

**THEORETICAL COMPUTATIONS FOR RING-PUCKERING  
POTENTIAL ENERGY FUNCTIONS OF FLUOROCYCLOBUTANES**

An Undergraduate Research Scholars Thesis

by

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## ABSTRACT

Theoretical Computations for Ring-Puckering Potential Energy Functions of Fluorocyclobutanes

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Quantum chemistry computational methods have long been utilized to understand and calculate potential and kinetic energies of a system. MP2 ab initio method, based on the Møller-Plesset Perturbation Theory, has been used in this study to calculate the potential energy functions (PEFs) of fluorocyclobutane molecules. All possible substitutions of fluoride on the four-membered ring and their conformations have been investigated and the puckering angle and puckering coordinates of each molecule were calculated. The barrier to planarity and puckering coordinates were used to derive the PEFs. It was found that the angle strain has less an effect on the conformation of the molecules than the torsional forces, which makes the puckered conformation more favorable than the planar one. The expected symmetrical PEFs for selected molecules were calculated using a quartic equation relating both torsional forces and angle strain constants. Furthermore, the kinetic expansion function  $g(44)_x$  was calculated for the selected

symmetrical PEFs. The reduced mass was then used to obtain energy spacings of lower energy levels on the constructed PEFs. The results have shown agreement with experimental data, which indicated the applicability of this method to further understand other vibrational potential functions, including non-symmetrical PEFs.

## DEDICATION

*This thesis is dedicated to:*

*My Mom, Dad, and sisters; Lubna, Israa, and Rana, for always supporting me and providing advice, comfort, confidence boosts, and unconditional love throughout my life. I would not have been where I am today without you.*

*My friends Umut Aydemir and Basak Sagcan, who I shared many study sessions with, you have been there since the start of my chemistry journey and stuck around at the hardest times.*

*Professor David Russell, who provided me with endless guidance. You have been the mentor anyone eager to thrive wishes for.*

*And finally, Bridget, Chris, and Rey, the people I met here in College Station who made my experience at Texas A&M University more special.*

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### **Contributors**

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Thanks also go to my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience.

All work conducted for the thesis was completed by the student independently.

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## 1. INTRODUCTION

Ring-puckering vibrations of four-membered rings have been extensively studied over the past fifty years [1]. Ring-puckering coordinates have been used to predict the vibrational PEFs of these molecules. Initially, Bell [2] postulated that PEFs of the vibrations of out-of-plane molecules is proportional to fourth power of the displacement, based on Raman and IR spectroscopy methods. Laane has shown that the quartic equation (Eq. 1) is needed for the one-dimensional PEF (Eq. 1) [1, 3-14]. Laane has shown that the one-dimensional symmetrical potential energy function is well estimated using the one-dimensional quartic equation:

$$V(x) = ax^4 + bx^2 \quad (\text{Eq. 1})$$

where  $x$  is the ring-puckering coordinate, as defined in Figure 2.  $a$  and  $b$  coefficients are related to torsional forces and initial angle strain. The  $a$  coefficient is always positive. The  $b$  coefficient can be positive, which would result in a harmonic oscillator shaped PEF curve. It can also be negative, which would result in a double minimum PEF curve with an energy barrier equal to Equation 5 [15].

A symmetrical PEF is expected when the puckered-up energy is equivalent to the puckered-down energy of the molecule. A non-substituted cyclobutane molecule was shown to have a symmetrical PEF [16] (Figure 1)



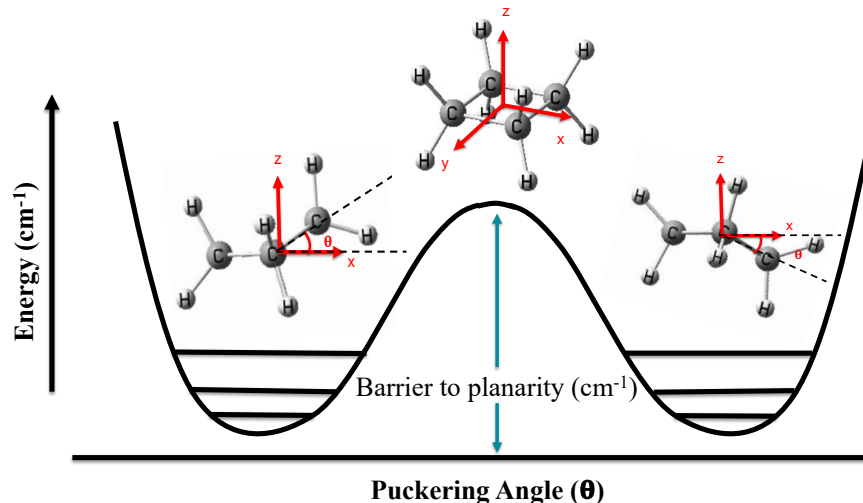


Figure 1: Symmetrical PEF of cyclobutane molecule.

