Computational and Theoretical Chemistry 1134 (2018) 8–14

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Ab inito study on the electronic structure and laser cooling of SiH

Yun-Guang Zhang[a,*], Ge Dou[a], Jian-Xia Qi[a,b], Jie Cui[a]

[a] School of Science, Xi'an University of Posts and Telecommunications, Xi'an 710121, China
[b] School of Physics and Information Technology, Shaanxi Normal University, Xi'an 710000, China

ARTICLE INFO

Keywords:
Spectroscopic constants
Franck-Condon factors
Radiative lifetimes
Laser cooling

ABSTRACT

Potential energy curves (PECs) of six electronic states ($X^2\Pi$, $a^4\Sigma^-$, $A^2\Delta$, $B^2\Sigma^-$, $C^2\Sigma^+$, and $D^2\Sigma^+$) are calculated based on multi-reference configuration interaction plus Davidson corrections (MRCI + Q), and the spin–orbit coupling (SOC) effects are considered at the MRCI + Q level. By solving the radical Schrödinger equation, the spectroscopic constants of these states are obtained, which agree well with the experimental results. The SOC effects have little influence on spectroscopic constants. The permanent dipole moments (PDMs) and transition dipole moments (TDMs) of SiH molecule are also calculated with the same method. Highly diagonally distributed Franck-Condon factors (FCFs) are determined for the transitions $X^2\Pi \leftrightarrow A^2\Delta$ ($f_{00} = 0.9858$) and $X^2\Pi \leftrightarrow C^2\Sigma^+$ ($f_{00} = 0.9676$). Furthermore, the suitable radiative lifetimes τ of the $A^2\Delta$ and $C^2\Sigma^+$ states are 3.4625×10^{-7} s and 1.6462×10^{-7} s, which are evaluated for rapid laser cooling. Schemes to laser cooling SiH molecule are designed, and the proposed laser cooling drives for the transition $X^2\Pi(v'') \leftrightarrow A^2\Delta(v')$ and $X^2\Pi(v'') \leftrightarrow C^2\Sigma^+(v')$ both use three wavelengths. Main pump laser λ_{00} for the two transitions are 401.31 and 319.64 nm. These results not only prove the feasibility of laser cooling SiH, but also provide a microkelvin cool temperature for this molecule.

1. Introduction

In recent years, laser cooling of diatomic molecules has attracted more and more research interests, since ultracold molecules can be used in many fields of research, such as quantum computation [1], measurements [2,3], dynamics [4], and Ultracold chemistry [5]. Although direct laser cooling of molecules is a challenge because of their complex molecular structure, the direct cooling of SrF molecule was successfully reported by Shuman *et al.* in 2010. [6] Since then, many potential laser cooling diatomic molecules (YO [7], CaF [8], and BaH [9]) have been performed experimentally. Summing up the previous researches, the criteria of candidates for laser cooling must follow these keys: (i) highly diagonal Franck-Condon factors (FCFs), which can describe the overlap of the vibartional wave functions for transitions for direct laser cooling. (ii) shortly radiative lifetimes τ for rapid laser cooling, and (iii) a closed laser cooling cycle transition from the upper state to the ground state, if the upper state can radiate and stop the cycling transition, that is to say, if intervening electronic states exist, it is necessary to ensure that they have no effect on the laser cooling cycle.

Until now, many studies for laser cooling candidates (such as BeF [10], BeCl [11], BeBr [11] MH (M = Be, Mg, Ca, Sr, Ba) [12,13], and CuF [14]) have been investigated theoretically. Some molecules have no intervening states between the upper state and the ground state, for example BeCl and BeBr [11] have no intervening states between the $A^2\Pi$ state and $X^2\Sigma^+$ state. Some molecules have intervening states between their transitions. For example, laser cooling the SiO^+ molecule was studied by Nguyen and Odom [15]. The SiO^+ exist an intervening state $A^2\Sigma^+$ between $B^2\Sigma^+$ and $X^2\Sigma^+$ states, and the state $A^2\Sigma^+$ has a short lifetime, so the intervening state $A^2\Sigma^+$ has no influence on the transition $X^2\Sigma^+ \leftrightarrow B^2\Sigma^+$. In addition, Wells and Lane [16] have studied on laser cooling of the transition $X^1\Sigma^+ \leftrightarrow A^1\Pi$ for AlF molecules. The state $a^3\Pi$ is found between the states $A^1\Pi$ and $X^1\Sigma^+$. Although the $X^1\Sigma^+ \leftrightarrow a^3\Pi$ transition has highly diagonal FCFs and short radiative lifetimes, the transition is unsuitable for laser cooling since the state $a^3\Pi$ has a small emission rate. Besides the spin-allowed cooling transitions ($X^1\Sigma^+ \leftrightarrow A^1\Pi$, $X^2\Sigma^+ \leftrightarrow A^2\Sigma^+$, and $X^2\Sigma^+ \leftrightarrow B^2\Sigma^+$) are researched, the spin-forbidden transitions are also studied in the theory. For instance, we studied the spin-forbidden transition $X^1\Sigma^+ \leftrightarrow a^3\Pi$ for laser cooling of GaH in 2017 [17]. It is noted that the transition $X^2\Pi \leftrightarrow A^2\Delta$ has not been studied.

