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Research paper

Collisional rate coefficients of SiH($X^2\Pi$) open-shell molecule induced by its collision with He(^1S)

T. Tchakoua [a,b], M. Nsangou [c,*], O. Motapon [b,d]

[a] National Radiation Protection Agency of Cameroon, P.O. Box 33732, Yaounde, Cameroon
[b] LPF, UFD Mathématiques, Informatique Appliquée et Physique Fondamentale, Université de Douala, B.P. 24157, Douala, Cameroon
[c] Higher Teachers' Training College, University of Maroua, P.O. BOX 46, Maroua, Cameroon
[d] University of Maroua, Faculty of Science, P.O. BOX 814, Maroua, Cameroon

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ABSTRACT

New adiabatic potential energy surfaces (PESs) for $^2A'$ and $^2A''$ states of SiH($X^2\Pi$)-He(^1S) complex have been calculated at the restricted coupled cluster level of theory including single, double and triple excitation [RCCSD(T)]. The RKHS method was used for the analytic fit of these PESs. The resulting PESs were employed later in the close-coupling approach for the computation of the inelastic integral cross sections which take into account the fine-structure of the SiH radical. Scattering calculations, are done on a grid of collision energies large enough to ensure converged state-to-state rate coefficients for the temperature ranging from 8 K up to 300 K.

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1. Introduction

Understanding our planetary atmosphere, interstellar clouds, interstellar medium, often requires the knowledge of some physical constants, such as cross sections, rate coefficients of the molecular species present in these medium. These physical constants can be obtained experimentally or theoretically through the collision between the molecular species present in these medium. During this last decade, the theoretical studies of collisions have received much attention thanks to the use of accurate potential energy surfaces for the quantum treatments of the collision dynamics. Actually, both closed- and open-shell diatomic and triatomic molecules colliding with closed-shell partners are widely studied. Among these studies, some authors have reported the data of collisional rate coefficients for some radicals, such as CH($X^2\Pi$) [1], OH($X^2\Pi$) [2], NO($X^2\Pi$) [3], SH($X^2\Pi$) [4] colliding with He(^1S).

Since the discovery of the radical hydride CH [5] in the interstellar medium (ISM), astronomers have identified an important number of open-shell hydrides in the interstellar gas from the measurement of lines in their rotational spectra. Today we count many open-shell hydride radicals which have been detected in the ISM (OH [6], NO [7], SH [8]), or have been subject to a tentative of detection (SiH [9]). Thanks to significant abundance of Si, many silicon-containing molecules have been observed in interstellar medium, ranging from diatomics (SiC, SiN, SiO, SiS), to triatomics (SiCN, SiNC, SiCC, SiCSi), to tetratomics (SiC_3, SiCCH), and to five atoms systems (SiC_4, SiH_4). This justifies why there is a high probability that the SiH radical may be found in the ISM and stellar atmospheres [10,11]. SiH may be formed from SiH_2^+ as follows [12]: Firstly, SiH_2^+ is formed by one of the two mechanisms below

$$Si + H_3^+ \longrightarrow SiH_2^+ + H, \qquad (1)$$

$$Si^+ + H_2 \longrightarrow SiH_2^+ + h\nu, \qquad (2)$$

and SiH is then formed by dissociative recombinaison

$$SiH_2^+ + e \longrightarrow SiH + H. \qquad (3)$$

In addition, reaction of SiH as that of SiH_2^+ or SiH^+, with nitrogen, oxygen and sulphur compounds, initiate chemical sequences of molecular species such as SiO, SiO^+, SiN, SiS and HSiN [12]. Moreover, the observation of the electronic bands of SiH in the visible region has been used as the main justification of the existence of this molecule in the sun and cool stars [11]. In laboratory, SiH radical was first observed by optical spectroscopy in the 1930s [13]. The tentative detection of SiH($^2\Pi_{\frac{1}{2}}$, $J = \frac{3}{2} - \frac{1}{2}$, 625 GHz, 628 GHz) rotational transitions was made by Schilke et al. [9] at the Caltech Submillimeter Observatory (CSO). Its presence has not yet been

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* Corresponding author.

