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*Ab initio investigation of high multiplicity R<sub>p</sub>—R<sub>p</sub> [sigma superscript + - sigma superscript +] optical transitions in the spectra of CN and isoelectronic species*

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# *Ab initio* investigation of high multiplicity $\Sigma^+ - \Sigma^+$ optical transitions in the spectra of CN and isoelectronic species

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## Abstract

Based on high-level *ab initio* calculations, we predict the existence of a strong  ${}^4\Sigma^+ - {}^4\Sigma^+$  optical transition ( $\mathbf{d}_{\text{av}}=1.6$  D) near 328 nm ( $T_{00} = 30460$   $\text{cm}^{-1}$ ), analogous to the  $B {}^2\Sigma^+ - X {}^2\Sigma^+$  violet system, ( $\mathbf{d}_{\text{av}}=1.7$  D) in the near-ultraviolet spectrum of CN. The lower state of the predicted transition is the lowest-lying state of quartet multiplicity and has been observed previously through its perturbations of the  $B$  state. The predicted transition will enable determination of the equilibrium properties of the metastable lowest quartet state of CN. The lowest energy metastable sextet state of CN is also calculated to be quasibound ( $r_e=1.76$  Å,  $\omega_e = 365$   $\text{cm}^{-1}$ ), and a  ${}^6\Sigma^+ - {}^6\Sigma^+$  transition, analogous to those for the doublet and quartet multiplicities, is predicted ( $\mathbf{d}_{\text{av}}=2.2$  D). Investigation of the isoelectronic BO,  $\text{C}_2^-$ , and  $\text{N}_2^+$  molecules reveals that differences in  $2s^22p^x$  and  $2s^12p^{x+1}$  atomic energies play the key role in determining the magnitude of the  $5\sigma(2p) \leftarrow 4\sigma(2s)$ -derived  $\Sigma^+ - \Sigma^+$  transition energies for the different multiplets. Furthermore, the strong stabilization of  $2s^22p^x$  character with respect to  $2s^12p^{x+1}$  in BO and  $\text{N}_2^+$  leads to strongly bound lowest  ${}^6\Sigma^+$  states with binding energies as high as 2.0 eV. We believe that these newly predicted sextet states could be identified

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through their perturbations of quartet states of the relevant molecules.

*Key words:*

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## 1. Introduction

Low-lying metastable electronic states of small molecules often have very different chemical properties than the corresponding ground electronic states. Molecules in these metastable states may possess several eV of electronic energy but, due to the fact that they do not radiate to the ground electronic state, often elude detection by spectroscopic techniques. What is known about metastable electronic states is often derived from indirect experimental evidence, such as spectroscopic perturbations that arise from near degeneracies between rovibrational levels of the metastable state with rovibrational levels of well-characterized optically bright electronic states. Because these perturbations can occur at arbitrary degrees of vibrational and rotational excitation of the metastable electronic state, the spectroscopic parameters of the perturbing levels may be only tenuously related to the equilibrium properties of the metastable state. Further, as the “extra” lines in the spectrum correspond to only a small subset of the rovibrational structure, and the perturbing states are prone to fast collisional energy transfer into other states, it is not possible to determine from the spectrum the rovibrational distribution of population within the metastable state.

The lowest-lying quartet state of the CN radical,  $a\ ^4\Sigma^+$ , has been experimentally observed only through perturbations with the  $B\ ^2\Sigma^+$  state, the upper state of the CN violet bands. The perturbation of the  $B$  state at  $v = 11$ ,  $N = 20$  was first observed at high resolution by Coxon, Ramsay, and Setser[1], who argued that the perturbing state likely has  $^4\Sigma^+$  symmetry. A similar perturbation was later observed by Yenchu *et al.*[2] These observations were in accord with *ab initio* calculations by Schaefer and Heil[3] that predicted several low-lying quartet electronic states within 10 eV of the ground electronic state, with the lowest, a  $^4\Sigma^+$  state, 4 eV above the ground state minimum. Zeeman anticrossing measurements were used to characterize the rotational[4] and fine-structure[5] parameters of the perturbing level of the  $a\ ^4\Sigma^+$  state.

The  $B\ ^2\Sigma^+ - a\ ^4\Sigma^+$  perturbation causes intensity anomalies in the R(19) and P(21) emission lines of the  $(v', v'') = (11, 11)$  member of the  $B - X$  violet tail-band system when CN is produced by dissociative excitation of a cyanide-

containing molecule in the reaction with argon metastable atoms. These intensity anomalies indicate that a significant portion of the CN radicals are produced in metastable quartet states. Recently, Ito and coworkers[6] have identified the possibility that the nature of the metastable quartet electronic states contributes to precursor-dependent behavior in the chemical vapor deposition of amorphous-CN<sub>x</sub> films. Although subsequent investigations have favored ion-mediated processes as the determining factor for film hardness[7], quantification of the quartet state population is desirable. As the  $a\ ^4\Sigma^+$  state cannot decay radiatively by any spin-allowed transitions, emission spectroscopy unlikely to provide a definitive method for determining the doublet/quartet branching ratio.

Modern spectroscopic techniques are achieving the levels of sensitivity and resolution required to enable the analysis of the rotational structure of transitions within the high spin multiplicity manifolds of small molecules. A recent example is the determination of the spin-orbit constant of the  $C''\ ^5\Pi_{ui}$  state of N<sub>2</sub>[8, 9, 10].

Laser-induced fluorescence of the strong CN  $B - X$  transition has long been used an extremely convenient method of determining the internal state distribution of CN reaction products[11]. In order to locate a transition suitable for the detection of population in the low-lying quartet states, we require accurate predictions of the higher-lying quartet states. Although some high-level calculations of the lower quartet states have been reported[12, 13], the only predictions in the literature of the higher quartet excitations are due to Schaefer and Heil[3], who were limited by computing power to a very small basis set. In this work, we describe high-level *ab initio* calculations of the doublet, quartet, and sextet electronic states of CN in order to identify the appropriate frequency region to search for strong quartet-quartet transitions. Fluorescence detection is applicable only in cases where the radiative lifetime of the upper state of the transition is shorter than, or comparable to, the lifetime due to non-radiative processes, most notably predissociation. In the case of fast non-radiative decay, sensitive absorption-based methods such as cavity ringdown spectroscopy or frequency-modulation spectroscopy provide equivalent information.

