint[3]=oldarr[conatom,3]-t*G
distcmass=((planepoint[1]-cmass[1])^2+(planepoint[2]-cmass[2])^2+(planepoint[3]-cmass[3])^2)^.5
print
"distplane",distplane,"t",t,"planepoint",planepoint[1],planepoint[2],planepoint[3],"distcmass",distcmass,"aberror",aberror >>
"diagnostics"
if (distcmass>1.4) {
  vector[1]=planepoint[1]-cmass[1];vector[2]=planepoint[2]-cmass[2];vector[3]=planepoint[3]-cmass[3]
}

```

```

vector[1]=vector[1]*1.4/distcmass;vector[2]=vector[2]*1.4/distcmass;vector[3]=vector[3]*1.4/distcmass

```

```

planepoint[1]=cmass[1]+vector[1];planepoint[2]=cmass[2]+vector[2];planepoint[3]=cmass[3]+vector[3];
distcmass=((planepoint[1]-cmass[1])^2+(planepoint[2]-cmass[2])^2+(planepoint[3]-cmass[3])^2)^.5
distplane=((planepoint[1]-oldarr[conatom,1])^2+(planepoint[2]-oldarr[conatom,2])^2+(planepoint[3]-oldarr[conatom,3])^2)^.5
print "new
distplane",distplane,"newplanepoint",planepoint[1],planepoint[2],planepoint[3],"newdistcmass",distcmass >> "diagnostics"
}
delX=oldarr[conatom,1]-planepoint[1];delY=oldarr[conatom,2]-planepoint[2];delZ=oldarr[conatom,3]-planepoint[3]
if (applyforceplane==2) apforceplane=apforceplane*(distplane-apforceplaneX0)

```

```

unitX=apforceplane*delX/distplane;unitY=apforceplane*delY/distplane;unitZ=apforceplane*delZ/distplane
forceArr[conatom,1]=forceArr[conatom,1]-unitX;forceArr[conatom,2]=forceArr[conatom,2]-unitY;forceArr[conatom,3]=forceArr[conatom,3]-unitZ
for (i=2;i<8;i++) {
  if (afplaneatoms[i]>.5) {
    platom=afplaneatoms[i]
}
}

```

```

forceArr[platom,1]=forceArr[platom,1]+unitX/numplaneatoms;forceArr[platom,2]=forceArr[platom,2]+unitY/numplaneatoms;forceArr[platom,3]=forceArr[platom,3]+unitZ/numplaneatoms
}
}
}

```

```

function setinterlockingsphereatom() {
#apply force to one of a series of atoms, whichever is closest to
}

```

```

afatom[1]
for (i=3;i<8;i++) {
  if (afatom[i]>0) {

if(Distance(afatom[1],afatom[i])<Distance(afatom[1],afatom[2]))
afatom[2]=afatom[i]
}
  if (afatomB[i]>0) {

if(Distance(afatomB[1],afatomB[i])<Distance(afatomB[1],afatom
B[2])) afatomB[2]=afatomB[i]
}
  if (afatomC[i]>0) {

if(Distance(afatomC[1],afatomC[i])<Distance(afatomC[1],afatom
C[2])) afatomC[2]=afatomC[i]
}
}
}

```

```

function doapplyforce() {
# applyforce 1 puts a linear constant force.
# applyforce 2 puts on a harmonic restoring force to apforceX0
delX=oldarr[afatom[1],1]-
oldarr[afatom[2],1];delY=oldarr[afatom[1],2]-
oldarr[afatom[2],2];delZ=oldarr[afatom[1],3]-oldarr[afatom[2],3];
dstatoms=(delX^2+delY^2+delZ^2)^.5
if (applyforce==2) apforce=apforce*(dstatoms-apforceX0)
if (applyforce==3) apforce=apforce*(dstatoms-apforceX0) +
apforce2*(dstatoms-apforceX0)^2
if (applyforce==4) apforce=apforce*(dstatoms-apforceX0) +
apforce2*(dstatoms-apforceX0)^2 + apforce3*(dstatoms-
apforceX0)^3

unitX=apforce*delX/dstatoms;unitY=apforce*delY/dstatoms;;uni
tZ=apforce*delZ/dstatoms;
forceArr[afatom[1],1]=forceArr[afatom[1],1]-
unitX;forceArr[afatom[1],2]=forceArr[afatom[1],2]-
unitY;forceArr[afatom[1],3]=forceArr[afatom[1],3]-unitZ

forceArr[afatom[2],1]=forceArr[afatom[2],1]+unitX;forceArr[afat
om[2],2]=forceArr[afatom[2],2]+unitY;forceArr[afatom[2],3]=forc
eArr[afatom[2],3]+unitZ
}

```

```

function doapplyforceB() {
delX=oldarr[afatomB[1],1]-
oldarr[afatomB[2],1];delY=oldarr[afatomB[1],2]-
oldarr[afatomB[2],2];delZ=oldarr[afatomB[1],3]-
oldarr[afatomB[2],3];
dstatoms=(delX^2+delY^2+delZ^2)^.5
if (applyforceB==2) apforceB=apforceB*(dstatoms-
apforceX0B)
if (applyforceB==3) apforceB=apforceB*(dstatoms-
apforceX0B) + apforce2B*(dstatoms-apforceX0B)^2
if (applyforceB==4) apforceB=apforceB*(dstatoms-
apforceX0B) + apforce2B*(dstatoms-apforceX0B)^2 +
apforce3B*(dstatoms-apforceX0B)^3

unitX=apforceB*delX/dstatoms;unitY=apforceB*delY/dstatoms;;
unitZ=apforceB*delZ/dstatoms;
forceArr[afatomB[1],1]=forceArr[afatomB[1],1]-
unitX;forceArr[afatomB[1],2]=forceArr[afatomB[1],2]-
unitY;forceArr[afatomB[1],3]=forceArr[afatomB[1],3]-unitZ

forceArr[afatomB[2],1]=forceArr[afatomB[2],1]+unitX;forceArr[a
fatomB[2],2]=forceArr[afatomB[2],2]+unitY;forceArr[afatomB[2]
,3]=forceArr[afatomB[2],3]+unitZ
}

```

```

function doapplyforceC() {
delX=oldarr[afatomC[1],1]-
oldarr[afatomC[2],1];delY=oldarr[afatomC[1],2]-
oldarr[afatomC[2],2];delZ=oldarr[afatomC[1],3]-
oldarr[afatomC[2],3];
dstatoms=(delX^2+delY^2+delZ^2)^.5
if (applyforceC==2) apforceC=apforceC*(dstatoms-
apforceX0C)
if (applyforceC==3) apforceC=apforceC*(dstatoms-
apforceX0C) + apforce2C*(dstatoms-apforceX0C)^2
if (applyforceC==4) apforceC=apforceC*(dstatoms-
apforceX0C) + apforce2C*(dstatoms-apforceX0C)^2 +
apforce3C*(dstatoms-apforceX0C)^3

unitX=apforceC*delX/dstatoms;unitY=apforceC*delY/dstatoms;;
unitZ=apforceC*delZ/dstatoms;
forceArr[afatomC[1],1]=forceArr[afatomC[1],1]-
unitX;forceArr[afatomC[1],2]=forceArr[afatomC[1],2]-
unitY;forceArr[afatomC[1],3]=forceArr[afatomC[1],3]-unitZ

```

```

forceArr[afatomC[2],1]=forceArr[afatomC[2],1]+unitX;forceArr[a
fatomC[2],2]=forceArr[afatomC[2],2]+unitY;forceArr[afatomC[2]
,3]=forceArr[afatomC[2],3]+unitZ
}

```

```

function doempiricaldispersion() {
EdispHtotal=0
s6=empiricaldispersion
for (i=1;i<=numAtoms;i++) {
  if (atSym[i]=="H") {c6[i]=0.14;r0[i]=1.001}
# if (atSym[i]=="H") {c6[i]=0.16;r0[i]=1.11}
  if (atSym[i]=="He") {c6[i]=0.08;r0[i]=1.012}
  if (atSym[i]=="Li") {c6[i]=1.61;r0[i]=0.825}
  if (atSym[i]=="Be") {c6[i]=1.61;r0[i]=1.408}
  if (atSym[i]=="B") {c6[i]=3.13;r0[i]=1.485}
  if (atSym[i]=="C") {c6[i]=1.75;r0[i]=1.452}
# if (atSym[i]=="C") {c6[i]=1.65;r0[i]=1.61}
  if (atSym[i]=="N") {c6[i]=1.23;r0[i]=1.397}
# if (atSym[i]=="N") {c6[i]=1.11;r0[i]=1.55}
  if (atSym[i]=="O") {c6[i]=0.70;r0[i]=1.342}
# if (atSym[i]=="O") {c6[i]=0.70;r0[i]=1.49}
  if (atSym[i]=="F") {c6[i]=0.75;r0[i]=1.287}
  if (atSym[i]=="Ne") {c6[i]=0.63;r0[i]=1.243}
  if (atSym[i]=="Na") {c6[i]=5.71;r0[i]=1.144}
  if (atSym[i]=="Mg") {c6[i]=5.71;r0[i]=1.364}
  if (atSym[i]=="Al") {c6[i]=10.79;r0[i]=1.639}
  if (atSym[i]=="Si") {c6[i]=9.23;r0[i]=1.716}
  if (atSym[i]=="P") {c6[i]=7.84;r0[i]=1.705}
  if (atSym[i]=="S") {c6[i]=5.57;r0[i]=1.683}
  if (atSym[i]=="Cl") {c6[i]=5.07;r0[i]=1.639}
# if (atSym[i]=="Cl") {c6[i]=8.00;r0[i]=1.82}
  if (atSym[i]=="Ar") {c6[i]=4.61;r0[i]=1.595}
  if (atSym[i]=="K") {c6[i]=10.8;r0[i]=1.485}
  if (atSym[i]=="Ca") {c6[i]=10.8;r0[i]=1.474}
  if (atSym[i]=="Sc") {c6[i]=10.8;r0[i]=1.562}
  if (atSym[i]=="Ti") {c6[i]=10.8;r0[i]=1.562}
  if (atSym[i]=="V") {c6[i]=10.8;r0[i]=1.562}
  if (atSym[i]=="Cr") {c6[i]=10.8;r0[i]=1.562}
  if (atSym[i]=="Mn") {c6[i]=10.8;r0[i]=1.562}
  if (atSym[i]=="Fe") {c6[i]=10.8;r0[i]=1.562}
  if (atSym[i]=="Co") {c6[i]=10.8;r0[i]=1.562}
  if (atSym[i]=="Ni") {c6[i]=10.8;r0[i]=1.562}
  if (atSym[i]=="Cu") {c6[i]=10.8;r0[i]=1.562}
  if (atSym[i]=="Zn") {c6[i]=10.8;r0[i]=1.562}
  if (atSym[i]=="Ga") {c6[i]=16.99;r0[i]=1.65}
  if (atSym[i]=="Ge") {c6[i]=17.10;r0[i]=1.727}
  if (atSym[i]=="As") {c6[i]=16.37;r0[i]=1.76}
  if (atSym[i]=="Se") {c6[i]=12.64;r0[i]=1.771}
  if (atSym[i]=="Br") {c6[i]=12.47;r0[i]=1.749}
  if (atSym[i]=="Pd") {c6[i]=24.67;r0[i]=1.639}
}

```

```

    if (atSym[i]!="I") {c6[i]=31.5;r0[i]=1.892}
    r0[i]=r0[i]*radiusmultiplier
  }
  for (i=1;i<numAtoms;i++) {
    for (j=i+1;j<=numAtoms;j++) {
      Rij=Distance(i,j)
      if (Rij<8) { #cutoff of 8 angstroms to save time - later this
        can be parameterized
        #need to get units of force to Hartrees/Bohr, since that is the units
        of forceArr
          EdispK=Edisp(c6[i],c6[j],Rij,r0[i],r0[j])*1E6/4184 #in
          kcal/mol
          FdispK=Fdisp(c6[i],c6[j],Rij,r0[i],r0[j])*1E6/4184 #in
          kcal/mol per angstrom
          EdispH=EdispK/627.509
          EdispHtotal=EdispHtotal+EdispH
          FdispHB=FdispK*0.52917725/627.509
          # print i,j,Cij,Rij,r0[i],r0[j],fdmp," ",EdispK,FdispK,"
          ",EdispH,FdispHB,EdispHtotal
          delX=oldarr[i,1]-oldarr[j,1];delY=oldarr[i,2]-
          oldarr[j,2];delZ=oldarr[i,3]-oldarr[j,3];

          unitX=FdispHB*delX/Rij;unitY=FdispHB*delY/Rij;;unitZ=Fdisp
          HB*delZ/Rij;

          forceArr[i,1]=forceArr[i,1]+unitX;forceArr[i,2]=forceArr[i,2]+unit
          Y;forceArr[i,3]=forceArr[i,3]+unitZ
          forceArr[j,1]=forceArr[j,1]-
          unitX;forceArr[j,2]=forceArr[j,2]-
          unitY;forceArr[j,3]=forceArr[j,3]-unitZ
        }
      }
    }
    newPotentialE=newPotentialE+EdispHtotal
  }

function Edisp(c6i,c6j,rij,r0i,r0j) {
  cij=(c6i*c6j)^.5
  fdmp=1/(1+exp(-20*((rij/(r0i+r0j)-1))))
  return -s6*cij*fdmp/(rij^6)
}

function Fdisp(c6i,c6j,rij,r0i,r0j) {
  delta=0.001
  return (Edisp(c6i,c6j,rij-delta,r0i,r0j)-
  Edisp(c6i,c6j,rij+delta,r0i,r0j))/(2*delta)
}

function dozeroatom() {
  #routine to slowly move an atom toward the origin as set by a
  harmonic potential
  multiple=0.99996
  oldarr[zzeroatom,1]=multiple*oldarr[zzeroatom,1]
  oldarr[zzeroatom,2]=multiple*oldarr[zzeroatom,2]
  oldarr[zzeroatom,3]=multiple*oldarr[zzeroatom,3]
}

function dothermostat() {
  #print out some things to vellist and do thermostat
  # the damping in the thermostat is based on temperature based on
  old geo vs older geo
  if (diag<4) print "KEold",KEold,"desired
  temperature",temp,"apparent Temperature",apparentTemp >>
  "vellist"
  if (apparentTemp>temp) damping=thermostatmult
  if (apparentTemp<temp) damping=1/thermostatmult
}

function doDRP() {
  #routine for DRPs

```

```

    maxForce=0;oscillTest=0
    for (i=1;i<=numAtoms;i++) {
      for (j=1;j<=3;j++) {
        # conversions here take force to J/angstrom, 1E20 converts to kg
        angstroms / s^2, then mult time (s^s) and divide by weight in kg to
        get angstroms

        forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNu
        m))*(timestep^2)/(weight[i]/(avNum*1000))
        oscillTest=oscillTest+forceArr[i,j]*oldForce[i,j]
        if (forceArr[i,j]>maxForce) maxForce=forceArr[i,j]
        if ((0-forceArr[i,j])>maxForce) maxForce=-forceArr[i,j]
      }
      if (i==1) printf("% .8f % .8f % .8f
      \n",forceArr[1,1],forceArr[1,2],forceArr[1,3]) > "oldAdjForces"
      if (i>1) printf("% .8f % .8f % .8f
      \n",forceArr[i,1],forceArr[i,2],forceArr[i,3]) >> "oldAdjForces"
    }
    print "oscillTest",oscillTest >> "oldAdjForces"
    if (oscillTest<0) {
      maxAtomMove = maxAtomMove*0.5
      print maxAtomMove > "maxMove"
    }
    if (oscillTest>0) {
      maxAtomMove = maxAtomMove*1.2
      print maxAtomMove > "maxMove"
    }
    print "maxAtomMove ",maxAtomMove >> "oldAdjForces"
    forceMult=maxAtomMove/maxForce
    for (i=1;i<=numAtoms;i++) {
      for (j=1;j<=3;j++) {
        newarr[i,j]=oldarr[i,j]+forceMult*forceArr[i,j]
      }
    }
  }

function doVerlet() {
  #normal routine for Verlet
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      # conversions here take force to J/angstrom, 1E20 converts to kg
      angstroms / s^2, then mult time (s^s) and divide by weight in kg to
      get angstroms

      forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNu
      m))*(timestep^2)/(weight[i]/(avNum*1000))
      # if ((diag>1) && (i==1)) print
      "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
      "diagnostics"
      # if (diag>1) print
      i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >>
      "diagnostics"
      newarr[i,j]=oldarr[i,j]+damping*(oldarr[i,j]-
      olderarr[i,j])+forceArr[i,j]
      if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) ||
      (i==fixedatom4)) newarr[i,j]=oldarr[i,j]
      #turn around atoms outside the box
      if (boxon==1) {
        if (newarr[i,j]>boxsize) if (oldarr[i,j]>olderarr[i,j])
        newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-
        oldarr[i,j])+forceArr[i,j]
        if (newarr[i,j]<-1*boxsize) if (oldarr[i,j]<olderarr[i,j])
        newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-
        oldarr[i,j])+forceArr[i,j]
      }
    }
  }
}

#calculate the kinetic energy. This is for the point prior to the
current point. Corrected calculation
for (at=1;at<=numAtoms;at++) {

```

```

    atomVel=((olderarr[at,1]-newarr[at,1])^2 + (olderarr[at,2]-
newarr[at,2])^2 + (olderarr[at,3]-newarr[at,3])^2)^.5/2

KEnew=KEnew+0.5*weight[at]*(atomVel^2)/((timestep^2)*conv
er1)
}
KEave=KEnew # we used to average with KEold but that is
incorrect. This is better.
Etotal=newPotEK+KEave
#still basing apparent Temperature on velocities from old vs older,
even though the KE now represents an average of old and new
if (diag==4) print runpointnum,"KEave",KEave,"apparent
Temperature",apparentTemp,"newPotEK",newPotEK,"Etotal",Etot
al,"pressure in Atm",pressureAtm,"density in 0.9r",density >>
"vellist"
}

function writetraj() {
    print numAtoms >> "traj"
    print newPotentialE,title1,title2,title3,title4,"runpoint
",runpointnum,"runisomer ",isomernum >> "traj"
    for (i=1;i<=numAtoms;i++) {
        printf("%s %.7f %.7f
%.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "traj"
        print "" >> "traj"
    }
}

function writecomfile() {
    print "%nproc=" processors
    print "%mem=" memory
    if (killcheck!=1) print "%chk=" checkpoint
    if (nonstandard==0) {
        print "#p " method " force
scf=(xqc,maxconven=155,fulllinear,nosym) "
        if (meth2=="unrestricted") print "guess=mix" #for unrestricted
calculations
        if (meth2=="read") print "guess=tcheck" #for reading orbitals
from check, sometimes faster, sometimes not
        if (length(meth3)>2) print meth3
        if (length(meth4)>2) print meth4
    }
    if (nonstandard==1) {
        print "# "
        print "nonstd"
        system("cat nonstandard")
    }
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    if (DRP==1) {
        print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove
        print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove >>
"movelist"
    }
    print ""
    if (oniommult==0) print charge,multiplicity
    if (oniommult>0) print
charge,multiplicity,oniomcharge,oniommult
    for (i=1;i<=numAtoms;i++) {
        printf("%s %.7f %.7f
%.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3])
        if ((i>highlevel) && (i<=highlevel+linkatoms)) printf("
%s","M H")
        if (i>(highlevel+linkatoms)) printf(" %s","M")
        print ""
    }
}

```

```

print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
    for (i=1;i<=methodfilelines;i++) {
        getline < "methodfile"
        print $0
    }
}
if ((nmrtype>0) && (nmrdo==1)) {
    print "--link1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmeth " nmr=giao geom=check"
    if (nmrmeth==method) print "guess=tcheck"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
}
print ""
if ((nmrtype>1) && (nmrdo==1)) {
    print "--link1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmeth2 " nmr=giao geom=check"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
}
print ""
if ((nmrtype>2) && (nmrdo==1)) {
    print "--link1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmeth3 " nmr=giao geom=check"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
}
print ""
if ((nmrcc==1) && (nmrdo==1)) {
    print "CCSD(T) NMR calculation" > "ZMAT"
    for (i=1;i<=numAtoms;i++) {
        printf("%s %.7f %.7f
%.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "ZMAT"
        print "" >> "ZMAT"
    }
    print "" >> "ZMAT"
    print "*ACES2(CALC=CCSD[T],PROP=NMR,BASIS=dzp)
>> "ZMAT"
    print
"ABCDTYPE=AOBASIS,TREAT_PERT=SEQUENTIAL,CC_P
ROG=ECC" >> "ZMAT"
    print "COORD=CARTESIAN" >> "ZMAT"
    print "MEM_UNIT=GB,MEMORY=2)" >> "ZMAT"
}

```