E-mail addresses: tchaktheo@yahoo.fr, t.tchakoua@nrp.cm (T. Tchakoua), mnsangou@yahoo.com (M. Nsangou).

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confirmed in interstellar clouds, may be because SiH is destroyed by photodissociation,

$$SiH + h\nu \longrightarrow Si + H, \tag{4}$$

or by strong reaction with O, C, N, or S^+ [12]

$$SiH + O \longrightarrow SiO + H, \tag{5}$$

$$SiH + C \longrightarrow SiC + H, \tag{6}$$

$$SiH + N \longrightarrow SiN + H, \tag{7}$$

$$SiH + S^+ \longrightarrow SiS + H^+. \tag{8}$$

Eqs. (5)–(8) show that SiH probably initiates chemical sequences leading to molecules such as SiO (detected in Sgr B2 cloud and Ori A) [12], SiC, SiS and SiN (identified in IRC + 10216) [12,14].

SiH radical is useful in chemistry. It plays an important role in the process of chemical vapor deposition (CVD) of hydrogenated amorphous silicon thin films (a-Si:H). These silicon thin films, also known as solar cells, are promising and efficient clean energy source for the moment and near future [15]. Thanks to its important role [16], the SiH radical has been extensively studied. Today, we can count more than 150 articles on SiH. Complete documents on this radical can be found on the web site www.exomol.com/bibliography/SiH [17]. However, to the best of our knowledge, only the collision of this radical with electron had been studied [18].

In a previous work done on SiS by Lique et al. [19] in 2008, an estimate of H_2 ($j = 0$) rate coefficients from He rate coefficients was carried out. The aim of this investigation was to judge the validity of the model of collision with He. In 2014, Walker et al. [20] did similar investigation applied to CO. Both case studies, concluded that collision with He atom is a good model for para-H_2, but must be used with caution. To obtain reasonable predictions, one should use the ratio of the product of the reduced mass with the PES well depth, instead of the standard constant factor $\sim$1.4 [20]. The purpose of this present paper is to determine some data (the collisional rate coefficients and cross sections) induced by the collision of this radical with He atom, that are useful to astrophysicists or astronomers in the case of eventual detection.

Our paper is organized as follows, Section 2 gives the details of the ab initio calculations of new potential energy surfaces of SiH-He used in this work, and a brief description of theory and calculations. Section 3 presents the results and discussions. Conclusion and remarks are given in Section 4.

2. Potential energy surfaces (PESs)

2.1. Ab initio calculations of $^2A'$ and $^2A''$

The ground state of SiH is $X^2\Pi$ which corresponds to the $KL(3s\sigma)^2(3p\pi)^2 3p\pi$ configuration, and gives rise to two electronic states of SiH-He complex, $^2A'$ and $^2A''$ in C_s symmetry. These states are related to the orientation of the singly occupied π orbital of SiH with respect to SiH-He plane: the $^2A'$ corresponds to π orbital located in Si-H-He plane, and the $^2A''$ corresponds to π orbital perpendicular to the Si-H-He plane. In the present work, the calculations of the adiabatic potentials ($^2A'$ and $^2A''$) have been performed in the Jacobi coordinate. In this representation, r_{SiH} is the SiH bond length taken to its experimental value. R refers to the distance between He atom and the center of mass of SiH and θ is the angle between R and r_{SiH} with $\theta = 0^0$ refering to the SiH-He configuration. A grid defined by the internal coordinates r_{SiH}, R and θ was used to calculate the PESs. For r_{SiH}, we take four values around the equilibrium experimental value which is 2.87257 Bohr [21]. θ takes ten values from 0 to 180 with a uniform steps of 20 degree. R varies from 4 to 12 Bohr with a uniform steps of 0.25 Bohr, and from 12 to 20 Bohr with a uniform steps of 1 Bohr. The method used for the calculation of the interaction energy was the coupled clusters single and double excitation (CCSD) [22], associated with the perturbative contribution from triple excitation (i.e. RCCSD(T)) as defined by Watts et al. [23]. Some verifications of the calculations showed that the weight of the dominant configuration, for the ground state for each of the two symmetries $^2A'$ and $^2A''$, was greater than 0.94, and this confirms the choice of this method. The three atoms of the complex, Si, H, and He, were described by the cc-pVQZ-F12 basis sets of Peterson et al. [24]. In order to have accurate values of the complex interaction energy, the above-mentioned basis sets were further augmented respectively by the set of mid-bond functions, (3s3p2d2f1g), optimized by Cybulski and Toczylowski [25]. These mid-bond functions were placed at mid-distance between helium and the center of mass of SiH. Throughout the calculations of the potential energy surfaces, the basis set superposition error (BSSE) was corrected at all the geometries, as follows [26]:

