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RADIATIVE CHARGE TRANSFER IN COLLISIONS OF Li WITH H^+

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ABSTRACT

We present cross sections for the radiative charge transfer process $Li(2s) + H^+ \rightarrow Li^+(1s^2) + H(1s) + \hbar\omega$ for collision energies between 0.1 meV and 10 eV and rate coefficients for temperatures between 10 and 40,000 K. At 300 K, the rate coefficient is 1.3×10^{-13} cm^3 s^{-1}. The results are obtained through a fully quantum-mechanical method using completely ab initio molecular data. Cross sections for the total collision-induced radiative decay, radiative charge transfer plus radiative association, from the entrance $Li(2s) + H^+$ channel are calculated with the optical potential method. Radiative charge transfer dominates radiative association for the considered collision energies, but direct charge transfer will become important at higher energies. The emission spectrum, which has a peak at wavelengths near 158 nm, due to radiative charge transfer is given for several collision energies. Implications to the lithium ionization fraction in the postrecombination era of the early universe are discussed.

Subject headings: atomic processes — early universe

1. INTRODUCTION

The radiative charge transfer process

$$Li(2s) + H^+ \rightarrow Li^+(1s^2) + H(1s) + \hbar\omega \quad (1)$$

and the radiative association reaction

$$Li(2s) + H^+ \rightarrow LiH^+(X\ ^2\Sigma^+) + \hbar\omega \quad (2)$$

were previously investigated by Kimura, Dutta, & Shimakura (1994) using the optical potential method and molecular data obtained from a pseudopotential approach. Dalgarno, Kirby, & Stancil (1996) have studied reaction (2) by a fully quantum-mechanical method that incorporated ab initio molecular data at the configuration-interaction level. Although the molecular data in the two investigations are in agreement, Dalgarno et al. (1996) obtained cross sections for reaction (2) that are 10^2–10^3 times larger than that obtained by Kimura et al. (1994) for the summation of reactions (1) and (2). Further, the rate coefficients for the total of reactions (1) and (2) have been estimated semiclassically (cf. Stancil, Lepp, & Dalgarno 1996). The semiclassical rate coefficients are typically 10^3 times larger than the values of Kimura et al. (1994) but are in fair agreement with the quantal rates of Dalgarno et al. for reaction (2) at low temperatures where radiative association is expected to dominate.

Kimura et al. (1995) have found an error in their previous calculation so that their new rate coefficients for the summation of reactions (1) and (2) are typically $\sim 10^3$–10^4 times larger than their previous results. The new results of Kimura et al. (1995) are ~ 10 times larger than the radiative association rates of Dalgarno et al. but are in fair agreement with the semiclassical rate coefficients for the summation of reactions (1) and (2) for $T \gtrsim 1500$ K.

Since an accurate determination of the rate coefficients of reaction (1) is of interest because it may be an important process for establishing the ionization fraction of lithium in the postrecombination epoch of the early universe (Stancil et al. 1996), we present a new analysis using a fully quantum-mechanical approach (cf. Zygelman et al. 1989) incorporating the new ab initio data of Dalgarno et al. (1996). Atomic units are used throughout unless otherwise noted.

2. THEORY

The radiative charge transfer cross section is given by (Cooper, Kirby, & Dalgarno 1984; Zygelman et al. 1989)

$$\sigma = \int_{\omega_{\min}}^{\omega_{\max}} \frac{d\sigma}{d\omega}\, d\omega\ , \quad (3)$$

where

$$\frac{d\sigma}{d\omega} = \frac{8}{3}\left(\frac{\pi}{k_a}\right)^2 \frac{\omega^3}{c^3} \sum_J \times [JM^2_{J,J-1}(k_a, k_b) + (J+1)M^2_{J,J+1}(k_a, k_b)] \quad (4)$$

and

$$M_{J,J'}(k_a, k_b) = \int_0^\infty dR f^a_J(k_a R) D(R) f^b_{J'}(k_b R)\ . \quad (5)$$