SiH molecule has attracted many attentions of researchers. In theory, the potential energy curve (PEC) of ground state $X^2\Pi$ was evaluated by Cade and Huo [18] in 1967 using the Hartree–Fock method. Then the PECs of six Λ–S states with the self-consistent field molecular orbital and configuration interaction were reported by Wirsam [19] in 1971. Besides, the spectroscopically properties of states

* Corresponding author.
E-mail address: zygsr2010@163.com (Y.-G. Zhang).

https://doi.org/10.1016/j.comptc.2018.04.014
Received 28 January 2018; Received in revised form 10 April 2018; Accepted 23 April 2018
Available online 26 April 2018

$^4\Sigma^-$, $^2\Sigma^-$, and $2^2\Sigma^-$ were also reported. Meyer and Rosmus [20] researched the permanent dipole moment (PDM) for the state $X^2\Pi$ in 1975. The electronic structure of $^4\Sigma^-$ and $^2\Pi$ states were calculated using the Gaussian-type orbital basis set by Mavrldls and Harrison [21] in 1982. In the next year, the PECs, spectroscopic parameters and the properties of the ground and excited states of SiH, such as $B^2\Sigma^-$, $C^2\Sigma^+$, $D^2\Sigma^+$, and $E^2\Sigma^+$, were reported by Lewerenz *et al.* [22]. In 2013, Shi *et al.* [23] reported that the $B^2\Sigma^-$ and $C^2\Sigma^+$ states had two potential wells, and the corresponding spectroscopic parameters were also calculated. Experimentally, Davies *et al.* [24] observed hot band transitions and low Q-branch transitions in both $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states of the fundamental by diode laser absorption spectroscopy in 1984. Next year, Washida *et al.* [25] reported the emission spectra of the $X^2\Pi \leftrightarrow A^2\Delta$ in the VUV photolyses of silane. In 1986, Betrencourt *et al.* [26] found and analyzed the rovibrational bands 1–0, 2–1, and 3–2 in the $X^2\Pi$ ground state. At the third year, the spin–orbit coupling (SOC) effects on the $X^2\Pi$ state are observed by Seebass *et al.* [27]. Johnson and Hudgens [28] studied that the spectra of SiH radicals appeared over the laser wavelength interval between 426 and 430 nm by resonance-enhanced multiphoton ionization spectroscopy in 1989. In 1998 Ram *et al.* [29] observed the emission spectra of Λ−S transition of SiH at high resolution. More information was summarized in Refs [30–33]. Up to now, there are few papers to study the spectroscopic constants, PDMs of the states $B^2\Sigma^-$ and $C^2\Sigma^+$. Meanwhile, the transition properties of the transitions $X^2\Pi \leftrightarrow A^2\Delta$, $X^2\Sigma^+ \leftrightarrow B^2\Sigma^+$, and $X^2\Pi \leftrightarrow C^2\Sigma^+$ are seldom reported, which are not enough to judge the feasibility for laser cooling of these transitions. Accurate and systematic studies of SiH molecule are necessary.

In present paper, the task is to determine whether the SiH molecule can be cooled by laser. The PECs of six states $X^2\Pi$, $a^4\Sigma^-$, $A^2\Delta$, $B^2\Sigma^-$, $C^2\Sigma^+$, and $D^2\Sigma^+$ correlating to the three atomic dissociation limits $Si(^3P_g) + H(^2S_g)$, $Si(^1D_g) + H(^2S_g)$, and $Si(^1S_g) + H(^2S_g)$ are calculated. The spectroscopic constants, PDMs, transition dipole moments (TDMs), radiative lifetime, and Frank-Condon factors (FCFs) of the Λ−S bound states were obtained. The effects of spin-orbit coupling on PECs and spectroscopic constants are also computed with the MRCI + Q method. In Section 2, the *ab initio* method and basis sets are introduced. In Section 3, the results and analysis are given. The conclusions for this work are described in Section 4.

2. Computational details

In this paper, all the *ab initio* calculations of SiH molecule are computed by using the MOLPRO 2015 program package. [34] The energies of the $X^2\Pi$, $a^4\Sigma^-$, $A^2\Delta$, $B^2\Sigma^-$, $C^2\Sigma^+$, and $D^2\Sigma^+$ states are calculated via multi-reference configuration interaction (MRCI) plus Davidson corrections (MRCI + Q), [35–37] which based on the complete active space self-consistent-field (CASSCF) [38,39]. Scalar relativistic effects are considered throughout the Douglas-Kroll-Hess (DKH). [40,41] SOC effects are also taken into account following the MRCI + Q calculations.

