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QUANTUM-MECHANICAL STUDY OF RO-VIBRATIONAL TRANSITIONS IN H_2 INDUCED BY He ATOMS

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ABSTRACT

We describe quantum-mechanical scattering calculations of ro-vibrational transitions in H_2 induced by collisions with He. We use a close-coupled description of the dynamics which includes full ro-vibrational coupling and a reliable potential energy surface. Rate coefficients for rotational and vibrational transitions in ortho- and para-H_2 are presented in the temperature range $10 \leq T \leq 5000$ K.
Subject headings: molecular data — molecular processes

1. INTRODUCTION

Ro-vibrational excitations in H_2 induced by collisions with H and He atoms are important mechanisms in the cooling of shocked interstellar gas, cooling flow galaxies, and objects formed in the early universe. A number of recent measurements (Kunze et al. 1996; Rigopoulou et al. 1996; Sturm et al. 1996; Timmermann et al. 1996; Wright et al. 1996) performed aboard the *Infrared Space Observatory* have identified emissions arising from pure rotational transitions in H_2. The rate coefficients for these transitions play a central role in the interpretation of the observed spectral lines and the understanding of the physics of molecular clouds. The levels are excited by collisions with H, He, and H_2. Recent calculations of Flower (1997) and Forrey et al. (1997) of H–H_2 collisions have provided rate coefficients for rotational transitions in H_2 at temperatures prevailing in the interstellar medium. Here we report calculations for He–H_2 collisions.

Inelastic collisions of H_2 with He have been the subject of many studies (Gordon & Secrest 1970; Rabitz & Zarur 1974; McGuire & Kouri 1974; McGuire & Toennies 1975; Alexander & McGuire 1976; Alexander 1976; Clark 1977; Raczkowski, Lester, & Miller 1978; Schaefer & Köhler 1985; Flower, Roueff, & Zeippen 1998). The calculations of Eastes & Secrest (1972), McGuire & Kouri (1974), and Alexander & McGuire (1976) used an interaction potential which neglected the van der Waals well. Tsapline & Kutzelnigg (1973) performed ab initio calculations of the HeH_2 potential energy surface (PES) which was extended with an analytic form by Raczkowski & Lester (1977) and made use of by Alexander (1977) and Raczkowski et al. (1978) for extensive quantum scattering calculations. Recently, Muchnick & Russek (1994) provided a PES for the He–H_2 interaction which included more recent ab initio potential energy calculations by Meyer et al. (1980). An important feature of this PES is the inclusion of a dependence on the vibrational coordinate of H_2 so that it can be used to investigate ro-vibrational transitions. We have shown (Balakrishnan, Forrey, & Dalgarno 1998) that the low temperature rate coefficients computed on this surface give good agreement with the experimental results of Audibert et al. (1976) for the vibrational relaxation of $H_2(v = 1, j = 0)$ by He at temperatures between 50 to 300 K. The Muchnick & Russek (1994) PES was also employed by Flower et al. (1998) who used a harmonic oscillator approximation for the H_2 wave functions. In the present study we employ the Muchnick & Russek (1994) PES using exact vibrational wave functions in a close-coupled expansion of the scattering wave function. We present ro-vibrational transition rate coefficients and the corresponding cooling rate coefficients arising from collisions of He with ortho- and para-H_2.

2. QUANTUM-MECHANICAL APPROACH

We use the total angular momentum representation of Arthurs & Dalgarno (1960) in which the cross section for transitions from an initial vibrational-rotational level labeled by quantum numbers vj to a final level labeled by quantum numbers $v'j'$ is expressed in terms of the corresponding S-matrix elements

$$\sigma_{v,j\to v',j'}(E_k) = \frac{\pi\hbar^2}{2\mu E_k(2j+1)} \sum_{J=0}^{\infty} (2J+1) \times \sum_{l=|J-j|}^{|J+j|} \sum_{l'=|J-j'|}^{|J+j'|} |\delta_{jj'}\delta_{ll'}\delta_{vv'} - S^J_{jj'll'vv'}|^2 , \quad (1)$$

where μ is the three-body reduced mass, J is the total angular momentum quantum number, and l and l' are, respectively, the initial and final orbital angular momentum quantum numbers. The total energy E is related to the kinetic energy of the incoming atom according to $E = E_k + \epsilon_{vj}$ where ϵ_{vj} is the energy of the initial ro-vibrational level.

