THE ASTROPHYSICAL JOURNAL, 458:401–406, 1996 February 20

THE LITHIUM CHEMISTRY OF THE EARLY UNIVERSE

P. C. STANCIL AND S. LEPP
W. M. Keck Laboratory for Computational Physics, Department of Physics, University of Nevada, Las Vegas, Las Vegas, NV 89154-4002; stancil@physics.unlv.edu, lepp@nevada.edu

AND

A. DALGARNO
Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138; dalgarno@cfa.harvard.edu
Received 1995 June 2; accepted 1995 August 23

ABSTRACT

A comprehensive chemistry of lithium in the postrecombination epoch is presented, and calculations are carried out of the abundances of Li, Li^+, Li^-, LiH, and LiH^+ as a function of redshift z for several cosmological models. Atomic lithium is found to recombine at a redshift of about 450 but to remain significantly ionized with a fractional ionization of approximately 0.3 as $z \rightarrow 0$ due to the scarcity of electrons after hydrogen recombination. With the inclusion of a new quantal rate coefficient for the radiative association of lithium and hydrogen, the calculated fractional abundance of LiH is about 100 times smaller than in previous studies. The inclusion of additional gas-phase chemical reactions results in a further reduction by another factor of about 100. The fractional abundance of LiH^+ is predicted to approach 10% of that of the neutral LiH as $z \rightarrow 0$, but LiH^+ is much less abundant than LiH for $z > 30$. The fraction of lithium that is taken up in molecular form in the postrecombination epoch is predicted to be about 10^{-7}. Such small molecular abundances indicate that Thomson scattering between cosmic background radiation (CBR) photons and primordial LiH and LiH^+ plays an insignificant role in erasing primary anisotropies in the CBR field.

Subject headings: early universe — nuclear reactions, nucleosynthesis, abundances

1. INTRODUCTION

The first galaxies and stars formed from a gas of H and ^{4}He with trace amounts of D, ^{3}He, and ^{7}Li. In the absence of heavier elements, the radiative cooling at temperatures less than 8000 K is controlled by the presence of a small fraction of the gas that is molecular, and it is molecular cooling that allows primordial clouds to collapse (Palla, Salpeter, & Stahler 1983; Silk 1983; Lepp & Shull 1984). The details of the cooling mechanisms are important in the determination of the large-scale structure, represented by globular cluster and galaxy masses, and the small-scale structure, represented by the initial mass function. At the onset of collapse, the molecular abundances, evolved from the postrecombination epoch, constrain the cooling processes and subsequently the initial galactic and stellar evolution of the universe. It was suggested by Dubrovich (1993) that primordial molecules with large dipole moments might be detectable by their imprint on the cosmic background radiation (CBR) arising from the resonant enhancements of the Thomson scattering cross sections that occur at the transition frequencies of the molecules. Lepp & Shull (1984) carried out a preliminary study of the abundances of LiH that suggested a large fraction of the primordial lithium might be incorporated into LiH. The effects of the presence of LiH in the early universe have been explored by de Bernardis et al. (1993), Signore et al. (1994), and Maoli, Melchiorri, & Tosti (1994).

Molecular abundances in the postrecombination epoch have been calculated by Lepp & Shull (1984), Latter (1989), Puy et al. (1993), and Palla, Galli, & Silk (1995). The chemistry of the early universe has been reviewed by Dalgarno & Lepp (1987), Black (1988), and Dalgarno & Fox (1994). We concentrate in this paper on the lithium chemistry. We extend the previous studies by including additional reactions in a more comprehensive chemistry, and we employ the new rate coefficients for radiative association determined in the previous paper (Dalgarno, Kirby, & Stancil 1996, hereafter DKS).

2. EARLY UNIVERSE CHEMISTRY

As the universe expanded, atoms and molecules formed from the free nucleons and electrons as photoionization and photodissociation gradually became ineffective because of the cooling of the radiation temperature. The matter temperature T_m and the radiation temperature T_r remained the same until a redshift of about 1300, the beginning of the recombination era, after which Compton scattering was no longer able to overcome the cooling by the expansion and T_m fell below T_r. Subsequently, the primordial matter continued to cool until collapse was initiated in protoclouds.

