

Rotational excitation of HD molecules by He atoms

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Abstract. We present rate coefficients for rotational transitions induced in collisions between HD and He. Rotational levels and kinetic temperatures $T \leq 1000$ K are considered. The interaction potential surface calculated by Muchnick & Russek (1994) has been used, together with the quantal coupled-channel method for calculating the cross-sections. Very good agreement with previous calculations by Schaefer (1990) is obtained. The present work goes beyond the latter in that collision rates are calculated for all available rotational levels below the first excited vibrational level.

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

1. Introduction

Rate coefficients for rotational transitions in HD molecules induced by collisions with He atoms are of interest in different contexts. Indeed, pure rotational lines in HD have been detected in planetary atmospheres (Lelouch 1998) and in interstellar clouds (Bertoldi et al. 1998, Wright et al. 1998) with the help of the ISO satellite. Such transitions may also intervene in the cooling processes in pre-galactic clouds (Galli & Palla 1998, Stancil et al. 1998). On the theoretical side, Green (1974) was the first to calculate rotational excitation rates within the framework of a quantal close-coupling treatment by using the potential of Shafer & Gordon (1973). These calculations have been reconsidered by Schaefer (1990) on the basis of a new potential surface proposed by Meyer et al. (1980) and where long-range attractive terms were included. The maximum value of the rotational quantum number involved in the rotational de-excitation cross-sections was set to 4 in these calculations. A potential surface for the H₂-He system has since been calculated by Muchnick & Russek (1994) who provide an analytic fit to their *ab initio* results for the complete range of intermolecular distances. Flower et al. (1998) and Balakrishnan et al. (1998a) have used this analytical fit to perform calculations of rates for rovibrational collisional excitation of H₂ molecules by He atoms in a close-coupling quantal treatment. Good agreement between

available measurements of relaxation rate constants and theoretical results has been obtained.

In the present paper, we extend the previous rotational excitation calculations of Schaefer (1990) for the pure rotational excitation of HD molecules induced by He atoms to all levels below the first vibrational level. The techniques used are described in Sect. 2 and results are given in Sect. 3, where comparison with earlier calculations is also made. Sect. 4 includes a discussion of the present data and some concluding remarks.

2. Numerical methods

The quantal coupled-channel method introduced by Arthur & Dalgarno (1960) was used, as implemented in the computer code MOLSCAT developed by Hutson & Green (1995) and where different numerical methods allow for the propagation of the coupled, second-order differential equations. Among the various possibilities, the hybrid modified LOG-DERIVATIVE/AIRY propagator (Alexander & Manolopoulos 1987) and the R-MATRIX propagator (Stechel et al. 1978) have been tried, with mutually consistent results. The potential surface of Muchnick & Russek (1994) is expressed as a function of the distances between the three atoms in the system. So, the potential surfaces of the H₂-He and HD-He systems are identical from the adiabatic point of view where nuclei are fixed. However, for the purpose of the collision calculations, the interaction potential is most conveniently expressed in the form:

$$V(R, \theta) = \sum_{\lambda} v_{\lambda}(R) P_{\lambda}(\cos\theta) \quad (1)$$

where θ is the angle between \mathbf{r} , the vector linking H and D, and \mathbf{R} , the vector directed from the centre-of-mass of the HD molecule towards the He atom. The distance r between H and D is taken to be 1.442 a.u., which corresponds to the mean value for the $v=0$ state. P_{λ} is the Legendre polynomial of order λ . The MOLSCAT program includes a facility to expand the potential in terms of the Legendre polynomials. Now, contrary to the H₂-He case, the Legendre expansion of the HD-He interaction contains odd as well as even contributions of λ since the system is not symmetric with respect to the exchange of nuclei anymore. In the subsequent collision calculations, terms up to $\lambda = 15$ have been retained in the potential expansion. The collision equations

Table 1. Energies of HD rotational levels in the ground vibrational level.

