

THEORETICAL STUDY OF THE PHOTOELECTRON  
SPECTRUM OF  $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{NO})$

A Senior Honors Thesis

By

THOMAS F. MILLER III

Submitted to the Office of Honors Programs  
& Academic Scholarships  
Texas &M University  
In partial fulfillment of the requirements of the

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Group: Physical Sciences

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## ABSTRACT

Theoretical Study of the Photoelectron  
Spectrum of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ni(NO). (April 2000)

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The valence photoelectron spectrum of cyclopentadienyl nickel nitrosyl (CpNiNO) was computed to determine the ion state orbital ordering of the  $5e_1$ ,  $7a_1$ , and  $3e_2$  bands. Calculations were performed with Hartree-Fock theory, density functional theory, Møller-Plesset perturbation theory, and configuration interaction theory and, in all cases, utilized a triple- $\zeta$  basis set including polarization and diffuse functions (6-311+G\*). Density functional theory was also used with the same basis set to calculate the ion state orbital ordering of the lowest energy  $e_1$ ,  $a_1$ , and  $e_2$  bands in pentamethylcyclopentadienyl nickel nitrosyl (Cp\*NiNO). Recent experimental studies have proposed the conflicting ion state orbital orderings of  $5e_1(1), 5e_1(2) < 7a_1 \approx 3e_2(3)$  (band numbers are in parentheses) and  $5e_1(1) < 7a_1(2) < 3e_2(3)$  for CpNiNO. In this study, the ordering concluded from calculated energy differences between the neutral ground state and the cationic states is  $5e_1(1) < 7a_1(2) < 3e_2(3)$ , while comparison of the calculated band shifts between the CpNiNO and Cp\*NiNO spectra support the assignment of  $5e_1(1), 5e_1(2) < 7a_1 \approx 3e_2(3)$ .

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## Introduction

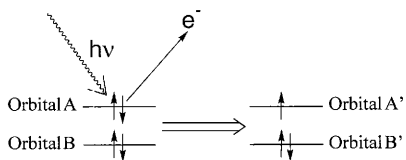
Spectroscopy is the study of the absorption and emission of light and other radiation by matter.<sup>1</sup> The numerous applications of spectroscopy to chemical analysis include techniques such as infrared spectroscopy which measures the rigidity of chemical bonds and nuclear magnetic resonance spectroscopy that indicates the electronic environment of nuclei in molecules.<sup>2</sup> In the special case of photoelectron spectroscopy<sup>3</sup> (PES), molecules are bombarded with high energy photons. A sufficiently energetic photon typically interacts with a neutral molecule in the ground state to eject a bound electron and yield a positively charged molecular ion, or cation (Fig. 1). The energy of the impinging photon,  $h\nu$ , is related to the kinetic energy  $E_k$  of the expelled electron by Einstein's photoelectric effect, namely

$$h\nu = E_k + E_I$$

where the ionization energy  $E_I$  corresponds to the difference between the energy of the neutral ground state of the molecule and the energy of the resulting cationic state. In the implementation of PES discussed hereafter, monochromatic radiation of known frequency  $\nu$  is directed at the molecular sample and the number of electrons ejected with particular values of  $E_k$  is accurately counted. Thus, the ionization energies  $E_I$  of a molecule and the relative probability of forming the corresponding cationic states (for the given frequency of impinging light) are determined.

PES is often explained within the conceptual framework of molecular orbital (MO) theory. That is, formation of a cationic state corresponds loosely to the removal of an electron from a particular molecular orbital in the neutral ground state configuration. The orbital from which the electron is ejected is called the ion state orbital. Throughout this work, each ionization process will be labeled according to its associated ion state orbital. For example, if the partially occupied molecular orbital in the MO approximation of the cationic state corresponds to the  $7a_1$  molecular orbital of the neutral ground state MO wavefunction, the  $7a_1$  orbital is said to be the ion state orbital for this ionization process.