$D(R)$ is the transition dipole moment connecting the two molecular electronic states and k_a and k_b are the entrance and exit momenta, given respectively by

$$k_a = \sqrt{2\mu[E - V_a(\infty)]} \quad (6)$$

and

$$k_b = \sqrt{2\mu[E - V_b(\infty) - \hbar\omega]}\ , \quad (7)$$

where E is the collision energy in the entrance channel, ω is the angular frequency of the emitted photon, and V_a and V_b are the adiabatic potential energies of the entrance and exit channels, respectively. R is the internuclear distance, μ the collision system reduced mass, and J the angular momentum quantum number. The partial wave $f^i_J(k_i R)$ (where i = a, b) is a regular solution of the homogeneous radial equation

$$\left\{\frac{d^2}{dR^2} - \frac{J(J+1)}{R^2} - 2\mu[V_i(R) - V_i(\infty)] + k_i^2\right\} f^i{}_J(k_i R) = 0\ , \quad (8)$$

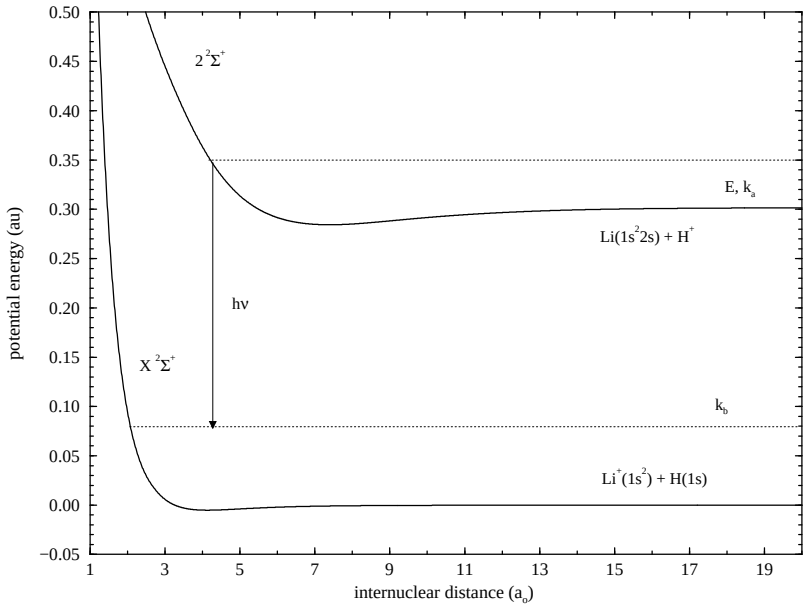

FIG. 1.—The LiH^+ $X\ ^2\Sigma^+$ and $2\ ^2\Sigma^+$ potentials

and is normalized asymptotically according to

$$f^i_J(k_i R) \rightarrow \sqrt{\frac{2\mu}{\pi k_i}} \sin\left(k_i R - \frac{J\pi}{2} + \delta^i_J\right). \tag{9}$$

A phase shift is denoted by δ^i_J, and equation (8) is solved by the renormalized Numerov method of Johnson (1977).

The cross section for total collision-induced radiative decay from the entrance channel, the sum of the cross sections for processes (1) and (2) can be obtained with the optical potential method (Zygelman & Dalgarno 1988; Zygelman et al. 1989) and is given by

$$\sigma = \frac{\pi}{k_a^2} \sum_J^{\infty} (2J+1)[1 - \exp(-4\eta_J)]\,. \tag{10}$$

The phase shift η_J is given within the distorted-wave approximation by

$$\eta_J = \frac{\pi}{2} \int_0^{\infty} dR\, |f^a_J(k_a R)|^2 A(R)\,, \tag{11}$$

where $A(R)$ is a transition probability given by

$$A(R) = \frac{4}{3} D^2(R) \frac{|V_b(R) - V_a(R)|^3}{c^3}\,. \tag{12}$$

3. RESULTS AND DISCUSSION

The LiH^+ potential curves, displayed in Figure 1, and the transition moment used in the current calculation are discussed in Dalgarno et al. (1996). Asymptotically, the potential energies are described to leading order by the

