LiHe$^+$ IN THE EARLY UNIVERSE: A FULL ASSESSMENT OF ITS REACTION NETWORK AND FINAL ABUNDANCES

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ABSTRACT

We present the results of quantum calculations based on entirely ab initio methods for a variety of molecular processes and chemical reactions involving the LiHe$^+$ ionic polar molecule. With the aid of these calculations, we derive accurate reaction rates and fitting expressions valid over a range of gas temperatures representative of the typical conditions of the pregalactic gas. With the help of a full chemical network, we then compute the evolution of the abundance of LiHe$^+$ as function of redshift in the early universe. Finally, we compare the relative abundance of LiHe$^+$ with that of other polar cations formed in the same redshift interval.

Key words: astrochemistry – atomic processes – cosmic background radiation – early Universe – molecular processes – radiative transfer

1. INTRODUCTION

The suggestion that chemical processes involving lithium atoms, as part of simple diatomic species formed with partner atoms and ions of expected significant abundances (i.e., H, He, H$^+$, and He$^+$), could play a role in the evolution of the early universe was put forward several years ago (e.g., see Lepp & Shull 1983; Stancil et al. 1996; Galli & Palla 1998). The formation of Li-bearing molecules results from the production of Li atoms a few minutes after the big bang and the concurrent formation of other light atoms like H, D, and He (Wagoner et al. 1967; Peebles 1993). The fractional abundances of these elements are sensitive to the values of the baryon density and temperature of the early universe and therefore imply specific physical constraints on their actual values (Cyburt et al. 2008). In fact, as the universe expanded its radiation temperature decreased and the atomic ions which had originated from the elements above gave rise to neutral atoms from ionic recombination with ambient electrons, thereby producing molecular species chiefly by radiative association. Neutral molecules include H$_2$, HD, and LiH.

Because of its large dipole moment and low ionization potential, LiH has been considered a potential candidate for inducing spatial and/or spectral distortions of the cosmic background radiation (CBR), as originally suggested by Dubrovich (1993) and observationally tested by Maoi et al. (1994) and Persson et al. (2010). It is, in fact, its possible role as a molecular coolant of the primordial gas because of the efficient radiative decay down its manifold of rovibrational levels that made its likely presence a very important issue in several earlier studies (Bougleux & Galli 1997). By the same token, other molecular species formed as cations after atomic ionization during gravitational collapse, e.g., LiH$^+$, HeH$^+$, HD$^+$, and LiHe$^+$, could also play a similar role as additional molecular coolants. Furthermore their non-equilibrium level populations may also have left possible signatures in protogalactic clouds, imprinting spatial or spectral distortions in the CBR spectrum (Schleicher et al. 2008).

In particular, in this work we analyze LiHe$^+$ via a series of quantum calculations to determine the relative role of several pathways to its formation and destruction within the chemical network acting at low redshift. In previous papers (Bovino et al. 2011a, 2012), we examined the photonic paths to the formation and destruction of LiHe$^+$. In the present paper, we extend that work by adding the chemical paths presiding over its evolution, i.e., the chemical reaction with hydrogen,

$$\text{LiHe}^+ + \text{H} \rightarrow \text{LiH}^+ + \text{He},$$

leading to its destruction, and the formation reaction from the lithium hydride cation:

$$\text{LiH}^+ + \text{He} \rightarrow \text{LiHe}^+ + \text{H},$$

the physical characteristics of which are discussed extensively in our recent work on this system (Tacconi et al. 2012).

An additional path that we shall consider in the present study is that driven by the presence of a residual electron fraction in the early universe (Stancil et al. 1996), i.e., the fragmentation of the polar cation by the dissociative recombination (DR) process:

$$\text{LiHe}^+ + e^- \rightarrow \text{LiHe}^+ \rightarrow \text{Li} + \text{He} + h\nu,$$

a reaction that, from the previous calculations, will turn out to be fairly efficient.