**Figure 1.** An impinging photon expels a bound electron in a photoionization process.

Moreover, we would call the difference in energy between the cationic and neutral ground states the  $7a_1$  ionization energy. This approach is useful because it reduces the behavior of the many-electron wavefunction down to that of a single electron. It should be noted, however, that there is a meaningful distinction between the energy of the ion state orbital and the true ionization energy. In the first place, the orbitals containing the remaining bound electrons will relax upon removal of an electron from the ion state orbital, and thus the occupied orbitals of the cation will differ in composition from those of the neutral ground state. A more fundamental flaw lies in the fact that single-configurational, one-particle MO wavefunction is, in general, a crude approximation to the true wavefunction. In cases requiring the inclusion of extensive dynamic electron correlation, the approximation of molecular orbitals simply does not hold. Nonetheless, the use of the ion state orbital from MO theory for a labeling scheme is simple and unambiguous in this study, and MO theory remains a useful tool in the qualitative understanding of PES.

Since both the neutral molecule and its cation exist in states with discrete energy, ionization energies of the molecule also take on discrete values. Figures 2 and 3 exhibit electronic transitions induced by photoionization. Each curve in the figures represents the energy of a particular adiabatic electronic state as a function of nuclear position. The horizontal lines about the minimum of each curve represent the lowest vibrational energies for that adiabatic surface. The neutral state vibrational quantum number is  $v''$ , and the cation state vibrational number is  $v'$ . In a PES experiment, the molecule begins in the lowest ( $v''=0$ ) vibrational level of the neutral ground state. Note that in Figure 2, the internuclear coordinate corresponding to the lowest point of the cation state potential surface approximately equals that of the ground state surface. This suggests that the ion state orbital for this photoionization has little bonding or anti-bonding character because the molecular geometry is invariant to its occupation. In Figure 3, however, the equilibrium geometry differs significantly between the two surfaces ( $\Delta Q$ ) which indicates that the ion state orbital has some net bonding character.

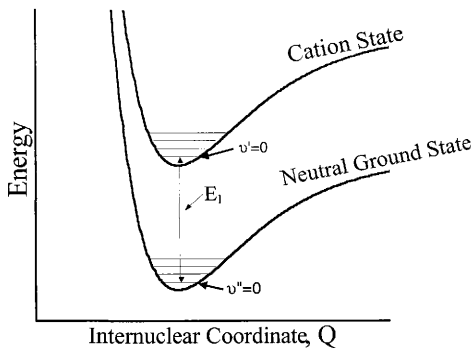


Figure 2. Ionization from a non-bonding ion state orbital.

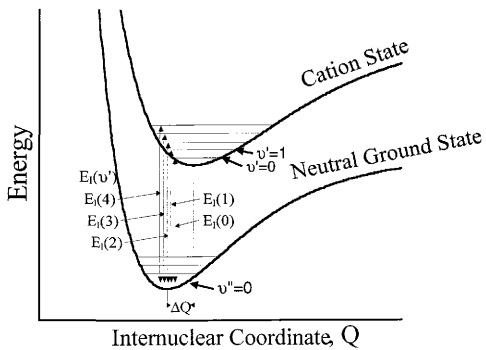


Figure 3. Ionization from an ion state orbital with net bonding character.

Figures 2 and 3 illustrate that multiple excited vibrational states are energetically accessible in a photoionization process, so an investigation of which cationic vibrational states actually become occupied is essential. The Frank-Condon principle<sup>4</sup> asserts that peak intensities in a photoelectron (PE) spectrum are proportional to the square of the overlap integral for the neutral state vibrational wavefunction and the cationic state vibrational wavefunction. The general characteristics of vibrational wavefunctions reveal that structures with significantly different geometries (Fig. 3) have very little overlap between their lowest state ( $v''=0$ ,  $v'=0$ ) vibrational wavefunctions. Thus, the most intense peak for the photoionization will correspond to a transition from  $v''=0$  in the ground state to an excited  $v'$  vibrational state in the cation. On the other hand, when the cation and neutral species are nearly identical in geometry (Fig. 2), the spectral peak arising from the  $v''=0$  to  $v'=0$  transition dominates.

