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THE RADIATIVE ASSOCIATION OF Li^+ AND H, Li AND H^+, AND Li AND H

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ABSTRACT

The rate coefficients for formation of LiH^+ and LiH by radiative association are determined for temperatures between 50 and 5000 K by quantum mechanical methods. The rate coefficients generally decrease slowly with temperature and have magnitudes at 300 K of 7.5×10^{-23}, 3.3×10^{-15}, and 3.3×10^{-20} cm^3 s^{-1} for $Li^+ + H$, $Li + H^+$, and Li + H, respectively. Radiative association cross sections and ab initio potentials and dipole moments for the ground and $2\,^2\Sigma^+$ states of LiH^+ are also given. We briefly discuss the importance of these formation rates for the lithium chemistry of the early universe.

Subject headings: ISM: abundances — molecular processes

1. INTRODUCTION

Of the molecules formed in the postrecombination era, lithium hydride is of particular interest because of its contribution to the cooling of the primordial gas and because of its possible effects on the cosmic blackbody background radiation. Searches for rotational-vibrational (RV) lines of LiH at high redshifts have been reported by de Bernardis et al. (1993) and Signore et al. (1994). Maoli, Melchiorri, & Tosti (1994) have suggested that Thomson scattering of cosmic background photons by LiH may partially erase anisotropies if the fractional abundance of LiH exceeds 10^{-10}.

Lepp & Shull (1984) pointed out that LiH would be formed in the early universe by the radiative association process

$$\mathrm{Li} + \mathrm{H} \rightarrow \mathrm{LiH} + h\nu\ . \tag{1}$$

They estimated a rate coefficient of 10^{-17} cm^3 s^{-1} for it and concluded that the fractional abundance (number density with respect to the total hydrogen nuclei number density) of LiH would lie between 10^{-11} and 10^{-13}, depending on the primordial lithium abundance. A more elaborate chemistry but with the same rate coefficient for reaction (1) has been used by Puy et al. (1993). Dalgarno & Lepp (1987) noted that because of its low ionization potential lithium remains almost fully ionized at the time of hydrogen recombination and that the lithium chemistry might be initiated by the radiative association process

$$\mathrm{Li}^+ + \mathrm{H} \rightarrow \mathrm{LiH}^+ + h\nu\ . \tag{2}$$

Bellini et al. (1994) remarked that the LiH^+ abundance would be limited by dissociative recombination and photodissociation, and they estimated an abundance ratio of $n(\mathrm{LiH}^+)/n(\mathrm{LiH})$ of about $10^{-3.5}$. The estimate is highly uncertain because the rate coefficient of reaction (2) was unknown.

In this paper, we present the cross sections and rate coefficients for the radiative association processes (1) and (2) and for the radiative association process

$$\mathrm{Li} + \mathrm{H}^+ \rightarrow \mathrm{LiH}^+ + h\nu\ . \tag{3}$$

These results are obtained using a fully quantum mechanical method. Ab initio calculations of the LiH^+ $X\,^2\Sigma^+$ and $2\,^2\Sigma^+$ potential energy curves, the $X\,^2\Sigma^+$ dipole moment, and the $X\,^2\Sigma^+ \rightarrow 2\,^2\Sigma^+$ transition moment are given. The consequences of the new rate coefficients for the formation of LiH and LiH^+ in the postrecombination epoch are addressed in the following paper (Stancil, Lepp, & Dalgarno 1996).

2. MOLECULAR DATA

2.1. *Lithium Hydride Ion*

The two lowest separated atom limits for LiH^+ are $Li^+(^1S) + H(^2S)$ and $Li(^2S) + H^+$, each of which correlates to a single molecular state of $^2\Sigma^+$ symmetry. Electronic energies and wave functions were calculated for these states as a function of internuclear separation using the configuration-interaction (CI) method.

An elementary basis set of Slater-type functions centered on the atomic nuclei was used to construct an orthonormal set of molecular orbitals. The basis set given in Table 1 consisted of 23σ, 12π, and 4δ functions. Because there were only three electrons, a full CI calculation within the complete space of one-electron functions was entirely tractable. CI wave functions consisted of 8304 configuration state functions (CSF) with each CSF constructed from the set of orthonormal molecular orbitals to have $^2\Sigma^+$ symmetry. Self-consistent–field calculations were used to obtain the basis of orthonormal molecular orbitals.