The non-symmetrical PEF on the other hand is more complicated and can be better described using the cubic equation:

$$V(x) = ax^4 + bx^2 + cx^3 \quad (\text{Eq. 2})$$

where  $c$  is a constant and the additional term describes the energy difference between the puckered-up and the puckered-down conformations.

The kinetic energy expansion function,  $g_{44}(x)$ , can be calculated and used to solve the quantum mechanical problem (Eq. 3)

$$-\frac{\hbar^2}{2} \frac{\partial}{\partial x} g_{44}(x) \frac{\partial}{\partial x} + V(x) = E\Psi \quad (\text{Eq. 3})$$

In this work, theoretical PEFs for all possible molecules of fluorocyclobutanes will be calculated through a developed MP2 ab initio method based on Møller-Plesset perturbation theory, from the Hartree-Fock ab initio method. The results of this study will facilitate the understanding of how halogen substitutions on the cyclobutane molecules affect the torsional and angle strain, which determine molecular conformations.

## 1.1 Potential Energy Function

The low frequency, large amplitude non-rigid four- and five-membered rings have PEFs directly related to their puckering coordinates. Puckering coordinate is the distance between two diagonals of the four-membered ring (Figure 2)

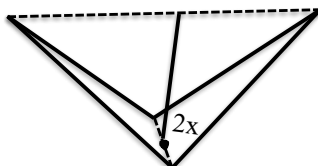


Figure 2: Puckering coordinates of a four-membered ring.

Puckering coordinates and puckering angle of the energy minima can be used to find the PEF. The barrier to planarity, the energy needed for a puckered molecule to reach a planar conformation, is used to find the constant a, subsequently finding constant b as follows:

$$x_{min} = \left(-\frac{b}{2a}\right)^{\frac{1}{2}} \text{ for } b < 0 \quad (\text{Eq. 4})$$

$$B = \frac{b^2}{4a} \quad (\text{Eq. 5})$$

$$a = \frac{B}{x_{min}^4} \quad (\text{Eq. 6})$$

Where  $x_{min}$  is the puckering coordinates of the energy minima and B is the barrier to planarity in  $\text{cm}^{-1}$ .

Non-symmetrical PEFs can be obtained using a best-fit cubic equation (Eq. 2) for the curve of the energy of a molecule as a function of the puckering coordinates.

## 1.2 Kinetic Expansion Function

It is well known that the reduced mass of a cyclic molecule changes as the puckering coordinates change. Numerical methods have been introduced by Malloy [17], and well

established and utilized by Laane [18,19], in order to obtain the reciprocal reduced mass as a function of puckering coordinates. The kinetic expansion function,  $g_{44}(x)$ , can thus be used to solve the quantum mechanical problem (Eq. 3).

### 1.3 MP2 ab initio method

MP ab initio method is a quantum chemistry computational method based on the Møller-Plesset Perturbation theory (MPPT) [20], which is a correction of the Hartree-Fock method. MPPT breaks up the Hamiltonian into two terms which describe the total energy, potential and kinetic, of the system [21].

$$H = H^0 + H' \quad (\text{Eq. 7})$$

The first Hamiltonian,  $H^0$  is unperturbed and is assumed to have known eigenfunctions and can be found as the sum of the Fock operators for each of the  $n$  electrons, where  $n$  is the number of electrons in the system

$$H^0 = \sum_{i=1,n} F(i) \quad (\text{Eq. 8})$$

The second Hamiltonian,  $H'$  is perturbed and is believed to be much smaller than the unperturbed Hamiltonian. The total Hamiltonian of the  $n$ -electrons and the unperturbed Hamiltonian, which is the sum of the Fock operators, describes the perturbation of MPPT.

MP2 is MPPT of the second order, which is a relatively simple and cost-effective method that includes electron correlation and energy corrections.

## 2. METHODS

### 2.1 Structure calculations

The theoretical computations were conducted utilizing Gaussian16 software. The geometrical structures of the molecules were calculated using MP2/cc-pVTZ ab initio computations. The puckering coordinates, along with the puckering angle, were obtained as shown in Figure 2 and Figure 3. The Energy of the planar conformation was calculated and the barrier to planarity was obtained.

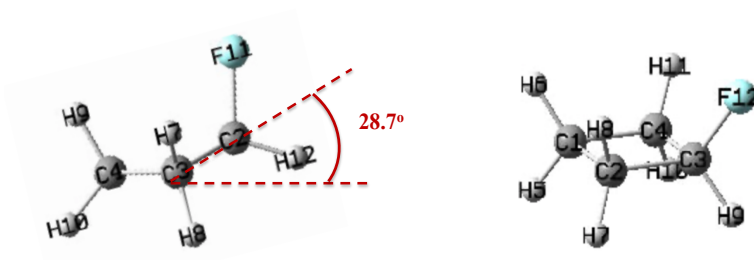


Figure 3: Puckering angle of fluorocyclobutane determination.