As an example, consider the two lowest ionization energies (Fig. 4) of carbon monoxide, CO. These photoionization processes correspond to ejection of electrons from the oxygen  $\sigma$  lone pair and bonding  $\pi$  orbitals. Because ejection of an electron from a lone pair does little to change the molecular structure, Figure 2 depicts photoionization from the  $\sigma$  ion state orbital and we thus expect to observe only the  $v''=0$  to  $v'=0$  transition in the spectrum. Indeed, Figure 4 shows that the  $\sigma$  ionization energy band at 14 eV is comprised almost entirely of a single peak. Conversely, the removal of bonding electrons from the  $\pi$  orbitals of CO leads to a significant increase in bond length, as in to Figure 3. The appearance of multiple vibrational contributions to the  $\pi$  photoionization band at ~17 eV in Figure 4 is thus not surprising. Ionization from the bonding  $\pi$  ion state orbitals in CO exhibits greatest intensity for the  $v''=0$  to  $v'=2$  transition.

An adiabatic ionization energy<sup>4</sup> is defined as the energy between the  $v''=0$  neutral state and the  $v'=0$  cationic state. The vertical ionization energy<sup>4</sup> corresponds to the  $v''=0$  to  $v'=n$  transition, where  $n$  is the quantum number for the cation vibrational state with

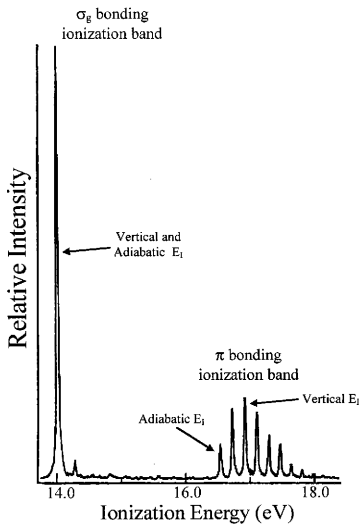
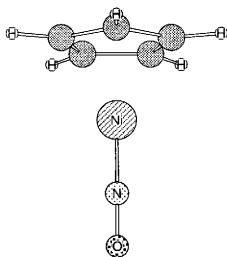


Figure 4. PE spectrum of carbon monoxide.<sup>5</sup>

greatest intensity. Note that for ionization of the  $\sigma$  lone pair of CO, the adiabatic and vertical ionization energies are the same. However, for the ionization from the  $\pi$  ion state orbital, the vertical ionization occurs at 16.9 eV, whereas the adiabatic ionization is 16.5 eV. We will assume throughout this study that all  $v''=0$  to  $v'=0$  ionizations are vertical.

The interpretation of photoelectron spectra with the methods of electronic structure theory is a natural interface between the realms of theory and experiment. Information regarding the environment of bound electrons obtained from a theoretical model provides an understanding of the ionization energies observed for a particular molecule. Conversely, photoelectron spectroscopy provides a direct experimental probe of the electronic structure in a molecule and tests the validity of a theoretical prediction. Among the most valuable features of this symbiosis is the capacity of one approach to clarify issues that are irresolvable from the perspective of the other. Such is the purpose of this work.

The fundamental nature and appealing properties of the ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)NiNO molecule rendered it an early subject of photoelectron spectroscopic analysis.<sup>6</sup> CpNiNO (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) is a volatile, highly-symmetric, closed-shell, half-sandwich molecule (Fig. 5). Figure 6 is a proposed molecular orbital diagram for CpNiNO. Because the molecule exhibits C<sub>5v</sub> symmetry, the five d orbitals are split into three irreducible representations. The d<sub>xz</sub> and d<sub>yz</sub> orbitals correspond to the e<sub>1</sub> irreducible representation, the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> and d<sub>xy</sub> orbitals exhibit e<sub>2</sub> symmetry, and the remaining d<sub>z<sup>2</sup></sub> orbital corresponds to the totally symmetric a<sub>1</sub> representation. The dominant valence orbitals introduced by the NO moiety is a partially-occupied pair of  $\pi^*$  e<sub>1</sub> orbitals which interact with the e<sub>1</sub> Ni<sup>+</sup> orbitals to obtain the left column of Figure 5. Now we can formally introduce the occupied e<sub>1</sub>  $\pi$  orbitals and unoccupied e<sub>2</sub>  $\pi^*$  orbitals from the frontier valence of the anionic Cp ring to obtain the final MO diagram for CpNiNO. Note that the four highest occupied CpNiNO MOs (5e<sub>1</sub>, 7a<sub>1</sub>, 3e<sub>2</sub>, 4e<sub>1</sub>) are considerably separated in energy from the rest of the valence orbitals. It is expected that electrons in these four sets of orbitals will be removed at considerably less