At 18 internuclear separations R over the range $R = 2.7$ to $R = 30$ (all quantities are in atomic units unless otherwise noted), calculations of potential energies, dipole moments, and dipole transition moments were carried out for the two lowest states of $^2\Sigma^+$ symmetry. The relevant quantities for describing the radiative association of LiH^+ (the energies of the lowest two states, the dipole moment of the ground state, and the dipole transition moment connecting the $X\,^2\Sigma^+$ and the $2\,^2\Sigma^+$ states) are listed in Table 2. The potential energy curves are shown in Figure 1. The energies agree well with the model potential calculation of Alikacem & Aubert-Frécon (1985) and at $R = 30$, the calculated energy splitting of the two states is 8.216 eV, in excellent agreement with the experimentally determined asymptotic splitting of 8.214 eV obtained from the ionization potentials of Li (5.392 eV) and H (13.6057 eV). The dipole moment of the ground state has been previously calculated by Tortorelli & Harriman (1978) and Dyer & Steiner (1986) at only one internuclear separation. Translating Dyer &

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TABLE 1

SLATER-TYPE FUNCTION BASIS SET FOR LiH$^+$

	EXPONENT (a_o^{-1})	
nl	Li	H
1*s*......	4.6351, 2.472	1.9883, 1.00, 0.70
2*s*......	1.033, 0.8237, 0.51	1.00, 0.50
2*p*......	3.9004, 2.1109, 1.0758, 0.7539, 0.51	1.50, 1.00, 0.50
3*s*......	2.6811	...
3*d*......	1.4974, 0.9866	1.5
4*f*......	1.7748	...

Steiner's moment at $R = 4.25$ of 0.2305 calculated relative to Li as the origin gives -0.3008 at the center of mass, which is in excellent agreement with our value of -0.294. Tortorelli & Harriman (1978) quote a value of 0.7599 relative to the center of mass for $R = 4.23$, but it appears that they used the wrong sign for the slope of the translation. Using the correct translation slope gives a moment of -0.2976, also in good agreement with the present work.

Beyond $R = 30$, the potentials of both states are described by the long-range form

$$V_L(R) = -\frac{\alpha_d}{2R^4} - \frac{C_6}{R^6} + E_\infty \, , \tag{4}$$

giving for the $X\,^2\Sigma^+$ state

$$V_L(R) = -\frac{4.5}{2R^4} - \frac{8.0}{R^6} - 7.7734527 \tag{5}$$

and for the $2\,^2\Sigma^+$ state

$$V_L(R) = -\frac{161.4}{2R^4} - \frac{712}{R^6} - 7.4713854 \, . \tag{6}$$

α_d is the dipole polarizability of the neutral atom, E_∞ is the separated atom energy, and the C_6 coefficient for the $2\,^2\Sigma^+$ state is taken from the recent calculation of the quadrupole polarizability of Li by Marinescu, Sadeghpour, & Dalgarno (1994). For $R < 2.7$, the short-range potential is fitted to the form $A \exp(-BR) + C$.

TABLE 2

ENERGIES, DIPOLE MOMENTS, AND TRANSITION MOMENTS FOR THE LOWEST TWO DOUBLET SIGMA STATES OF LiH$^+$

	ENERGIES (au)		DIPOLE MOMENT[a] (au)	TRANSITION MOMENT (au)
R (a_o)	$X\,^2\Sigma^+$	$2\,^2\Sigma^+$	$X\,^2\Sigma^+$	$X\,^2\Sigma^+ \rightarrow 2\,^2\Sigma^+$
2.7.......	−7.755753	−7.298033	−0.161	−0.278
2.8.......	−7.760545	−7.308581	−0.160	−0.318
3.0.......	−7.767688	−7.328415	−0.163	−0.402
3.5.......	−7.776395	−7.372772	−0.196	−0.603
4.0.......	−7.778549	−7.410190	−0.256	−0.734
4.25......	−7.778571	−7.425789	−0.294	−0.769
4.5.......	−7.778276	−7.439188	−0.335	−0.787
4.75......	−7.777826	−7.450466	−0.379	−0.792
5.0.......	−7.777321	−7.459795	−0.424	−0.786
6.0.......	−7.775573	−7.481886	−0.605	−0.700
7.0.......	−7.774586	−7.488692	−0.772	−0.576
8.0.......	−7.774092	−7.488360	−0.925	−0.454
10........	−7.773703	−7.481783	−1.204	−0.256
15........	−7,773506	−7.473231	−1.855	−0.034
20........	−7.773469	−7.471921	−2.489	−0.003
22........	−7.773463	−7.471746	−2.741	−0.001
25........	−7.773459	−7.471599	−3.118	−0.0002
30........	−7.7734555	−7.471486	−3.745	−0.0000

[a] Computed with respect to the center of mass of the molecule.

