

A quantum mechanical study of the rotational excitation of HD by H₂

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Abstract. Cross sections and rate coefficients have been computed for rotational transitions within the vibrational ground state of HD, induced in collisions with H₂ molecules. Where possible, our results are compared with previous calculations by Schaefer; the overall level of agreement is found to be good. Rate coefficients are available for kinetic temperatures $T \leq 1000$ K and rotational levels of the HD molecule $J \leq 8$.

1. Introduction

The ISO satellite has enabled emission in pure rotational transitions of HD to be observed, for the first time, in the interstellar medium (Bertoldi *et al* 1999, Wright *et al* 1998). These observations enable the HD/H₂ abundance ratio to be determined, and hence the D/H elemental abundance ratio. The latter is predicted by cosmological models, which are constrained by these observations. Because of its permanent dipole moment, HD is potentially an important coolant of the interstellar gas (Dalgarno and McCray 1972) and of the primordial gas (Galli and Palla 1998). In order to determine the cooling rate, and to interpret the observations of HD, rate coefficients are required for the rotational excitation of HD by the most abundant perturbers, H, He and H₂.

Schaefer (1990) calculated rate coefficients for the excitation of HD by He and H₂, but only for rotational levels $J \leq 4$ and $J \leq 2$, respectively. Until very recently, no data were available for the excitation of HD by H. Results for excitation by He have been extended to higher rotational levels and temperatures by Roueff and Zeippen (1999), and analogous results for excitation by H have been obtained by Roueff and Flower (1999). We now complement these recent studies by performing calculations of the excitation of HD by ortho- and para-H₂.

In our calculations, we have chosen to use a different (*ab initio*) potential from that employed by Schaefer (1990) in his work on H₂–HD scattering. The potential that we have adopted (Schwenke 1988) will additionally enable the vibrational inelasticity of the collision process to be studied. Comparison with the cross sections computed by Schaefer—for pure rotational transitions—is an important preliminary to such larger-scale calculations. Furthermore, by using a much larger rotational basis set on the HD molecule, we place ourselves in a position to check the suggestion made by Schaefer (1990) that the de-excitation rate coefficients for transitions in HD in which $\Delta J = 1$ and the initial value of $J > 2$ are likely to be close to that for $J = 2 \rightarrow 1$.

2. Theory and numerical methods

2.1. Interaction potential

For the purposes of the collision calculations, it is convenient to expand the H₂–HD interaction potential in terms of products of spherical harmonics (Launay 1977, Schwenke 1988),

$$V(R, \hat{R}_1, \hat{R}_2) = \sum_{q_1 q_2 \mu \geq 0} v_{q_1 q_2 \mu}(R) \frac{4\pi}{[2(1 + \delta_{\mu 0})]^{1/2}} [Y_{q_1 \mu}(\hat{R}_1) Y_{q_2 - \mu}(\hat{R}_2) + Y_{q_1 - \mu}(\hat{R}_1) Y_{q_2 \mu}(\hat{R}_2)] \quad (1)$$

where \hat{R}_1 and \hat{R}_2 are the angular coordinates of the H₂ and the HD molecules, relative to a body-fixed coordinate frame in which the vector \mathbf{R} , connecting the centre of mass of the H₂ molecule (1) to that of the HD molecule (2), coincides with the z -axis. The intramolecular distances are kept fixed at their equilibrium values in the ground vibrational state, $v = 0$: $R_1 = 1.449 a_0$ and $R_2 = 1.442 a_0$.

An alternative expansion of the interaction potential, used for example by Schaefer (1990), is

$$V(\mathbf{R}, \hat{r}_1, \hat{r}_2) = \sum_{q_1 q_2 q} A_{q_1 q_2 q}(R) \sum_{m_1 m_2 m} C_{m_1 m_2 m}^{q_1 q_2 q} Y_{q_1 m_1}(\hat{r}_1) Y_{q_2 m_2}(\hat{r}_2) Y_{qm}^*(\hat{R}) \quad (2)$$

where $C_{m_1 m_2 m}^{q_1 q_2 q}$ is a Clebsch–Gordan coefficient, and the intramolecular vectors, \hat{r}_1 and \hat{r}_2 , are now referred to a space-fixed frame, as is the intermolecular vector, \mathbf{R} . The coefficients of the expansions (1) and (2) are related through (Flower *et al* 1979)

$$A_{q_1 q_2 q}(R) = 4\pi \left(\frac{4\pi}{2q+1} \right)^{1/2} \sum_{\mu \geq 0} v_{q_1 q_2 \mu}(R) C_{\mu - \mu 0}^{q_1 q_2 q} \left(\frac{2}{1 + \delta_{\mu 0}} \right)^{1/2} \quad (q_1 + q_2 + q \text{ even}) \quad (3)$$

$$= 0 \quad (q_1 + q_2 + q \text{ odd}).$$

We note that the definitions of the positive sense of the vectors \mathbf{r}_2 and \mathbf{R} (taken here to be H \rightarrow D and H₂ \rightarrow HD, respectively) determine the signs of the coefficients $A_{q_1 q_2 q}$ with q_2 or q odd (q_1 is even because H₂ is homonuclear) through the relations

$$Y_{q_2 m_2}(-\hat{r}_2) = (-1)^{q_2} Y_{q_2 m_2}(\hat{r}_2)$$

$$Y_{qm}(-\hat{R}) = (-1)^q Y_{qm}(\hat{R}).$$

Expansions (1) and (2) above apply equally to the H₂–HD and H₂–H₂ interaction potentials. However, in the former case, the centre of mass of the HD molecule is displaced from the mid-point of the internuclear axis. It follows that terms with q_2 odd contribute to the H₂–HD expansion, whereas such terms vanish in the H₂–H₂ expansion.

For the purposes of the collision calculations reported below, we derived the coefficients $v_{q_1 q_2 \mu}(R)$ of the body-fixed expansion (1) using two independent approaches. First, the potential was evaluated on a grid of values of the intermolecular distance R for the set of 25 independent interaction geometries which derive from the following:

$$\Theta_1 = 0, 90 \quad \Theta_2 = 0, 30, 45, 60, 90, 120, 135, 150, 180 \quad \Phi = \Phi_2 - \Phi_1 = 0, 90.$$

We use the notation $\hat{R}_1 = (\Theta_1, \Phi_1)$ and $\hat{R}_2 = (\Theta_2, \Phi_2)$, and the angles are expressed in degrees. A matrix inversion then yields the 25 coefficients $v_{q_1 q_2 \mu}(R)$ with $q_1 = 0, 2$, $q_2 \leq 6$, $0 \leq \mu \leq \min(q_1, q_2) \leq 2$. Alternatively, using the orthogonality of the (real) angular functions

$$\Psi_{q_1 q_2 \mu}(\hat{R}_1, \hat{R}_2) = \frac{4\pi}{[2(1 + \delta_{\mu 0})]^{1/2}} [Y_{q_1 \mu}(\hat{R}_1) Y_{q_2 - \mu}(\hat{R}_2) + Y_{q_1 - \mu}(\hat{R}_1) Y_{q_2 \mu}(\hat{R}_2)]$$

