

Can we estimate $H_2(j = 0)$ rate coefficients from He rate coefficients? Application to the SiS molecule

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ABSTRACT

Context. Over the next few years, the ALMA and Herschel missions will perform high spatial and spectral resolution studies at infrared and sub-millimeter wavelengths. Modeling of molecular emission requires excitation calculations using radiative, as well as collisional rates, with the most abundant species. In the interstellar medium, the dominant collision partner is H_2 , but little data is available for collisions with H_2 . If data for collisions with He are available, it has often been proposed to use the more available rate coefficients for collision with He, with the appropriate reduced mass correction, as a first estimate of rate coefficients with $H_2(j = 0)$. The validity of this approximation is not known.

Aims. The present paper focuses on the calculation of rate coefficients among the first rotational levels of the SiS molecule in its ground vibrational state in collision with para- H_2 and compares these new data with recently published He ones to investigate the validity of using He rate coefficients to estimate $H_2(j = 0)$ rate coefficients.

Methods. A new potential energy surface for the SiS-para- H_2 system was obtained using highly correlated ab initio calculations. Dynamical calculations of pure rotational (de)excitation of SiS by para- H_2 were performed for the first rotational levels within the coupled-states approximation.

Results. Collisional cross sections among the 51 first rotational levels of SiS were calculated for kinetic energies up to 2500 cm^{-1} . State-to-state rate coefficients are calculated for temperatures ranging from 5 K up to 300 K. A propensity rule that favors even Δj transitions is found and is explained by the near homonuclear symmetry of the SiS-para- H_2 potential energy surface. A detailed comparison with recent SiS-He rate coefficients is also presented. We demonstrate that collision with He is a reasonable model for collisions with para- H_2 , although this approximation must be used with caution.

Key words. ISM: molecules – molecular data – molecular processes

1. Introduction

Silicon monosulfide (SiS) is one of the numerous diatomic species to be detected in the interstellar and circumstellar media. The first detection of the interstellar SiS molecule was reported more than 30 years ago by Morris et al. (1975). SiS was detected through the $j = 6 \rightarrow 5$ and $j = 5 \rightarrow 4$ radio line emission near the circumstellar envelope of the carbon star IRC+10216. Since then, the SiS molecule has been extensively observed (Olofsson et al. 1982; Turner 1987; Biegging & Nguyen-Quang-Rieu 1989; Fonfría Expósito et al. 2006). As it has a dipole moment ($\mu = 1.73 \text{ D}$, Tiemann et al. 1972), SiS is a good candidate for radioastronomy. Modeling SiS molecular emissions requires excitation calculations using radiative, as well as collisional, rate coefficients with the most abundant interstellar species: He, H, and H_2 .

The Herschel satellite of the European Space Agency (ESA) will provide high spectral resolution observations of molecular emission in the submillimeter and far-IR domains. SiS lines involving high- j levels will be observed with high signal-to-noise ratio given the expected sensitivity of the Herschel

instruments. Interpreting the Herschel data will require new rate coefficients involving high- j levels. Accurate collisional rate coefficients both for a wide temperature range and for high- j levels are thus needed.

As far as we know, no collisional data exist for collisions of the SiS molecule with the most abundant interstellar species, H_2 . In the absence of available collisional data for the SiS molecule, astronomers frequently used the SiO rate coefficients (Schöier et al. 2005) to estimate the abundance of SiS in molecular clouds. Another way to estimate H_2 rate coefficients would be to use available rate coefficients for collisions with He, along with the appropriate reduced mass correction.

Recent studies (Lique et al. 2006; Daniel et al. 2006) have shown that the degree of excitation of molecules crucially depends on the set of collisional rate coefficients used. Consequently, inaccurate rates can induce important errors when determining the molecular abundance in molecular clouds. Vincent et al. (2007) have shown that SiO and SiS rate coefficients are very different, so that it is inaccurate to use SiO data as a model for SiS. In general, the propensity for collisional

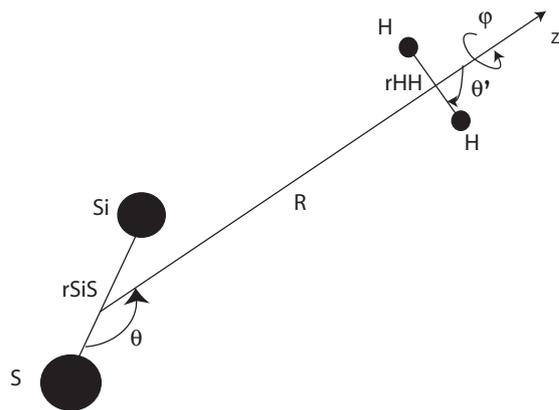


Fig. 1. Definition of the body-fixed coordinate system for the SiS–H₂ system.

excitation is very specific to the molecule in question, so that it may be risky to use rate coefficients for one molecule to estimate those for another. It is thus very important to know if a good estimate of rate coefficients for collision with H₂ ($j = 0$) can be obtained from those for collision with He. This question is important for astrophysical modeling since it is far more difficult to determine rate coefficients for excitation of molecules with H₂, especially if ro-vibrational transitions are allowed.