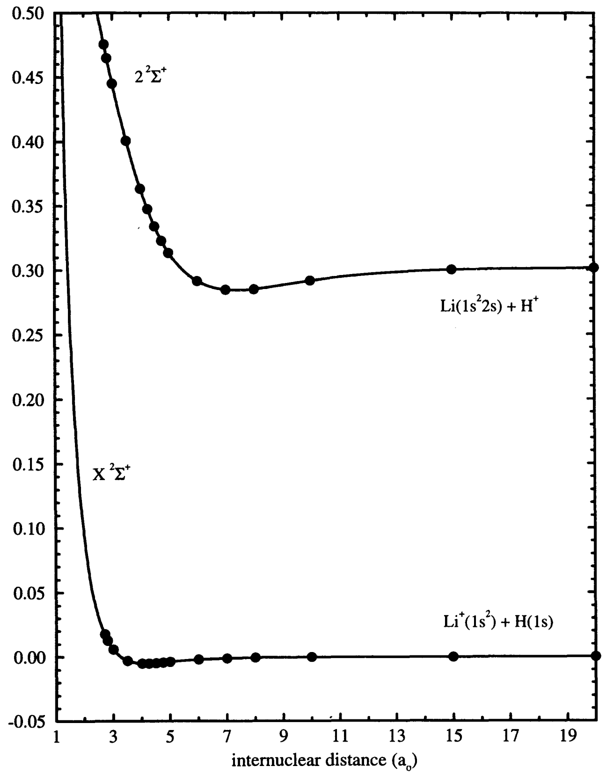

FIG. 1.—The LiH$^+$ $X\,^2\Sigma^+$ and $2\,^2\Sigma^+$ potentials

A third-order cubic spline fit to the ground-state ab initio results gives 0.1404 eV and 4.13 for the dissociation energy D_e and equilibrium distance R_e in excellent agreement with the values 0.14 eV and 4.12 and 0.13 eV and 4.08 obtained by Rosmus & Meyer (1977) and Alikacem & Aubert-Frécon (1985), respectively. We obtain a value of 422.1 cm^{-1} for the equilibrium vibrational constant ω_e compared to 443.4 cm^{-1} given by Rosmus & Meyer (1977). We find six vibrational levels in agreement with Tortorelli & Harriman (1978) and a total of 64 RV levels. Table 3 gives the vibrational level spacings with a comparison to the calculations of Tortorelli & Harriman (1978).

Fitting the $2\,^2\Sigma^+$ energies via a cubic spline yields $D_e = 0.480$ eV and $R_e = 7.39$ in good agreement with Alikacem & Aubert-Frécon (1985) who give $D_e = 0.50$ eV and $R_e = 7.35$. The energy splitting T_e between the minima of these two $^2\Sigma^+$ states is 7.878 eV. The dissociation energy of the $2\,^2\Sigma^+$ is con-

TABLE 3

VIBRATIONAL LEVEL SPACINGS AND MAXIMUM ROTATIONAL QUANTUM NUMBERS

		$\Delta G(v'', v''+1)$ (cm^{-1})	
v''	$N''_{\max}$	This Work	Tortorelli & Harriman 1978
0	16	354.09	313.85
1	13	261.63	245.81
2	11	169.48	175.58
3	8	90.311	105.35
4	6	35.585	37.310
5	4	...	...

siderably larger than that of the ground state because of the much greater dipole polarizability of Li compared to that of H.

For the ground-state dipole moment, we use the long-range form $-R/8$, while for $R < 2.7$ the dipole moment is fitted to the form $AR^2 + BR$. The $X\,^2\Sigma^+ \rightarrow 2\,^2\Sigma^+$ transition moment falls off exponentially at large R but is found to fit well to the function $-4.77 \times 10^{11}/R^{11}$. At short range, the transition moment is fitted to the united-atom limit of 1.32 for the Be^+ $2\,^2S - 2\,^2P$ transition.