## 2. Methods

First principles calculations were carried out using the MOLPRO 2006.1 quantum chemistry package[14]. For multi-configuration self-consistent field

(MCSCF) and subsequent multi-reference configuration interaction (MRCI) calculations, we employed the aug-cc-pVTZ basis set. Relative energies from aug-cc-pVTZ calculations were compared with the larger basis set, aug-cc-pVQZ, and found to be converged within less than 0.5% for equilibrium bond lengths and fundamental frequencies. The data collected at the aug-cc-pVQZ basis-set level was across a large range of internuclear separations ( $r = 1 - 5$  Å). Dissociation limits, which were derived either from taking the asymptotic limit of the potential energy curve or from the direct atomic energies, were determined to be overestimated by as much as 0.05 eV (around 0.5-1%), but typically on the order of 0.005-0.02 eV, for the aug-cc-pVTZ basis when compared against aug-cc-pVQZ. The basis-set-dependent difference in doublet, quartet, or sextet  $\Sigma^+ - \Sigma^+$  energetic splittings was found to be on the order of 0.006 eV or less. The symmetry of each electronic state was determined from the expectation value of  $\hat{L}_z^2$ . For the majority of MRCI calculations, a state-averaged approach was used for the underlying MCSCF calculations in order to converge the lowest two to four roots. The dominant configuration, which was used to identify nominal electron configurations, consisted of at least 80% of the total wavefunction. Additionally, transition dipole moments were calculated between several key states over a large range of internuclear separation. Finally, the potential energy curve of each state was determined over a 0.005 Å mesh in order to ensure a sufficient data set to allow for smooth interpolation. A linear fit to the derivative at the minimum of each curve was used to determine the equilibrium bond length and harmonic frequency of each state. Leroy’s LEVEL code[15] was used for the calculation of vibrational levels and Franck-Condon factors using potentials obtained from the *ab initio* calculations. Spin-orbit coupling calculations were carried out using the full Breit-Pauli SO-operator on the MCSCF wavefunctions.

### 3. Results and Analysis

#### 3.1. Doublet states of CN

The ground state of CN is well-known to be  $X^2\Sigma^+$ , and our theoretical bond length, 1.18 Å, and fundamental frequency, 2035  $\text{cm}^{-1}$ , are in good agreement with experiments (1.172 Å, 2068.68  $\text{cm}^{-1}$ )[16]. The qualitative electron configuration of this state is  $3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 2\pi^{*,0}$ , corresponding to a bond order of roughly 2 to 2.5 as a result of the weakly bonding character of  $5\sigma$  (see Fig. 1). The next lowest state,  $A^2\Pi$ , differs from the ground state by preferential population of the  $5\sigma$  in the minority spin in place of

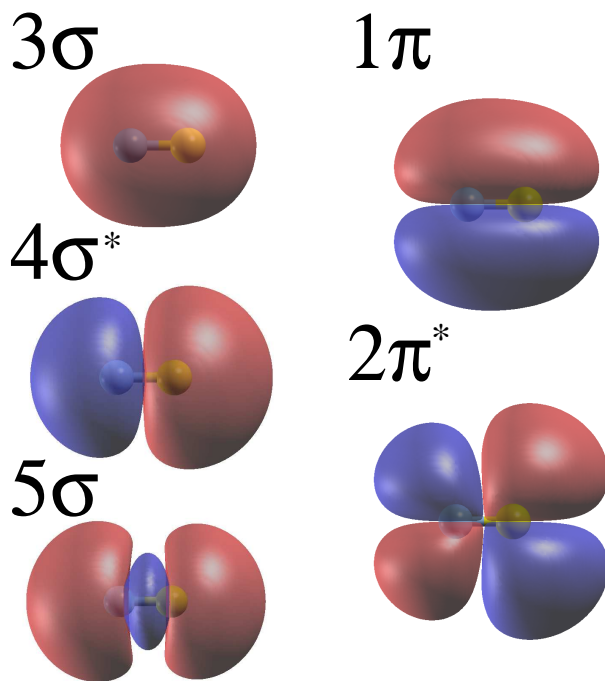


Figure 1: Canonical occupied valence molecular orbitals relevant for both doublet and quartet low-lying states of CN. In each molecular orbital isosurface diagram, N appears to the left and C to the right.

one of the occupied  $1\pi$  orbitals in  $X \ ^2\Sigma^+$ , also corresponding to a slight decrease in bond order. The  $A \ ^2\Pi$  state resides 1.13 eV above the ground state, with a bond length of 1.2 Å and frequency of  $1821 \text{ cm}^{-1}$  consistent with the qualitative change in bond order (see Table 1). Both the  $X$  and  $A$  states dissociate adiabatically to the first dissociation limit, C ( $1s^22s^22p^2 \ ^3P$ ) + N ( $1s^22s^22p^3 \ ^4S$ ), but there exist several higher energy states that are derived from higher dissociation limits.

The next lowest state,  $B \ ^2\Sigma^+$ , is 3.23 eV above the ground state and is the upper state of a strong  $B - X$  optical transition known as the CN violet band system[18, 19]. This state corresponds to a  $5\sigma \leftarrow 4\sigma$  excitation from an anti-bonding orbital to a weakly bonding but very diffuse orbital, which has very little effect on bond order. The result is that the  $B \ ^2\Sigma^+$  equilibrium bond length, 1.16 Å, and frequency,  $2133 \text{ cm}^{-1}$ , are both very close to the values of the ground state (see Table 1). The next six higher

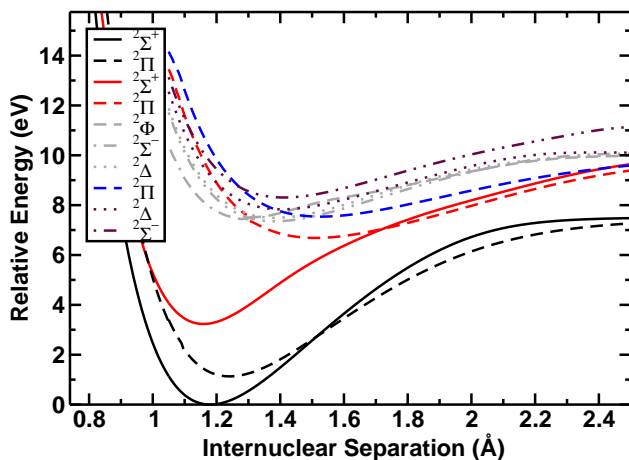


Figure 2: Potential energy curves (in eV) of the lowest lying states of doublet CN including the ground state,  $X\ ^2\Sigma^+$  (black, solid line), and the next few excited states,  $A\ ^2\Pi$  (black, dashed line),  $B\ ^2\Sigma^+$  (red, solid line), and  $C\ ^2\Pi$  (red, dashed line). For reference, several higher energy states are shown, many of which lie within a narrow 1 eV band around 7-8 eV above the ground state.

energy states all reside in an energy window 6-8 eV above the ground state and consist primarily of states in which there is a  $2\pi^* \leftarrow 1\pi$  excitation and thus longer bond lengths of around 1.4 Å and lower frequencies around 1700  $\text{cm}^{-1}$  (see Table 1 and Fig. 2). The structure and relative energies differ only slightly among these states; for example, the  $^2\Sigma^-$  and  $^2\Delta$  states are essentially identical except for the electronic orbital angular momentum.

