

CAN WE ESTIMATE RATE COEFFICIENTS FOR COLLISIONS WITH PARA-H₂(J=0) FROM HELIUM RATE COEFFICIENTS ? APPLICATION TO SiS

L. F. M. Vincent¹, F. Lique^{1,2}, A. Spielfiedel¹, N. Feautrier¹, R. Tobola³ and J. Klos

Abstract. The theoretical determination of collisional rate coefficients is a two steps process: determination of the interaction potential V between the colliding systems and calculation of the collision dynamics. In the interstellar medium, the dominant collision partner is H₂, but only few data are available for collisions with H₂. If data for collisions with He are available, it is often proposed to use He-rate coefficients with the appropriate reduced mass correction as a first estimate of rate coefficients with H₂($j = 0$). This approximation assumes that He- and H₂-collisions have the same cross sections. As shown from our recent results on SiS in collision with He and H₂($j = 0$), some caution may be exercised concerning this approximation.

1 Introduction

Analysis of light emission from different regions of the interstellar medium (ISM) is a powerful tool to investigate the physical and chemical conditions of the medium. Modelling of the gas emission in those regions requires the simultaneous resolution of radiative transfer and steady state equations for populations of each ro-vibrational level of the considered molecule. When the local thermodynamical equilibrium (LTE) conditions are not fulfilled, in shocks for instance, a competition between radiative and collisional processes occurs and thus accurate collisional rates with the most abundant species are needed. The dominant collision partner in the ISM is H₂ but, in the absence of available collisional data, rate coefficients with helium are often used with a scaling factor of about 1.4 (Schöier et al 2005). This approximation is based on the assumption of equal collision cross sections for He and H₂($j = 0$). Hereafter, our purpose is to check the validity and the accuracy of this approximation in the particular case of rotational excitation of SiS by collisions with He and with para-H₂($j = 0$). Sect. 2 describes the calculations of rate coefficients for both systems and gives the results which are discussed in Sect. 3.

2 Collisional rate coefficients

Within the Born-Oppenheimer approximation, the determination of collisional rate coefficients requires two different steps. Firstly we determine the potential energy surface (PES). It consists in the resolution of Schrödinger equation with fixed nuclei. Then, this PES is used for scattering calculations. For SiS, the distance between the two atoms is frozen to its experimental equilibrium value $r_{SiS} = r_e = 3.6459$ bohr. For collisions at low temperature, the probability of rotational excitation of H₂ is low so we further restrict H₂ to its lowest rotational level $j=0$. As a consequence, the SiS-H₂ cross sections are calculated by using an interaction potential obtained by an average over the angular motion of the H₂ molecule. Figure 1 shows the two Jacobi coordinates R and θ used to describe the PESs. For the resolution of scattering equations, the interaction potential is expanded in terms of Legendre functions.

$$V(R, \theta) = \sum_{\lambda=0}^{\lambda_{max}} V_{\lambda}(R) P_{\lambda}(\cos\theta) \quad (2.1)$$

¹ LERMA, CNRS UMR 8112, Observatoire de Paris - Section de Meudon, France

² Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742-2021

³ Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warszawa, Poland

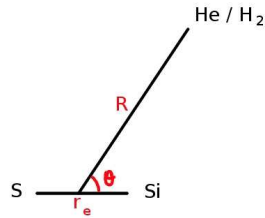


Fig. 1. Coordinates for both systems.

The determination of the PES is an *ab initio* quantum calculation, performed with the MOLPRO package (2002). We used the supermolecular approach with a single- and double-excitation coupled cluster method with perturbative contributions of triple excitations (CCSD(T)). The basis set used for all the atoms is the standard correlation-consistent polarized-valence-quadruple-zeta of Dunning (1989) augmented with diffuse functions of s, p, d, f and g symmetries (aug-cc-pVQZ) and bond functions placed equidistant between the SiS center of mass and He or the H₂ center of mass. Contour plots of the potential for both systems are shown in Fig. 2.

