

LETTER TO THE EDITOR

Rotational excitation of H₂ by H at low energies

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Abstract. Cross sections and rate coefficients are reported for rotational transitions within the vibrational ground state of H₂, induced in collisions with H atoms at low energies. The quantal close-coupling method is employed together with a recently published interaction potential. Comparison is made with previous results.

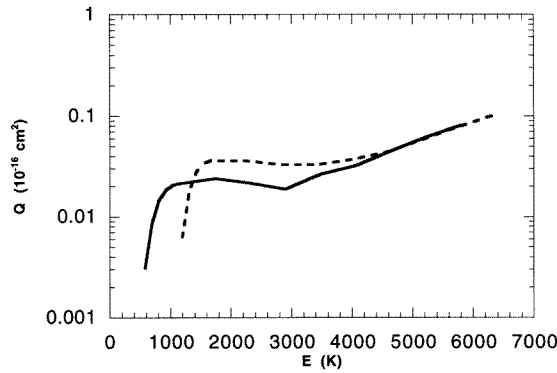
Low-energy scattering of hydrogen atoms and hydrogen molecules, leading to rotational excitation of the molecule, is one of the most fundamental processes in the domain of molecular collisions. Whilst justified for this reason alone, the study of this process receives further motivation from the realm of astrochemistry. In the so-called ‘photon-dominated regions’ of the interstellar medium, H₂ molecules are partly dissociated into hydrogen atoms, and rotational excitation of the molecules by the atoms might be expected to become competitive with excitation by other abundant species. The degree to which this is the case depends on the relative magnitudes of the cross sections for excitation of H₂ by H, H₂ and He.

Both reactive (proton transfer) and non-reactive (vibrationally and rotationally inelastic) collisions between H and H₂ have been studied by Mandy and Martin (1993) and by Lepp *et al* (1995) using quasi-classical trajectory Monte Carlo methods. Wolken *et al* (1972), Chu and Dalgarno (1975), McGuire and Krueger (1975), Green and Truhlar (1979) and Sun and Dalgarno (1994), on the other hand, have studied rotational excitation by means of quantum mechanical techniques. One of the conclusions that may be drawn from these studies is that the pure rotational excitation cross sections were sensitive to the H–H₂ interaction potential that was employed. This potential is predominantly repulsive, with only a shallow Van der Waals minimum of about 20 K at a separation of the atom from the centre of mass of the molecule of 7 *a*₀ (Boothroyd *et al* 1991, Partridge *et al* 1993). In the present letter, we use the recent potential of Boothroyd *et al* (1991) and the quantum mechanical method to compute the rotational excitation cross sections. The latter method is desirable, even indispensable near threshold, where classical techniques become unreliable.

The calculations reported here were carried out using two similar but independent programs, in order to cross-check the results obtained. We have used both the MOLSCAT code (Hutson and Green 1994) and the quantal close-coupling code originally developed by Launay (1977). Calculations were performed for both para and ortho H₂, which, in the absence of reactive collisions, may be treated as independent species. The work of Mandy and Martin (1993) and of Lepp *et al* (1995) suggests that the contribution of reactive collisions to rotational excitation is more important for ortho than for para H₂ but does not

Table 1. Eigenenergies of the rotational states of H_2 included in the bases, expressed in K through division by Boltzmann's constant.

J	E_J (K)
0	0
1	170
2	510
3	1015
4	1682
5	2504
6	3475
7	4587
8	5830
9	7199

**Figure 1.** Cross sections for the $J = 2 \rightarrow 0$ (full curve) and $3 \rightarrow 1$ (broken curve) transitions, in units of 10^{-16} cm^2 . The centre of mass collision energy is expressed in K, relative to the $J = 0$ level.

exceed about 10% of the total. The energy eigenvalues of the rotational levels included in the bases are given in table 1.

Rotational cross sections were computed on a grid of collision energies extending up to almost 7000 K ($1 \text{ cm}^{-1} = 1.4388 \text{ K}$). We have verified that, even at the highest energy, the rotational basis was sufficient to converge the cross sections. The grid was adjusted to adequately delineate the threshold behaviour of the $\Delta J = 2$ transitions, which were found to dominate those with $\Delta J > 2$. The predominantly repulsive character of the potential results in a smooth variation of the cross sections with the collision energy. The transitions which are particularly important for astrophysical applications are $J = 0 \rightarrow 2$ and $1 \rightarrow 3$. The corresponding de-excitation cross sections are plotted as functions of the collision energy in figure 1.