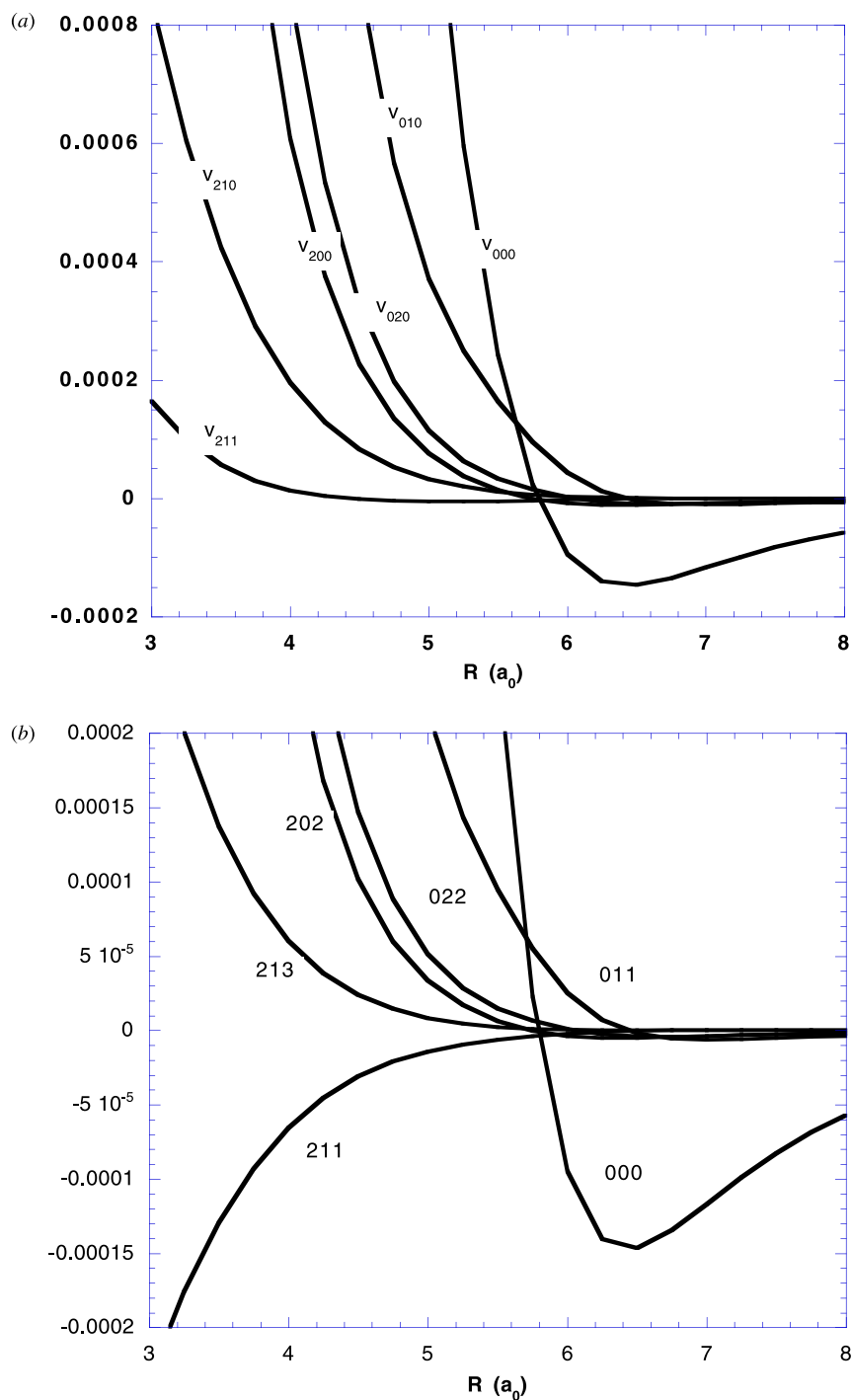


Figure 1. (a) The six lowest-order coefficients, $v_{q_1q_2\mu}(R)$, (expressed in Hartree) of the body-fixed expansion, equation (1), of the H₂–HD interaction potential. (b) The corresponding coefficients, $A_{q_1q_2q}(R)/(4\pi)^{3/2}$, of the space-fixed expansion, equation (2). Each curve is labelled by the values of q_1q_2q .

in the expansion (1) above, namely,

$$\int \Psi_{q'_1 q'_2 \mu'}(\hat{R}_1, \hat{R}_2) \Psi_{q_1 q_2 \mu}(\hat{R}_1, \hat{R}_2) d\hat{R}_1 d\hat{R}_2 = (4\pi)^2 \delta_{q'_1 q_1} \delta_{q'_2 q_2} \delta_{\mu' \mu} \quad (4)$$

the coefficients $v_{q_1 q_2 \mu}(R)$ may be determined by projection, the angular integrals being evaluated numerically.

In the calculations reported below, the interaction potential calculated by Schwenke (1988) has been employed. Schaefer (1990) used a potential which derived from work by Schaefer and Meyer (1979) and Monchick and Schaefer (1980) and which was ultimately published by Schaefer and Köhler (1989). Differential scattering cross sections had been calculated with the aid of this potential and compared with measurements for D₂-H₂ (Buck *et al* 1983a) and D₂-HD (Buck *et al* 1981, 1983b). However, the potential published by Schaefer and Köhler (1989) cannot be used to study vibrationally inelastic scattering, whereas the potential of Schwenke (1988) incorporates the additional information—the dependence of the interaction energy on the magnitudes of the intramolecular distances—which enables such calculations to be performed. It is instructive to compare the cross sections for pure rotational transitions, obtained with these two independent potential energy surfaces, before embarking on larger-scale collision calculations. This comparison will be made in section 3 below.

In figure 1(a) we plot the first few coefficients of the expansion (1), derived using the projection procedure outlined above. (We have omitted the results obtained following the matrix inversion procedure, which are discernibly different from those generated by the projection procedure only for the highest-order term, $v_{211}(R)$). The dominant contributor is $v_{000}(R)$, the isotropic (angle-independent) term. Higher-order terms contribute directly to rotationally inelastic scattering. In particular, $v_{010}(R)$ is primarily responsible for the magnitudes of transitions in which $\Delta J = 1$ in HD. Using the transformation (3), the corresponding space-fixed coefficients $A_{q_1 q_2 q}(R)/(4\pi)^{3/2}$ can be derived; these are plotted in figure 1(b). Comparison may then be made with the coefficients of Schaefer (1990), plotted in his figure 3. (Schaefer defined HD as molecule 1 and H₂ as molecule 2, and so the indices q_1 and q_2 are inverted in figure 1(b) compared with his figure 3. Furthermore, coefficients with q odd have opposite sign, for the reason given above.) Generally good quantitative agreement is found. The isotropic coefficient $A_{000}(R)/(4\pi)^{3/2}$ which derives from Schwenke's potential displays a deeper potential well; but we have already noted that the cross sections for inelastic scattering are determined directly by coefficients of higher order.

2.2. Cross sections

In the present work, we are concerned with the integral cross sections for rotational transitions in HD, induced in collisions with H₂ molecules. In all our calculations, the quantal coupled channels method (cf Flower 1990) has been employed, in the implementation of Launay (1977). The basis sets will be specified at appropriate points in the following presentation of the results.

