Spectroscopic properties and transition probabilities of SiC+ cation

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ABSTRACT

This study calculates the potential energy curves of 12 Λ-S and 27 Ω states, which belong to the first dissociation channel of SiC+ cation. The potential energy curves are computed with the complete active space self–consistent field method, which is followed by the valence internally multireference configuration interaction approach with the Davidson correction. The transition dipole moments are determined. Core-valence correlation and scalar relativistic correction, as well as extrapolation of the potential energies to the complete basis set limit are included. The spin-orbit coupling effect on the spectroscopic parameters and vibrational properties is evaluated. The vibrational band origins, Franck–Condon factors, and Einstein coefficients of spontaneous emissions are calculated. The rotationless radiative lifetimes of the vibrational levels are approximately 10^{-5} s long for the $e^2\Pi$ state. The partial radiative lifetimes of vibrational levels are approximately 10^{-7} s long for the $2^4\Pi$ and $2^4\Sigma^-$ states, 10^{-5} to 10^{-6} s long for the $2^2\Sigma^-$ state and the first well of the $1^4\Pi$ state, and very short for the second well of the $1^4\Pi$ state. Overall, the emissions are strong for the $2^2\Sigma^-$–$c^2\Sigma^-$, $2^4\Sigma^-$–$X^4\Sigma^-$, $2^4\Pi$–$X^4\Sigma^-$ transitions, and for the second well of the $1^4\Pi$–$1^4\Sigma^+$ transition. The spectral range of emissions is determined. In terms of the radiative lifetimes and transition probabilities obtained in this paper, some guidelines for detecting these states are proposed via spectroscopy. These results can be used to measure the emissions from the SiC+ cation, in particular, in interstellar clouds.

1. Introduction

The SiC radical is astrophysically important [1–3]. Early in 1979, Suzuki [4] theoretically studied the evolutional feature of all molecules containing Si and C atoms in interstellar clouds. Cernicharo et al. [5] in 1989 first detected the rotational spectra of this radical in the ground state in the circumstellar shell of IRC + 10216. Naturally, it is expected that the SiC+ cation would be observed in these places. Since the observations require accurate spectroscopic information and transition knowledge, the SiC radical has been widely studied for several decades both experimentally and theoretically, as reviewed in the previous works [6, 7]. Unfortunately, no spectroscopic experimental investigations have been performed for the SiC+ cation, although three groups of spectroscopic calculations have been reported in the literature [8–10].

Theoretically, Bruna et al. [8] in 1981 first reported the ab initio calculations of potential energy curves (PECs) for the 12 low–lying quartet and doublet states of SiC+ cation using the multireference configuration interaction (MRCI) approach. With the PECs obtained in their work, they evaluated the spectroscopic parameters of six states. Boldyrev et al. [9] in 1994 predicted the R_e and ω_e values of the $X^4\Sigma^-$, $b^2\Pi$, and $d^2\Sigma^+$ states of this cation with the second-order Møller–Plesset perturbation theory. Pramanik et al. [10] in 2008 calculated the PECs of 14 Λ-S states and 14 Ω states of this cation with the multireference singles and doubles configuration interaction approach. Using their PECs, they evaluated the T_e, R_e, and ω_e values of these states. In addition, they also calculated some transition dipole moments (TDMs), estimated the partial radiative lifetimes of the vibrational levels, and briefly discussed few transition probabilities of this cation.

Summarizing the above results, we confirm that few transition probabilities are currently available, although the transition properties are necessary for observing the SiC+ cation in the interstellar clouds. For this reason, this work will investigate the vibrational band origins, Franck–Condon (FC) factors, and Einstein coefficients of all the spontaneous emissions between several low–lying states, so as to accurately understand the transition probabilities of this cation.

This paper is organized as follows. The methodology employed will be briefly introduced in the next section. The PECs and TDMs are reported in Section 3. The spectroscopic parameters, vibrational levels G_v and rotational constants B_v are predicted. The vibrational band origins, Franck–Condon factors, and Einstein coefficients of all spontaneous emissions are calculated. The rotationless radiative lifetimes of vibrational levels are estimated for the $e^2\Pi$, $2^4\Sigma^-$, $2^2\Sigma^-$, $2^4\Pi$, and $1^4\Pi$ states. The spectral range of the spontaneous emissions is briefly evaluated. The transition probabilities are discussed. The spin–orbit coupling (SOC) effect on the spectroscopic parameters and vibrational levels of each state is briefly studied. A summary is presented in Section 4.