**Figure 5.** The CpNiNO molecule.

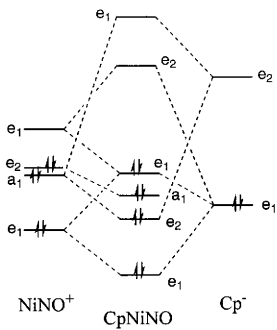


Figure 5. Molecular Orbital Diagram for CpNiNO.



energetic cost than electrons from more stable occupied orbitals. Because of small spatial overlap between the nickel  $e_2$  orbitals and the two set of  $e_2$  orbitals on the Cp ring, the  $3e_2$  orbital in Figure 6 displays primarily metal character. The  $7a_1$  orbital of CpNiNO is also largely metallic in composition because of the absence of frontier orbitals of  $a_1$  symmetry in the ligands. The nickel  $e_1$  orbitals, however, interact relatively strongly with orbitals from both Cp and NO. Thus, the CpNiNO  $5e_1$  orbital and  $4e_1$  orbitals are considerably more delocalized and less metallic than the other occupied frontier orbitals.

The PE spectrum (Fig. 7) of CpNiNO exhibits three well-resolved bands in the ionization energy region below 12 eV that correspond to four ionization processes. The lowest energy band is comprised of two peaks separated by approximately 0.2 eV. Although it is widely accepted that the peaks correspond to photoionization from the  $5e_1$ ,  $7a_1$ ,  $3e_2$ , and  $4e_1$  orbitals of Figure 6, recently reported variable-energy PES studies disagree on the assignment of the peaks in the spectrum to their corresponding ion state orbitals. In concurrence with the original assignment, Bancroft and coworkers<sup>8</sup> indicate that each peak in the spectrum corresponds to a distinct orbital and report an ion state orbital ordering of  $5e_1 < 7a_1 < 3e_2 < 4e_1$  in order of increasing binding energy (Table 1). Green and coworkers<sup>9</sup> suggest the alternative assignment  $5e_1 < 7a_1 \approx 3e_2 < 4e_1$ . They propose that the peaks resulting from ionization out of the  $7a_1$  and  $3e_2$  orbitals overlap at 9.35 eV and that the two low-energy peaks at 8.33 eV and 8.56 eV result exclusively from elimination of electrons in the  $5e_1$  orbital. They argue that splitting in the  $5e_1$  band arises from a non-vertical ionization to a vibrationally excited state of the nitrosyl moiety. A subsequent publication by Green<sup>10</sup> contends that the observed band shifts in the PE spectrum between CpNiNO and Cp\*NiNO (Cp\* =  $\eta^5\text{-C}_5\text{Me}_5$ ) confirm their recommended ion state orbital ordering of  $5e_1 < 7a_1 \approx 3e_2 < 4e_1$ .

