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MRCI study on spectroscopic and molecular properties of several low-lying electronic states of the CN radical

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ABSTRACT

The potential energy curves (PECs) of eight low-lying electronic states ($X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, $a^4\Sigma^+$, $D^2\Pi$, $E^2\Sigma^+$, $1^2\Sigma^-$ and $F^2\Delta$) of the CN radical have been studied using the *ab initio* quantum chemical method. The calculations have been performed using the complete active space self-consistent field (CASSCF) method followed by the valence internally contracted multireference configuration interaction (MRCI) approach in combination with the correlation-consistent basis sets of Dunning and co-workers. The effects on the PECs by the core–valence correlation and relativistic corrections are taken into account. The way to consider the relativistic correction is to use the second-order Douglas–Kroll Hamiltonian approximation. The core–valence correlation correction calculations are performed with the cc-pCVQZ basis set. The relativistic correction is carried out at the level of cc-pV5Z basis set. In order to obtain more reliable results, the PECs determined by the MRCI calculations are also corrected for size-extensivity errors by means of the Davidson modification (MRCI+*Q*). The PECs are extrapolated to the complete basis set (CBS) limit by the total-energy extrapolation scheme. With these PECs, the spectroscopic parameters (T_e, R_e, ω_e, $\omega_e x_e$, $\omega_e y_e$, B_e, α_e and γ_e) are determined and compared with those reported in the literature. Finally, with the PECs obtained by the MRCI+*Q*/CV+DK+*Q*5 calculations, the complete vibrational states are computed for the eight electronic states by solving the ro-vibrational Schrödinger equation for the non-rotating radical, and the vibrational levels and inertial rotation and centrifugal distortion constants of the first 11 vibrational states are reported, which agree favorably with the available experimental data. The spectroscopic parameters of $1^2\Sigma^-$ and $F^2\Delta$ electronic states obtained by the MRCI+*Q*/CV+DK+*Q*5 calculations should be good predictions for future laboratory experiments.

1. Introduction

The spectra of the CN radical have been observed in many extraterrestrial sources such as the planets, comets, stellar atmospheres and interstellar molecular clouds [1] by the techniques of microwave, infrared and ultraviolet spectroscopy. Its spectroscopic knowledge has fundamental applications in chemical kinetics, flame diagnostics, molecular cloud chemistry and astronomy [2]. For the reason, the CN radical has been the subject of extensive investigations for a long time, both experimentally and theoretically.

As we know, the CN radical possesses a very rich spectrum in the visible and near ultraviolet range. In the experiment, although its spectra were observed more than a century ago, most of transition bands were investigated in detail only in the past several decades. For example, the first detection of its pure rotation spectrum was via the radio astronomical observations by Penzias et al. [3] in 1974. The first laboratory detection of the

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radical was performed by Dixon and Woods [4] in 1977. As of 1979, many transition bands of the radical had been observed and analyzed, and a number of spectroscopic parameters and molecular constants had been determined. Some accurate results were summarized by Huber and Herzberg [5] in 1979, and a summary of the previous work on the radical available prior to 1992 has been provided by Prasad et al. [6,7] in 1992. Now in the laboratory, the CN radical could be produced by a wide variety of sources such as active nitrogen after glows, flames, carbon arcs, shock tubes and electrical discharges of all types [7,8]. Its spectroscopic and molecular properties have been extensively studied by various experimental approaches, such as concentration-modulation laser spectroscopy [2], Fourier transform spectroscopy [1,7–9], millimeter and submillimeter spectroscopic technique [10], diode laser absorption spectroscopy [11] and laser-induced fluorescence spectroscopy [12]. With the aid of these experimental results, a number of improved spectroscopic parameters and molecular constants [1,2,6–15] have also been determined in the past forty years.

In theory, Guerin [16] in 1970 made the early calculations of the CN radical by the self-consistent field (SCF) orbitals, in which no more than three configurations were included for the $A^2\Pi$, $D^2\Pi$, $F^2\Delta$ and $J^2\Delta$ electronic states. In the next year, Schaefer and Heil [17] performed the electronic structure and potential energy curve (PEC) calculations of some low-lying molecular states by the configuration interaction (CI) approach with the Hartree-Fork (HF) atomic orbitals at eleven internuclear separations, and evaluated several spectroscopic parameters (excitation energy term T_e, equilibrium internuclear separation R_e, harmonic frequency ω_e, anharmonic constants $\omega_e x_e$ and $\omega_e y_e$, rotational constant B_e, rotation–vibration coupling constant α_e and rotation–vibration interaction constant γ_e). Up to now, a number of theoretical investigations [18–28] have been made, and some spectroscopic parameters have been determined. Of these investigations, several high-level quantum chemistry calculations [18–23,25–28] have been carried out.