2.2. *Lithium Hydride*

We adopt the ab initio CI results of Partridge & Langhoff (1981) for the $X\,^1\Sigma^+$ ground-state potential between $R = 1.75$ and $R = 7.5$, which compare well to the earlier CI calculation of Docken & Hinze (1972a). Corrections to the potential from $R = 7.5$ to $R = 11$ are taken from Verma & Stwalley (1982), where an unpublished calculation of Partridge & Langhoff is presented graphically and the D_e is forced to match the experimental value of 2.515 eV. For $R > 11$, we use the long-range form

$$V_L(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} + E_\infty\,, \tag{7}$$

where C_6, C_8, and C_{10} are taken from Proctor & Stwalley (1977).

We obtain 1390.4 cm^{-1} and 3.02 for ω_e and R_e, which compare well to the experimental values of 1405.65 cm^{-1} and 3.015 given in Stwalley & Zemke (1993) and the theoretical results of 1387.47 cm^{-1} and 3.05 found by Docken & Hinze (1972b). We find 23 vibrational levels with spacings agreeing to within 10 cm^{-1} for the 12 that are experimentally observed (cf. Partridge & Langhoff 1981). The total number of RV levels is found to be 932.

The $X\,^2\Sigma^+$ dipole moment is taken from Partridge & Langhoff (1981) for $R = 1.75$ to $R = 17.5$, which is in good agreement with the CI calculation of Docken & Hinze (1972b) and to within 0.3% of the accurate coupled-cluster double-excitation polarization propagator computation of Ogilvie, Oddershede, & Sauer (1994) given only between $R = 2.215$ and $R = 4.115$. For $R > 17.5$, the long-range form d_7/R^7 (Bottcher & Dalgarno 1974) is used, where $d_7 = 4.55 \times 10^5$ is obtained by fitting the ab initio data between $R = 12$ and $R = 17.5$. At short range the form $AR^2 + BR$ is used.

3. RADIATIVE ASSOCIATION

A molecule is formed when two atomic species approach with a relative energy E, initially in the vibrational continuum of a molecular electronic state, and radiate to a bound RV level of either the same or a lower bound electronic state through spontaneous emission. The quantum mechanical theory of radiative association is outlined in Zygelman & Dalgarno (1990) and Stancil, Babb, & Dalgarno (1993).

Following the notation of Stancil et al. (1993), the radiative association cross section is given by

$$\sigma(E) = \sum_{N'} \sum_{v''} \sigma_{N'}(v'', E)\,, \tag{8}$$

where

$$\sigma_{N'}(v'', E) = \frac{64}{3} \frac{\pi^5}{c^3} \frac{\nu^3}{k^2}\, p[N' M^2_{v'',\,N'-1;\,k,\,N'} + (N' + 1) M^2_{v'',\,N'+1;\,k,\,N'}]\,. \tag{9}$$

For equation (9), ν is the photon frequency, k is the wavenumber of relative motion, p is the probability of approach in the initial electronic state, N' is the initial rotational quantum number, v'' is the final vibrational quantum number, and M is the electric dipole matrix element connecting the initial and final nuclear and electronic states. Apart from external factors, the product of ν^3 and the factor in brackets is the spontaneous transition probability during the collision. The probability p for reactions (1), (2), and (3) is, respectively, $\frac{1}{4}$, 1, and 1 according to the degeneracy of the molecular state correlating to the relevant separated atom limits. The reduced masses used are as given in Stwalley & Zemke (1993). In Figure 2, we present the radiative association cross sections $\sigma(E)$ given by equation (8) for the formation of the LiH and LiH^+ molecules. The great disparity in magnitudes is primarily related to the difference in photon energies and to the fact that reactions (1) and (2) involve RV transitions from continuum to bound levels within the LiH $X\,^1\Sigma^+$ and LiH^+ $X\,^2\Sigma^+$ ground states, respectively, while process (3) is governed by the $2\,^2\Sigma^+ \rightarrow X\,^2\Sigma^+$ electronic transition in LiH^+. The peaks appearing in the cross sections of processes (1) and (2) are orbiting resonances due to long-range rotational barriers (cf. Stancil et al. 1993).

The rate coefficients $\alpha(T)$ for reactions (1), (2), and (3) are given in Table 4 and were determined by averaging over the cross sections with a Maxwellian velocity distribution. The results are fitted to the form

$$\alpha(T) = a_1 \left(\frac{T}{300}\right)^{a_2} \exp\left(\frac{-T}{a_3}\right) \tag{10}$$

with an accuracy better than 10% over the range $T = 300$–5000 K. The coefficients a^1 ($\mathrm{cm}^3\ \mathrm{s}^{-1}$), a_2, and a^3 (K) are 3.8×10^{-20}, -0.28, and 3300; 8×10^{-23}, -0.9, and 7000; and 3.25×10^{-15}, -0.49, and ∞ for reactions (1), (2), and (3), respectively. Our quantum mechanically determined rate coefficient for reaction (1) is 3 orders of magnitude smaller than the value estimated by Lepp & Shull (1984).