In this paper, we focus on rate coefficients for the rotational excitation of SiS by para-H₂ for temperatures ranging from 5 up to 300 K. These rate coefficients are determined by coupled-states quantum scattering calculations based on a potential energy surface (PES) determined using highly-correlated coupled-cluster methods. We consider here rotational transitions between the 51 first rotational levels of SiS. We compare the present results with the results obtained by Vincent et al. (2007) for the SiS molecule in collision with He. We then ascertain the validity of the approximation frequently used by astronomers for astrophysical systems: collisional rate coefficients with para-H₂ can be obtained from collisional rate coefficients with He by a simple multiplication of a factor of 1.4 (Schöier et al. 2005) corresponding to the square root of the ratio of the masses of the targets.

The paper is organized as follows. Section 2 describes the ab initio calculation of the potential energy surface. Section 3 then provides a brief description of the theory and the calculations. In Sect. 4 we present and discuss our results.

2. Potential energy surface

In the present work, we focus on low/moderate temperature collisions so that vibrational excitation does not occur. The collision partners may thus be considered as rigid. As shown previously (Faure et al. 2005; Jankowski & Szalewicz 2005), a better description of the intermolecular potential is obtained by fixing the molecular distance at its average value in the ground vibrational level rather than at the equilibrium distance. Accordingly, we used a H₂ bond distance $r_{\text{H-H}} = 1.44876$ bohr. For SiS, we used the experimental equilibrium distance ($r_{\text{SiS}} = 3.6459$ bohr (Huber & Herzberg 1979)), which differs by less than 0.01 bohr from the calculated value obtained by averaging over the $v = 0$ wave function.

For the purposes of the calculation, we defined the body-fixed coordinate system in Fig. 1. The geometry of the SiS–H₂ system with H₂ and SiS treated as rigid rotors is then

characterized by three angles θ , θ' , and ϕ , and the distance R between the centers of masses of H₂ and SiS. The polar angles of the SiS and H₂ molecules with respect to \mathbf{R} are denoted, respectively, by θ and θ' , while ϕ denotes the dihedral angle, which is the relative polar angle between the SiS and H₂ bonds.

For the solution of the close-coupling scattering equations, it is most convenient to expand, at each value of R , the interaction potential $V(R, \theta, \theta', \phi)$ in angular functions. For the scattering of two linear rigid rotors, we used (Green 1975):

$$V(R, \theta, \theta', \phi) = \sum_{l, l', \mu} v_{l, l', \mu}(R) s_{l, l', \mu}(\theta, \theta', \phi). \quad (1)$$

The basis functions $s_{l, l', \mu}(\theta, \theta', \phi)$ are products of associated Legendre functions P_{lm} :

$$s_{l, l', \mu}(\theta, \theta', \phi) = \left(\frac{2l+1}{4\pi} \right)^{1/2} \{ \langle l0l'0 | l'l'\mu0 \rangle P_{l0}(\theta) P_{l'0}(\theta') \\ + \sum_m (-)^m 2 \langle lml' - m | l'l'\mu0 \rangle \\ P_{lm}(\theta) P_{l'm}(\theta') \cos(m\phi) \} \quad (2)$$

where $\langle \dots | \dots \rangle$ is a Clebsch-Gordan coefficient. The P_{lm} functions are related to spherical harmonics through $Y_{lm}(\theta, \phi) = P_{lm}(\theta, \phi) e^{im\phi}$. Here l, l' are associated respectively with the rotational motion of SiS and H₂. In Eq. (1), the homonuclear symmetry of H₂ forces the index l' to be even.

For collisions at low/moderate temperature, the probability of rotational excitation of H₂ is low (the energy spacing between the $j = 0$ and $j = 2$ levels in para-H₂ is 510 K) so we further restrict H₂ to its lowest rotational level. In this case, only the leading term $l' = \mu = 0$ need be retained in the expansion of the interaction potential given in Eq. (2). The resulting expansion then can be simplified to:

$$V_{\text{av}}(r = r_e, R, \theta) = \sum_l V_l(R) P_l(\cos \theta) \quad (3)$$

where $V_{\text{av}}(r = r_e, R, \theta)$ is obtained by an average over the angular motion $\{\theta', \phi\}$ of the H₂ molecule.

The ground electronic state of the SiS–H₂ van der Waals system is of $^1A'$ symmetry. The potential energy surface was calculated in the supermolecular approach with a single- and double-excitation coupled cluster method (Hampel et al. 1992) (CCSD) with perturbative contributions from connected triple excitations computed as defined by Watts et al. (1993) [CCSD(T)]. The MOLPRO package (2002) was used. The four atoms were described by the standard correlation consistent, polarized-valence-triple-zeta atomic orbital bases of Dunning (1989) (cc-pVTZ) augmented with the diffuse functions of s, p, d, f , and g symmetries of Kendall (1992) (aug-cc-pVTZ). This basis set was further augmented by the (3s, 2p, 1d) set of bond functions defined by William et al. (1995), and placed equidistant between the SiS and H₂ centers of mass. Lique et al. (2005) have shown recently that using aug-cc-pVTZ basis sets with additional bond functions gives results comparable in accuracy to those obtained with the larger aug-cc-pVQZ basis sets. The Boys & Bernardi (1970) counterpoise procedure is used at all geometries to correct for basis set superposition error (BSSE), as follows:

$$V(R, \theta, \theta', \phi) = E_{\text{SiS-H}_2}(R, \theta, \theta', \phi) \\ - E_{\text{SiS}}(R, \theta, \theta', \phi) - E_{\text{H}_2}(R, \theta, \theta', \phi), \quad (4)$$

