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THE RADIATIVE ASSOCIATION OF H AND D

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ABSTRACT

The formation of the deuterated hydrogen molecule HD by the radiative association of H and D is investigated. Spontaneous association and stimulated association in a blackbody radiation field are considered. For a collision temperature of 1000 K, the rate coefficient for spontaneous radiative association is $1.0 \times 10^{-26} \text{ cm}^3 \text{ s}^{-1}$. At the same collision temperature, the rate coefficient is enhanced by stimulated association to $1.8 \times 10^{-26} \text{ cm}^3 \text{ s}^{-1}$ for a radiation temperature of 10,000 K. The role of radiative association in the deuterium chemistry of the early universe is discussed.

Subject headings: atomic processes — early universe

1. INTRODUCTION

The deuterated hydrogen molecule HD is the second most abundant molecule after H_2 predicted to be produced in the postrecombination era of the early universe (Lepp & Shull 1984). During the collapse of primordial clouds it could become a significant coolant as the rotational-vibrational (RV) lines of H_2 become optically thick (Dalgarno & Wright 1972). HD has been observed by the Infrared Space Observatory in the atmospheres of Jupiter (Encrenaz et al. 1996) and Saturn (Griffin et al. 1996). Through exchange reactions

and abstraction reactions

HD participates in the deuterium fractionation of complex molecular ions XH^+ in interstellar clouds (see Rodgers & Millar 1996). In these environments, HD is formed primarily by the exchange reaction

(Dalgarno, Weisheit, & Black 1973).

In the postrecombination era, reaction (3) is effective for redshifts $z \lesssim 200$. For larger redshifts other processes may contribute more to the formation of HD, such as the radiative association of hydrogen and deuterium,

Its thermal rate coefficient was estimated by Lepp & Shull (1984) from classical arguments to be $\sim 10^{-25} \text{ cm}^3 \text{ s}^{-1}$.

We present a calculation of the rate coefficients for reaction (4) using a fully quantum mechanical method. With the extension of the theory of radiative association to include stimulated association (Stancil & Dalgarno 1997), we also calculate the rate coefficients for the formation of HD in a blackbody radiation field of temperature T_b . For a frequency ν_b the process may be represented by

The effect of reactions (4) and (5) is briefly discussed. Atomic units are used throughout unless otherwise noted.

2. MOLECULAR DATA

We adopt the accurate variational Born-Oppenheimer calculation of Wolniewicz (1993) for the $X^1\Sigma^+$ electronic ground-state potential energy for internuclear distances $R = 0.2a_0$ to $R = 12a_0$ with additional points computed by L. Wolniewicz (1996, private communication) for $13a_0 \leq R \leq 20a_0$. Adiabatic, relativistic, and radiative corrections (Wolniewicz 1993) are included. For $R > 20a_0$, the long-range dispersion expansion

$$V_L(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \frac{C_{11}}{R^{11}} - \frac{C_{12}}{R^{12}} \quad (6)$$

is fitted smoothly to the variational data with C_6 , C_8 , and C_{10} taken from Yan et al. (1996) and C_{11} and C_{12} from Bukta & Meath (1974). Further details on the potential are given by Zygelman et al. (1997).

A third-order cubic spline fitted to the potential gives a ground vibrational state dissociation energy D_0 of 36405.45 cm^{-1} , in good agreement with the calculated value 36405.774 cm^{-1} of Wolniewicz (1993) and the recent measurements of 36405.88 and 36405.83 cm^{-1} of Eyler & Melikechi (1993) and Balakrishnan, Vallet, & Stoicheff (1993), respectively. We find 18 vibrational levels and a total of 393 rotational levels.

Unlike H_2 , HD has a dipole moment that is nonzero as a consequence of the coupling of the electronic and nuclear motions. We adopt the ab initio HD dipole moment function of Ford & Browne (1977) for $R = 0.5a_0$ to $R = 3a_0$. For larger R , the dipole moment function is fitted to the form $A \exp(-BR)$. While there has been a long-standing discrepancy between the experimental and calculated HD dipole moment, the recent measurement of $(8.1 \pm 0.5) \times 10^{-4} \text{ D}$ (Wishnow, Ozier, & Gush 1992) is in good agreement with the theoretical value $8.31 \times 10^{-4} \text{ D}$ obtained by Ford & Browne (1977). As a further check, we calculated the rotational-vibrational transition probabilities, previously computed by Abgrall, Roueff, & Viala (1982), using the dipole moment function of Ford & Browne (1977), but an older potential. A random comparison finds agreement to better than 5% for transitions between vibrational levels with $v \lesssim 6$ for all rotational quantum numbers. For higher v the differences increase, with the greatest discrepancies occurring for large Δv . They may be caused by

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the assumed form of the dipole moment function for $R > 3a_0$, which is not explicitly given in Abgrall et al. (1982).

3. THEORY

In reaction (4), the formation of HD is stabilized by the spontaneous emission of a photon of frequency ν as the atoms approach with relative energy E in the vibrational continuum of the ground electronic state $X^1\Sigma^+$. The emission occurs into all bound states $v''J''$ of the X state, where v'' and J'' are the vibrational and rotational quantum numbers, respectively. The cross section for the spontaneous radiative association process, reaction (4), is given by (see Zygelman & Dalgarno 1990)

$$\sigma^{\text{sp}}(E) = \sum_{J'} \sum_{v''} p \sigma_J^{\text{sp}}(v'', E), \quad (7)$$

where the partial cross section is

$$\sigma_J^{\text{sp}}(v'', E) = \frac{64}{3} \frac{\pi^5}{c^3} \frac{\nu^3}{k^2} [J' M_{v'', J' - 1; k, J'}^2 + (J' + 1) M_{v'', J' + 1; k, J'}^2] \quad (8)$$

In equation (8), k is the momentum of relative motion; p is the probability of approach in the initial electronic state; J' is the initial rotational quantum number; and M is the electric dipole matrix element connecting the initial continuum and final RV states of the ground electronic state. The parameter p is equal to $\frac{1}{4}$ for the $X^1\Sigma^+$ state of HD. Since the dipole probabilities for bound-bound transitions are typically over 100 times larger than the quadrupole prob-

abilities (Abgrall et al. 1982), we neglect contributions from the latter.

