

## ROTATIONAL EXCITATION OF H<sub>2</sub> IN COLLISION WITH H

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Received 1993 October 15; accepted 1993 December 3

### ABSTRACT

Rate coefficients for the reactive processes of ortho-para conversion in which the  $j = 0$  rotational level of molecular hydrogen is excited to the  $j = 1$  and  $j = 3$  level by impacts with hydrogen atoms are calculated for temperatures between 30 K and 1000 K using a fully converged complete close-coupled method. Rate coefficients are also obtained for the excitation from the  $j = 0$  to the  $j = 2$  rotational level and from the  $j = 1$  to the  $j = 3$  rotational level. The interference between the direct and reactive channels is taken into account as is the geometric phase resulting from the adiabatic separation of electronic and nuclear motion that generates the potential energy surface. Convenient analytic representations of the rate coefficients are presented.

*Subject headings:* atomic processes — molecular processes

### 1. INTRODUCTION

The distribution of molecular hydrogen between its ortho and para forms is an important aspect of the physics and chemistry of the atmospheres of the Jovian planets (Massie & Hunten 1982; Conrath & Gierasch 1984), and of interstellar molecular clouds (Dalgarno, Black, & Weisheit 1973; Spitzer, Cochran, & Hirshfeld 1974; Jura 1975; Dalgarno & Black 1977; Takayanagi, Sakimoto, & Onda 1987; Pineau des Forêts, Flower, & McCarroll 1991; Abgrall et al. 1992). Depending on the physical environments, conversions between ortho and para forms may be effected by reactive collisions between H and H<sub>2</sub> in which the rotational quantum number  $j$  changes by an odd number. Rotational excitations in which  $j$  changes by an even number in nonreactive and reactive collisions of H with H<sub>2</sub> are important to the distribution of the relative populations of the rotational levels of H<sub>2</sub> and to the cooling efficiency of hydrogen-rich gas.

Because of its fundamental significance to the theory of chemical reactions, the reactive scattering of H by H<sub>2</sub> has received considerable attention, and powerful methods have been developed for and applied to the calculation of the cross sections (Schatz & Kuppermann 1976; Mladenovic et al. 1988; Zhang & Miller 1988, 1989; Park & Light 1989; Walker & Light 1989a, b; Manolopoulos & Wyatt 1989, 1990; Launay & Le Dourneuf 1989; Miller & Zhang 1991). Most of the effort has been devoted to an exploration of the dynamical resonances that may or may not have been detected experimentally at energies near 1 eV (Nieh & Valentini 1988, 1990; Kliner, Adelman, & Zare 1991), but some calculations of reactive scattering at lower temperatures have been carried out (Park & Light 1989; Takayanagi & Masaki 1991), and Mandy & Martin (1991, 1992, 1993) have used a semiclassical procedure to calculate rate coefficients for all the possible reactive and nonreactive rovibrational transitions in H<sub>2</sub> for temperatures down to 600 K.

No calculations of rotational transitions at lower temperatures have been reported since the calculations of Green & Truhlar (1979) who did close-coupling calculations of nonreactive rotational excitation processes within the rigid rotor approximation, neglecting any interference between reactive and nonreactive channels. They obtained rate coefficients considerably smaller than the results of earlier close-coupling calculations of Allison & Dalgarno (1967), Wolken, Miller, & Karplus (1972), Chu & Dalgarno (1975), and McGuire & Kruger (1975).

In many astrophysical applications, rate coefficients determined by Elitzur & Watson (1978) by interpolation and extrapolation of the early calculations (Dalgarno, Henry, & Roberts 1966; Allison & Dalgarno 1967; Nishimura 1968) have been used.