Chemistry began with the appearance of the first neutral molecule H_2 soon after the production of neutral atomic hydrogen through radiative recombination of protons and electrons. There were no grains and H_2 was formed through the H_2^+ and H^- sequences,

$$H^+ + H \rightarrow H_2^+ + \nu , \quad (1)$$

$$H_2^+ + H \rightarrow H_2 + H^+ , \quad (2)$$

$$H + e^- \rightarrow H^- + \nu , \quad (3)$$

$$H^- + H \rightarrow H_2 + e^- \quad (4)$$

(cf. Lepp & Shull 1984).

The lithium chemistry was initiated by the recombination of lithium, which occurred near $z = 450$ through radiative recombination,

$$Li^+ + e^- \rightarrow Li + \nu , \quad (5)$$

mutual neutralization,

$$Li^+ + H^- \rightarrow Li + H , \tag{6}$$

and radiative association,

$$Li^+ + H \rightarrow LiH^+ + \nu , \tag{7}$$

followed by dissociative recombination,

$$LiH^+ + e^- \rightarrow Li + H , \tag{8}$$

and the exchange reaction,

$$LiH^+ + H \rightarrow Li + H_2^+ . \tag{9}$$

Some Li^+ was recovered by photoionization,

$$Li + \nu \rightarrow Li^+ + e^- , \tag{10}$$

by the charge transfer processes,

$$Li + H^+ \rightarrow Li^+ + H , \tag{11}$$

$$Li + H_2^+ \rightarrow Li^+ + H_2 , \tag{12}$$

by radiative charge transfer,

$$Li + H^+ \rightarrow Li^+ + H + \nu , \tag{13}$$

and by the exchange reaction,

$$LiH^+ + H \rightarrow Li^+ + H_2 . \tag{14}$$

The molecular ion LiH^+ formed by reaction (7) and by the radiative association process,

$$Li + H^+ \rightarrow LiH^+ + \nu , \tag{15}$$

was removed by reactions (8) and (9), by photodissociation,

$$LiH^+ + \nu \rightarrow Li^+ + H , \tag{16}$$

$$LiH^+ + \nu \rightarrow Li + H^+ , \tag{17}$$

by electron-impact dissociation,

$$LiH^+ + e^- \rightarrow Li^+ + H + e^- , \tag{18}$$

and by the exchange reactions,

$$LiH^+ + H \rightarrow LiH + H^+ \tag{19}$$

and (14).

With the production of neutral lithium, lithium hydride could be formed by radiative association,

$$Li + H \rightarrow LiH + \nu , \tag{20}$$

and by associative detachment,

$$Li + H^- \rightarrow LiH + e^- . \tag{21}$$

The negative ion Li^- was formed by radiative attachment,

$$Li + e^- \rightarrow Li^- + \nu , \tag{22}$$

and removed by photodetachment,

$$Li^- + \nu \rightarrow Li + e^- , \tag{23}$$

and mutual neutralization,

$$Li^- + H^+ \rightarrow Li + H . \tag{24}$$

Some Li^- survived to participate in associative detachment,

$$Li^- + H \rightarrow LiH + e^- , \tag{25}$$

which provided a major source of LiH. The neutral molecule LiH undergoes photodissociation,

$$LiH + \nu \rightarrow Li + H , \tag{26}$$

charge transfer,

$$LiH + H^+ \rightarrow LiH^+ + H , \tag{27}$$

producing LiH^+, and the exchange reactions,

$$LiH + H \rightarrow Li + H_2 , \tag{28}$$

$$LiH + H^+ \rightarrow Li^+ + H_2 , \tag{29}$$

and

$$LiH + H^+ \rightarrow Li + H_2^+ . \tag{30}$$

The rate coefficients that we adopted for the various reactions together with the energy excess and the sources of the data are given in Table 1. Some are from explicit calculations or measurements, others are from experimental or theoretical results for related systems, while the remainder are estimates and are subject to considerable uncertainty. The reactions are generally listed for the exothermic direction.