The partial cross section for the sum of spontaneous association and stimulated association in a blackbody radiation field is given by

$$\sigma_J(v'', E) = \frac{\sigma_J^{\text{sp}}(v'', E)}{1 - \exp(-h\nu/k_b T_b)} \quad (9)$$

(Stancil & Dalgarno 1997). The rate coefficients are obtained by averaging the product of the relative velocity and the cross section over a Maxwellian velocity distribution characterized by the matter, or collision, temperature T_m .

4. RESULTS AND DISCUSSION

The total cross sections for stimulated and spontaneous radiative association are given in Figure 1 as a function of the energy E for radiation temperatures up to 10,000 K. The cross sections for $T_m = 0$ correspond to spontaneous radiative association (reaction [4]). The pronounced structures that appear are orbiting resonances in the elastic scattering of H and D.

The rate coefficients are displayed in Figure 2 as functions of T_m and T_b and are listed in Table 1. At $T_b = 5000$, 7000, and 10,000 K, stimulated emission increases the rate coefficients by factors of about 1.3, 1.5, and 1.8, respectively, for $T_m = 1000$ K.

Reaction (4) was included in the deuterium chemistry model of Stancil, Lepp, & Dalgarno (1997) for the postre-

TABLE 1
TOTAL, SPONTANEOUS PLUS STIMULATED, RADIATIVE ASSOCIATION RATE COEFFICIENTS
 α ($10^{-26} \text{ cm}^3 \text{ s}^{-1}$) FOR H + D AS A FUNCTION OF MATTER TEMPERATURE T_m AND
BLACKBODY RADIATION TEMPERATURE T_b

T_m (K)	T_b (K)							
	0	1000	3000	4000	5000	7000	9000	10000
10.....	0.65	0.65	0.68	0.71	0.75	0.83	0.93	0.98
20.....	0.83	0.83	0.87	0.91	0.96	1.08	1.20	1.27
30.....	0.83	0.83	0.88	0.92	0.97	1.08	1.21	1.28
40.....	0.81	0.81	0.86	0.90	0.95	1.06	1.19	1.25
50.....	0.79	0.80	0.85	0.89	0.94	1.05	1.17	1.24
60.....	0.79	0.79	0.84	0.89	0.93	1.05	1.17	1.24
70.....	0.79	0.80	0.85	0.89	0.94	1.06	1.19	1.26
80.....	0.80	0.81	0.87	0.91	0.96	1.08	1.21	1.28
90.....	0.82	0.83	0.88	0.93	0.98	1.11	1.24	1.32
100.....	0.83	0.84	0.90	0.95	1.01	1.13	1.28	1.35
150.....	0.91	0.93	1.00	1.06	1.12	1.27	1.44	1.52
200.....	0.97	0.99	1.07	1.13	1.21	1.37	1.55	1.65
300.....	1.04	1.05	1.14	1.21	1.29	1.48	1.68	1.78
400.....	1.06	1.07	1.16	1.24	1.33	1.52	1.73	1.84
500.....	1.06	1.07	1.17	1.25	1.34	1.54	1.75	1.86
600.....	1.06	1.07	1.17	1.25	1.34	1.54	1.76	1.87
700.....	1.05	1.06	1.16	1.24	1.33	1.53	1.75	1.85
800.....	1.04	1.05	1.15	1.23	1.32	1.52	1.73	1.84
900.....	1.02	1.03	1.13	1.21	1.30	1.50	1.71	1.81
1000.....	1.01	1.02	1.12	1.20	1.28	1.48	1.69	1.79
1500.....	0.95	0.97	1.06	1.13	1.21	1.39	1.59	1.68
2000.....	0.86	0.88	0.95	1.01	1.08	1.24	1.41	1.49
3000.....	0.76	0.77	0.82	0.87	0.93	1.06	1.20	1.26
4000.....	0.70	0.71	0.76	0.81	0.86	0.97	1.10	1.16
5000.....	0.63	0.64	0.68	0.71	0.76	0.86	0.96	1.02
6000.....	0.57	0.58	0.61	0.64	0.68	0.76	0.85	0.90
7000.....	0.52	0.52	0.55	0.58	0.61	0.68	0.76	0.80
8000.....	0.47	0.47	0.50	0.53	0.55	0.62	0.69	0.72
9000.....	0.44	0.44	0.46	0.48	0.51	0.56	0.63	0.66
10000.....	0.40	0.40	0.43	0.44	0.47	0.52	0.57	0.60

FIG. 1.—Cross sections (a_0^2) for stimulated plus spontaneous radiative association of H and D for various blackbody radiation temperatures T_b . $T_b = 0, 1000, 3000, 4000, 5000, 7000, 9000$, and $10,000$ K from bottom to top.

combination era. Radiative association was found to give a negligible contribution to the formation of HD since its rate coefficient is very slow. HD is rapidly destroyed by the reverse of process (3) and

The modest enhancement in the abundance of HD from the stimulated association process (5) is insignificant.

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FIG. 2.—Rate coefficients for stimulated plus spontaneous radiative association of H and D for various blackbody radiation temperatures T_b . $T_b = 0, 1000, 3000, 4000, 5000, 7000, 9000$, and $10,000$ K from bottom to top.

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