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Rotational excitation and de-excitation
of HF molecules by He atoms⋆

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Abstract. We report Close Coupling calculations of the rotational transitions induced in collisions between HF molecules and He atoms. We consider transitions for levels up to $J = 9$ and for temperatures up to 300 K. We use a new global 3D potential energy surface which we proposed recently and is the best available at the moment. This surface exhibits two minima associated both with linear geometries ($V = -43.70$ cm^{-1} for He–HF and $V = -25.88$ cm^{-1} for He-FH). Close Coupling calculations are performed in the collision energy 10^{-6} to 2000 cm^{-1} interval. Our results validate the estimate, by Neufeld et al., of the abundance of HF in the interstellar medium which was detected recently.

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

1. Introduction

The first detection of interstellar hydrogen Fluoride was reported recently by Neufeld et al. (1997) using the Long Wavelength Spectrometer of the Infrared Space Observatory (ISO). They detected the $J = 2-1$ line of HF in absorption toward the far-infrared continuum source Sagittarius B2 and presented a brief description of the fluorine chemistry from which they concluded that gaseous fluorine exists in interstellar clouds almost entirely in the form of the molecule HF. A more comprehensive accounts of the chemistry of HF in interstellar clouds was then given by Zhu et al. (2002). They confirmed the conclusion of Neufeld et al. (1997) after considering in detail the spin orbit quenching of F(^{2}P$_{1/2}$) and the reaction of F(^{2}P$_{3/2}$) atoms colliding with H$_2$. In the absence of available collisional data for the He–HF system Neufeld et al. (1997) used the rate coefficient for collisional de-excitation of HCl by He to estimate the abundance of HF in Sgr B2. The purpose of the present work is to propose a more realistic estimation of He–HF collisional rate.

The He–HF complex is a relatively simple system for ab initio calculations and it has been the object of numerous studies (Rodwell et al. 1981; Sapse 1983; Raimondi 1984). The widely used potential energy surface of Rodwell et al. (1981) suffers, however from several weaknesses. It is too shallow and the anisotropic terms are too large in the repulsive

wall region. Moszynski et al. (1994, 1996) have computed the He–HF potential energy surface using symmetry-adapted perturbation theory for three internuclear distances of the HF molecule (1.6078, 1.7328 and 1.9180 Bohr). They have shown that the shape of the potential results from a balance between the dispersion, exchange, electrostatic and induction interactions, the main contribution resulting from dispersion. They however did not obtain an analytical potential energy surface.

We calculated a new surface in a recent work (Stoecklin et al. 2003) dedicated to the study of the vibrational quenching of the $\nu = 1$ state of the HF molecule. This surface which is the best available currently is based on a grid of ab initio points calculated at the coupled cluster BCCD(T) level using Brueckner orbitals (Handy et al. 1989) and an aug-cc-pVQZ basis set (Woon & Dunning 1993). We then applied the reproducing kernel Hilbert space method (Ho & Rabitz 1996) to construct an analytical model of the potential energy surface. This method has proved to be very effective for the description of several van der Waals systems including He–N$_2$ (Stoecklin et al. 2002), He–F$_2$ (Stoecklin et al. 2003) and H–F$_2$ (Stoecklin et al. 2004) which we studied.

On the dynamical side, the experimental data concern only the moderate and high collision energies. The first calculations are quite old and were obtained using the Infinite Order Sudden Approximation (IOSA) (Gianturco et al. 1983) and the potential energy surface of Rodwell et al. (1981). In a recent study Moszynski et al. (1996) improved their surface from 1994 and performed Close Coupling calculations but only for three collision energies and in the rigid rotor approximation. Very

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⋆ Tables 1 and 2 are only available in electronic form at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via http://cdsweb.u-strasbg.fr/cgi-bin/qcat?J/A+A/430/1139

recently the same surface was also used by Bodo & Gianturco (2003) to perform Close Coupling calculations but only for collision energies below 1 cm^{-1}. In this work we perform close coupling calculations using our new surface for collision energies ranging from 10^{-6} to 2000 cm^{-1}.

The paper is organised as follows. In Sect. 2 the method and the parameters used to make the scattering calculations are briefly discussed in Sect. 3. The results of inelastic, elastic cross sections and quenching rate coefficients calculations are presented and discussed in Sect. 4.