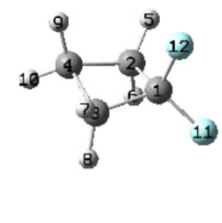
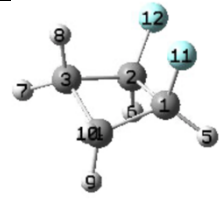
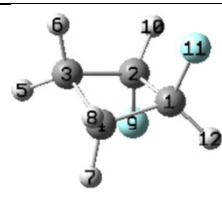
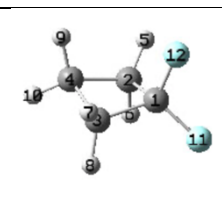
### 2.2 Kinetic energy calculations

The kinetic energy expansion functions were calculated using Laane RDMS4 program based on the vector approach [16, 17]. The bond distances, bond angles, and atomic masses were used in the input file from the computed planar conformation for selected molecules.

Energy levels and energy spacings were obtained using Meinander-Laane DA1OPTN program [22].

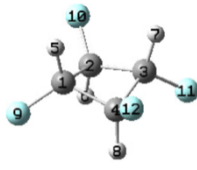
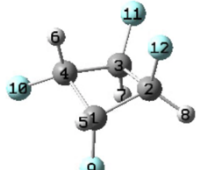
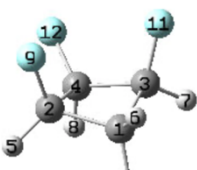
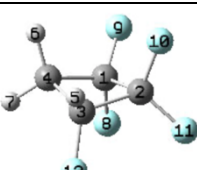
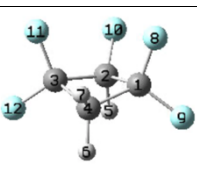
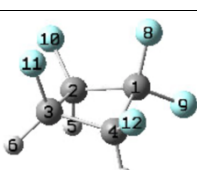
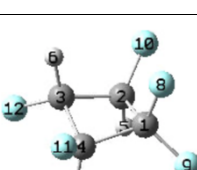
### 3. RESULTS

Both the minimum puckered conformation energy and the planar conformation energy were calculated in Hartree. The barrier to planarity was calculated in wavenumbers. The theoretical puckering coordinates, puckering angles, and barrier to planarity of fluorocyclobutane molecules are summarized in Table 1.

Molecule	Energy minima (Hartree)	Puckering coordinates (x)	Puckering angle	Planar Energy (Hartree)	Barrier to planarity (cm <sup>-1</sup> )	Structure
fluorocyclobutane	-255.973	0.137	28.7	-255.971	402.5	
cis-1,2-difluorocyclobutane	-355.101	0.160	33.7	-355.096	1194.4	
trans-1,2-difluorocyclobutane	-355.100	0.126	27.1	-355.100	21.7	
1,1-difluorocyclobutane	-355.121	0.133	28.2	-355.118	520.4	

cis-1,3-difluorocyclobutane	-355.106	0.147	31.1	-355.101	1105.3	
trans-1,3-difluorocyclobutane	-355.105	0.185	30.3	-355.101	800.4	
1,1,3-trifluorocyclobutane	-454.250	0.131	28.1	-454.247	658.9	
cis-1,2,3-trifluorocyclobutane	-454.222	0.141	24.2	-454.218	852.7	
trans-1,2,3-trifluorocyclobutane	-454.234	0.159	33.7	-454.226	1786.1	
1-trans-2,3-trifluorocyclobutane	-454.230	0.151	31.3	-454.223	697.1	
1,1,2-trifluorocyclobutane	-454.246	0.163	34.2	-454.242	1016.6	

1,1,2,2-tetrafluorocyclobutane	-553.385	0.134	28.0	-553.382	574.8	
cis-1,1,2,3-tetrafluorocyclobutane	-553.367	0.136	28.6	-553.363	839.9	
trans-1,1,2,3-tetrafluorocyclobutane	-553.373	0.189	31.6	-553.367	1276.0	
trans-1,1,2,4-tetrafluorocyclobutane	-553.368	0.146	30.7	-553.364	861.9	
cis-1,1,2,4-tetrafluorocyclobutane	-553.368	0.147	30.9	-553.363	1036.1	
1,1,3,3-tetrafluorocyclobutane	-553.390	0.096	20.6	-553.390	167.7	
cis-1,2,3,4-tetrafluorocyclobutane	-553.339	0.156	32.0	-553.333	1398.9	

trans-1,2,3,4-tetrafluorocyclobutane	-553.358	0.160	33.6	-553.349	2107.0	
trans-1,2-trans-3,4-tetrafluorocyclobutane	-553.350	0.163	34.1	-553.344	1399.4	
1-trans-2,3,4-tetrafluorocyclobutane	-553.344	0.134	28.4	-553.342	390.2	
1,1,2,2,3-pentafluorocyclobutane	-652.504	0.119	24.8	-652.503	344.1	
1,1,2,3,3-pentafluorocyclobutane	-652.508	0.125	26.7	-652.505	678.2	
cis-1,1,2,3,4-pentafluorocyclobutane	-652.482	0.148	30.8	-652.477	1187.1	
trans-1,1,2,3,4-pentafluorocyclobutane	-652.492	0.153	32.3	-652.485	1502.1	



