Theoretical studies of molecular ions. Ionization potentials of CN⁻ and BO⁻

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The ${}^{1}\Sigma^{+} \rightarrow {}^{2}\Sigma^{+}$ vertical ionization potentials of BO⁻ and CN⁻ and the ${}^{1}\Sigma^{+} \rightarrow {}^{2}\Pi$ vertical ionization potential of CN⁻ are reported for several internuclear distances. The estimated adiabatic electron affinities of BO (2.79 eV) and CN (3.69 eV) are in good agreement with experimental determinations. The 5 σ orbital electron density in CN⁻ and BO⁻ is analyzed and compared to that in N₂ and CO. Curve crossing behavior in the ${}^{2}\Sigma^{+}$ and ${}^{2}\Pi$ states of CN is discussed.

I. INTRODUCTION

Although the cyanide anion is an important species in several areas of chemistry and in studies of the upper atmosphere, surprisingly little theoretical work has been done to investigate its electronic structure and properties.¹ The intentions of this study are to use the equations-of-motion (EOM) method developed by one of us in Ref. 2 to obtain accurate values for the $X^{1}\Sigma^{+}$ $-X^2\Sigma^+$ ionization potentials of CN⁻ and the isoelectronic BO⁻ ion, and to provide a qualitative description of the bonding in these systems. The EOM method permits us to obtain the ion-molecule energy differences through third order in perturbation theory from a single calculation rather than from two separate variational calculations on the parent and the daughter. Ionization energies accurate to within 0.2 eV of known experimental values have previously been obtained using this theory for a variety of ion-molecule systems.³

The basis sets used in the calculations reported here are described in Sec. II along with a brief review of the EOM method. Section III contains our results, including ion-molecule energy differences and a discussion of the SCF-level potential curves obtained for the ${}^{2}\Sigma^{+}$ and ${}^{2}\Pi$ states of CN. The electron density in the highest occupied (5 σ) orbitals of CN⁻ and BO⁻ is described and related to the electron density in the corresponding 5 σ orbitals of the isoelectronic N₂ and CO molecules. Concluding remarks are contained in Sec. IV.

II. PROCEDURE

A. EOM method

In the theory of electron affinities and ionization potentials derived in Ref. 2, the excitation operator Ω_{μ} , which generates the eigenstate $|\mu^{N-1}\rangle$ of the neutral molecule when operating on the true ground state of the negative ion $|g^N\rangle$, is approximated in terms of the second-quantized Hartree-Fock creation (C_i^*) and annihilation (C_i) operators as follows⁴:

$$\Omega_{\mu} = \sum_{i} X_{i}(\mu) C_{i} + \sum_{m \leq n, \alpha} Y_{n\alpha m}(\mu) C_{n} C_{\alpha}^{*} C_{m} + \sum_{\alpha \leq \beta, m} Y_{\alpha m \beta}(\mu) C_{\alpha} C_{m}^{*} C_{\beta} \quad .$$
(1)

By assuming that $|g^N\rangle$ and $|\mu^{N-1}\rangle$ are eigenfunctions of the Born-Oppenheimer Hamiltonian, one obtains the basic equation of motion,

$$[H, \Omega_{\mu}] |g^{N}\rangle = (E_{\mu}^{N-1} - E_{g}^{N}) \Omega_{\mu} |g^{N}\rangle , \qquad (2)$$

which forms the basis for the derivation of the matrix pseudoeigenvalue problem involving the ionization potential, $\Delta E_{\mu} = E_{\mu}^{N-1} - E_{\xi}^{N}$:

$$\sum_{j} H_{ij} \left(\Delta E_{\mu} \right) X_{j}(\mu) = \Delta E_{\mu} X_{i}(\mu) .$$
⁽³⁾