In this study, we utilize an assortment of *ab initio* theoretical methods to determine the assignment of the three lowest energy bands in the CpNiNO PE spectrum. However, this objective can be conveniently reformulated upon consideration of the aforementioned

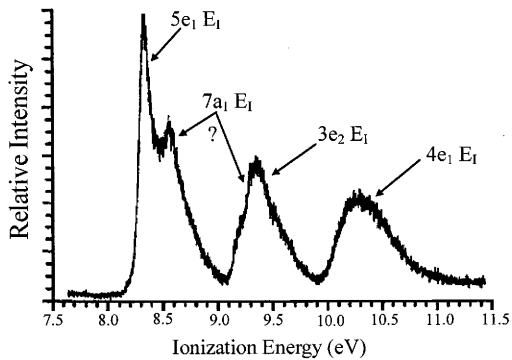


Figure 7. PE spectrum of CpNiNO.<sup>7</sup>

**Table 1.** Experimentally Determined Ionization Energies (eV) of CpNiNO

Ion State Orbital	Green <sup>y</sup>	Bancroft <sup>z</sup>
5e <sub>1</sub>	8.33, 8.56	8.29
7a <sub>1</sub>	9.35	8.48
3e <sub>2</sub>	9.35	9.30

dispute. Both recent experimental reports agree that ionization from the  $5e_1$  orbital occurs at about 8.3 eV and ionization from the  $3e_2$  orbital requires about 9.3 eV. The only remaining question is whether the  $7a_1$  ionization energy is very close to the  $5e_1$  ionization energy or the  $3e_2$  ionization energy. We also investigate the difference in energies of ionization from the highest occupied  $e_1$ ,  $a_1$ , and  $e_2$  molecular orbitals of CpNiNO and Cp\*NiNO to compare with the findings of Green.

### Theoretical Methods

Calculation of the ground state energy and lowest  ${}^2E_1$ ,  ${}^2A_1$ , and  ${}^2E_2$  cationic state energies for CpNiNO was performed with the Hartree-Fock (HF) method,<sup>11</sup> the second- and third-order Møller-Plesset (MPx, x=2,3) perturbation methods,<sup>12</sup> the configuration interaction method with all single and double substitutions (CISD),<sup>13</sup> and the B3LYP density functional method which includes the Becke three-parameter (B3) exchange functional<sup>14</sup> and the Lee-Yang-Parr (LYP) correlation functional.<sup>15</sup> The ground and cationic state energies for Cp\*NiNO were computed only with the B3LYP density functional method. All reported calculations in this work were performed with the Gaussian 98 program<sup>16</sup> and utilized the same basis set. The basis set contains Pople's standard 6-311+G\* basis<sup>17</sup> for the H, C, N, and O atoms and the Wachter-Hay augmented nickel basis set<sup>18</sup> with a contracted set of six primitives and nine uncontracted primitives in the s shell, a contracted set of five primitives and six uncontracted primitives in the p shell, a contracted set of three primitives and three uncontracted primitives in the d shell, and a single primitive of f symmetry.

Both CpNiNO and Cp\*NiNO exhibit geometries of  $C_{5v}$  symmetry. All CpNiNO calculations were run at the experimental geometry,<sup>19</sup> but the Cp\*NiNO geometry was optimized at the B3LYP level with the basis set described above. Our calculated Cp\*NiNO geometry agreed well with previously published results<sup>20</sup> and was verified with a frequency

calculation to be a local minimum for the B3LYP method. All ionization energies were assumed to be vertical.

All open-shell calculations performed with the Gaussian 98 program utilized the Symm and Dsymm options for the self consistent field (SCF) calculation, which require the number of occupied orbitals of each symmetry type to remain constant throughout the calculation and constrain the density matrix to match the symmetry of the molecule at every SCF iteration. To prevent collapse of the wavefunction to a spin-contaminated single determinant, the  ${}^2E_2$  state's density-based HF convergence criterion was relaxed to  $10^4$ , rather than the default value of  $10^7$  for the reference wavefunction in MPx and CISD calculations. For the same post-HF methods, the  ${}^2E_1$  and  ${}^2E_2$  reference SCF wavefunctions exhibited slightly negative HOMO-LUMO gaps. Although this is unlikely to significantly affect the CISD results, the MPx perturbation methods are expected to be impacted detrimentally.