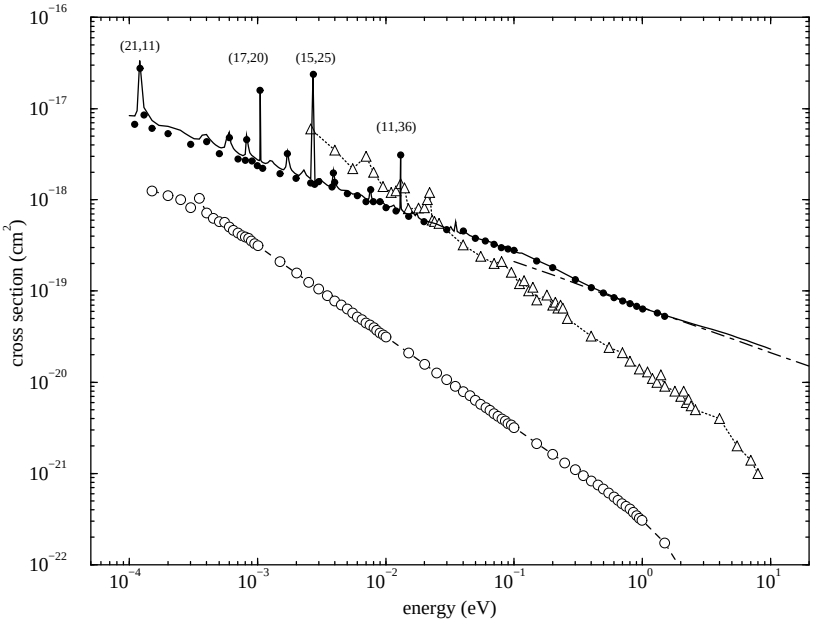

FIG. 2.—Cross sections for radiative charge transfer and radiative association as a function of relative energy. Reaction (1), this work (*filled circles*). Reaction (2), Dalgarno et al. (1996) (*open circles*). The sum of reactions (1) and (2) obtained with eq. (10), this work (*solid line*); Kimura et al. (1995) (*open triangles*); and semiclassically with eq. (13) (*dot-dashed line*). The resonances are labeled by (v, J).

TABLE 1

RATE COEFFICIENTS FOR RADIATIVE CHARGE TRANSFER $Li + H^+ \rightarrow Li^+ + H + \hbar\omega$

T (K)	$\alpha(T)$[a]
10	1.43
15	1.49
20	1.51
30	1.48
50	1.44
70	1.41
100	1.37
200	1.34
300	1.30
500	1.30
600	1.29
700	1.27
800	1.27
1000	1.25
1500	1.21
2000	1.17
3000	1.12
4000	1.09
5000	1.07
6000	1.05
8000	1.04
10000	1.03
20000	1.03
30000	1.04
40000	1.05

[a] In units of 10^{-13} cm^3 s^{-1}.

polarization interaction, and its form is given quantitatively in Dalgarno et al. Cross sections for processes (1) and (2) are presented in Figure 2. Reaction (1) is the dominant process for the energy range considered in this work, so that the present fully quantal results for reaction (1) obtained with equation (3) can be compared to the optical potential calculation of Kimura et al. (1995) for the sum of (1) and (2). The two cross sections are in fair agreement, although the latter are smaller for $E \gtrsim 30$ meV and larger for $E \lesssim 10$ meV. The discrepancy in the cross section slope is puzzling since the transition probability $A(R)$, which is plotted in Figure 3, and the potential energies of Dalgarno et al. (1996) are in good agreement with the data given graphically in Kimura et al. (1994). The difference between the two values of $A(R)$ for $R < 2.5$ is inconsequential since the wave function overlap is nearly zero in this region. For the asymptotic, separated-atom energy difference of V_a and V_b, we have used Dalgarno et al.'s (1996) ab initio value of 8.2197 eV compared to Kimura et al.'s (1994) result of 8.2 eV. This difference is not significant, and both compare well to the experimental value of 8.2067 eV.