2. Scattering calculations

We performed Close Coupling calculations using our code. This program, written by T. Stoecklin, is based on the Magnus propagator introduced by Light and coworkers (Anderson et al. 1978; Stechel et al. 1978). The scattering equations are propagated in the spaced fixed coordinates and the asymptotic matching to diagonal spherical Bessel functions of the first and second kind follows the lines described by Launay (1977).

The T matrix elements obtained are used to calculate the cross section for a transition from an initial vibrational-rotational level labeled by the quantum numbers vj to a final level labeled by the quantum numbers $v'j'$:

$$\sigma_{vj \to v'j'}\left(E_{vj}\right) =$$

$$\frac{\pi}{(2j+1)\,k_{vj}^2} \sum_{J=0}^{\infty} (2J+1) \sum_{l=|J-j|}^{|J+j|} \sum_{l'=|J-j'|}^{|J+j'|} \left|T_{vj,v'j'}^J\right|^2 \quad (1)$$

where J and l are respectively the total and the orbital angular momentum quantum numbers. The wave vector is defined by $k_{vj}^2 = \frac{2\mu}{\hbar^2}\left[E - \varepsilon_{vj}\right]$, ε_{vj} being the eigen energy of the initial rovibrational state vj, E the total energy, μ the relative mass of the system and $E_{vj} = \frac{\hbar^2 k_{vj}^2}{2\mu}$.

The de-excitation rate coefficient are calculated by averaging the cross sections over a Boltzman distribution of the relative kinetic energy

$$k_{vj \to v'j'}^{\text{In}}(T) = \sqrt{\frac{8}{\pi\mu}}\,(k_B T)^{-\frac{3}{2}} \int_0^{\infty} dE_{vj} E_{vj} \sigma_{vj \to v'j'}^{\text{In}}\left(E_{vj}\right) e^{-\frac{E_{vj}}{k_B T}}. \quad (2)$$

The excitation rate coefficient is calculated using the detailed balance relationship.

$$k_{v'j' \to vj}^{\text{In}}(T) = \frac{(2j+1)}{(2j'+1)} e^{-\frac{\left[E_{vj}-E_{v'j'}\right]}{k_B T}} k_{vj \to v'j'}^{\text{In}}(T). \quad (3)$$

Because the rotational constant of HF ($v = 0$) is quite large (around 20 cm^{-1}), the highest occupied rotational level of the first vibrational level is $j = 13$. We included 15 rotational states in the basis set for each of the two vibrational levels $v = 0$ and $v = 1$ considered in the calculations. With this basis set we believe the cross section to be converged to better than 1%. The maximum propagation distance was 300 Bohr and convergence was checked as a function of the propagator step size. At each point of the propagation grid the matrix elements of the potential were evaluated by expanding the potential in Legendre polynomials retaining terms up to $l = 6$ on
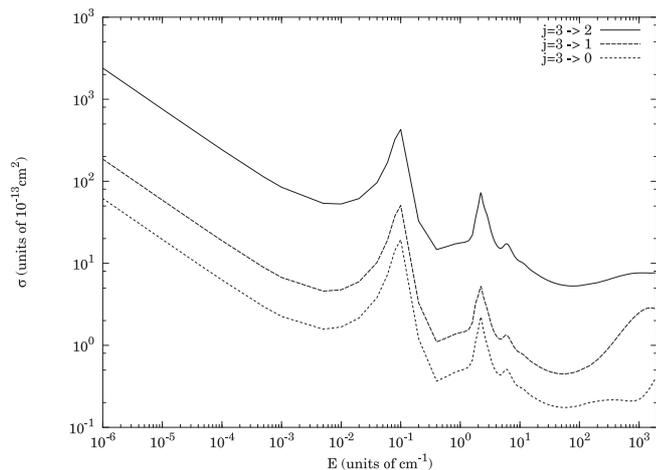