Transition dipole moments were calculated between the low-lying doublet valence states. First, the strong and optically accessible  $B - X$  transition was found to have a dipole moment of about 1.7 D at its maximum value at 1.17 Å, corresponding to the average bond length for the two states (see Fig. 7). The transition dipole decreases smoothly as one moves away from the minimum in either direction. In the case of  $B - A$  and  $A - X$  transitions, the magnitude of the transition dipole moment is less than that for the  $B - X$  transition (see Fig. 3). For the  $A\ ^2\Pi - X\ ^2\Sigma^+$  transition, a single maximum of 0.8 D at a bond length of 1.15 Å, about half of the calculated transition dipole moment for  $B - X$ . The  $B\ ^2\Sigma^+ - A\ ^2\Pi$  transition dipole moment maximum is even smaller, at about 0.4 D. Notably, the transition dipole moment exhibits two maxima at differing interatomic distances, one at a very short distance around 0.8 Å and one at around 1.6 Å (see Fig. 3). The

second maximum is likely a result of the avoided  $B - X$  crossing at around this distance, which induces some mixing between the  $B$  and  $X$  states. The  $B - A$  transition is enhanced via  $B - X$  mixing as a direct result of a very strong  $B - X$  transition dipole moment that makes the character of the  $B - A$  transition equivalent to the  $A - X$  transition dipole moment for that range of internuclear distances. This argument has been invoked earlier to explain the internuclear distance dependence of the electronic dipole moments of the  $X$ ,  $A$  and  $B$  states by Knowles, *et al.*[20]. At short bond lengths, the  $B$  and  $A$  curves are very close in energy, and they likely are derived from the same united atom limit, thus a maximum in the  $B - A$  transition dipole moment is also observed at a short bond length.

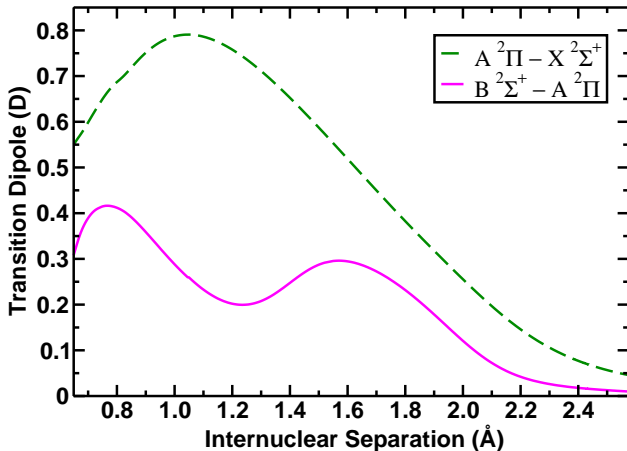


Figure 3: Transition dipole moments (in Debye) of the  $A \ ^2\Pi - X \ ^2\Sigma^+$  (green, dashed line) and  $B \ ^2\Sigma^+ - A \ ^2\Pi$  transitions shown as a function of internuclear separation (in Å). The stronger  $A - X$  transition exhibits a maximum at a bond length of 1.15 Å, near the minimum of the ground state PES, while the weaker  $B - A$  transition exhibits two maxima at 0.8 and 1.6 Å.

### 3.2. Quartet states of CN

While the lowest-lying states of CN all exhibit doublet character, two excited quartet states,  $a \ ^4\Sigma^+$  and  $b \ ^4\Pi$ , have been previously experimentally observed[1, 4, 5, 2, 21, 22, 23, 24, 25]. The lowest quartet state,  $a \ ^4\Sigma^+$ , is calculated to reside 4.80 eV above the doublet ground state. This large separation in energy is due to the higher energy valence orbitals that are by necessity occupied in quartet states as a result of a greater imbalance between



spin-up and spin-down electrons. That is, all of the lowest energy calculated quartet states exhibit a  $1\pi^3 2\pi^{*,1}$  configuration before additional excitations are considered. In the case of the doublets,  $2\pi^* \leftarrow 1\pi$  excitation produces states residing roughly 6 eV above the ground state. These excitation energies are consistent with the 4.8-8.6 eV energy window in which we find the first six quartet electronic states (see Table 2). The lowest quartet state  $a\ ^4\Sigma^+$  electron configuration is, in fact,  $3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^{*,1}$ , which corresponds to a bond order roughly of 1 to 1.5. The structural parameters of the  $a\ ^4\Sigma^+$  state are a bond length of 1.37 Å and a frequency of 1333  $\text{cm}^{-1}$ .

The next lowest quartet state,  $b\ ^4\Pi$ , lies 1.07 eV above the lowest quartet, consistent with the 1.13 eV energy separation between  $^2\Sigma^+$  and  $^2\Pi$ . In this case, as in the case of the doublet, the  $\Pi$  state favors enhanced  $5\sigma$  occupation in the minority spin in lieu of population of  $1\pi$ . This difference corresponds to an apparent decrease in bond order again with the  $b\ ^4\Pi$  state having an equilibrium bond length of 1.52 Å and a frequency of 1030  $\text{cm}^{-1}$ . While only the two lowest quartet states of CN have been experimentally observed, we predict several other quartet states to reside within 2-3 eV of the previously observed states. Namely, permutations of the orientation of the electron configuration similar to that in the ground state gives rise to  $^4\Delta$  and  $^4\Sigma^-$  states. Additionally, one of the excited states,  $^4\Pi$ , exhibits a shorter bond length of about 1.23 Å and frequency of 1860  $\text{cm}^{-1}$ . This state has a higher apparent bond order as a result of preferential occupation of  $1\pi$  in lieu of  $4\sigma$  in the minority spin with respect to the ground state.