As a check of our results, we have calculated the cross sections for the sum of reactions (1) and (2) using the optical potential method. The cross sections using equation (10) are equal to the sum of the cross sections for (1) using equation (3) and the cross sections for reaction (2) from Dalgarno et al. (1996) to within 1.4%, 3.3%, 0.7%, and 2.3% at 1, 10, 100, and 1000 meV, respectively. The current optical potential cross section behaves as $1/E^{1/2}$ while that of Kimura et al. (1995) has a $1/E$ dependence. The semiclassical approximation for the radiative decay cross section is given by (cf. Zygelman & Dalgarno 1988)

$$\sigma = 2\pi \sqrt{\frac{2\mu}{E}} \int p\, dp \int_{R_a^{ctp}}^{\infty} \frac{A(R)}{\sqrt{1 - V_a(R)/E - p^2/R^2}}\,, \quad (13)$$

where R_a^{ctp} is the classical turning point in the incoming channel. For large energies ($E \gg V_a$), the double integral is nearly energy independent, and we find numerically $\sigma = 6.6 \times 10^{-20} E^{-1/2}$ cm^2 with E given in electronvolts. This result is plotted in Figure 2 and is in excellent agreement with our optical potential calculations.

The resonant-like structures in the low-energy cross sections are due to quasi-bound rotational-vibrational (RV) levels of the initial molecular state. The RV levels responsible for the resonances are labeled in Figure 2 by the vibrational quantum number v and J. For $T \lesssim 1000$ K, the rate coefficients are enhanced by the resonances contributing as much as 30% to the rate coefficient at 20 K.

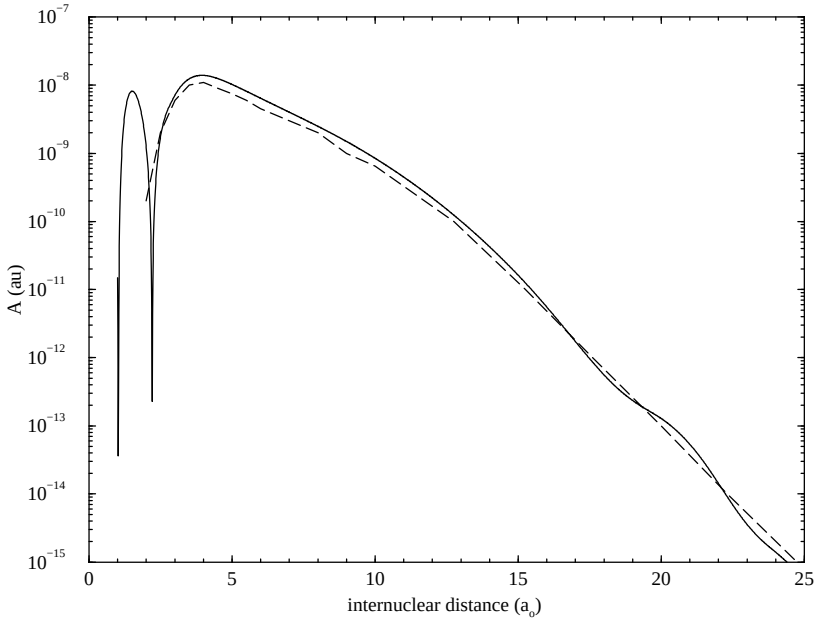

FIG. 3.—The transition probability $A(R)$. This work (*solid line*); Kimura et al. (1994) (*long-dashed line*).