J	E(cm ⁻¹)	E(K)
0	0.00	0.00
1	89.23	128.4
2	267.12	384.3
3	532.32	765.9
4	883.30	1270.7
5	1317.45	1895.4
6	1832.55	2635.8
7	2424.14	3487.5
8	3089.46	4445.3
9	3824.92	5503.5

in the space-fixed reference frame are:

$$\left[\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} + k_j^2 \right] F(jlpJ|R) = 2\mu \sum_{j'l'\lambda} v_\lambda(R) f_\lambda(jl, j'l'; J) F(j'l'pJ|R)$$

with

$$f_\lambda(jl, j'l'; J) = (-1)^{j+j'-J} [(2j+1)(2j'+1)(2l+1)(2l'+1)]^{1/2} \begin{pmatrix} j' & j & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l & \lambda \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} j & l & J \\ l' & j' & \lambda \end{matrix} \right\} \quad (2)$$

where j, l, p, J refer respectively to the rotational quantum number, the relative orbital angular momentum, the parity and the total angular momentum which determine the dimension of the coupling matrix (see for example Flower 1990). The integral cross-sections are obtained by summing the partial cross-sections σ_J until convergence is reached. A step of 1 is taken for energies smaller than 5000 cm⁻¹. Larger step values may be used for the high energy calculations since the partial cross-sections vary smoothly with J and a large number of partial cross-sections are present. The basis expansion is made of 10 rotational levels whose energies are displayed in Table 1 and are taken from Dabrowski & Herzberg (1976) and Abgrall et al. (1982). Level $J = 9$ is above the first vibrational excited level. Cross-sections for rotational transitions were then calculated on a grid of barycentric collision energies extending from the threshold of the first rotational level (89.23 cm⁻¹) up to 200,000 cm⁻¹.

3. Results

We may compare our results with the values given by Schaefer (1990) for the first rotational levels. Fig. 1 shows the comparison between the de-excitation cross-sections of the three first rotational levels as a function of the relative velocity between HD and He. The agreement is excellent despite the fact that the potentials are not strictly identical. It should be noted, however, that both surfaces include the effects of the long-range weakly attractive interactions. A similar level of agreement is obtained for the other cross-sections. At very low energies above the threshold of

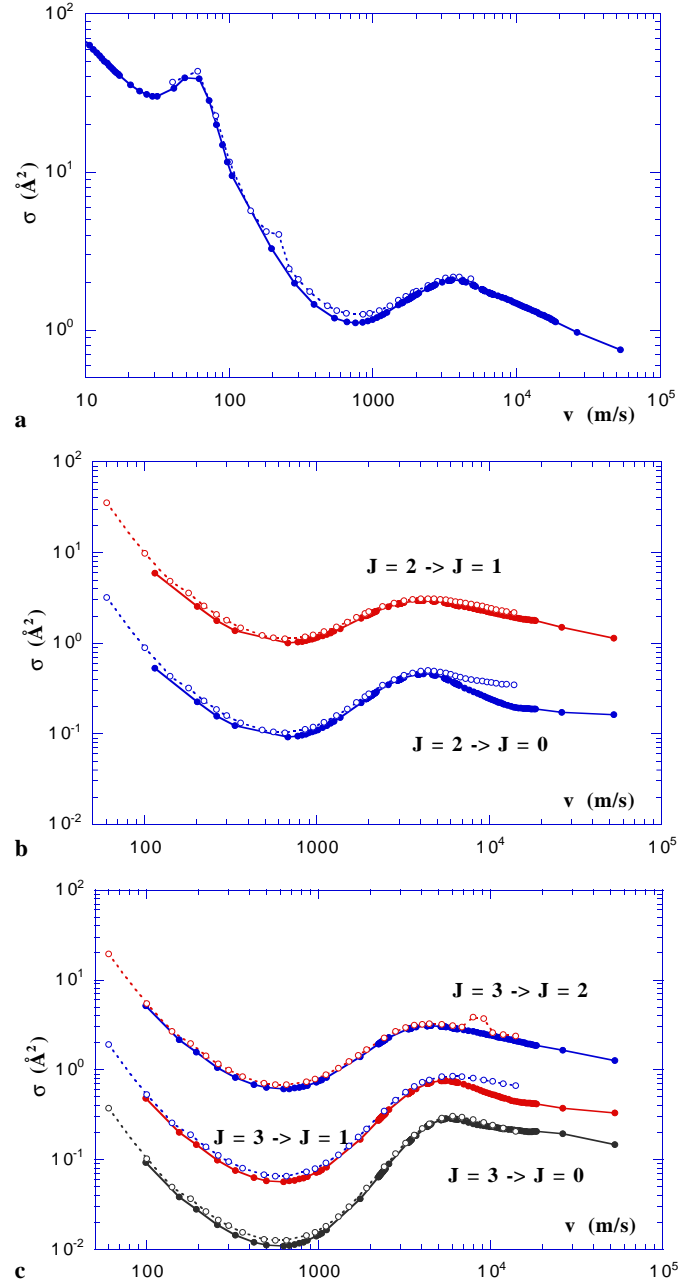


Fig. 1a–c. Comparison between present (filled points) and Schaefer (1990)'s (open points) results for the deexcitation collisional cross-sections as a function of the relative center of mass velocity. **a** deexcitation from the $J=1$ level, **b** deexcitation from the $J=2$ level, **c** deexcitation from the $J=3$ level.