We note that one of these higher-lying quartet states, a second  $^4\Sigma^+$  state, is analogous to the  $B\ ^2\Sigma^+$  state. This state has an electron configuration of  $3\sigma^2 4\sigma^1 5\sigma^2 1\pi^3 2\pi^{*,1}$ , which results from promotion of a minority spin orbital from  $4\sigma$  to  $5\sigma$ . The resulting bond length in this case increases only very slightly from 1.37 Å in the lowest quartet state to 1.38 Å and the vibrational frequency is slightly decreased from 1333  $\text{cm}^{-1}$  to 1184  $\text{cm}^{-1}$ . The trend from the lower to higher  $\Sigma^+$  states in the quartets is reversed very slightly from that in the case of the doublets, but in either case the change in structural properties is minimal as a result of  $5\sigma$  being only very weakly bonding. The  $2\ ^4\Sigma^+ - a\ ^4\Sigma^+$  splitting is 3.79 eV, an increase from the splitting value for the doublets. Importantly, this  $2\ ^4\Sigma^+$  state is not the third lowest quartet state as a number of lower energy quartet states reside between the two  $^4\Sigma^+$  states as a result of the greater open shell character of the quartets.

In addition to considering the similarities of the  $2\ ^4\Sigma^+ - a\ ^4\Sigma^+$  transition in the quartets and the  $B - X$  transition in the doublets, we also examined the

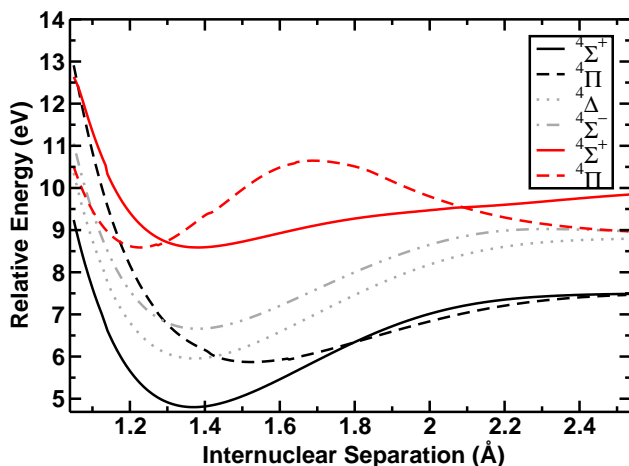


Figure 4: Potential energy curves (in eV) of the lowest lying states of quartet CN including the lowest,  $a\ 4\Sigma^+$  (black, solid line) and  $b\ 4\Pi$  (black, dashed line) as well as  $a\ 4\Sigma^+$  (red, solid line), which is analogous to the  $B\ 2\Sigma^+$  state observed in the doublet case. The relative energies are determined with respect to the doublet ground state,  $X\ 2\Sigma^+$ , and, therefore, the first quartet state resides at about 4.8 eV.

transitions between the two lowest quartet states and the higher energy  $2\ 4\Sigma^+$  state. We observed the  $b\ 4\Pi - a\ 4\Sigma^+$  transition dipole moment to be smaller than that for  $2\ 4\Sigma^+ - b\ 4\Pi$ , in an apparent reversal of the trend observed in the doublets. In both cases, a single maximum exists in the transition dipole moments at short bond lengths around 1.3 Å. The maximum for the  $b - a$  transition is around 0.4 D, while that for the  $2\ \Sigma^+ - b$  transition is around 0.6 D (see Fig. 5). These transition dipole moments, however, are of similar magnitude to those for previously experimentally observed transitions between doublet states.

The strong doublet  $B - X$  transition has been provided a convenient method of probing CN radical population and has been instrumental in identification of other electronic states of CN via rotational perturbations. We will now demonstrate that there is an equally strong analogous transition in the quartet manifold. A comparison of the lowest and first excited  $\Sigma^+$  states of doublet and quartet multiplicity shows that, in both cases, the lowest state dissociates adiabatically to the first dissociation limit, C ( $1s^22s^22p^2\ 3P$ ) + N ( $1s^22s^22p^3\ 4S$ ), while the excited state,  $B\ 2\Sigma^+$  or  $2\ 4\Sigma^+$ , correlates with a higher dissociation limit. In both spin cases, the excited state exhibits a slightly shorter bond length, indicative of promotion from a weakly anti-

bonding  $4\sigma$  orbital to a weakly bonding but more diffuse  $5\sigma$  orbital. The doublet and quartet excitations are of similar magnitude in energy, 3.23 eV and 3.79 eV, respectively, but we will later show that this small increase in the quartet excitation energy is symptomatic of a hybridization-dependent trend. When we compare the transition dipole moments (see Fig. 7) for both doublet and quartet  $\Sigma^+ - \Sigma^+$  transitions, we see that the maximum transition moment and the dependence on interatomic distance are comparable for the two manifolds. In fact, the quartet curve appears to be only slightly shifted outward with respect to the doublet, proportional to the difference in average equilibrium bond lengths between the doublet and quartet states. Therefore, since the  $B - X$  optical transition in the doublets is quite strong, one would expect this analogous quartet transition also to be observable experimentally in a sample containing metastable quartet CN.

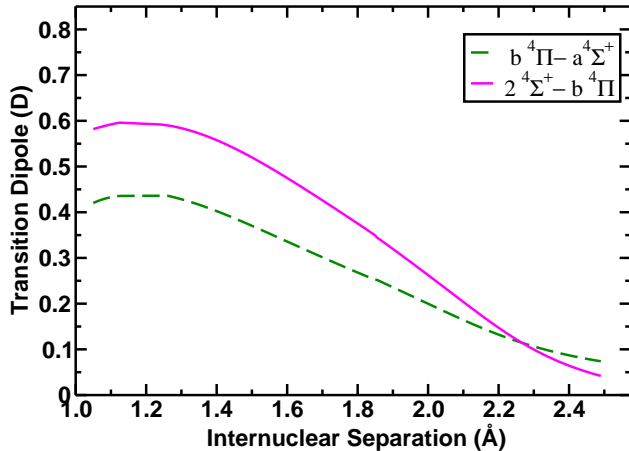


Figure 5: Transition dipole moments (in Debye) of the  $b\ ^4\Pi - a\ ^4\Sigma^+$  (green, dashed line) and  $2\ ^4\Sigma^+ - b\ ^4\Pi$  transitions, shown as a function of internuclear separation (in Å). The  $2\ ^4\Sigma^+ - b$  transition moment, while stronger than the  $b - a$  transition, exhibits a maximum at roughly the same bond length, 1.15 Å.

