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The electronic spectrum of the SiC radical: A theoretical study

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Abstract

Electronic structure and spectroscopic properties of the low-lying electronic states of the SiC radical have been determined from the ab initio based configuration interaction calculations. Potential energy curves of 32 Λ–S states of singlet, triplet, and quintet spin multiplicities have been constructed. Spectroscopic constants (r_e, T_e, and ω_e) of 23 states within 6 eV are reported and compared with the existing data. The dipole moments (μ_e) of most of these states at their respective equilibrium bond lengths have been computed. Effects of the spin–orbit coupling on the spectroscopic properties of SiC have been studied. The $E^3\Pi$ state is found to be an important one which has not been studied before. A transition of the type $E^3\Pi$–$X^3\Pi$ is predicted to take place in the range 25000–26000 cm^{-1}. The partial radiative lifetimes for several electric dipole allowed transitions such as $A^3\Sigma^+$–$X^3\Pi$, $B^3\Sigma^+$–$X^3\Pi$, $C^3\Pi$–$X^3\Pi$, $D^3\Delta$-$X^3\Pi$, $E^3\Pi$–$X^3\Pi$ etc. have been reported.

Keywords: Silicon carbide; Configuration interaction; Electronic spectrum; Spectroscopic constants; Potential energy curves

1. Introduction

The simple diatomic SiC radical is known to be an important component of the carbon star. It is also present in interstellar regions of space [1]. Though astrophysically important, the spectroscopy of this radical was not observed in laboratory for a long time. The major difficulty to study the silicon–carbon compounds was that it needed a very high temperature to vaporize these elements. Bondybey [2] and Michalopoulos et al. [3] attempted experiments using laser vaporization of silicon carbide rod. But the detection of the SiC radical was unsuccessful. Although Si_2 and C_2 are spectroscopically well known species, the spectroscopic identification of SiC has been made much later. However, ab initio calculations of SiC are performed before the experimental detection. Lutz and Ryan [4] have performed the configuration interaction (CI) calculations and found that the ground state of the mixed first row–second row diatomic is $^3\Pi$. Bruna et al. [5] have also carried out large scale CI calculations for the potential curves of the isovalent series of diatomic species, CN^+, Si_2, SiC, CP^+, and SiN^+ in their low-lying states. The results of these calculations for the SiC radical have agreed well with those of the previous calculations [4]. Rohlfing and Martin [6] have studied the structure and spectroscopic properties of the isovalent diatomic molecules such as C_2, Si_2, and SiC. These authors have used Moller–Plesset perturbation theory based on UHF reference function as well as externally contracted CI based on a multireference function of the complete-active-space type for determining the spectroscopic constants of a few low-lying states. Meanwhile, low-lying electronic states of SiC^- and electron affinity of SiC have been studied by Anglada et al. [7] from large scale CI calculations. Dohman et al. [8] have made a comparison among various isoelectronic radicals possessing eight valence electrons. The CASSCF and contracted CI calculations have been performed by Larsson [9] to study the potential curves of $X^3\Pi$, $B^3\Sigma^+$, and $C^3\Pi$ states of the SiC molecule. The author has predicted transitions between the ground state and the B and C states to occur in the wave length range 4000–6000 Å. Bauschlicher and Langhoff [10] have performed CI calculations at various levels of electron correlation to compute the spectroscopic

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constants of $X^3\Pi$ and $A^3\Sigma^-$ states of SiC. Their best estimates of r_e, ω_e, and D_e for the ground state of the radical were 1.719 Å, 962 cm^{-1}, and 4.4 eV, respectively.