The rate coefficient for a given transition is obtained by averaging the appropriate cross section over a Boltzmann distribution of velocities of the incoming atom at a specified temperature T:

$$k_{v,j\to v',j'}(T) = (8/\pi\mu\beta)^{1/2}\beta^2 \int_0^{\infty} E_k\, \sigma_{v,j\to v',j'}(E_k) \times \exp(-\beta E_k) dE_k , \quad (2)$$

where $\beta = (k_B T)^{-1}$ and k_B is the Boltzmann constant. The rate coefficient for the reverse transition may be obtained by detailed balance:

$$k_{v',j'\to v,j}(T) = \frac{(2j+1)}{(2j'+1)} \exp[\beta(\epsilon_{v'j'} - \epsilon_{vj})] k_{v,j\to v',j'}(T) . \quad (3)$$

3. RESULTS

The quantum-mechanical calculations were performed by adapting the nonreactive scattering program MOLSCAT developed by Hutson & Green (1994) for the present system. The *R*-matrix approach (Stechel, Walker, & Light 1978) was used to solve the coupled equations for the radial motion. We obtained the diatomic vibrational wave functions of H_2 as expansions in Hermite polynomials with the H_2 potential taken from Schwenke (1988). The energies of selected ro-vibrational levels below the $v = 2$ excitation threshold of H_2 used in the calculations are shown in Table 1. Sufficient H_2 ro-vibrational levels and total angular momentum partial waves have been included in the calculations to secure convergence.

In Table 2 we present rate coefficients for pure rotational excitations within the $v = 0$ vibrational level of both ortho and para H_2 in the temperature range 100 to 5000 K. They are typically several times larger than those for collisions with H.

In Table 3 we present rate coefficients for the quenching of even and odd rotational levels of H_2 within the $v = 0$ vibrational level as a function of temperature from $T = 10$ to 5000 K. Our calculations show that the cross sections for quenching collisions exhibit a minimum near a translational energy of 40 K ($E_k = k_B T$) and increase with further decrease of kinetic energy. The enhancement of the cross section at low energies is predominantly due to the long-range attractive forces in the potential and has an important effect on the low temperature rate coefficients (Balakrishnan et al. 1998). A similar behavior occurs for H–H_2 collisions (Forrey et al. 1997). The various rate coefficients may be represented by the analytical form

$$\log_{10} k_{v,j\to v',j'}(T) = \sum_{n=0}^{N} a^{(n)}_{v,j\to v',j'} x^n , \qquad (4)$$

where $x = 1/T^{1/3}$. Table 4 gives the values of $a^{(n)}_{v,j\to v',j'}$ for the rate coefficients given in Table 3 with $N = 5$. A fifth-order polynomial is required to cover the wide range of temperatures in Table 3. The uncertainty arising from the fit is usually less than 5%.

In Table 5, we present excitation rate coefficients for ro-vibrational transitions between selected rotational levels in the $v = 0$ and $v = 1$ vibrational levels of ortho- and para-H_2. The coefficients of the polynomial which fit to these rate coefficients in the temperature range $100 \le T \le 3000$ are given in Table 6. An extensive tabulations of rate coefficients for ro-vibrational transitions in H_2 has been presented by Flower et al. (1998). Their results are in good agreement with the present results for pure rotational transitions indicating that the harmonic oscillator approximation that they used is valid for rotationally inelastic He–H_2 collisions. The agreement is less satisfactory for ro-vibrational transitions below a temperature of 500 K, but for temperatures higher than that their results agree with the present calculations. The sensitivity of the low-energy ro-vibrational transition cross sections to the choice of the diatomic vibrational wave function was pointed out previously by Alexander & McGuire (1976). We believe the results presented here provide reliable estimates of ro-