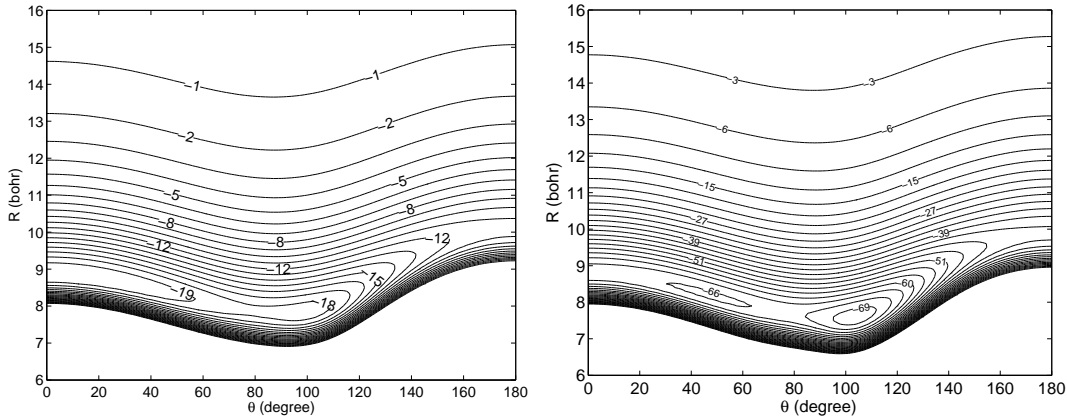


Fig. 2. Contour plots of the SiS-He PES (on the left) and the SiS-H₂ PES (on the right) as a function of R and θ . Energies are in cm⁻¹ and the zero of energy is taken as that of the SiS+He and SiS+H₂ asymptote respectively.

The PESs were used to determine rotational excitation and de-excitation cross sections of SiS by He atoms and H₂ molecules. All the scattering calculations were performed using the MOLSCAT code (Hutson and Green 1994). In the case of collisions of SiS with He, the full close coupling approach (CC) was used to calculate the cross sections involving the first 26 rotational levels up to 200 K, with a basis set of 36 rotational levels. More details can be found in Vincent et al. (2007). In the case of collisions of SiS with H₂, the full CC approach is overly computationally intensive, so we have used the coupled-states approximation (CS) to calculate the cross sections involving the first 51 rotational levels up to 300 K, with a basis set of 71 rotational levels (Lique et al. 2007). From the rotationally inelastic cross sections, one obtains the corresponding thermal rate coefficients by an average over the collision energy E_k .

$$k_{j \rightarrow j'}(T) = \left(\frac{8}{\pi \mu k^3 T^3} \right)^{\frac{1}{2}} \times \int_0^{\infty} \sigma_{j \rightarrow j'}(E_k) E_k \exp(-E_k/kT) dE_k \quad (2.2)$$

where k is Boltzmann's constant. The typical variation with temperature of the downward rate coefficients is shown in Fig. 3. We notice that rate coefficients increase with increasing j for a given $\Delta j = j - j'$.

As shown in Fig. 4, in both systems, the rate coefficients exhibit a propensity in favor of transitions with even Δj .

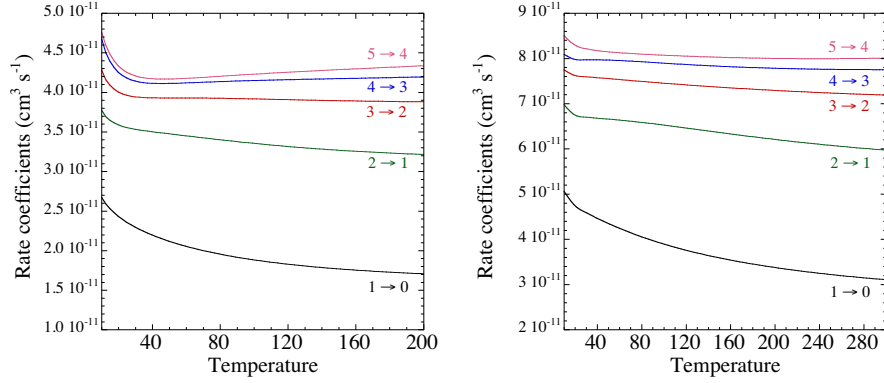


Fig. 3. Temperature variation of the de-excitation rate coefficients for the first $\Delta j = -1$ transitions for SiS-He (left) and SiS-H₂ (right).