The C_{2V} point group symmetry has four irreducible representations (A_1, B_1, B_2, and A_2). The A_1 irreducible representation yields Σ^+ state and a component of Δ state, B_1 provides the Π state, and A_2 yields Σ^- state and the other components of Δ state. In the CASSCF calculations, five molecular orbitals are selected as the active space ($4\sigma 5\sigma 6\sigma 2\pi_x 2\pi_y$), including the $3s^23p^2$ shells of Si and $1s^1$ shell of H. In addition, five electrons are distributed in a (3, 1, 1, 0) active space, and $1s^22s^22p^6$ orbit of silicon is closed-shell orbit, which keeps doubly occupation. In following MRCI + Q step, the Si(1s) shell is used for the core-valence correlation for the SiH molecule, i.e. there are altogether 15 electrons in the correlation energy calculations. The aug-cc-pV5Z basis set is chosen for hydrogen atom, and the aug-cc-pwCV5Z basis set is for silicon atom.

Einstein spontaneous emission coefficient $A_{\nu'\nu''}$ from initial level to final level (ν'',J'') is evaluated by the expression: [42,43]

$$A_{\nu'\nu''} = 3.1361891 \times 10^{-7} \frac{S(J',J'')}{2J'+1} \nu^3 \langle \Psi_{\nu',J'} | M(r) | \Psi_{\nu'',J''} \rangle$$

In the formula, where $A_{\nu'\nu''}$ is the Einstein spontaneous emission coefficient in units of s^{-1}, $M(r)$ is the transition dipole function in units of D, ν is the emission frequency in units of cm^{-1}, $S(J',J'')$ is the Hönl–London rotational intensity factor, $\Psi_{\nu',J'}$ and $\Psi_{\nu'',J''}$ are normalized radial wavefunctions. The radiative lifetimes can be calculated as the reciprocal of the total Einstein spontaneous emission coefficient:

$$\tau_{\nu'} = 1 \Big/ \sum_{\nu''} A_{\nu'\nu''}$$

The spectroscopic constants (R_e, ω_e, $\omega_e\chi_e$, B_e, D_e, T_e) including the equilibrium internuclear distance (R_e), harmonic frequency (ω_e), first anharmonicities ($\omega_e\chi_e$), rotational constants (B_e), depth well (D_e) and adiabatic relative electronic energy referred to the ground state (T_e) are calculated by solving the radical Schrödinger equation using the LEVEL8.2 program. [44] The PECs are calculated over the distance from 0.7 Å to 10 Å. The interval value is 0.01 Å near equilibrium bound distance to achieve results. The PDMs and TDMs are calculated by MRCI + Q method. The Einstein spontaneous emission coefficients, FCFs and radiative lifetimes of Λ−S states are also determined with the LEVEL8.2 program.

3. Results and discussion

In the section, the PECs and spectroscopic constants of the six Λ−S states are studied with the MRCI + Q method firstly. Secondly, six Λ−S states split into nine Ω states after considering the SOC effect, and the PECs and spectroscopic constants are discussed with the same method. Thirdly, the transitions properties, including PDMs, TDMs, FCFs and radiative lifetimes, are calculated to determine the suitability for laser cooling. Lastly, the reasonable laser cooling schemes are developed.

3.1. PECs and spectroscopic constants of the Λ−S states

To accurately study their feasibility for laser cooling, the PECs and spectroscopic parameters of the six Λ−S states ($X^2\Pi$, $a^4\Sigma^-$, $A^2\Delta$, $B^2\Sigma^-$, $C^2\Sigma^+$, and $D^2\Sigma^+$ states) are computed. Detailed PECs of internuclear distance from 0.6 to 7 Å are plotted in Fig. 1. The dissociation limits of SiH for the states $X^2\Pi$, $a^4\Sigma^-$, and $B^2\Sigma^-$ are $Si(^3P_g) + H(^2S_g)$, for the states $A^2\Delta$ and $C^2\Sigma^+$ are $Si(^1D_g) + H(^2S_g)$, for state $D^2\Sigma^+$ is $Si(^1S_g) + H(^2S_g)$. In addition, the spectroscopic parameters of $X^2\Pi$, $a^4\Sigma^-$, $A^2\Delta$, $C^2\Sigma^+$, and $D^2\Sigma^+$ states together with available experimental value [32,33] of SiH are listed in Table 1.

In the Table 1, the states $X^2\Pi$ and $A^2\Delta$ have detailed experimental

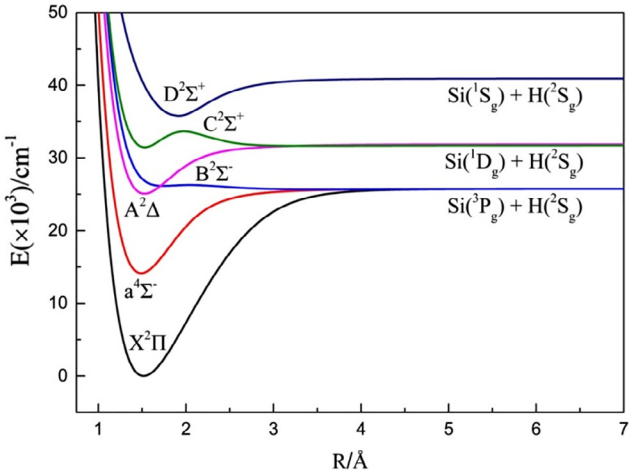

Fig. 1. The PECs of the Λ−S states of SiH.