TABLE 1

ENERGIES (in cm^{-1}) OF RO-VIBRATIONAL LEVELS OF H_2

v	j	ϵ_{vj}
0.....	0	2168
0.....	1	2287
0.....	2	2522
0.....	3	2873
0.....	4	3336
0.....	5	3908
0.....	6	4582
0.....	7	5354
0.....	8	6218
0.....	9	7168
1.....	0	6329
1.....	1	6442
1.....	2	6666
1.....	3	6999
1.....	4	7439
1.....	5	7981
1.....	6	8622
1.....	7	9354
1.....	8	10174
1.....	9	11075

TABLE 2

PURE ROTATIONAL EXCITATION RATE COEFFICIENTS $k_{0,j\to 0,j'}(T)$ (in $cm^3\ s^{-1}$) FOR ORTHO- AND PARA-H_2 IN THE $v = 0$ VIBRATIONAL LEVEL IN COLLISIONS WITH He AS FUNCTIONS OF TEMPERATURE

T(K)	$k_{0,0\to 0,2}(T)$	$k_{0,0\to 0,4}(T)$	$k_{0,2\to 0,4}(T)$	$k_{0,1\to 0,3}(T)$	$k_{0,1\to 0,5}(T)$	$k_{0,3\to 0,5}(T)$
100	2.66(−14)	1.19(−21)	1.91(−18)	1.76(−16)	2.58(−25)	2.25(−20)
200	7.79(−13)	2.14(−17)	2.27(−15)	3.63(−14)	1.51(−19)	1.60(−16)
300	3.09(−12)	8.93(−16)	3.54(−14)	2.93(−13)	2.14(−17)	4.69(−15)
500	1.20(−11)	2.88(−14)	4.66(−13)	2.14(−12)	2.02(−15)	1.09(−13)
700	2.48(−11)	1.71(−13)	1.75(−12)	6.01(−12)	1.20(−14)	5.46(−13)
1000.....	4.78(−11)	8.17(−13)	5.60(−12)	1.50(−11)	1.46(−13)	2.22(−12)
1500.....	8.97(−11)	3.54(−12)	1.64(−11)	3.56(−11)	9.19(−13)	8.10(−12)
2000.....	1.31(−10)	8.46(−12)	3.10(−11)	5.93(−11)	2.71(−12)	1.73(−11)
2500.....	1.69(−10)	1.52(−11)	4.75(−11)	8.39(−11)	5.61(−12)	2.87(−11)
3000.....	2.03(−10)	2.33(−11)	6.48(−11)	1.08(−10)	9.52(−12)	4.13(−11)
3500.....	2.34(−10)	3.23(−11)	8.20(−11)	1.31(−10)	1.42(−11)	5.45(−11)
4000.....	2.61(−10)	4.16(−11)	9.86(−11)	1.52(−10)	1.94(−11)	6.77(−11)
4500.....	2.86(−10)	5.10(−11)	1.14(−10)	1.72(−10)	2.50(−11)	8.05(−11)
5000.....	3.07(−10)	6.01(−11)	1.29(−10)	1.89(−10)	3.06(−11)	9.25(−11)

TABLE 3

PURE ROTATIONAL DE-EXCITATION RATE COEFFICIENTS $k_{0,j\to 0,j'}(T)$ (in $cm^3\ s^{-1}$) FOR ORTHO- AND PARA-H_2 IN THE $v = 0$ VIBRATIONAL LEVEL IN COLLISIONS WITH He AS FUNCTIONS OF TEMPERATURE