This result is obtained by substituting in Eq. (2) the approximation to Ω_{μ} given in Eq. (1) and the first order Rayleigh-Schrödinger approximation to $|g^N\rangle$:

$$\left|g_{\rm RS}^{N}\right\rangle = N_{0}^{-1/2} \left[\left|0\right\rangle + \sum_{m < n, \alpha < \beta} \frac{\langle mn \mid \alpha\beta \rangle}{\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_{m} - \epsilon_{n}} \times C_{m}^{*} C_{n}^{*} C_{\beta} C_{\alpha} \mid 0\right\rangle\right].$$

$$(4)$$

 N_0 is a normalization constant, ϵ_i is the Hartree-Fock energy of spin orbital ϕ_i , and the $\langle mn \mid \alpha\beta \rangle$ are antisymmetrized two-electron integrals over the spin orbitals $\phi_m, \phi_n, \phi_{\alpha}, \phi_{\beta}$, where greek indices α, β label "occupied" Hartree-Fock spin orbitals, m, n label "unoccupied" orbitals, and i, j label either set. The Hartree-Fock wavefunction of the negative ion parent is represented by $|0\rangle$. Explicit formulas giving the elements of the $H(\Delta E_{\mu})$ matrix in terms of the orbital energies and two-electron integrals are given in Ref. 2. This method determines the ion-molecule energy difference from only a single calculation due to the formal cancellation of terms contributing equally to the energies of the parent and the daughter. Changes in correlation energy associated with the ionization process as well as contributions to the energy difference resulting from the adjustment of the Hartree-Fock orbitals of the parent (orbital relaxation) are included in the theory so as to provide second and third order corrections to the Koopmans' theorem estimate of the parent-daughter energy difference. The reader is referred to Ref. 2 for examples of the application of this theory to other positive and negative ions.

B. Basis sets

The starting point for the construction of the double zeta basis sets used in these calculations was Roetti and Clementi's excellent set of double zeta functions⁵ for the component atoms. To better describe the charge distribution in the resultant negative molecular ions, the orbital exponents of the functions with large expansion coef-

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TABLE I. Basis sets (STO's) for CN" and BO".

_	CN*					BO					
0	σorbitals		π orbitals			σ	orbita	ls	π orbitals		
center	nl	ζ	center	nl	ζ	center	nl	ζ	center	nl	ζ
С	1s	5,1231	С	2p	1,2566	В	15	4,2493	В	2p	0,9500
С	1s	7,5223	С	2p	2.7304	в	1s	6.5666	в	2p	2.2173
С	2s	0,9750	N	2p	1.3380	в	2s	0.8250	0	2p	1.5200
С	2s	1,9400	Ν	2p	3,2493	в	2s	1.6500	0	2p	3.6944
С	2p	1,2566		-		в	2p	0.8500		-	
с	2p	2,8700				в	2p	2.2173			
N	1s	5,9864				0	1_s	6.8377			
N	1s	8.4960				0	1s	9.4663			
N	2 <i>s</i>	2,3500				0	2s	2.8200			
N	2s	1,3750				0	2 s	1.6754			
N	2p	1,4992				0	2p	1.6586			
N	2p	3,2493				0	$\hat{2p}$	3.6944			

ficients in the highest occupied molecular orbital (HOMO) of CN⁻ and of BO⁻ were varied to maximize the ionization energies. The greatest changes in each case were produced by modifying the exponents of the 2s and $2p\sigma$ functions on the less electronegative atom in the ion.

Since little is known about the geometry of BO⁻, its basis set was optimized at R = 2.278 bohr, which corresponds to the equilibrium separation of the neutral BO molecule.⁶ The total energy before optimization was - 99.550 hartree and the corresponding $X^1\Sigma^* \rightarrow X^2\Sigma^*$ ionization potential was 2.16 eV. The final basis gave a slightly lower SCF energy, - 99.554 hartree, and a vertical ionization potential of 2.81 eV.

The CN⁻ basis set optimizations were performed at R = 2.2 bohr, the internuclear separation corresponding to the lowest energy found after a few preliminary SCF calculations on CN⁻ with the starting basis. The initial energy at 2.2 bohr was -92.2634 hartree, and the vertical ionization energy for the starting basis was 3.04 eV.