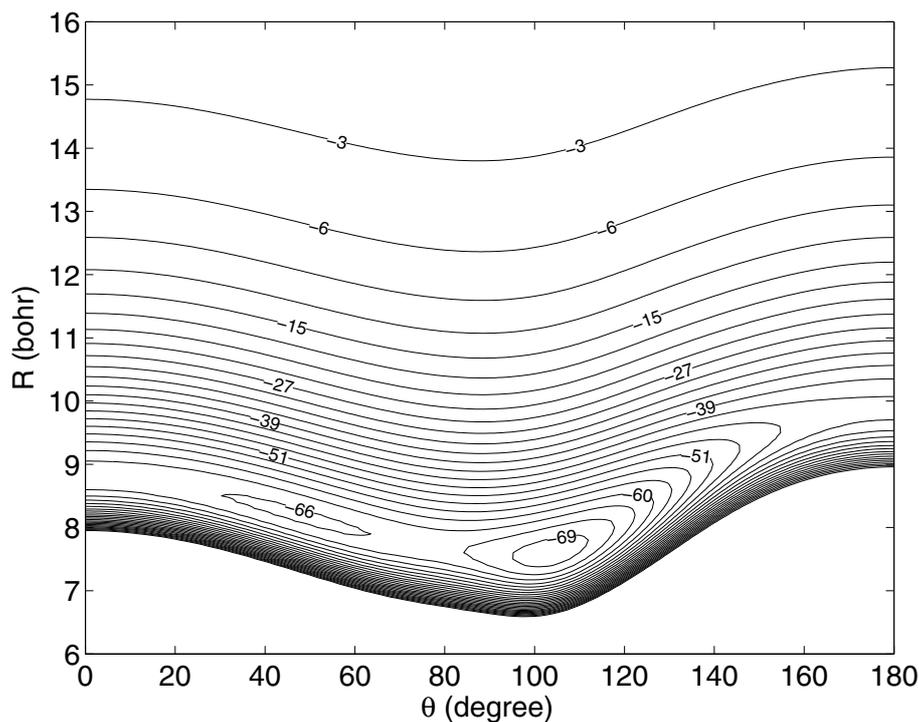


Fig. 2. Contour plot of the PES of SiS–para-H₂ as a function of R and θ with the Si–S separation fixed at $r_c = 3.6459$ bohr. The energies are in cm^{-1} with a spacing of 3 cm^{-1} , and the zero of energy is taken as that of the SiS($r = r_c$)+H₂ asymptote.

where the energies of the SiS and H₂ subsystems are computed with the full (four atom plus bond functions) basis set.

For a weakly-bound system, where the ground state is described well by a single electron occupancy configuration at all computed geometries, this level of theory is expected to yield reliable results.

The radial scattering coordinate R was assigned 36 values ranging from 25.0 bohr to 4.0 bohr [$R = 25, 20, 18, 16, 15, 14.5, 14, 13.5, 13, 12.5, 12, 11.5, 11, 10.5, 10, 9.75, 9.5, 9.25, 9, 8.75, 8.5, 8.25, 8, 7.75, 7.5, 7.25, 7, 6.75, 6.5, 6.25, 6, 5.75, 5.5, 5, 4.5, 4$], the θ grid ranged from 0 to 180 degrees in steps of 22.5 degrees. Three sets of (θ', ϕ) angles for each set of (R, θ) are calculated. Those are $a_1 = (0, 0)$; $a_2 = (\pi/2, 0)$; $a_3 = (\pi/2, \pi/2)$. This resulted in a total of 966 geometries computed for the SiS–H₂ system.

As mentioned above, V_{av} is obtained by averaging the total PES over θ' and ϕ . We approximate this here by an equipoise averaging of the a_1 , a_2 , and a_3 geometries, namely:

$$V_{av} = \frac{1}{3} (V_1 + V_2 + V_3). \quad (5)$$

The 4-dimensional SiS–H₂($j_2 = 0$) PES is thus reduced to a 2D PES. The resulting PES can, in principle, be extended to include the $l, \mu > 0$ terms that would be required for treating collisions of SiS with ortho-H₂ and/or para-H₂($j > 0$). Finally the fitting procedure described by Werner et al. (1988) for the CN–He system was adapted in order to obtain the $V_{av}(r = r_c, R, \theta)$ numerical expansion required to perform the scattering calculations.

A contour plot of the 2D PES is shown in Fig. 2. For this van der Waals system, the global minimum of the interaction energy was found to be -69 cm^{-1} ($R = 7.80$ bohr, $\theta = 112.5$ degree).