In a previous study of the lithium chemistry in the early universe (Bovino et al. 2011b), we found that the abundances of LiH and LiH$^+$ were of the order of about $10^{-17}$ (number fraction), i.e., too diluted for direct detection with presently available tools. Hence it is of interest to see what the abundance would be for the LiHe$^+$, a molecular partner not considered in previous studies because of lack of reliable data. To this goal, we shall avail ourselves of the new, and accurate, cross sections and reaction rates obtained here with fully quantum methods.

In the next section, we will briefly summarize the computational findings for reactions (1)–(3) and report the corresponding computed reaction rates at the relevant temperatures, while in Section 3 we will discuss the relative role of the formation/destruction channel rates of LiHe$^+$ at low $z$, together with its fractional abundance compared to those of other molecules present in the early universe. Finally, in Section 4 we summarize our conclusions.
2. THE COMPUTED QUANTUM RATES

As mentioned in Section 1, our previous study on the photon-induced evolution of LiHe\(^+\) under early universe conditions (Bovino et al. 2011a, 2012) has shown efficient formation of the latter molecule by resonant radiative recombination but also competitive destruction by photodissociation at low redshifts. Hence, it was suggested by the ensuing modeling of its relative abundances that the LiHe\(^+\) number fraction at \(z \sim 30–1\) would be lower than \(10^{-11}\) by photon-induced paths only, i.e., much lower that the corresponding values obtained for LiH\(^+\) (∼\(10^{-14}\)) and for HeH\(^+\) (∼\(10^{-9}\)) under the same conditions. On the other hand, a more realistic picture should be obtained by the additional implementation in the evolution scheme of the chemical routes outlined in the previous section, in order to achieve a fuller comparison with the data which already exist for the other polar cations formed in the early universe.

The chemical reaction route for both processes,

\[
\text{LiH}^+(2\Sigma^+) + \text{He}(1S) \rightleftharpoons \text{LiHe}^+(1\Sigma^+) + \text{H}(2S),
\]  

(4)

of formation (with a threshold) and of destruction (without threshold) have been studied in detail earlier by us (Tacconi et al. 2012) using accurately computed potential energy surfaces for the reactive paths (Wernli et al. 2009). The quantum reactive cross sections were obtained using a negative imaginary potential approach within a coupled-state description of the quantum dynamics (Bovino et al. 2011c). Full details of the computations have been reported by Tacconi et al. (2011) and in earlier papers on ionic reactions (Bovino et al. 2010, 2011c): we therefore refer the interested reader to those papers for further details. In order to put the present results in a more specific context, we show in Figure 1 the behavior of the computed rates for the formation (left panel) and destruction (right panel) reactions given by Equation (4) and obtained from our recent calculations (Tacconi et al. 2012).

It is interesting to note at the outset the contrasting behavior between the formation of the cation, which presents an energy barrier of ∼0.05 eV (Tacconi et al. 2012) and therefore becomes negligibly small at lower redshifts, and the same process when the LiH\(^+\) formed is taken to be vibrationally excited (dashed line in the left panel). Since the amount of internal energy is sufficient to overcome the barrier to reaction, the formation process now shows a rather mild dependence on temperature and exhibits much larger formation rates around \(10^{-10}\) cm\(^3\) s\(^{-1}\).

Entirely different, however, is the behavior of the exothermic destruction reaction, reported in the right panel of Figure 1. In that case the reaction rates are largely independent of temperature but, even for LiHe\(^+\) in its ground rotovibrational state, remain of the order of \((3–4) \times 10^{-10}\) cm\(^3\) s\(^{-1}\) at the lower temperature values. It is therefore natural to expect that the different sizes of the two reaction channels will play an important role when generating the final abundances, as we shall discuss further in the next section.

Another “chemical” process which we need to consider concerns the effects of the ambient electrons on the cationic molecule formed as described by reaction (3), i.e., the destruction of LiHe\(^+\) following the DR mechanism outlined there. The DR process has been studied before and corresponding data under early universe conditions already exist for HeH\(^+\) (Haxton & Greene 2009) and LiH\(^+\) (Čurík & Greene 2007). No data, however, were available for the present system.