Fig. 1. Rotational deactivation transition cross section (in Angstrom^2) of HF ($v = 0$, $j = 3$) in collision with He as a function of the kinetic energy in cm^{-1}.
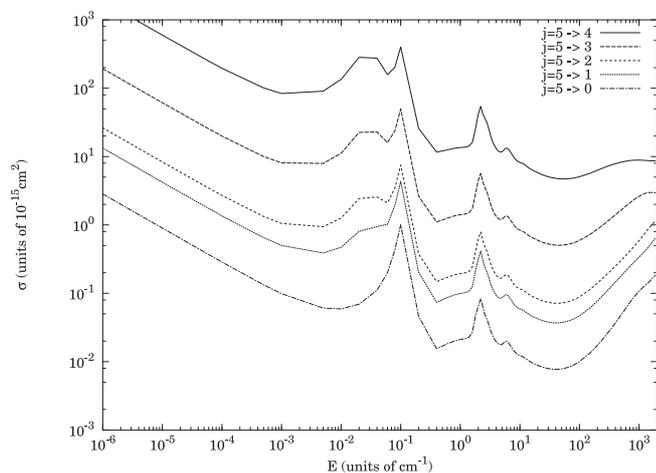

Fig. 2. Rotational deactivation transition cross section (in Angstrom^2) of HF ($v = 0$, $j = 5$) in collision with He as a function of the kinetic energy in cm^{-1}.

a grid of 8 points used to calculate the Gauss Hermite quadrature of the vibrational part of the integral. A Discrete Variable Representation (DVR) along the Gauss Hermite grid of the diatomic rovibrational wave functions was calculated by solving the exact diatomic equations using the diatomic potential described in our previous work (Stoecklin et al. 2003) and a Finite Basis Representation (FBR) of 150 imaginary exponential wave functions as described for example by Colbert & Miller (1982).

3. Results and discussion

Cross sections for rotationally inelastic scattering were computed for kinetic energy in the range $[10^{-6}; 2000]$ cm^{-1}. The convergence of the cross section was checked as a function of the total angular momentum for each value of the kinetic energy. The maximum value of the total angular momentum J used in the calculations was $J = 50$. Figures 1−4 show the de-excitation cross section for rotational levels (respectively
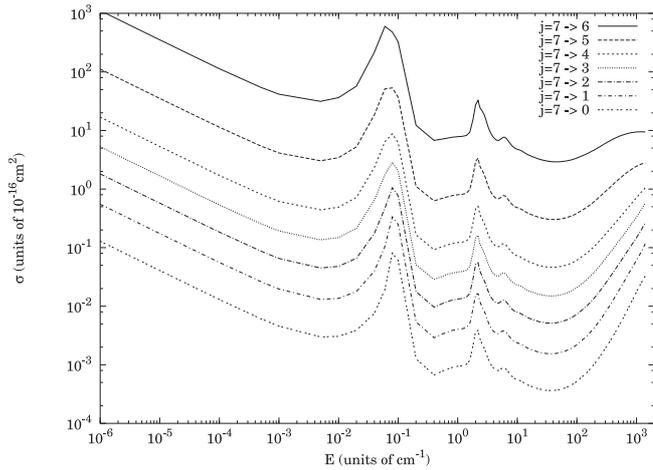
Fig. 3. Rotational deactivation transition cross section (in Angstrom^2) of HF ($v = 0$, $j = 7$) in collision with He as a function of the kinetic energy in cm^{-1}.
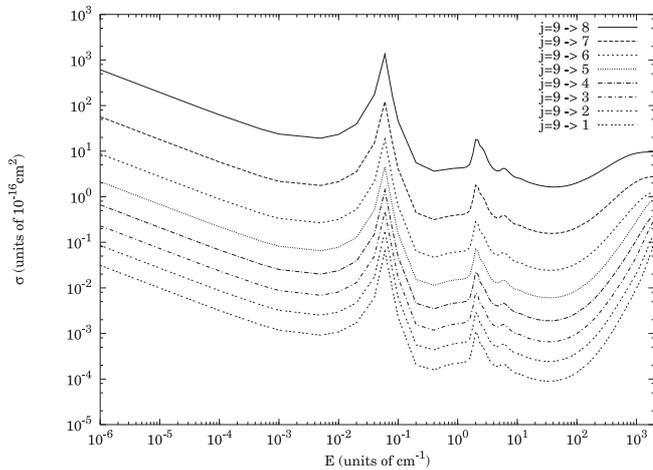

Fig. 4. Rotational deactivation transition cross section (in Angstrom^2) of HF ($v = 0$, $j = 9$) in collision with He as a function of the kinetic energy in cm^{-1}.