T(K)	$k_{0,2\to 0,0}(T)$	$k_{0,4\to 0,0}(T)$	$k_{0,4\to 0,2}(T)$	$k_{0,3\to 0,1}(T)$	$k_{0,5\to 0,1}(T)$	$k_{0,5\to 0,3}(T)$
10	2.33(−13)	6.27(−16)	3.40(−14)	8.13(−14)	1.64(−16)	8.21(−15)
20	2.69(−13)	6.08(−16)	3.28(−14)	9.60(−14)	1.94(−16)	9.64(−15)
30	3.22(−13)	7.17(−16)	3.83(−14)	1.18(−13)	2.45(−16)	1.20(−14)
40	3.83(−13)	8.78(−16)	4.65(−14)	1.44(−13)	3.09(−16)	1.50(−14)
50	4.52(−13)	1.08(−15)	5.67(−14)	1.75(−13)	3.89(−16)	1.86(−14)
60	5.26(−13)	1.33(−15)	6.87(−14)	2.09(−13)	4.86(−16)	2.29(−14)
70	6.06(−13)	1.62(−15)	8.25(−14)	2.47(−13)	6.02(−16)	2.80(−14)
80	6.90(−13)	1.96(−15)	9.82(−14)	2.89(−13)	7.37(−16)	3.38(−14)
90	7.79(−13)	2.34(−15)	1.16(−13)	3.35(−13)	8.99(−16)	4.04(−14)
100	8.73(−13)	2.79(−15)	1.36(−13)	3.84(−13)	1.09(−15)	4.79(−14)
200	2.00(−12)	1.08(−14)	4.47(−13)	1.08(−12)	4.90(−15)	1.79(−13)
300	3.38(−12)	2.71(−14)	9.81(−13)	2.12(−12)	1.41(−14)	4.31(−13)
500	6.65(−12)	9.25(−14)	2.70(−12)	4.98(−12)	5.88(−14)	1.38(−12)
700	1.03(−11)	2.10(−13)	5.19(−12)	8.62(−12)	1.53(−13)	2.92(−12)
1000.....	1.60(−11)	4.88(−13)	1.00(−11)	1.50(−11)	4.12(−13)	6.28(−12)
1500.....	2.52(−11)	1.21(−12)	2.00(−11)	2.68(−11)	1.19(−12)	1.39(−11)
2000.....	3.37(−11)	2.18(−12)	2.21(−11)	3.88(−11)	2.37(−12)	2.31(−11)
2500.....	4.14(−11)	3.31(−12)	4.22(−11)	5.04(−11)	3.89(−12)	3.31(−11)
3000.....	4.82(−11)	4.54(−12)	5.32(−11)	6.13(−11)	5.65(−12)	4.32(−11)
3500.....	5.42(−11)	5.80(−12)	6.37(−11)	7.13(−11)	7.55(−12)	5.31(−11)
4000.....	5.94(−11)	7.04(−12)	7.34(−11)	8.05(−11)	9.50(−12)	6.25(−11)
4500.....	6.40(−11)	8.23(−12)	8.24(−11)	8.87(−11)	1.14(−11)	7.13(−11)
5000.....	6.79(−11)	9.34(−12)	9.05(−11)	9.60(−11)	1.33(−11)	7.93(−11)

TABLE 4

COEFFICIENTS OF THE POLYNOMIAL FIT (eq. [4]) TO THE RATE COEFFICIENTS IN TABLE 3[a]

n	$a^{(n)}_{0,2\to 0,0}$	$a^{(n)}_{0,4\to 0,0}$	$a^{(n)}_{0,4\to 0,2}$	$a^{(n)}_{0,3\to 0,1}$	$a^{(n)}_{0,5\to 0,1}$	$a^{(n)}_{0,5\to 0,3}$
0.....	−9.464	−9.320	−8.983	−9.099	−8.852	−8.914
1.....	−6.508	−21.841	−9.652	−9.031	−25.832	−9.515
2.....	−133.513	−192.235	−206.642	−163.126	−231.377	−262.627
3.....	822.577	1432.446	1279.298	1020.071	1752.927	1626.641
4.....	−1798.540	−3334.971	−2791.453	−2229.331	−4130.745	−3593.403
5.....	1385.131	2656.107	2142.288	1708.834	3311.615	2782.833

[a] The rate coefficients resulting from the fit are in $cm^3\ s^{-1}$ and are valid in the temperature range $100 \le T \le 5000$ K.