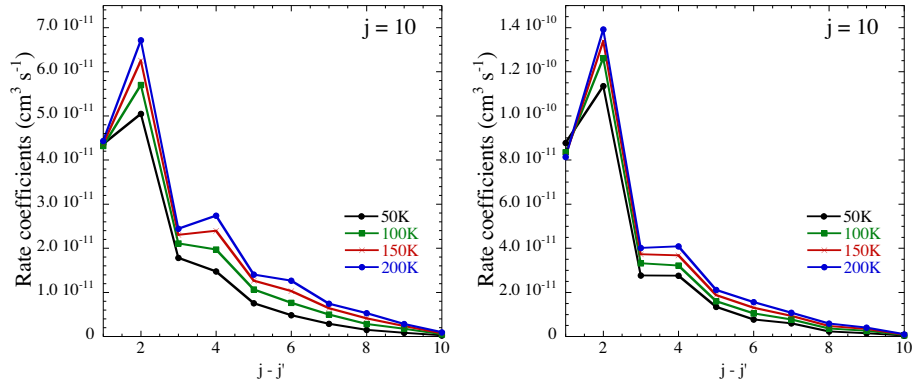


Fig. 4. De-excitation rate coefficients out of $j = 10$ at 50, 100, 150 and 200 K for SiS-He (left) and the SiS-H₂ (right).

3 Discussion

Although the two PESs are qualitatively similar, the minimum of the SiS-H₂ PES (-69 cm⁻¹) is three times deeper than that of the SiS-He PES (-19.97 cm⁻¹). This leads to important differences in the resonance energy area, and hence significant differences in the corresponding rate coefficients at low temperature. We compare

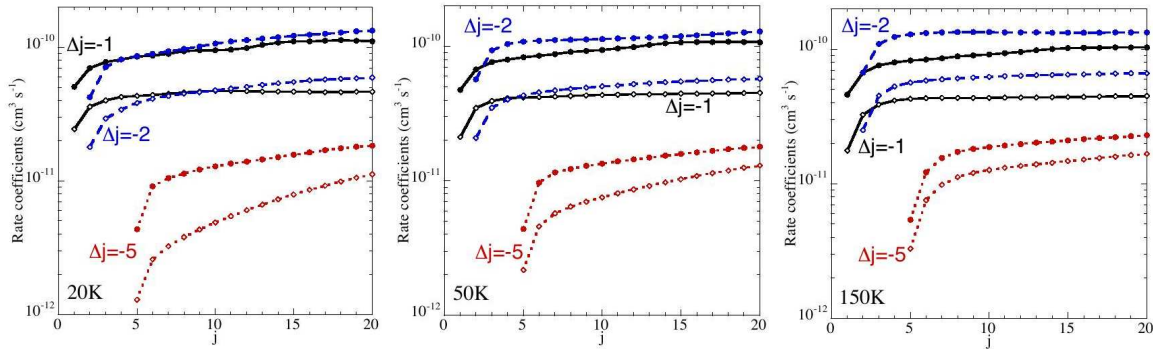


Fig. 5. Calculated SiS-H₂ rate coefficients (filled circles) at 20 K (left panel), 50 K (middle panel) and 150 K (right panel) compared with SiS-He rate coefficients (empty diamonds).

in Fig. 5 the rate coefficients for both systems for $\Delta j = j' - j = -1, -2,$ and -5 transitions at temperatures of 20, 50 and 150 K. The ratio of the two sets of rate coefficients differs from the often used scaling factor of 1.4,

and varies with the temperature, the initial level and the value of Δj .

4 Conclusion

This work confirms that accurate collisional rate coefficients with para-H₂ cannot be obtained from collisional rates with He. The latter give an order of magnitude, sufficient for actual observations, but the high resolution observations expected from Herschel and ALMA will require accurate rate coefficients with both para- and ortho-H₂.

References

Dunning, T. H. 1989, *J. Chem. Phys.*, 90, 1007

Hutson J. M. and Green S., MOLSCAT computer code, version 14 (Collaborative Computational Project No. 6 of the Science and Engineering Research Council, United Kingdom, 1994)

Lique, F. et al., 2007, *A&A*, submitted

MOLPRO is a package of ab initio programs written by :

Werner, H.-J. and Knowles, P. J. with contributions from Almlöf, J., Amos, R. D., Deegan, M. J., Elbert, S. T., Hampel, C., Meyer, W., Peterson, K., Pitzer, R., Stone, A. J., Taylor, P. R., Lindh, R., Mura, M. E. and Thorsteisson T.

Schöier, F. L., van der Tak, F. F. S., van Dishoeck, E. F. and Black, J. H., 2005, *A&A*, 432, 369

Vincent, L., Lique, F., Spielfiedel, A. and Feautrier, N., 2007, *A&A*, 472, 1037