

Quantal coupled channels calculations of the rates of self-relaxation of *ortho*- and *para*-H₂

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Received 10 August 2000

Abstract. We have computed thermally averaged rate coefficients for vibrational self-relaxation $v = 1 \rightarrow 0$ of *ortho*- and *para*-H₂. The quantum mechanical, coupled channels method was employed, with bases which are adequate to ensure convergence of the results at the kinetic temperatures ($T = 300$ and 500 K) considered. Although the inclusion of excited rotational states of the perturber molecule leads to increases in the rate coefficients for vibrational relaxation, these increases are insufficient to reconcile the theoretical results with experimental measurements.

1. Introduction

The infrared space observatory (ISO) and, more recently, the far-ultraviolet spectroscopic explorer (FUSE) satellites have given new impetus to studies of the H₂ molecule in the interstellar medium. First detected beyond the solar system by Carruthers (1970), by means of a rocket-borne ultraviolet spectrometer, H₂ was subsequently observed, again in ultraviolet absorption against hot stars, by the Copernicus satellite (Spitzer *et al* 1973). Although observable from the ground through atmospheric windows in the near infrared, more comprehensive observational studies have to be made from above the Earth's atmosphere.

Molecular hydrogen in interstellar space may be rovibrationally excited by three mechanisms: collisions in hot gas, produced, for example, by the passage of shock waves; absorption of stellar ultraviolet radiation in the Lyman and Werner bands, followed by cascade to rovibrationally excited states; and association of two hydrogen atoms to form H₂ on the surface of a dust grain. When the density of the gas is sufficiently high, collisionally induced vibrational relaxation of H₂ molecules leads to heating of the gas. The reverse process—collisional excitation—results in cooling of the gas when the density is low. Thus, the thermal balance of the medium and its kinetic temperature depend on the rates of rovibrationally inelastic collision processes.

The rate coefficients for vibrational relaxation of H₂ have been both measured in the laboratory and calculated. The experiments of Audibert *et al* (1974, 1975) and of Dove and Teitelbaum (1974) served to determine the rates of self-relaxation of H₂ at temperatures extending from 40 to 3000 K. Various attempts have been made to calculate the cross sections, and hence the rate coefficients, using semiclassical methods (Cacciatore *et al* 1989, Cacciatore and Billing 1992, Billing and Kolesnick 1993, Kolesnick and Billing 1993, Zenevich and Billing 1999) and the quantum mechanical coupled channels method (Flower and Roueff 1998, 1999, Flower 2000). The more recent calculations, semiclassical and quantum mechanical alike, have used the H₂–H₂ potential computed by Schwenke (1988). Whilst it is clear that the

quantum mechanical method is intrinsically sounder, particularly at low collision energies (low kinetic temperatures), this method is restricted in terms of basis set size. Zenevich and Billing (1999) have suggested that limitations to the rotational basis set used to describe the perturber H_2 molecule, in the quantum mechanical calculations of Flower and Roueff (1998, 1999), led to the rate coefficients for vibrational relaxation of the target molecule being underestimated by large factors. It is important to establish whether the discrepancies between the semiclassical and quantum mechanical results arise from approximations made in one, the other or both methods.

In an initial study (Flower 2000), I extended our calculations of the vibrational relaxation $v = 1 \rightarrow 0$ of *para*- H_2 (Flower and Roueff 1998) by including the first rotationally excited state ($j_1 = 2$) of the perturber molecule, which lies 510 K above the $j_1 = 0$ ground state. The target molecule was represented by the states $v_2 = 0$, $j_2 = 0, 2, 4, 6, 8, 10$ and $v_2 = 1$, $j_2 = 0, 2, 4, 6, 8$. At the kinetic temperature $T = 500$ K, for which the results of Flower and Roueff (1998) lie below both the measurements and the semiclassical calculations by about an order of magnitude, it was found that the inclusion of $j_1 = 2$ on the perturber molecule led to an increase in the Boltzmann-weighted value of the relaxation rate coefficient, but by a factor of only 1.6. Introducing $j_1 = 2$ increases the number of coupled channels, and hence the computing time, by substantial factors; but, in view of the importance of the H_2 – H_2 system, I have since extended these computations by adding the $j_1 = 4$ state of the perturber *para*- H_2 molecule. Furthermore, the analogous calculations for *ortho*- H_2 , in which the perturber molecule was represented by the three states $v_1 = 0$, $j_1 = 1, 3, 5$, have been carried out. These calculations are reported in sections 2 and 3 below. Concluding remarks are given in section 4.