It is now practical to carry out numerically exact calculations of the rotational excitation cross sections at low velocities which do not use the rigid rotor approximation and which include all the important reactive and nonreactive channels. We employ here the generalized Newton variational principle GNVP (Schwenke et al. 1988; Sun et al. 1989) to calculate the cross sections for the  $j = 0 \rightarrow 1, 2, 3$  and  $j = 1 \rightarrow 0, 2, 3$  transitions of H<sub>2</sub> in its lowest vibrational state with H at total energies below 0.9 eV. We include all the contributing states, both open and closed, and obtain the nonreactive and reactive  $S$  matrix elements in the same calculation. The nonreactive calculations of Green & Truhlar (1979) were based on the LSTH potential energy surface (Truhlar & Horowitz 1978, 1979). We make use of the modified DMBE version (Varandas et al. 1987) which is designed to be more accurate at large separations of H and H<sub>2</sub>.

### 2. THEORY

In the Arthurs-Dalgarno (1960) representation, the cross section for the rotational transition of a diatom from rotational level  $j$  to rotational level  $j'$  by atom impact at a total energy  $E$  is given by

$$\sigma(E, j \rightarrow j') = \frac{\pi}{k_j^2} P(E, j \rightarrow j'), \quad (1)$$

where  $k_j$  is the wavenumber of the relative motion of the colliding particles and  $P(E, j \rightarrow j')$  is given in terms of the  $S$ -matrix element  $S^J$  for the  $J$ th partial wave by the expression

$$P(E, j \rightarrow j') = (2j + 1)^{-1} \sum_{J=0}^{J_{\max}} (2J + 1) \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} |S^J(E, jl \rightarrow j'l')|^2. \quad (2)$$

The  $S$ -matrix for collisions of H and H<sub>2</sub> is given by

$$|S^J(E, jl \rightarrow j'l')|^2 = \begin{cases} |S_n^J(E, jl \rightarrow j'l') + S_r^J(E, jl \rightarrow j'l')|^2, & j'j', \text{ even}; \\ |S_n^J(E, jl \rightarrow j'l') - S_r^J(E, jl \rightarrow j'l')|^2 + 2|S_n^J(E, jl \rightarrow j'l')|^2, & j, j' \text{ odd}; \\ 3|S_r^J(E, jl \rightarrow j'l')|^2, & j \text{ even}, j' \text{ odd}; \\ |S_r^J(E, jl \rightarrow j'l')|^2, & j \text{ odd}, j' \text{ even}; \end{cases} \quad (3)$$

where  $S_n^J$  and  $S_r^J$  are the nonreactive and reactive  $S$ -matrix elements, respectively. Equation (3) was obtained from the formalism of Miller (1969) except that here we have reversed the sign in front of  $S_r^J$  to compensate for the geometric phase arising from the adiabatic separation of the electronic and nuclear motion (Mead & Truhlar 1979; Mead 1980; Lepetit & Kuppermann 1990). The permutation symmetry for three identical nuclei leads to an irreducible representation, which reduces the size of the problem to one third (Miller 1969; Schwenke et al. 1989).

The rate coefficient is defined as

$$k(T, j \rightarrow j') = \frac{\hbar^2}{2\pi} \left( \frac{2\pi}{\mu k_B T} \right)^{3/2} \int_{E_0}^{\infty} dE \exp \left( -\frac{E - E_j}{k_B T} \right) P(E, j \rightarrow j'), \quad (4)$$

where  $k_B$  is Boltzmann's constant;  $T$  is the temperature;  $\mu$  is the reduced mass of the colliding system, H-H<sub>2</sub>;  $E_j$  is the rotational energy of level  $j$  of H<sub>2</sub>; and  $E_0$  is the larger value of  $E_j$  and  $E_{j'}$ .

### 3. CALCULATIONS

We calculated the  $S$ -matrix up to a total energy of 0.9 eV, varying the basis function size to ensure numerical convergence to better than 5%. As the energy increases, more partial waves contribute, requiring more extensive calculations.

Reactive processes only occur at low values of the angular momentum  $J$  at which the projectile may overcome the centrifugal barrier and enter the short-range reaction region. At high  $J$ , the reactive channels may be neglected and the calculation simplifies to a nonreactive problem which requires much less computational effort. Near  $E = 0.8$  eV, for example, the reactive transition amplitudes become very small beyond  $J = 15$ , but the nonreactive ones do not until  $J = 40$ . According to equation (3), the integral cross section has more contributions from high- $J$   $S$ -matrix elements due to the weighting factor  $2J + 1$  and is less sensitive to the reactive processes that occur at low  $J$ . This is not true for differential cross sections where the low- $J$  contributions may dominate at particular scattering angles. In practice, we found also that below 1000 K it is a valid approximation to neglect the closed rovibrational channels and the reactive channels for the para-para and ortho-ortho transitions.