The SiC radical was first observed [11] by high-resolution Fourier transform emission spectroscopy from a composite wall hollow cathode. The 0–0 band of the $d^1\Sigma^+$–$b^1\Pi$ system of SiC has been observed near 6100 cm^{-1}. This has been confirmed by ab initio calculations performed at different level of accuracy. Molecular constants of several low-lying states, namely $X^3\Pi$, $A^3\Sigma^-$, $a^1\Sigma^+$, $b^1\Pi$, $c^1\Delta$, and $d^1\Sigma^+$ of SiC are predicted from these calculations. The results are found to be comparable with the predictions of Bauschlicher and Langhoff [10]. The ground state of SiC has been characterized from the microwave transition observed by Cernicharo et al. [12]. The $A^3\Sigma^-$–$X^3\Pi$ system of SiC is analogous to the Ballik–Ramsay system of C_2. Brazier et al. [13] have observed the 0–0 band of this system in emission near 4500 cm^{-1} and the reported bond lengths are 1.81356 and 1.72187 Å for $A^3\Sigma^-$ and $X^3\Pi$ states, respectively. The A–X band was found to be weak because of the difficulty in making the SiC radical. Multireference CI calculations have been performed by Langhoff and Bauschlicher [14] to study the $A^3\Sigma^-$–$X^3\Pi$ infrared transition in the radical. The 0–0 band of the A–X transition has also been reassigned in another theoretical study [15]. The dipole moment functions of $A^3\Sigma^-$ and $X^3\Pi$, and the transition moment functions as well as radiative lifetimes of the A–X transition have also been reported. Martin et al. [16] have computed three lowest states, $X^3\Pi$, $A^3\Sigma^-$, and $a^1\Sigma^+$ of SiC using augmented coupled cluster methods and different basis sets. Thermochemistry of the radical has also been reported by these authors. Butenhoff and Rohlfing [17] have studied the $C^3\Pi$–$X^3\Pi$ band system of the jet-cooled SiC radical using a laser induced fluorescence (LIF) spectroscopy. The vibrational energies and rotational constants for the lowest few vibrational levels of both $C^3\Pi$ and $X^3\Pi$ states of SiC have been determined by these authors. Almost at the same time, Ebben et al. [18] have measured seven rovibronic bands belonging to the $C^3\Pi$–$X^3\Pi$ transition in SiC produced by the laser vaporization in combination with supersonic cooling. The radiative lifetimes of the $C^3\Pi$ state were found to vary from 2886 to 499 ns in the lowest seven vibrational levels. Singles and doubles CI calculations from single SCF configuration have been carried out by McLean et al. [19] on a series of diatomic species including SiC and SiC^-. Some spectroscopic information of $X^3\Pi$, $A^3\Sigma^-$, $b^1\Pi$, and $c^1\Delta$ states of SiC and the $^2\Pi$ state of SiC^- have been reported. The millimeter-wave rotational spectra with hyperfine structure of two stable isotopes with nuclear spin, namely ^{29}SiC and $Si^{13}C$, were detected in the ground state [20,21]. The vibrational and adiabatic ionization energies and electron affinities of Si_nC and Si_nO ($n = 1$–3) molecules have been reported by Boldyrev et al. [22] from large-scale ab initio calculations at different levels of correlation.

Grutter et al. [23] have identified the electronic absorption spectra of SiC^- and SiC in 5 K neon matrices using mass-selected deposition. The neutralization of the anion leads to the observation of a new band system $B^3\Sigma^+ \leftarrow X^3\Pi$ of SiC in addition to the known systems, namely $A^3\Sigma^- \leftarrow X^3\Pi$ and $C^3\Pi \leftarrow X^3\Pi$. The B–X band has the origin at 11 749 cm^{-1}, while the ω_e value for the $B^3\Sigma^+$ state of SiC in neon matrix has been reported to be 1178 cm^{-1}. However, no gas phase data is available for this state. Recently [24], the infrared emission spectrum of the $A^3\Sigma^-$–$X^3\Pi$ electronic transition of the SiC radical in the gas phase has been observed using a high resolution Fourier transform spectrometer. Three bands, 0–1, 0–0, and 1–0 of this system are found in 2770, 3723, and 4578 cm^{-1}, respectively.

In this paper, we have performed ab initio based multireference singles and doubles CI (MRDCI) calculations to study the electronic structure and spectroscopic properties of the SiC radical in low-lying singlet, triplet, and quintet states. The effects of the spin-coupling on the spectroscopic properties of these states have been studied. Potential energy curves of the low-lying states of SiC have been constructed with and without spin–orbit coupling. The radiative lifetimes of some of the excited states have been predicted and compared with the available data.

2. Method of computations

The average relativistic effective potentials (AREP) of Pacios and Christiansen [25] are used to replace the $1s^22s^22p^6$ core electrons of the Si atom and $3s^23p^2$ valence electrons are kept available for the CI calculations. For the carbon atom, the AREP of the same authors have been employed. The total number of active electrons in the CI space is, therefore eight. The 4s4p Gaussian basis sets of Pacios and Christiansen [25] for Si are augmented with some diffuse and polarization functions. Three s functions ($\xi_s = 0.04525$, 0.02715, and $0.0163a_0^{-2}$), two p functions ($\xi_p = 0.06911$ and $0.02499a_0^{-2}$), five d functions ($\xi_d = 4.04168$, 1.46155, 0.52852, 0.19112, and $0.06911a_0^{-2}$), and two f functions ($\xi_f = 0.19112$ and $0.06911a_0^{-2}$) are added [26]. The first two sets of d functions are contracted using coefficients of 0.054268 and 0.06973. Similarly, the two f functions are contracted using the coefficients of 0.29301 and 0.536102. The final basis set for Si used in the present CI calculations is (7s6p5d2f/7s6p4d1f). For the carbon atom, the (4s4p) basis set of Pacios and Christiansen [25] has been enhanced by adding two sets of d functions of exponents 1.2 and 0.35.

At each internuclear distance of SiC, we have performed self-consistent-field (SCF) calculations for the $(\sigma^2\sigma^2\pi^2)$ $^3\Sigma^-$ state using the above mentioned basis sets. The entire calculations are carried out in the C_{2v} subgroup keeping Si at the origin and C in the $+z$ axis. The symmetry adapted SCF-MOs are subsequently used for the generation of configurations in the CI calculations. Throughout the calculations we have employed the MRDCI methodology of Buenker and coworkers [27–33] which uses perturbative correction and energy extrapolation techniques. The