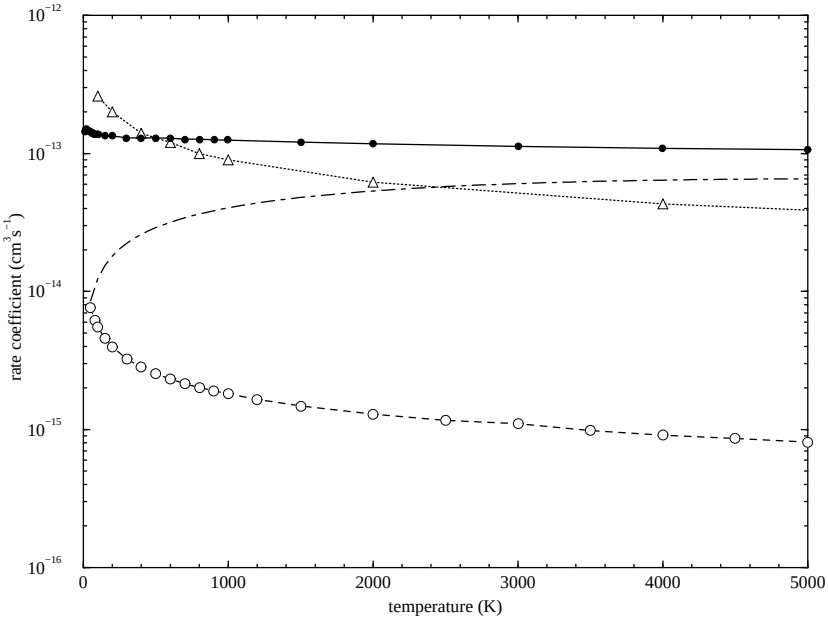

FIG. 4.—Rate coefficients for radiative charge transfer and radiative association as a function temperature. Reaction (1), this work (*filled circles*). Reaction (2), Dalgarno et al. (1996) (*open circles*). The sum of reactions (1) and (2), Kimura et al. (1995) (*open triangles*); Stancil et al. (1996), semiclassical (*dot-dash line*).

The rate coefficients for reaction (1) are obtained by averaging the cross sections of equation (3) over a Maxwellian velocity distribution. The results are displayed in Figure 4 and Table 1. The rate coefficients are fitted to the relation

$$\alpha(T) = a\left(\frac{T}{10{,}000}\right)^b \exp\left(\frac{-T}{c}\right) \qquad (14)$$

with the parameters $a = 1.08 \times 10^{-13}$ cm^3 s^{-1}, $b = -0.051$, and $c = 2.82 \times 10^5$ K. The fit is reliable to within 5% over the temperature range 20 to 10,000 K. Rate coefficients for reaction (2) from Dalgarno et al. (1996) and for the sum of reactions (1) and (2) obtained by Kimura et al. (1995) with the optical potential approach and by Stancil et al. (1996) with a semiclassical method (cf. Butler, Guberman, & Dalgarno 1977) are given in Figure 4 for comparison. The rate coefficients for reaction (1) are greater than (2) by a factor of 10 to 100 over the given temperature range, indicating that radiative charge transfer is the dominant collision process for removal of Li for temperatures $T \lesssim 4000$ K, above which direct, nonradiative charge transfer will become important (Kimura et al. 1994, 1995) The current quantal, optical potential, and semiclassical methods give rate coefficients for reaction (1) that agree to within a factor of ~ 2 for $T \gtrsim 1500$ K, but have significantly different low-temperature behaviors.

Figure 5 displays the emission spectrum $d\sigma/d\omega$ for the single incoming partial wave $J = 0$ at various collision energies. Its oscillatory structure is related to the mapping of the

