Theoretical study of spectroscopic constants and transition properties of silicon hydride cation

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ABSTRACT

The potential energy curves and dipole moments for the lowest seven $\Lambda - S$ states correlating to three dissociation limits $Si^+(^2P_u) + H(^2S_g)$, $Si^+(^4P_g) + H(^2S_g)$, and $Si(^1D_g) + H^+(^1S_g)$ of SiH^+ cation are computed using multi-reference configuration interaction plus Davidson corrections method with the AWCV5Z-DK basis set. By solving the radical Schrödinger equation, the spectroscopic parameters of these states are obtained, which are in excellent agreement with available experimental values. The spin-orbit coupling effect is taken into account in the computations via the Breit-Pauli Hamiltonian operator, which causes the seven $\Lambda - S$ states to split into fifteen Ω states. It is the first time that the spin-orbit coupling calculation is carried out on SiH^+. The spin-orbit coupling leads to avoided crossing between $B^1\Delta_2$ and $d^3\Pi_2$ states, $c^3\Sigma_1^-$ and $b^3\Sigma_1^+$ states, respectively. The $B^1\Delta_2$ state has a double-well potential resulting from the avoided crossing. The potential energy curves and spectroscopic constants of the Ω electronic states are also depicted with the aid of the avoided crossing between electronic states of the same symmetry. In addition, the transition dipole moments, Franck-Condon factors and the radiative lifetimes for the $X^1\Sigma \leftrightarrow A^1\Pi$, $A^1\Pi \leftrightarrow B^1\Delta$, $a^3\Pi \leftrightarrow d^3\Pi$, $a^3\Pi \leftrightarrow c^3\Sigma^-$, $c^3\Sigma^- \leftrightarrow d^3\Pi$, $X^1\Sigma_{0^+}^+ \leftrightarrow a^3\Pi_{0^+}$, and $X^1\Sigma_{0^+}^+ \leftrightarrow a^3\Pi_1$ transitions are obtained.

1. Introduction

The molecular ions are generally existent material form in nature. The electronic structure and spectral properties of the cation could permit us to understand the physical and chemical processes that take place in the comet tails, stellar atmospheres, and interstellar space [1–4]. Moreover, the cation can also be used as a monitoring probe for chemical dynamics in the research of combustion processes. The SiH^+ cation is one of the most important molecules in the study of plasma physics, chemical reaction processes, and astrophysics. It was observed in the solar photospheric spectrum by Grevesse and Sauval in 1970 [1]. In the same year, Douglas and Lutz detected SiH^+ cation in the laboratory for the first time [2]. Since then, investigations of this molecular ion are very active in both experiment and theory.

The emission of the $A^1\Pi \leftrightarrow X^1\Sigma^+$ transition was firstly observed by Grevesse and Sauval [3]. They estimated the absorption oscillator strength f_{00} of $A^1\Pi \leftrightarrow X^1\Sigma^+(0,0)$ band from the spectra. Later, Sing et al. determined the vertical excitation energy from first excited state to ground state in the laboratory [4,5]. Carlson et al. measured the radiative lifetimes of the $A^1\Pi$ states ($v' = 0 - 3$) by using the high frequency deflection technique [6]. Some accurate spectroscopic constants of the $X^1\Sigma^+$ and $A^1\Pi$ states were summarized by Huber and Herzberg in 1979 [7]. Hishikawa and Karawajczyk remeasured the relative intensities of the $v' = 0$ progression, and analyzed the rotational levels of the (0, 3) and (0, 4) bands of the $A^1\Pi \leftrightarrow X^1\Sigma^+$ transition for the first time in 1993 [8]. Photodissociation cross sections from LTE distributions of rotational and vibrational levels of the ground state $X^1\Sigma^+$ to first excited state $A^1\Pi$ were obtained for temperatures between 1000 and 9000 K in 1997 [9]. In the same year, Whitham et al. gained photodissociation spectra through laser-induced excitation from the ground state to near-threshold levels of electronic states correlating with the lowest dissociation limits $^2P_{3/2,1/2}(Si^+) + ^2S(H)$ [10]. Recently, the photoexcitation cross sections and energies of the main resonances in the inner shell spectrum of SiH^+ cation were measured by Mosnier et al. [11].