TABLE 5

RO-VIBRATIONAL EXCITATION RATE COEFFICIENTS $k_{0,j\to 1,j'}(T)$ (in $cm^3\ s^{-1}$) FOR ORTHO- AND PARA-H_2 BETWEEN THE $v = 0$ AND $v = 1$ VIBRATIONAL LEVELS IN COLLISIONS WITH He AS FUNCTIONS OF TEMPERATURE

T(K)	$k_{0,0\to 1,0}(T)$	$k_{0,0\to 1,2}(T)$	$k_{0,2\to 1,0}(T)$	$k_{0,2\to 1,2}(T)$	$k_{0,1\to 1,1}(T)$	$k_{0,1\to 1,3}(T)$	$k_{0,3\to 1,1}(T)$	$k_{0,3\to 1,3}(T)$
100	5.50(−46)	1.80(−48)	6.40(−44)	9.10(−46)	5.89(−46)	1.12(−49)	7.11(−42)	1.94(−45)
200	4.06(−32)	1.82(−33)	3.39(−31)	6.56(−32)	4.74(−32)	4.96(−34)	7.58(−30)	1.20(−31)
300	4.14(−27)	4.98(−28)	1.39(−26)	7.27(−27)	4.90(−27)	2.10(−28)	1.71(−25)	1.17(−26)
500	1.02(−22)	3.12(−23)	1.49(−22)	2.06(−22)	1.30(−22)	1.94(−23)	1.21(−21)	3.12(−22)
700	1.32(−20)	6.55(−21)	1.24(−20)	2.93(−20)	1.81(−20)	4.91(−21)	8.80(−20)	4.42(−20)
1000.....	7.80(−19)	5.88(−19)	4.99(−19)	1.88(−18)	1.14(−18)	5.15(−19)	3.21(−18)	2.86(−18)
1500.....	2.99(−17)	3.27(−17)	1.38(−17)	7.65(−17)	4.67(−17)	3.27(−17)	7.99(−17)	1.18(−16)
2000.....	2.46(−16)	3.25(−16)	9.96(−17)	6.38(−16)	4.00(−16)	3.49(−16)	5.16(−16)	9.90(−16)
2500.....	1.01(−15)	1.48(−15)	3.88(−16)	2.61(−15)	1.70(−15)	1.68(−15)	1.83(−15)	4.08(−15)
3000.....	2.79(−15)	4.35(−15)	1.05(−15)	7.13(−15)	4.93(−15)	5.23(−15)	4.70(−15)	1.14(−14)

TABLE 6

COEFFICIENTS OF THE POLYNOMIAL FIT (eq. [4]) TO THE RATE COEFFICIENTS IN TABLE 5[a]

n	$a^{(n)}_{0,0\to1,0}$	$a^{(n)}_{0,0\to1,2}$	$a^{(n)}_{0,2\to1,0}$	$a^{(n)}_{0,2\to1,2}$	$a^{(n)}_{0,1\to1,1}$	$a^{(n)}_{0,1\to1,3}$	$a^{(n)}_{0,3\to1,1}$	$a^{(n)}_{0,3\to1,3}$
0.....	−10.121	−12.443	−6.061	−11.150	−8.838	−10.999	−7.767	−9.611
1.....	−15.632	94.748	−196.112	36.346	−56.184	41.736	−123.121	−21.277
2.....	−981.917	−2678.132	1672.781	−1659.294	−326.964	−1830.963	883.057	−678.269
3.....	6049.637	17545.374	−11905.109	10039.422	509.518	10548.295	−8357.904	1759.806
4.....	−30772.201	−69490.906	28826.544	−42073.520	−7887.635	−41975.637	25015.562	−7911.484
5.....	42235.591	92321.294	−33566.778	55036.462	6000.653	49532.745	−39124.439	888.212

[a] The rate coefficients resulting from the fit are in $cm^3\ s^{-1}$ and are valid in the temperature range $100 \leq T \leq 3000$ K.

vibrational transition rates in He–H_2 collisions over a wide range of temperature.

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