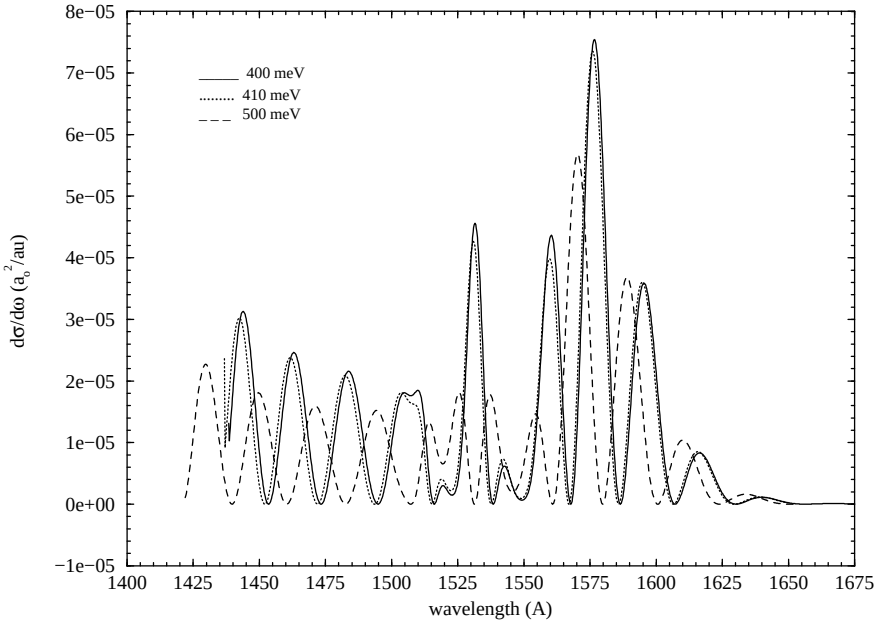

FIG. 5.—Spectra for the $J = 0$ incoming partial wave at collision energies of 0.4 eV (*solid line*), 0.41 eV (*dotted line*), 0.5 eV (*dashed line*)