```

    print "" >> "ZMAT"
}
}

```

## randgen.py

```

import random
random.seed()
for i in range(100000):
    print(random.random())

```

## toxyz.py

```

import numpy as np
import sys
from math import cos, pi, sin
np.set_printoptions(precision=2)

```

```

arglist = []
for arg in sys.argv[1:]:
    arglist.append(arg)
assert len(arglist) > 0, "You need to specify an input file"
atSym = []; lengthlist = []; anglelist = []; dihedrallist = []; atcon_1 =
[]; atcon_a = []; atcon_d = []

```

```

with open(arglist[0], 'r') as f:
    for line in f:
        if len(line) > 5:
            words = line.split()
            assert len(words[6]) > 0
            atSym.append(words[0])
            lengthlist.append(float(words[1]))
            anglelist.append(float(words[2]))
            dihedrallist.append(float(words[3]))
            atcon_1.append(int(words[4])-1)
            atcon_a.append(int(words[5])-1)
            atcon_d.append(int(words[6])-1)

```

```

anglelist = [pi * (180 - x) / 180 for x in anglelist]
dihedrallist = [pi * x / 180 for x in dihedrallist]
numAtoms = int(len(atSym))
geoArr = np.zeros([numAtoms,3])

```

```

for i in range(1,numAtoms):
    if i == 1:
        geoArr[1,0] = lengthlist[i]
    if i == 2:
        geoArr[i,0] = geoArr[atcon_1[i],0] +
        lengthlist[i]*cos(anglelist[i])
        geoArr[i,2] = geoArr[atcon_1[i],2] +
        lengthlist[i]*sin(anglelist[i])
    if i > 2:
        ab = geoArr[atcon_a[i],:] - geoArr[atcon_d[i],:]
        bc = geoArr[atcon_l[i],:] - geoArr[atcon_a[i],:]
        bc /= np.linalg.norm(bc)
        ucaret = np.cross(ab, bc)
        ucaret = ucaret / np.linalg.norm(ucaret)
        cd0 = bc * lengthlist[i]
        cd1 = cos(anglelist[i])*cd0 +
        np.cross(ucaret,sin(anglelist[i])*cd0) +
        np.dot(cd0,ucaret)*ucaret*(1-cos(anglelist[i]))
        cd2 = cos(dihedrallist[i])*cd1 +
        np.cross(bc,sin(dihedrallist[i])*cd1) + np.dot(cd1,bc)*bc*(1-
        cos(dihedrallist[i]))
        geoArr[i,:] = geoArr[atcon_l[i],:] + cd2

```

```

for i in range(0,numAtoms):
    print(atSym[i],"% 12.8f" % geoArr[i,0], "% 12.8f" %

```

```

geoArr[i,1], "% 12.8f" % geoArr[i,2])

```

## tozmat.py

```

import numpy as np
import sys
from math import cos, pi, sin, sqrt

```

```

def distance(Atom1,Atom2):
    if Atom1 < 0 or Atom2 < 0:
        return 0.
    return sqrt((geoArr[Atom1,0]-geoArr[Atom2,0])**2 +
    (geoArr[Atom1,1]-geoArr[Atom2,1])**2 + (geoArr[Atom1,2]-
    geoArr[Atom2,2])**2)

```

```

def angle(Atom1,Atom2,Atom3):
    ba = geoArr[Atom1,:]- geoArr[Atom2,:]
    bc = geoArr[Atom3,:]- geoArr[Atom2,:]
    cosine_angle = np.dot(ba, bc) / (np.linalg.norm(ba) *
    np.linalg.norm(bc))
    angle = np.arccos(cosine_angle)
    return np.degrees(angle)

```

```

def dihedral(Atom1,Atom2,Atom3,Atom4):
    p0 = geoArr[Atom1,:]
    p1 = geoArr[Atom2,:]
    p2 = geoArr[Atom3,:]
    p3 = geoArr[Atom4,:]
    b0 = -1.0*(p1 - p0)
    b1 = p2 - p1
    b2 = p3 - p2
    b1 /= np.linalg.norm(b1)
    v = b0 - np.dot(b0, b1)*b1
    w = b2 - np.dot(b2, b1)*b1
    x = np.dot(v, w)
    y = np.dot(np.cross(b1, v), w)
    return np.degrees(np.arctan2(y, x))

```

```

arglist = []
for arg in sys.argv[1:]:
    arglist.append(arg)
assert len(arglist) > 0, "You need to specify an input file"
atSym = []; lengthlist = []; anglelist = []; dihedrallist = []; atcon_1 =
[]; atcon_a = []; atcon_d = []

```

```

lengthlist = [0.]
anglelist = [0., 0.]
dihedrallist = [0., 0., 0.]
atcon_1 = [-1]
atcon_a = [-1, -1]
atcon_d = [-1, -1, -1]
atom_x = []
atom_y = []
atom_z = []
distance_adjustment = {'H': 0.5, 'O': 0.3}

```

```

with open(arglist[0], 'r') as f:
    for line in f:
        if len(line) > 5:
            words = line.split()
            assert len(words[3]) > 0, "Problem with input file format. It
            should be ElementSymbol number number number"
            atSym.append(words[0])
            atom_x.append(float(words[1]))
            atom_y.append(float(words[2]))
            atom_z.append(float(words[3]))

```

```

numAtoms = int(len(atSym))
geoArr = np.array(list(zip(atom_x,atom_y,atom_z)))

#internally leaving the numbering starting at zero, but will add one
for all output
# the atcons and length for the first atom are assigned in the
initialization
for i in range(1,numAtoms):
    shortest_distance = 100
    closest_atom = 0
    for j in range(0,i):
        if (distance(i,j) + distance_adjustment.get(atSym[j], 0.0)) <
shortest_distance:
            shortest_distance = distance(i,j)
            closest_atom = j
    lengthlist.append(shortest_distance)
    atcon_l.append(closest_atom)

for i in range(2,numAtoms):
    shortest_distance = 100
    closest_atom = 0
    for j in range(0,i):
        consistency_pref = 0
        if j != atcon_l[i]:
            if j == atcon_l[atcon_l[i]]:
                consistency_pref = 1
            if (distance(j,atcon_l[i]) + distance_adjustment.get(atSym[j],
0.0) - consistency_pref) < shortest_distance:
                shortest_distance = distance(j,atcon_l[i]) +
distance_adjustment.get(atSym[j], 0.0) - consistency_pref
                closest_atom = j
        if atcon_l[atcon_l[i]] > 1:
            if atcon_l[atcon_l[i]] != i:
                closest_atom = atcon_l[atcon_l[i]]
# print("default angle atom",i+1,atcon_l[i]+1,closest_atom+1)
atcon_a.append(closest_atom)
anglelist.append(angle(i,atcon_l[i],atcon_a[i]))

for i in range(3,numAtoms):
    shortest_distance = 100
    closest_atom = 0
    for j in range(0,i):
        consistency_pref = 0
        if j != atcon_l[i] and j != atcon_a[i]:
            if j == atcon_l[atcon_a[i]]:
                consistency_pref = 1
            if (distance(j,atcon_a[i]) + distance_adjustment.get(atSym[j],
0.0) - consistency_pref) < shortest_distance:
                shortest_distance = distance(j,atcon_a[i]) +
distance_adjustment.get(atSym[j], 0.0) - consistency_pref
                closest_atom = j
        if atcon_l[atcon_a[i]] > 0:
            if atcon_l[atcon_a[i]] != i:
                if atcon_l[atcon_a[i]] != atcon_l[i]:
                    closest_atom = atcon_l[atcon_a[i]]
# print("default dihedral
atom",i+1,atcon_l[i]+1,atcon_a[i]+1,closest_atom+1)
atcon_d.append(closest_atom)
dihedrallist.append(dihedral(i,atcon_l[i],atcon_a[i],atcon_d[i]))

for i in range(0,numAtoms):
    print(atSym[i],"% 12.9f" % lengthlist[i], "% 10.7f" %
anglelist[i], "% 10.7f" % dihedrallist[i], "% 4s" % str(atcon_l[i] +
1), "% 4s" % str(atcon_a[i] + 1), "% 4s" % str(atcon_d[i] + 1))

```

## proganal

```

BEGIN {
nmrset=0
blankLineTester=10
while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="NMRtype") nmrtype=$2
    if ($1=="title") {
        title1=$2
        title2=$3
        title3=$4
        title4=$5
    }
    blankLineTester=length($0)
}

firsttitle=1
getline < "isomernumber"
isomer=$1
}
/transCyhex/ {
if (firsttitle==1) {
    titlestring=$1 " $2" " $3" " $4" " $6" " $7" " $8
    printf("%s %s %s %s %s %s %s %s ",$1,$2,$3,$4,$6,$7,$8)
    runpoint=$6
}
firsttitle++
}
/Standard orientation/,/Rotational constants/ {
if (($1>.5) && ($1<.99)) {
    A[$1]=$4;B[$1]=$5;C[$1]=$6
}
}
END {
    CB=Distance(6,17)
    CCold=Distance(8,6)
    CCnew=Distance(8,5)
    difference=((CCold-CCnew)^2)^0.5
    CET=Distance(6,19)
    if (Distance(6,18)<CET) CET=Distance(6,18)
    if (Distance(6,20)<CET) CET=Distance(6,20)
    DihInv=Dihedral(18,17,6,5)
    DihRet=Dihedral(20,17,6,5)
    DihAnti=Dihedral(18,17,6,8)
    printf("%s %.2f %s %.3f %s %.3f %s %.3f %s %.1f %s %.1f
", "CB",CB,"CCold",CCold,"CCnew",CCnew,"CET",CET,"DihInv",
DihInv,"DihRet",DihRet)
    if (difference<0.02) printf("%s %.1f ", "DihAnti",DihAnti)
    if ((CCnew<1.6) && (CET>2.3)) printf("%s ", "Str14")
    if ((CET<2.3) && (CET>1.7)) printf("%s ", "LastMigration")
    if (runpoint>500) {
        print "Too many points. XXXXX"
    }
    if (CET<1.7) {
        if (Distance(6,18)<1.7) print "C18 C18 C18 XXXX"
        if (Distance(6,20)<1.7) print "C20 C20 C20 XXXX"
        if (Distance(6,19)<1.7) print "C19 C19 C19 XXXX"
    }
    if ((CCold<1.6) && (CCnew>2.25)) {
        print "INT INT INT XXXX"
    }
    system("date +%b:%d:%Y %T")
    system("tail -1 Echeck | grep XXXX")
}

function Distance(Atom1,Atom2) {
    return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2
+ (C[Atom1]-C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {

```



```

value=(-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(
Atom2,Atom3)^2)/(2*Distance(Atom1,Atom2)*Distance(Atom2,
Atom3))
return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
B1x=A[Atom2]-A[Atom1]
B1y=B[Atom2]-B[Atom1]
B1z=C[Atom2]-C[Atom1]
B2x=A[Atom3]-A[Atom2]
B2y=B[Atom3]-B[Atom2]
B2z=C[Atom3]-C[Atom2]
B3x=A[Atom4]-A[Atom3]
B3y=B[Atom4]-B[Atom3]
B3z=C[Atom4]-C[Atom3]
modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
yAx=modB2*(B1x)
yAy=modB2*(B1y)
yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
CP2x=(B2y*B3z)-(B2z*B3y)
CP2y=(B2z*B3x)-(B2x*B3z)
CP2z=(B2x*B3y)-(B2y*B3x)
termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
CPx=(B1y*B2z)-(B1z*B2y)
CPy=(B1z*B2x)-(B1x*B2z)
CPz=(B1x*B2y)-(B1y*B2x)
termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
dihed4=(180/3.141592)*atan2(termY,termX)
return dihed4
}

function killdyn(isomer) {
system("rm -f dyn")
}

```

## progdyn.conf

```

#This is the configuration file for PROGDYN. This file is read by
progdynstarterHP and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and
progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely
to be what you want.
#Do not delete lines - rather, comment out lines for unwanted
options.
#The values here are read repeatedly and most can be changed in
the middle of running jobs
***The keywords are case sensitive. The following keywords
should always be defined:***
***method, charge, multiplicity, memory, processors, title

```

```

*** method --The following word is copied exactly to the
gaussian input file.
method M11/6-31+G**
#To do a nonstandard route, make nonstandard 1. For normal
calcs, use nonstandard 0 or else leave it out.
#Then make a file called "nonstandard" containing the nonstandard
route with no extra lines.
nonstandard 0
# NMRoptions As is NMRtype=1 will add a section for an NMR
calc at every NMRevery intervals. If you want to combine the two
use nonstandard
#NMRtype 1
#NMRmethod2 B97D/6-31G*
#NMRmethod LC-wPBE/6-31G*
#NMRmethod3 B3LYP/cc-pvtz
#NMRevery 4
#NMRrand 1
#NMRcc 1
#loadlimit 10.0
#geometry linear
rotationmode 1
*** method2 --The options here are restricted, unrestricted, and
read. restricted is the default
#If the method is U..., put unrestricted here and the .com files will
have in them guess=mix.
#If you put read here, the .com files will contain guess=tcheck,
which sometimes makes things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file
name using the keyword checkpoint.
method2 read
charge 0
multiplicity 1
#onionchargemult 1 1
processors 4
*** memory --The following "word" is copied exactly to the
gaussian input file after %mem=.
memory 6gb
*** killcheck and checkpoint -- You can use a specifically
defined checkpoint file name by putting
#the name after the keyword checkpoint. This is necessary if you
use the read option with method2.
#Defined checkpoint names are an unnecessary modest hassle and
if you do not want to bother, use killcheck 1
killcheck 0
checkpoint g16.chk
*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out
extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file
"vellist"
#4 adds the apparent temperature to vellist, but this is meaningless
with quasiclassical calculations
diagnostics 0
*** title -- the title keyword must be followed by exactly four
words
title transCyhexD2 BEt3 M11PS 298dis2
*** initialdis -- 0 (default) turns off displacement of the normal
modes, so that all trajectories start from the same place
# and only the energies and signs of the motion in the modes are
randomized
# 1 gives a flat distribution of displacements where all of the
possible values are equally likely
# 2 (recommended) gives a QM-like gaussian distribution of
displacements, so that displacements in the middle are more likely
that
# those at the end by 1/e
initialdis 2
*** timestep -- this is the time between points in the trajectory.
Typical values would be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
*** scaling -- this lets you scale the gaussian frequencies by a

```

```

constant
scaling 1.0
temperature 298.15
**** thermostat 1 puts in a damping factor so as to bring the
classical temperature toward the desired temperature.
**** use a thermostatmult between 0.95 and 1, typically 0.995, so
the damping happens slowly - otherwise there will be
**** overadjustment in response to random variation
**** the thermostat is not exact. The second traj point ignores
this, so it only applies to later points handled by progdynb.
#thermostat 1
#thermostatmult 0.999
**** method3, method4, method5, and method6 -- These
keywords let you add extra lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the
lines defining the method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank
line of course
#only a single term with no spaces can be added, one per method
line. Here are some examples to uncomment if needed
#method3 empiricaldispersion=gd3
#method3 IOp(3/76=0572004280)
#method3 scrf=(pcm,solvent=ethanol)
#method3 scrf=(solvent=chloroform)
#add the line below with big structures to get it to put out the
distance matrix and the input orientation
#method4 empiricaldispersion=gd3
#method3 scf=(conver=5)
method4 int(finegrid)
#method4 iop(3/124=3)
#method4 scrf=(pcm,solvent=dms0,read)
#method5 radii=bondi
#method6
**** methodfile -- This keyword lets you add more complicated
endings to gaussian input files
#such as a gen basis set. Put after the keyword the number of lines
in a file you create called
#methodfile that contains the test you want to add to the end of the
gaussian input
methodfile 0
**** numimag --This tells the program the number of imaginary
frequencies in the starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the
direction defined by searchdir
#if 2, only lowest freq will go direction of searchdir and other imag
mode will go in random direction
numimag 1
**** searchdir -- This keyword says what direction to follow the
mode associated with the imaginary frequency.
#The choices are "negative" and "positive". Positive moves in the
direction defined in the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the
opposite direction. The correct choice can be made either
#by a careful inspection of the normal modes and standard
orientation geometry, or by trial and error.
searchdir positive
**** classical -- for quassical dynamics, the default, use 0.
for classical dynamics, use 1
#if there are no normal modes and the velocities are to be
generated from scratch, use classical 2
classical 0
**** DRP, saddlepoint, and maxAtomMove --to run a DRP use
'DRP 1' in the line below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so
use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no

```

```

#maxAtomMove 0.01
**** cannonball -- The program can "fire" a trajectory from a
starting position toward a particular target, such as toward
#a ts. To use this, make a file cannontraj with numAtom lines and
three numbers per line that defines the vector
#for firing the trajectory, relative to the starting geometry's
standard orientation. The number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
**** keepevery --This tells the program how often to write the
gaussian output file to file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to
save on disk space or molden loading time.
keepevery 9999
**** highlevel --For ONIOM jobs, the following line states the
number of highlevel atoms,
#which must come before the medium level atoms. Use some high
value such as 999 if not using ONIOM
highlevel 9999
**** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These
fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up,
while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three
distances, not just two
#in current form fixed atoms only are meant to work with no
displacements, that is, initialdis=0
#fixedatom1 16
#fixedatom2 1
#fixedatom3 4
#fixedatom4 20
#applyforce 1 lets one push atoms together or appart - a positive
force pushes them together
#format is applyforce force - with the units on force the same as
in the Gaussian output file
#applyforce 2 or 3 or 4 applies a polynomial force centered at
dist0. 2 is just harmonic, 3 is second order, 4 is third order
#format is applyforce 4 forcecoefficient dist0 forcecoefficient2
forcecoefficient3
#then use afatoms to chose the atoms with format afatoms
firstatom secondatom [additional atoms]
#applyforce 2 0.1 2.1
#afatoms 16 1 2 3 4 5 6
#applyforceB 2 0.01 5.2
#afatomsB 8 15
#applyforceC 2 0.01 5.2
#afatomsC 8 15
#zeroatom pushes the numbered atom toward the origin with a
small harmonic potential - good with boxon when you want to
keep the reaction in the center
#zeroatom 16
**** boxon and boxsize - With boxon 1, a cubic box is set such
that atoms that reach the edge
#are reflected back toward the middle. Useful for dynamics with
solvent molecules. This is a crude
#implementation that is ok for a few thousand femtoseconds but
will not conserve energy long term.
#Set the box size so as to fit the entire initial molecule but not have
too much extra room.
#The dimensions of the box are two times the boxsize, e.g. boxsize
7.5 leads to a box that is 15 x 15 x 15 angstroms
#boxon 1
#boxsize 11.2
**** sphereon and spheresize and sphereforce - uses a force to
push atoms within a sphere. notice that if the atom is far outside of
#the sphere then the force is large unless sphereforce is set small
#sphereon 1
#spheresize 12.9
#sphereforce .01
#setting a value for empiricaldispersion sets its s6 value with the

```