3. Results

3.1. Cross sections

In figure 2, we compare the present values of the de-excitation cross sections (J_1, J_2) = (0, 1) → (0, 0), (0, 2) → (0, 1) and (0, 2) → (0, 0) with the corresponding calculations of Schaefer (1990, table 4); J_1 and J_2 denote the rotational quantum numbers of the H₂ and HD molecules, respectively. The excitation energies of the $J_2 = 1$ and 2 levels, relative to $J_2 = 0$, are 128.4 and 384.2 K (Dabrowski and Herzberg 1976). We note that a centre-of-mass velocity

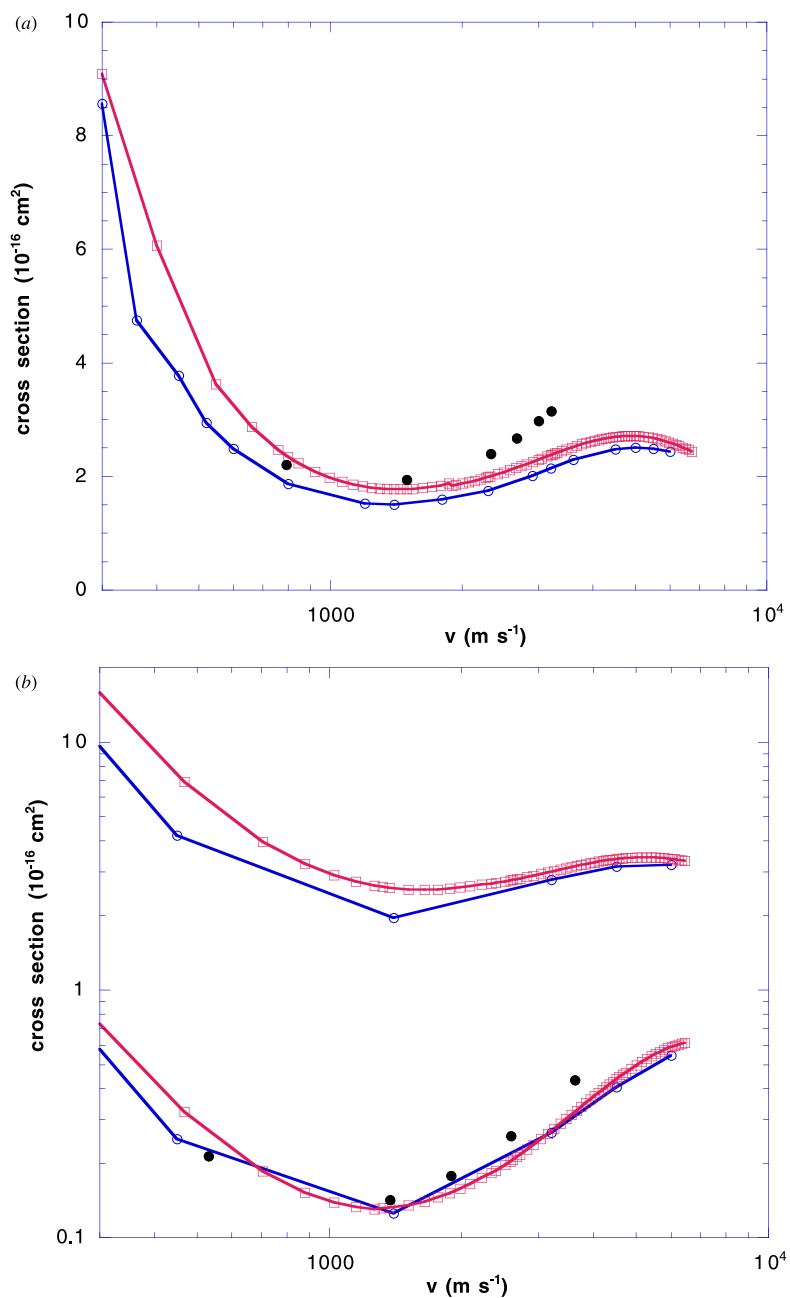


Figure 2. Cross sections for rotationally inelastic transitions in HD, induced by para- H_2 : (a) $J_2 = 1 \rightarrow 0$ (upper panel); (b) $J_2 = 2 \rightarrow 1$ (upper set of curves in the lower panel) and $J_2 = 2 \rightarrow 0$ (lower set of curves). The present cross sections are shown as open squares, the values calculated by Schaefer (1990) by open circles, and the results of Chu (1975) by full circles. The abscissa is the centre-of-mass collision velocity, relative to the initial (upper) level of the transition.

(This figure can be viewed in colour in the electronic version of the article; see <http://www.iop.org>)

of 300 m s^{-1} (the lower limit of the abscissa in figure 2) is equivalent to 6.5 K, whereas the upper limit of 6000 m s^{-1} to Schaefer's results corresponds to approximately 2600 K (these centre-of-mass energies are relative to the initial (upper) state of the transition). The basis set used in our calculations was $J_1 = 0, 2, 0 \leq J_2 \leq 8$; the latter includes all the rotational levels of the vibrational ground state of HD which lie below the first vibrationally excited state. Schaefer (1990) used a smaller basis, in which $J_2 \leq 4$; the excitation energy of the $J_2 = 5$ level is 1895 K.

Figure 3 displays the corresponding results for excitation by H_2 ($J_1 = 1$). The first excited state of ortho- H_2 , $J_1 = 3$, lies 845 K above the $J_1 = 1$ state, and its exclusion from the basis set will have only minor consequences for transitions $\Delta J_2 = 1$ in HD, as Schaefer (1990) has shown. In figures 2 and 3, we have plotted only those data points actually calculated by Schaefer, and not the additional points that he obtained by means of an interpolation procedure. We have also included in figures 2 and 3 the results of early calculations by Chu (1975). The latter tabulated excitation cross sections, for the transitions $(J_1, J_2) = (0, 0) \rightarrow (0, 1)$, $(0, 0) \rightarrow (0, 2)$, $(1, 0) \rightarrow (1, 1)$, $(1, 0) \rightarrow (1, 2)$, from which we have derived de-excitation cross sections from detailed balance.

We remark first on the strong similarity of the results for transitions induced by ortho- and by para- H_2 : the cross sections for rotational transitions in HD are evidently insensitive to the rotational state of the H_2 molecule. The overall level of agreement between the present results and those of Schaefer (1990) (and even of Chu 1975) is, we believe, good. The remaining discrepancies probably arise from differences in the potentials employed, rather than to differences in the basis sets. We do not claim that the results of the present calculations are more accurate than those of Schaefer (1990) (although they are almost certainly more accurate than the much earlier calculations by Chu 1975). Indeed, Schaefer and his collaborators have gone to considerable lengths to refine the potential that he used through its comparison with experimental data. As stated in the introduction, our objective is to establish, through these comparisons of integral cross sections for rotational transitions, the viability of the potential of Schwenke (1988), which has the considerable merit of being extendible to the study of vibrationally inelastic scattering.