Fig. 5. Rotational deactivation rate coefficient of HF ($v = 0$, $j = 3$) in collision with He as a function of temperature. The inverse rotational transitions rate coefficients are also represented.

Fig. 6. Rotational deactivation rate coefficient of HF ($v = 0$, $j = 5$) in collision with He as a function of temperature. The inverse rotational transitions rate coefficients are also represented.

$j = 3$, 5, 7 and 9) states of HF. The profiles we find as a function of energy are identical to the quenching cross section profile which we analysed in our previous work (Stoecklin et al. 2003). This the usual profile for similar Van der Waals complexes with a very low energy Wigner regime, an intermediate regime with resonances for energies below the well depth and a translation − (vibration rotation) energy transfer regime for energies above. In the present case, however, because the rotational constant of HF is so large, the Feshbach resonances are not superimposed on the shape resonances as for example is the case for He–CO (Balakrishnan et al. 2000). The two peaks around 2 and 7 cm^{-1} are then isolated. More details about the analysis of the nature of the resonances can be found in our previous work (Stoecklin et al. 2003). Another point of importance which we found in this previous study is that the vibrational transition cross sections are quite small compared to pure rotational transitions cross sections as a result of the weak dependence of the potential as a function of the HF stretching coordinate in contrast to its strong variation as a function of the
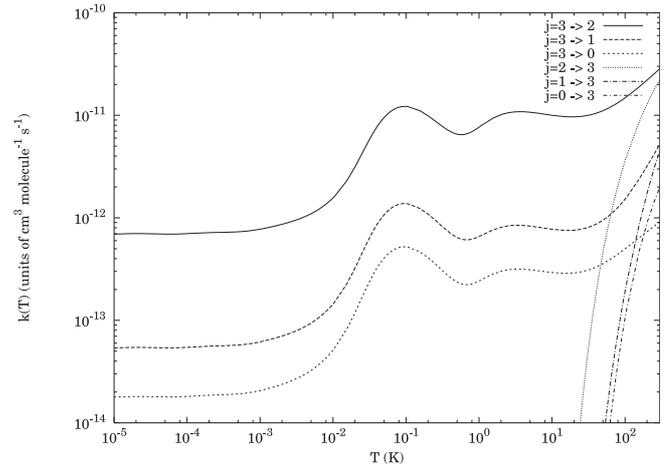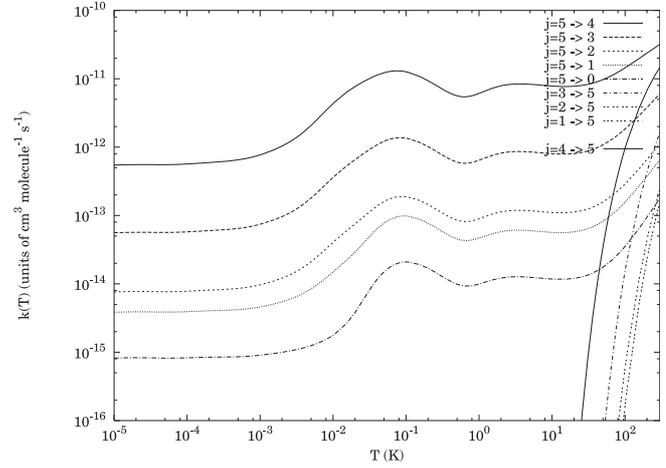
angle. This point was illustrated in Fig. 2 of our previous work (Stoecklin et al. 2003).

Figures 5–8 show the corresponding de-excitation and excitation rate coefficients as a function of temperature for rotational level (respectively $j = 3$, 5, 7 and 9) states of HF. The excitation rate coefficients increase monotonously as a function of temperature. Conversely, the de-excitation rate coefficients exhibit a maximum around 0.1 K. This low temperature maximum is as usual a direct consequence of the resonances shown in Figs. 1−4. Rate coefficients for rotational de-excitation of the HF ($j_i = 9$, 8, 7, 6) and for HF ($j_i = 5$, 4, 3, 2, 1) are respectively given in Tables 1 and 2 for 10 temperatures in the [0.1; 300] temperature interval. The corresponding excitation rate coefficient can be obtained using the detailed balance relationship (6) using the diatomic energies calculated with our potential given in Table 3.