```

    printf("  %s ", "sixth")
  }
  if ((runpoint-Str14begin)==150) {
    printf("%s %.1f %s %.1f ", "CCC  ", "CCC", "  ", "CCCop")
    printf("  %s ", "seventh")
  }
  if ((runpoint-Str14begin)==175) {
    printf("%s %.1f %s %.1f ", "CCC  ", "CCC", "  ", "CCCop")
    printf("  %s ", "eighth")
  }
  if ((runpoint-Str14begin)==200) {
    printf("%s %.1f %s %.1f ", "CCC  ", "CCC", "  ", "CCCop")
    printf("  %s ", "ninth")
  }
}
if ((CCnew<1.6) && (CEt>2.3)) {
  if (DihInv + DihRet > 0) invangleless=0
  if (intermediateyet==0) {
    printf("%s %.1f %s %.1f ", "CCC  ", "CCC", "  ", "CCCop")
    printf("  %s ", "first")
    Str14begin=runpoint
    intlinecount=0
    CCreboundmax50=0
    CCreboundmax100=0
    CCreboundmax150=0
  }
  printf("%s ", "  Str14")
  intermediateyet=1
}
if ((intermediateyet==1) && (DihInv + DihRet > 0))
invangleless=0
if ((CEt<2.3) && (CEt>1.7)) {
  printf("%s ", "LastMigration")
  finalyet=1
  if (intermediateyet==0) printf("%s ", "ConcertedMaybe")
}
if ((intermediateyet==1) && (finalyet==0)) {
  intlinecount++
  count14[intlinecount]++
  CCCtot[intlinecount]=CCCtot[intlinecount]+CCC
  CCCoptot[intlinecount]=CCCoptot[intlinecount]+CCCop
}
velsqCCnewtot[intlinecount]=velsqCCnewtot[intlinecount]+(CCnew-oldCCnew)^2
velsqCC23tot[intlinecount]=velsqCC23tot[intlinecount]+(CC23-oldCC23)^2
  CCnewtot[intlinecount]=CCnewtot[intlinecount]+CCnew
  CC23tot[intlinecount]=CC23tot[intlinecount]+CC23
  if ((intlinecount<51) && (CCreboundmax50<CCnew))
  CCreboundmax50=CCnew
  if ((intlinecount<101) && (intlinecount>50) &&
(CCreboundmax100<CCnew)) CCreboundmax100=CCnew
  if ((intlinecount<151) && (intlinecount>100) &&
(CCreboundmax150<CCnew)) CCreboundmax150=CCnew
}
if (runpoint>500) {
  print "Too many points. XXXXXN"
  printon=0
}
if (CEt<1.7) {
  printf("%s %i ", "InvAngleLess", invangleless)
  if (intermediateyet==0) printf("%s ", "first")
  if (Distance(6,18)<1.7) print "C18 C18 C18 XXXX"
  if (Distance(6,20)<1.7) print "C20 C20 C20 XXXX"
  if (Distance(6,19)<1.7) print "C19 C19 C19 XXXX"
  printon=0
  intermediateyet=0
  if ((Distance(6,20)<1.7) && (intlinecount>50) &&
(CCreboundmax50>0)) print

```

```

intlinecount, "\t", CCreboundmax50, "\t", CCreboundmax100, "\t", CC
reboundmax150 > "C20reboundlist"
  if ((intlinecount>50) && (CCreboundmax50>0)) print
intlinecount, "\t", CCreboundmax50, "\t", CCreboundmax100, "\t", CC
reboundmax150 > "C20reboundlist"
  CCreboundmax50=0; CCreboundmax100=0;
  CCreboundmax150=0;
}
  if ((CCold<1.6) && (CCnew>2.25)) {
    print "INT INT INT XXXX"
    printon=0
    intermediateyet=0
  }
  print ""
}
}
linenumber++
if (linenumber>0.5) {
  A[linenumber]=$2; B[linenumber]=$3; C[linenumber]=$4
}
}
END {
  CB=Distance(6,17)
  CCold=Distance(8,6)
  CCnew=Distance(8,5)
  difference=((CCold-CCnew)^2)^0.5
  CEt=Distance(6,18)
# if (Distance(6,19)<CEt) CEt=Distance(6,19)
# if (Distance(6,20)<CEt) CEt=Distance(6,20)
  CE20=Distance(6,20)
  CCC=Angle(8,5,6)
  DihInv=Dihedral(18,17,6,5)
  DihRet=Dihedral(20,17,6,5)
  Dih19=Dihedral(19,17,6,5)
  DihAnti=Dihedral(18,17,6,8)
  if (printon==1) {
    printf("%s %.2f %s %.3f %s %.3f %s %.3f %s %.1f %s %.1f
", "CB", "CB", "CCold", "CCold", "CCnew", "CCnew", "CEt", "CEt", "DihInv",
DihInv, "DihRet", "DihRet)
    printf("%s %.1f ", "Dih19", "Dih19)
    printf("%s %.3f ", "CE20", "CE20)
    if (difference<0.01) printf("%s %.1f ", "DihAnti", "DihAnti)
  if ((CCnew<1.6) && (CEt>2.3)) {
    printf("%s ", "  Str14")
    if (DihInv + DihRet > 0) invangleless=0
    if (intermediateyet==0) {
      printf("%s %.1f ", "CCC  ", "CCC)
      printf("%s ", "first")
    }
    intermediateyet=1
  }
  if ((intermediateyet==1) && (DihInv + DihRet > 0))
invangleless=0
  if ((CEt<2.3) && (CEt>1.7)) {
    printf("%s ", "LastMigration")
    if (intermediateyet==0) printf("%s ", "ConcertedMaybe")
  }
  if (runpoint>500) {
    print "Too many points. XXXXXN"
    printon=0
  }
  if (CEt<1.7) {
    printf("%s %i ", "InvAngleLess", invangleless)
    if (intermediateyet==0) printf("%s ", "first")
    if (Distance(6,18)<1.7) print "C18 C18 C18 XXXX"
    if (Distance(6,20)<1.7) print "C20 C20 C20 XXXX"
    if (Distance(6,19)<1.7) print "C19 C19 C19 XXXX"
    printon=0
    intermediateyet=0
  }
}

```

```

    }
    if((CCold<1.6) && (CCnew>2.25)) {
        print "INT INT INT XXXX"
        printon=0
        intermediateyet=0
    }
    print ""
}
for (i=1;i<=250;i++) {
    print
    i,"t",count14[i],"t",CCCtot[i]/count14[i],"t",CCCopptot[i]/count
14[i],"t",velsqCCnewtot[i]/count14[i],"t",velsqCC23tot[i]/count1
4[i] > "CCclist"
    print
    i,"t",count14[i],"t",CCnewtot[i]/count14[i],"t",CC23tot[i]/count1
4[i] > "CClist"
}
}

function Distance(Atom1,Atom2) {
    return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2
+ (C[Atom1]-C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
    value=0
    if (Distance(Atom2,Atom3)>0) {
        value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(
Atom2,Atom3)^2)/(2*Distance(Atom1,Atom2)*Distance(Atom2,
Atom3)))
    }
    return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
    B1x=A[Atom2]-A[Atom1]
    B1y=B[Atom2]-B[Atom1]
    B1z=C[Atom2]-C[Atom1]
    B2x=A[Atom3]-A[Atom2]
    B2y=B[Atom3]-B[Atom2]
    B2z=C[Atom3]-C[Atom2]
    B3x=A[Atom4]-A[Atom3]
    B3y=B[Atom4]-B[Atom3]
    B3z=C[Atom4]-C[Atom3]
    modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
    yAx=modB2*(B1x)
    yAy=modB2*(B1y)
    yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
    CP2x=(B2y*B3z)-(B2z*B3y)
    CP2y=(B2z*B3x)-(B2x*B3z)
    CP2z=(B2x*B3y)-(B2y*B3x)
    termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
    CPx=(B1y*B2z)-(B1z*B2y)
    CPy=(B1z*B2x)-(B1x*B2z)
    CPz=(B1x*B2y)-(B1y*B2x)
    termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
    dihed4=(180/3.141592)*atan2(termY,termX)
    return dihed4
}

```

```

function killdyn(isomer) {
    system("rm -f dyn")
}

```

## progcount

```

grep XXX n2?/?/dynfollowfile > temp589
echo "collected XXX from corrected dynfollowfiles into temp589.
Here is the line count:"
wc temp589
date
echo ""

# Organize the results including director and isomernumber and
time for each direction. The directory and isomernumber will be
used
# to associate the results with a particular geoPlusVel
awk 'BEGIN {
    dirstart=1
    dirend=9999
    }
{
    dirnum=substr($1,2,3)
    if (dirnum!=olddirnum) isomernumber=""
    direction=1
    if ((dirnum==olddirnum) && ($7==oldisomernumber))
    direction=2
    if ($7>0) {
        isomernumber=$7
        maxres[dirnum]=isomernumber
        result[dirnum,isomernumber,direction]=$20
        time[dirnum,isomernumber,direction]=$5
    }
    olddirnum=dirnum;oldisomernumber=isomernumber
# print dirnum,oldisomernumber
}
END {
    for (d=dirstart;d<=dirend;d++) {
        for (i=1;i<=maxres[d];i++) {
            if (time[d,i,2]>0) print
d,i,time[d,i,2],time[d,i,1],result[d,i,2],result[d,i,1]
        }
    }
}' temp589 > temp590
echo "summarized the results in temp590. Line count:"
wc temp590
date
echo ""

# Count all of the results and output the count
awk 'BEGIN {
    Invnum=0;Recross=0;totalresults=0;Toomany=0;intrecross=0
    InvT50=0;InvT100=0;InvT150=0;InvT200=0;InvT250=0;InvT300
=0;InvT350=0;InvT400=0;InvT450=0;InvTG=0
    Ret50=0;Ret100=0;Ret150=0;Ret200=0;Ret250=0;Ret300=0;Ret3
50=0;Ret400=0;Ret450=0;RetG=0
    invtime=0
    rettime=0
}
{
    totalresults++
    if (($5=="INT") && ($6=="C18")) {
        Invnum++
        invtime=invtime + $4
        invtimelist[totalresults]=$4
        if ($4<=50) InvT50++
        else if ($4<=100) InvT100++
        else if ($4<=150) InvT150++
    }
}

```

```

else if ($4<=200) InvT200++
else if ($4<=250) InvT250++
else if ($4<=300) InvT300++
else if ($4<=350) InvT350++
else if ($4<=400) InvT400++
else if ($4<=450) InvT450++
else InvTG++
}
if (($5=="INT") && ($6=="C20")) {
  Recross++
  revtime = revtime + $4
  revtimelist[totalresults]=$4
  if ($4<=50) Ret50++
  else if ($4<=100) Ret100++
  else if ($4<=150) Ret150++
  else if ($4<=200) Ret200++
  else if ($4<=250) Ret250++
  else if ($4<=300) Ret300++
  else if ($4<=350) Ret350++
  else if ($4<=400) Ret400++
  else if ($4<=450) Ret450++
  else RetG++
}
if (($5=="Too") && ($6=="C18")) Toomany++
if (($5=="Too") && ($6=="INT")) Toomany++
if (($6=="Too") && ($5=="C18")) Toomany++
if (($6=="Too") && ($5=="INT")) Toomany++
if (($5=="INT") && ($6=="INT")) intrecross++
if (($5=="C18") && ($6=="C18")) prodrecross++
if (($5=="C18") && ($6=="C20")) prodrecross++
if (($5=="C20") && ($6=="C18")) prodrecross++
if (($5=="Too") && ($6=="Too")) Toomany++
if (($5=="C18") && ($6=="INT")) InvnumBackwards++
}
END {
print "Total results",totalresults
print "Results unaccounted for",totalresults-Invnum-Recross-
Toomany-intrecross-InvnumBackwards-prodrecross
print ""
totalresults = totalresults - intrecross - InvnumBackwards -
prodrecross
print "Productive results",totalresults
}
print "Forms inversion product",Invnum," Percent",
(int(10000*Invnum/totalresults))/100
print " average time",invtime/Invnum
print "Forms retention product",Recross," Percent",
(int(10000*Recross/totalresults))/100
print " average time",revtime/Recross
percentinv = (int(10000*Invnum/(Invnum+Recross)))/100
print "Ratio of inversion to retention = ",percentinv," : ",100-
percentinv
print "Forms product but backwards",InvnumBackwards
print "Too many points one or both ways, all
possibilities",Toomany
print "Recrossing from intermediate to intermediate",intrecross
print "Recrossing from product to product",prodrecross
print "productive trajectories"
print "<50 51-100 101-150 151-200 201-250 251-300 301-350
351-400 401-450 >450"
print " ",InvT50," ",InvT100," ",InvT150," ",InvT200,"
",InvT250," ",InvT300," ",InvT350," ",InvT400,"
",InvT450," ",InvTG
print "Recrossing times"
print "<50 51-100 101-150 151-200 201-250 251-300 301-350
351-400 401-450 >450"
print " ",Ret50," ",Ret100," ",Ret150," ",Ret200,"
",Ret250," ",Ret300," ",Ret350," ",Ret400," ",Ret450,"
",RetG
print ""
print "list of inv times"
for (i=1;i<=totalresults;i++) {
  if (invtimelist[i]>1) print invtimelist[i]
}
print "list of ret times"
for (i=1;i<=totalresults;i++) {
  if ( revtimelist[i]>1) print revtimelist[i]
}
}' temp590
echo "done with counting. Check to make sure time list was in
correct direction."
date
echo

```

### GAUSSRATE / POLYRATE input files

```

p.dat
16 H
17 B
18 C
*General
19 C
20 C
TITLE
21 H
LARIONOV
22 H
END
23 H
24 H
ATOMS
25 H
1 C
26 H
2 C
27 H
3 H
28 H
4 H
29 H
5 C
END
6 C
7 H
NOSUPERMOL
8 C
9 H
WRITEFU31 ON
10 C
INPUNIT AU
11 H
*OPTIMIZATION
12 H
OPTMIN OHOOK
13 H
OPTTS OHOOK
14 H
15 H

```

*SECOND	13
	14
	15
HESSCAL HHOOK	16
	17
*REACT1	18
SPECIES NONLINRP	19
INITGEO HOOKS	20
GEOM	21
1	22
2	23
3	24
4	25
5	26
6	27
7	28
8	29
9	END
10	ELEC
11	1 0.0
12	END
13	
14	
15	
16	
END	*START
ELEC	SPECIES NONLINTS
1 0.0	INITGEO HOOKS
END	GEOM
	1
	2
	3
	4
*REACT2	5
SPECIES NONLINRP	6
INITGEO HOOKS	7
GEOM	8
17	9
18	10
19	11
20	12
21	13
22	14
23	15
24	16
25	17
26	18
27	19
28	20
29	21
END	22
ELEC	23
1 0.0	24
END	25
	26
	27
	28
	29
*PROD1	END
INITGEO HOOKS	ELEC
SPECIES NONLINRP	1 0.0
GEOM	END
1	
2	
3	
4	# end of start section
5	
6	*PATH
7	
8	SCALEMASS 1.00
9	
10	RODS ON
11	
12	INTMU 3

```

SSTEP 0.010
INH 10

SRANGE

  SLP 20.50
  SLM -0.50
END

RPM pagem

SIGN PRODUCT

IDIRECT 1

COORD CART

# INTDEF
# 5-6 18-19 5-6-1 9-12-18
# 2-1 3-2 4-3 5-4 6-1 7-3 8-7 9-8 10-9 11-7 12-9 13-4
# 14-5 15-6 16-1 17-2 18-11 19-8 20-8 3-2-1 4-3-2 5-4-3
# 6-1-2 7-3-2 8-7-3 9-8-7 10-9-8 11-7-3 12-9-8 13-4-3
# 14-5-4 15-6-1 16-1-2 17-2-1 18-11-7 19-8-7 20-8-7
# 4-3-2-1 5-4-3-2 6-1-2-3 7-3-2-1 8-7-3-2 9-8-7-3
# 10-9-8-7 11-7-3-2 12-9-8-7 13-4-3-2 14-5-4-3 15-6-1-2
# 16-1-2-3 17-2-1-6 18-11-7-3 19-8-7-3 20-8-7-3
# END

FREQSCALE 1.00

PRPATH
COORD 8 9
INTERVAL 1
XMOL
END

*TUNNEL

QUAD
NQE 40
NQTH 40
END

# LCT
# SCT

*RATE

FORWARDK
VPFEXP 350
SIGMAF 1
CVT
PRDELG ON
# PRGIGT ON

TEMP
10
20
30
40
50
60
70
80
90
100
120
140
160
180

```

```

200
220
240
260
273.15
298.15
323.15
350
400
END

```

## p.71

```

nproc=20
%mem=40gb
%chk=g09.chk
#p M11/6-31+G** opt fchk NOSYMM
scf=tight int(grid=ultrafine)

trans-cyclohexene

0 1
C,0,-1.5720283101,-0.089332252,0.0482600216
C,0,-0.6814186321,1.2056074341,-0.1902628084
H,0,-1.7764048237,-0.2065426809,1.122529418
H,0,-2.5228525962,-0.0072443179,-0.4970660727
C,0,-0.5838766884,-1.1031437441,-0.4536013527
C,0,0.4886954536,-1.1902100643,0.3600739437
H,0,-0.3782471743,-1.0150516463,-1.5296328406
C,0,1.559735429,-0.2160776289,-0.0392159068
H,0,0.2867196402,-1.1972845018,1.4403201511
C,0,0.7789375845,1.117185198,0.33500982
H,0,2.5116659962,-0.2697583938,0.507721166
H,0,1.758312606,-0.2389946517,-1.1206958322
H,0,1.3425071002,1.9885442624,-0.0319569722
H,0,0.7657657698,1.192021444,1.4340880053
H,0,-0.6576409226,1.3918921433,-1.275786337
H,0,-1.1718704322,2.0783893999,0.2672155968

```

## p.72

```

%nproc=20
%mem=40gb
%chk=g09.chk
#p M11/6-31+G** opt fchk NOSYMM
scf=tight int(grid=ultrafine)

```

trimethylborane

```

0 1
B,0,0.00082,0.00057,-0.00113
C,0,1.57463,-0.11881,-0.01929
C,0,-0.68591,1.42154,-0.00406
C,0,-0.89121,-1.30175,0.02789
H,0,1.89847,-0.57988,0.92984
H,0,1.91035,-0.81413,-0.80425
H,0,2.11219,0.83197,-0.13179
H,0,-1.42203,-1.33979,0.99458
H,0,-1.68644,-1.25031,-0.73238
H,0,-0.34375,-2.24551,-0.09499
H,0,-0.18908,2.119,0.68712
H,0,-0.54171,1.85765,-1.00845
H,0,-1.76453,1.41674,0.20201

```

## p.73

```

%nproc=20
%mem=40gb
%chk=g09.chk

```



```
#p M11/6-31+G** opt fchk NOSYMM
scf=tight int(grid=ultrafine)
```

reaction product

```
0 1
C,0,-1.0756472421,-0.3070242073,0.4860151466
C,0,-0.8646130919,1.0771405058,-0.1432376618
H,0,-0.9769028865,-0.2378930136,1.5816258485
H,0,-2.0587330969,-0.7465997932,0.2634540237
C,0,0.0921311193,-1.1242879149,-0.0848752918
C,0,0.3241144008,-2.533203908,0.5293072816
H,0,-0.0977835353,-1.2565265418,-1.1657054849
C,0,1.2772733858,-0.1444894152,0.0614157594
H,0,-0.5103907973,-3.1645350291,0.1724098736
C,0,0.6761715206,1.2672681662,-0.1653718822
H,0,1.6934023192,-0.2223261822,1.0785742703
H,0,2.0993689793,-0.3718134779,-0.6353498539
H,0,1.0078152887,1.6993699925,-1.118957372
H,0,1.0000137678,1.9601883914,0.622972533
H,0,-1.2596853304,1.0753471448,-1.1703081778
H,0,-1.3808502728,1.8795625255,0.4001932117
B,0,1.6581485844,-3.066680372,-0.1439640469
C,0,0.3096781872,-2.5300331206,2.0641344912
C,0,1.6714286432,-3.3791306022,-1.6927579433
C,0,2.982543011,-3.231456095,0.6978652857
H,0,-0.6919145359,-2.3214863766,2.4664546473
H,0,0.6280236823,-3.503256455,2.465186012
H,0,0.9943968772,-1.7738735546,2.4780189228
H,0,2.8948978584,-4.1728566883,1.2702295062
H,0,3.8964938988,-3.3059937037,0.0933480447
H,0,3.1094931844,-2.441025094,1.4527100746
H,0,2.2553488958,-4.2826040063,-1.9243677665
H,0,0.6791094557,-3.4654529148,-2.1568746981
H,0,2.2021312092,-2.5520490898,-2.1976864036
```

## p.75

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p M11/6-31+G** opt=(ts,calcfc,noeigentest) fchk NOSYMM
int(grid=ultrafine)
```

hexenebme3ts

```
0 1
C,0,-1.5653299515,-0.1070547645,0.0386957079
C,0,-0.6461177337,1.1808959703,-0.2186880258
H,0,-1.7683110788,-0.2003230916,1.1135706745
H,0,-2.4989584634,-0.0224540305,-0.531184831
C,0,-0.5644214114,-1.0797733433,-0.4378938407
C,0,0.5158681612,-1.3033739084,0.3676842979
H,0,-0.4061398333,-1.1208567382,-1.5255386969
C,0,1.5433262317,-0.2379734274,-0.0328390064
H,0,0.2994285651,-1.2610692355,1.4451211822
C,0,0.7874581987,1.0803765715,0.3500709142
H,0,2.4899339003,-0.3344319865,0.5160000004
H,0,1.7575431209,-0.2640303375,-1.1120856912
H,0,1.362087468,1.9572186557,0.0148876035
H,0,0.7393444196,1.1356553411,1.4491987699
H,0,-0.6004543734,1.3466974275,-1.3058856548
H,0,-1.1650901777,2.0476004915,0.2151482344
B,0,1.2799590421,-3.212743501,-0.0229948207
C,0,0.2146123973,-4.1280682726,0.7611171222
C,0,1.2871312336,-3.3074942942,-1.6285756055
C,0,2.7165739579,-3.0570673796,0.6838259971
H,0,0.5724072408,-5.1725518584,0.7426691052
H,0,0.1059078183,-3.8581186607,1.823930136
H,0,-0.7867313378,-4.1221647405,0.3031037805
```

```
H,0,3.1664532326,-4.0638328838,0.7426537108
H,0,3.4278620604,-2.4276280479,0.1264390722
H,0,2.6606006635,-2.6838649133,1.719753803
H,0,1.8745996047,-4.1962992376,-1.9164882212
H,0,0.2869574721,-3.4318419032,-2.0732668189
H,0,1.7804995721,-2.4524279013,-2.1214288985
```