The reactions involving collisions of H_2 or H_2^+ with Li or Li^+ are not included. The reverse of reactions (14), (28), and (29) are endothermic by 4.336 eV, 1.961 eV, and 10.191 eV, respectively, and have significant rate coefficients only at large z, but when the abundances of H_2, H_2^+, and Li are negligible. We checked by trial calculations that the reverse of reactions (9) and (30) had no influence on the resulting abundances of LiH and LiH^+. Process (12) is not important since the fractional abundance of H_2^+, relative to the total abundance of hydrogen nuclei, is typically less than 10^{-12}. We omitted the sequence

$$Li^+ + H_2 \rightarrow LiH_2^+ + \nu , \tag{31}$$

$$LiH_2^+ + e^- \rightarrow LiH + H , \tag{32}$$

which had been suggested as a possible source of LiH in interstellar clouds (Kirby & Dalgarno 1978). With the extreme upper limit of 10^{-17} cm^3 s^{-1} for the rate of reaction (31), the production of LiH_2^+ would be comparable to the production of LiH^+ through reaction (7), but LiH^+ is formed primarily by reaction (15) (see § 4 below). Formation of LiH_2^+ through the process

$$Li + H_2^+ \rightarrow LiH_2^+ + \nu \tag{33}$$

in comparison to reaction (15) would be negligible because of the low H_2^+ abundance. Using the rate coefficient of reaction (15) for reaction (33), a trial calculation resulted in a LiH_2^+ fractional abundance of approximately 10^{-22} formed through reactions (31) and (33). Adopting a rate coefficient of $1.7 \times 10^{-7}(300/T)^{0.5}$ cm^3 s^{-1} for reaction (32) produced negligible LiH. Reaction (18) was also neglected since its rate is unlikely to exceed that of the dissociative recombination process (8).

3. EVOLUTIONARY MODELS

To estimate the particle abundances in the expanding universe, we took into account the chemical reactions listed in Table 1. The corresponding chemical rate equations form a set of coupled stiff differential equations for the particle densities $n(x)$ of the form

$$\frac{dn(x)}{dt} = \alpha_{\rm form}\, n(y)n(w) - \zeta_{\rm dest}\, n(x) + \cdots , \tag{34}$$

TABLE 1

GAS-PHASE REACTIONS AND THEIR RATE COEFFICIENTS USED IN THE MODELS

	Reaction	a_1 (cm^3 s^{-1})	a_2	a_3 (K)	Notes
(5)	$Li^+ + e^- \rightarrow Li + \nu$	3.1–12[a]	−0.68	-	1
(10)	$Li + \nu \rightarrow Li^+ + e^-$	-	-	-	2
(6)	$Li^+ + H^- \rightarrow Li + H$	1.2–7	−0.36	−16500	3
(11)	$Li + H^+ \rightarrow Li^+ + H$	4.0–20	6.8	1800	4
(13)	$Li + H^+ \rightarrow Li^+ + H + \nu$	2.3–14	0.55	10000	5
(22)	$Li + e^- \rightarrow Li^- + \nu$	1.85–15	−0.62	9300	6
(23)	$Li^- + \nu \rightarrow Li + e^-$	-	-	-	2
(24)	$Li^- + H^+ \rightarrow Li + H$	1.2–7	−0.36	−16500	7
(7)	$Li^+ + H \rightarrow LiH^+ + \nu$	8.0–23	−0.9	7000	8
(16)	$LiH^+ + \nu \rightarrow Li^+ + H$	-	-	-	2
(15)	$Li + H^+ \rightarrow LiH^+ + \nu$	3.25–15	−0.49	-	8
(17)	$LiH^+ + \nu \rightarrow Li + H^+$	-	-	-	2
(8)	$LiH^+ + e^- \rightarrow Li + H$	2.6–8	−0.47		9
(9)	$LiH^+ + H \rightarrow Li + H_2^+$	9.0–10	-	66400[b]	10
(14)	$LiH^+ + H \rightarrow Li^+ + H_2$	3.0–10	-	-	11
(19)	$LiH^+ + H \rightarrow LiH + H^+$	1.0–11	-	67900[b]	12
(20)	$Li + H \rightarrow LiH + \nu$	3.8–20	−0.28	3300	8
(26)	$LiH + \nu \rightarrow Li + H$	-	-	-	2
(21)	$Li + H^- \rightarrow LiH + e^-$	4.0–10	-	-	13
(25)	$Li^- + H \rightarrow LiH + e^-$	4.0–10	-	-	14
(27)	$LiH + H^+ \rightarrow LiH^+ + H$	1.0–9	-	-	15
(28)	$LiH + H \rightarrow Li + H_2$	2.0–11	-	-	16
(29)	$LiH + H^+ \rightarrow Li^+ + H_2$	1.0–9	-	-	17
(30)	$LiH + H^+ \rightarrow Li + H_2^+$	1.0–9	-	-	18

