

QUANTUM MECHANICAL CALCULATIONS OF ROTATIONAL TRANSITIONS IN H-H₂ COLLISIONS

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ABSTRACT

We report quantum mechanical cross sections and rate coefficients for rotational transitions due to collisions of hydrogen atoms with hydrogen molecules. The sensitivity of the results to the nature of the potential energy surface and to the scattering formulation is investigated. We find that the rigid rotor and harmonic oscillator approximations are inadequate to describe the dynamics. We make use of the most reliable of the potential energy surfaces in a close-coupled description of the nonreactive scattering that takes the vibrational motion into account, and we calculate rate coefficients for rotational transitions at temperatures below 1000 K, where the reactive channels may be neglected.

Subject headings: molecular data — molecular processes

1. INTRODUCTION

The rate coefficients of rotational transitions of H₂ induced by collisions with hydrogen atoms are central parameters in the interpretation of the rotational populations of H₂ derived from observations of ultraviolet interstellar absorption lines. They also enter into the quantitative analysis of the infrared emission of H₂ seen in photon-dominated regions and shocked regions of the interstellar medium. Rotational excitation is a major cooling mechanism in interstellar clouds and in objects formed in the early universe. Pure rotational transitions have been observed in emission from several extragalactic sources using the short-wavelength spectrometer on board the *Infrared Space Observatory* (Kunze et al. 1996; Rigolopou et al. 1996; Sturm et al. 1996; Timmerman et al. 1996; Wright et al. 1996).

Rotational transitions in collisions of hydrogen atoms with hydrogen molecules have been the subject of many theoretical investigations (Allison & Dalgarno 1967; Green & Truhlar 1979; Sun & Dalgarno 1994; Flower & Wroe 1996; Boothroyd et al. 1996; Flower 1997). Full quantum calculations of rotational excitation cross sections at low velocities that go beyond the rigid rotor approximation and include all the important reactive and nonreactive channels were performed by Sun & Dalgarno (1994). These calculations were based on the DMBE potential (Varandas et al. 1987), which was thought to be more accurate than the older LSTH potential (Truhlar & Horowitz 1978). It gave rate coefficients much larger than those obtained using the LSTH potential (Green & Truhlar 1979). Lepp, Buch, & Dalgarno (1995), who carried out semiclassical calculations with several interaction potentials, demonstrated that these differences are largely due to the potential energy surfaces. Boothroyd et al. (1996) conducted a critical examination of the LSTH and DMBE potentials, along with their own BKMP (Boothroyd et al. 1991) potential, which we label BKMP1. They concluded that the LSTH and DMBE potentials were too unconstrained at the intermediate distances (~ 3 – 5 a.u.) most responsible for low-energy rotational excitation. The BKMP1 potential extended the

LSTH potential to include new data, but it too was weakly constrained in the critical interaction region. A refined potential was developed, BKMP2 (Boothroyd et al. 1996), that used the same functional form as BKMP1, but with additional constraints.

At about the same time, calculations of nonreactive cross sections within the rigid rotor approximation were performed by Flower & Wroe (1996) and Flower (1997) using the BKMP1 potential. Their resulting cross sections are about an order of magnitude smaller than those obtained by Sun & Dalgarno (1994) using the DMBE potential. However, because the rigid rotor approximation may underestimate the magnitude of the rotational cross sections, it is not clear how much of this difference is due to the potential and how much to the scattering approximation.

In their detailed study of H₃ potential energy surfaces, Boothroyd et al. (1996) also performed quasi-classical trajectory calculations for the LSTH, DMBE, BKMP1, and BKMP2 potential surfaces, and confirmed the sensitivity of the low-energy rotational transition rate coefficients to the nature of the surface. As a result, they suggested that in order to obtain reliable low-temperature rate coefficients, new quantum mechanical calculations using the BKMP2 surface are required.

In the present paper, we complete the investigation by performing full quantum mechanical calculations of the rotational cross sections and rate coefficients for each of the four potential energy surfaces. We compare the results obtained using the rigid rotor approximation with those that incorporate the vibrational motion. The contribution from reactive scattering is small at low velocities (Park & Light 1989; Takayanagi & Masaki 1991; Sun & Dalgarno 1994), so we consider only nonreactive collisions. For this purpose, we employed the close-coupling computer code MOLSCAT developed by Hutson & Green (1994).