$$V(R,\theta) = \Delta E_{SiH/He}(R,\theta) = E_{SiH/He} - E_{SiH} - E_{He}. \tag{9}$$

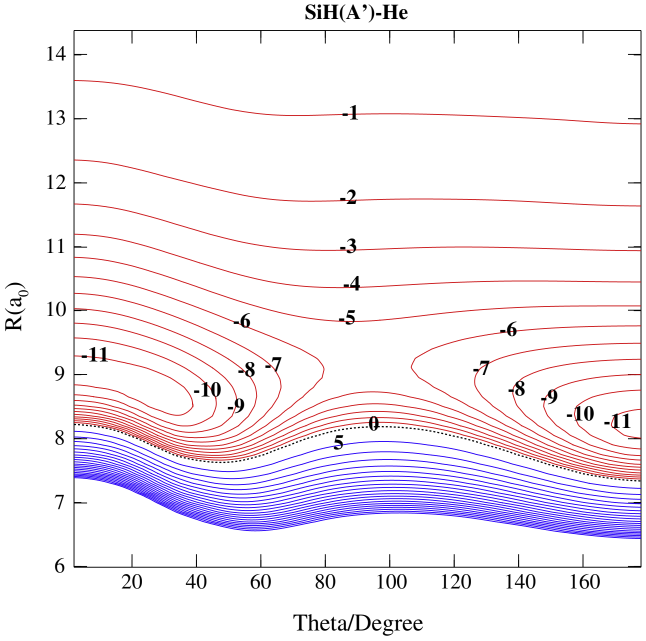

Fig. 1. Contour plot of the SiH($^2A'$)-He in the Jacobi coordinate computed at the RCCSD(T)/cc-pVQZ-F12 level of theory.

Both surfaces ($^2A'$ and $^2A''$) were calculated using the MOLPRO package (2002) [27]. The resulted complex was then treated in the C_s symmetry point group. Figs. 1 and 2 display the contour plots of the PESs of $^2A'$ and $^2A''$ states respectively. These surfaces are calculated at the RCCSD(T)/cc-pVQZ-F12 level of theory. The PES of the $^2A'$ state has two minima. Both minima occur at almost linear geometries, one is located at ($R = 8.8a_0$, $\theta = 24°$ and $D_e = -11.6\ cm^{-1}$), and the other is located at ($R = 8.2a_0$, $\theta = 180°$ and $D_e = -11.4\ cm^{-1}$). Both minima show that in the $^2A'$ state, the complex is almost linear. For the $^2A''$ state, there is only one minimum, and at this minimum located at ($R = 5.6a_0$, $\theta = 72°$ and $D_e = -84.7\ cm^{-1}$) the complex has an almost T-shaped geometry.

2.2. Analytic potential energy surface

To allow for the dynamics calculations, the ab initio points were fitted by using the reproducing kernel Hilbert space (RKHS) of Ho

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