## Calculations and Sample Input Files for Chapter IV

### *Dimerization of cyclopentadiene*

#### **finalkieprediction.py**

```
import numpy as np
import sys
import os
os.environ["CUDA_VISIBLE_DEVICES"]="-1"
import time
import h5py
from keras import layers, regularizers
from keras.layers import Input, Dense, Activation,
BatchNormalization, Flatten, Dropout
from keras.models import Sequential, load_model
from keras.metrics import categorical_crossentropy
from keras.optimizers import Adam, RMSprop
from keras.utils import layer_utils, to_categorical
import keras.backend as K
from keras.callbacks import ReduceLROnPlateau,
LearningRateScheduler, EarlyStopping
import warnings
warnings.filterwarnings("ignore")
os.environ["TF_CPP_MIN_LOG_LEVEL"] = '3'

def schedule(epochnum):
    lr = 0.002
    if epochnum > 40:
        lr = 0.0006
    if epochnum > 80:
        lr = 0.0002
    if epochnum > 350:
        lr = 0.0001
    if epochnum > 380:
        lr = 0.00004
    # print ("epoch",epochnum,"lr",lr)
    return lr

def confusion_matrix(ytrue, ypred):
    assert (ytrue.shape == ypred.shape), "Inputs to
confusion matrix have different dimensions"
    dim = ytrue.shape[1]
    outmat = np.zeros([dim,dim], dtype=int)
    for i in range(0,dim):
        for j in range(0,dim):
            outmat[i,j] = int(np.sum(ytrue[:,i] * ypred[:,j]))
    return outmat

#prepare the training and test arrays. Split into
validation is done automatically.
lambda=0.004
```

```
print("lambda original",lambda)
fullarray =
np.loadtxt("/scratch/user/vroytman/cpdim2019/temp
in500.csv",delimiter=",")
outside_test_array =
np.loadtxt("/scratch/user/vroytman/cpdim2019/bincp
dimer/million.csv",delimiter=",")
trimedarray = fullarray
Yset = trimedarray[:,128:132]
print(Yset)
Xset = Yset # temporary for appending, then will
delete first three columns
Youtside_test_array = outside_test_array[:,128:132]
#Sometimes this will be real, sometimes not if we
don't know answers, but something has to be there in
file.
Xoutside_test_array = Youtside_test_array #
temporary, silly, but makes for easy programming by
fitting with how Xset handled
IDset = trimedarray[:,132:135]
featurelist = [0, 1, 2, 3, 4, 5, 6, 7, 8, 12, 13, 18, 60,
61, 62, 64, 67]

print("featurelist original",featurelist)
if len(sys.argv) > 1 and sys.argv[1] == "add":
    for arg in sys.argv[2:]:
        featurelist.append(int(arg))
    print("featurelist after adding",featurelist)
if len(sys.argv) > 1 and sys.argv[1] == "remove":
    mylist = []
    for arg in sys.argv[2:]:
        mylist.append(int(arg))
    featurelist = [x for x in featurelist if x not in mylist]
    print("featurelist after removal",featurelist)
if len(sys.argv) > 1 and sys.argv[1] == "lambda":
    lambda = sys.argv[2]
    print("revised lambda",lambda)
for feature in featurelist:
    a = np.reshape(trimedarray[:,feature],(-1,1))
    Xset = np.concatenate((Xset,a), axis=1)
    b = np.reshape(outside_test_array[:,feature],(-1,1))
    Xoutside_test_array =
np.concatenate((Xoutside_test_array,b), axis=1)
#remove Y values from Xset and normalize
Xset = Xset[:,4::]
print("Xset",Xset)
xmean = Xset.mean(axis=0)
Xset = Xset - xmean
```

```

xstd = Xset.std(axis=0)
Xset = Xset / xstd
np.savetxt('normoff',[xstd,xmean])
#remove Y values from Xoutside_test_array and set
to same scale as Xset
Xoutside_test_array = Xoutside_test_array[:,4::]
Xoutside_test_array = Xoutside_test_array - xmean
Xoutside_test_array = Xoutside_test_array / xstd
print("full X shape",Xset.shape,"full Y
shape",Yset.shape)
print("outside test shape",Xoutside_test_array.shape)
class_weight = {0:1, 1:1, 2:2, 3:1.5}
print("class_weight",class_weight)
tic = time.time()
for ind in range(0,1):
    m = Yset.shape[0]
    i = int(0.95*m)
    Xtest=Xset[i:m,:]
    Ytest=Yset[i:m,:]
    IDtest=IDset[i:m,:]
    Xset=Xset[1:i,:]
    Yset=Yset[1:i,:]
    IDset=IDset[1:i,:]
    costlist=[]
    XSAlist=[]
    valcostlist=[]
    valXSAlist=[]
    for seed in range(100):
        np.random.seed()
        m = Yset.shape[0]
        print(m)
        permutation = list(np.random.permutation(m))
        X_train = Xset[permutation, :]
        Y_train = Yset[permutation, :]
        print ("number of training examples = " +
str(X_train.shape[0]))
        print ("X_train shape: " + str(X_train.shape))
        print ("Y_train shape: " + str(Y_train.shape))
        print ("Xtest shape: " + str(Xtest.shape))
        print ("Ytest shape: " + str(Ytest.shape))

        model = Sequential([
            Dense(300, input_shape=(Xtest.shape[1]),
activation='relu',
kernel_regularizer=regularizers.l2(lambd)),
            Dense(4, activation='softmax'),
        ])
        reduce_lr = LearningRateScheduler(schedule)
        early_stop =
EarlyStopping(monitor='val_loss',min_delta=0,
patience=80, verbose=1)
        model.summary()
        model.compile(RMSprop(lr=0.002, rho=0.99),
loss='categorical_crossentropy', metrics=['accuracy'])
        losshist = model.fit(X_train, Y_train,
validation_split=0.02, batch_size=512, epochs=400,

```

```

class_weight=class_weight, shuffle=True,
callbacks=[reduce_lr, early_stop], verbose=0)
        if seed == 0:
            model.save('cpdimer.h5')
            val_loss = round(losshist.history.get('val_loss')[-
1],5)
            val_acc = round(losshist.history.get('val_acc')[-
1],5)
            valcostlist.append(losshist.history.get('val_loss')[-
1])

valXSAlist.append(losshist.history.get('val_acc')[-1])
        print("loss = ", round(losshist.history.get('loss')[-
1],4),
            "acc = ", round(losshist.history.get('acc')[-1],4),
            "val_loss = ", val_loss,
            "val_acc = ", val_acc)
        loss_and_metrics = model.evaluate(Xtest, Ytest,
batch_size=16, verbose=0)
        XSA = int(100000*loss_and_metrics[1])/1000
        print(loss_and_metrics)
        cost = int(100000*loss_and_metrics[0])/100000
        print("")
        print("loss for test set ", cost, " accuracy for
test set: ", XSA,"%")
        costlist.append(cost)
        XSAlist.append(XSA)
        print("running", seed, " ",
round(np.mean(XSAlist),4),"% layers
",str(sys.argv[1:]))
        print("valRunning", seed, "
",100*round(np.mean(valXSAlist),4),"%
cost",round(np.mean(valcostlist),4),"% arguments
",str(sys.argv[1:]))
        rounded_predictions =
to_categorical(model.predict_classes(Xtest,
batch_size=16, verbose=1), num_classes=4)
        print(" ")
        print("shape of rounded
predictions",rounded_predictions.shape,"shape of
Ytest", Ytest.shape)
        print("predictions by
category:",int(np.sum(rounded_predictions[:,0])),
int(np.sum(rounded_predictions[:,1])),int(np.sum(rounded_predictions[:,2])),int(np.sum(rounded_predictions[:,3]))))
        print("test
percentage",round(100*np.sum(rounded_predictions[:,0])/Ytest.shape[0],2),
round(100*np.sum(rounded_predictions[:,1])/Ytest.s
hape[0],2),
round(100*np.sum(rounded_predictions[:,2])/Ytest.s
hape[0],2),

```

```

round(100*np.sum(rounded_predictions[:,3])/Ytest.shape[0],2)
    total_correct = int(np.sum(Ytest *
rounded_predictions))
    print("total in test set",Ytest.shape[0],"Total
correct",total_correct," Percent
",round(100*total_correct/Ytest.shape[0],2))
    if seed == 0: #print out the errors ID info for
seed==0
        print(" identifiers      Y actual  Y
predicted")
        for index in range(Ytest.shape[0]):
            if np.sum(Ytest[index, :] *
rounded_predictions[index, :]) == 0:
                print(IDtest[index, :],Ytest[index,
:],rounded_predictions[index, :])
#            print(Ytest[index, :] *
rounded_predictions[index, :])
            cm =
confusion_matrix(Ytest,rounded_predictions)
            print("confusion matrix")
            print(" A   B   Rec ProdRec")
            print(cm)
            print(" ")
            print("predictions for outside test array")
            outside_rounded_predictions =
to_categorical(model.predict_classes(Xoutside_test_a
rray, batch_size=16, verbose=1))
            print(" ")
            print("shape of outside rounded
predictions",outside_rounded_predictions.shape,"sha
pe of
Youtside_test_array",Youtside_test_array.shape)
            print("outside predictions by
category:",int(np.sum(outside_rounded_predictions[:,
0])),
int(np.sum(outside_rounded_predictions[:,1])),int(np.
sum(outside_rounded_predictions[:,2])),int(np.sum(o
utside_rounded_predictions[:,3])))
            print("outside
percentage",round(100*np.sum(outside_rounded_pre
dictions[:,0])/Youtside_test_array.shape[0],2),
round(100*np.sum(outside_rounded_predictions[:,1])
/Youtside_test_array.shape[0],2),
round(100*np.sum(outside_rounded_predictions[:,2])
/Youtside_test_array.shape[0],2),
round(100*np.sum(outside_rounded_predictions[:,3])
/Youtside_test_array.shape[0],2))
            outside_total_correct =
int(np.sum(Youtside_test_array *
outside_rounded_predictions))

```

```

    print ("total in outside
set",Youtside_test_array.shape[0],"Total
correct",outside_total_correct," percent correct",
100*outside_total_correct/Youtside_test_array.shape
[0])
    cm =
confusion_matrix(Youtside_test_array,outside_roun
ed_predictions)
    print("confusion matrix for outside test")
    print(" A   B   Rec ProdRec")
    print(cm)
    K.clear_session()
    toc = time.time()
    print("")
    print("time so far",round(toc-tic,2))
    print("-----")
    print("-----",str(seed) * 10)
    print(" ")
    print(" ")
    print("Test Ave Acc
",round(np.mean(XSAlist),2),"% Test Ave cost
",round(np.mean(costlist),4)," Test Med Acc
",round(np.median(XSAlist),4),"% layers
",str(sys.argv[1:]))
    print("Val Ave Acc
",100*round(np.mean(valXSAlist),4),"% Val Ave
cost ",round(np.mean(valcostlist),4)," Val Med Acc
",100*round(np.median(valXSAlist),4),"% layers
",str(sys.argv[1:]))
    toc = time.time()
    print("wall run time after loading",round(toc-tic,2))

```

### groundhog.py

```

import os.path
import os
os.environ["CUDA_VISIBLE_DEVICES"]="-1"
os.environ["TF_CPP_MIN_LOG_LEVEL"] = '3'
import sys
import keras.models
import numpy as np
import warnings
warnings.filterwarnings("ignore")
featurelist = [0, 1, 2, 3, 4, 5, 6, 7, 8, 12, 13, 18, 60,
61, 62, 64, 67]
#this program takes arguments /dataline/location and
/normoff/location
data =
np.loadtxt(os.path.join(sys.argv[1],'data.line'),delimit
er=',')[featurelist]
#print("data allowing for featurelist")
#print(data)
normoff =
np.loadtxt(os.path.join(sys.argv[2],'normoff,))
#offset and normalization constants for the data are
needed; these are in normoff
data = data - normoff[1]

```

```

data = data/normoff[0]
#print("data allowing for normoff")
#print(data)

makemodel.py
import numpy as np
import sys
import os
os.environ["CUDA_VISIBLE_DEVICES"]="-1"
import time
import h5py
from keras import layers, regularizers
from keras.layers import Input, Dense, Activation,
BatchNormalization, Flatten, Dropout
from keras.models import Sequential, load_model
from keras.metrics import categorical_crossentropy
from keras.optimizers import Adam, RMSprop
from keras.utils import layer_utils, to_categorical
import keras.backend as K
from keras.callbacks import ReduceLROnPlateau,
LearningRateScheduler, EarlyStopping
import warnings
warnings.filterwarnings("ignore")
os.environ['TF_CPP_MIN_LOG_LEVEL'] = '3'

def schedule(epochnum):
    lr = 0.002
    if epochnum>40:
        lr = 0.0006
    if epochnum > 80:
        lr = 0.0002
    if epochnum > 350:
        lr = 0.0001
    if epochnum > 380:
        lr = 0.00004
    # print ("epoch",epochnum,"lr",lr)
    return lr

def confusion_matrix(ytrue, ypred):
    assert (ytrue.shape == ypred.shape), "Inputs to
confusion matrix have different dimensions"
    dim = ytrue.shape[1]
    outmat = np.zeros([dim,dim], dtype=int)
    for i in range(0,dim):
        for j in range(0,dim):
            outmat[i,j] = int(np.sum(ytrue[:,i] * ypred[:,j]))
    return outmat

#prepare the training and test arrays. Split into
validation is done automatically.
lambda=0.004
print("lambda original",lambda)
fullarray =
np.loadtxt("/scratch/user/vroytman/cpdim2019/tempb
in500.csv",delimiter=",")

```

```

mymodel =
keras.models.load_model(os.path.join(sys.argv[2],'cp
dimer.h5'))
results = mymodel.predict(np.array([data]))[0]
print(int(100*max(results)))
outside_test_array =
np.loadtxt("/scratch/user/vroytman/cpdim2019/binho
g/regularitest.csv",delimiter=",")
trimedarray = fullarray
Yset = trimedarray[:,128:132]
print(Yset)
Xset = Yset # temporary for appending, then will
delete first three columns
Youtside_test_array = outside_test_array[:,128:132]
#Sometimes this will be real, sometimes not if we
don't know answers, but something has to be there in
file.
Xoutside_test_array = Youtside_test_array #
temporary, silly, but makes for easy programming by
fitting with how Xset handled
IDset = trimedarray[:,132:135]
featurelist = [0, 1, 2, 3, 4, 5, 6, 7, 8, 12, 13, 18, 60,
61, 62, 64, 67]

print("featurelist original",featurelist)
if len(sys.argv) > 1 and sys.argv[1] == "add":
    for arg in sys.argv[2:]:
        featurelist.append(int(arg))
    print("featurelist after adding",featurelist)
if len(sys.argv) > 1 and sys.argv[1] == "remove":
    mylist = []
    for arg in sys.argv[2:]:
        mylist.append(int(arg))
    featurelist = [x for x in featurelist if x not in mylist]
    print("featurelist after removal",featurelist)
if len(sys.argv) > 1 and sys.argv[1] == "lambda":
    lambda = sys.argv[2]
    print("revised lambda",lambda)
for feature in featurelist:
    a = np.reshape(trimedarray[:,feature],(-1,1))
    Xset = np.concatenate((Xset,a), axis=1)
    b = np.reshape(outside_test_array[:,feature],(-1,1))
    Xoutside_test_array =
np.concatenate((Xoutside_test_array,b), axis=1)
#remove Y values from Xset and normalize
Xset = Xset[:,4::]
print("Xset",Xset)
xmean = Xset.mean(axis=0)
Xset = Xset - xmean
xstd = Xset.std(axis=0)
Xset = Xset / xstd
np.savetxt('normoff',[xstd,xmean])
#remove Y values from Xoutside_test_array and set
to same scale as Xset
Xoutside_test_array = Xoutside_test_array[:,4::]
Xoutside_test_array = Xoutside_test_array - xmean

```

```

Xoutside_test_array = Xoutside_test_array / xstd
print("full X shape",Xset.shape,"full Y
shape",Yset.shape)
print("outside test shape",Xoutside_test_array.shape)
class_weight = {0:1, 1:1, 2:2, 3:1.5}
print("class_weight",class_weight)
tic = time.time()
for ind in range(0,1):
    m = Yset.shape[0]
    i = int(0.95*m)
    Xtest=Xset[i:m,:]
    Ytest=Yset[i:m,:]
    IDtest=IDset[i:m,:]
    Xset=Xset[1:i,:]
    Yset=Yset[1:i,:]
    IDset=IDset[1:i,:]
    costlist=[]
    XSAlist=[]
    valcostlist=[]
    valXSAlist=[]
    for seed in range(1):
        np.random.seed()
        m = Yset.shape[0]
        print(m)
        permutation = list(np.random.permutation(m))
        X_train = Xset[permutation, :]
        Y_train = Yset[permutation, :]
        print ("number of training examples = " +
str(X_train.shape[0]))
        print ("X_train shape: " + str(X_train.shape))
        print ("Y_train shape: " + str(Y_train.shape))
        print ("Xtest shape: " + str(Xtest.shape))
        print ("Ytest shape: " + str(Ytest.shape))

        model = Sequential([
            Dense(300, input_shape=(Xtest.shape[1]),
activation='relu',
kernel_regularizer=regularizers.l2(lambd)),
            Dense(4, activation='softmax'),
        ])
        reduce_lr = LearningRateScheduler(schedule)
        early_stop =
EarlyStopping(monitor='val_loss',min_delta=0,
patience=80, verbose=1)
        model.summary()
        model.compile(RMSprop(lr=0.002, rho=0.99),
loss='categorical_crossentropy', metrics=['accuracy'])
        losshist = model.fit(X_train, Y_train,
validation_split=0.02, batch_size=512, epochs=400,
class_weight=class_weight, shuffle=True,
callbacks=[reduce_lr, early_stop], verbose=0)
        if seed == 0:
            model.save('cpdimer.h5')
            val_loss = round(losshist.history.get('val_loss')[-
1],5)

```

```

            val_acc = round(losshist.history.get('val_acc')[-
1],5)
            valcostlist.append(losshist.history.get('val_loss')[-
1])
            valXSAlist.append(losshist.history.get('val_acc')[-1])
            print("loss = ", round(losshist.history.get('loss')[-
1],4),
                "acc = ", round(losshist.history.get('acc')[-1],4),
                "val_loss = ", val_loss,
                "val_acc = ", val_acc)
            loss_and_metrics = model.evaluate(Xtest, Ytest,
batch_size=16, verbose=0)
            XSA = int(100000*loss_and_metrics[1])/1000
            print(loss_and_metrics)
            cost = int(100000*loss_and_metrics[0])/100000
            print("")
            print("loss for test set ", cost, " accuracy for
test set: ", XSA,"%")
            costlist.append(cost)
            XSAlist.append(XSA)
            print("running", seed, " ",
round(np.mean(XSAlist),4),"% layers
",str(sys.argv[1:]))
            print("valRunning", seed, "
",100*round(np.mean(valXSAlist),4),"%
cost",round(np.mean(valcostlist),4),"% arguments
",str(sys.argv[1:]))
            rounded_predictions =
to_categorical(model.predict_classes(Xtest,
batch_size=16, verbose=1), num_classes=4)
            print(" ")
            print("shape of rounded
predictions",rounded_predictions.shape,"shape of
Ytest",Ytest.shape)
            print("predictions by
category:",int(np.sum(rounded_predictions[:,0])),
int(np.sum(rounded_predictions[:,1])),int(np.sum(rou
nded_predictions[:,2])),int(np.sum(rounded_predictio
ns[:,3])))
            print("test
percentage",round(100*np.sum(rounded_predictions[
:,0])/Ytest.shape[0],2),
round(100*np.sum(rounded_predictions[:,1])/Ytest.s
hape[0],2),
round(100*np.sum(rounded_predictions[:,2])/Ytest.s
hape[0],2),
round(100*np.sum(rounded_predictions[:,3])/Ytest.s
hape[0],2))
            total_correct = int(np.sum(Ytest *
rounded_predictions))