3.2. Rate coefficients

The rate coefficients, $q(T)$, for collisional de-excitation were obtained from the relation

$$q(T) = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \int_0^\infty Q(y) y e^{-y} dy \quad (5)$$

in which $Q(y)$ is the de-excitation cross section and $y = E/kT$; μ is the reduced mass of the H_2 -HD system and E is the barycentric collision energy, relative to the initial (upper) level. The integral was evaluated numerically, using a trapezoidal rule on a fine grid of the integration variable, y ; $Q(y)$ was generated at the grid points by cubic spline interpolation of its computed values. Rate coefficients for excitation were generated by means of the detailed balance relation

$$(2J_1 + 1)(2J_2 + 1)q_{J_1 J_2 \rightarrow J'_1 J'_2}(T) = (2J'_1 + 1)(2J'_2 + 1)q_{J'_1 J'_2 \rightarrow J_1 J_2}(T) \times \exp[-(E_{J'_1 J'_2} - E_{J_1 J_2})/kT]. \quad (6)$$

In table 1, we compare our de-excitation (i.e. the sum of the internal energies of the molecules, relative to their respective ground states, is initially greater than it is finally) rate coefficients with the corresponding results of Schaefer (1990), for three representative temperatures. Overall, the level of agreement is more than satisfactory and improves as T

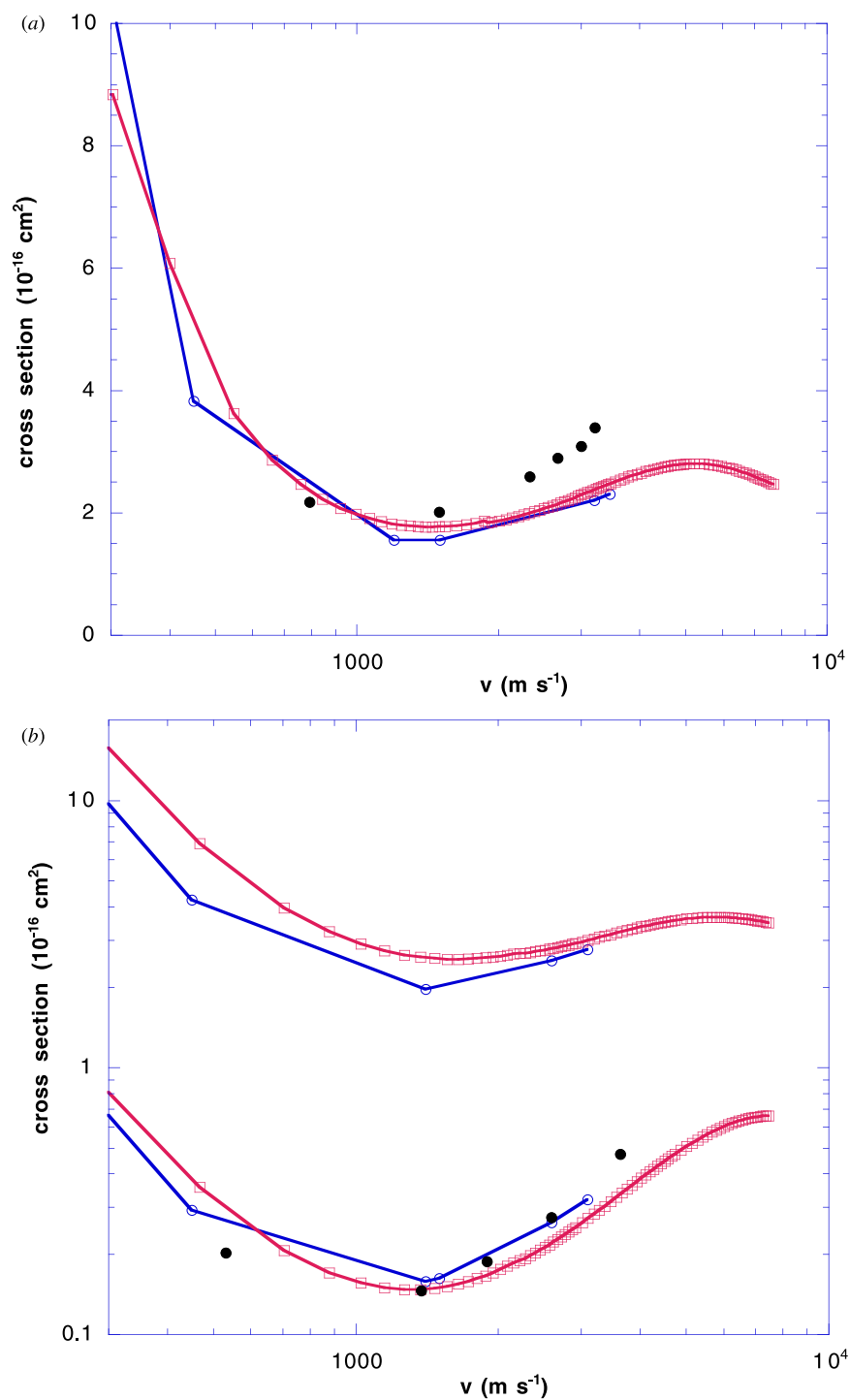


Figure 3. As figure 2, but for collisions with ortho- H_2 .

(This figure can be viewed in colour in the electronic version of the article; see <http://www.iop.org>)

Table 1. Rate coefficients (in units of $\text{cm}^3 \text{s}^{-1}$) for de-excitation transitions $(J_1, J_2) \rightarrow (J'_1, J'_2)$, occurring in H_2 –HD collisions. For each of the three values of the kinetic temperature, T , the present result is followed by that of Schaefer (1990). Numbers in parentheses are powers of 10.

	T					
	50 K		100 K		200 K	
0, 1–0, 0	2.2(–11)	1.8(–11)	2.7(–11)	2.3(–11)	3.9(–11)	3.4(–11)
0, 2–0, 0	1.6(–12)	1.3(–12)	2.1(–12)	1.9(–12)	3.6(–12)	3.4(–12)
0, 2–0, 1	3.3(–11)	2.2(–11)	3.9(–11)	2.9(–11)	5.3(–11)	4.4(–11)
2, 0–0, 0	3.9(–13)	3.4(–13)	4.7(–13)	4.8(–13)	6.8(–13)	7.7(–13)
2, 0–0, 1	1.8(–13)	1.0(–13)	3.1(–13)	2.1(–13)	6.9(–13)	5.2(–13)
2, 0–0, 2	9.3(–13)	1.1(–14)	9.9(–13)	3.2(–14)	1.1(–12)	1.4(–13)
2, 1–0, 0	8.4(–14)	7.1(–14)	1.2(–13)	1.1(–13)	2.3(–13)	2.4(–13)
2, 1–0, 1	4.0(–13)	4.2(–13)	5.3(–13)	6.1(–13)	8.0(–13)	1.0(–12)
2, 1–0, 2	7.9(–14)	1.4(–13)	1.6(–13)	2.9(–13)	4.3(–13)	7.3(–13)
2, 1–2, 0	2.0(–11)	1.8(–11)	2.6(–11)	2.3(–11)	3.8(–11)	3.5(–11)
1, 1–1, 0	2.2(–11)	1.8(–11)	2.7(–11)	2.3(–11)	3.9(–11)	3.5(–11)
1, 2–1, 0	1.8(–12)	1.6(–12)	2.3(–12)	2.4(–12)	3.9(–12)	4.4(–12)
1, 2–1, 1	3.3(–11)	2.2(–11)	3.9(–11)	2.9(–11)	5.3(–11)	4.4(–11)

Table 2. Rate coefficients (in units of $\text{cm}^3 \text{s}^{-1}$) for de-excitation transitions $J_2 \rightarrow J'_2$ in HD, induced in collisions with ground state ortho- H_2 ($J_1 = 1$) and para- H_2 ($J_1 = 0$). The result for ortho- H_2 is followed by that for para- H_2 at each value of the kinetic temperature, T . Numbers in parentheses are powers of 10.