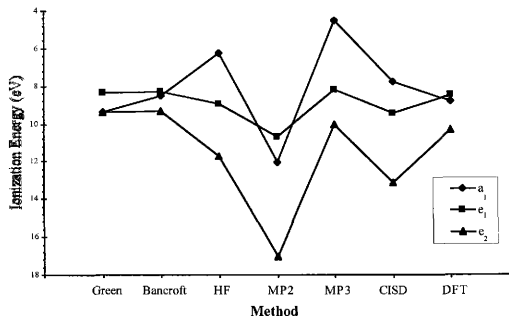
## Results and Discussion

In this study, the CpNiNO ionization energies  $E_I$  were calculated using the formula

$$E_I = E_{\text{neutral}} - E_{\text{cation}}$$

where  $E_{\text{neutral}}$  is the energy of the neutral ground state and  $E_{\text{cation}}$  is the energy of one of the cation states. This relationship was introduced graphically in Figures 2 and 3. It follows that for each reported ionization energy, two computations are needed.

**CpNiNO.** The three lowest ionization energies for CpNiNO are cataloged in Table 2 and displayed graphically in Figure 8. Several significant conclusions can be drawn from these data. Recall from the Introduction that the correct assignment of the PE spectrum can be determined from the relative closeness of the  $7a_1$  and  $5e_1$  ionization energies and the  $7a_1$  and  $3e_2$  ionization energies. In Table 3, the absolute value of these ionization energy differences are displayed. Note that every theoretical method employed predicts the energy difference between the  $7a_1$  and  $5e_1$  ionization processes to be significantly smaller than that



**Figure 8.** Calculated and Experimental Ionization Energies for CpNiNO

**Table 2.** Ionization Energies (eV) of CpNiNO

Ion State Orbital	Exp. (Green <sup>a</sup> )	Exp. (Bancroft <sup>8</sup> )	HF	MP2	MP3	CISD	B3LYP
5e <sub>1</sub>	8.33,8.56	8.29	8.93	10.65	8.17	9.43	8.46
7a <sub>1</sub>	9.35	8.48	6.22	12.04	4.52	7.75	8.80
3e <sub>2</sub>	9.35	9.30	11.70	17.00	9.99	13.10	10.32

**Table 3.** Absolute Values of the Difference Between the 7a<sub>1</sub> and 5e<sub>1</sub> Ionization Energies (eV) and the 7a<sub>1</sub> and 3e<sub>2</sub> Ionization Energies (eV) of CpNiNO

Ion State Orbitals	Exp. (Green <sup>a</sup> )	Exp. (Bancroft <sup>8</sup> )	HF	MP2	MP3	CISD	B3LYP
7a <sub>1</sub> ,5e <sub>1</sub>	1.02 <sup>a</sup>	0.19	2.71	1.39	3.65	1.68	0.34
7a <sub>1</sub> ,3e <sub>2</sub>	0.00	0.82	5.48	4.96	5.47	5.35	1.52

<sup>a</sup>The dominant spectral peak at 8.33 eV was used in calculating the difference.

for the  $7a_1$  and  $3e_2$  ionizations and thus supports the findings of Bancroft. The results calculated with the B3LYP method correlate particularly well with the experimental spectrum with respect to the absolute magnitude, relative spacing, and relative ordering of the ionization energies.

Despite the strong qualitative agreement between these calculations and the findings of Bancroft, the theoretical results fall short of an indisputable resolution of the controversy. Of particular concern is the dramatic variance in calculated ionization energies from method to method. The progression of wavefunction methods (HF,MP2,MP3,CISD) formally approach the exact solution within a given basis set, but Figure 8 clearly indicates that a suitable convergence has not been reached. The CISD method is the most sophisticated of the employed wavefunction methods and still fails to exhibit quantitative agreement with the experimental spectrum.