Figures 1 and 2 show the calculated cross sections for the  $j = 0 \rightarrow 1, 2, 3$  and  $j = 1 \rightarrow 0, 2, 3$  transitions, from which we obtained rate coefficients with an error of less than 15%. We used cubic-spline fitting for the calculated  $P(E)$ , or  $\log P(E)$  in the lower energy region where  $P(E)$  grows exponentially.

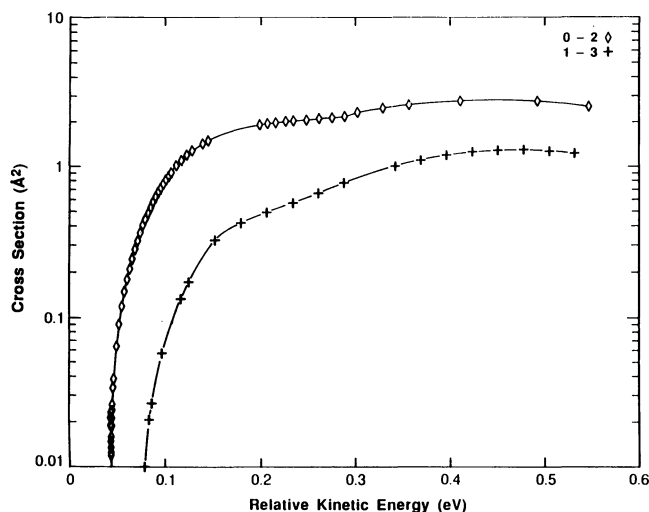


FIG. 1

FIG. 1.—The cross sections for the transition from  $j = 0$  to  $j = 2$  and from  $j = 1$  to  $j = 3$

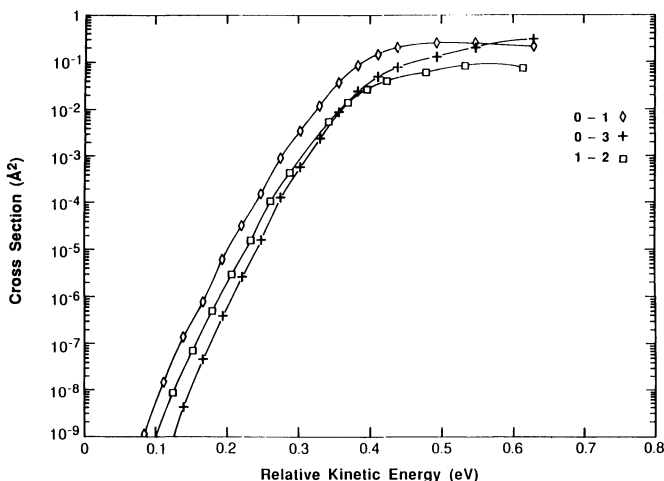


FIG. 2

FIG. 2.—The cross sections for the transition from  $j = 0$  to  $j = 1, 3$  and from  $j = 1$  to  $j = 2$

Table 1 lists our calculated rate coefficients  $k(j \rightarrow j')$  for the nonactive rotational excitations  $j = 0 \rightarrow 2$  and  $j = 1 \rightarrow 3$ . The rate coefficients of the inverse transitions can be obtained according to

$$k(j' \rightarrow j) = \frac{2j+1}{2j'+1} \exp\left(\frac{E_j - E_{j'}}{k_B T}\right) k(j \rightarrow j') \times \begin{cases} 3 & j \text{ even and } j' \text{ odd} , \\ \frac{1}{3} & j \text{ odd and } j' \text{ even} , \\ 1 & \text{otherwise} . \end{cases} \quad (5)$$

The energies of the rotational levels of H<sub>2</sub> are  $(E_j - E_0)/k_B = 170$  K, 509 K, and 1014 K for  $j = 1, 2, 3$ , respectively.