	T					
	50 K		100 K		200 K	
1–0	2.2(–11)	2.2(–11)	2.7(–11)	2.7(–11)	3.9(–11)	3.9(–11)
2–1	3.3(–11)	3.3(–11)	3.9(–11)	3.9(–11)	5.3(–11)	5.3(–11)
3–2	2.8(–11)	2.8(–11)	3.4(–11)	3.4(–11)	5.0(–11)	4.9(–11)
4–3	1.8(–11)	1.8(–11)	2.4(–11)	2.4(–11)	3.8(–11)	3.7(–11)
5–4	1.3(–11)	1.3(–11)	1.6(–11)	1.5(–11)	2.6(–11)	2.5(–11)
6–5	4.8(–12)	4.7(–12)	7.8(–12)	7.6(–12)	1.6(–11)	1.5(–11)
7–6	2.7(–12)	2.6(–12)	4.1(–12)	4.0(–12)	9.5(–12)	9.2(–12)
8–7	1.5(–12)	1.4(–12)	2.1(–12)	2.0(–12)	5.6(–12)	5.5(–12)

increases, reflecting the behaviour of the cross sections with energy, considered in section 3.1. An exception is the transition $(J_1, J_2) = (2, 0) \rightarrow (0, 2)$, which involves simultaneous de-excitation of the H_2 molecule and excitation of the HD molecule; the net effect is exoergic. For this transition, the rate coefficients that we have calculated are much larger than those tabulated by Schaefer (1990), particularly at low temperatures. This is the extreme case of those transitions for which comparison can be made ($0 \leq J_1, J_2 \leq 2$), as it involves the maximal simultaneous change ($|\Delta J| = 2$) of *both* the rotational quantum numbers. Consequently, its cross section (and rate coefficient) might be expected to be small. On the other hand, as de-excitation of the H_2 molecule is accompanied by excitation of the HD molecule, the energy defect is only 126 K; this tends to act in the opposite sense, that of enhancing the cross section. It is unclear to us which, if either, of the results (Schaefer's or ours) for this transition is accurate. Fortunately, this issue is unimportant from the viewpoint of the application of the results in astrophysical contexts, where the large rate coefficients for the $\Delta J_1 = 0$, $\Delta J_2 = 1$ transitions dominate collisional population transfer in the HD molecule.

Table 3. Rate coefficients (in units of cm³ s⁻¹) for ortho-H₂-HD collisions. The columns are labelled by the initial, the rows by the final state of the transition.

<i>T</i> = 50 K									
	(1, 0)	(1, 1)	(1, 2)	(1, 3)	(1, 4)	(1, 5)	(1, 6)	(1, 7)	(1, 8)
(1, 0)	1.3D-09	2.2D-11	1.8D-12	1.9D-13	1.8D-14	2.3D-15	1.6D-16	2.1D-17	2.6D-18
(1, 1)	5.0D-12	1.5D-09	3.3D-11	2.0D-12	1.7D-13	1.9D-14	1.3D-15	1.5D-16	1.8D-17
(1, 2)	4.1D-15	3.3D-13	1.5D-09	2.8D-11	1.3D-12	1.2D-13	7.7D-15	8.7D-16	9.8D-17
(1, 3)	3.0D-19	1.3D-17	1.9D-14	1.6D-09	1.8D-11	9.5D-13	4.6D-14	4.7D-15	5.0D-16
(1, 4)	1.5D-24	6.0D-23	4.7D-20	9.7D-16	1.6D-09	1.3D-11	3.3D-13	2.8D-14	2.6D-15
(1, 5)	8.6D-31	3.1D-29	2.0D-26	2.3D-22	6.2D-17	1.5D-09	4.8D-12	1.9D-13	1.6D-14
(1, 6)	2.7D-38	9.2D-37	5.5D-34	4.9D-30	6.7D-25	2.1D-18	1.4D-09	2.7D-12	1.1D-13
(1, 7)	1.6D-46	5.1D-45	2.9D-42	2.3D-38	2.6D-33	3.8D-27	1.2D-19	1.6D-09	1.5D-12
(1, 8)	1.1D-55	3.3D-54	1.8D-51	1.3D-47	1.3D-42	1.7D-36	2.7D-29	8.0D-21	2.6D-09
<i>T</i> = 100 K									
	(1, 0)	(1, 1)	(1, 2)	(1, 3)	(1, 4)	(1, 5)	(1, 6)	(1, 7)	(1, 8)
(1, 0)	1.7D-09	2.7D-11	2.3D-12	2.8D-13	2.8D-14	3.2D-15	3.1D-16	3.4D-17	3.5D-18
(1, 1)	2.2D-11	1.5D-09	3.9D-11	2.7D-12	2.6D-13	2.6D-14	2.4D-15	2.5D-16	2.5D-17
(1, 2)	2.5D-13	5.0D-12	1.5D-09	3.4D-11	1.9D-12	1.6D-13	1.4D-14	1.4D-15	1.3D-16
(1, 3)	9.2D-16	1.1D-14	1.1D-12	1.5D-09	2.4D-11	1.2D-12	8.3D-14	7.5D-15	6.9D-16
(1, 4)	7.8D-19	8.4D-18	4.8D-16	2.0D-13	1.6D-09	1.6D-11	5.9D-13	4.5D-14	3.6D-15
(1, 5)	2.1D-22	2.0D-21	9.9D-20	2.3D-17	3.7D-14	1.5D-09	7.8D-12	3.0D-13	2.2D-14
(1, 6)	1.5D-26	1.3D-25	6.1D-24	1.2D-21	1.0D-18	5.6D-15	1.5D-09	4.1D-12	1.5D-13
(1, 7)	3.6D-31	3.2D-30	1.4D-28	2.4D-26	1.8D-23	5.0D-20	9.4D-16	1.5D-09	2.1D-12
(1, 8)	2.9D-36	2.5D-35	1.1D-33	1.7D-31	1.1D-28	2.8D-25	2.8D-21	1.6D-16	2.0D-09
<i>T</i> = 200 K									
	(1, 0)	(1, 1)	(1, 2)	(1, 3)	(1, 4)	(1, 5)	(1, 6)	(1, 7)	(1, 8)
(1, 0)	1.7D-09	3.9D-11	3.9D-12	5.6D-13	7.0D-14	8.8D-15	1.0D-15	1.2D-16	1.3D-17
(1, 1)	6.1D-11	1.6D-09	5.3D-11	4.7D-12	5.7D-13	6.6D-14	7.6D-15	8.8D-16	9.3D-17
(1, 2)	2.9D-12	2.5D-11	1.6D-09	5.0D-11	3.6D-12	3.9D-13	4.3D-14	4.8D-15	5.0D-16
(1, 3)	8.5D-14	4.5D-13	1.0D-11	1.6D-09	3.8D-11	2.5D-12	2.3D-13	2.5D-14	2.5D-15
(1, 4)	1.1D-15	5.7D-15	7.8D-14	3.9D-12	1.6D-09	2.6D-11	1.5D-12	1.3D-13	1.3D-14
(1, 5)	7.4D-18	3.5D-17	4.5D-16	1.4D-14	1.4D-12	1.6D-09	1.6D-11	8.6D-13	7.1D-14
(1, 6)	2.6D-20	1.2D-19	1.4D-18	3.8D-17	2.3D-15	4.6D-13	1.6D-09	9.5D-12	4.9D-13
(1, 7)	5.0D-23	2.2D-22	2.6D-21	6.5D-20	3.4D-18	4.1D-16	1.5D-13	1.6D-09	5.6D-12
(1, 8)	5.0D-26	2.2D-25	2.6D-24	6.2D-23	3.1D-21	3.2D-19	7.5D-17	5.3D-14	1.8D-09
<i>T</i> = 500 K									
	(1, 0)	(1, 1)	(1, 2)	(1, 3)	(1, 4)	(1, 5)	(1, 6)	(1, 7)	(1, 8)
(1, 0)	1.8D-09	7.1D-11	9.8D-12	2.0D-12	3.8D-13	7.1D-14	1.3D-14	2.2D-15	3.4D-16
(1, 1)	1.6D-10	1.7D-09	9.3D-11	1.3D-11	2.4D-12	4.4D-13	7.8D-14	1.3D-14	2.1D-15
(1, 2)	2.3D-11	9.3D-11	1.8D-09	9.3D-11	1.2D-11	2.1D-12	3.6D-13	6.1D-14	9.7D-15
(1, 3)	3.1D-12	8.3D-12	6.1D-11	1.8D-09	8.2D-11	9.5D-12	1.6D-12	2.6D-13	4.1D-14
(1, 4)	2.7D-13	7.5D-13	3.5D-12	3.8D-11	1.8D-09	6.6D-11	7.3D-12	1.1D-12	1.7D-13
(1, 5)	1.8D-14	4.7D-14	2.2D-13	1.6D-12	2.3D-11	1.8D-09	5.0D-11	5.4D-12	7.5D-13
(1, 6)	8.5D-16	2.2D-15	1.0D-14	6.8D-14	6.9D-13	1.4D-11	1.9D-09	3.8D-11	3.9D-12
(1, 7)	3.0D-17	8.1D-17	3.7D-16	2.4D-15	2.2D-14	3.0D-13	7.9D-12	1.9D-09	2.8D-11
(1, 8)	8.0D-19	2.1D-18	9.8D-18	6.4D-17	5.7D-16	7.1D-15	1.4D-13	4.6D-12	1.9D-09