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2. Theory and Method

The ionization energies of Si and C atoms are 65,747.76 and 90,820.35 cm^{-1} [11], respectively. In terms of these ionization energies, the ionization of a C atom is easier than that of a Si atom. Therefore, the first dissociation limit of SiC$^+$ cation is Si$^+(^2P_u)$ + C(^3P_g). According to the Wigner–Witmer rules [12], the C(^3P_g) atom and the Si$^+(^2P_u)$ ion generate a total of 12 Λ-S states. These states are X$^4\Sigma^-$, 1$^2\Delta$ (a$^2\Delta$), 1$^2\Pi$ (b$^2\Pi$), 1$^2\Sigma^-$ (c$^2\Sigma^-$), 1$^2\Sigma^+$ (d$^2\Sigma^+$), 2$^2\Pi$ (e$^2\Pi$), 1$^4\Delta$ (A$^4\Delta$), 1$^4\Sigma^+$, 2$^2\Sigma^-$, 1$^4\Pi$, 2$^4\Sigma^-$, and 2$^4\Pi$.

All the PECs are calculated employing the complete active space self-consistent field (CASSCF) method, which is followed by the valence internally contracted MRCI (icMRCI) approach with the Davidson correction (icMRCI + Q) [13, 14]. Thus, the CASSCF is used as the reference wavefunctions for the icMRCI calculations. The basis sets used here are aug-cc-pV5Z (AV5Z) and aug-cc-pV6Z (AV6Z). The point spacing interval is 0.02 nm for each state. As with the previous work [15], to determine the detailed information of each PEC, the point spacing is 0.005 nm near the internuclear equilibrium separations of these states. It should be noticed that the point spacing intervals stated here are employed to calculate all the PECs, including the calculations of core-valence correlation and scalar relativistic corrections as well as the SOC effect.

All the PECs and TDMs are calculated within the MOLPRO 2010.1 program package [16] in the C$_{2v}$ point group. The state–averaged technique is used in the CASSCF calculations. As with the previous work [17], the molecular orbitals (MOs) used for the icMRCI calculations are generated by the CASSCF calculations. Eight outermost MOs (4a$_1$, 2b$_1$, and 2b$_2$) are put into the active space, corresponding to the 5–8σ, 2π and 3π MOs in the SiC$^+$ cation. The seven valence electrons are distributed into the eight valence MOs. Hence, this active space is referred to as CAS [7, 8]. The remaining 12 inner electrons are put into the six lowest MOs (4a$_1$, 1b$_1$, and 1b$_2$), corresponding to the 1–4σ and 1π MOs in the SiC$^+$ cation. No additional MOs are added into the active spaces when we calculate the core–valence correlation and scalar relativistic corrections as well as the SOC effect. For the icMRCI calculations with the AV6Z basis set, the total of external orbitals is 368, which are 126a$_1$, 90b$_1$, 90b$_2$, and 62a$_2$, respectively. In the CASSCF calculations with the AV6Z basis set, the A$_1$, A$_2$, B$_1$, and B$_2$ symmetries corresponding to the doublet states have 616, 560, 588, and 588 configuration–state functions (CSFs), and those corresponding to the quartet states have 320, 352, 336, and 336 CSFs, respectively. In the icMRCI calculations with the AV6Z basis set, the totals of contracted configurations of A$_1$, A$_2$, B$_1$, and B$_2$ symmetries corresponding to the doublet states are 2451432, 3550576, 2450380, and 2450380, and those corresponding to the quartet states are 2379112, 3483208, 2380616, and 2380616, respectively.

To improve the quality of PECs, core–valence correlation and scalar relativistic corrections are included into the PECs with the cc-pCV5Z and cc-pV5Z-DK basis sets, whose approaches have been introduced in our previous paper [18]. For purposes of clarity, the PECs including the core–valence correlation correction is denoted as "+ CV"; and the PECs including the scalar relativistic correction is denoted as "+ DK". For example, when the PECs are obtained by the icMRCI + Q/AV5Z calculations and the PECs have included the core–valence correlation and scalar relativistic corrections, the method calculated is denoted as "icMRCI + Q/AV5Z + CV + DK".