Theoretically, the potential energy curves (PECs) of ground and ten excited states of SiH$^+$ cation have been computed by Bruna and Peyerimhoff [12]. But they only listed the vertical excitation energy of the four lowest-lying excited states, and the spectroscopic constants of all bound states have not been reported. Hirst calculated the PECs of $X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$, and $^3\Sigma$ states in 1986, and the spectroscopic constants of $X^1\Sigma^+$ state were in good agree with the experimental results [13]. For the ground state Roos used the complete active space method and also obtained accurate values for its spectroscopic constants [14]. Also, accurate lifetime and spectroscopic constants of the $A^1\Pi$ state have been calculated by Ahlrichs et al. [15] and Matos et al. [16] using the coupled pair functional method. In 1995, Sannigrahi et al. have carried out *ab initio* configuration interaction calculations for SiH$^+$ cation using a large Gaussian basis set, who gained exact spectroscopic constants of the $X^1\Sigma^+$ and $A^1\Pi$ states [17]. In addition, they also predicted excitation energy, spectroscopic constants, and lifetimes for a large number of higher excited states. The PECs and dipole transition moments of ground and six excited states have been calculated for the SiH$^+$ cation in 1997 [9]. Obviously, most experimental and theoretical studies were focused on the $X^1\Sigma^+$ and $A^1\Pi$ states, and the only qualitative research on PECs and spectroscopic constants for higher excited states were presented. Theoretically, highly correlated method with inclusion of various corrections should be implemented for calculation of the SiH$^+$ cation. In addition, the effect of spin-orbit coupling was not taken into account in the previous work, which may play an important role in spectroscopic and dynamic properties of the electronic states [18–21]. It is well known that the spin-orbit coupling effect could result in avoided crossing of two different $\Lambda - S$ states with same Ω components, and the PECs near the region of avoided crossing may become very complicated.

In this letter, the PECs of lowest seven $\Lambda - S$ states $X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$, $b^3\Sigma^+$, $c^3\Sigma^-$, $d^3\Pi$, and $B^1\Delta$ correlating to the three atomic dissociation limits $Si^+(^2P) + H(^2S)$, $Si^+(^4P) + H(^2S)$, and $Si(^1D) + H^+(^1S)$ for SiH$^+$ cation are calculated. The scalar relativistic effect and core-valence correlation are also taken into account in the calculations. The spectroscopic constants, permanent dipole moments (PDMs), transition dipole moments (TDMs), radiative lifetime, and Frank-Condon factors (FCFs) of the $\Lambda - S$ bound states are obtained from the calculated PECs. The spin-orbit interaction makes seven $\Lambda - S$ states split and recombine to fifteen Ω states. The PECs and spectroscopic constants of Ω states are computed by using the same method. Finally, the properties of spin-forbidden transitions ($X^1\Sigma_{0^+}^+ \leftrightarrow a^3\Pi_{0^+}$ and $X^1\Sigma_{0^+}^+ \leftrightarrow a^3\Pi_1$) are also evaluated. This paper is organized as follows. In Section 2, we describe the *ab initio* method and basis sets chosen for calculations. The results and discussion of the data are provided in Section 3. Finally, we reach some conclusions for this work in Section 4.

2. Methods and computational details

In present work, the *ab initio* calculations on the electronic structure of SiH$^+$ cation are performed with the quantum chemistry MOLPRO 2015 program package [22]. First, the energy of ground state $X^1\Sigma^+$ is computed by spin-restricted Hartree-Fock (RHF) method. Then, the complete active space self-consistent-field (CASSCF) method is used to obtain the multi-reference wavefunction [23,24]. The initial values for orbital optimization of CASSCF derive from the RHF orbits. Finally, the energies are calculated by using the high-level multi-reference configuration interaction plus Davidson corrections (MRCI + Q) method [25–27]

with the CASSCF wave functions as a zero-order function. Scalar relativistic corrections are implemented through Douglas-Kroll Hamilton at third-order level [28,29]. And this method has been applied to some molecules to be accurately calculated [30–34]. SOC effects are also taken into account in the calculation of SiH$^+$ because of spin forbidden for the $X^1\Sigma_{0^+}^+ \leftrightarrow a^3\Pi_{0^+}$ and $X^1\Sigma_{0^+}^+ \leftrightarrow a^3\Pi_1$ transitions. The SOC effects are evaluated with Breit-Pauli operators [35] at MRCI + Q level.