### 3.3. Metastable sextet states

The high spin nature of the isolated atomic fragments of CN naturally gives rise to a number of high spin sextet molecular states that have not been observed experimentally. While, in general, these states lie quite high in energy or tend to not be very strongly bound, we believe that they could be found to perturb states of the quartet manifold. The lowest calculated

Table 1: Symmetry, bond length,  $r_e$  (Å), harmonic frequency,  $\omega_e$  (cm<sup>-1</sup>), energy,  $T_e$  (eV), and nominal electron configuration for nine low-lying doublet states of CN. States which have been identified experimentally are identified by their spectroscopic labels.

State	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$T_e$ (eV)	<i>Configuration</i>
X <sup>2</sup> Σ <sup>+</sup>	1.180	2035	0.00	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 2\pi^{*,0}$
A <sup>2</sup> Π	1.241	1821	<b>1.13</b>	$3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3 2\pi^{*,0}$
B <sup>2</sup> Σ <sup>+</sup>	1.159	2133	<b>3.23</b>	$3\sigma^2 4\sigma^1 5\sigma^2 1\pi^4 2\pi^{*,0}$
D <sup>2</sup> Π	1.527	986	6.69	$3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 2\pi^{*,1}$
E <sup>2</sup> Σ <sup>+</sup>	1.331	1681	7.34	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^{*,1}$
<sup>2</sup> Σ <sup>-</sup>	1.382	1261	7.35	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^{*,1}$
F <sup>2</sup> Δ	1.384	1272	7.49	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^{*,1}$
<sup>2</sup> Π	1.512	1001	7.54	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^2 2\pi^{*,1}$
<sup>2</sup> Δ	1.412	1189	7.83	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^{*,1}$
<sup>2</sup> Σ <sup>-</sup>	1.405	1194	8.31	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^{*,1}$

Table 2: Symmetry, bond length,  $r_e$  (Å), harmonic frequency,  $\omega_e$  (cm<sup>-1</sup>), energy with respect to the lowest doublet and quartet states,  $T_e$  and  $T'_e$  (eV), and nominal electron configuration for six low-lying quartet states of CN. States which have been identified experimentally are noted.

State	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$T_e$ (eV)	$T'_e$ (eV)	<i>Configuration</i>
a <sup>4</sup> Σ <sup>+</sup>	1.370	1333	4.80	0.00	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^{*,1}$
b <sup>4</sup> Π	1.523	1030	5.87	<b>1.07</b>	$3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2 2\pi^{*,1}$
<sup>4</sup> Δ	1.373	1295	5.95	1.15	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^{*,1}$
<sup>4</sup> Σ <sup>-</sup>	1.381	1281	6.66	1.86	$3\sigma^2 4\sigma^2 5\sigma^1 1\pi^3 2\pi^{*,1}$
<sup>4</sup> Π	1.228	1860	8.59	3.79	$3\sigma^2 4\sigma^1 5\sigma^1 1\pi^4 2\pi^{*,1}$
<sup>4</sup> Σ <sup>+</sup>	1.380	1184	8.59	<b>3.79</b>	$3\sigma^2 4\sigma^1 5\sigma^2 1\pi^3 2\pi^{*,1}$

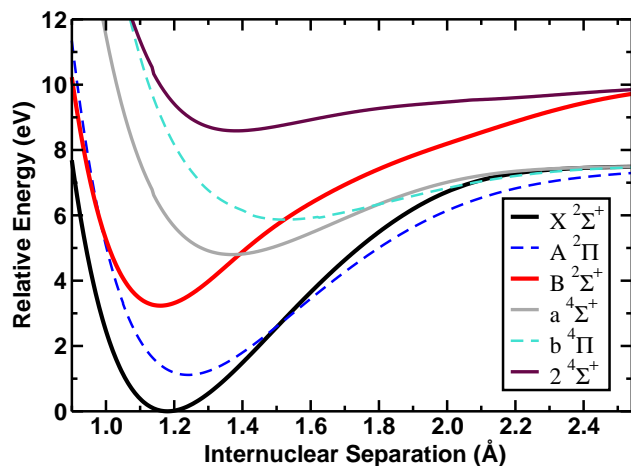


Figure 6: Potential energy curves (in eV) of the lowest lying doublet and quartet states of CN. For both multiplicities, the lowest  $\Sigma^+$  state (in black or gray) is shown, as well as the first excited  $\Sigma^+$  state (in red or maroon). Additionally, the lowest  $\Pi$  state is shown for both the doublet and quartet (in blue or light blue dashed lines, respectively). The lowest doublet and quartet  $\Sigma^+$  states share the same first dissociation limit along with both  $\Pi$  states, while the excited doublet and quartet  $\Sigma^+$  states both correspond to a higher dissociation limit.

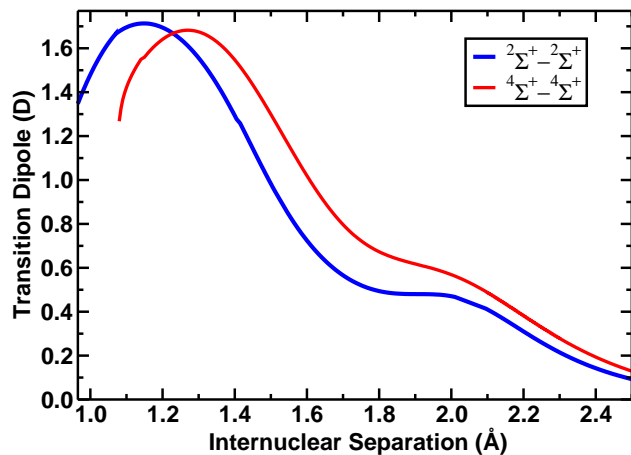


Figure 7: Transition dipole moments (in Debye) of the  $\Sigma^+ - \Sigma^+$  transitions for the doublet ( $B - X$ , in thick, blue line) and quartet ( $2 \Sigma^+ - a$ , thinner, red line) shown as a function of internuclear separation (in Å).

sextet state of CN,  $^6\Sigma^+$ , correlates adiabatically with the first dissociation limit and is bound only by roughly 0.06 eV. This very weakly bound state

has an equilibrium bond length around 1.76 Å and a vibrational frequency of 365 cm<sup>-1</sup>. This very shallow binding curve is explained by the nominal electron configuration: in the majority spin, it has 3σ<sup>1</sup>4σ<sup>1</sup>5σ<sup>1</sup>1π<sup>2</sup>2π<sup>\*2</sup> and in the minority it has 3σ<sup>1</sup>4σ<sup>1</sup>. The net bonding interaction in this state is derived exclusively from the 5σ molecular orbital, which we have already previously demonstrated to be quite diffuse in nature and to only weakly contribute to the net bond order of the molecule in most cases. The small number of possible configurations with net bonding interactions also gives rise to numerous repulsive states, which have avoided crossings with the quasi-bound states that do have net bonding interactions.