To obtain more reliable PECs, we extrapolate the potential energies to the complete basis set (CBS) limit with the AV5Z and AV6Z basis sets. It has been proved that the convergence speed of the reference energy is faster than that of the correlation energy [19]. Therefore, in order to improve the accuracy of PECs, we separately extrapolate the reference and correlation energies in this study. The extrapolation scheme is as follows [19],

$$\Delta E_X^{ref} = E_\infty^{ref} + A^{ref}X^{-\alpha}, \tag{1}$$

$$\Delta E_X^{corr} = E_\infty^{corr} + A^{corr}X^{-\beta}. \tag{2}$$

Here, ΔE_X^{ref} and ΔE_X^{corr} are the reference and correlation energies, respectively, calculated by the aug-cc-pVXZ basis set (here X = 5 and 6). ΔE_∞^{ref} and ΔE_∞^{corr} are the reference and correlation energies, respectively, obtained by the CBS extrapolation. The extrapolation parameters α and β are taken as 3.4 and 2.4 for the reference and correlation energies [19], respectively. Here, the PECs obtained by the CBS extrapolation with the AV5Z and AV6Z basis sets is denoted as "56". For example, when the PECs are obtained by the icMRCI + Q calculations and the PECs have included the extrapolation noted above, the approach calculated is denoted as "icMRCI + Q/56" for convenience of description in this paper.

The SOC effect is calculated by the state interaction approach [20] at the level of icMRCI theory with the all–electron cc-pCV5Z basis set. The calculations are performed within the MOLPRO 2010.1 program package in the C$_{2v}$ point group. The all–electron cc-pCV5Z basis set with and without the SOC operator is used to determine the potential energies, respectively. The difference between the two energies is the contribution to the total energy by the SOC effect, which is denoted as SOC in this paper. For example, when the PECs are obtained by the "icMRCI + Q/56 + CV + DK" calculations and the PECs have included the SOC effect, the approach calculated is denoted as "icMRCI + Q/56 + CV + DK + SOC". Employing the PECs obtained by the icMRCI + Q/56 + CV + DK and icMRCI + Q/56 + CV + DK + SOC calculations, we evaluate the spectroscopic parameters, T_e, D_e, R_e, ω_e, $\omega_e x_e$, $\omega_e y_e$, α_e, and B_e with MOLCAS program [21].

The TDMs are calculated by the valence icMRCI approach along with the AV6Z basis set. In this paper, we use these TDMs and PECs to calculate the transition probabilities and FC factors of all the spontaneous emissions, with the LEVEL program [22].

Supposing that the upper and lower vibrational levels are v' and v'', respectively, the total transition probability of a certain upper level is obtained by summing the Einstein coefficients of emissions from this level to all the levels of lower states. The rotationless radiative lifetime of a certain upper level is determined as the reciprocal of total transition probability [23–25],

$$A_{v'} = \sum_{v''} A_{v'v''} \tag{3}$$

$$\tau_{v'} = \frac{1}{A_{v'}} \tag{4}$$

Here, $A_{v'v''}$ is the rotationless Einstein coefficient of spontaneous emissions from an upper–level v' to the lower–level v''; $A_{v'}$ is the total transition probability of an upper–level v'; and $\tau_{v'}$ is the radiative lifetime of level v'.

Sometimes, the total Einstein coefficient of an upper level is determined by several contributions. To explain how this value is calculated, we take the 2$^4\Pi$ state as an example. According to transition selection rules, the spontaneous emissions from the 2$^4\Pi$ state to the X$^4\Sigma^-$, A$^4\Delta$, 1$^4\Sigma^+$, 1$^4\Pi$, and 2$^4\Sigma^-$ states can occur. That is, the total Einstein coefficient of a certain vibrational–level v' of the 2$^4\Pi$ state comes from the contributions of five groups of transitions, 2$^4\Pi$–X$^4\Sigma^-$, 2$^4\Pi$–A$^4\Delta$, 2$^4\Pi$–1$^4\Sigma^+$, 2$^4\Pi$–1$^4\Pi$, and 2$^4\Pi$–2$^4\Sigma^-$. When several spontaneous emission systems (i = 1, 2, …) are generated from a certain upper state, the total Einstein coefficient of emissions from an upper–level v' is,

$$A_{v'} = \sum_i A_{i,v'} \tag{5}$$

Here, $A_{i, v'}$ is the total Einstein coefficient of emissions from an upper–level v' for the ith emission system.