the first rotational level, the deexcitation cross-section increases continuously following a Wigner law as shown on Fig. 1a. Recently, such collisions have received attention (Balakrishnan et al. 1998b). They allow the determination of the imaginary part of the scattering length. We have calculated the collision rates $q(T)$ from the Maxwellian average of the cross-sections:

$$q(T) = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \left(\frac{1}{kT} \right)^2 \int_0^\infty \sigma(E) E dE e^{-E/kT} \quad (3)$$

Table 2. Collision rate coefficients in cubic centimeters per second for a temperature $T = 300$ K. xy denotes $x \times 10^y$.

ji	0.0	1.0	2.0	3.0	4.0
jf					
0.0		3.3e-11	5.5e-12	1.5e-12	3.1e-13
1.0	6.5e-11		4.2e-11	5.8e-12	1.5e-12
2.0	7.6e-12	3.0e-11		3.7e-11	4.7e-12
3.0	8.3e-13	1.6e-12	1.4e-11		2.9e-11
4.0	4.0e-14	1.0e-13	4.4e-13	7.0e-12	
5.0	1.3e-15	3.0e-15	1.4e-14	1.2e-13	3.3e-12
6.0	3.0e-17	6.5e-17	3.0e-16	2.4e-15	3.9e-14
7.0	3.7e-19	8.2e-19	3.5e-18	2.8e-17	3.9e-16
8.0	4.3e-21	9.2e-21	3.9e-20	2.8e-19	3.7e-18
ji	5.0	6.0	7.0	8.0	
jf					
0.0	6.7e-14	1.5e-14	2.8e-15	6.8e-16	
1.0	3.0e-13	6.4e-14	1.2e-14	2.9e-15	
2.0	1.0e-12	2.1e-13	3.6e-14	8.6e-15	
3.0	3.4e-12	6.7e-13	1.1e-13	2.5e-14	
4.0	2.2e-11	2.5e-12	3.7e-13	7.7e-14	
5.0		1.7e-11	1.6e-12	2.6e-13	
6.0	1.7e-12		1.1e-11	1.1e-12	
7.0	1.1e-14	7.7e-13		8.4e-12	
8.0	8.1e-17	3.6e-15	3.9e-13		

Table 3. Collision rate coefficients in cubic centimeters per second for a temperature $T = 500$ K.

ji	0.0	1.0	2.0	3.0	4.0
jf					
0.0		4.6e-11	8.7e-12	3.1e-12	7.8e-13
1.0	1.1e-10		6.2e-11	1.1e-11	3.5e-12
2.0	2.0e-11	6.2e-11		5.8e-11	9.3e-12
3.0	4.7e-12	6.9e-12	3.8e-11		5.0e-11
4.0	5.5e-13	1.1e-12	2.9e-12	2.3e-11	
5.0	5.3e-14	9.5e-14	2.8e-13	1.3e-12	1.4e-11
6.0	3.9e-15	6.6e-15	1.9e-14	8.3e-14	5.7e-13
7.0	2.1e-16	3.6e-16	9.8e-16	4.2e-15	2.5e-14
8.0	9.5e-18	1.6e-17	4.5e-17	1.8e-16	1.1e-15
ji	5.0	6.0	7.0	8.0	
jf					
0.0	2.1e-13	5.8e-14	1.5e-14	4.1e-15	
1.0	8.8e-13	2.3e-13	6.0e-14	1.6e-14	
2.0	2.6e-12	6.6e-13	1.6e-13	4.4e-14	
3.0	7.6e-12	1.9e-12	4.5e-13	1.2e-13	
4.0	4.1e-11	6.1e-12	1.3e-12	3.2e-13	
5.0		3.3e-11	4.5e-12	9.4e-13	
6.0	8.9e-12		2.5e-11	3.5e-12	
7.0	2.5e-13	5.4e-12		2.0e-11	
8.0	8.8e-15	1.2e-13	3.3e-12		

where σ is the cross-section and μ the reduced mass of the system. Rate coefficients for excitation and deexcitation are given in Tables 2, 3 and 4 for three temperatures, $T = 300$, 500 and 1000.