After optimization of 2s and $2p\sigma$ functions on carbon and 2s functions on nitrogen, the total energy was -92.2645 hartree and the $X^1\Sigma^* - X^2\Sigma^*$ vertical ionization energy was 3.69 eV. The diffuse $2p\pi$ function on nitrogen was varied slightly in an attempt to obtain a reasonable ${}^1\Sigma - {}^2\Pi$ ionization potential. However, the ${}^2\Pi$ state of CN is not expected to be well described in our basis since the optimization of the pi functions was not extensive. The final optimized CN^{*} and BO⁻ basis sets shown in Table I were used to compute ion-molecule energy differences at several internuclear separations; these differences were added to the total SCF energies at corresponding R values of the negative ions to generate SCF-level potential curves for BO and CN.

III. RESULTS

Examination of the ground state potential curves for BO, BO⁻, CN, and CN⁻ allows us to determine the adiabatic electron affinities of BO and CN, which we can compare with existing experimental data. Our predicted electron affinity for BO, 2.79 ± 0.2 eV, ⁷ is within the range of experimental estimates⁸ which vary from 2.4 eV to 3.1 ± 0.1 eV. Experimental studies of CN have yielded more precise results. Chupka *et al.*⁹ have reported an electron affinity of 3.82 ± 0.02 eV, which was obtained from photodissociation measurements on HCN. Our calculated electron affinity, 3.70 ± 0.02 eV, is in good agreement with this value.

The results of our EOM calculations and Koopmans' theorem estimates for vertical ionization potentials of CN⁻ and BO⁻ are shown in Table II for selected internuclear separations. The Koopmans' theorem values deviate considerably from EOM results for the ${}^{1}\Sigma^{*} \rightarrow {}^{2}\Sigma^{*}$ ionization of CN⁻, less so for the ${}^{1}\Sigma^{*} \rightarrow {}^{2}\Sigma^{*}$ BO⁻ ionization, and are actually very close to EOM results for the ${}^{1}\Sigma^{*} \rightarrow {}^{2}\Pi$ ionization of CN⁻.

The large difference between Koopmans' theorem and

TABLE II. Selected CH" and BO" ionization potentials.

		CN ⁻	BO				
<i>R</i> (a.u.)	$^{1}\Sigma^{+} \rightarrow ^{2}\Sigma^{+}$		$1\Sigma^{+} \rightarrow 2\Pi$			$^{1}\Sigma^{+} \rightarrow ^{2}\Sigma^{+}$	
	I. P. (eV)	$-\epsilon_{5\sigma}(eV)$	I. P. (eV)	$-\epsilon_{1r}(eV)$	<i>R</i> (a.u.)	I. P. (eV)	$-\epsilon_{5\sigma}(eV)$
2,75	3.74	4.62	3.60	3.53	2.80	3.10	3.56
2.70	3.74	4.70	3.76	3.70	2.35ª	2.88	3.23
2,35 ^b	3.71	5.14	4.93	5.01	2.278^{c}	2.81	3.14
2.30	3.70	5.18	5.11	5.21	2.20	2.72	3.04
2,25 ^{a,c}	3.69	5.21	5.29	5.43			
2.00	3.65	5.23	6.28	6.60			

^aR_e of the ion.

^bR_o of ²II state of the neutral.

^cR_e of ${}^{2}\Sigma^{+}$ state of the neutral.

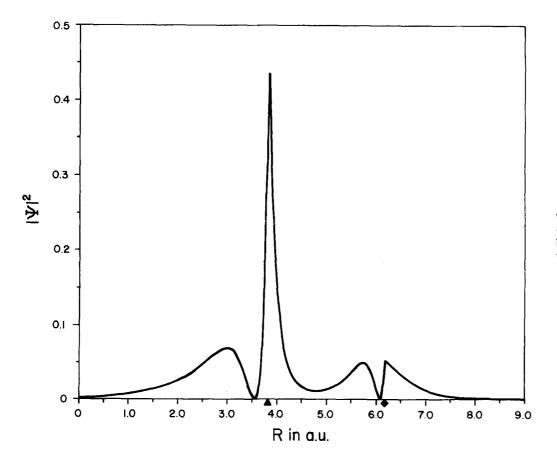


FIG. 1. A plot along the internuclear axis of the square of the BO⁻ wavefunction (\triangle boron center; \blacklozenge oxygen center).