The values for the  $0 \rightarrow 2$  and  $1 \rightarrow 3$  transitions are much larger than the rate coefficients calculated by Green & Truhlar (1979) and by Mandy & Martin (1993) which are also listed in Table 1. Although the calculations of Green & Truhlar (1979) used the rigid rotor approximation and neglected closed channels and reactive channels, there seems little question that the large discrepancies arise primarily from the different potential energy surfaces employed in the two calculations. Given that they used a semiclassical method which tends to overestimate the rate coefficients at low temperatures, the calculations of Mandy & Martin (1993), who also adopted the LSTH surface but did not use the rigid rotor approximation or neglect the reactive channels, are consistent with the results of Green & Truhlar (1979).

Further evidence is provided by unpublished semiclassical calculations by S. Lepp (1993, private communication) and by W. J. Keogh and P. G. Martin (1993, private communication) who obtain much larger values of  $k(0 \rightarrow 2)$  and  $k(1 \rightarrow 3)$  for the DMBD surface than for the LSTH surface.

It is claimed by Varandas et al. (1987) that their potential is superior to the LSTH potential at intermediate and long-range separations of H and H<sub>2</sub>. If so, the rate coefficients we have presented in Table 1 are preferable to those of Green & Truhlar (1979) and Mandy & Martin (1993). By chance, they are of the same order of magnitude as the early calculations of Allison & Dalgarno (1967). However P. G. Martin (1993, private communication) has informed us of a recent extension of the calculations of Boothroyd et al. (1991), and it yields a potential energy surface closer to the LSTH surface.

Our calculated rate coefficients for the reactive excitation and deexcitation processes are presented in Table 2. In contrast to the nonreactive excitation process, the values agree well at least at the common temperature of 1000 K with the semiclassical results of Mandy & Martin (1993). At 1000 K we obtain  $k(0 \rightarrow 1) = 7.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ ,  $k(0 \rightarrow 3) = 2.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , and  $k(1 \rightarrow 2) = 2.1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , whereas they calculated, respectively,  $6.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ ,  $4.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , and  $1.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ . The different potential energy surfaces used are quite similar at shorter distances of approach where reaction occurs. The agreement supports the utility of the semiclassical method above 600 K (Mandy & Martin 1993). Takayanagi & Masaki (1991) have used a simplified  $J_z$ -conserving coupled states method. With the LSTH surface they obtain  $k(1 \rightarrow 0) = 1.9 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$  and  $4.4 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$  at 200 K and 100 K, while we obtain  $9.8 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$  and  $5.4 \times 10^{-22} \text{ cm}^3 \text{ s}^{-1}$ . At low temperatures, the  $J_z$  conserving method is probably inadequate though some of the differences are due to the potentials. Experimental data are available for thermal rate coefficients between 300 K and 444 K. Schultz & LeRoy (1965) give an analytic fit to the data, reproduced in the review of Schofield (1967). We have complete results only for initially populated  $j = 0$  and  $j = 1$  levels so that no comparison is possible.

TABLE 1  
RATE COEFFICIENTS FOR THE  $0 \rightarrow 2$  AND  $1 \rightarrow 3$  ROTATIONAL EXCITATION TRANSITION OF  
H<sub>2</sub> BY H IMPACT<sup>a</sup>