```

```

    print("total in test set",Ytest.shape[0],"Total
correct",total_correct," Percent
",round(100*total_correct/Ytest.shape[0],2))
    if seed == 0: #print out the errors ID info for
seed==0
    print(" identifiers      Y actual  Y
predicted")
    for index in range(Ytest.shape[0]):
        if np.sum(Ytest[index, :] *
rounded_predictions[index, :]) == 0:
            print(IDtest[index, :],Ytest[index,
:],rounded_predictions[index, :])
#         print(Ytest[index, :] *
rounded_predictions[index, :])
        cm =
confusion_matrix(Ytest,rounded_predictions)
        print("confusion matrix")
        print(" A  B  Rec ProdRec")
        print(cm)
        print(" ")
        print("predictions for outside test array")
        outside_rounded_predictions =
to_categorical(model.predict_classes(Xoutside_test_a
rray, batch_size=16, verbose=1))
        print(" ")
        print("shape of outside rounded
predictions",outside_rounded_predictions.shape,"sha
pe of
Youtside_test_array",Youtside_test_array.shape)
        print("outside predictions by
category:",int(np.sum(outside_rounded_predictions[:,
0])),
int(np.sum(outside_rounded_predictions[:,1])),int(np.
sum(outside_rounded_predictions[:,2])),int(np.sum(o
utside_rounded_predictions[:,3])))
        print("outside
percentage",round(100*np.sum(outside_rounded_pre
dictions[:,0])/Youtside_test_array.shape[0],2),
round(100*np.sum(outside_rounded_predictions[:,1])
/Youtside_test_array.shape[0],2),
round(100*np.sum(outside_rounded_predictions[:,2])
/Youtside_test_array.shape[0],2),
round(100*np.sum(outside_rounded_predictions[:,3])
/Youtside_test_array.shape[0],2))
        outside_total_correct =
int(np.sum(Youtside_test_array *
outside_rounded_predictions))
        print ("total in outside
set",Youtside_test_array.shape[0],"Total
correct",outside_total_correct," percent correct",
100*outside_total_correct/Youtside_test_array.shape
[0],"      ,m)

```

```

    cm =
confusion_matrix(Youtside_test_array,outside_round
ed_predictions)
    print("confusion matrix for outside test")
    print(" A  B  Rec ProdRec")
    print(cm)
    K.clear_session()
    toc = time.time()
    print("")
    print("time so far",round(toc-tic,2))
    print("-----
-----",str(seed) * 10)

    print(" ")
    print(" ")
    print("Test Ave Acc
",round(np.mean(XSAlist),2),"% Test Ave cost
",round(np.mean(costlist),4)," Test Med Acc
",round(np.median(XSAlist),4),"% layers
",str(sys.argv[1:]))
    print("Val Ave Acc
",100*round(np.mean(valXSAlist),4),"% Val Ave
cost ",round(np.mean(valcostlist),4)," Val Med Acc
",100*round(np.median(valXSAlist),4),"% layers
",str(sys.argv[1:]))
    toc = time.time()
    print("wall run time after loading",round(toc-tic,2))
progbraintrepcpdimer
# Get a list of all of the trajectory results
grep XXX n??/dynfollowfile > temp589

# Organize the results including director and
isomernumber and time for each direction. The
directory and isomernumber will be used
# to associate the results with a particular geoPlusVel
awk 'BEGIN {
dirstart=100
dirend=999
}
{
dirnum=substr($1,2,3)
direction=1
if ((dirnum==olddirnum) &&
($7==oldisomernumber)) direction=2
if ($7>0) {
isomernumber=$7
maxres[dirnum]=isomernumber
result[dirnum,isomernumber,direction]=$14
time[dirnum,isomernumber,direction]=$5
}
olddirnum=dirnum;oldisomernumber=isomernumber
}
END {
for (d=dirstart;d<=dirend;d++) {
for (i=1;i<=maxres[d];i++) {
if (time[d,i,2]>0) print
d,i,time[d,i,2],time[d,i,1],result[d,i,2],result[d,i,1]

```

```

    }
  }
}' temp589 > temp590

# Count all of the results and output the count
awk 'BEGIN {
Acnum=0;MVKnum=0;Recross=0;totalresults=0;Toomany=0;prodrecross=0
prodaT50=0;prodaT100=0;prodaT150=0;prodaT200=0;prodaT250=0;prodaT300=0;prodaT350=0;prodaT400=0;prodaT450=0;prodaTG=0
prodbT50=0;prodbT100=0;prodbT150=0;prodbT200=0;prodbT250=0;prodbT300=0;prodbT350=0;prodbT400=0;MVK450=0;prodbTG=0
toT50=0;toT100=0;toT150=0;toT200=0;toT250=0;toT300=0;toT350=0;toT400=0;MVK450=0;toTG=0
}
{
totalresults++
if (($6=="PRODA") && ($5=="Returned")) {
  Acnum++
  if ($4<=50) prodaT50++
  else if ($4<=100) prodaT100++
  else if ($4<=150) prodaT150++
  else if ($4<=200) prodaT200++
  else if ($4<=250) prodaT250++
  else if ($4<=300) prodaT300++
  else if ($4<=350) prodaT350++
  else if ($4<=400) prodaT400++
  else if ($4<=450) prodaT450++
  else prodaTG++
}
if (($6=="PRODB") && ($5=="Returned")) {
  MVKnum++
  if ($4<=50) prodbT50++
  else if ($4<=100) prodbT100++
  else if ($4<=150) prodbT150++
  else if ($4<=200) prodbT200++
  else if ($4<=250) prodbT250++
  else if ($4<=300) prodbT300++
  else if ($4<=350) prodbT350++
  else if ($4<=400) prodbT400++
  else if ($4<=450) prodbT450++
  else prodbTG++
}
if (($6=="Returned") && ($5=="Returned")) {
  Recross++
  if ($4<=50) toT50++
  else if ($4<=100) toT100++
  else if ($4<=150) toT150++
  else if ($4<=200) toT200++
  else if ($4<=250) toT250++
  else if ($4<=300) toT300++
  else if ($4<=350) toT350++
  else if ($4<=400) toT400++
  else if ($4<=450) toT450++
}
}
}

```

```

    else toTG++
  }
  if (($6=="Too") && ($5=="Returned"))
  Toomany++
  if (($6=="Too") && ($5=="PRODA"))
  Toomany++
  if (($6=="Too") && ($5=="PRODB"))
  Toomany++
  if (($6=="Too") && ($5=="Returned"))
  Toomany++
  if (($6=="Too") && ($5=="PRODA"))
  Toomany++
  if (($6=="Too") && ($5=="PRODB"))
  Toomany++
  if (($5=="PRODA") && ($6=="PRODB"))
  prodrecross++
  if (($5=="PRODB") && ($6=="PRODA"))
  prodrecross++
  if (($5=="PRODA") && ($6=="PRODA"))
  prodrecross++
  if (($5=="PRODB") && ($6=="PRODB"))
  prodrecross++
  if (($5=="Too") && ($6=="Too")) Toomany++
  if (($6=="Returned") && ($5=="PRODA"))
  AcnumBackwards++
  if (($6=="Returned") && ($5=="PRODB"))
  MVKnumBackwards++
}
END {
print "Forms PRODA from SM",Acnum
print "Forms PRODB from SM",MVKnum
print "Recrosses to Starting both ways",Recross
print "Forms PRODA from SM but backwards",AcnumBackwards
print "Forms PRODB from SM but backwards",MVKnumBackwards
print "Too many points one or both ways, all possibilities",Toomany
print "Recrossing from product to product, all possibilities",prodrecross
print "Total results",totalresults
print "Results unaccounted for",totalresults-Acnum-MVKnum-Recross-Toomany-prodrecross-AcnumBackwards-MVKnumBackwards
print "Prod A times"
print "<50 51-100 101-150 151-200 201-250 251-300 301-350 351-400 401-450 >450"
print prodaT50," ",prodaT100," ",prodaT150," ",prodaT200," ",prodaT250," ",prodaT300," ",prodaT350," ",prodaT400," ",prodaT450," ",prodaTG
print "Prod B times"
print "<50 51-100 101-150 151-200 201-250 251-300 301-350 351-400 401-450 >450"
print prodbT50," ",prodbT100," ",prodbT150," ",prodbT200," ",prodbT250," ",prodbT300,"

```



```

",prodbT350," ",prodbT400," ",prodbT450,"
",prodbTG
print "Recrossing times"
print "<50 51-100 101-150 151-200 201-250 251-300
301-350 351-400 401-450 >450"
print toT50," ",toT100," ",toT150," ",toT200,"
",toT250," ",toT300," ",toT350," ",toT400,"
",toT450," ",toTG
}' temp590

```

```

# create a big full that combines all of the
geoRecords, with an extra label that includes the
directory name
awk '
/trajectory/ {printf("%s ",substr(FILENAME,2,3));}
{print}' n??/geoRecord > temp591

```

```

# prep for output files
rm -f temp*.csv

```

```

# combine the results summary in temp590 and the
geoRecords in temp591 to output files for bringing in
to neural nets
awk 'BEGIN {
totalline=0
dirstart=100
dirend=999
oldanswer=" , 0, 0, 0, 0"
CCmax=0;CCmin=10;COAcmax=0;COAcmin=10;C
OMVKmax=0;COMVKmin=10;CCdotmax=0;CCdot
min=10;COAcdotmax=0;COAcdotmin=10;COMVK
dotmax=0;COMVKdotmin=10
CCaimmax=0; CCaimmin=10; COAcaimmax=0;
COAcaimmin=10; COMVKaimmax=0;
COMVKaimmin=10
}
/trajectory/ {
dirnum=$1
isomernumber=$2
linenumber=0
maxres[dirnum]=isomernumber
badgeo=0
}
{
totalline++
linenumber++
if ((linenumber>=3) && (linenumber<=24)) {
if ($2==0) badgeo=1
if ($2=="nan") badgeo=1
i=linenumber-2
weight[i]=$5
atSym[i]=$1
for (j=1;j<=3;j++) {
geoArr[i,j]=$1+j
}
}
}

```

```

if ((linenumber>=25) && (linenumber<=46)) {
i=linenumber-22
velMult=50
for (j=1;j<=3;j++) {
velArr[i,j]=$j
aimGeo[i,j]=geoArr[i,j]+velMult*velArr[i,j]
}
}
# now extract any key geometry and velocity
parameters
if ((badgeo==0) && (linenumber==47)) {
# CC
delX=geoArr[1,1]-geoArr[10,1];delY=geoArr[1,2]-
geoArr[10,2];delZ=geoArr[1,3]-geoArr[10,3];
velX=velArr[1,1]-velArr[10,1];velY=velArr[1,2]-
velArr[10,2];velZ=velArr[1,3]-velArr[10,3];
delaimX=aimGeo[1,1]-
aimGeo[10,1];delaimY=aimGeo[1,2]-
aimGeo[10,2];delaimZ=aimGeo[1,3]-aimGeo[10,3];
distatoms=(delX^2+delY^2+delZ^2)^.5
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.5
CC[dirnum,isomernumber]=distatoms
CCaim[dirnum,isomernumber]=distaim
if (distatoms==0) print
FILENAME,"totalline",totalline,"zero problem here"
if (distatoms!=0) {
unitX=delX/distatoms;unitY=delY/distatoms;;unitZ=
delZ/distatoms;
}
CCdot[dirnum,isomernumber]=-
25*(unitX*velX+unitY*velY+unitZ*velZ)
if (CCdot[dirnum,isomernumber]>CCdotmax)
CCdotmax=CCdot[dirnum,isomernumber]; if
(CCdot[dirnum,isomernumber]<CCdotmin)
CCdotmin=CCdot[dirnum,isomernumber];
if (CC[dirnum,isomernumber]<CCmin)
CCmin=CC[dirnum,isomernumber];if
(CC[dirnum,isomernumber]>CCmax)
CCmax=CC[dirnum,isomernumber];
if (CCaim[dirnum,isomernumber]<CCaimmin)
CCaimmin=CCaim[dirnum,isomernumber];if
(CCaim[dirnum,isomernumber]>CCaimmax)
CCaimmax=CC[dirnum,isomernumber];
# COAc
delX=geoArr[8,1]-geoArr[2,1];delY=geoArr[8,2]-
geoArr[2,2];delZ=geoArr[8,3]-geoArr[2,3];
velX=velArr[8,1]-velArr[2,1];velY=velArr[8,2]-
velArr[2,2];velZ=velArr[8,3]-velArr[2,3];
delaimX=aimGeo[8,1]-
aimGeo[2,1];delaimY=aimGeo[8,2]-
aimGeo[2,2];delaimZ=aimGeo[8,3]-aimGeo[2,3];
distatoms=(delX^2+delY^2+delZ^2)^.5
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.5
COAc[dirnum,isomernumber]=distatoms
COAcaim[dirnum,isomernumber]=distaim

```

```

if (distatoms==0) print dirnum, isomernumber

unitX=delX/distatoms;unitY=delY/distatoms;;unitZ=
delZ/distatoms;
COAc[dot][dirnum,isomernumber]=
25*(unitX*velX+unitY*velY+unitZ*velZ)
if
(COAc[dot][dirnum,isomernumber]>COAc[dot]max)
COAc[dot]max=COAc[dot][dirnum,isomernumber];if
(COAc[dot][dirnum,isomernumber]<COAc[dot]min)
COAc[dot]min=COAc[dot][dirnum,isomernumber];
if (COAc[dirnum,isomernumber]<COAcmin)
COAcmin=COAc[dirnum,isomernumber];if
(COAc[dirnum,isomernumber]>COAcmax)
COAcmax=COAc[dirnum,isomernumber];
if
(COAc[aim][dirnum,isomernumber]<COAc[aim]min)
COAc[aim]min=COAc[aim][dirnum,isomernumber];if
(COAc[aim][dirnum,isomernumber]>COAc[aim]max)
COAc[aim]max=COAc[aim][dirnum,isomernumber];
# COMVK
delX=geoArr[4,1]-geoArr[12,1];delY=geoArr[4,2]-
geoArr[12,2];delZ=geoArr[4,3]-geoArr[12,3];
velX=velArr[4,1]-velArr[12,1];velY=velArr[4,2]-
velArr[12,2];velZ=velArr[4,3]-velArr[12,3];
delaimX=aimGeo[4,1]-
aimGeo[12,1];delaimY=aimGeo[4,2]-
aimGeo[12,2];delaimZ=aimGeo[4,3]-aimGeo[12,3];
distatoms=(delX^2+delY^2+delZ^2)^.5
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.5
COMVK[dirnum,isomernumber]=distatoms
COMVK[aim][dirnum,isomernumber]=distaim

unitX=delX/distatoms;unitY=delY/distatoms;;unitZ=
delZ/distatoms;
COMVK[dot][dirnum,isomernumber]=
25*(unitX*velX+unitY*velY+unitZ*velZ)
if
(COMVK[dot][dirnum,isomernumber]>COMVK[dot]max)
COMVK[dot]max=COMVK[dot][dirnum,isomernumber]
]; if
(COMVK[dot][dirnum,isomernumber]<COMVK[dot]min)
COMVK[dot]min=COMVK[dot][dirnum,isomernumber]
];
if (COMVK[dirnum,isomernumber]<COMVKmin)
COMVKmin=COMVK[dirnum,isomernumber];if
(COMVK[dirnum,isomernumber]>COMVKmax)
COMVKmax=COMVK[dirnum,isomernumber];
if
(COMVK[aim][dirnum,isomernumber]<COMVK[aim]min)
COMVK[aim]min=COMVK[aim][dirnum,isomernumber]
];if
(COMVK[aim][dirnum,isomernumber]>COMVK[aim]

```

```

max)
COMVK[aim]max=COMVK[aim][dirnum,isomernumber]
];
}
if ((badgeo==0) && (linenumber>=47) &&
(linenumber<=106)) {
mv[dirnum,isomernumber,linenumber]=$4/3e13;
mdis[dirnum,isomernumber,linenumber]=$5
}
if (FILENAME=="temp590") {
# By the time we get here we should be done with
all of the extractions from geoRecords

d=$1;i=$2;time[d,i,1]=$3;time[d,i,2]=$4;result[d,i,1]
=$5;result[d,i,2]=$6
answer[d,i]=999
if (($6=="PRODA") && ($5=="Returned")) {
answer[d,i]=", 1, 0, 0, 0"
}
if (($6=="PRODB") && ($5=="Returned")) {
answer[d,i]=", 0, 1, 0, 0"
}
if (($5=="Returned") && ($6=="Returned")) {
answer[d,i]=", 0, 0, 1, 0"
}
if (((($6=="PRODA") || ($6=="PRODB")) &&
(($5=="PRODA") || ($5=="PRODB")))) {
answer[d,i]=", 0, 0, 0, 1"
}
if (answer[d,i]==999) countunassigned++
if (answer[d,i]!=999) {
for (timebin=50;timebin<=500;timebin+=50) {
filestring="tempbin"timebin".csv"
if (time[d,i,2]<timebin) {
for (disline=47;disline<=106;disline++) {
printf("%.5f, ",mv[d,i,disline]) >> filestring
}
for (disline=48;disline<=106;disline++) {
printf("%.6f, ",mdis[d,i,disline]) >>
filestring
}
printf("%.5f, %.5f, %.5f, %.5f, %.5f, %.5f, ",
CC[d,i], COAc[d,i], COMVK[d,i], CC[dot][d,i],
COAc[dot][d,i], COMVK[dot][d,i]) >> filestring
printf("%.5f, %.5f, %.5f", CC[aim][d,i],
COAc[aim][d,i], COMVK[aim][d,i]) >> filestring
print answer[d,i], "time[d,i,2]", "d", "i" >>
filestring
}
}
oldanswer=answer[d,i]
}
}
}
END {
print "unassigned",countunassigned

```

```

print
"CCmax,CCmin,COAcmax,COAcmin,COMVKmax,
COMVKmin"
print
CCmax,CCmin,COAcmax,COAcmin,COMVKmax,
COMVKmin
print "CCdotmax,CCdotmin"
print CCdotmax,CCdotmin
print "COAcdotmax,COAcdotmin"
print COAcdotmax,COAcdotmin
print "COMVKdotmax,COMVKdotmin"
print COMVKdotmax,COMVKdotmin
print "CCaimmax, CCaimmin"
print CCaimmax, CCaimmin
print "COAcaimmax, COAcaimmin"
print COAcaimmax, COAcaimmin
print "COMVKaimmax, COMVKaimmin"
print COMVKaimmax, COMVKaimmin
}' temp591 temp590

```

```

rm -f temp589 temp590 temp591
wc *csv
module load Anaconda/3-5.0.0.1
#module load myPython/3.5.2-intel-2017A &&
source /scratch/user/vroytman/myPython/3.5.2-intel-
2017A/bin/activate
sed -i '/0.00000, 0.00000, 0.00000, 0.00000/d' *.csv
mv tempbin500.csv test
python shuffle.py > tempbin500.csv
mv tempbin450.csv test
python shuffle.py > tempbin450.csv
mv tempbin400.csv test
python shuffle.py > tempbin400.csv
mv tempbin350.csv test
python shuffle.py > tempbin350.csv
mv tempbin300.csv test
python shuffle.py > tempbin300.csv
mv tempbin250.csv test
python shuffle.py > tempbin250.csv
mv tempbin200.csv test
python shuffle.py > tempbin200.csv
mv tempbin150.csv test
python shuffle.py > tempbin150.csv
mv tempbin100.csv test
python shuffle.py > tempbin100.csv
mv tempbin50.csv test
python shuffle.py > tempbin50.csv
wc *csv

```

### **progdyn.conf for Groundhog**

```

#This is the configuration file for PROGDYN. This
file is read by progdynstarterHP and
# the awk programs proggenHP, prog1stpoint,
prog2ndpoint, and progdynb.
#The programs won't read anything past the first
blank line,
#and this file must end with a blank line.