However, we note that the lowest <sup>6</sup>Σ<sup>+</sup> state is connected to an excited <sup>6</sup>Σ<sup>+</sup> state by a single 5σ ← 4σ electron excitation similar to that observed in the doublet and quartet cases. The roughly nonbonding character of the 5σ orbital is consistent with a slight elongation of the bond to 2.14 Å and lower frequency of 267 cm<sup>-1</sup> for the excited <sup>6</sup>Σ<sup>+</sup>. Both <sup>6</sup>Σ<sup>+</sup> states are weakly bound with binding energies on the order of 0.05-0.10 eV, but transition dipole moments with a maximum of 2.2 D are comparable to, or even slightly stronger than, the transition dipoles calculated within the doublet or quartet manifolds. The sextet Σ<sup>+</sup> – Σ<sup>+</sup> splitting also follows the trend of increased splitting in the higher multiplicities, with the splitting of 3.98 eV between the two states being an increase over that for the quartet or doublet at 3.79 and 3.23 eV, respectively. This trend suggests that the decreased presence of alternatively 2*p*-derived π density in the minority spin channel, which goes from two electrons in the doublet to one electron in the quartet and, finally, to zero electrons in the sextet, increases the 5σ ← 4σ splitting.

### 3.4. Franck-Condon factors for Σ<sup>+</sup> – Σ<sup>+</sup> excitations

Following the identification of excitations of quartet and sextet Σ<sup>+</sup> CN via promotion of 4σ to 5σ in an analogous manner to that which has been experimentally observed in the doublet manifold, we calculated Franck-Condon factors and energetics of the relevant transitions. Comparison of the Franck-Condon factors for the lowest vibrational states of the *B* – *X* transition in the doublet manifold with the 2 <sup>4</sup>Σ<sup>+</sup> – *a* transition in the quartet manifold shows that both are dominantly diagonal in vibrational quantum number (see Tables 4 and 5).

Both doublet and quartet Franck-Condon matrices show comparable values for the 0-0 transition, but the F-C factors for the quartet case are more

Table 3: Summary of calculated energies (in  $\text{cm}^{-1}$ ) of the lowest few excitations for the analogous doublet, quartet, and sextet  $\Sigma^+ - \Sigma^+$  transitions. For comparison, the experimentally derived transition energies from Ref. [16] for the  $B - X$  band system are listed in parentheses.

$v' - v''$	Doublet	Quartet	Sextet
0-0	26135 (25798)	30460	32048
1-1	26209 (25879)	30213	–
2-2	26268 (25946)	29925	–
3-3	26308 (25998)	29597	–
4-4	26327 (26030)	29229	–

Table 4: Franck-Condon factors for the transition between the  $X^2\Sigma^+$  and  $B^2\Sigma^+$  states of CN.

		$B^2\Sigma^+ v'$				
		0	1	2	3	4
$X^2\Sigma^+$ $v''$	0	0.9169	0.0818	0.0013	0.0000	0.0000
	1	0.0768	0.7728	0.1474	0.0030	0.0000
	2	0.0059	0.12854	0.6620	0.1991	0.0042
	3	0.0004	0.0153	0.1597	0.5808	0.2390
	4	0.0000	0.0014	0.0263	0.1740	0.5261

Table 5: Franck-Condon factors for the transition between the  $a^4\Sigma^+$  and  $2^4\Sigma^+$  states of CN. This transition is analogous to the  $B - X$  transition in the doublet manifold.

		$2^4\Sigma^+ v'$				
		0	1	2	3	4
$a^4\Sigma^+$ $v''$	0	0.9814	0.0174	0.0007	0.0004	0.0000
	1	0.0143	0.9064	0.0774	0.0000	0.0015
	2	0.0041	0.0567	0.7366	0.1939	0.0052
	3	0.0001	0.0181	0.1261	0.4734	0.3332
	4	0.0000	0.0012	0.0509	0.1915	0.1901

strongly diagonal at low excitation and less strongly diagonal at higher excitation than in the doublet case. We note that, while omitted here, the 0-0 Franck-Condon factor for the sextet case is much smaller, at around 0.03, because of the large mismatch in bond lengths and structure. We summarize in Table 3 the predicted frequencies of the strongest observable  $\Sigma^+ - \Sigma^+$  transitions. As there exists the possibility of a slight systematic shift in the energies of the upper states calculated with respect to their true experimental energies, we compare the energetics of the experimentally known doublet transitions with the quartet transitions to provide an estimate in the size of the experimental search window required locate the predicted transitions. The agreement between the calculated values of the  $B - X$  transition energies and those experimentally reported by Ram *et al.*[16] is quite good, with the calculations overestimating the transition energies by approximately 300  $\text{cm}^{-1}$ . Further evidence of the quality of the calculated potentials is the excellent agreement between the calculated Franck-Condon factors for the  $B - X$  transition (Table 4) and those derived from experiment by Prasad and Bernath[17]. For the  $\Delta v = 0$  transitions, the agreement is better than 1%. For the much weaker  $\Delta v = 1$  transitions, the agreement is better than 5%.