1,1,2-trans-3,4-pentafluorocyclobutane	-652.485	0.134	28.0	-652.483	553.5	
1,1,2,2,3,3-hexafluorocyclobutane	-751.642	0.055	11.4	-751.640	347.9	
cis-1,1,2,2,3,4-hexafluorocyclobutane	-751.619	0.152	31.6	-751.616	624.8	
trans-1,1,2,2,3,4-hexafluorocyclobutane	-751.620	0.107	22.4	-751.620	44.8	
cis-1,1,2,3,3,4-hexafluorocyclobutane	-751.623	0.135	27.9	-751.618	888.2	
trans-1,1,2,3,3,4-hexafluorocyclobutane	-751.623	0.136	28.2	-751.620	519.5	
Hepptafluorocyclobutane	-850.756	0.172	36.0	-850.753	642.0	

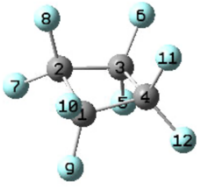
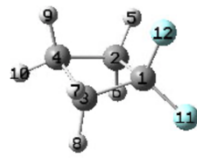
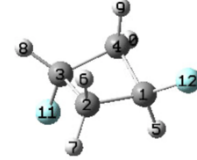
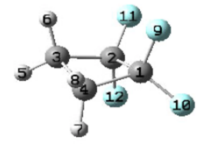
perfluorocyclobutane	-949.887	0.126	16.6	-949.885	346.8	
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Table 1: Ring-puckering coordinates, puckering angle, and the barrier to planarity of possible *m*-fluorocyclobutane molecules (*m* = 1-8).

For the molecules that are expected to have a symmetrical PEFs, their *a* and *b* values were calculated and summarized in Table 2. As described earlier, *b* constant is more related to the torsional forces while *a* constant is more related to the angle strain of the ring. Nevertheless, both constants contribute to both torsional forces and angle strain. As seen in Table 2, *b* values have a higher contribution to the conformation of the ring, due to the nature of the symmetrical PEF, (Eq. 1), which explains why the puckered conformation would result in a lower energy than the planar conformation.

Molecule	Barrier to Planarity (cm <sup>-1</sup> )	<i>a</i>	<i>b</i>	Structure
1,1-difluorocyclobutane	520.4	1.684E+06	-5.921E+04	
trans-1,3-difluorocyclobutane	800.4	6.777E+05	-4.658E+04	
1,1,2,2-tetrafluorocyclobutane	574.6	1.808E+06	-6.446E+04	

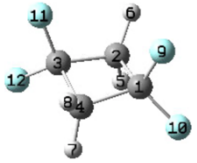
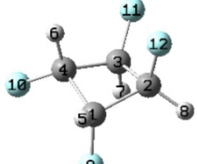
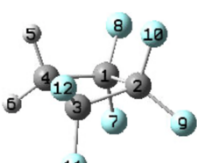
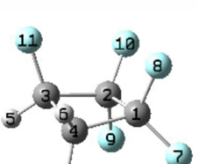
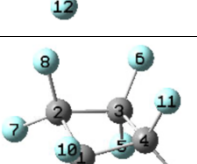
1,1,3,3-tetrafluorocyclobutane	167.5	1.983E+06	-3.644E+04	
trans-1,2-trans-3,4-tetrafluorocyclobutane	1399.4	1.989E+06	-1.055E+05	
1,1,2,2,3,3-hexafluorocyclobutane	347.9	3.733E+07	-2.279E+05	
trans-1,1,2,2,3,4-hexafluorocyclobutane	44.8	3.402E+05	-7.806E+03	
perfluorocyclobutane	346.8	1.382E+06	-4.378E+04	

Table 2: calculated  $a$  &  $b$  values of molecules with expected symmetrical potential energy functions.

The kinetic energy was calculated for the selected molecules in Figure 4. 1,1,3,3-tetrafluorocyclobutane (13TFCB) belongs to the symmetry group  $C_{2v}$ . 1,1,2,2,3,3-hexafluorocyclobutane (123HFCB) belong to the symmetry group  $C_s$ . Perfluorocyclobutane (PFCB) belongs to the symmetry group  $D_{2d}$ . The geometrical parameters of each structure were taken from the planar conformation.