2. CALCULATIONS

The Arthurs-Dalgarno (1960) formalism is used to represent the cross section for transition of a diatom from rotational level j to rotational level j' by collision with an atom

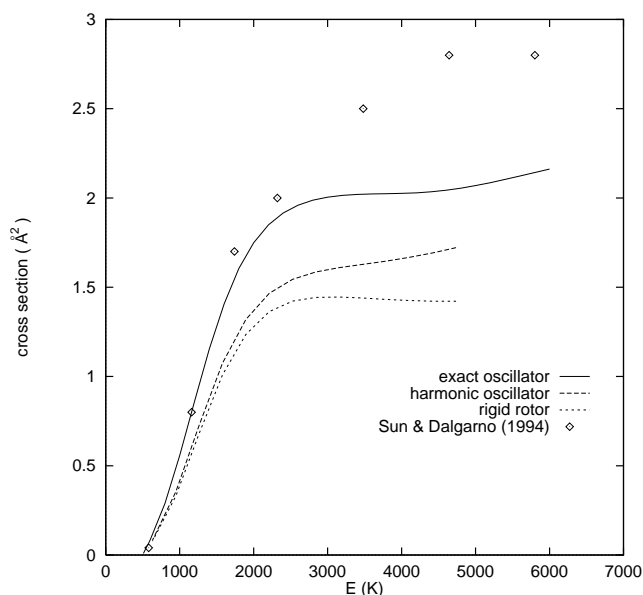


FIG. 1a

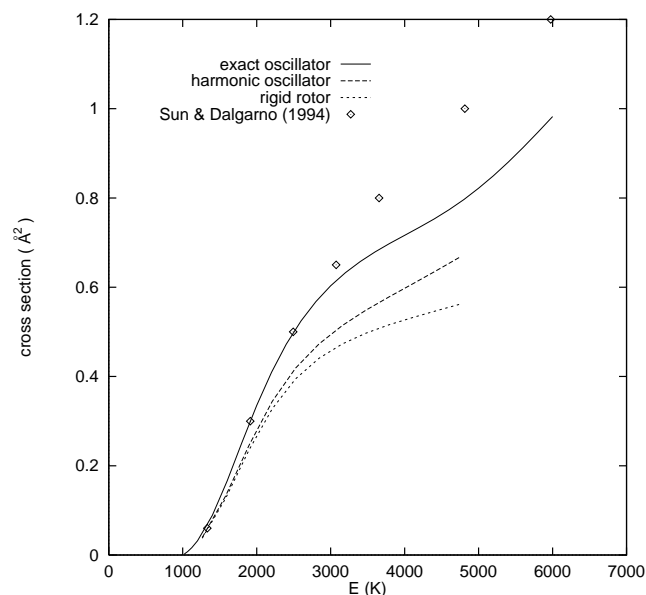


FIG. 1b

FIG. 1.—Rotational cross sections using DMBE potential surface. The present results are compared with those of Sun & Dalgarno (1994) and also with rigid rotor and harmonic oscillator approximations for (a) $0 \rightarrow 2$ and (b) $1 \rightarrow 3$ transitions.

at total energy E as

$$\sigma_{jj'}(E) = \frac{\pi}{k_j^2} \sum_{j=0}^{J_{\max}} \left(\frac{2J+1}{2j+1} \right) \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} |S_{jl,j'l'}^J(E)|^2. \quad (1)$$

The ground-state vibrational wave function was expanded in a Hermite polynomial basis set consisting of 10 functions, with an angular frequency parameter of 4000 cm^{-1} . The harmonic oscillator approximation, with an angular frequency of 4395 cm^{-1} , was also considered. Vibrational coupling was neglected in all calculations described below.

Figures 1a and 1b show $\sigma_{02}(E)$ and $\sigma_{13}(E)$, respectively, for the DMBE potential obtained using numerically exact

and harmonic oscillator approximations to the vibrational wave function, and using the rigid rotor approximation where the vibrational motion is neglected. The total energy E is expressed as an effective temperature $E = k_B T$, where k_B is Boltzmann's constant; threshold energies are 510 K and 845 K, respectively, for the $0 \rightarrow 2$ and $1 \rightarrow 3$ transitions. Also shown in Figures 1a and 1b are the calculated cross sections of Sun & Dalgarno (1994), which include reactive channels and take vibrational motion into account. The rigid rotor and harmonic oscillator approximations significantly underestimate the rotational cross sections, while the calculations using the exact vibrational wave functions give excellent agreement at low energy with those of Sun & Dalgarno (1994).