NOTE.—The rate coefficients are given by the relation $\alpha = a_1\ (T/300)^{a_2} \exp(-T/a_3)$. (1) Fit to the data of Caves & Dalgarno 1972; (2) detailed balance applied to the reverse reaction; (3) determined from cross sections of Janev & Radulović 1978 and Peart & Hayton 1994; (4) fit to data of Kimura, Dutta, & Shimakura 1994; (5) semiclassical calculation using molecular data of DKS; (6) determined by detailed balance from photodetachment cross section of Ramsbottom, Bell, & Berrington 1994; (7) same rate coefficient as reaction (6); (8) DKS; (9) estimate; (10) endothermic by 5.722 eV, estimate; (11) exothermic by 4.336 eV, estimate; (12) endothermic by 5.855 eV, estimate; (13) determined from cross section of Fedchak et al. 1994; (14) same rate coefficient as reaction (21); (15) exothermic by 5.855 eV, estimate; (16) exothermic by 1.961 eV, see Boldyrev & Simons 1993, estimate; (17) exothermic by 10.191 eV, estimate; (18) exothermic by 0.133 eV, estimate.

[a] The notation 3.1 − 12 corresponds to 3.1×10^{-12}.

[b] For the indicated reactions the exponential term in the rate relation has the form $\exp(-a_3/T)$.

which must be integrated in time t and which depend upon the total density and the temperature. The photo-destruction rate ζ_{dest} was obtained by detailed balance using the appropriate equilibrium constant and the corresponding formation rate α_{form}. Partition functions are taken from Irwin (1981), while the equilibrium constants are given by Sauval & Tatum (1994) except for LiH^+, which is given by Stancil (1996).

For the recombination epoch we assumed that the hydrogen density is given by

$$n_H = 8.02 \times 10^{-6} \Omega_b h^2 (1 + z)^3 \mathrm{cm}^{-3} , \quad (35)$$

where Ω_b is the ratio of the baryonic-matter density to the critical density required to close the universe, h is the Hubble constant in units of 100 km s^{-1} Mpc^{-1}, and the redshift z is related to the time by the expression

$$\frac{dt}{dz} = \frac{3.086 \times 10^{17}}{h(1 + z)^2 (1 + \Omega_0 z)^{1/2}} \quad (36)$$

(cf. Peebles 1993). The radiation temperature is given by $T_r = 2.726(1 + z)$. The matter temperature is taken from the models of Puy et al. (1993). Though Puy et al. (1993) overestimate the LiH abundance (see § 4 below), the LiH heating and cooling rates are low and have an insignificant effect on the matter temperature.

We investigate three different cosmological models. Their parameters are given in Table 2, and all incorporate the closure parameter $\Omega_0 = 1.0$. Model I corresponds to the standard big bang nucleosynthesis (SBBN) model of Wagoner, Fowler, & Hoyle (1967) and Yang et al. (1984). Model I was adopted by Lepp & Shull (1984). Model III differs from model I by incorporating the recent parameter values used by Palla et al. (1995), which are based on the recent SBBN models of Walker et al. (1991) and Smith, Kawano, & Malaney (1993). Model II assumes a larger lithium abundance taken from the inhomogeneous BBN (IBBN) model of Applegate & Hogan (1985), Sale & Mathews (1986), and Mathews et al. (1990). Model II also assumes a baryonic-matter dominated universe. Model II was used in the abundance calculations of Puy et al. (1993).