TABLE 4

RADIATIVE ASSOCIATION RATE COEFFICIENTS

	$\alpha(T)$ ($\mathrm{cm}^3\ \mathrm{s}^{-1}$)		
T (K)	$\mathrm{Li}^+(1s^2) + \mathrm{H}(1s)$	$\mathrm{Li}(2s) + \mathrm{H}^+$	$\mathrm{Li}(2s) + \mathrm{H}(1s)$
50	1.62 − 22[a]	7.66 − 15	3.00 − 20
80	1.43 − 22	6.15 − 15	3.12 − 20
100	1.33 − 22	5.53 − 15	3.17 − 20
150	1.13 − 22	4.55 − 15	3.26 − 20
200	9.76 − 23	3.96 − 15	3.29 − 20
300	7.53 − 23	3.25 − 15	3.25 − 20
400	6.01 − 23	2.82 − 15	3.11 − 20
500	4.94 − 23	2.53 − 15	2.94 − 20
600	4.14 − 23	2.32 − 15	2.75 − 20
700	3.54 − 23	2.14 − 15	2.57 − 20
800	3.07 − 23	2.01 − 15	2.39 − 20
900	2.69 − 23	1.90 − 15	2.23 − 20
1000......	2.39 − 23	1.81 − 15	2.08 − 20
1200......	1.93 − 23	1.65 − 15	1.82 − 20
1500......	1.46 − 23	1.48 − 15	1.51 − 20
2000......	1.01 − 23	1.29 − 15	1.15 − 20
2500......	7.55 − 24	1.16 − 15	9.11 − 21
3000......	5.9 − 24	1.1 − 15	7.4 − 21
3500......	4.8 − 24	9.8 − 16	6.2 − 21
4000......	4.0 − 24	9.1 − 16	5.3 − 21
4500......	3.4 − 24	8.6 − 16	4.6 − 21
5000......	2.9 − 24	8.1 − 16	4.0 − 21

[a] The notation 1.62 − 22 corresponds to 1.62×10^{-22}.

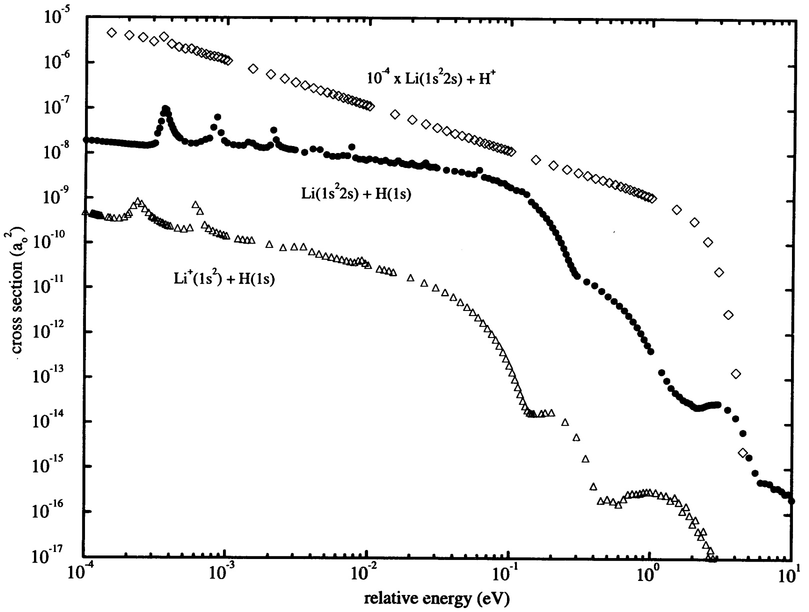

FIG. 2.—The cross sections for radiative association as a function of relative energy. Reaction (1), Li + H, is given by the filled circles; reaction (2), Li^+ + H, by the open triangles; and reaction (3), Li + H^+, by the open diamonds. Note that the reaction (3) cross section is multiplied by 10^{-4}.

With these new rates, it is now possible to estimate the abundance of LiH^+ in the early universe and improve previous LiH abundance estimates. This is the subject of the following paper (Stancil et al. 1996).

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