It is interesting to compare this PES with the earlier SiS–He PES of Vincent et al. (2007). Although the two PES are qualitatively similar, the minimum of the SiS–para-H₂($j = 0$)

PES is three times deeper than that of the SiS–He PES. The consequences for the collisional excitation cross sections and rate coefficients will be discussed below.

3. Collision dynamics

The main focus of this paper is the use of the fitted SiS–para-H₂($j = 0$) PES to determine rotational excitation and de-excitation cross sections of SiS molecules by para-H₂($j = 0$). The rotational energy levels of the ²⁸Si³²S molecule is computed using the experimental spectroscopic constants of Tiemann et al. (1972).

Because the full CC approach of Arthurs & Dalgarno (1960) is much too computationally intensive for molecules with very small rotational constants, we used the coupled-states approximation (CS) (McGuire & Kouri 1974) for the determination of collision cross sections. The integral cross sections were obtained by summing the partial cross sections over a sufficiently large number of values of the total angular momentum J until convergence was reached.

The standard time-independent coupled scattering equations were solved using the MOLSCAT (Hutson & Green 1994) code. Calculations were carried out at values of the total energy ranging from 0.8 to 2500 cm^{-1} . The integration parameters were chosen to ensure convergence of the cross sections over this range. In most of the calculations the integration range extended from 3.5 to 40 bohr.

We extended the rotational basis to ensure convergence of the inelastic cross sections. At the highest total energy considered (2500 cm^{-1}), the rotational basis extended to $j = 70$. The maximum value of the total angular momentum J used in the calculations was set large enough that the inelastic cross sections were converged to within 0.005 \AA^2 .

From the rotationally inelastic cross sections $\sigma_{j \rightarrow j'}(E_k)$, one can obtain the corresponding thermal rate coefficients

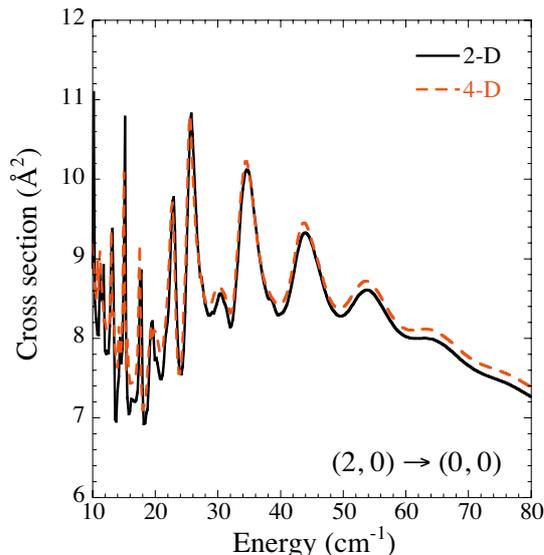


Fig. 3. Rotational de-excitation cross sections for the SiS molecule in collision with para-H₂($j = 0$) as a function of the collision energy obtained from present calculation black lines, with a full PES, and including coupling with $j = 2$ levels of H₂ (Lique & Klos 2007): dashed red lines.

at temperature T by an average over the collision energy (E_k) (Smith 1980):

$$k_{j \rightarrow j'}(T) = \left(\frac{8}{\pi \mu k^3 T^3} \right)^{\frac{1}{2}} \times \int_0^{\infty} \sigma_{j \rightarrow j'}(E_k) E_k \exp(-E_k/kT) dE_k \quad (6)$$

where k is Boltzmann's constant. The numerical integration in Eq. (6) was performed using a repeated Simpson's rule. To obtain precise values for the rate constants, the energy grid was chosen to be fine enough to include the numerous scattering resonances that will be described below.

It could be argued that our description of the collision of SiS with para-H₂($j = 0$) is inaccurate because (i) only three H₂ angles are used to obtain the average over the full orientation of the H₂ molecule and (ii) coupling with the $j = 2$ (and higher) states of H₂ is not taken into account. To ascertain the error introduced by these approximations, we compare in Fig. 3 and Table 1 several SiS de-excitation cross sections (for H₂ in $j = 0$) with results determined with a PES retaining the dependence on all three Jacobi angles (θ, θ', ϕ) and from scattering calculations including coupling with $j = 2$ levels of H₂. (Lique & Klos 2007)

As can be seen, the differences everywhere are less than 10% between these two sets of results even at energies where the $j = 2$ level of H₂ is open ($E_k > 355 \text{ cm}^{-1}$). For the $2 \rightarrow 0$ transition, the difference was 5.1%, for the $5 \rightarrow 3$ transition, 5.7%. To explain these differences, we integrated the full 4-D PES over the H₂ θ' and ϕ angles and compared it to the one averaged over 3 H₂ orientations. Very small differences exist between these two PES. Indeed, although these differences could lead to small deviations in the cross sections, the major differences between the two sets of results arise mainly from the neglect of $j = 2$ and higher H₂ rotational states. Consequently, we believe that an accurate description of the scattering of SiS with para-H₂ can be obtained by the simplified treatment described here in which we use three points to average over the rotational motion of the H₂ molecule before the scattering calculation.

Table 1. Comparison between present cross sections (a) and those (b) obtained with the full 4D PES including coupling with the $j = 2$ levels of H₂ (Lique & Klos 2007).