The cross sections plotted in figure 1 are found to be much smaller than the analogous results of Sun and Dalgarno (1994). The differences stem from the interaction potentials employed. Sun and Dalgarno used an earlier potential of Varandas *et al* (1987); with this potential, we obtain cross sections very similar to those published by Sun and Dalgarno (1994). The interaction potential of Boothroyd *et al* (1991) is believed to be more accurate, as noted by Lepp *et al* (1995). These authors have already shown, using classical trajectory methods, that the rotational cross sections obtained with the more recent potential are much

Table 2. The coefficients of the cubic fit to the temperature dependence of the rate coefficients for rotational de-excitation $J = 3 \rightarrow 1$ and $4 \rightarrow 2$. Numbers in parentheses are powers of 10.

n	c_n
0	1.17(−18)
1	3.31(−21)
2	−1.50(−24)
3	2.34(−28)

Table 3. Rate coefficients, in units of $10^{-11} \text{ cm}^3 \text{ s}^{-1}$, for excitation of the $J = 0 \rightarrow 2$ and $1 \rightarrow 3$ transitions of H_2 by H at $T = 1000 \text{ K}$.

$J \rightarrow J'$	This work	Lepp <i>et al</i> (1995)	Sun and Dalgarno (1994)	Mandy and Martin (1993)	Green and Truhlar (1979)
$0 \rightarrow 2$	0.50	1.6	7.3	0.93	0.21
$1 \rightarrow 3$	0.25	0.38	2.0	0.36	0.12

The present results were obtained with the potential of Boothroyd *et al* (1991) and the quantal close coupling (CC) scattering method. The quoted results of Lepp *et al* (1995) derive from the same potential but the quasi-classical trajectory (QCT) scattering technique. Sun and Dalgarno (1994) used the potential by Varandas *et al* (1987) and the CC method. Mandy and Martin (1993) employed QCT with the potential fit of Truhlar and Horowitz (1978). Green and Truhlar (1979) used the latter fit and the CC method. Numbers in parentheses are powers of 10.

smaller than those obtained with the potential of Varandas *et al* (1987).

Directly required for astrophysical applications are the rate coefficients as functions of the kinetic temperature, obtained from the cross sections by integrating over a Maxwellian distribution:

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

where $(8kT/\pi\mu)^{1/2}$ is the mean collision speed, μ is the reduced mass, Q the cross section, and $y = E/kT$, where E is the centre of mass collision energy. We shall take Q in this equation to be the cross section for a $\Delta J = 2$ rotational de-excitation transition and E to be the energy relative to the initial (upper) level. The cross section may be satisfactorily approximated by a third-order polynomial in E

$$Q(E) = \sum_{n=0}^3 c_n \left(\frac{E}{k} \right)^n$$

in which case the integral in the expression for the de-excitation rate coefficient may be trivially evaluated, yielding

$$q(T) = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \sum_{n=0}^3 (n+1)! c_n T^n.$$

To within the uncertainties in the calculations, we find that the rate coefficients for the transitions $J = 3 \rightarrow 1$ and $4 \rightarrow 2$ may be adequately fitted by the same set of coefficients, c_n , given in table 2; q is in units of $\text{cm}^3 \text{ s}^{-1}$ when T is in K and the mean collision speed $(8kT/\pi\mu)^{1/2}$ is in cm s^{-1} . The rate coefficient for the $2 \rightarrow 0$ transition is smaller by a factor of 1.5. Rate coefficients for excitation may be readily obtained from those for de-excitation using detailed balance:

$$(2J+1)q_{J \rightarrow J'}(T) = (2J'+1)q_{J' \rightarrow J}(T) \exp[-(E_{J'} - E_J)/kT].$$

The fit is satisfactory for temperatures $T \leq 1000$ K.

Table 3 compares the rate coefficients obtained by various authors for the $0 \rightarrow 2$ and $1 \rightarrow 3$ transitions at $T = 1000$ K. The reasons for the variations have already been mentioned. Subject to the reliability of the potential of Boothroyd *et al* (1991), the present results should be the most accurate.

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