the equations of motion results for the ${}^{1}\Sigma^{*} - {}^{2}\Sigma^{*}$ ionization of CN⁻ indicates that orbital relaxation and electron correlation effects are important in the process of removing an electron from the 5σ orbital of CN⁻. Analogously, relaxation and correlation effects appear to be less important in the ionization of BO'. The electron densities in the highest occupied 50 orbitals of BO⁻ and CN⁻, shown in Figs. 1 and 2, suggest a possible interpretation of this trend. The 50 orbital of BO⁻ is composed primarily of diffuse 2s and diffuse $2p\sigma$ functions on boron combined to form an sp-hybrid lobe directed away from the more electronegative oxygen nucleus. The electrons therefore reside primarily at the boron end of the diatomic system, with little electron density in the internuclear region, creating a nonbonding or slightly antibonding orbital. In the case of CN⁻, though, the electronegativity difference between the constituent atoms is not as great as the corresponding difference for BO⁻. The 5 σ orbital of CN⁻ contains diffuse 2s and 2p_{σ} functions on carbon as well as a diffuse $2p_{\sigma}$ nitrogen function, which results in the electron density being distributed on both ends of the molecule, with slightly more density on the carbon and a small amount in the internuclear region. The electrons in the HOMO of CN⁻ thus are seen to exist in regions of the molecule where there is high probability of interaction with the other electrons in the molecule. Electrons in the 5σ orbital of BO, however, reside primarily in a region of space essentially unoccupied by other electrons. The electron correlation effects associated with the loss of an electron in the 5σ orbital are therefore expected to be larger in CN⁻ compared to BO⁻.

Another consequence of the nature of the electron density in the HOMO's is the relative ease of ionization for electrons in the 5σ orbital of CN⁻ and BO⁻. Consider that the electrons in the BO⁻ HOMO are most likely to be found at the boron end of the diatom in a lone pair type orbital whereas the electrons in the HOMO of CN⁻ are distributed near both the carbon and the nitrogen nuclei. Boron is less electronegative than either carbon or nitrogen, so the electrons in the BO⁻ HOMO feel a smaller effective nuclear charge than those in the HOMO of CN⁻. Thus it should be easier to remove an electron from the 5σ orbital of BO⁻ than from the 5σ orbital of CN⁻. Our vertical ionization energies, 2.88 eV for BO⁻ and 3.69 eV for CN⁻, do show this behavior.

This discussion of the nature of the highest occupied molecular orbitals in CN⁻ and BO⁻ can be extended to include a comparison with the 5σ orbitals in the isoelectronic molecules N₂ and CO. The 5σ molecular orbital of N₂ is totally symmetric, being a combination of 2s and $2p\sigma$ functions on each center. The overlap of the sphybrids which point away from the internculear region results in little bonding, so this molecular orbital is mostly a nonbonding or "lone pair" orbital.

The 5σ orbital of CO is similar to the corresponding N_2 orbital, but it is strongly polarized toward the carbon center. It is a 2s-2p hybrid lobe whose dominant component is on the less electronegative atom, which contributes very little to the bonding. Thus we can see a trend as we move along the isoelectronic series from N_2 , CN⁻, CO to BO⁻; the electronegativity difference between the constituent atoms increases and the elec-

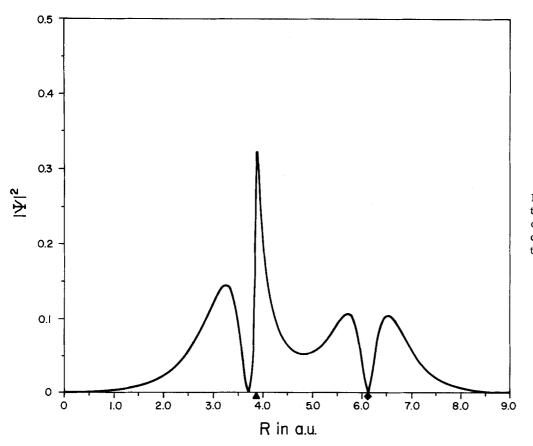


FIG. 2. A plot along the internuclear axis of the square of the CN⁻ wavefunction (\triangleleft carbon center; \blacklozenge nitrogen center).

tron density in the 5σ molecular orbital becomes more strongly polarized toward the less electronegative atom.