The H, H^+, and e^- abundances are at least 10^5 times larger than the lithium species and are not affected by the lithium chemistry. For our calculations, we used the results of Rybicki & Dell'Antonio (1995), who made a careful study of the recombination epoch, including the radiative transfer of Lyα photons.

4. RESULTS AND DISCUSSION

We determined the fractional abundances of H^-, Li, Li^+, Li^-, LiH, and LiH^+ for the three different cosmological models as a function of redshift. The results for model III are presented in Figure 1, while the lithium fractional abundances as $z \rightarrow 0$ for each of the models are given in Table 2 with a comparison to previous calculations.

The abundance of H^- is in agreement with the calculations of Latter (1989) (cf. Black 1988). We consider formation of H^-

TABLE 2

COSMOLOGICAL MODEL PARAMETERS AND FRACTIONAL ABUNDANCES AT $z = 10$ AND CLOSURE PARAMETER $\Omega_0 = 1$ FOR ALL MODELS

A.

Parameters	Model I	Model II	Model III
Ω_b	0.1	1.0	0.0367
h	0.5	0.5	0.67
Li/H	1.0 − 10	1.0 − 8	2.3 − 10

B.

	MODEL I			MODEL II		MODEL III	
SPECIES	Reference 1[a]	Reference 2[b]	This Work	Reference 2[b]	This Work	Reference 3[c]	This Work
H^+, e^-	...	...	3.2 − 4[d]	...	3.3 − 5[d]	7.8 − 4	6.5 − 4[d]
H^-	...	...	7.6 − 13	...	5.3 − 14	1.8 − 12	1.4 − 12
Li	...	...	7.0 − 11	...	9.1 − 9	1.9 − 10	1.6 − 10
Li^+	...	...	3.0 − 11	...	2.4 − 9	3.7 − 11	8.2 − 11
Li^-	...	...	1.1 − 18	...	2.6 − 17	...	3.7 − 18
LiH	1.8 − 13	6.0 − 11	2.1 − 17	6.0 − 10	5.9 − 16	5.4 − 13	6.8 − 17
LiH^+	...	...	1.8 − 18	...	3.4 − 17	9.0 − 17	6.7 − 18

NOTE.—The notation 3.2 − 4 corresponds to 3.2×10^{-4}.

[a] Lepp & Shull 1984.

[b] Puy et al. 1993.

[c] Palla, Galli, & Silk 1995.

[d] Rybicki & Dell'Antonio 1995.

only through the radiative attachment process (3). It is destroyed mostly by the reverse process of photodetachment, but for $z < 100$ mutual neutralization with H^+ and (4) dominate. Processes (6) and (21) are minor H^- destruction mechanisms but are included since they create Li and LiH, respectively. For H^- and all other species whose formation depends on the abundances of H, H^+, or e^-, a peak, inflection, or plateau in the abundance occurs near $z = 1300$ when H is recombined. The features are less pronounced than obtained by previous calculations because radiation trapping (Rybicki & Dell'Antonio 1995) delays the loss of electrons to H recombination. The effective redshift of formation z_f for H^- is about 100, but the abundance decreases slightly for smaller z.