Transition $j \rightarrow j'$	$E = 100 \text{ cm}^{-1}$		$E = 200 \text{ cm}^{-1}$		$E = 500 \text{ cm}^{-1}$	
	(a)	(b)	(a)	(b)	(a)	(b)
$1 \rightarrow 0$	3.43	3.39	1.93	1.95	1.01	1.00
$2 \rightarrow 0$	6.60	6.75	4.63	4.80	2.67	2.82
$2 \rightarrow 1$	6.06	5.81	4.01	3.82	2.13	2.02
$5 \rightarrow 3$	12.46	12.72	9.05	9.37	6.07	6.44
$5 \rightarrow 4$	7.63	7.20	5.22	4.84	3.18	2.88

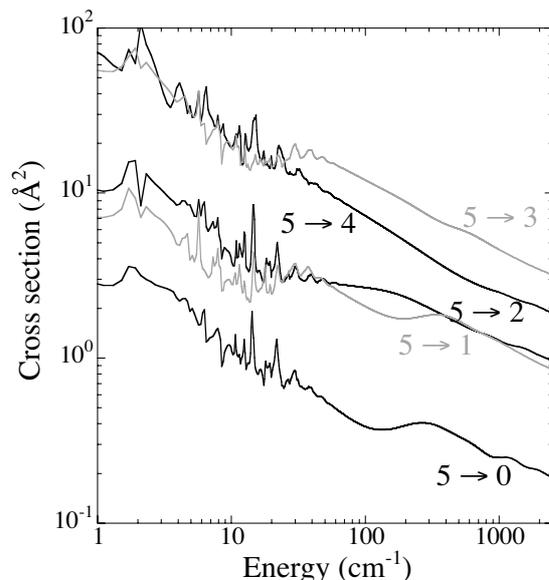


Fig. 4. Typical rotational de-excitation cross sections for the SiS molecule in collision with para-H₂($j = 0$) as a function of the collision energy. Black lines: odd Δj transitions; grey lines: even Δj transitions.

4. Results

Figure 4 illustrates the typical energy dependence of the collisional de-excitation cross sections obtained from the present CS calculations. At collision energies about $\approx 100 \text{ cm}^{-1}$ numerous sharp spikes appear. These are a consequence of the attractive potential wells. Quasibound states may arise from tunneling through the centrifugal energy barrier (shape resonances) or from excitation of the para-H₂-SiS complex to a bend-stretch level that is energetically accessible because of the attractive wells but is asymptotically closed (Feshbach resonances). Because of the small energy spacing between the SiS rotational levels, there are many of these Feshbach resonances. It is the temporary trapping that leads to narrow spikes or dips in the integral cross sections (Smith et al. 1979; Christoffel & Bowman 1983). Because of the averaging over collision energy (Eq. (6)), these narrow resonances will have little, if any, effect on the relaxation rate coefficients.

The CS approach used in the present calculations is expected to give accurate results at high energies and for transitions between high rotational levels for a heavy system like SiS. However, errors can arise whenever weak collisions at a large impact parameter make a significant contribution, as will occur at low energies or for transitions between closely-spaced levels.

To check the validity of the CS approach, CC calculations were performed at selected low total energies for the first

Table 2. Comparison between cross sections obtained by CC and CS methods.

Transitions $j \rightarrow j'$	$E = 10 \text{ cm}^{-1}$		$E = 20 \text{ cm}^{-1}$		$E = 50 \text{ cm}^{-1}$		$E = 100 \text{ cm}^{-1}$		$E = 200 \text{ cm}^{-1}$	
	CC	CS	CC	CS	CC	CS	CC	CS	CC	CS
1 → 0	16.75	10.53	9.41	12.29	5.78	5.72	3.54	3.43	1.98	1.93
2 → 0	11.12	9.41	9.57	6.92	8.23	8.37	5.58	6.60	4.07	4.63
2 → 1	25.20	17.53	13.63	13.09	8.56	8.54	6.04	6.06	4.03	4.01
3 → 0	1.86	1.71	1.03	1.02	0.847	1.06	0.982	1.06	0.921	0.93
3 → 1	21.97	17.47	16.00	12.52	13.09	14.84	9.21	10.49	6.97	7.56
3 → 2	31.30	23.76	17.44	18.28	9.75	9.92	6.73	6.84	4.64	4.67
5 → 0	4.82	2.86	0.82	1.10	0.46	0.62	0.33	0.39	0.35	0.38
5 → 1	11.28	7.19	3.61	2.79	2.77	3.16	2.21	2.14	1.90	1.72
5 → 2	14.94	10.57	4.28	5.11	2.51	3.08	2.46	2.69	2.29	2.37
5 → 3	72.82	56.26	20.70	22.25	16.23	17.25	11.20	12.46	8.46	9.05
5 → 4	93.67	74.66	26.95	22.73	11.55	11.40	7.51	7.63	5.20	5.22
10 → 5	2.36	2.40	1.27	1.46	1.27	1.36
10 → 6	5.81	4.94	3.54	3.22	2.84	2.61
10 → 7	5.03	4.82	3.01	3.19	2.86	2.97
10 → 8	25.18	20.77	14.41	13.96	9.74	10.12
10 → 9	22.71	22.67	8.87	8.99	5.47	5.52

rotational levels. Table 2 presents a comparison between cross sections predicted by both approaches. As anticipated, significant differences exist between the CC and CS approaches at very low energy, but these differences decrease rapidly with increasing energies. At $E_c = 50 \text{ cm}^{-1}$ and above, we find excellent agreement between cross sections obtained by these two methods ($\sim 10\text{--}15\%$). Hence, we can be confident of the accuracy of the CS results presented in this paper even though rate coefficients at very low temperature (10–20 K) can present an inaccuracy of 20–30%.