```

```

#The program has a number of default values but
they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for
unwanted options.
#The values here are read repeatedly and most can be
changed in the middle of running jobs
****The keywords are case sensitive. The following
keywords should always be defined:****
****method, charge, multiplicity, memory,
processors, title
**** method --The following word is copied exactly
to the gaussian input file.
method B3LYP/6-31G*
#To do a nonstandard route, make nonstandard 1.
For normal calcs, use nonstandard 0 or else leave it
out.
#Then make a file called "nonstandard" containing
the nonstandard route with no extra lines.
nonstandard 0
# NMRoptions As is NMRtype=1 will add a section
for an NMR calc at every NMRevery intervals. If
you want to combine the two use nonstandard
#NMRtype 1
#NMRmethod2 B97D/6-31G*
#NMRmethod LC-wPBE/6-31G*
#NMRmethod3 B3LYP/cc-pvtz
#NMRevery 4
#NMRrand 1
#NMRcc 1
#loadlimit 10.0
#geometry linear
rotationmode 1
**** method2 --The options here are restricted,
unrestricted, and read. restricted is the default
#If the method is U..., put unrestricted here and the
.com files will have in them guess=mix.
#If you put read here, the .com files will contain
guess=tcheck, which sometimes makes things faster,
sometimes not.
#The use of read requires a specifically defined
checkpoint file name using the keyword checkpoint.
method2 restricted
charge 0
multiplicity 1
#oniomchargemult 1 1
processors 4
**** memory --The following "word" is copied
exactly to the gaussian input file after %mem=.
memory 6gb
**** killcheck and checkpoint -- You can use a
specifically defined checkpoint file name by putting
#the name after the keyword checkpoint. This is
necessary if you use the read option with method2.
#Defined checkpoint names are an unnecessary
modest hassle and if you do not want to bother, use
killcheck 1

```

```

killcheck 0
checkpoint g16.chk
**** diagnostics -- 0 prints out nothing extra, 1
(default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds
velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is
meaningless with quasiclassical calculations
diagnostics 0
**** title -- the title keyword must be followed by
exactly four words
title cpdim norm B3LYPSB 298dis4
**** initialdis -- 0 (default) turns off displacement of
the normal modes, so that all trajectories start from
the same place
# and only the energies and signs of the motion in the
modes are randomized
# 1 gives a flat distribution of displacements where
all of the possible values are equally likely
# 2 (recommended) gives a QM-like gaussian
distribution of displacements, so that displacements
in the middle are more likely than
# those at the end by 1/e
initialdis 4
**** timestep -- this is the time between points in the
trajectory. Typical values would be 1E-15 or 0.5E-
15 or 0.25E-15
timestep 1E-15
**** scaling -- this lets you scale the gaussian
frequencies by a constant
scaling 1.0
temperature 298.15
**** thermostat 1 puts in a damping factor so as to
bring the classical temperature toward the desired
temperature.
**** use a thermostatmult between 0.95 and 1,
typically 0.995, so the damping happens slowly -
otherwise there will be
**** overadjustment in response to random variation
**** the thermostat is not exact. The second traj
point ignores this, so it only applies to later points
handled by progdynb.
#thermostat 1
#thermostatmult 0.999
**** method3, method4, method5, and method6 --
These keywords let you add extra lines to the
gaussian input file.
#method3 and method4 add lines at the top of the
input after the lines defining the method, and
#this is useful to implement things like the iop for
mPW1k
#method5 and method6 add lines after the geometry,
after a blank line of course
#only a single term with no spaces can be added, one
per method line. Here are some examples to
uncomment if needed

```

```

#method3 IOp(3/76=0572004280)
#method3 scrf=(pcm,solvent=ethanol)
#method3 scrf=(solvent=chloroform)
#add the line below with big structures to get it to put
out the distance matrix and the input orientation
#method4 empiricaldispersion=gd3
#method3 scf=(conver=5)
#method4 iop(3/124=3)
#method4 scrf=(pcm,solvent=dmsol,read)
#method5 radii=bondi
#method6
**** methodfile -- This keyword lets you add more
complicated endings to gaussian input files
#such as a gen basis set. Put after the keyword the
number of lines in a file you create called
#methodfile that contains the test you want to add to
the end of the gaussian input
methodfile 0
**** numimag --This tells the program the number
of imaginary frequencies in the starting structure.
#if 0, treats as ground state and direction of all modes
is random
#if 1, motion along the reaction coordinate will start
out in the direction defined by searchdir
#if 2, only lowest freq will go direction of searchdir
and other imag mode will go in random direction
numimag 1
**** searchdir -- This keyword says what direction
to follow the mode associated with the imaginary
frequency.
#The choices are "negative" and "positive". Positive
moves in the direction defined in the gaussian
frequency calculation
#for the imaginary frequency, while negative moves
in the opposite direction. The correct choice can be
made either
#by a careful inspection of the normal modes and
standard orientation geometry, or by trial and error.
searchdir positive
**** classical -- for quasiclassical dynamics, the
default, use 0. for classical dynamics, use 1
#if there are no normal modes and the velocities are
to be generated from scratch, use classical 2
classical 0
**** DRP, saddlepoint, and maxAtomMove --to run
a DRP use 'DRP 1' in the line below, otherwise leave
it at 0 or comment it out
#the treatment of starting saddlepoints is not yet
implemented so use saddlepoint no
#if DRP shows oscillations then decrease
maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01

```

```

**** cannonball -- The program can "fire" a
trajectory from a starting position toward a particular
target, such as toward
#a ts. To use this, make a file cannontraj with
numAtom lines and three numbers per line that
defines the vector
#for firing the trajectory, relative to the starting
geometry's standard orientation. The number
following cannonball sets
#the extra energy being put into the structure in
kcal/mol
#cannonball 10
**** keepevery --This tells the program how often to
write the gaussian output file to file dyn, after the
first two points.
#Use 1 for most dynamics to start with, but use a
higher number to save on disk space or molden
loading time.
keepevery 9999
**** highlevel --For ONIOM jobs, the following line
states the number of highlevel atoms,
#which must come before the medium level atoms.
Use some high value such as 999 if not using
ONIOM
highlevel 9999
**** fixedatom1, fixedatom2, fixedatom3, and
fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and
messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of
fixing three distances, not just two
#in current form fixed atoms only are meant to work
with no displacements, that is, initialdis=0
#fixedatom1 16
#fixedatom2 1
#fixedatom3 4
#fixedatom4 20
#applyforce 1 lets one push atoms together or apart -
a positive force pushes them together
#format is applyforce force - with the units on force
the same as in the Gaussian output file
#applyforce 2 or 3 or 4 applies a polynomial force
centered at dist0. 2 is just harmonic, 3 is second
order, 4 is third order
#format is applyforce 4 forcecoefficient dist0
forcecoefficient2 forcecoefficient3
#then use afatoms to chose the atoms with format
afatoms firstatom secondatom [additional atoms]
#applyforce 2 0.1 2.1
#afatoms 16 1 2 3 4 5 6
#applyforceB 2 0.01 5.2
#afatomsB 8 15
#applyforceC 2 0.01 5.2
#afatomsC 8 15
#zeroatom pushes the numbered atom toward the
origin with a small harmonic potential - good with

```

```

boxon when you want to keep the reaction in the
center
#zeroatom 16
**** boxon and boxsize - With boxon 1, a cubic box
is set such that atoms that reach the edge
#are reflected back toward the middle. Useful for
dynamics with solvent molecules. This is a crude
#implementation that is ok for a few thousand
femtoseconds but will not conserve energy long term.
#Set the box size so as to fit the entire initial
molecule but not have too much extra room.
#The dimensions of the box are two times the
boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15
x 15 angstroms
#boxon 1
#boxsize 11.2
**** sphereon and spheresize and sphereforce - uses
a force to push atoms within a sphere. notice that if
the atom is far outside of
#the sphere then the force is large unless sphereforce
is set small
#sphereon 1
#spheresize 12.9
#sphereforce .01
#setting a value for empiricaldispersion sets its s6
value with the Grimme 2006 algorithm. Default is 0,
with no empiricaldispersion
#empiricaldispersion 1.0
**** displacements -- This keyword lets you set the
initialdis of particular modes by using a series of
lines of the format
# displacements NumberOfMode
InitialDisForThatMode, as in the example below.
You should be able to do as many of these as you like
# you might consider this for rotations where a
straight-line displacement goes wrong at large
displacements
# The choices for InitialDisForThatMode are 0, 1, 2,
and 10, where 10 does the same thing as 0 but is
maintained for now because
# a previous version of the program had a bug that
made 0 not work.
#displacements 2 0
#displacements 3 0
#displacements 4 0
#displacements 5 0
#displacements 6 0
#displacements 7 0
#displacements 8 0
#displacements 9 0
#displacements 10 0
**** etolerance --This sets the allowable difference
between the desired energy in a trajectory and the
actual
#energy, known after point 1 from the potential
energy + the kinetic energy in the initial velocities.

```

#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems. For very large and floppy molecules, a larger value  
 #may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).  
 #If initialdis is not 0 and few trajectories are being rejected, decrease the value.  
 etolerance 10  
 \*\*\* controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.  
 #The format is controlphase  
 numberOfModeToControl positive or controlphase  
 numberOfModeToControl negative.  
 #controlphase 2 positive  
 \*\*\* damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities  
 #by the damping factor. A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range  
 #from 0.95 to 1.05. The use of damping lets one do simulated annealing - you add energy until the structure is moving enough  
 #to sample the kinds of possibilities you are interested in, then you take away the energy slowly.  
 damping 1.000  
 #at a damping of .9995, the energy is cut in half in 693 points  
 \*\*\* reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.  
 reversetraj true  
 #for groundhog put in a value of interesting between 50 and 99  
 interesting 60  
 #anharmonic corrections  
 readdzdm  
 anharmonicmode 2 2.397 -0.017  
 anharmonicmode 3 2.889 -0.045  
 anharmonicmode 4 5.121 -1.729  
 anharmonicmode 5 9.543 -0.178  
 anharmonicmode 6 16.544 0.009  
 anharmonicmode 7 14.917 0.285  
 anharmonicmode 8 16.107 -0.396  
 anharmonicmode 9 37.923 2.581  
 anharmonicmode 10 36.433 0.573  
 anharmonicmode 11 27.856 0.558

anharmonicmode 12 26.824 -0.125  
 anharmonicmode 13 32.275 0.374  
 anharmonicmode 14 34.542 0.756  
 anharmonicmode 15 82.240 -0.773  
 anharmonicmode 16 111.231 -4.627  
 anharmonicmode 17 129.138 6.328  
 anharmonicmode 18 119.374 3.376  
 anharmonicmode 19 69.568 -13.382  
 anharmonicmode 20 69.629 2.728  
 anharmonicmode 21 59.619 1.871  
 anharmonicmode 22 55.026 0.489  
 anharmonicmode 23 54.734 -1.683  
 anharmonicmode 24 61.524 2.004  
 anharmonicmode 25 67.074 4.720  
 anharmonicmode 26 78.502 -6.782  
 anharmonicmode 27 60.577 6.034  
 anharmonicmode 28 68.251 -0.848  
 anharmonicmode 29 97.606 -22.010  
 anharmonicmode 30 61.380 -1.658  
 anharmonicmode 31 59.165 -2.983  
 anharmonicmode 32 66.264 -2.929  
 anharmonicmode 33 69.227 10.317  
 anharmonicmode 34 73.173 6.921  
 anharmonicmode 35 62.683 7.099  
 anharmonicmode 36 72.889 2.029  
 anharmonicmode 37 134.072 11.919  
 anharmonicmode 38 127.233 8.206  
 anharmonicmode 39 102.723 0.577  
 anharmonicmode 40 115.259 -4.412  
 anharmonicmode 41 239.010 -49.040  
 anharmonicmode 42 249.121 -33.704  
 anharmonicmode 43 213.918 61.729  
 anharmonicmode 44 226.389 70.293  
 anharmonicmode 45 106.668 15.729  
 anharmonicmode 46 105.634 12.989  
 anharmonicmode 47 351.787 162.289  
 anharmonicmode 48 429.288 -337.378  
 anharmonicmode 49 418.313 620.581  
 anharmonicmode 50 412.795 -17.360  
 anharmonicmode 51 452.294 -662.682  
 anharmonicmode 52 450.549 9.984  
 anharmonicmode 53 471.849 1.848  
 anharmonicmode 54 463.889 669.967  
 anharmonicmode 55 479.512 67.921  
 anharmonicmode 56 488.624 -671.120  
 anharmonicmode 57 486.697 -633.783  
 anharmonicmode 58 491.956 744.092  
 anharmonicmode 59 500.596 699.963  
 anharmonicmode 60 498.458 -742.886

## progmakeline

```
#!/bin/awk
BEGIN {
}
/trajectory/ {
i=1
d=600
dirnum=600
isomernumber=1
linenumber=0
}
{
linenumber++
if ((linenumber>=3) && (linenumber<=24)) {
i=linenumber-2
weight[i]=$5
atSym[i]=$1
for (j=1;j<=3;j++) {
geoArr[i,j]=$ (1+j)
}
}
if ((linenumber>=25) && (linenumber<=46)) {
i=linenumber-22
velMult=50
for (j=1;j<=3;j++) {
velArr[i,j]=$j
aimGeo[i,j]=geoArr[i,j]+velMult*velArr[i,j]
}
}
# now extract any key geometry and velocity
parameters
if (linenumber==47) {
# CC1-10-heavyside10
delX=geoArr[1,1]-geoArr[10,1];
delY=geoArr[1,2]-geoArr[10,2]; delZ=geoArr[1,3]-
geoArr[10,3];
velX=velArr[1,1]-velArr[10,1]; velY=velArr[1,2]-
velArr[10,2]; velZ=velArr[1,3]-velArr[10,3];
delaimX=aimGeo[1,1]-aimGeo[10,1];
delaimY=aimGeo[1,2]-aimGeo[10,2];
delaimZ=aimGeo[1,3]-aimGeo[10,3];
distatoms=(delX^2+delY^2+delZ^2)^.5
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.5
CC1[dirnum,isomernumber]=distatoms
CC1aim[dirnum,isomernumber]=distaim
if (distatoms==0) print
FILENAME,"totalline",totalline,"zero problem here"
if (distatoms!=0) {

unitX=delX/distatoms;unitY=delY/distatoms;;unitZ=
delZ/distatoms;
}
CC1dot[dirnum,isomernumber]=-
25*(unitX*velX+unitY*velY+unitZ*velZ)
# CC2-8
```

```
delX=geoArr[2,1]-geoArr[8,1]; delY=geoArr[2,2]-
geoArr[8,2]; delZ=geoArr[2,3]-geoArr[8,3];
velX=velArr[2,1]-velArr[8,1]; velY=velArr[2,2]-
velArr[8,2]; velZ=velArr[2,3]-velArr[8,3];
delaimX=aimGeo[2,1]-aimGeo[6,1];
delaimY=aimGeo[2,2]-aimGeo[8,2];
delaimZ=aimGeo[2,3]-aimGeo[8,3];
distatoms=(delX^2+delY^2+delZ^2)^.5
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.5
CC2[dirnum,isomernumber]=distatoms
CC2aim[dirnum,isomernumber]=distaim
if (distatoms==0) print
FILENAME,"totalline",totalline,"zero problem here"
if (distatoms!=0) {

unitX=delX/distatoms;unitY=delY/distatoms;;unitZ=
delZ/distatoms;
}
CC2dot[dirnum,isomernumber]=-
25*(unitX*velX+unitY*velY+unitZ*velZ)
# CC4-12
delX=geoArr[12,1]-geoArr[4,1];
delY=geoArr[12,2]-geoArr[4,2]; delZ=geoArr[12,3]-
geoArr[4,3];
velX=velArr[12,1]-velArr[4,1]; velY=velArr[12,2]-
velArr[4,2]; velZ=velArr[12,3]-velArr[4,3];
delaimX=aimGeo[12,1]-aimGeo[4,1];
delaimY=aimGeo[12,2]-aimGeo[4,2];
delaimZ=aimGeo[12,3]-aimGeo[4,3];
distatoms=(delX^2+delY^2+delZ^2)^.5
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.5
CC3[dirnum,isomernumber]=distatoms
CC3aim[dirnum,isomernumber]=distaim
if (distatoms==0) print
FILENAME,"totalline",totalline,"zero problem here"
if (distatoms!=0) {

unitX=delX/distatoms;unitY=delY/distatoms;;unitZ=
delZ/distatoms;
}
CC3dot[dirnum,isomernumber]=-
25*(unitX*velX+unitY*velY+unitZ*velZ)
}
if ((linenumber>=47) && (linenumber<=106)) {
mv[dirnum,isomernumber,linenumber]=$4/3e13;
mdis[dirnum,isomernumber,linenumber]=$5
}
}
END {
d=600;i=1
answer[d,i]="0, 0, 0"
time[d,i,1]=2
for (disline=47;disline<=106;disline++) {
printf("%.5f, ",mv[d,i,disline])
}
for (disline=48;disline<=106;disline++) {
```

```

    printf("%.5f, ",mdis[d,i,disline])
}
printf("%.5f, %.5f, %.5f, %.5f, %.5f, %.5f, ",
CC1[d,i], CC1dot[d,i], CC1aim[d,i], CC2[d,i],
CC2dot[d,i], CC2aim[d,i])

```

### groundhog.py (modified)

```

import os.path
import os
os.environ["CUDA_VISIBLE_DEVICES"]="-1"
os.environ["TF_CPP_MIN_LOG_LEVEL"] = '3'
import sys
import keras.models
import numpy as np
import warnings
warnings.filterwarnings("ignore")
featurelist = [0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13,
14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27,
28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41,
42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55,
58, 60]
#this program takes arguments /dataline/location and
/normoff/location
data =
np.loadtxt(os.path.join(sys.argv[1],'data.line'),delimit
er=',')[featurelist]
print("data allowing for featurelist")
print(data)
normoff =
np.loadtxt(os.path.join(sys.argv[2],'normoff,))
#offset and normalization constants for the data are
needed; these are in normoff
data = data - normoff[1]
data = data/normoff[0]
print("data allowing for normoff")
print(data)
mymodel =
keras.models.load_model(os.path.join(sys.argv[2],'de
carb.h5'))
results = mymodel.predict(np.array([data]))[0]
results[2]=results[2]+0.3333
#print(results)

```

```
print(int(100*max(results)))
```

### makemodel.py

```

import numpy as np
import sys
import os
os.environ["CUDA_VISIBLE_DEVICES"]="-1"
import time
from keras import layers
from keras import regularizers
from keras.layers import Input, Dense, Activation,
BatchNormalization, Flatten, Dropout
from keras.models import Sequential, load_model
from keras.metrics import categorical_crossentropy

```

```

printf("%.5f, %.5f, %.5f, ", CC3[d,i], CC3dot[d,i],
CC3aim[d,i] )
print answer[d,i]", "time[d,i,1]", ".d", ".i
}

```

### Acetone cation radical dissociation

```

from keras.optimizers import Adam, RMSprop
from keras.utils import layer_utils, to_categorical
import keras.backend as K
from keras.callbacks import ReduceLROnPlateau,
LearningRateScheduler, EarlyStopping
import warnings
warnings.filterwarnings("ignore")
os.environ["TF_CPP_MIN_LOG_LEVEL"] = '3'

def schedule(epochnum):
    lr = 0.002
    if epochnum>80:
        lr = 0.0006
    if epochnum > 160:
        lr = 0.0002
    if epochnum > 240:
        lr = 0.0001
    if epochnum > 380:
        lr = 0.00005
    # print ("epoch",epochnum,"lr",lr)
    return lr

def confusion_matrix(ytrue, ypred):
    assert (ytrue.shape == ypred.shape), "Inputs to
confusion matrix have different dimensions"
    dim = ytrue.shape[1]
    outmat = np.zeros([dim,dim], dtype=int)
    for i in range(0,dim):
        for j in range(0,dim):
            outmat[i,j] = int(np.sum(ytrue[:,i] * ypred[:,j]))
    return outmat

```

```

#prepare the training and test arrays. Split into
validation is done automatically.
lambd=0.0060
hidden1=800
print("lambd original",lambd,"hidden1
original",hidden1)
fullarray =
np.loadtxt("tempbin550.csv",delimiter=",")
###changed outside from Feb 5 to Feb12 on feb 12
2020##
outside_test_array =
np.loadtxt("binhog/tempbin550.csv",delimiter=",")
trimedarray = fullarray
Yset = trimedarray[:,61:64]
print(Yset)
Xset = Yset # temporary for appending, then will
delete first three columns