2. Method

The quantum mechanical coupled channels method has been used, without any approximations beyond the use of finite basis sets to represent the target and perturber molecules. When calculating cross sections for self-relaxation of *para*- H_2 , I employed the basis $v_1 = 0$, $j_1 = 0, 2, 4$ on the perturber molecule and $v_2 = 0$, $j_2 = 0, 2, 4, 6, 8, 10$ and $v_2 = 1$, $j_2 = 0, 2, 4, 6, 8$ on the target. For the study of self-relaxation of *ortho*- H_2 , the basis was $v_1 = 0$, $j_1 = 1, 3, 5$ on the perturber and $v_2 = 0$, $j_2 = 1, 3, 5, 7, 9, 11$ and $v_2 = 1$, $j_2 = 1, 3, 5, 7, 9$ on the target. The process being considered is collisional de-excitation of the target molecule, initially in a state $v_2 = 1$, j_2 , to a final state $v_2' = 0$, j_2' , by a perturber molecule $v_1 = 0$, j_1 . At the kinetic temperatures considered ($T = 300$ and 500 K), most of the population of *para*- H_2 is in the levels $j_1 = 0$ and 2 , and practically all the population of *ortho*- H_2 is in the levels $j_1 = 1$ and 3 . The additional levels, $j_1 = 4$ and $j_1 = 5$, which have excitation energies of 1682 and 2334 K above their respective ground states ($j_1 = 0$ and $j_1 = 1$), were included in the basis sets in order to ensure convergence of the rovibrational de-excitation cross sections for $j_1 \leq 3$.

The scattering code which has been employed is described by Flower *et al* (2000). We have used both the de Vogelaere (see Launay 1976) and Johnson–Manolopoulos (Johnson 1973, Manolopoulos 1986) methods to integrate the coupled differential equations, obtaining practically identical results. Sets of up to 1413 coupled, second-order, ordinary differential equations were solved by these means, for barycentric collision energies in the range $6000 \leq E \leq 12\,000$ K, relative to the ground state of the system ($v_1 = v_2 = 0$, $j_1 = j_2 = 0$ for *para*- H_2 and $j_1 = j_2 = 1$ for *ortho*- H_2).

3. Results

Rate coefficients for rovibrational de-excitation $v_2 = 1, j_2 \rightarrow v'_2 = 0, j'_2$ of the target molecules, induced by projectile molecules $v_1 = 0, j_1$, have been determined by numerical integration of the corresponding de-excitation cross sections Q over a Maxwellian distribution

$$q(T) = \left(\frac{8kT}{\pi m} \right)^{1/2} \int_0^\infty Q(x) x e^{-x} dx \quad (1)$$

where $x = E/kT$; E is the barycentric collision energy, T is the kinetic temperature and m is the reduced mass of the colliding molecules. Results are presented in tables 1 and 2 for self-relaxation of *ortho*- and *para*-H₂ at temperatures $T = 300$ and 500 K, for which converged values of the integral in equation (1) have been obtained. The energies of the states involved, $E(v_1 j_1 v_2 j_2)$, are listed in table 3, where they are expressed relative to $E(0101) = 0.0$ in *ortho*-H₂ and $E(0000) = 0.0$ in *para*-H₂.

Table 1. Rate coefficients (cm³ s⁻¹) for the transitions in *ortho*-H₂ $v_1 = 0, j_1, v_2 = 1, j_2 \rightarrow v'_1 = 0, j'_1, v'_2 = 0, j'_2$. The columns are labelled by the initial rotational states (j_1, j_2) and the rows by the final rotational states (j'_1, j'_2).