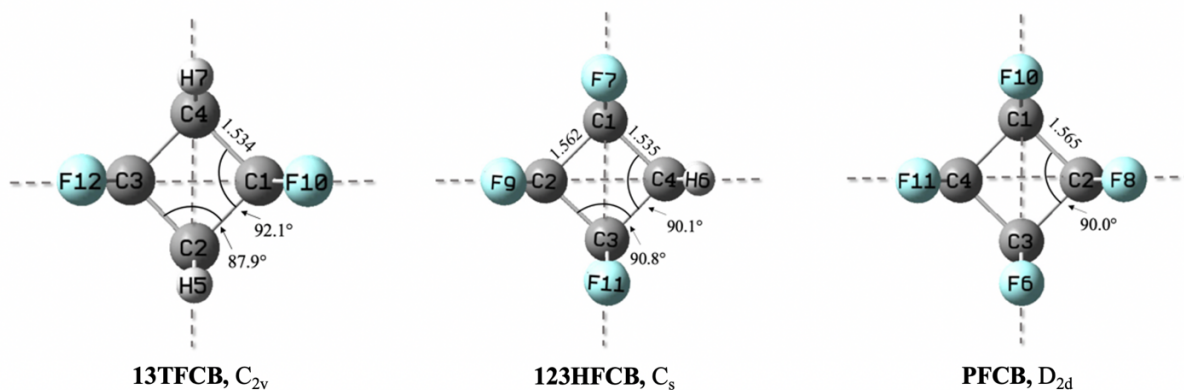


Figure 4: Calculated structural parameter of 13TF CB, 123HF CB, and PFCB in their planar energy conformation.

No previous experimental barriers of 13TF CB were found, but previous results of MP2-cc-pVTZ computations have shown to be sufficient enough to obtain a good estimation of the barrier and PEF [16]. The PEF is given in Equation 9.

$$V(x) = 1982752.4 x^4 - 36443.3 x^2 \quad (\text{Eq. 9})$$

The  $g_{44}(x)$  function was calculated as a function of puckering coordinates and fitted to the 6<sup>th</sup> order, given in Equation 10.

$$g_{44}(x) = 0.0016 - 0.0049 x^2 + 0.0127 x^4 - 0.0547 x^6 \quad (\text{Eq. 10})$$

The reduced mass obtained from Equation 10 was calculated to be 614.8 at  $x=0$ . This value was used to obtain the energy spacings related to the lower energy levels of this PEF (Figure 5).

The PEF has an inversion barrier of  $167.5 \text{ cm}^{-1}$ ,  $x_{\min} = \pm 0.096$  and  $\theta_{\min} = \pm 20.6^\circ$ .