Subsequently, we used the calculated inelastic cross sections to obtain, by energy averaging, de-excitation rate coefficients for the first 51 ($j = 0\text{--}50$) rotational levels of SiS, from CS cross sections. The representative variation with temperature is illustrated in Fig. 5.

The complete set of (de)excitation rate coefficients obtained from the CS cross sections for transitions with $j, j' \leq 50$ is available on-line from the BASECOL website¹. Excitation rate coefficients can be easily obtained by detailed balance:

$$k_{j \rightarrow j'}(T) = k_{j' \rightarrow j}(T) \frac{2j' + 1}{2j + 1} \exp\left[-(\varepsilon_{j'} - \varepsilon_j)/kT\right] \quad (7)$$

where ε_j and $\varepsilon_{j'}$ are, respectively, the energies of the rotational levels j and j' .

We are also interested in the propensity rules of pure rotational transitions. Figure 6 presents downward rotational rate coefficients out of $j = 10$ levels at 20, 50, 100, and 300 K.

The downward rate coefficients decrease with increasing Δj , which is the usual trend, and a strong propensity towards transitions with even Δj exist. This last propensity is due to the near-homonuclear symmetry of the potential energy surface (see Fig. 1). This effect has been seen both experimentally (for NO–Ar collisions, Andresen et al. 1982) and theoretically (for CO–He collisions, Chapman & Green 1977), and was first explained by Brumer (1974), and later by McCurdy & Miller (1977).

4.1. Comparison with SiS–He rate coefficients

It is interesting to compare the present SiS rate coefficients for collision with para-H₂ ($j = 0$) with SiS rate coefficients for collision with He calculated recently by Vincent et al. (2007) using

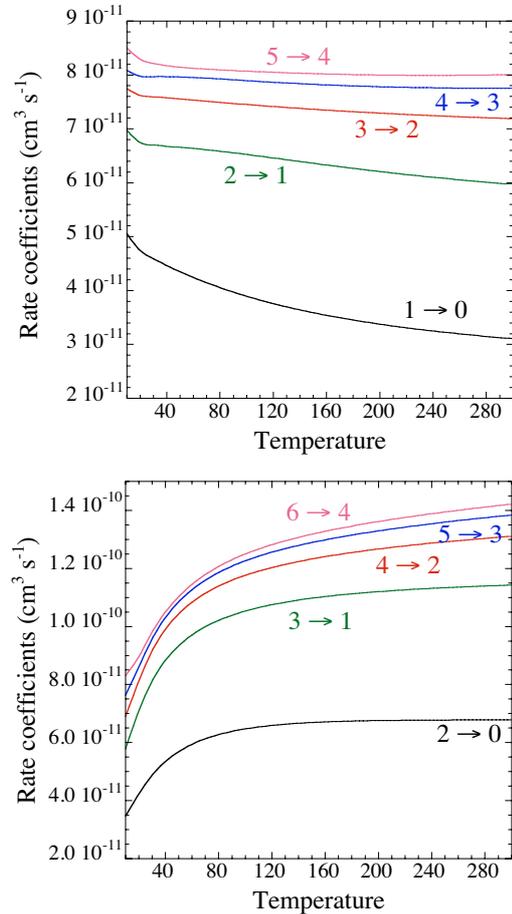


Fig. 5. Typical variation with temperature of the collisional de-excitation rate coefficients of SiS by para-H₂ corresponding to $\Delta j = -1$ (upper panel) and $\Delta j = -2$ (lower panel) transitions.

very similar methodology to the one here. By comparing the two sets of rate coefficients, we mostly analyze the effect of the different perturber masses and PESs. Collisions with helium are often used to model collisions with para-H₂ ($j = 0$). It is generally assumed that rate coefficients with para-H₂ ($j = 0$) should be larger than He rate coefficients, owing to the smaller collisional reduced mass and the larger size of H₂. A scaling factor

¹ <http://www.obspm.fr/basecol/>

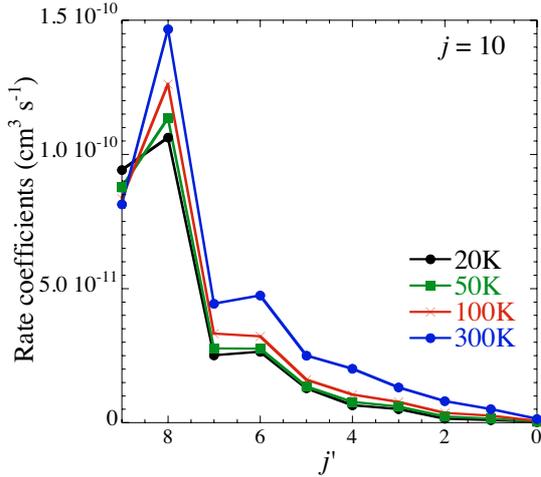


Fig. 6. De-excitation rate coefficients out of $j = 10$ at 20, 50, 100, and 300 K.