The low-lying quartet states of CN have been exclusively identified through their perturbations of the  $B^2\Sigma^+$  state, and as a test of the quality of our potentials, we verified the previously assigned perturbations. We confirmed the identification of the perturbation of the  $B^2\Sigma^+$  state by  $a^4\Sigma^+$  as  $(v_B, v_a) = (11, 7)$ , as has been previously suggested[13]. Our identifications of the known perturbations by  $b^4\Pi$ [22, 23, 24] were more problematic owing to poor quality of the calculated  $b^4\Pi$  potential, as well as an overestimate of its relative energy. Overall, we were still able to recover the qualitative positions of likely perturbations and the associated non-negligible vibrational overlaps. In addition, we found systematic near-degeneracies between the vibrational levels of  $B^2\Sigma^+$  and  $c^4\Delta$ . Our results show reasonably large Franck-Condon factors, around 0.10-0.20, for a variety of vibrational levels in of the range of  $(v_B, v_c) = (16, 5)$  to  $(20, 9)$ . However, perturbations between  $B$  and  $c$  states cannot occur directly due to the  $\Delta\Lambda = 0, \pm 1$  restriction on the spin-orbit matrix elements. It is possible that higher-order effects could give rise to observable features in the spectrum, but such features would likely be overshadowed by the  $b^4\Pi - B^2\Sigma^+$  perturbations that also occur in this energy range.

As we were able to confirm the likelihood of quasi-bound  $^6\Sigma^+$  states,



we attempted to identify which quartet states might be perturbed by these states as a means of identification of the sextet states. Exploration of all candidate quartet states showed that the  ${}^4\Sigma^-$  state, which is nominally the fourth lowest quartet state, is likely to experience spin-orbit perturbations  $(v_{4\Sigma^-}, v_{6\Sigma^+}) = (5, 0)$  to  $(6, 0)$  with a Franck-Condon factor of about 0.08. Perturbations of the  ${}^4\Sigma^-$  state are not likely to be observed experimentally. However, we will show that several similar molecules exhibit more strongly bound sextet states, which may be more straightforwardly identified by their perturbations of quartet states.

### 3.5. Predissociation

Because of the long history of spectroscopy on CN, it is perhaps surprising that a transition as strong as the one predicted in this work would have escaped detection. We are not aware of any features present in the classical spectra that may be associated with the  ${}^4\Sigma^+ - {}^4\Sigma^+$  transition. Douglas and Routly reported the existence of some unidentified bands in their analyses of the spectra of  $\text{CN}^+$ [26] and CN[27], but provided a rotational analysis of only one of these bands, which was determined to arise from a  $\Pi - \Sigma$  transition. Either the upper state of the transition is predissociated rapidly, thus preventing detectable emission, or the state is not generated in significant quantity in the sources traditionally used in CN spectroscopy. The classical emission spectroscopy of CN was generally performed using a flowing active nitrogen source[28] or a hollow cathode discharge of helium with trace  $\text{C}_2\text{N}_2$ [26, 27, 29]. Using the helium discharge, Carroll observed emission from states with up to 8 eV of electronic excitation ( $J^2\Pi_i$ ,  $T_e = 65\,258\text{ cm}^{-1}$ ), demonstrating both that states that lie above the first dissociation limit ( $D_0 \sim 7.7\text{ eV}$ ) are formed in the discharge source and that these states are not universally predissociated. Later experiments demonstrated that an argon discharge containing BrCN was significantly more effective at producing quartet CN[5], but the degree of electronic excitation in these sources is likely insufficient to populate the higher-lying quartet states.

In order to assess the likelihood of predissociation of the  $2\,{}^4\Sigma^+$  state, calculations were carried out with the goal of locating states with potential energy curves that cross that of  $2\,{}^4\Sigma^+$ . Attention was focussed on those states that correlate with the lowest dissociation limit. Of these, only the  ${}^6\Sigma^+$  and  ${}^6\Pi$  states cross  $2\,{}^4\Sigma^+$  state in the range of internuclear separation relevant for the lowest few vibrational wavefunctions on the  $2\,{}^4\Sigma^+$  potential. The  ${}^6\Sigma^+$  state crosses  $2\,{}^4\Sigma^+$  near the minimum of the latter state, however

the interaction between them is forbidden by the spin-orbit selection rule  $\Sigma^+ \leftrightarrow \Sigma^+$ . The  $2^4\Sigma^+$  is crossed on its outer limb, at approximately 2 Å, by the lowest  $^6\Pi$  state. These states may interact via the spin-orbit operator, but the electronic matrix element at the crossing is calculated to be relatively small, on the order of  $1\text{ cm}^{-1}$ . The contribution of the sextet states to the nonradiative decay of  $2^4\Sigma^+$  is therefore expected to be minor. It is possible that contributions to the non-radiative decay may arise from states that correlate to higher dissociation limits such as the the second  $^4\Pi$ , which correlates to  $\text{C } (^1\text{D}) + \text{N } (^4\text{S})$ . This  $^4\Pi$  state is quasibound (see Fig. 4) and crossings with the  $2^4\Sigma^+$  occur both near the minimum of the  $^4\Sigma^+$  state and on its outer limb. The minimum of the  $2^4\Sigma^+$  state lies very near the  $\text{C } (^1\text{D}) + \text{N } (^4\text{S})$  dissociation limit; consequently, the lowest few vibrational levels have wavefunctions that do not sample the outer limb crossing and are unlikely to be rapidly predissociated by this interaction.

### 3.6. Variations among isoelectronic molecules: $\text{BO}$ , $\text{C}_2^-$ , $\text{N}_2^+$ and $\text{CN}$

We consider here the properties of the first  $\Sigma^+$  state and the excited  $\Sigma^+$  state connected by  $5\sigma \leftarrow 4\sigma$  electronic excitation of a few molecules isoelectronic with  $\text{CN}$ . The goal is to further understand the relative sensitivity of properties of these  $\Sigma^+$  states to the nuclear character and relative  $2s$  and  $2p$  configurations. Comparison of  $\text{C}_2^-$ ,  $\text{N}_2^+$ , and  $\text{BO}$  to previously reported  $\text{CN}$  results shows that the subtle differences between these molecules can actually result in quite large energetic and structural differences (see Table 6). However,  $\text{CN}$ ,  $\text{C}_2^-$ , and  $\text{N}_2^+$  all exhibit an increase in energy splitting going from low spin to high spin as the minority spin  $2p$  occupation decreases. The  $\text{CN}$  doublet multiplicity  $\Delta E$  is 0.56 eV smaller than the quartet and 0.75 eV smaller than the sextet;  $\text{C}_2^-/\text{N}_2^+$  molecules exhibit comparable increases of 0.42 eV/0.73 eV to the quartet 1.43 eV/2.29 eV to the sextet. While  $\text{C}_2^-$ ,  $\text{N}_2^+$ , and  $\text{CN}$  generally exhibit comparable structural and energetic trends, study of the  $\text{BO}$  molecule shows that it behaves significantly differently.  $\text{BO}$  is the most ionic of the molecules, and it exhibits a much larger  $\Delta E$  between the two  $\Sigma^+$  states for doublets, quartets, and sextets. The two  $\Sigma^+$  states of the same molecule also often have radically different structural properties, as evidenced by large values for  $\Delta r_e$  and  $\Delta\omega_e$ . Mulliken populations of the various  $\text{BO}$  electronic states reveals that the populations on  $\text{B}$  and  $\text{O}$  are roughly around 5.5 and 7.5 electrons, respectively, but these values vary with electronic state symmetry. For the  $\Sigma^+ - \Sigma^+$  excitation,  $\text{O}$   $2p$  population generally increases in the excited state, with some commensurate decrease in  $2s$