We have already remarked on the insensitivity of the cross sections for rotational transitions in HD to the rotational state of the H₂ molecule. This insensitivity is clearly apparent in table 2, where we list the rate coefficients for such transitions up to $J_2 = 8$, for ground state ortho-H₂ ($J_1 = 1$) and para-H₂ ($J_1 = 0$). It may be seen that the results for ortho- and para-H₂ are almost the same. As J_2 increases beyond $J_2 = 2$, the rate coefficients decrease in magnitude;

Table 4. As table 3, but for para-H₂-HD.

$T = 50 \text{ K}$														
(0, 0)	(0, 1)	(0, 2)	(2, 0)	(2, 1)	(0, 3)	(2, 2)	(0, 4)	(2, 3)	(2, 4)	(0, 5)	(2, 5)	(0, 6)	(2, 6)	
(0, 0)	1.4D-09	2.2D-11	1.6D-12	3.9D-13	8.4D-14	1.6D-13	5.8D-15	1.5D-14	2.0D-15	3.5D-16	1.9D-15	3.6D-17	1.3D-16	7.0D-18
(0, 1)	5.0D-12	1.5D-09	3.3D-11	1.8D-13	4.0D-13	2.0D-12	1.2D-13	1.5D-13	1.2D-14	2.3D-15	1.7D-14	2.4D-16	1.1D-15	4.6D-17
(0, 2)	3.7D-15	3.3D-13	1.5D-09	9.3D-13	7.9D-14	2.8D-11	4.0D-13	1.3D-12	1.2D-13	1.3D-14	1.2D-13	1.2D-15	7.2D-15	2.3D-16
(2, 0)	7.2D-17	1.5D-16	7.5D-14	1.6D-09	2.0D-11	1.4D-13	1.8D-12	1.8D-14	1.9D-13	1.8D-14	2.8D-15	1.2D-15	2.2D-16	1.6D-16
(2, 1)	3.6D-18	7.4D-17	1.5D-15	4.6D-12	1.4D-09	1.7D-12	3.3D-11	1.7D-13	2.0D-12	1.7D-13	2.0D-14	1.0D-14	1.4D-15	1.3D-15
(0, 3)	2.5D-19	1.4D-17	1.9D-14	1.1D-15	6.3D-14	1.6D-09	8.3D-14	1.8D-11	3.9D-13	9.8D-14	9.6D-13	7.2D-15	4.6D-14	1.2D-15
(2, 2)	2.5D-21	2.3D-19	7.4D-17	4.1D-15	3.3D-13	2.3D-14	1.6D-09	6.8D-13	2.8D-11	1.4D-12	9.8D-14	6.7D-14	6.3D-15	8.0D-15
(0, 4)	1.2D-24	5.5D-23	4.8D-20	8.1D-21	3.2D-19	9.5D-16	1.3D-16	1.6D-09	5.6D-14	4.3D-13	1.3D-11	4.8D-14	3.3D-13	6.7D-15
(2, 3)	5.8D-25	1.5D-23	1.5D-20	2.9D-19	1.3D-17	7.3D-17	1.9D-14	2.0D-13	1.6D-09	1.9D-11	2.8D-13	5.1D-13	2.4D-14	4.8D-14
(2, 4)	5.4D-30	1.5D-28	8.8D-26	1.5D-24	6.2D-23	9.7D-22	4.9D-20	8.1D-17	1.0D-15	1.6D-09	1.1D-12	7.0D-12	7.4D-14	3.5D-13
(0, 5)	7.0D-31	2.8D-29	2.0D-26	5.8D-27	1.8D-25	2.3D-22	8.7D-23	6.1D-17	3.6D-19	2.7D-14	1.5D-09	3.1D-13	4.7D-12	4.4D-14
(2, 5)	2.6D-36	7.4D-35	3.7D-32	4.5D-31	1.7D-29	3.3D-28	1.1D-26	4.1D-23	1.2D-22	3.2D-17	5.7D-17	9.1D-10	5.5D-13	5.1D-12
(0, 6)	2.2D-38	8.1D-37	5.2D-34	2.0D-34	5.6D-33	4.9D-30	2.5D-30	6.6D-25	1.4D-26	8.0D-22	2.0D-18	1.3D-15	1.4D-09	4.7D-13
(2, 6)	2.2D-43	6.1D-42	3.1D-39	2.7D-38	9.4D-37	2.3D-35	5.8D-34	2.5D-30	5.1D-30	7.0D-25	3.6D-24	2.2D-18	8.8D-17	1.5D-09
$T = 100 \text{ K}$														
(0, 0)	(0, 1)	(0, 2)	(2, 0)	(2, 1)	(0, 3)	(2, 2)	(0, 4)	(2, 3)	(2, 4)	(0, 5)	(2, 5)	(0, 6)	(2, 6)	
(0, 0)	1.7D-09	2.7D-11	2.1D-12	4.7D-13	1.2D-13	2.3D-13	8.7D-15	2.4D-14	3.2D-15	5.7D-16	2.6D-15	8.4D-17	2.5D-16	1.3D-17
(0, 1)	2.2D-11	1.5D-09	3.9D-11	3.1D-13	5.3D-13	2.7D-12	1.7D-13	2.4D-13	1.8D-14	3.6D-15	2.3D-14	5.5D-16	2.1D-15	8.3D-17
(0, 2)	2.3D-13	5.0D-12	1.5D-09	9.9D-13	1.6D-13	3.4D-11	5.1D-13	1.9D-12	1.6D-13	1.9D-14	1.6D-13	2.7D-15	1.3D-14	4.1D-16
(2, 0)	1.4D-14	1.1D-14	2.8D-13	1.5D-09	2.6D-11	1.7D-13	2.3D-12	2.7D-14	2.7D-13	2.8D-14	3.7D-15	2.7D-15	4.0D-16	3.0D-16
(2, 1)	3.1D-15	1.6D-14	3.7D-14	2.2D-11	1.5D-09	1.9D-12	3.9D-11	2.3D-13	2.7D-12	2.6D-13	2.5D-14	2.2D-14	2.6D-15	2.3D-15
(0, 3)	7.7D-16	1.1D-14	1.1D-12	1.8D-14	2.5D-13	1.6D-09	1.1D-13	2.4D-11	5.1D-13	1.4D-13	1.2D-12	1.5D-14	8.3D-14	2.0D-15
(2, 2)	2.8D-17	6.6D-16	1.6D-14	2.5D-13	5.0D-12	1.1D-13	1.5D-09	9.1D-13	3.4D-11	1.9D-12	1.2D-13	1.4D-13	1.1D-14	1.4D-14
(0, 4)	6.5D-19	7.8D-18	4.9D-16	2.4D-17	2.5D-16	1.9D-13	7.6D-15	1.6D-09	7.8D-14	5.6D-13	1.5D-11	9.7D-14	5.8D-13	1.1D-14
(2, 3)	3.2D-19	2.2D-18	1.5D-16	9.0D-16	1.1D-14	1.6D-14	1.1D-12	2.9D-13	1.6D-09	2.4D-11	3.3D-13	1.0D-12	4.2D-14	8.3D-14
(2, 4)	4.7D-22	3.6D-21	1.5D-19	7.6D-19	8.4D-18	3.5D-17	4.9D-16	1.7D-14	2.0D-13	1.6D-09	1.1D-12	1.3D-11	1.2D-13	5.9D-13
(0, 5)	1.7D-22	1.8D-21	9.7D-20	7.9D-20	6.5D-20	2.4D-17	2.4D-18	3.6D-14	2.1D-16	8.5D-14	1.5D-09	5.5D-13	7.6D-12	7.3D-14
(2, 5)	1.7D-25	1.3D-24	4.9D-23	1.7D-22	1.7D-21	9.0D-21	8.6D-20	7.0D-18	2.0D-17	3.1D-14	1.7D-14	1.3D-09	7.4D-13	7.8D-12
(0, 6)	1.2D-26	1.2D-25	5.8D-24	6.1D-25	4.8D-24	1.2D-21	1.6D-22	9.9D-19	2.0D-20	6.6D-18	5.4D-15	1.7D-14	1.5D-09	6.5D-13
(2, 6)	1.8D-29	1.4D-28	5.5D-27	1.4D-26	1.3D-25	8.8D-25	6.1D-24	5.8D-22	1.2D-21	1.0D-18	1.6D-18	5.6D-15	2.0D-14	1.6D-09

Table 4. Continued.