As we know, both the core–valence correlation and the relativistic corrections have important effect on the quality of spectroscopic parameters and molecular constants in high-level quantum chemistry calculations. Of these studies [16–28] concerned with the spectroscopic parameters of the CN radical, however, only two groups of calculations [23,24] have taken into account the core–valence correlation corrections, and none of them are involved in the relativistic effect. In detail, Pradhan et al. [23] in 1994 employed the valence internally contracted multireference CI (MRCI) approach in combination with a series of correlation-consistent basis sets to carry out the dissociation energy calculations of CN and C_2. For CN, the 1s correlation is computed by the averaged coupled pair functional (ACPF) approach. However, only the ground-state properties were studied. Baboul et al. [24] in 1999 employed a variation of Gaussian-3 theory to investigate the geometries and zero-point energies of a number of molecules. At the level of MP2 theory, all electrons were correlated in their calculations. However, they calculated only the ground-state equilibrium internuclear separation R_e for the CN radical. When we compare these spectroscopic parameters [16–28] with the experimental data [5], we find that a room still exists for improvement by theory.

The paper is organized as follows. First, the PECs of $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, $a^4\Sigma^+$, $D^2\Pi$, $E^2\Sigma^+$, $1^2\Sigma^-$ and $F^2\Delta$ electronic states of the CN radical for internuclear separations from 0.05 to 1.92 nm are calculated employing the complete active space self-consistent field (CASSCF) method followed by the MRCI approach [29,30] with the aug-cc-pVQZ (AVQZ) and aug-cc-pV5Z (AV5Z) correlation-consistent basis sets of Dunning and co-workers [31,32]. In order to obtain more reliable PECs, the core–valence correlation and relativistic corrections are taken into account, and the PECs determined by the MRCI calculations are also corrected for size-extensivity errors by means of the Davidson modification (MRCI+Q) [33,34]. Then, the PECs of these electronic states are extrapolated to the complete basis set (CBS) limit by using the total-energy extrapolation scheme so as to eliminate the incomplete basis set errors. The spectroscopic parameters are determined with the aid of module VIBROT in MOLCAS 7.4 program package [35]. The detailed discussion is made about the effects on the spectroscopic parameters by the Davidson modification, core–valence correlation and relativistic corrections and total-energy extrapolation. Finally, the complete vibrational states are computed for the eight electronic states by solving the ro-vibrational Schrödinger equation for the non-rotating radical using the PECs determined by the MRCI+*Q*/CV+DK+*Q*5 calculations.

2. Summary of calculations

Here we compute the PECs of eight valence states ($X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, $a^4\Sigma^+$, $D^2\Pi$, $E^2\Sigma^+$, $1^2\Sigma^-$ and $F^2\Delta$) of the CN radical by the CASSCF method, which is followed by the MRCI calculations. Therefore, the full valence CASSCF is employed as the reference wavefunction for the MRCI calculations in the present work. For such PEC calculations, the MRCI theory has particularly been proved to be successful. Using this approach, we have reported a number of high-quality spectroscopic results for a number of diatomic molecules [36–40] in recent years. The basis sets used here are the augmented correlation-consistent polarized AV5Z basis set [31,32]. The present PEC calculations are made in the MOLPRO 2008.1 program package [41] for internuclear separations from 0.05 to 1.92 nm.

MOLPRO uses only the Abelian point group symmetry. For molecules with degenerate symmetry, an Abelian subgroup must be used. That is, for a diatomic molecule such as CN with $C_{\infty v}$ symmetry, it will be substituted by C_{2v} symmetry with the order of irreducible representations being $a_1/b_1/b_2/a_2$. In the CASSCF and subsequent MRCI calculations, for the CN radical, these four kinds of states would be evaluated. In detail, for the $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, $a^4\Sigma^+$, $D^2\Pi$, $E^2\Sigma^+$, $1^2\Sigma^-$ and $F^2\Delta$ electronic states, eight molecular orbitals (MOs) are put into the active space, including four a_1, two b_1 and two b_2 symmetry MOs which correspond to the 2s2p shell of these two atoms, C and N. The rest of the electrons in the CN radical are put into the closed-shell orbitals, here including only two a_1 symmetry MOs. For the eight low-lying electronic