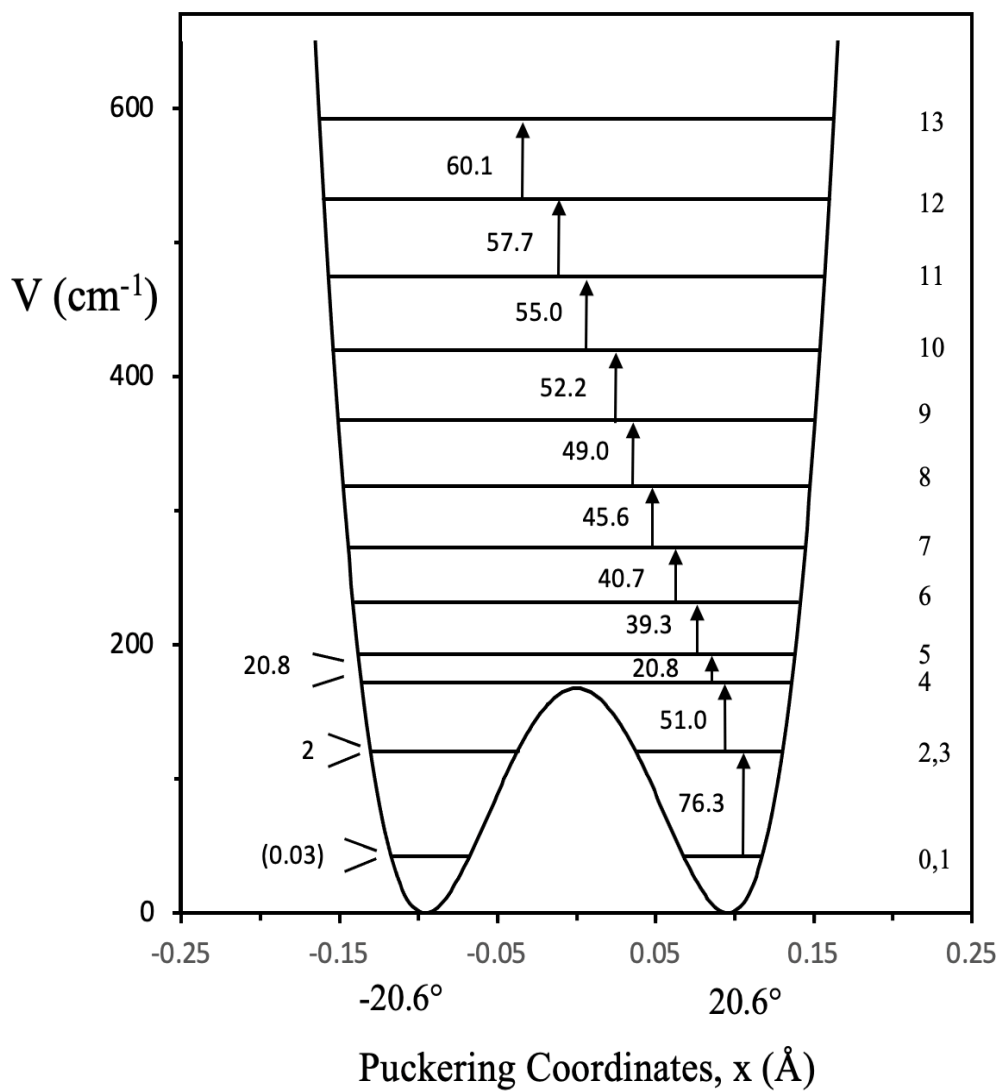


Figure 5: Theoretical ring-puckering PEF of lower energy levels of 13TF CB showing predicted transitions. The energy minima are at  $x_{min} = \pm 0.096 \text{ \AA}$  and  $\theta_{min} = \pm 20.6^\circ$

Similarly, the PEF of 123HF CB is given in Equation 11.

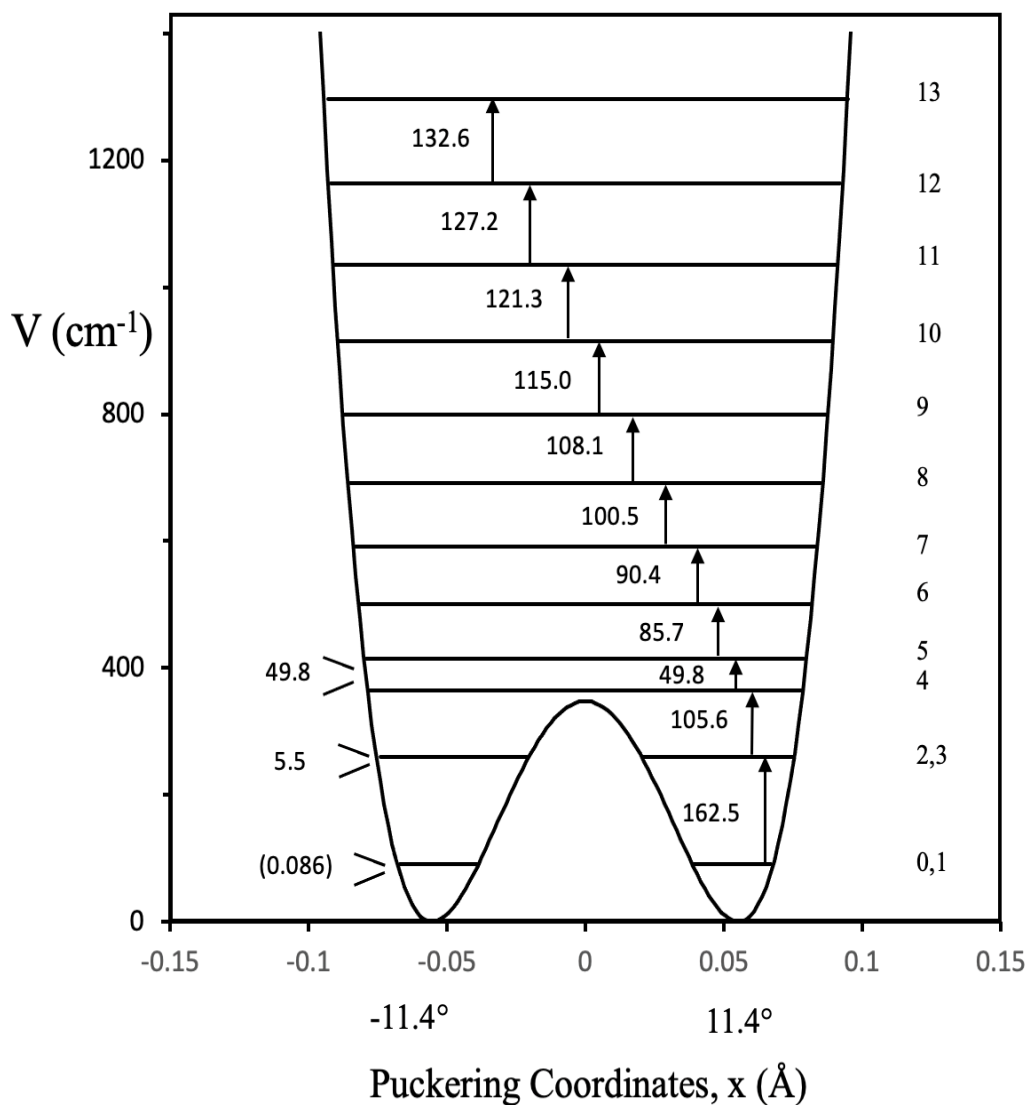
$$V(x) = 37332270.4 x^4 - 227918.2 x^2 \quad (\text{Eq. 11})$$

The kinetic expansion function was calculated as a function of puckering coordinates and fitted to the 6<sup>th</sup> order, given in Equation 12.

$$g_{44}(x) = 0.0012 - 0.0013 x^2 - 0.0043 x^4 - 0.0003 x^6 \quad (\text{Eq. 12})$$

The reduced mass obtained from Equation 10 was calculated to be 847.7 at  $x=0$ . Approximations were made in order to obtain the PEF energy spacings of this molecule due to its relatively heavy weight and broader puckering barrier. The reduced mass value, however, was used as is to obtain the energy spacings related to the lower energy levels of this PEF (Figure 6).