Much of the inaccuracy in our calculated results arises from the nature of the CpNiNO electronic structure. Even the closed-shell neutral species has numerous low-lying unoccupied molecular orbitals which undermine the assumption in the Hartree-Fock method of a single-configurational wavefunction. The open-shell  $^2E_1$  and  $^2E_2$  states of the cation are inherently more troublesome because they contain partially occupied degenerate orbitals. Perturbative corrections introduced by the MP2 and MP3 methods to the poor HF wavefunction are insufficient to incorporate a satisfactory degree of multi-reference character. Even the CISD method, which explicitly includes all singly- and doubly-excited configurations of the HF wavefunction, provides at best a semi-quantitative description of the CpNiNO wavefunction. Very little formal evidence suggests that the B3LYP method (another single-reference approach) should fully describe the effects of electron correlation in the CpNiNO wavefunction. The excellent consistency of the B3LYP calculations with the experimental spectrum must thus be considered somewhat fortuitous.

The shortcomings inherent to each employed theoretical method underline the necessity for an analytical approach that invokes a cancellation of method-dependent error.



Such is the utility of the above examination of the differences in calculated ionization energies (Table 3). Note that each ionization energy is itself a difference in the absolute neutral and cation state energies and thus includes a cancellation of error in the absolute energy of the doubly-occupied orbitals. However, each ionization energy carries a method-dependence in its component due to the removal of an electron to form an open shell. By considering the difference in the energy of two open-shell states (or equivalently, the difference in two ionization energies) for a given method, a more even-handed cancellation of error is achieved. This point is illustrated most clearly by the highly consistent difference in the  $7a_1$  and  $3e_2$  ionization energies of approximately 4.5-5.5 eV determined by the HF, MP2, MP3 and CISD wavefunction methods (Fig. 8). As discussed in the Introduction, both the  $7a_1$  and  $3e_2$  orbitals are localized and primarily metallic in character. They will thus be treated similarly by each of the wavefunction methods. That is, despite the significant variance in the absolute  $7a_1$  and  $3e_2$  ionization energies from method to method, the difference between them is notably consistent. The variation of the energy of ionization from the delocalized, ligand-based  $5e_1$  orbital with respect to the  $7a_1$  and  $3e_2$  ionization energies indicates that the variable responsible for most of the remaining method-dependence in our analysis is the composition of the partially occupied orbital in the cation.

**Cp\*NiNO.** The similarity between the electronic structures of CpNiNO and Cp\*NiNO makes useful a comparison of their PE spectra. Like the CpNiNO molecule, Cp\*NiNO exhibits  $C_{5v}$  symmetry and has high-lying occupied molecular orbitals of  $e_1$ ,  $a_1$ , and  $e_2$  symmetry that are analogous in character to the CpNiNO  $5e_1$ ,  $7a_1$ , and  $3e_2$ , respectively. The  $a_1$  and  $e_2$  orbitals are localized and primarily metallic in composition whereas the  $e_1$  molecular orbital is more delocalized and exhibits greater ligand character. The fundamental difference in the PE spectra of CpNiNO and Cp\*NiNO is that ionization from the  $e_1$ ,  $a_1$ , and  $e_2$  orbitals of the latter molecule generally occur at lower energy. However, the magnitude of the shift in the ionization energy for each corresponding ion state orbital depends on the composition of that orbital. Generally, one would expect that the shift in

the energy of ionization from orbitals with Cp character ( $e_1$ ) is greater than that of metallic orbitals ( $a_1$  and  $e_2$ ).<sup>21</sup>

Table 4 includes the ionization energies of CpNiNO and Cp\*NiNO measured and assigned by Green and coworkers<sup>10</sup> and our calculated ionization energies for the two molecules using the B3LYP method. Also displayed in the table are the differences in the energy of ionization from corresponding orbitals for each method. Aside from the shift of band energies, the PE spectrum for Cp\*NiNO is virtually indistinguishable from the CpNiNO spectrum. That is, ionization from the three highest molecular orbitals yield only two well-resolved spectral bands, the first of which is split into two peaks. Analysis of the B3LYP results for Cp\*NiNO in terms of the relative closeness of the  $a_1$  and  $e_1$  ionization energies and the  $a_1$  and  $e_2$  ionization energies again supports the original spectral assignment of Bancroft<sup>4</sup>. It can be seen in Table 4 that the calculated difference in the  $a_1$  and  $e_1$  ionization energies of Cp\*NiNO is 0.69 eV which is significantly smaller than the calculated difference in the  $a_1$  and  $e_2$  ionization energies of 1.4 eV.