	(1, 1)	(1, 3)	(3, 1)	(3, 3)	(1, 5)	(5, 1)	(3, 5)	(5, 3)
<i>T</i> = 300 K								
(1, 1)	1.46D-17	3.83D-19	4.40D-19	8.69D-20	2.62D-20	2.39D-20	7.58D-21	6.50D-21
(1, 3)	4.85D-18	1.44D-17	6.98D-19	7.27D-19	4.55D-19	3.27D-20	1.01D-19	3.33D-20
(3, 1)	3.91D-18	5.25D-19	1.34D-17	5.43D-19	3.55D-20	3.11D-19	2.79D-20	7.02D-20
(3, 3)	1.24D-17	4.53D-18	4.07D-18	1.50D-17	4.60D-19	3.67D-19	4.81D-19	4.66D-19
(1, 5)	1.08D-18	1.82D-17	3.28D-19	2.01D-18	1.51D-17	2.16D-20	1.11D-18	6.14D-20
(5, 1)	1.39D-19	1.57D-19	6.75D-18	9.71D-19	2.29D-20	1.35D-17	5.81D-20	6.20D-19
(3, 5)	1.26D-18	3.46D-17	2.14D-18	1.62D-17	8.37D-18	2.30D-19	1.54D-17	1.25D-18
(5, 3)	3.62D-19	8.03D-19	2.94D-17	9.40D-18	3.26D-19	3.31D-18	8.78D-19	1.52D-17
(1, 7)	1.22D-20	8.45D-19	1.66D-20	4.68D-19	1.17D-16	5.76D-21	9.23D-18	9.01D-20
(5, 5)	1.01D-18	7.60D-19	2.26D-18	1.55D-16	4.51D-18	4.23D-18	1.58D-17	1.39D-17
(3, 7)	1.41D-20	1.72D-18	5.07D-20	2.18D-18	2.02D-16	8.16D-20	1.00D-16	6.90D-19
<i>T</i> = 500 K								
(1, 1)	2.44D-17	1.24D-18	1.51D-18	3.42D-19	1.08D-19	9.34D-20	3.32D-20	2.66D-20
(1, 3)	3.27D-17	2.93D-17	3.74D-18	2.89D-18	1.71D-18	2.04D-19	3.66D-19	1.76D-19
(3, 1)	1.80D-17	2.42D-18	2.45D-17	1.77D-18	2.01D-19	1.11D-18	1.38D-19	2.42D-19
(3, 3)	7.65D-17	2.19D-17	2.73D-17	3.02D-17	2.16D-18	2.26D-18	2.02D-18	2.23D-18
(1, 5)	8.67D-18	1.31D-16	2.22D-18	1.32D-17	3.68D-17	1.72D-19	5.08D-18	6.91D-19
(5, 1)	1.26D-18	1.08D-18	3.98D-17	5.82D-18	1.75D-19	2.22D-17	5.31D-19	1.85D-18
(3, 5)	9.25D-18	2.33D-16	1.67D-17	1.11D-16	3.62D-17	1.39D-18	5.03D-17	9.77D-18
(5, 3)	3.42D-18	6.24D-18	2.04D-16	5.18D-17	1.82D-18	2.47D-17	4.78D-18	3.85D-17
(1, 7)	2.12D-19	7.14D-18	1.84D-19	3.33D-18	5.73D-16	4.60D-20	5.39D-17	6.91D-19
(5, 5)	4.01D-18	8.64D-18	1.83D-17	7.54D-16	2.20D-17	2.40D-17	7.83D-17	1.32D-16
(3, 7)	2.26D-19	8.91D-18	6.20D-19	1.80D-17	8.82D-16	5.44D-19	4.86D-16	3.93D-18

The relaxation rate coefficient is obtained by weighting the de-excitation rate coefficients by the relative populations of the $v_1 = 0, j_1, v_2 = 1, j_2$ initial levels, assuming that these are determined by a Boltzmann distribution at temperature T , and summing over the $v'_1 = 0, j'_1, v'_2 = 0, j'_2$ final states,

$$q_{1 \rightarrow 0}(T) = \sum_{v'_1 j'_1 v'_2 j'_2} n(v_1 j_1) n(v_2 j_2) q(v_1 j_1 v_2 j_2 \rightarrow v'_1 j'_1 v'_2 j'_2) \quad (2)$$

Table 2. Rate coefficients ($\text{cm}^3 \text{s}^{-1}$) for the transitions in para- H_2 $v_1 = 0$, j_1 , $v_2 = 1$, $j_2 \rightarrow v'_1 = 0$, j'_1 , $v'_2 = 0$, j'_2 . The columns are labelled by the initial rotational states (j_1 , j_2) and the rows by the final rotational states (j'_1 , j'_2).