population. The population on B behaves oppositely, with B  $2s$  population increasing while B  $2p$  population decreases. The large splitting and underlying high energetic cost for  $5\sigma \leftarrow 4\sigma$  promotion may be derived from the fact that a  $2s^2 2p^4$  configuration is highly stabilized for the isolated oxygen atom, and  $2s^1 2p^5$  configurations would be highly unstable. Strictly speaking, strong  $s - p$  hybridization means that  $5\sigma$  has only slightly more  $p$  character than  $4\sigma$ . The analysis of Mulliken populations reflects this trend.

Table 6: Summary of features of doublet, quartet, and sextet  $\Sigma^+ - \Sigma^+$  excitations for the isoelectronic series, CN,  $C_2^-$ ,  $N_2^+$ , and BO. The differences in bond length,  $\Delta r_e$  (Å), frequency  $\Delta\omega_e$  ( $\text{cm}^{-1}$ ), and energy,  $\Delta E$  (eV), are determined as the excited state value minus the initial value. The transition dipole moment,  $\mathbf{d}_{\text{av}}$ , is computed at the average between the equilibrium bond lengths of the two states and is reported in Debye.

		CN	$C_2^-$	$N_2^+$	BO
2	$\Delta r_e$	-0.02	-0.04	-0.04	0.10
	$\Delta\omega_e$	97	156	173	-533
	$\Delta E$	3.23	2.22	3.21	5.30
	$\mathbf{d}_{\text{av}}$	1.71	2.60	1.87	0.67
4	$\Delta r_e$	0.01	-0.08	0.07	0.64
	$\Delta\omega_e$	-149	234	-108	-650
	$\Delta E$	3.79	2.64	3.94	4.80
	$\mathbf{d}_{\text{av}}$	1.59	2.70	1.83	0.45
6	$\Delta r_e$	0.38	-0.27	-	-
	$\Delta\omega_e$	-98	489	-	-
	$\Delta E$	3.98	3.65	5.50	6.55
	$\mathbf{d}_{\text{av}}$	0.91	3.01	-	-

Following the analysis of the Mulliken populations of BO and the associated separated atom energies, we predict that  $C_2^-$  and CN will have smaller  $\Sigma^+ - \Sigma^+$  splittings than  $N_2^+$  because the atomic energy splitting between  $2s^2 2p^x$  and  $2s^1 2p^{x+1}$  states of C is experimentally much smaller than for N. These trends are apparent in Table 6, where  $C_2^-$  exhibits the smallest splittings, while  $N_2^+$  exhibits slightly larger splittings than CN. Mulliken population analysis shows that the partitioning of  $s$  and  $p$  electron populations for individual C and N atoms within  $C_2^-$  and  $N_2^+$ , respectively, are virtually identical, further highlighting the role that differences in the dissociation limits play in the state splitting. For CN, on the other hand, Mulliken population trends are opposite for the C and N atoms. That is, while in N atoms there is

generally an increase in  $2p$  population, the C experiences also some increase in  $2s$  population, as the CN  $5\sigma$  orbital is a strong mixture of dominantly  $2s$  orbitals from C and  $2p$  from N. For both BO and  $\text{N}_2^+$ , the large energetic splitting between lower and higher dissociation limits and their adiabatically correlated states, as well as a large number of repulsive states correlated to the lower dissociation limit, gives rise to upper quartet or sextet  $\Sigma^+$  states which are only quasi-bound. Consequently, the lower  ${}^6\Sigma^+$  states are both well bound, with dissociation energies in the range of 0.75-2.0 eV. While outside the scope of this work, the structural properties of these states suggest that characterization of the  ${}^6\Sigma^+$  state in these molecules by identification of perturbations of quartets in a similar energy range would be quite possible.

#### 4. Conclusion

MRCI calculations predict the presence of a strong  ${}^4\Sigma^+ - {}^4\Sigma^+$  transition in the CN radical, near 328 nm. This transition in the quartet manifold is analogous to the  $B {}^2\Sigma^+ - X {}^2\Sigma^+$  violet band system in CN. The large transition moment in the quartet ( $\sim 1.6$  D vs. 1.7 D in the doublet) of the predicted transition should make it an ideal means of detecting metastable quartet CN using laser-induced fluorescence or multiphoton ionization techniques. The energetic shift between the analogous doublet and quartet band systems, and to a lesser extent the sextet system, is due to a progression of decreasing minority spin  $2p$  density in each of these systems. As the  $2p$  density declines, the upper state's  $5\sigma(2p)$  orbital becomes increasingly destabilized with respect to the  $4\sigma$  state. When we compare doublets, quartets, and sextets, we go from as many as two other  $2p$  derived minority spin electrons in the doublet to one in the quartet and essentially zero in the sextet. Looking more broadly at the isoelectronic molecules,  $\text{C}_2^-$ ,  $\text{N}_2^+$ , and BO, differences between the  $\Sigma^+ - \Sigma^+$  splitting and structural changes of these molecules are determined by the extent to which  $2s^2 2p^x$  atomic configurations are preferred over  $2s^1 2p^{x+1}$ . In the cases of  $\text{N}_2^+$  and BO, where the  $2s^1 2p^{x+1}$  occupation is energetically quite unfavorable, bound upper  $\Sigma^+$  states are often nonexistent in the quartet and sextet manifolds. On the other hand, these molecules give rise to strongly bound lower quartet and sextet  $\Sigma^+$  states, which may potentially be characterized experimentally by their perturbations of high-energy, lower-spin states.

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