<i>T</i> (K)	0 → 2			1 → 3		
	1 <sup>b</sup>	2 <sup>c</sup>	3 <sup>d</sup>	1 <sup>b</sup>	2 <sup>c</sup>	3 <sup>d</sup>
30.....	2.7 (−19)	...	...	9.2 (−25)	...	...
40.....	2.1 (−17)	...	...	1.2 (−21)	...	...
50.....	3.0 (−16)	...	...	9.4 (−20)	...	...
60.....	1.8 (−15)	...	...	1.8 (−18)	...	...
70.....	6.6 (−15)	...	...	1.5 (−17)	...	...
80.....	1.8 (−14)	...	...	7.5 (−17)	...	...
90.....	4.0 (−14)	...	...	2.7 (−16)	...	...
100.....	7.7 (−14)	1.0 (−15)	...	7.7 (−16)	7.5 (−17)	...
150.....	6.2 (−13)	...	...	1.9 (−14)	...	...
200.....	1.9 (−12)	...	...	1.1 (−13)	...	...
300.....	7.2 (−12)	9.7 (−14)	...	7.4 (−13)	4.4 (−14)	...
400.....	1.5 (−11)	...	...	2.1 (−12)	...	...
500.....	2.4 (−11)	3.6 (−13)	...	4.1 (−12)	2.0 (−13)	...
600.....	3.4 (−11)	...	...	6.7 (−12)	...	...
700.....	4.4 (−11)	...	...	9.7 (−12)	...	...
800.....	5.4 (−11)	...	...	1.3 (−11)	...	...
900.....	6.4 (−11)	...	...	1.6 (−11)	...	...
1000.....	7.3 (−11)	2.1 (−12)	9.5 (−12)	2.0 (−11)	1.2 (−12)	4.0 (−12)

<sup>a</sup> Units:  $\text{cm}^3 \text{ s}^{-1}$ ; number in parentheses is the power of 10.

<sup>b</sup> This work.

<sup>c</sup> Green & Truhlar 1979.

<sup>d</sup> Mandy & Martin 1993.

TABLE 2  
RATE COEFFICIENTS FOR THE  $0 \rightarrow 1$ ,  $3$ , AND  $1 \rightarrow 2$   
ROTATIONAL EXCITATION TRANSITION OF  $\text{H}_2$   
BY H IMPACT<sup>a</sup>

$T(\text{K})$	$0 \rightarrow 1$	$0 \rightarrow 3$	$1 \rightarrow 2$
100.....	1.0 (−22)	1.0 (−24)	1.8 (−23)
150.....	8.5 (−21)	5.1 (−22)	1.9 (−21)
200.....	4.2 (−19)	5.7 (−20)	1.1 (−19)
300.....	9.3 (−17)	2.2 (−17)	2.3 (−17)
400.....	2.1 (−15)	6.1 (−16)	5.2 (−16)
500.....	1.5 (−14)	5.0 (−15)	3.7 (−15)
600.....	5.6 (−14)	2.1 (−14)	1.4 (−14)
700.....	1.4 (−13)	6.0 (−14)	3.7 (−14)
800.....	2.9 (−13)	1.3 (−13)	7.6 (−14)
900.....	5.1 (−13)	2.4 (−13)	1.3 (−13)
1000.....	7.8 (−13)	3.9 (−13)	2.1 (−13)

<sup>a</sup> Units:  $\text{cm}^3 \text{s}^{-1}$ ; number in parentheses is the power of 10.

The uncertainties in the calculated rate coefficients may be as large as 15% at the lowest and largest temperatures. For the transitions from  $j = 0$  to  $j = 1, 3$  and  $j = 1$  to  $j = 2$ , the analytical expressions

$$k(0 \rightarrow 1) = \exp [(5.30 - 460/T)^2 - 21.2] \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}, \quad (6)$$

$$k(0 \rightarrow 3) = \exp [(6.36 - 373/T)^2 - 34.5] \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}, \quad (7)$$

$$k(1 \rightarrow 2) = \exp [(5.35 - 454/T)^2 - 23.1] \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}. \quad (8)$$

provide fits to our results to within the accuracy of the calculated rate coefficients.

The rate coefficients for reactive scattering should be reliable in that they are determined by the attractive potential at separations where the three potential energy surfaces do not differ much. The rate coefficients for the nonreactive  $0 \rightarrow 2$  and  $1 \rightarrow 3$  pure rotational transitions are sensitive to the intermediate and long-range interactions which are still uncertain.

We are indebted to S. Green, W. J. Keogh, S. Lepp, M. E. Mandy, P. G. Martin, and W. Huo for discussions and for showing us unpublished data. This work was supported by NASA grant NAGW-1561. It utilized the Cray-2 supercomputer of the National Center for Supercomputing Applications, University of Illinois at Urbana-Champaign.

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