```



```

Youtside_test_array = outside_test_array[:,61:64]
#Sometimes this will be real, sometimes not if we
don't know answers, but something has to be there in
file.
Xoutside_test_array = Youtside_test_array #
temporary, silly, but makes for easy programming by
fitting with how Xset handled
featurelist = [0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13,
14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27,
28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41,
42, 43,44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55,
58, 60]

print("featurelist original",featurelist)
if len(sys.argv) > 1 and sys.argv[1] == "add":
    for arg in sys.argv[2:]:
        featurelist.append(int(arg))
    print("featurelist after adding",featurelist)
if len(sys.argv) > 1 and sys.argv[1] == "remove":
    mylist = []
    for arg in sys.argv[2:]:
        mylist.append(int(arg))
    featurelist = [x for x in featurelist if x not in mylist]
    print("featurelist after removal",featurelist)
if len(sys.argv) > 1 and sys.argv[1] == "lambd":
    lambd = sys.argv[2]
    print("revised lambd",lambd)
if len(sys.argv) > 1 and sys.argv[1] == "hidden1":
    hidden1 = int(sys.argv[2])
    print("revised hidden1",hidden1)
for feature in featurelist:
    a = np.reshape(trimedarray[:,feature],(-1,1))
    Xset = np.concatenate((Xset,a), axis=1)
    b = np.reshape(outside_test_array[:,feature],(-1,1))
    Xoutside_test_array =
np.concatenate((Xoutside_test_array,b), axis=1)
#remove Y values from Xset and normalize
Xset = Xset[:,3::]
print(Xset)
xmean = Xset.mean(axis=0)
Xset = Xset - xmean
xstd = Xset.std(axis=0)
Xset = Xset / xstd
np.savetxt('normoff',[xstd,xmean])
#remove Y values from Xoutside_test_array and set
to same scale as Xset
Xoutside_test_array = Xoutside_test_array[:,3::]
Xoutside_test_array = Xoutside_test_array - xmean
Xoutside_test_array = Xoutside_test_array / xstd
print("full X shape",Xset.shape,"full Y
shape",Yset.shape)
print("outside test shape",Xoutside_test_array.shape)
class_weight = {0:1, 1:1, 2:1}
print("class_weight",class_weight)
tic = time.time()
for ind in range(1):

```

```

    m = Yset.shape[0]
##### vlad changed the 0.98 to 0.90 on Feb
12 2020  changed back 0.98 on Feb 15 2020, changed
to 0.85 on feb 16 2020 ###
    i = int(0.98*m)
    Xtest=Xset[i:m,:]
    Ytest=Yset[i:m,:]
    Xset=Xset[1:i,:]
    Yset=Yset[1:i,:]
    step_per_ep = int(Xset.shape[0]/2048)
    if step_per_ep < 1:
        step_per_ep = 1
    my_batch_size =
int(2+0.98*Xset.shape[0]/step_per_ep)
    print("steps per epoch",step_per_ep,"batch
size",my_batch_size)
# IDset=IDset[1:i,:]
    costlist=[]
    XSAlist=[]
    valcostlist=[]
    valXSAlist=[]
    outsideAccList=[]
    for seed in range(3):
        np.random.seed(seed)
        m = Yset.shape[0]
        print(m)
        permutation = list(np.random.permutation(m))
        X_train = Xset[permutation, :]
        Y_train = Yset[permutation, :]
        print ("number of training examples = " +
str(X_train.shape[0]))
        print ("X_train shape: " + str(X_train.shape))
        print ("Y_train shape: " + str(Y_train.shape))
        print ("Xtest shape: " + str(Xtest.shape))
        print ("Ytest shape: " + str(Ytest.shape))

        model = Sequential([
            Dense(hidden1, input_shape=(Xtest.shape[1]),
activation='relu',
kernel_regularizer=regularizers.l2(lambd)),
            Dense(3, activation='softmax')
        ])
        reduce_lr = LearningRateScheduler(schedule)
        early_stop =
EarlyStopping(monitor='val_loss',min_delta=0,
patience=80, verbose=1)
        model.summary()
        model.compile(Adam(lr=0.002, beta_1=0.95,
beta_2=0.99), loss='categorical_crossentropy',
metrics=['accuracy'])
        losshist = model.fit(X_train, Y_train,
validation_split=0.02, epochs=400,
batch_size=my_batch_size,
class_weight=class_weight, shuffle=True,
callbacks=[reduce_lr, early_stop], verbose=0)
        if seed == 0:

```

```

        model.save('decarb.h5.new')
    val_loss = round(losshist.history.get('val_loss')[-1],5)
    val_acc = round(losshist.history.get('val_acc')[-1],5)
    valcostlist.append(losshist.history.get('val_loss')[-1])

valXSAlist.append(losshist.history.get('val_acc')[-1])
    print("loss = ", round(losshist.history.get('loss')[-1],4),
        "acc = ", round(losshist.history.get('acc')[-1],4),
        "val_loss = ", val_loss,
        "val_acc = ", val_acc)
    loss_and_metrics = model.evaluate(Xtest, Ytest,
batch_size=16, verbose=0)
    XSA = int(100000*loss_and_metrics[1])/1000
    cost = int(100000*loss_and_metrics[0])/100000
    print("")
    print("loss for test set ", cost, " accuracy for
test set: ", XSA,"%")
    costlist.append(cost)
    XSAlist.append(XSA)
    print("running", seed, " ",
round(np.mean(XSAlist),4),"% layers
",str(sys.argv[1:]))
    print("valRunning", seed, "
",100*round(np.mean(valXSAlist),4),"%
cost",round(np.mean(valcostlist),4),"% arguments
",str(sys.argv[1:]))
    rounded_predictions =
to_categorical(model.predict_classes(Xtest,
batch_size=16, verbose=1), num_classes=3)
    print(" ")
    print("shape of rounded
predictions",rounded_predictions.shape,"shape of
Ytest", Ytest.shape)
    print("predictions by
category:",int(np.sum(rounded_predictions[:,0])),

int(np.sum(rounded_predictions[:,1])),int(np.sum(rou
nded_predictions[:,2])))
    print("test
percentage",round(100*np.sum(rounded_predictions[
:,0])/Ytest.shape[0],2),

round(100*np.sum(rounded_predictions[:,1])/Ytest.s
hape[0],2),

round(100*np.sum(rounded_predictions[:,2])/Ytest.s
hape[0],2))

    total_correct = int(np.sum(Ytest *
rounded_predictions))

```

```

    print("total in test set",Ytest.shape[0],"Total
correct",total_correct," Percent
",round(100*total_correct/Ytest.shape[0],2))
    cm =
confusion_matrix(Ytest,rounded_predictions)
    print(" Confusion matrix")
    print(" R L Too")
    print(cm)
    print(" ")
    print("predictions for outside test array")
    outside_rounded_predictions =
to_categorical(model.predict_classes(Xoutside_test_a
rray, batch_size=16, verbose=1), num_classes=3)
    print(" ")
    print("shape of outside rounded
predictions",outside_rounded_predictions.shape,"sha
pe of
Youtside_test_array",Youtside_test_array.shape)
    print("outside predictions by
category:",int(np.sum(outside_rounded_predictions[
:,0])),

int(np.sum(outside_rounded_predictions[:,1])),int(np.
sum(outside_rounded_predictions[:,2])))
    print("outside
percentage",round(100*np.sum(outside_rounded_pre
dictions[:,0])/Youtside_test_array.shape[0],2),

round(100*np.sum(outside_rounded_predictions[:,1])
/Youtside_test_array.shape[0],2),

round(100*np.sum(outside_rounded_predictions[:,2])
/Youtside_test_array.shape[0],2))

    outside_total_correct =
int(np.sum(Youtside_test_array *
outside_rounded_predictions))

outsideAccList.append(100*outside_total_correct/Yo
utside_test_array.shape[0])
    print ("total in outside
set",Youtside_test_array.shape[0],"Total
correct",outside_total_correct," percent correct",
100*outside_total_correct/Youtside_test_array.shape
[0]," ",m)
    cm =
confusion_matrix(Youtside_test_array,outside_roun
ed_predictions)
    print("confusion matrix for outside test")
    print(" R L Too")
    print(cm)
    K.clear_session()
    toc = time.time()
    print("")
    print("time so far",round(toc-tic,2))

```

```

print("-----")
-----",str(seed) * 10)
print(" ")
print(" ")
print("average outside percentage
",round(np.mean(outsideAccList),4)," ",m)
print("Test Ave Acc
",round(np.mean(XSAList),2),"% Test Ave cost
",round(np.mean(costlist),4)," Test Med Acc
",round(np.median(XSAList),4),"% layers
",str(sys.argv[1:]))
print("Val Ave Acc
",100*round(np.mean(valXSAList),4),"% Val Ave
cost ",round(np.mean(valcostlist),4)," Val Med Acc
",100*round(np.median(valXSAList),4),"% layers
",str(sys.argv[1:]))
toc = time.time()
print("wall run time after loading",round(toc-tic,2))
progbrainpacetone
# Get a list of all of the trajectory results
grep XXX n??/dynfollowfile > temp589
echo "collected XXX from dynfollowfiles into
temp589. Here is the line count:"
wc temp589
date
echo ""

# Get a list of all of the energy results into temp592
grep e n??/Echeck > temp592
echo "completed Echeck collection in temp592"
wc temp592
echo

# Organize the energies into a file temp593
awk 'BEGIN {
dirstart=100
dirend=999
}
/trajectory/ {isomernumber=$3}
/potential/ {PE=$5; KE=$10; TE=$12}
/desired/ {
dirnum=substr($1,2,3)
maxres[dirnum]=isomernumber
DE=$4
error[dirnum,isomernumber]=TE-DE
PEarr[dirnum,isomernumber]=PE;
KEarr[dirnum,isomernumber]=KE;
TEarr[dirnum,isomernumber]=TE;
DEarr[dirnum,isomernumber]=DE;
# Note - the KE here is the KE from modes and does
not include rotational energy - it is ultimately gotten
by prog2ndpoint from geoPlusVel
# and was chosen because it makes for easy math.
# The PE here is observed, not desired! - not a fit
with an unrun number
}

```

```

END {
for (d=dirstart;d<=dirend;d++) {
for (i=1;i<=maxres[d];i++) {
if (PEarr[d,i]>0) print
d,i,error[d,i],PEarr[d,i],KEarr[d,i],TEarr[d,i],DEarr[d,
i]
}
}
}' temp592 > temp593
echo "completed organization of energies into
temp593"
wc temp593
echo ""

# Organize the results including director and
isomernumber and time for each direction. The
directory and isomernumber will be used
# to associate the results with a particular geoPlusVel
awk 'BEGIN {
dirstart=100
dirend=899
}
{
dirnum=substr($1,2,3)
direction=1
if ((dirnum==olddirnum) &&
($7==oldisomernumber)) direction=2
if ($7>0) {
isomernumber=$7
maxres[dirnum]=isomernumber
result[dirnum,isomernumber,direction]=$28
time[dirnum,isomernumber,direction]=$5
}
olddirnum=dirnum;oldisomernumber=isomernumber
if (FILENAME=="temp593") {
error[$1,$2]=$3; PEarr[$1,$2]=$4;
KEarr[$1,$2]=$5; TEarr[$1,$2]=$6;
DEarr[$1,$2]=$7
}
}
END {
for (d=dirstart;d<=dirend;d++) {
for (i=1;i<=maxres[d];i++) {
if (time[d,i,2]>0) print
d,i,time[d,i,1],time[d,i,2],result[d,i,1],result[d,i,2],err
or[d,i],PEarr[d,i],KEarr[d,i],TEarr[d,i],DEarr[d,i]
if ((error[d,i]>10) || (error[d,i]<-10)) print
d,i,1,1,"bad","bad",error[d,i],PEarr[d,i],KEarr[d,i],TE
arr[d,i],DEarr[d,i]
}
}
}' temp589 temp593 > temp590
echo "summarized the results in temp590. Line
count:"
wc temp590
date

```



```

print "<50 51-100 101-150 151-200 201-250 251-300
301-350 351-400 401-450 >450"
print prodaT50," ",prodaT100," ",prodaT150,"
",prodaT200," ",prodaT250," ",prodaT300,"
",prodaT350," ",prodaT400," ",prodaT450,"
",prodaTG
print "Prod B times"
print "<50 51-100 101-150 151-200 201-250 251-300
301-350 351-400 401-450 >450"
print prodbT50," ",prodbT100," ",prodbT150,"
",prodbT200," ",prodbT250," ",prodbT300,"
",prodbT350," ",prodbT400," ",prodbT450,"
",prodbTG
print "Recrossing times"
print "<50 51-100 101-150 151-200 201-250 251-300
301-350 351-400 401-450 >450"
print toT50," ",toT100," ",toT150," ",toT200,"
",toT250," ",toT300," ",toT350," ",toT400,"
",toT450," ",toTG
}' temp590

```

```

# create a big full that combines all of the
geoRecords, with an extra label that includes the
directory name
awk '
/trajectory/ {printf("%s ",substr(FILENAME,2,3));
{print}' n??*/geoRecord > temp591
echo "Gathered geoRecords"
date
echo ""

```

```

# prep for output files
rm -f temp*.csv

```

```

# combine the results summary in temp590 and the
geoRecords in temp591 to output files for bringing in
to neural nets
awk 'BEGIN {
totalline=0
dirstart=100
dirend=999
CCrmax=0;CCrmin=10;CClmax=0;CClmin=10;CH
max=0;CHmin=10;CCrdotmax=0;CCrdotmin=10;CC
ldotmax=0;CCldotmin=10;CHdotmax=0;CHdotmin=
10
CCraimax=0; CCraimin=10; CClaimmax=0;
CCclaimmin=10; CHaimmax=0; CHaimmin=10
}
/trajectory/ {
dirnum=$1
isomernumber=$2
linenumber=0
maxres[dirnum]=isomernumber
badgeo=0
}

```

```

{
totalline++
linenumber++
if ((linenumber>=3) && (linenumber<=12)) {
if ($2==0) badgeo=1
if ($2=="nan") badgeo=1
i=linenumber-2
weight[i]=$5
atSym[i]=$1
for (j=1;j<=3;j++) {
geoArr[i,j]=$i+j
}
}
if ((linenumber>=13) && (linenumber<=22)) {
i=linenumber-12
velMult=10
for (j=1;j<=3;j++) {
velArr[i,j]=$j
aimGeo[i,j]=geoArr[i,j]+velMult*velArr[i,j]
}
}
}
# now extract any key geometry and velocity
parameters
#####
if ((badgeo==0) && (linenumber==23)) {
#CCr
delX=geoArr[1,1]-geoArr[6,1];delY=geoArr[1,2]-
geoArr[6,2];delZ=geoArr[1,3]-geoArr[6,3];
velX=velArr[1,1]-velArr[6,1];velY=velArr[1,2]-
velArr[6,2];velZ=velArr[1,3]-velArr[6,3];
delaimX=aimGeo[1,1]-
aimGeo[6,1];delaimY=aimGeo[1,2]-
aimGeo[6,2];delaimZ=aimGeo[1,3]-aimGeo[6,3];
distatoms=(delX^2+delY^2+delZ^2)^.5
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.5
CCr[dirnum,isomernumber]=distatoms
CCraim[dirnum,isomernumber]=distaim
if (distatoms==0) print
FILENAME,"totalline",totalline,"zero problem here"
if (distatoms!=0) {
unitX=delX/distatoms;unitY=delY/distatoms;;unitZ=
delZ/distatoms;
}
CCrdot[dirnum,isomernumber]=-
25*(unitX*velX+unitY*velY+unitZ*velZ)
if (CCrdot[dirnum,isomernumber]>CCrdotmax)
CCrdotmax=CCrdot[dirnum,isomernumber]; if
(CCrdot[dirnum,isomernumber]<CCrdotmin)
CCrdotmin=CCrdot[dirnum,isomernumber];
if (CCr[dirnum,isomernumber]<CCrmin)
CCrmin=CCr[dirnum,isomernumber];if
(CCr[dirnum,isomernumber]>CCrmax)
CCrmax=CCr[dirnum,isomernumber];
}
}

```

```

if (CCraim[dirnum,isomernumber]<CCraimmin)
CCraimmin=CCraim[dirnum,isomernumber];if
(CCraim[dirnum,isomernumber]>CCraimax)
CCraimax=CCr[dirnum,isomernumber];
#CCI
delX=geoArr[1,1]-geoArr[3,1];delY=geoArr[1,2]-
geoArr[3,2];delZ=geoArr[1,3]-geoArr[3,3];
velX=velArr[1,1]-velArr[3,1];velY=velArr[1,2]-
velArr[3,2];velZ=velArr[1,3]-velArr[3,3];
delaimX=aimGeo[1,1]-
aimGeo[3,1];delaimY=aimGeo[1,2]-
aimGeo[3,2];delaimZ=aimGeo[1,3]-aimGeo[3,3];
dstatoms=(delX^2+delY^2+delZ^2)^.5
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.5
CCI[dirnum,isomernumber]=dstatoms
CCLAIM[dirnum,isomernumber]=distaim
if (dstatoms==0) print dirnum, isomernumber

```

```

unitX=delX/dstatoms;unitY=delY/dstatoms;;unitZ=
delZ/dstatoms;
CCldot[dirnum,isomernumber]=-
25*(unitX*velX+unitY*velY+unitZ*velZ)
if (CCldot[dirnum,isomernumber]>CCldotmax)
CCldotmax=CCldot[dirnum,isomernumber]; if
(CCldot[dirnum,isomernumber]<CCldotmin)
CCldotmin=CCldot[dirnum,isomernumber];
if (CCI[dirnum,isomernumber]<CCLmin)
CCLmin=CCI[dirnum,isomernumber];if
(CCI[dirnum,isomernumber]>CCLmax)
CCLmax=CCI[dirnum,isomernumber];
if (CCLAIM[dirnum,isomernumber]<CCLAIMmin)
CCLAIMmin=CCLAIM[dirnum,isomernumber];if
(CCLAIM[dirnum,isomernumber]>CCLAIMmax)
CCLAIMmax=CCLAIM[dirnum,isomernumber];
#CH
delX=geoArr[6,1]-geoArr[7,1];delY=geoArr[6,2]-
geoArr[7,2];delZ=geoArr[6,3]-geoArr[7,3];
velX=velArr[6,1]-velArr[7,1];velY=velArr[6,2]-
velArr[7,2];velZ=velArr[6,3]-velArr[7,3];
delaimX=aimGeo[6,1]-
aimGeo[7,1];delaimY=aimGeo[6,2]-
aimGeo[7,2];delaimZ=aimGeo[6,3]-aimGeo[7,3];
dstatoms=(delX^2+delY^2+delZ^2)^.5
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.5
CH[dirnum,isomernumber]=dstatoms
CHaim[dirnum,isomernumber]=distaim

```

```

unitX=delX/dstatoms;unitY=delY/dstatoms;;unitZ=
delZ/dstatoms;
CHdot[dirnum,isomernumber]=-
25*(unitX*velX+unitY*velY+unitZ*velZ)
if (CHdot[dirnum,isomernumber]>CHdotmax)
CHdotmax=CHdot[dirnum,isomernumber]; if
(CHdot[dirnum,isomernumber]<CHdotmin)
CHdotmin=CHdot[dirnum,isomernumber];

```

```

if (CH[dirnum,isomernumber]<CHmin)
CHmin=CH[dirnum,isomernumber];if
(CH[dirnum,isomernumber]>CHmax)
CHmax=CH[dirnum,isomernumber];
if (CHaim[dirnum,isomernumber]<CHaimmin)
CHaimmin=CHaim[dirnum,isomernumber];if
(CHaim[dirnum,isomernumber]>CHaimmax)
CHaimmax=CHaim[dirnum,isomernumber];
}
if ((badge==0) && (linenumber>=23) &&
(linenumber<=46)) {
mv[dirnum,isomernumber,linenumber]=$4/3e13;
mdis[dirnum,isomernumber,linenumber]=$5
}
if (FILENAME=="temp590") {
# By the time we get here we should be done with
all of the extractions from geoRecords