of 1.4 is often used (Schöier et al. 2005). This approximation is based on the assumption of equal collisional cross sections for He and para-H₂($j = 0$). The factor 1.4 reflects the difference in the collision reduced mass factor in the thermal average leading to the corresponding rate coefficients (Eq. (6)). As only a few systems have been studied with both He and H₂, the validity of this scaling law must be ascertained. The present system is an ideal candidate for this.

We compare in Fig. 7 the present rate coefficients with the rate coefficients obtained for the SiS–He system for $\Delta j = j' - j = -1, -2,$ and -5 transitions at temperatures of 20, 50, and 150 K. As we see, the ratio of the two sets of rate coefficients differs from 1.4, and varies both with the temperature and with the transition considered. Typically, for the temperature range considered in this work, the H₂($j = 0$) rate coefficients are larger within a factor of 1–3 of the He rate coefficients. This delimits the accuracy of collisional rate coefficients with para-H₂ obtained from collisional rates with He. This result confirms previous results obtained for other diatomic molecules like SO (Lique et al. 2007) or CO (Wernli et al. 2006). To analyze these differences in more detail, we plot in Fig. 8 the energy variation of collisional cross sections with He and para-H₂($j = 0$). The difference is most pronounced at low energy. This is to be expected, since low energy collisions will be most sensitive to the well depth in the PES. Here, the well depth is three times larger (63 cm^{-1} vs. 20 cm^{-1}) with H₂ than with He. Consequently, too, the position of the quasi-bound resonance states will be different.

At higher energy, the SiS–He cross sections are consistently smaller. In addition, the same even/odd propensity rules characterize collisions of SiS with both He and para-H₂($j = 0$). Overall, then, the He cross sections agree reasonably well with those for para-H₂($j = 0$), but are not the same.

This comparison confirms that the rate coefficients for excitation of SiS by collision with para-H₂($j = 0$) cannot be predicted accurately as a constant multiple of rate coefficients for collisions with He. Notwithstanding, the multiplication of the He rate coefficients by the square root of the reduced mass ratio does correctly predict the order of magnitude of the para-H₂($j = 0$) rate coefficients. The results obtained here for the SiS molecule confirm recent results for the SO molecule (Lique et al. 2007). The present conclusion about the accuracy of using He rate coefficients to predict those for para-H₂($j = 0$) should

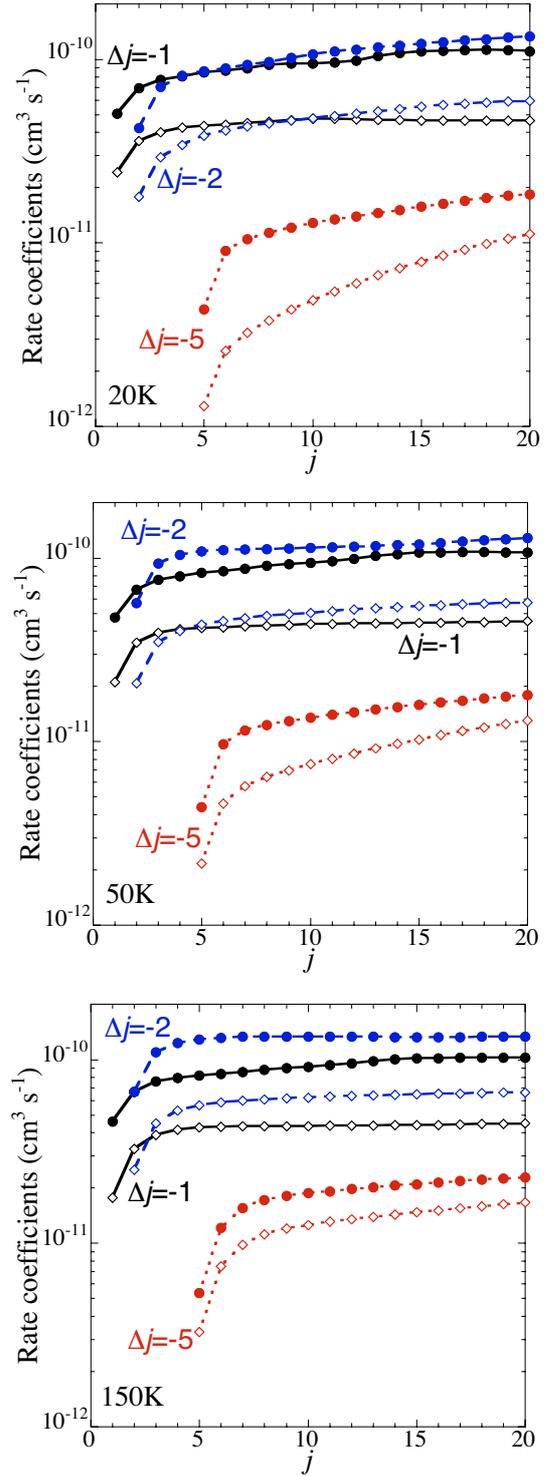


Fig. 7. Calculated SiS–para-H₂($j = 0$) rate coefficients (this work: filled circles) at 20 K (up panel), 50 K (middle panel), and 150 K (down panel) compared with SiS–He rate coefficients calculated by Vincent et al. (2007) (empty diamonds).

be extended by a systematic study of (de)excitation of other diatomic molecules.