	(0, 0)	(0, 2)	(2, 0)	(2, 2)	(0, 4)	(4, 0)	(2, 4)	(4, 2)
<i>T</i> = 300 K								
(0, 0)	1.24D-17	2.00D-19	2.76D-19	3.93D-20	8.50D-21	1.18D-20	3.71D-21	3.19D-21
(0, 2)	2.39D-18	1.30D-17	5.40D-19	4.92D-19	2.70D-19	2.64D-20	6.26D-20	2.26D-20
(2, 0)	2.76D-18	4.81D-19	1.28D-17	3.79D-19	2.69D-20	2.59D-19	1.83D-20	4.12D-20
(2, 2)	1.11D-17	4.55D-18	3.50D-18	1.42D-17	4.73D-19	3.57D-19	4.40D-19	4.23D-19
(0, 4)	1.10D-18	5.23D-18	2.56D-19	8.04D-19	1.31D-17	1.77D-20	7.46D-19	3.83D-20
(4, 0)	8.04D-20	1.22D-19	2.32D-18	5.05D-19	1.52D-20	1.32D-17	4.23D-20	4.63D-19
(2, 4)	1.66D-18	1.77D-17	2.12D-18	7.35D-18	6.84D-18	3.03D-19	1.50D-17	8.42D-19
(4, 2)	3.87D-19	5.83D-19	1.54D-17	5.26D-18	2.65D-19	2.77D-18	7.28D-19	1.48D-17
(4, 4)	1.07D-18	9.37D-19	2.51D-18	3.08D-17	1.63D-18	3.37D-18	8.50D-18	5.66D-18
(0, 6)	2.37D-20	5.00D-19	1.79D-20	1.83D-19	3.83D-17	5.44D-21	3.39D-18	3.68D-20
(2, 6)	5.44D-20	1.14D-18	9.92D-20	1.14D-18	5.48D-17	7.16D-20	4.20D-17	4.21D-19
(4, 6)	2.41D-20	1.45D-18	6.24D-20	1.48D-18	3.79D-18	1.97D-19	1.78D-16	6.30D-18
(0, 8)	3.57D-23	1.94D-21	5.41D-23	1.18D-21	5.30D-19	4.72D-23	2.48D-19	3.89D-21
<i>T</i> = 500 K								
(0, 0)	1.88D-17	3.14D-19	6.26D-19	1.32D-19	2.99D-20	3.67D-20	1.69D-20	1.22D-20
(0, 2)	1.13D-17	2.17D-17	2.34D-18	1.58D-18	8.75D-19	1.31D-19	2.52D-19	1.01D-19
(2, 0)	8.08D-18	1.87D-18	2.06D-17	9.53D-19	1.50D-19	7.15D-19	8.81D-20	1.42D-19
(2, 2)	6.17D-17	1.83D-17	1.78D-17	2.67D-17	2.18D-18	1.67D-18	1.73D-18	1.63D-18
(0, 4)	7.51D-18	4.35D-17	1.61D-18	5.66D-18	2.63D-17	1.14D-19	2.75D-18	2.87D-19
(4, 0)	6.05D-19	6.84D-19	1.16D-17	3.06D-18	1.20D-19	1.88D-17	3.01D-19	9.55D-19
(2, 4)	1.22D-17	1.09D-16	1.52D-17	5.54D-17	2.81D-17	1.62D-18	3.32D-17	4.98D-18
(4, 2)	3.87D-18	4.36D-18	9.30D-17	2.94D-17	1.55D-18	1.47D-17	3.49D-18	2.42D-17
(4, 4)	6.71D-18	9.92D-18	1.97D-17	2.14D-16	1.13D-17	2.06D-17	4.36D-17	4.69D-17
(0, 6)	3.03D-19	4.19D-18	1.92D-19	1.47D-18	2.33D-16	4.67D-20	2.11D-17	2.52D-19
(2, 6)	7.59D-19	8.06D-18	1.14D-18	1.06D-17	3.57D-16	5.47D-19	2.52D-16	2.36D-18
(4, 6)	3.13D-19	5.79D-18	6.56D-19	9.93D-18	3.66D-17	2.24D-18	8.25D-16	3.22D-17
(0, 8)	1.50D-21	3.27D-20	1.87D-21	2.65D-20	3.60D-18	1.30D-21	1.75D-18	2.93D-20

where

$$n(vj) = \frac{(2j+1) \exp[-\varepsilon(vj)/T]}{\sum_{vj} (2j+1) \exp[-\varepsilon(vj)/T]} \quad (3)$$

and $\varepsilon(vj)$ is the excitation energy of level vj . The results given in tables 4 and 5 were obtained for $j_1 = 1$ and 3 of *ortho*- H_2 and $j_1 = 0$ and 2 of *para*- H_2 . We see that the contributions to vibrational relaxation from perturber molecules in their first excited states, relative to those in their ground states, are greater at the higher temperature, as might have been anticipated. Thus, the total relaxation rate coefficients, which are given in the last columns of tables 4 and 5, exceed the values computed by Flower and Roueff (1999)—who neglected excited states of the perturber molecule—by factors of approximately 2 at 300 K and 3 at 500 K. However, the measured values of the total relaxation rate coefficients, $1 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ at 300 K and $1 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ at 500 K for both *ortho*- and *para*- H_2 (Audibert *et al* 1974, 1975), exceed the present results by similar factors. It follows that the inclusion in the calculations of excited states of the perturber molecule goes only part of the way to resolving the discrepancies with the measurements, as was indicated by my preliminary study (Flower 2000).