```

```

d=$1;i=$2;time[d,i,2]=$3;time[d,i,1]=$4;result[d,i,1]
=$5;result[d,i,2]=$6;error[d,i]=$7;PEarr[d,i]=$8;KEa
rr[d,i]=$9;TEarr[d,i]=$10;DEarr[d,i]=$11;
answer[d,i]=999
if (($5=="RIGHT") && ($6=="SM")) {
answer[d,i]=", 1, 0, 0"
}
if (($5=="LEFT") && ($6=="SM")) {
answer[d,i]=", 0, 1, 0"
}
if (($5=="Too") && ($6=="SM")) {
answer[d,i]=", 0, 0, 1"
}
if (answer[d,i]==999) countunassigned++
if (answer[d,i]!=999) {
for (timebin=50;timebin<=550;timebin+=50) {
filestring="tempbin"timebin".csv"
if (time[d,i,2]<timebin) {
for (disline=23;disline<=46;disline++) {
printf("%.5f, ",mv[d,i,disline]) >> filestring
}
for (disline=24;disline<=46;disline++) {
printf("%.6f, ",mdis[d,i,disline]) >>
filestring
}
printf("%.5f, %.5f, %.5f, %.5f, %.5f, %.5f, ",
CCr[d,i], CCI[d,i], CH[d,i], CCrdot[d,i], CCldot[d,i],
CHdot[d,i]) >> filestring
printf("%.5f, %.5f, %.5f, ", CCraim[d,i],
CCLAIM[d,i], CHaim[d,i]) >> filestring
printf("%.3f, %.3f, %.3f, %.3f, %.3f",
error[d,i], PEarr[d,i], KEarr[d,i], TEarr[d,i],
DEarr[d,i]) >> filestring
print answer[d,i], "time[d,i,2]", "d", "i >>
filestring
}
}
oldanswer=answer[d,i]

```

```

    }
  }
}
END {
print "unassigned",countunassigned
print
"CCrmax,CCrmin,CClmax,CClmin,CHmax,CHmin"
print
CCrmax,CCrmin,CClmax,CClmin,CHmax,CHmin
print "CCrdotmax,CCrdotmin"
print CCrdotmax,CCrdotmin
print "CCldotmax,CCldotmin"
print CCldotmax,CCldotmin
print "CHdotmax,CHdotmin"
print CHdotmax,CHdotmin
print "CCraimax, CCraimin"
print CCraimax, CCraimin
print "CClaimmax, CClaimmin"
print CClaimmax, CClaimmin
print "CHaimmax, CHaimmin"
print CHaimmax, CHaimmin
}' temp591 temp590
echo "finished first pass at creating csv files"
date
echo ""

#rm -f temp589 temp590 temp591
module load Anaconda/3-5.0.0.1
#module load myPython/3.5.2-intel-2017A &&
source /scratch/user/vroytman/myPython/3.5.2-intel-
2017A/bin/activate
module load numpy/1.14.1-foss-2017b-Python-3.6.3
#
wc *csv
sed -i '/0.00000, 0.00000, 0.00000, 0.00000/d' *.csv
mv tempbin500.csv test
python3.6 shuffle.py > tempbin500.csv
mv tempbin450.csv test
python3.6 shuffle.py > tempbin450.csv
mv tempbin400.csv test
python3.6 shuffle.py > tempbin400.csv
mv tempbin350.csv test
python3.6 shuffle.py > tempbin350.csv
mv tempbin300.csv test
python3.6 shuffle.py > tempbin300.csv
mv tempbin250.csv test
python3.6 shuffle.py > tempbin250.csv
mv tempbin200.csv test
python3.6 shuffle.py > tempbin200.csv
mv tempbin150.csv test
python3.6 shuffle.py > tempbin150.csv
mv tempbin100.csv test
python3.6 shuffle.py > tempbin100.csv
mv tempbin50.csv test
python3.6 shuffle.py > tempbin50.csv
wc *csv

```

### progdyn.conf for Groundhog

```

#This is the configuration file for PROGDYN. This
file is read by progdynstarterHP and
# the awk programs proggenHP, prog1stpoint,
prog2ndpoint, and progdynb.
#The programs won't read anything past the first
blank line,
#and this file must end with a blank line.
#The program has a number of default values but
they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for
unwanted options.
#The values here are read repeatedly and most can be
changed in the middle of running jobs
***The keywords are case sensitive. The following
keywords should always be defined:***
***method, charge, multiplicity, memory,
processors, title
*** method --The following word is copied exactly
to the gaussian input file.
method B2PLYP/6-31+G**
#To do a nonstandard route, make nonstandard 1.
For normal calcs, use nonstandard 0 or else leave it
out.
#Then make a file called "nonstandard" containing
the nonstandard route with no extra lines.
nonstandard 0
# NMRoptions As is NMRtype=1 will add a section
for an NMR calc at every NMRevery intervals. If
you want to combine the two use nonstandard
#NMRtype 1
#NMRmethod2 B97D/6-31G*
#NMRmethod LC-wPBE/6-31G*
#NMRmethod3 B3LYP/cc-pvtz
#NMRevery 4
#NMRrand 1
#NMRcc 1
#loadlimit 10.0
#geometry linear
rotationmode 1
*** method2 --The options here are restricted,
unrestricted, and read. restricted is the default
#If the method is U..., put unrestricted here and the
.com files will have in them guess=mix.
#If you put read here, the .com files will contain
guess=tcheck, which sometimes makes things faster,
sometimes not.
#The use of read requires a specifically defined
checkpoint file name using the keyword checkpoint.
method2 unrestricted
charge 1
multiplicity 2
#oniomchargemult 1 1

```

processors 4  
 \*\*\*\* memory --The following "word" is copied exactly to the gaussian input file after %mem=.  
 memory 6gb  
 \*\*\*\* killcheck and checkpoint -- You can use a specifically defined checkpoint file name by putting #the name after the keyword checkpoint. This is necessary if you use the read option with method2.  
 #Defined checkpoint names are an unnecessary modest hassle and if you do not want to bother, use  
 killcheck 1  
 killcheck 0  
 checkpoint g16.chk  
 \*\*\*\* diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a #file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"  
 #4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical calculations  
 diagnostics 0  
 \*\*\*\* title -- the title keyword must be followed by exactly four words  
 title acetonerad harm PLYPXPS 298dis2  
 \*\*\*\* initialdis -- 0 (default) turns off displacement of the normal modes, so that all trajectories start from the same place  
 # and only the energies and signs of the motion in the modes are randomized  
 # 1 gives a flat distribution of displacements where all of the possible values are equally likely  
 # 2 (recommended) gives a QM-like gaussian distribution of displacements, so that displacements in the middle are more likely that  
 # those at the end by 1/e  
 initialdis 2  
 \*\*\*\* timestep -- this is the time between points in the trajectory. Typical values would be 1E-15 or 0.5E-15 or 0.25E-15  
 timestep 1E-15  
 \*\*\*\* scaling -- this lets you scale the gaussian frequencies by a constant  
 scaling 1.0  
 temperature 298.15  
 \*\*\*\* thermostat 1 puts in a damping factor so as to bring the classical temperature toward the desired temperature.  
 \*\*\*\* use a thermostatmult between 0.95 and 1, typically 0.995, so the damping happens slowly - otherwise there will be  
 \*\*\*\* overadjustment in response to random variation  
 \*\*\*\* the thermostat is not exact. The second traj point ignores this, so it only applies to later points handled by progdynb.  
 #thermostat 1  
 #thermostatmult 0.999

\*\*\*\* method3, method4, method5, and method6 --  
 These keywords let you add extra lines to the gaussian input file.  
 #method3 and method4 add lines at the top of the input after the lines defining the method, and #this is useful to implement things like the iop for mPW1k  
 #method5 and method6 add lines after the geometry, after a blank line of course  
 #only a single term with no spaces can be added, one per method line. Here are some examples to uncomment if needed  
 #method3 IOp(3/76=0572004280)  
 #method3 scrf=(pcm,solvent=ethanol)  
 #method3 scrf=(solvent=chloroform)  
 #add the line below with big structures to get it to put out the distance matrix and the input orientation  
 #method4 empiricaldispersion=gd3  
 #method3 scf=(conver=5)  
 #method4 iop(3/124=3)  
 #method4 scrf=(pcm,solvent=dmsol,read)  
 #method5 radii=bondi  
 #method6  
 \*\*\*\* methodfile -- This keyword lets you add more complicated endings to gaussian input files #such as a gen basis set. Put after the keyword the number of lines in a file you create called #methodfile that contains the test you want to add to the end of the gaussian input  
 methodfile 0  
 \*\*\*\* numimag --This tells the program the number of imaginary frequencies in the starting structure.  
 #if 0, treats as ground state and direction of all modes is random  
 #if 1, motion along the reaction coordinate will start out in the direction defined by searchdir  
 #if 2, only lowest freq will go direction of searchdir and other imag mode will go in random direction  
 numimag 1  
 \*\*\*\* searchdir -- This keyword says what direction to follow the mode associated with the imaginary frequency.  
 #The choices are "negative" and "positive". Positive moves in the direction defined in the gaussian frequency calculation  
 #for the imaginary frequency, while negative moves in the opposite direction. The correct choice can be made either  
 #by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.  
 searchdir positive  
 \*\*\*\* classical -- for quasiclassical dynamics, the default, use 0. for classical dynamics, use 1  
 #if there are no normal modes and the velocities are to be generated from scratch, use classical 2  
 classical 0



```

**** DRP, saddlepoint, and maxAtomMove --to run
a DRP use 'DRP 1' in the line below, otherwise leave
it at 0 or comment it out
#the treatment of starting saddlepoints is not yet
implemented so use saddlepoint no
#if DRP shows oscillations then decrease
maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
**** cannonball -- The program can "fire" a
trajectory from a starting position toward a particular
target, such as toward
#a ts. To use this, make a file cannontraj with
numAtom lines and three numbers per line that
defines the vector
#for firing the trajectory, relative to the starting
geometry's standard orientation. The number
following cannonball sets
#the extra energy being put into the structure in
kcal/mol
#cannonball 10
**** keepevery --This tells the program how often to
write the gaussian output file to file dyn, after the
first two points.
#Use 1 for most dynamics to start with, but use a
higher number to save on disk space or molden
loading time.
keepevery 9999
**** highlevel --For ONIOM jobs, the following line
states the number of highlevel atoms,
#which must come before the medium level atoms.
Use some high value such as 999 if not using
ONIOM
highlevel 9999
**** fixedatom1, fixedatom2, fixedatom3, and
fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and
messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of
fixing three distances, not just two
#in current form fixed atoms only are meant to work
with no displacements, that is, initialdis=0
#fixedatom1 16
#fixedatom2 1
#fixedatom3 4
#fixedatom4 20
#applyforce 1 lets one push atoms together or apart -
a positive force pushes them together
#format is applyforce force - with the units on force
the same as in the Gaussian output file
#applyforce 2 or 3 or 4 applies a polynomial force
centered at dist0. 2 is just harmonic, 3 is second
order, 4 is third order
#format is applyforce 4 forcecoefficient dist0
forcecoefficient2 forcecoefficient3

```

```

#then use afatoms to chose the atoms with format
afatoms firstatom secondatom [additional atoms]
#applyforce 2 0.1 2.1
#afatoms 16 1 2 3 4 5 6
#applyforceB 2 0.01 5.2
#afatomsB 8 15
#applyforceC 2 0.01 5.2
#afatomsC 8 15
#zeroatom pushes the numbered atom toward the
origin with a small harmonic potential - good with
boxon when you want to keep the reaction in the
center
#zeroatom 16
**** boxon and boxsize - With boxon 1, a cubic box
is set such that atoms that reach the edge
#are reflected back toward the middle. Useful for
dynamics with solvent molecules. This is a crude
#implementation that is ok for a few thousand
femtoseconds but will not conserve energy long term.
#Set the box size so as to fit the entire initial
molecule but not have too much extra room.
#The dimensions of the box are two times the
boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15
x 15 angstroms
#boxon 1
#boxsize 11.2
**** sphereon and spheresize and sphereforce - uses
a force to push atoms within a sphere. notice that if
the atom is far outside of
#the sphere then the force is large unless sphereforce
is set small
#sphereon 1
#spheresize 12.9
#sphereforce .01
#setting a value for empiricaldispersion sets its s6
value with the Grimme 2006 algorithm. Default is 0,
with no empiricaldispersion
#empiricaldispersion 1.0
**** displacements -- This keyword lets you set the
initialdis of particular modes by using a series of
lines of the format
# displacements NumberOfMode
InitialDisForThatMode, as in the example below.
You should be able to do as many of these as you like
# you might consider this for rotations where a
straight-line displacement goes wrong at large
displacements
# The choices for InitialDisForThatMode are 0, 1, 2,
and 10, where 10 does the same thing as 0 but is
maintained for now because
# a previous version of the program had a bug that
made 0 not work.
#displacements 2 0
#displacements 3 0
#displacements 4 0
#displacements 5 0

```

```

#displacements 6 0
#displacements 7 0
#displacements 8 0
#displacements 9 0
#displacements 10 0
**** etolerance --This sets the allowable difference
between the desired energy in a trajectory and the
actual
#energy, known after point 1 from the potential
energy + the kinetic energy in the initial velocities.
#The unit is kcal/mol and 1 is a normal value for
mid-sized organic systems. For very large and floppy
molecules, a larger value
#may be needed, but the value must stay way below
the average thermal energy in the molecule (not
counting zpe).
#If initialdis is not 0 and few trajectories are being
rejected, decrease the value.
etolerance 1
**** controlphase --It is sometimes useful to set the
phase of particular modes in the initialization of
trajectories.
#The format is controlphase
numberOfModeToControl positive or controlphase
numberOfModeToControl negative.
#controlphase 2 positive
**** damping -- The damping keyword lets you add
or subtract energy from the system at each point, by
multiplying the velocities
#by the damping factor. A damping of 1 has no
effect, and since you mostly want to change the
energy slowly, normal values range
#from 0.95 to 1.05. The use of damping lets one do
simulated annealing - you add energy until the
structure is moving enough
#to sample the kinds of possibilities you are
interested in, then you take away the energy slowly.
damping 1.000
#at a damping of .9995, the energy is cut in half in
693 points
**** reversiontraj --This keyword sets the trajectories
so that both directions from a transition state are
explored.
reversiontraj true
#for groundhog put in a value of interesting between
50 and 99
interesting 75
##anharmonic corrections
readdzdm
anharmonicmode 2 3.974 0.003
anharmonicmode 3 27.523 -61.050
anharmonicmode 4 228.487 2.733
anharmonicmode 5 216.999 1.869
anharmonicmode 6 82.100 -1.578
anharmonicmode 7 40.600 0.024
anharmonicmode 8 151.893 -98.993
anharmonicmode 9 55.244 -0.077
anharmonicmode 10 63.254 6.513
anharmonicmode 11 56.252 0.080
anharmonicmode 12 318.281 -4.225
anharmonicmode 13 134.261 25.182
anharmonicmode 14 101.647 -9.172
anharmonicmode 15 176.666 32.604
anharmonicmode 16 110.423 0.530
anharmonicmode 17 94.454 0.031
anharmonicmode 18 322.872 518.972
anharmonicmode 19 175.271 75.024
anharmonicmode 20 414.643 -492.738
anharmonicmode 21 461.456 1.610
anharmonicmode 22 447.724 629.533
anharmonicmode 23 492.965 781.025
anharmonicmode 24 515.274 2.861
#updated Aug 9, 2007 to include the possibility of
classical dynamics by the keyword classical
#updated Jan 2008 to include fixed atoms, ONIOM
jobs, keepvery, and box size
#update Feb 2008 to include methodfile parameter
# updated Nov 2008 to allow for start without an
initial freq calc using classical = 2
# update Aug 2010 to include etolerance, damping
controlphase and reversiontraj

```

```

progmakeline
#!/bin/awk
BEGIN {
}
/trajectory/ {
dirnum=$1
isomernumber=$2
linenumber=0
badgeo=0
}
{
totalline++
linenumber++
if ((linenumber>=3) && (linenumber<=12)) {
if ($2==0) badgeo=1
if ($2=="nan") badgeo=1
i=linenumber-2
weight[i]=$5
atSym[i]=$1
for (j=1;j<=3;j++) {
geoArr[i,j]=$1+j
}
}
if ((linenumber>=13) && (linenumber<=22)) {
i=linenumber-12
velMult=10
for (j=1;j<=3;j++) {
velArr[i,j]=$j
aimGeo[i,j]=geoArr[i,j]+velMult*velArr[i,j]
}
}
# now extract any key geometry and velocity
parameters
if ((badgeo==0) && (linenumber==23)) {
# CCr
delX=geoArr[1,1]-
geoArr[6,1];delY=geoArr[1,2]-
geoArr[6,2];delZ=geoArr[1,3]-geoArr[6,3];
velX=velArr[1,1]-
velArr[6,1];velY=velArr[1,2]-
velArr[6,2];velZ=velArr[1,3]-velArr[6,3];
delaimX=aimGeo[1,1]-
aimGeo[6,1];delaimY=aimGeo[1,2]-
aimGeo[6,2];delaimZ=aimGeo[1,3]-
aimGeo[6,3];
distatoms=(delX^2+delY^2+delZ^2)^.5
}
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.
5
CCr[dirnum,isomernumber]=distatoms
if (distatoms>4) print dirnum, isomernumber
CCraim[dirnum,isomernumber]=distaim

```

```

if (distatoms==0) print
FILENAME,"totalline",totalline,"zero problem
here"
if (distatoms!=0) {
unitX=delX/distatoms;unitY=delY/distatoms;;u
nitZ=delZ/distatoms;
}
CCrdot[dirnum,isomernumber]=-
25*(unitX*velX+unitY*velY+unitZ*velZ)
#CCI
delX=geoArr[1,1]-
geoArr[3,1];delY=geoArr[1,2]-
geoArr[3,2];delZ=geoArr[1,3]-geoArr[3,3];
velX=velArr[1,1]-
velArr[3,1];velY=velArr[1,2]-
velArr[3,2];velZ=velArr[1,3]-velArr[3,3];
delaimX=aimGeo[1,1]-
aimGeo[3,1];delaimY=aimGeo[1,2]-
aimGeo[3,2];delaimZ=aimGeo[1,3]-
aimGeo[3,3];
distatoms=(delX^2+delY^2+delZ^2)^.5
}
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.
5
CCI[dirnum,isomernumber]=distatoms
CClaim[dirnum,isomernumber]=distaim
if (distatoms==0) print dirnum, isomernumber
unitX=delX/distatoms;unitY=delY/distatoms;;u
nitZ=delZ/distatoms;
CCldot[dirnum,isomernumber]=-
10*(unitX*velX+unitY*velY+unitZ*velZ)
#CH
delX=geoArr[6,1]-
geoArr[7,1];delY=geoArr[6,2]-
geoArr[7,2];delZ=geoArr[6,3]-geoArr[7,3];
velX=velArr[6,1]-
velArr[7,1];velY=velArr[6,2]-
velArr[7,2];velZ=velArr[6,3]-velArr[7,3];
delaimX=aimGeo[6,1]-
aimGeo[7,1];delaimY=aimGeo[6,2]-
aimGeo[7,2];delaimZ=aimGeo[6,3]-
aimGeo[7,3];
distatoms=(delX^2+delY^2+delZ^2)^.5
}
distaim=(delaimX^2+delaimY^2+delaimZ^2)^.
5
CH[dirnum,isomernumber]=distatoms
CHaim[dirnum,isomernumber]=distaim
unitX=delX/distatoms;unitY=delY/distatoms;;u
nitZ=delZ/distatoms;

```

```

    CHdot[dirnum,isomernumber]=-
    20*(unitX*velX+unitY*velY+unitZ*velZ)
  }
  if ((badgeo==0) && (linenumber>=23) &&
    (linenumber<=46)) {

    mv[dirnum,isomernumber,linenumber]=$4/3e13
  ;
    mdis[dirnum,isomernumber,linenumber]=$5
  }
}
/Total mode energy desired/ {
  DEarr[600,1]=$5
}
/KE initial from modes/ {
  KEarr[600,1]=$5
}
END {
d=600;i=1
answer[d,i]="0, 0, 0"
time[d,i,1]=2
for (disline=23;disline<=46;disline++) {
  printf("%.5f, ",mv[d,i,disline])
}
for (disline=24;disline<=46;disline++) {
  printf("%.5f, ",mdis[d,i,disline])
}
printf("%.5f, %.5f, %.5f, %.5f, %.5f, %.5f, ",
CCr[d,i], CCl[d,i], CH[d,i], CCrdot[d,i],
CCldot[d,i], CHdot[d,i])
printf("%.5f, %.5f, %.5f, ", CCraim[d,i],
CClaim[d,i], CHaim[d,i])
printf("%.3f, %.3f, %.3f, %.3f, %.3f, ",
error[d,i], PEarr[d,i], KEarr[d,i], TEarr[d,i],
DEarr[d,i])
print answer[d,i], "time[d,i,1]", "d", "i"
}

```