Unlike the case for the 5σ orbital of CN⁻, electron correlation and orbital relaxation effects do not provide significant corrections to Koopmans' theorem in ionization from the CN⁻ 1π orbital. This causes an interesting behavior as the internuclear separation of CN⁻ increases. The energy of the 1π orbital approaches that of the 5σ orbital; however, due to different magnitudes of correlation and relaxation effects for the $^{2}\Sigma^{+}$ and $^{2}\Pi$ ionizations, the energy of the ${}^{2}\Pi$ state of CN approaches that of the $^{2}\Sigma$ state at a different R value. That is, the $^2\Pi$ state of CN is found to lie higher in energy than the $^{2}\Sigma^{+}$ state at all R values up to 2.75 bohr, whereas the ordering of the 5σ and 1π orbital energies of CN⁻ indicates that the ${}^{2}\Pi$ state of CN should be the lower state at all R values greater than 2.35 bohr. The situation in the region from 2.35 to 2.75 bohr is similar to that encountered in the nitrogen molecule.¹⁰ Calculations on N₂ place the 5σ orbital lower in energy than the 1π . so the highest occupied molecular orbital is 1π . However, when N_2 is ionized, the ground state of N_2^* is found to be ${}^{2}\Sigma_{g}^{*}$; that is, the electron is more easily removed from the 5σ orbital even though that orbital is lower in energy than the 1π orbital. This situation is found for CN⁻ only over a short range of internuclear distances and is not found at all for BO".

IV. CONCLUSION

We have used the equations of motion method to study the stability of BO⁻ and CN⁻ and to investigate the nature of the highest occupied molecular orbital in each of these species. Our calculations show a ${}^{1}\Sigma^{+} \rightarrow {}^{2}\Sigma^{+}$ ionization energy of 2.88 eV for BO⁻ at 2.35 bohr, the equilibrium internuclear separation (R_e) of the ion, and an ionization potential of 2.81 eV at the R_e of BO, 2.278 bohr. The resulting adiabatic electron affinity of BO, 2.79 eV, falls within the range of experimental values obtained for this quantity. The EOM ionization potential (${}^{1}\Sigma^{+}$ $\rightarrow {}^{2}\Sigma^{+}$) of CN⁻ was found to be 3.69 eV at R = 2.25 bohr, the equilibrium separation of both the ion and the molecule. This result is very close to the experimental electron affinity of CN determined from photodissociation experiments.

In each of these ions, the electron is ionized out of a nonbonding 5σ molecular orbital consisting mainly of diffuse 2s and $2p_{\sigma}$ functions on the less electronegative atom in the ion. For CN⁻, there is also some contribution from the diffuse $2p_{\sigma}$ nitrogen function. The character of the 5σ orbital in the isoelectronic sequence, N₂, CN⁻, CO, BO⁻ changes in a regular fashion; the electron density in the 5σ orbital becomes more polarized toward the less electronegative atom as the electronegativity difference between the constituent atoms increases.

The ${}^{2}\Sigma^{*}$ and ${}^{2}\Pi$ states of CN were found to cross at about 2.75 bohr, whereas the Koopmans' theorem ionization energies predict the crossing at 2.35 bohr. The situation in the region from 2.35-2.75 bohr is analogous to the observed energy ordering of N₂ orbitals and N₂^{*} states, and is interpreted in terms of the larger correlation energy correction to Koopmans' theorem for ionization from the 5σ orbital of CN⁻ than from the 1π orbital.

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