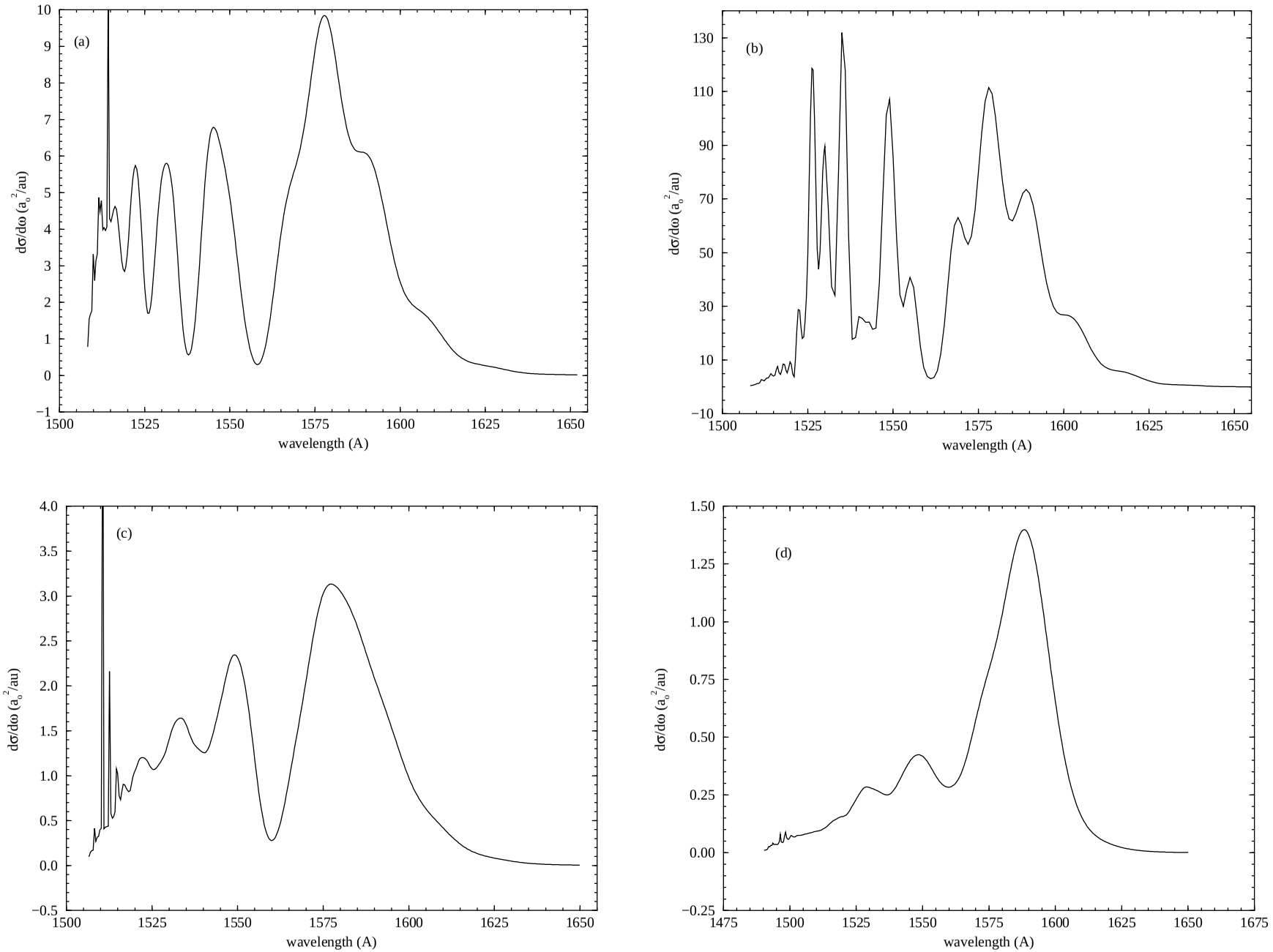

FIG. 6.—Total emission spectra at collision energies of (*a*) 1 meV, (*b*) 2.7 meV, (*c*) 10 meV, and (*d*) 100 meV. 2.7 meV is a resonance energy

phase of the outgoing wave of momentum k_b (related to the emitted photon frequency by energy conservation) at R_a^{ctp} of the incoming partial wave of momentum k_a. Total emission spectra for various collision energies are shown in Figures 6. The spectra reveal resonance-like structures at short wavelengths near threshold presumably due to orbiting effects in the ground state and a pronounced peak near 1580 Å which reaches a maximum wavelength of 1588 Å for a collision energy of 0.1 eV. This peak does not correspond to the wavelength of the asymptotic energy defect (1508 Å) as seen in the $He^+ + H$ system (Zygelman et al. 1989[1]). In the $He^+ + H$ case, f_J^a approaches the asymptotic sinusoidal behavior given by equation (9) for internuclear distances just longer than R_a^{ctp} because the entrance channel is repulsive. $f_{J'}^b$ is also sinusoidal for R near R_a^{ctp} since $R_b^{ctp} < R_a^{ctp}$. $M_{J,J'}$, and therefore $d\sigma/d\omega$, is largest when the overlap of f_J^a and $f_{J'}^b$ is optimal, or have nearly equal phases, in the region where $D(R)$ is significant. Since both f_J^a and $f_{J'}^b$ have asymptotic behaviors near R_a^{ctp} and $D(R)$ is maximum near R_a^{ctp}, $M_{J,J'}$ is maximized when $k_a \sim k_b$ or $\hbar\omega \sim V_a(\infty) - V_b(\infty)$. Conversely, for $Li + H^+$, the entrance channel is bound by 0.48 eV (Dalgarno et al. 1996). The attraction of the potential well affects f_J^a, and as a result, for R between R_a^{ctp} and the effective outer edge of the well, the phase is nearly that of the last bound vibrational level. This phase is larger than the asymptotic phase of f_J^a, and therefore the optimization of $M_{J,J'}$ requires $k_b > k_a$ giving $\hbar\omega \sim V_a(R_e) - V_b(\infty)$, where R_e is the equilibrium distance.

[1] The radiative rate coefficients for the formation of $He + H^+$ and HeH^+ given in Zygelman et al. (1989) and Zygelman & Dalgarno (1990), respectively, must be multiplied by a factor of $\frac{1}{4}$ to properly account for the statistical weight of the $A\,^1\Sigma^+$ channel formed during the initial approach of the atoms.

4. EARLY UNIVERSE

In modeling the lithium chemistry in the postrecombination epoch of the early universe, Stancil et al. (1996) adopted the semiclassical radiative charge transfer rate coefficients for reaction (1), which is one mechanism for increasing the lithium ionization fraction. Stancil et al. (1996) found $n(Li^+)/n_{Li} = 0.341$ (their model III) at redshift $z = 10$. We have rerun the early universe model III of Stancil et al. (1996) neglecting reaction (1), using the Kimura et al. (1995) rate coefficients, and using the current quantal values. The lithium ionization fraction is found to be 0.339, 0.347, and 0.348, respectively. The differences in the ionization fractions are primarily related to differences in the low temperature dependence of the rate coefficients and are negligible compared to other uncertainties in the early universe model. Removal of neutral Li is dominated by photoionization instead of the radiative charge transfer reaction (1).

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