$T = 200\text{ K}$														
(0, 0)	(0, 1)	(0, 2)	(2, 0)	(2, 1)	(0, 3)	(2, 2)	(0, 4)	(2, 3)	(2, 4)	(0, 5)	(2, 5)	(0, 6)	(2, 6)	
(0, 0)	1.7D-09	3.9D-11	3.6D-12	6.8D-13	2.3D-13	4.7D-13	2.0D-14	5.9D-14	7.7D-15	1.6D-15	7.1D-15	2.9D-16	8.3D-16	4.7D-17
(0, 1)	6.1D-11	1.6D-09	5.3D-11	6.9D-13	8.0D-13	4.6D-12	3.1D-13	5.2D-13	3.9D-14	9.5D-15	5.9D-15	1.8D-15	6.7D-15	2.9D-16
(0, 2)	2.6D-12	2.4D-11	1.6D-09	1.1D-12	4.3D-13	4.9D-11	8.0D-13	3.7D-12	3.1D-13	4.3D-14	3.8D-13	7.9D-15	4.0D-14	1.4D-15
(2, 0)	2.7D-13	1.7D-13	6.0D-13	1.6D-09	3.8D-11	2.6D-13	3.8D-12	5.1D-14	5.5D-13	6.8D-14	8.4D-15	8.3D-15	1.1D-15	1.0D-15
(2, 1)	1.4D-13	3.1D-13	3.6D-13	6.0D-11	1.6D-09	2.4D-12	5.3D-11	4.0D-13	4.6D-12	5.7D-13	5.2D-14	6.4D-14	7.0D-15	7.4D-15
(0, 3)	7.2D-14	4.5D-13	1.0D-11	1.0D-13	5.9D-13	1.6D-09	2.7D-13	3.7D-11	8.2D-13	2.8D-13	2.5D-12	3.9D-14	2.3D-13	6.1D-15
(2, 2)	5.6D-15	5.6D-14	3.1D-13	2.8D-12	2.5D-11	5.0D-13	1.6D-09	1.4D-12	5.0D-11	3.6D-12	2.3D-13	3.8D-13	2.8D-14	4.2D-14
(0, 4)	9.2D-16	5.2D-15	7.9D-14	2.1D-15	1.0D-14	3.8D-12	7.6D-14	1.6D-09	1.7D-13	8.9D-13	2.5D-11	2.3D-13	1.5D-12	3.0D-14
(2, 3)	4.6D-16	1.5D-15	2.5D-14	8.3D-14	4.5D-13	3.2D-13	1.0D-11	6.3D-13	1.6D-09	3.8D-11	5.7D-13	2.4D-12	1.0D-13	2.3D-13
(2, 4)	9.7D-18	3.7D-17	3.6D-16	1.1D-15	5.6D-15	1.1D-14	7.8D-14	3.5D-13	3.9D-12	1.6D-09	1.5D-12	2.5D-11	2.3D-13	1.5D-12
(0, 5)	6.0D-18	3.2D-17	4.3D-16	1.8D-17	7.1D-17	1.4D-14	6.9D-16	1.4D-12	8.1D-15	2.1D-13	1.6D-09	9.6D-13	1.5D-11	1.8D-13
(2, 5)	9.5D-20	3.7D-19	3.6D-18	7.0D-18	3.4D-17	8.4D-17	4.4D-16	4.8D-15	1.3D-14	1.3D-12	3.8D-13	1.5D-09	1.1D-12	1.6D-11
(0, 6)	2.0D-20	1.0D-19	1.3D-18	7.1D-20	2.8D-19	3.7D-17	2.4D-18	2.3D-15	4.2D-17	9.3D-16	4.5D-13	8.2D-14	1.6D-09	1.1D-12
(2, 6)	4.5D-22	1.7D-21	1.8D-20	2.5D-20	1.2D-19	3.8D-19	1.4D-18	1.8D-17	3.7D-17	2.3D-15	2.0D-15	4.6D-13	4.2D-13	1.6D-09
$T = 500\text{ K}$														
(0, 0)	(0, 1)	(0, 2)	(2, 0)	(2, 1)	(0, 3)	(2, 2)	(0, 4)	(2, 3)	(2, 4)	(0, 5)	(2, 5)	(0, 6)	(2, 6)	
(0, 0)	1.8D-09	7.0D-11	9.4D-12	1.3D-12	1.8D-12	8.9D-14	3.2D-13	4.0D-14	1.2D-14	5.7D-14	3.0D-15	9.7D-15	7.0D-16	
(0, 1)	1.6D-10	1.7D-09	9.1D-11	2.4D-12	1.2D-11	9.2D-13	2.2D-12	1.7D-13	5.8D-14	3.8D-13	1.6D-14	6.5D-14	3.7D-15	
(0, 2)	2.2D-11	9.1D-11	1.7D-09	1.4D-12	9.0D-11	1.7D-12	1.1D-11	9.7D-13	2.0D-13	1.9D-12	5.7D-14	3.2D-13	1.5D-14	
(2, 0)	2.4D-12	1.9D-12	1.1D-12	1.7D-09	7.0D-11	5.4D-13	1.6D-13	2.0D-12	3.7D-13	3.9D-14	6.9D-14	8.2D-15	1.2D-14	
(2, 1)	3.0D-12	3.0D-12	3.1D-12	1.6D-10	1.7D-09	3.5D-12	9.8D-13	1.3D-11	2.4D-12	2.0D-13	4.3D-13	4.3D-14	7.5D-14	
(0, 3)	2.6D-12	8.1D-12	5.9D-11	4.5D-13	1.3D-12	1.8D-09	7.8D-11	1.8D-12	9.6D-13	9.3D-12	2.0D-13	1.5D-12	5.1D-14	
(2, 2)	3.7D-13	1.7D-12	3.0D-12	2.2D-11	9.2D-11	3.6D-12	2.6D-12	9.2D-11	1.1D-11	7.2D-13	2.0D-12	1.4D-13	3.5D-13	
(0, 4)	2.3D-13	6.7D-13	3.5D-12	6.1D-14	1.7D-13	3.6D-11	1.8D-09	9.1D-13	1.9D-12	6.3D-11	8.9D-13	7.0D-12	1.9D-13	
(2, 3)	1.1D-13	2.0D-13	1.1D-12	3.0D-12	3.2D-12	6.0D-11	3.5D-12	1.8D-09	8.0D-11	1.5D-12	9.4D-12	4.3D-13	1.5D-12	