Table 3. Energies of the initial and final states of the transitions considered in tables 1 and 2 (from Dabrowski (1984)).

v_1	j_1	v_2	j_2	Energy (K)
(a) <i>ortho</i>				
0	1	0	1	0.0
0	1	0	3	844.7
0	3	0	1	844.7
0	3	0	3	1689.4
0	1	0	5	2333.5
0	5	0	1	2333.5
0	3	0	5	3178.2
0	5	0	3	3178.2
0	1	0	7	4416.1
0	5	0	5	4667.0
0	3	0	7	5260.8
0	1	1	1	5979.0
0	1	1	3	6781.4
0	3	1	1	6823.7
0	3	1	3	7626.1
0	1	1	5	8195.2
0	5	1	1	8312.5
0	3	1	5	9039.9
0	5	1	3	9114.9
(b) <i>para</i>				
0	0	0	0	0.0
0	0	0	2	509.9
0	2	0	0	509.9
0	2	0	2	1019.8
0	0	0	4	1681.8
0	4	0	0	1681.8
0	2	0	4	2191.7
0	4	0	2	2191.7
0	4	0	4	3363.6
0	0	0	6	3474.6
0	2	0	6	3984.5
0	4	0	6	5156.4
0	0	0	8	5830.0
0	0	1	0	5987.5
0	0	1	2	6471.9
0	2	1	0	6497.4
0	2	1	2	6981.8
0	0	1	4	7585.0
0	4	1	0	7669.3
0	2	1	4	8094.9
0	4	1	2	8153.7

4. Concluding remarks

We believe that the results presented above, which derive from large-scale quantum mechanical calculations, are essentially converged with respect to the basis sets used to represent the pair of colliding molecules. It is clear that the neglect of excited states of the perturber molecule in the calculations of Flower and Roueff (1998, 1999) led to the total relaxation rate coefficients

Table 4. Thermally averaged rate coefficients ($\text{cm}^3 \text{s}^{-1}$) for rovibrational de-excitation of a target *ortho*-H₂ molecule in states $v_2 = 1$, j_2 by a perturber *ortho*-H₂ molecule initially in the states $v_1 = 0$, j_1 . The values listed were obtained by weighting the rovibrational de-excitation rate coefficients (cf tables 1 and 2) by the relative populations of the initial levels, assumed to be given by a Boltzmann distribution at the temperature, T . Numbers in parentheses are powers of ten.

v_2	j_2	$j_1 = 1$	$j_1 = 3$
$T = 300 \text{ K}$			
1	1	3.00(−17)	6.27(−18)
1	3	9.46(−18)	3.46(−18)
1	5	6.05(−19)	2.37(−19)
1	7	3.97(−21)	3.71(−21)
		4.00(−17) +	9.97(−18) = 5.00(−17)
$T = 500 \text{ K}$			
1	1	8.05(−17)	6.59(−17)
1	3	9.62(−17)	9.14(−17)
1	5	3.15(−17)	2.30(−17)
1	7	5.53(−18)	1.18(−17)
		2.14(−16) +	1.92(−16) = 4.06(−16)

Table 5. As table 4, but for self-relaxation of *para*-H₂.

v_2	j_2	$j_1 = 0$	$j_1 = 2$
$T = 300 \text{ K}$			
1	0	8.32(−18)	9.20(−18)
1	2	1.15(−17)	1.44(−17)
1	4	1.37(−18)	2.55(−18)
1	6	3.35(−20)	5.77(−20)
		2.12(−17) +	2.62(−17) = 4.74(−17)
$T = 500 \text{ K}$			
1	0	1.29(−17)	3.25(−17)
1	2	4.21(−17)	1.20(−16)
1	4	2.57(−17)	7.82(−17)
1	6	4.01(−18)	1.18(−17)
		8.48(−17) +	2.42(−16) = 3.27(−16)

being underestimated, but by factors which are insufficient to reconcile the theoretical results with the experiments. We consider that progress in resolving the remaining discrepancies with the measurements will require a re-evaluation of the H₂–H₂ interaction potential and fresh experimental initiatives.

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