Table 4. Collision rate coefficients in cubic centimeters per second for a temperature $T = 1000$ K.

ji	0.0	1.0	2.0	3.0	4.0
jf					
0.0		6.7e-11	1.4e-11	6.9e-12	2.3e-12
1.0	1.8e-10		9.5e-11	2.1e-11	9.1e-12
2.0	4.7e-11	1.2e-10		9.6e-11	2.0e-11
3.0	2.2e-11	2.5e-11	9.1e-11		9.0e-11
4.0	5.9e-12	8.7e-12	1.5e-11	7.0e-11	
5.0	1.4e-12	2.0e-12	3.8e-12	9.5e-12	5.3e-11
6.0	3.0e-13	4.1e-13	7.7e-13	1.9e-12	6.1e-12
7.0	5.5e-14	7.5e-14	1.3e-13	3.2e-13	9.5e-13
8.0	8.5e-15	1.2e-14	2.1e-14	4.9e-14	1.5e-13
ji	5.0	6.0	7.0	8.0	
jf					
0.0	8.6e-13	3.3e-13	1.2e-13	4.2e-14	
1.0	3.2e-12	1.1e-12	4.3e-13	1.5e-13	
2.0	7.9e-12	2.8e-12	9.9e-13	3.6e-13	
3.0	1.9e-11	6.5e-12	2.3e-12	7.9e-13	
4.0	8.1e-11	1.7e-11	5.2e-12	1.8e-12	
5.0		7.2e-11	1.4e-11	4.3e-12	
6.0	4.0e-11		6.1e-11	1.2e-11	
7.0	3.8e-12	3.0e-11		5.3e-11	
8.0	5.2e-13	2.7e-12	2.3e-11		

Table 5. Critical densities (cm^{-3}) of the HD rotational levels in a mixture H-He. Parentheses indicate powers of 10.

Transition $J \rightarrow J'$	$T = 300$ K	$T = 500$ K	$T = 1000$ K
$1 \rightarrow 0$: 112.07 μm	3.1(3)	8.6(2)	5.1(2)
$2 \rightarrow 1$: 56.23 μm	2.3(4)	6.6(3)	3.9(3)
$3 \rightarrow 2$: 37.70 μm	9.4(4)	2.4(4)	1.4(4)
$4 \rightarrow 3$: 28.50 μm	2.9(5)	6.3(5)	3.4(4)
$5 \rightarrow 4$: 23.03 μm	8.0(5)	1.4(5)	7.2(4)
$6 \rightarrow 5$: 19.43 μm	1.8(6)	2.8(5)	1.3(5)
$7 \rightarrow 6$: 16.89 μm	3.9(6)	5.3(5)	2.3(5)
$8 \rightarrow 7$: 15.25 μm	7.2(5)	9.3(5)	3.8(5)

Collision rate coefficients for other temperatures are available on request from one of us (Evelyne.Roueff@obspm.fr).

4. Discussion and conclusion

Similar calculations have been performed on the HD-H system by Roueff and Flower (1998). The magnitudes of the rate coefficients are similar for the two systems with a tendency for the collisions with H atoms to be more efficient for $\Delta J = 1$. Table 5 displays the critical densities of the rotational levels of HD in a mixture of atomic hydrogen and helium gas ($\text{He}/\text{H} = 0.1$) at different temperatures. The critical density is defined as the ratio between the spontaneous emission Einstein coefficient and the total deexcitation collision rate coefficient where a proper weighting procedure has been applied to take into account the relative abundance of the perturbers.

Helium is sometimes taken as a prototype of the H_2 molecule in its ground state $J = 0$ in view of rotationally inelastic dynamics. The rate coefficients are then evaluated by scaling the values with the square root of the ratio of the reduced masses of the two systems:

$$\left(\frac{\mu_{HD-He}}{\mu_{HD-H_2}}\right)^{1/2} = 1.1934 \quad (4)$$

However, this procedure cannot be recommended since the collision cross-sections depend on the detailed variation of the intermolecular potentials with the different parameters. Unfortunately, there is no other simple way of estimating HD- H_2 collision cross-sections which are of major interest.

In this work, we have extended the previous calculations of Schaefer (1990) for the pure rotational excitation and deexcitation of HD due to collisions with He for all rotational levels inside the ground vibrational level and to higher collision energies. The agreement with previous calculations is excellent.

The data presented here are crucial to interpret the recent and future observations of HD excitation and to help with the determination of the relevant physical conditions. We now plan to calculate the rovibrational excitation of HD which, to our knowledge, has not been studied yet. These collisions are important to interpret future observations of the infrared emissivity of HD in shocked regions (Timmermann 1996, 1998)

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