The PEF has an inversion barrier of  $347.9 \text{ cm}^{-1}$ ,  $x_{\min} = \pm 0.055$  and  $\theta_{\min} = \pm 11.4^\circ$ .



*Figure 6: Theoretical ring-puckering PEF of the lower energy levels of 123HFCB showing predicted transitions. The energy minima are at  $x_{\min} = \pm 0.055 \text{ \AA}$  and  $\theta_{\min} = \pm 11.4^\circ$*

Multiple studies have reported the theoretical and experimental Raman and infrared (IR) spectra of PFCB (octafluorocyclobutane) [23-25]. In this study, the calculated PEF is given in Equation 13.

$$V(x) = 1381504.9 x^4 - 43775.1x^2 \quad (\text{Eq. 13})$$

The PEF has an inversion barrier of  $346.8 \text{ cm}^{-1}$ ,  $x_{\min} = \pm 0.126$  and  $\theta_{\min} = \pm 16.6^\circ$ . The energy spacings were calculated for higher energy levels, compared to 13TFCB and 123HFCB, due to the higher barrier to planarity observed in this structure (Figure 7). Blake et al. reports the inversion barrier to be between  $120\text{-}536 \text{ cm}^{-1}$  based on different levels of theory. The barrier obtained from MP2/cc-pVTZ computations was reported to be the same as the one presented in this paper; however, the best estimate of the ring-puckering barrier was determined to be  $132 \text{ cm}^{-1}$ , obtained from CCSD level of theory (based on the coupled-cluster theory) [25]. Ocola has also reported more accurate results through CCSD computations [16], but the MP2 computational approach was chosen in this report due to the elongated computational times required to conduct CCSD computations. Nevertheless, MP2 computations proved to yield more accurate vibrational transitions for perfluorocyclobutane than CCSD level of theory [25]. Additionally, the experimental puckering angle was determined to be  $17.4^\circ$ , which is in strong agreement with the theoretical value obtained here;  $16.6^\circ$ .