The abundances of Li and Li^+ have been given previously by Palla et al. (1995), who include only reactions (5) and (10). We obtain the same Li formation redshift, $z_f \sim 450$, but otherwise the current results deviate for the same cosmological parameters (model III of Table 2). For $z < 450$, Palla et al. (1995) find that Li is mostly neutral with the ionization fraction $n(Li^+)/n_{Li} \rightarrow 0.16$ as $z \rightarrow 0$. Our calculation indicates that Li will remain ionized with $n(Li^+)/n_{Li} \rightarrow 0.34$ for model III. The current result is in agreement with the suggestions of Dalgarno

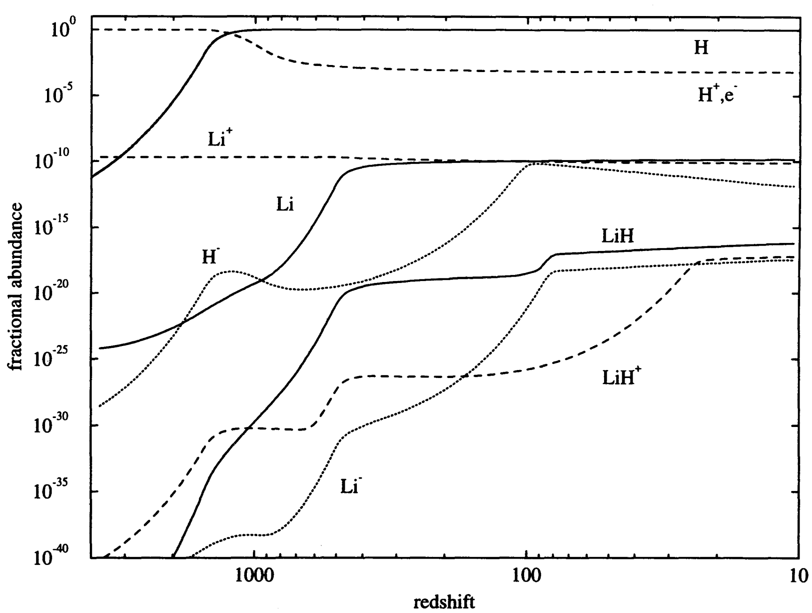

FIG. 1.—Fractional abundances of atoms, ions, and molecules for the lithium chemistry of the primordial gas for model III (see Table 2 for parameters)

& Lepp (1987) and Dalgarno & Fox (1994). Since Li has a lower ionization potential than H, it is still ionized by the background radiation field when H combines. After most of the H combines, the number density of electrons is very small, and the timescale for neutralization of the remaining H^+ and the Li^+ is longer than the age of the universe. Comparison of models I and II suggests that the lithium ionization fraction depends weakly on Ω_b. For the slightly larger Ω_b of model I, the ionization fraction decreases slightly to 0.3, and for the probably unrealistic baryon-dominated universe of model II, the ionization fraction decreases only to 0.21. Increasing Ω_b enhances the density and the Li recombination rate, but the H recombination is also enhanced, so that the additional electrons are removed to form H and not Li. We form Li mostly through process (5). The rate was determined by detailed balance from model potential photoionization cross sections (Caves & Dalgarno 1972) for which the ground state cross section is in fair agreement with the experimental curve. Inclusion of mutual neutralization (6) and charge transfer (11) and (13) has only minor effects. Processes that form the lithium hydrides have a negligible effect on the Li abundance.

Abundances of Li^- are presented for the first time in the present work. Li^- is formed by the radiative attachment process (22) and removed by photodetachment for $z > z_f \sim 80$ and by reaction (24) and the LiH forming process (25) for $z < z_f$.

The abundance of LiH has received considerable attention. It has been calculated by Lepp & Shull (1984), Puy et al. (1993), and Palla et al. (1995). They all overestimated the abundance by using a rate coefficient for the radiative association process (20) deduced by Lepp & Shull (1984) through semiclassical collision arguments. Including the new quantum-mechanically determined rate coefficient for reaction (20) obtained in DKS and the LiH destruction by process (26), we find the LiH abundance as $z \to 0$ to be reduced typically by about 100 for all three models in comparison to the previous calculations. Inclusion of the gas-phase reactions (27), (29), (30), and particularly (28) reduces the abundance further for $z < 1300$. The rate coefficients are uncertain. Reactions (19), (21), and (25) increase the abundance slightly, the associative attachment (25) of Li^- and H being the most effective for $z < 80$. The formation redshift z_f of about 450 is in agreement with the predictions of both Puy et al. (1993) and Palla et al. (1995).