Collision rate coefficients for other transitions and other temperatures are available on request from the corresponding author. If we compare these results with those of He–HCl used

Table 3. Energies of HF rotational levels in the ground vibrational level.

J	0	1	2	3	4	5	6	7	8	9
E/cm^{-1}	0.00	40.64	121.88	243.62	405.74	608.07	850.37	1132.40	1453.85	1814.37
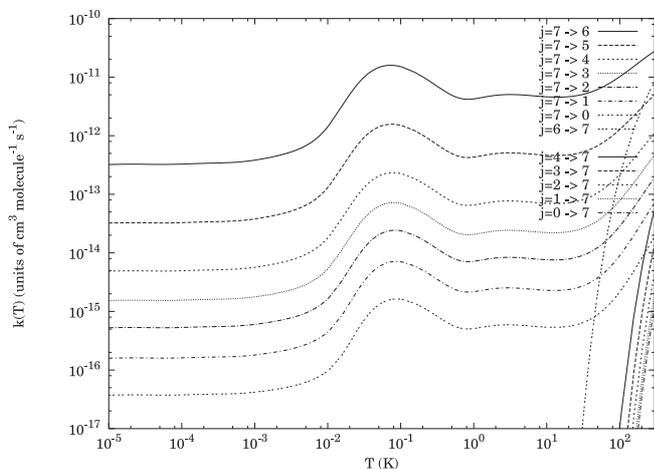
Fig. 7. Rotational deactivation rate coefficient of HF ($v = 0$, $j = 7$) in collision with He as a function of temperature. The inverse rotational transitions rate coefficients are also represented.
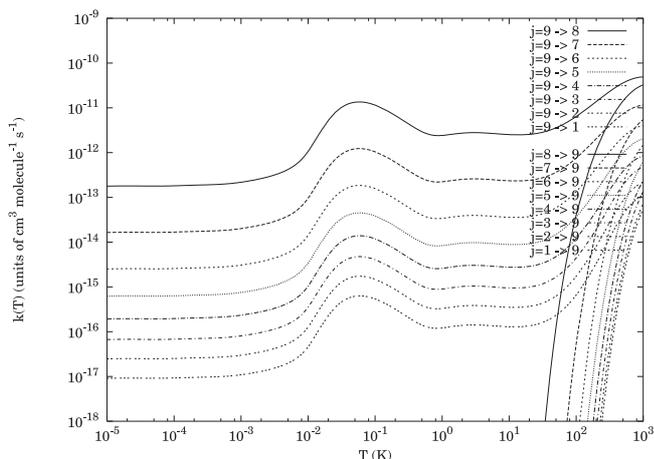
Fig. 8. Rotational deactivation rate coefficient of HF ($v = 0$, $j = 9$) in collision with He as a function of temperature. The inverse rotational transitions rate coefficients are also represented.

by Neufeld et al. (1997) to estimate the abundance of HF and calculated by them in another study (Neufeld et al. 1994) we see that our results are smaller by a factor of 10. This means that collisions with He have very little effect on the rotational population of HF compared to radiative transition in agreement with their hypothesis and this validates the value of the abundance of HF proposed by them.

4. Conclusion

We presented Close Coupling calculations of the rotational transitions induced in collisions between HF molecules and He atoms. Transitions for levels up to $J = 9$ and for temperatures up to 300 K were computed. We used a new global 3D potential energy surface which we proposed recently and that is the best available currently. The rotational deactivation rate coefficients all exhibit a very low temperature maximum around 0.1 K which is a consequence of the resonances supported by the Van der Waals well. We compared our results with those calculated by Neufeld et al. for the He–HCl system to estimate the abundance of HF in Sgr–B2. We find values smaller by a factor of 10. This means that collisions of He have very little effect on the rotational population of HF compared to radiative transitions, in agreement with their hypothesis and this validates the value of the abundance of HF proposed by them.

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