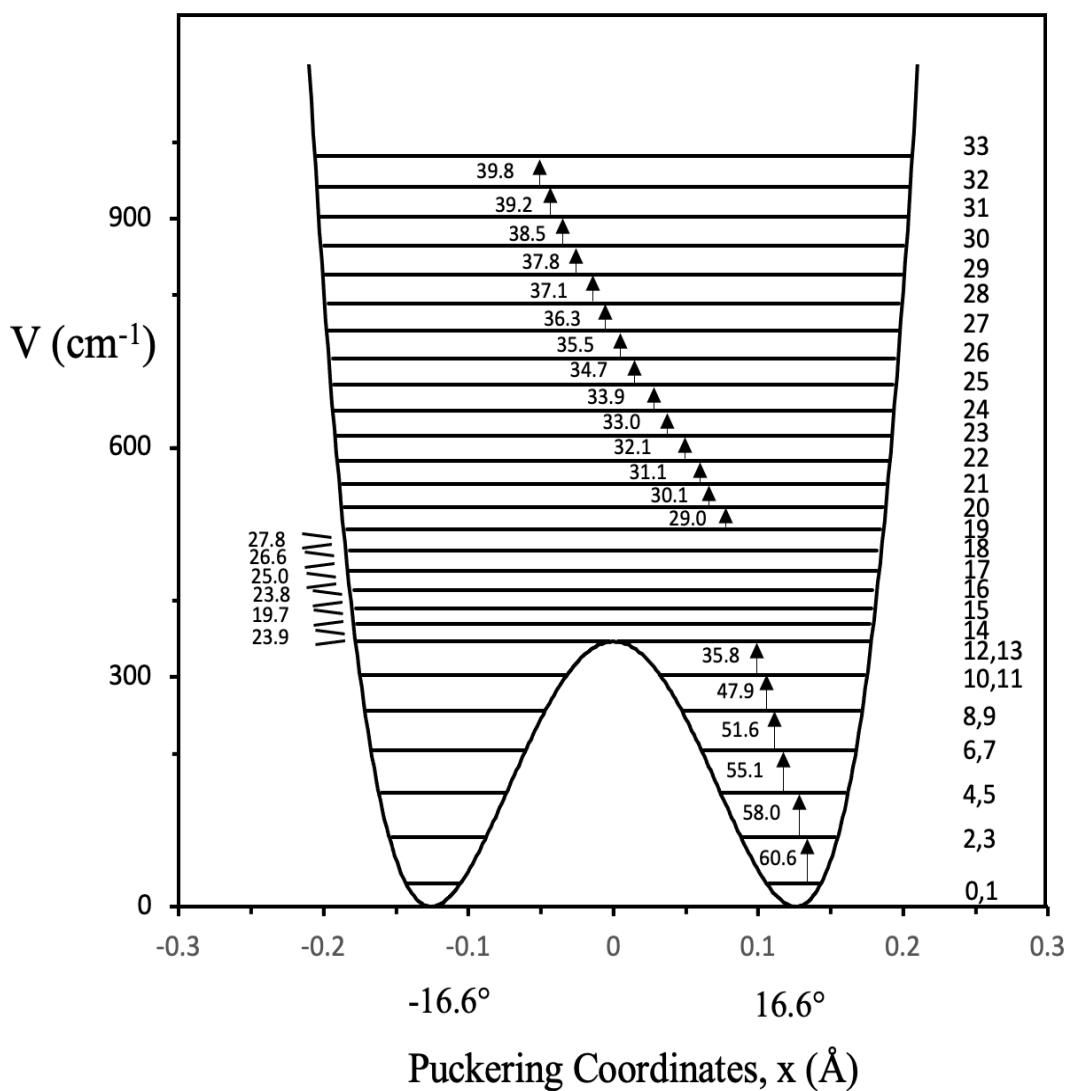


Figure 7: Theoretical ring-puckering PEF of the energy levels of PFCB showing predicted transitions. The energy minima are at  $x_{min} = \pm 0.126 \text{ \AA}$  and  $\theta_{min} = \pm 16.6^\circ$

Although the error for the barrier using MP2/cc-pVTZ level of theory is relatively high, ranging from 35-86%, the error for the puckering angle,  $\theta_{min}$ , ranges only from 1-16% [16]. Through the agreement of the experimental and calculated puckering angle, in conjunction with relatively low error margins, it can be estimated that the puckering angle, and thus puckering coordinates of



low-frequency, high-amplitude molecules can be determined using MP2/cc-pVTZ computations with acceptable accuracy.

## 4. CONCLUSION

Vibrational puckering coordinates of low-frequency, high-amplitude four-membered rings have been extensively studied. These puckering coordinates have proven to provide reliable PEFs. In this work, the symmetrical PEFs of fluorocyclobutane molecules were calculated using MP2 ab initio computational methods, revealing inversion barriers and puckering angles of energy minima. The lower vibrational energy spacings were constructed using the inverse reduced mass function,  $g_{44}(x)$ . Having both the PEFs and the energy spacing allows the understanding of molecules inversions and other processes such as isomerization. Not only did this study provide a better understanding of how fluoride substitution on a four-membered ring affects energies of puckered and planar conformations, but it also allowed the prediction of IR vibrational transition. Furthermore, the agreement of the MP2/cc-pVTZ computational results and experimental data establishes a wider area of possible PEFs and spectroscopic investigations of any type of molecules, especially the ones that are hard to synthesize or handle in a laboratory environment. Additionally, this method can be applied to non-symmetrical PEFs, which provides even better understanding of how symmetry plays a role in inter- and intramolecular processes.

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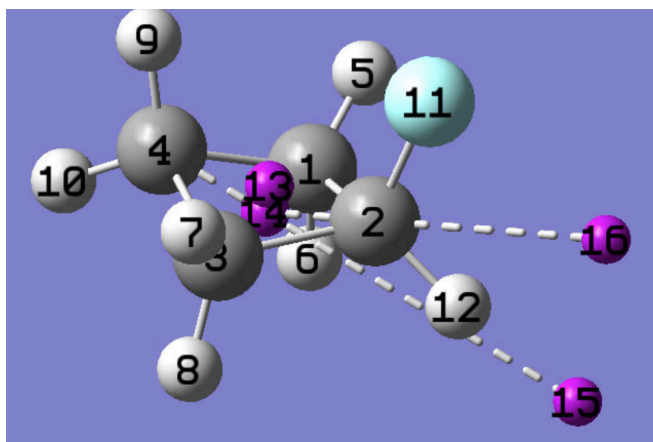
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## APPENDIX: CALCULATING PUCKERING COORDINATES

The method to obtain the puckering coordinates and the puckering angle were done as shown in Figure A.1. Dummy atoms 13 and 14 were placed on the diagonals of the four-membered rings. The distance between those two atoms is two times the puckering coordinates,  $2x$ . The puckering angle was measured using another two dummy atoms, 15 and 16, placed at a  $180^\circ$  with opposite atoms on the ring and one of the centered dummy atoms.



*Figure A.1: Fluorocyclobutane ring puckering coordinates and puckering angle visualized using Gaussian 16 software..*

For the energy minima calculations, “opt” function was used to optimize molecules to an energy minimum. For the planar conformations, “popt=z-matrix” function was used to calculate the energy. The dihedral angle (C1-C2-C3-C4) was set to zero.