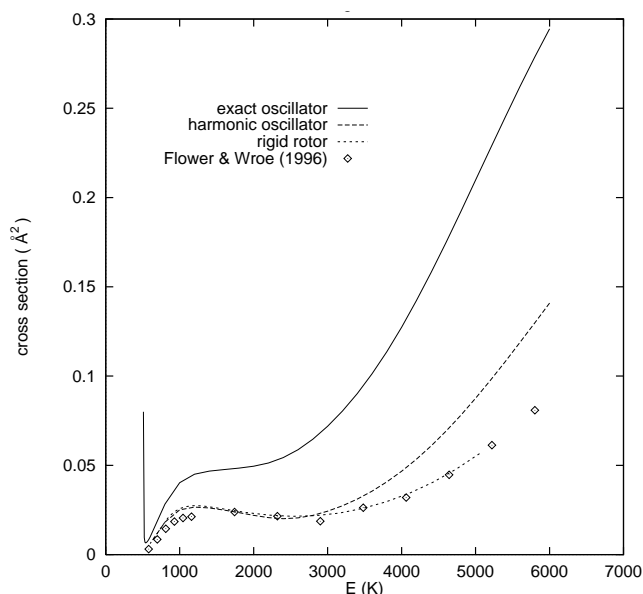


FIG. 2a

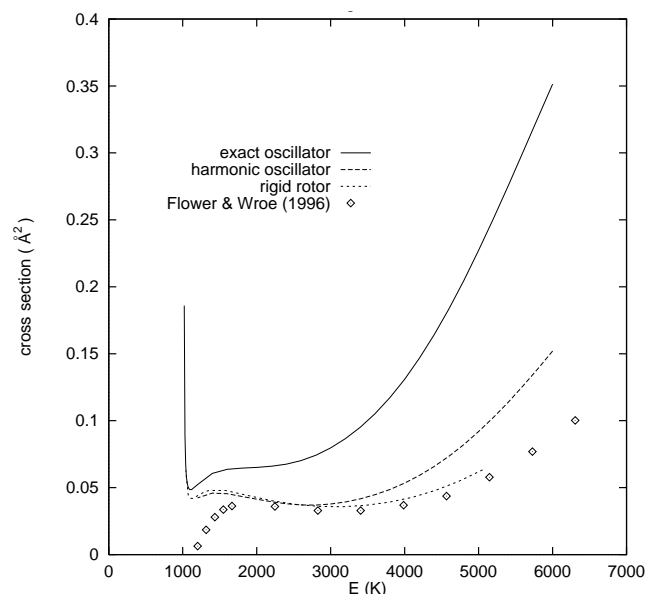


FIG. 2b

FIG. 2.—Rotational cross sections using BKMP1 potential surface. The present results are compared with those of Flower & Wroe (1996) and also with rigid rotor and harmonic oscillator approximations for (a) $2 \rightarrow 0$ and (b) $3 \rightarrow 1$ transitions.

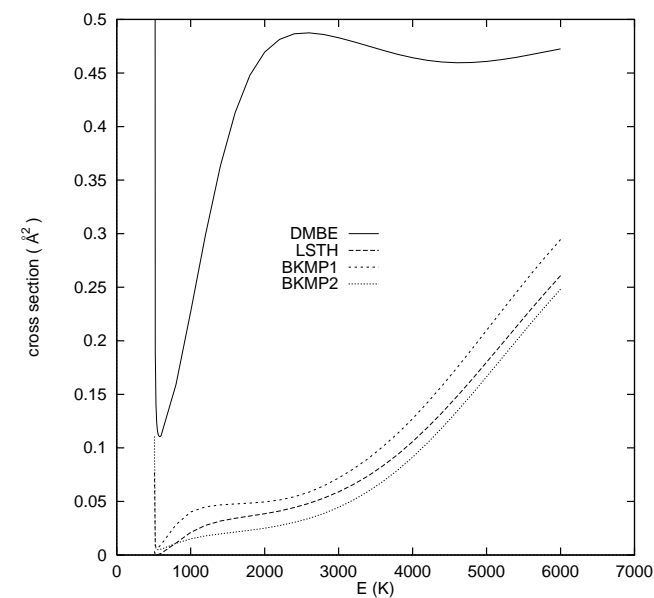


FIG. 3a

FIG. 3.—Rotational cross sections using DMBE, LSTH, BKMP1, and BKMP2 potential surfaces. The results are shown for (a) 2 → 0 and (b) 3 → 1 transitions.