With the realization that Li remains ionized, Dalgarno & Lepp (1987) inferred that initially the molecular ion LiH^+ would be preferentially produced over LiH and Bellini et al. (1994) have pointed out that the LiH^+ abundance would be limited by photodissociation and dissociative recombination. The actual situation is more interesting. The molecular ion can be formed by the *two* radiative association processes (7) and (15) and destroyed by the reverse reactions (16) and (17). Rates for reactions (7) and (15) were calculated in the preceding paper (DKS). Cross sections and early universe dissociation rates for (16) and (17) will be presented in a future publication (Stancil, Kirby, & Dalgarno 1996).

Figure 1 displays the unusual behavior of the LiH^+ fractional abundance with redshift. The first plateau at $z \sim 1300$ is due to formation by (7) and the second plateau at $z \sim 450$ to (15). The abundance is kept low because of the extreme effectiveness of the photodissociation reaction (16), as noted by Bellini et al. (1994), and to the small dissociation energy, 0.14 eV, of LiH^+. The photodissociation reaction (17) plays a minor role becoming negligible for $z < 450$, but as z approaches 100 the effectiveness of (16) also diminishes, so that the LiH^+ abundance rises sharply. The production of LiH^+ at late times in the primordial gas evolution with an effective redshift of formation $z_f \sim 25$ is unexpected. For $z < 25$, LiH^+ is removed by the dissociative recombination reaction (8) but mostly by the gas-phase reaction (14). We find the LiH^+ abundance to be negligible at large redshifts, but for $z < 25$ $n(LiH^+)/n(LiH)$ approaches 0.1. Palla et al. (1995) have carried out a calculation of the LiH^+ abundance with results that differ considerably from the current work. They considered formation by radiation association and destruction through photodissociation, but they adopted LiH rate coefficients.

Comparison between the three models suggests that the asymptotic abundances of H^- and Li and Li^+ are proportional to the electron and total lithium abundances, respectively. Li^-, LiH, and LiH^+ have a more complicated dependence on the electron and lithium abundances, so that model II or model III cannot be obtained from model I through simple scaling arguments. The primordial lithium abundance may be larger than in our models (Deliyannis et al. 1994; Deliyannis, Boesgaard, & King 1995). Within a particular model, if Ω_b and h are held fixed, the abundances of the lithium species scale linearly with the adopted primordial total lithium abundance.

5. IMPLICATIONS

5.1. *Cosmic Background Radiation Anisotropies*

It is difficult to reconcile measurements of spatial anisotropies in the CBR spectrum with current galaxy formation theories (cf. Maoli et al. 1994). One remedy is a secondary reionization in the postrecombination epoch near $z \sim 100$. If ionized, the primordial matter would scatter CBR photons, changing the frequency and spatial distribution. An alternative resolution was put forth by Dubrovich (1993) in which Thomson scattering of CBR photons with molecules would erase the spatial anisotropies. Following this suggestion, Maoli et al. (1994) have shown that the primary anisotropies may be attenuated for frequencies less than 50 GHz and angular scales between approximately 10°–50° if the fractional LiH abundance exceeds 10^{-10}. Assuming that LiH is destroyed by high-energy photons from the first primordial objects for $z = 7$–50, Maoli et al. (1994) obtained optical depths of $\sim 10^{-2}$ and ~ 1 for LiH abundances of 10^{-11} and 10^{-9}, respectively. For comparable LiH^+ abundances, the optical depth was predicted to be about a factor of 10 smaller. Palla et al. (1995) have recently shown, using their lower LiH abundance, that the optical depth is less than $\sim 10^{-4}$. Our improved lithium chemistry results in a further reduction of the LiH abundance and suggests that the opacity could not exceed $\sim 10^{-6}$ even for the baryon-dominated universe of model II. It seems unlikely that Thomson scattering will have an appreciable effect on the primary spatial CBR anisotropies. It may prove necessary to subscribe to a late reionization scenario to bring the observed anisotropies into agreement with galaxy formation models.