(2, 4)	1.5D-14	3.2D-14	1.1D-13	2.6D-13	8.1D-13	3.5D-12	3.5D-12	3.8D-11	1.8D-09	4.0D-12	6.5D-11	8.4D-13	7.2D-12	
(0, 5)	1.4D-14	4.1D-14	2.1D-13	5.4D-15	1.2D-14	1.5D-12	2.2D-11	1.4D-13	7.8D-13	1.8D-09	2.2D-12	4.8D-11	8.0D-13	
(2, 5)	1.4D-15	3.0D-15	1.1D-14	1.7D-14	4.6D-14	6.1D-14	2.2D-13	1.5D-12	2.3D-11	3.9D-12	1.8D-09	3.3D-12	5.0D-11	
(0, 6)	6.5D-16	1.9D-15	9.2D-15	3.0D-16	6.9D-16	6.5D-14	6.6D-13	1.0D-14	4.4D-14	1.3D-11	4.9D-13	1.9D-09	2.4D-12	
(2, 6)	8.4D-17	1.9D-16	7.5D-16	8.1D-16	2.2D-15	4.1D-15	3.2D-14	6.7D-14	6.7D-14	3.9D-13	1.3D-11	4.3D-12	1.9D-09	

we believe this is due to the increase of the energy defect of the transition, which is proportional to J_2 . Thus, between $J_2 = 2$ and $J_2 = 8$, the rate coefficients for $\Delta J_2 = 1$ transitions decrease by about an order of magnitude.

For the sake of completeness, we give the matrices of rate coefficients for temperatures $T = 50, 100, 200$ and 500 K in table 3, for collisions with ortho- H_2 , and in table 4, for collisions with para- H_2 ; in the latter case, results are given for rotational levels of HD $J_2 \leq 6$. Additional results, on a finer grid of values of T , will be made available on the CCP7 server (<http://ccp7.dur.ac.uk/>) or may be obtained directly from the author (email address: david.flower@dur.ac.uk).

4. Concluding remarks

We have computed cross sections and rate coefficients for rotational transitions in HD, induced by collisions with ortho- and para- H_2 . Rotational states of HD $J_2 \leq 8$ were considered. Rate coefficients are available for temperatures up to $T = 1000$ K. Comparison with the results of Schaefer (1990) shows generally good agreement over the limited temperature range ($T \leq 300$ K) and for the restricted number of levels of HD ($J_2 \leq 2$) for which comparison is possible. Considerations based on the interaction potentials employed suggest that, at low temperatures ($T \leq 100$ K), the results of Schaefer (1990) may be the more accurate. However, the potential used by Schaefer (Schaefer and Köhler 1989) cannot be applied to the study of vibrationally inelastic scattering, whereas the potential that we have employed here (Schwenke 1988) possesses this additional flexibility, that we now intend to exploit.

Cross sections (and hence rate coefficients) for the dominant transitions in HD, involving $\Delta J_2 = 1$, are found to be insensitive to the rotational state of the H_2 molecule. Consequently, it is unnecessary to know the ortho- to para- H_2 ratio in order to calculate the rates of population transfer in HD, due to collisions with H_2 . At a given temperature, rate coefficients for $\Delta J_2 = 1$ de-excitation transitions decrease with increasing J_2 , owing to the increasing energy defects of these transitions. The results presented here obviate the need to extrapolate the results of Schaefer (1990), for $J_2 \leq 2$, to higher values of J_2 , a procedure which is hazardous even for the wary.

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