All calculations are performed in the C_{2v} subgroup of $C_{\infty v}$ point group symmetry because of the limitation of MOLPRO program. The C_{2v} point group has four irreducible representations a_1, b_1, b_2, and a_2. The a_1 yields Σ^+ state and a component of Δ state, b_1 and b_2 provide the Π state, a_2 yields Σ^- state and the other one component of Δ state. In the CASSCF calculations, eight molecular orbitals are chosen as the active space ($3\sigma1\pi_x1\pi_y4\sigma5\sigma6\sigma2\pi_x2\pi_y$), including four a_1, two b_1, and two b_2 symmetry MOs, which correspond to the 2p3s3p shells of the Si atom and 1s shell of the H atom. Ten electrons are distributed in a (4, 2, 2, 0) active space, and the 1s2s orbit of Si is closed-shell orbit which keeps doubly occupation. In following MRCI + Q step, Si 1s shell is used for core-valence correlation for SiH$^+$ cation, i.e. there are altogether 14 electrons in the correlation energy calculations. In all electronic structure calculations for the $\Lambda - S$ and Ω states, the aug-cc-pV5Z-DK basis set is used for H atom, and the primary and contracted atomic basis sets are (8s, 4p, 3d, 2f, 1g)→(5s, 4p, 3d, 2f, 1g) [36]. But because the core-valence correlation on silicon is essential for accurate calculations, the aug-cc-pwCV5Z-DK basis set is chosen for Si atom. The primary and contracted atomic basis set is (20s, 12p, 4d, 3f, 2g, 1h)→(7s, 6p, 4d, 3f, 2g, 1h) [37].

Single point energy calculated on SiH$^+$ is performed to gain PECs. The adiabatic PECs of the electronic states of SiH$^+$ cation are constructed from 142 single point energies corresponding to internuclear distances from 0.6 to 8 Å. To achieve accurate results, the interval value is reduced to 0.02 Å near equilibrium bond distance. The PDMs and TDMs are also obtained by MRCI + Q method. On the basis of the calculated PECs, spectroscopic constants of the bound electronic states are determined by solving the radial Schrödinger equation with the LEVEL8.2 program [38]. The Einstein spontaneous emission coefficients, radiative lifetimes and FCFs of $\Lambda - S$ and Ω states are also determined from this program with the PECs and TDMs of different electronic states.

3. Results and discussions

In this section, the transitions properties of the low-lying electronic states of SiH$^+$ will be reported, including seven $\Lambda - S$ states and fifteen Ω states. At first, the PECs and spectroscopic parameters are determined by solving the radial Schrödinger equation. Secondly, the PDMs of the $\Lambda - S$ states and the TDMs are presented. Finally, the Franck-Condon factors and the radiative lifetimes are calculated.

3.1. The PECs and spectroscopic constants of the $\Lambda - S$ states

In this paper, PECs of the lowest seven $\Lambda - S$ states, $X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$, $b^3\Sigma^+$, $c^3\Sigma^-$, $d^3\Pi$, and $B^1\Delta$ are obtained by our fitting procedures. In order to more clearly illustrate this figure, detailed PECs of internuclear distance from 0.6 to 8 Å are presented in Fig. 1. Apparently, the $b^3\Sigma^+$ is a typical repulsive state, while the other six states are bound states. The dissociation limits of SiH$^+$ are the $Si^+(^2P) + H(^2S)$ for the states $X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$, and $b^3\Sigma^+$, $Si^+(^4P) + H(^2S)$ for $c^3\Sigma^-$ and $d^3\Pi$, $Si(^1D) + H^+(^1S)$ for the state $B^1\Delta$. The spectroscopic parameters including the equilibrium internuclear