Figures 2a and 2b show $\sigma_{20}(E)$ and $\sigma_{31}(E)$, respectively, for the BKMP1 potential obtained using the numerically exact vibrational wave functions along with the rigid rotor and harmonic oscillator approximations. Also shown in Figures 2a and 2b are the calculated cross sections of Flower & Wroe (1996), which use the rigid rotor approximation. Our rigid rotor calculations reveal slight differences, presumably numerical in origin, from those of Flower & Wroe (1996) for $\sigma_{31}(E)$. The upturn of the cross sections near threshold, apparent in Figures 2a and 2b, is a real physical effect arising from Wigner’s law (Balakrishnan, Forrey, & Dalgarno 1997).

Figures 3a and 3b compare $\sigma_{20}(E)$ and $\sigma_{31}(E)$, respectively, for all four potentials, using the numerically exact vibrational wave functions. The DMBE cross sections are significantly greater than those obtained from the LSTH, BKMP1, and BKMP2 potentials, thus supporting the conclusions of Lepp et al. (1995) and Boothroyd et al. (1996).

The cross sections are not sensitive to vibrational coupling when $E < 3000$ K and should therefore provide reliable rotational rate coefficients when $T < 1000$ K.

The rotational rate coefficients are calculated from the definition

$$k_{jj'}(T) = \sqrt{\frac{8}{\pi \mu k_B^3 T^3}} \int_0^\infty \sigma_{jj'}(E') \exp\left(-\frac{E'}{k_B T}\right) E' dE', \quad (2)$$

where T is here the kinetic temperature, μ is the reduced mass, and E' is the center of mass collision energy. Table 1 com-

TABLE 1

RATE COEFFICIENTS FOR ROTATIONAL TRANSITIONS AT $T = 1000$ K					
$J \rightarrow J'$	LSTH	DMBE ^a	BKMP1 ^b	BKMP1	BKMP2
0 → 2.....	1.1	7.3	0.50	1.3	0.86
1 → 3.....	0.4	2.0	0.25	0.6	0.34

NOTE.—Rate coefficients are in units of $10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Unless indicated otherwise, all calculations use the exact $v = 0$ vibrational wave function.
^a Sun & Dalgarno 1994.
^b Flower & Wroe 1996.

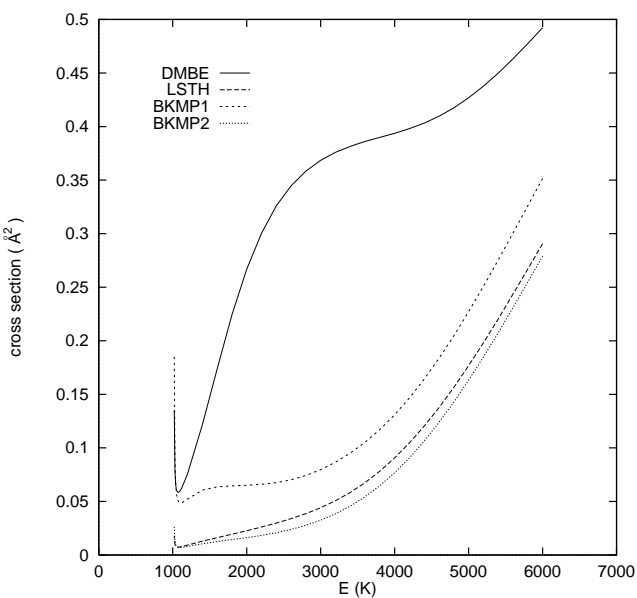


FIG. 3b

pares the rate coefficients for rotational excitation from nonreactive scattering at 1000 K using each of the four potential energy surfaces. The results are very sensitive to the choice of the potential. Table 2 shows rate coefficients for rotational excitation from nonreactive scattering using the BKMP2 potential, which we believe to be the most reliable. The rate coefficients in Table 2 should replace the values for nonreactive collisions given in Sun & Dalgarno (1994). The rate coefficients for reactive collisions of Sun & Dalgarno (1994) are less sensitive to the potential energy surface and are the most accurate available.