5.2. LiH *in Protoclouds*

The earlier calculations of Lepp & Shull (1984) and Puy et al. (1993), which indicate relatively large LiH abundances, have motivated searches for highly redshifted LiH rotational-vibrational (RV) lines in protoclouds (de Bernardis et al. 1993; Signore et al. 1994). de Bernardis et al. (1993) reported a 95% upper limit of a about 20 mK intensity for $(v = 0, j) \to (v = 1, j \pm 1)$ RV lines near 1300 cm^{-1} reshifted to about 7 cm^{-1}

($\sim$220 GHz) for $z \sim 180$. To estimate possible contamination from the atmosphere and local galactic emission, they also made observations at 90 GHz corresponding to a redshift of about 450 for the LiH RV lines. LiH lines were not expected to be present at this frequency since the formation of LiH was predicted by Lepp & Shull (1984) to occur at $z \sim 200$. de Bernardis et al. (1993) also modeled the emission for a 2 kpc cloud and estimated from their observed upper limits that the cloud density could be no greater than 10^7 cm^{-3} if the LiH fractional abundance were 10^{-10}. Recent measurements of greater precision have established the more severe upper limit of 1 mK for the intensity at 220 GHz, which reduces the inferred upper limit to the cloud density (Maoli et al. 1996). However, if our predicted LiH abundances are correct, the inferred upper limit of the cloud density is much increased.

The frequency of 90 GHz may not be optimal for estimating the background intensity. In our calculations, the LiH abundance at $z = 180$ is about 10 times the abundance at $z = 450$ and more than 100 times at $z > 500$, corresponding to frequencies less than 80 GHz.

It may still be possible to observe LiH lines in the early universe, perhaps in pregalactic clouds undergoing gravitational collapse for $z \sim 50$. As the density rises, the production of LiH will be enhanced by the three-body association reactions,

$$\mathrm{Li + H + H \rightarrow LiH + H}\,, \quad (37)$$

$$\mathrm{Li + H + H_2 \rightarrow LiH + H_2}\,. \quad (38)$$

5.3. *The Primordial Lithium Abundance and Nucleosynthesis Models*

A major motivation for investigating the effects of Thomson scattering on LiH and LiH emission lines in protoclouds is the possibility of placing constraints on the primordial lithium abundance, which would discriminate between standard big bang nucleosynthesis (SBBN) and inhomogeneous BBN (IBBN). SBBN predicts a ^{7}Li fractional abundance of $\sim 10^{-10}$ and IBBN a maximum of $\sim 10^{-8}$. Observations of a ^{7}Li fractional abundance of $\sim 10^{-10}$ in population II stars seems to confirm SBBN, but an abundance of $\sim 10^{-9}$ in population I stars is consistent with a IBBN scenario (cf. Signore et al. 1994). Use of these stellar measurements to constrain the primordial lithium abundance presumes an accurate understanding of lithium depletion in stellar evolution and galactic lithium production. de Bernardis et al. (1993) and Signore et al. (1994) propose to circumvent this problem by observing primordial LiH directly at high z. Maoli et al. (1994) and Signore et al. (1994) further suggest that CBR anisotropy data can be used to constrain the lithium abundance because elastic Thomson scattering of CBR photons with LiH may erase the anisotropies. Both methods require a large LiH abundance of $\sim 10^{-10}$, while our calculations place the LiH abundance closer to $\sim 10^{-16}$. Even considering the most optimal LiH-production parameters (model III, but with $n_{\rm Li}/n_{\rm H} = 10^{-8}$), the fractional abundance of LiH can be no greater than 10^{-15}.

We thank I. Dell'Antonio for providing us with his data prior to publication, K. Kirby for helpful discussions, and F. Palla, F. Melchiorri, D. Puy, and M. Signore for useful comments on the manuscript. This work was supported by the National Science Foundation, Cooperative Agreement OSR-9353227 (P. C. S. and S. L.) and Division of Astronomical Sciences, grant AST 93-01099 (A. D.).

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