Comparison of the shift of the energy of ionization from corresponding orbitals in the CpNiNO and Cp\*NiNO molecules, however, provides evidence in favor of the spectral assignment suggested by Green. In agreement with the conventional wisdom,<sup>21</sup> Table 4 shows that the B3LYP method predicts the  $a_1$  and  $e_2$  ionization energies to shift by similar amounts and slightly less than the  $e_1$  ionization energy. Such a result contradicts the assignment by Bancroft for which the  $a_1$  and  $e_1$  ionization energies would have to shift nearly identically. Moreover, the B3LYP ionization energy shifts agree well with those obtained from Green's assignment of the PE spectra.

Although comparing the shift in the corresponding ionization may provide a more sensitive experimental means of resolving this dispute, it is not immediately obvious that the same should hold for the theoretical data. The experimental evidence alone seems to point to the assignment of Green, so long as the heuristic dependence of ionization energy shift as a function of orbital composition holds true. However, in light of the calculations

**Table 4.** CpNiNO and Cp\*NiNO Ionization Energies and Ionization Energy Differences (eV)

Ion State Orbital	Exp. <sup>9</sup> CpNiNO	Exp. <sup>10</sup> Cp*NiNO	$\Delta E_1$ Exp.	B3LYP CpNiNO	B3LYP Cp*NiNO	$\Delta E_1$ B3LYP
e <sub>1</sub>	8.33, 8.56	7.30, 7.52	1.03 <sup>d</sup>	8.46	7.59	0.88
a <sub>1</sub>	9.35	8.64	0.71	8.80	8.28	0.52
e <sub>2</sub>	9.35	8.64	0.71	10.32	9.68	0.64

<sup>d</sup>The dominant spectral peaks at 8.33 eV and 7.30 eV were used in calculating the difference.

reported in Table 2, it is entirely possible that the calculated ionization energies deviate from the correct results by several electronvolts. Even a fraction of this error could lead to fallacious conclusions when comparing energy shifts. Note that the computational component of the above argument hinges entirely on the fact that the  $a_1$  ionization energy shifts approximately 0.3 eV less than the  $e_1$  ionization energy. Within the reasonable error for the calculations, either assignment can be substantiated.

The most appealing theoretical feature of the analysis of ionization energy band shifts in similar molecules is that it removes the dominant source of method-dependence inherent to the comparison of relative ionization energies within a single molecule, namely differences in the composition of the ion state orbital. However, this advantage is achieved only by introducing two potential hazards. The primary concern is that comparison of energy shifts involves differentiating between relatively small calculated quantities which requires an accuracy seldom obtained. Secondly, comparison of ionization energy shifts requires the employment of an empirical rule based on orbital composition. Such arguments can be very easily misemployed. Despite the general agreement that the  $e_1$  orbital has significant ligand character and the  $a_1$  and  $e_2$  orbitals are primarily metallic, none of the molecular orbitals are composed entirely of the orbitals from these fragments. In particular, the  $e_1$  most certainly contains non-negligible contributions from the nickel d orbitals. The unclear dependence of ionization energy shifts on the mixing of composition in the corresponding ion state orbitals hinder an unambiguous conclusion.

## Conclusions

In this study, the HF, MP2, MP3, CISD, and B3LYP methods were used to assign the region of the CpNiNO PE spectrum corresponding to the three lowest energy ionization processes. Based on the relative closeness of the calculated  $7a_1$  and  $5e_1$  ionization energies and the  $7a_1$  and  $3e_2$  ionization energies, all methods confirmed the ion state orbital assignment of  $5e_1 < 7a_1 < 3e_2$  reported by Bancroft. However, a comparison of the shifts

in the energy of ionization from corresponding orbitals in the CpNiNO and Cp\*NiNO molecules with the B3LYP method supports the ion state orbital ordering of  $5e_1 < 7a_1, 3e_2$  proposed by Green. Calculations of greater accuracy are required to conclusively resolve the dispute.

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