The rate coefficients for de-excitation can be reproduced to within the accuracy of the calculations when $10 < T < 1000$ K by the cubic fit

$$k_{jj'}(T) = \sum_{n=0}^3 c_{jj'}^{(n)} T^n, \quad (3)$$

where the $c_{jj'}^{(n)}$ are given in Table 3. The flexibility afforded by polynomial interpolation such as given by equation (3) allows a large range of temperatures to be covered. However, the fits fail outside the given temperature range and should not be used when $T < 10$ K or $T > 1000$ K. The

TABLE 2
RATE COEFFICIENTS FOR ROTATIONAL TRANSITIONS

T (K)	$k_{02}(T)$	$k_{13}(T)$	$k_{24}(T)$	$k_{35}(T)$
100.....	4.4(−15)	7.9(−17)	1.6(−18)	1.8(−20)
200.....	1.2(−13)	9.0(−15)	8.8(−16)	6.0(−17)
300.....	4.2(−13)	5.5(−14)	9.2(−15)	1.3(−15)
400.....	8.9(−13)	1.6(−13)	3.7(−14)	8.4(−15)
500.....	1.5(−12)	3.3(−13)	1.0(−13)	3.2(−14)
600.....	2.4(−12)	6.2(−13)	2.2(−13)	8.9(−14)
700.....	3.5(−12)	1.0(−12)	4.3(−13)	2.0(−13)
800.....	4.8(−12)	1.6(−12)	7.5(−13)	4.0(−13)
900.....	6.6(−12)	2.4(−12)	1.2(−12)	6.9(−13)
1000.....	8.6(−12)	3.4(−12)	1.8(−12)	1.1(−12)

NOTE.—Rate coefficients in units of $\text{cm}^3 \text{ s}^{-1}$ for rotational transitions using the exact $v = 0$ vibrational wave function with the BKMP2 potential.

TABLE 3

COEFFICIENTS OF THE POLYNOMIAL FITS TO THE TEMPERATURE
DEPENDENCE OF THE RATE COEFFICIENTS FOR
ROTATIONAL DE-EXCITATION

n	$c_{20}^{(n)}$	$c_{31}^{(n)}$	$c_{42}^{(n)}$	$c_{53}^{(n)}$
0.....	2.93(−14)	8.34(−14)	7.57(−14)	2.95(−14)
1.....	1.21(−15)	5.97(−16)	2.65(−16)	−1.21(−16)
2.....	2.16(−19)	7.76(−19)	2.14(−19)	5.53(−19)
3.....	1.32(−21)	1.72(−21)	2.65(−21)	2.51(−21)

NOTE.—Fits are valid when $10 < T < 1000$ K.

corresponding excitation rate coefficients are obtained from detailed balance,

$$(2j+1)k_{jj'}(T) = (2j'+1)k_{j'j}(T) \exp [-(E_{j'} - E_j)/k_B T]. \quad (4)$$

The cooling rate coefficients are obtained from the excitation rate coefficients by multiplying them by the energy difference between the initial and final rotational states. These are given in Table 4 for $70 < T < 1000$ K.

TABLE 4

COOLING RATE COEFFICIENTS FOR ROTATIONAL EXCITATION

T (K)	$q_{02}(T)$	$q_{13}(T)$	$q_{24}(T)$	$q_{35}(T)$
70	2.6(−29)	2.1(−31)	1.6(−33)	5.3(−36)
80	7.1(−29)	9.9(−31)	1.3(−32)	8.1(−35)
90	1.6(−28)	3.4(−30)	7.0(−32)	6.8(−34)
100	3.1(−28)	9.2(−30)	2.7(−31)	3.8(−33)
200	8.3(−27)	1.0(−27)	1.4(−28)	1.2(−29)
300	3.0(−26)	6.4(−27)	1.5(−27)	2.7(−28)
400	6.3(−26)	1.8(−26)	5.9(−27)	1.7(−27)
500	1.1(−25)	3.9(−26)	1.6(−26)	6.6(−27)
600	1.7(−25)	7.2(−26)	3.6(−26)	1.8(−26)
700	2.4(−25)	1.2(−25)	7.0(−26)	4.1(−26)
800	3.4(−25)	1.9(−25)	1.2(−25)	8.0(−26)
900	4.6(−25)	2.8(−25)	1.9(−25)	1.4(−25)
1000.....	6.0(−25)	3.9(−25)	2.9(−25)	2.2(−25)

NOTE.—Cooling rate coefficients $q_{jj'}(T)$ in units of $\text{ergs cm}^3 \text{s}^{-1}$ for rotational excitation using the exact $v = 0$ vibrational wave function with the BKMP2 potential.

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