5. Summary and discussion

We have used quantum scattering calculations to investigate rotational energy transfer in collisions of SiS with

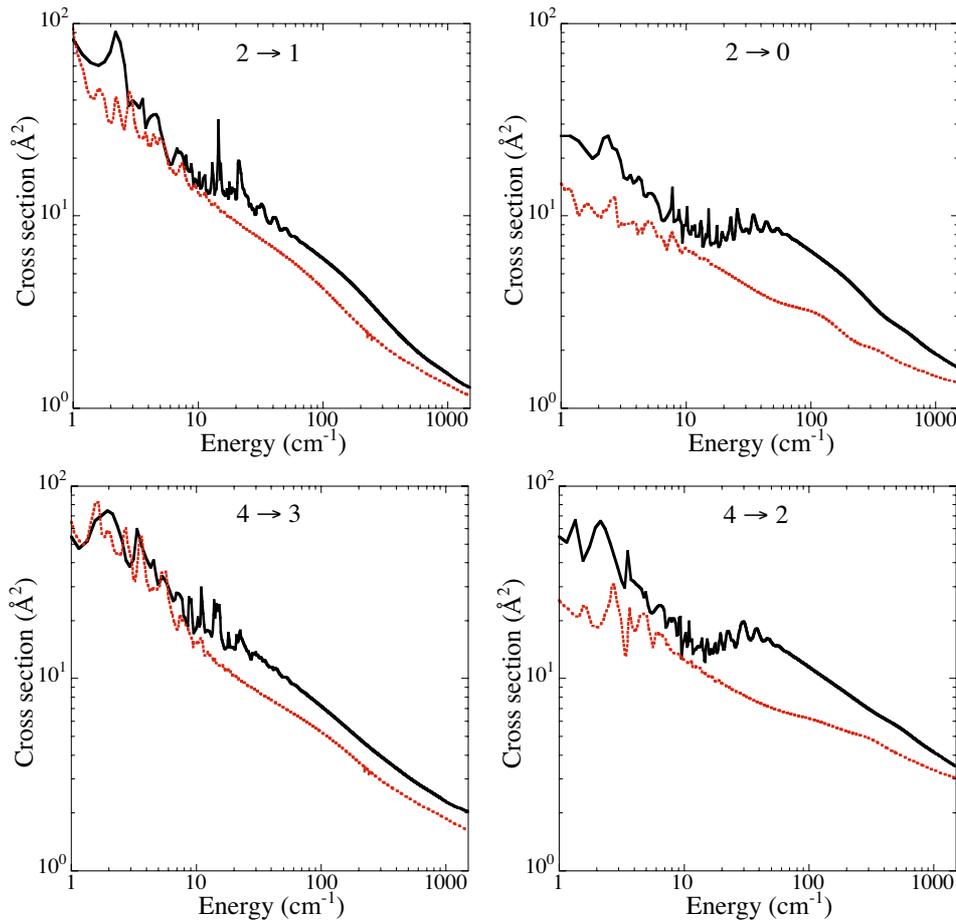


Fig. 8. Comparison between rotationally inelastic cross sections for collisions of SiS with para-H₂ (solid black line) and with He (dashed red line).

para-H₂ ($j = 0$) molecules. The calculations were based on a new 4D potential energy surface averaged over the motion of the H₂ moiety. Rate coefficients for transitions involving the lowest 51 levels of the SiS molecule were determined for temperatures ranging from 5 to 300 K. Strong propensity rules for even Δj were found. In particular, the rate coefficients for $|\Delta j| = 2$ transitions were about twice as large as those for $|\Delta j| = 1$ transitions, especially at high temperatures. This strong propensity can have important astrophysical consequences. As shown by Wernli et al. (2007) for HC₃N collisions, a Δj even propensity can amplify population inversion if local thermodynamic equilibrium (LTE) conditions are not met. In any case, the full set of rate coefficients presented here will enhance our ability to understand and interpret future SiS observations.

The comparison of the new SiS–para-H₂ rate coefficients with previously calculated SiS–He rate coefficients (Vincent et al. 2007) shows that significant differences exist. Nonetheless, when scaled by the square root of the collision reduced mass, the He rate coefficients are a reasonable approximation with a maximum error of a factor 2 to the para-H₂ rate coefficients at moderate temperature.

Finally, it is important to note that the rate coefficients obtained for the SiS molecule are very different from those for the SiO molecule (Dayou & Balança 2006), especially the propensity rules. Hence, the use of the SiO rate coefficients to simulate the collisional properties of SiS could lead to large errors in the interpretation of SiS molecular emission from molecular clouds and high-mass stars forming regions.

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