



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 ($d_{av} = 1.6$ D) near 328 nm ($T_{00} = 30460$ cm⁻¹), analogous to the $B^2\Sigma^+ - X^2\Sigma^+$ violet system, ($d_{av} = 1.7$ 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 quasi-bound ($r_e = 1.76$ Å, $\omega_e = 365$ cm⁻¹), and a $6\Sigma^+ - 6\Sigma^+$ transition, analogous to those for the doublet and quartet multiplicities, is predicted ($d_{av} = 2.2$ D). Investigation of the isoelectronic BO, C₂, and N₂⁺ molecules reveals that differences in $2s^2 2p^x$ and $2s^1 2p^{x+1}$ 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 multiplicities. Furthermore, the strong stabilization of $2s^2 2p^x$ character with respect to $2s^1 2p^{x+1}$ in BO and N₂⁺ 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 through their perturbations of quartet states of the relevant molecules.

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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 et al. [1], who argued that the perturbing state likely has $4\Sigma^+$ symmetry. A similar perturbation was later observed by Yencha 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 et al. [6] have identified the possibility that the nature of the metastable quartet electronic states contributes to precursor-dependent behavior in

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the chemical vapor deposition of amorphous-CN_x 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 is 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 $C''^5\Pi_{ii}$ state of N₂ [8–10].

Laser-induced fluorescence of the strong CN $B-X$ transition has long been used as 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 2–4 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 cm⁻¹, are in good agreement with experiments (1.172 Å, 2068.68 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 2–2.5 as a result of the weakly bonding character of 5σ (see Fig. 1). The next lowest state, $A^2\Pi$, differs from the ground state by preferential population of the 5σ in the minority spin in place of one of the occupied 1π 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 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, $C(1s^2 2s^2 2p^2 \ ^3P) + N(1s^2 2s^2 2p^3 \ ^4S)$, 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 cm⁻¹, are both very close to the values of the ground state (see Table 1). The next six higher 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 that yields longer bond lengths of around 1.4 Å and lower frequencies around 1700 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 accessi-

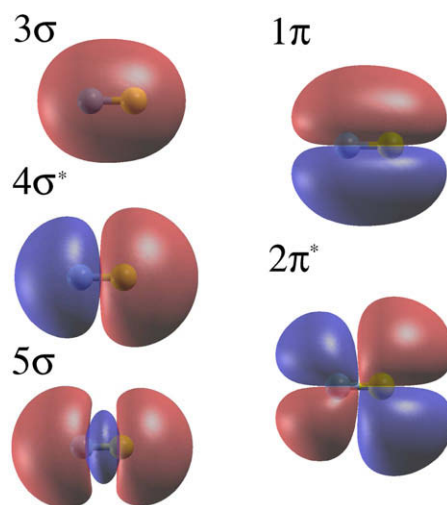


Fig. 1. Canonical occupied valence molecular orbitals relevant for both doublet and quartet low-lying states of CN. In each molecular orbital isosurface diagram, N appears to the left and C to the right.

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