Therefore we have analyzed the electron-assisted destruction of LiHe\(^+\), with the ensuing production of Li and He atoms (the details of the calculations will be presented elsewhere: R. Čurík et al. 2012, in preparation). Here, it suffices to say that the recombinative process, similar to the case of LiH\(^+\) (Čurík & Greene 2007), is not a direct curve-crossing process with a dissociative, neutral potential but rather an indirect process which involves Rydberg states of the lithium atom perturbed by the presence of He. The final destruction is therefore...
caused by vibrational Feshbach resonances within the (Li\(^+\)He\(^*\)) collisional complex which lead to the efficient break-up between a radiatively stabilized lithium and a neutral helium atom (see R. Ćurčík et al. 2012, in preparation for further details).

The general behavior of the computed rates as a function of the temperature of the gas \(T_g\) (assumed equal to the electron temperature) is given by the calculations shown in Figure 2. The figure clearly indicates the marked dependence of such rates on the internal energy of the initial target, while the definition of a global equilibrium temperature is the one which can be used within the calculation of the relative abundances, as we shall report in the following section.

3. THE CHEMICAL NETWORK AND EVOLUTIONARY MODELING

The evolution of the pregalactic gas is usually considered within the framework of a Friedmann cosmological model and the cosmological abundances of the main atomic components are taken from standard big bang nucleosynthesis results (Smith et al. 1993). The numerical values of the cosmological parameters used in the calculation are obtained from WMAP5 data (Komatsu et al. 2009). For additional details on the model, see Galli & Palla (1998), Coppola et al. (2011), and Bovino et al. (2011b).

In order to obtain the abundances of LiHe\(^*\) which evolve from the network of the relevant processes, a set of differential coupled rate equations of the form

\[
\frac{dn_i}{dt} = \alpha_{\text{form}} n_j n_k - \alpha_{\text{dest}} n_i + \cdots
\]

has been solved. In Equation (5), \(\alpha_{\text{form}}\) and \(\alpha_{\text{dest}}\) are the formation and destruction rates of the species under discussion, and \(n_i\) is the number density of the reactant species \(i\). The rate coefficients involved in the lithium chemistry network are basically the same as those reported in Bovino et al. (2012), with the exception of the reactions involving the LiHe\(^*\) molecule which now come from the present quantum calculations. Table 1 shows the reactions and the fitting formulas of the rate coefficients adopted. The equations governing the temperature and redshift evolutions have been reported in earlier papers (see, e.g., Galli & Palla 1998; Bovino et al. 2011b) and will not be repeated here.

4. LIHE\(^*\) EVOLUTION AND FINAL ABUNDANCES

As mentioned in the previous sections, it is instructive to model, from the present data plus the network of rate equations outlined before, the way in which the production of LiHe\(^*\) molecules evolves, as a function of redshift, in its interplay with the coexisting destruction channels.

The complex evolution of all the species considered is shown in Figure 3, where the labels \(p_i\) indicate production channels whereas the labels \(d_i\) identify the destruction channels (same notation as in Table 1). The production of LiHe\(^*\) is dominated at all redshifts by radiative association of Li\(^+\) with He, both spontaneous and stimulated (reactions \(p_1\) and \(p_2\), respectively). The LiH\(^+\) channel is never effective because of a threshold at \(\nu \approx 60\) K in the reaction of LiH\(^+\)\((\nu = 0)\) with He (reaction \(p_3\)). The reaction of LiH\(^+\)\((\nu = 1)\) with He (reaction \(p_4\)), although characterized by a much larger rate than its \(\nu = 0\) counterpart, is also not important because of the rapid decay of the \(\nu = 1\) level population of LiH\(^+\) at low redshifts. The destruction of LiHe\(^+\) is due to photodissociation for \(z \gtrsim 60\) (reaction \(d_1\)) and to collisions with H for \(z \gtrsim 60\) (reaction \(d_3\)), with a significant contribution from DR (reaction \(d_2\)).

The above data are considered reliable down to \(z\) values of about \(z = 10\) since at that stage the first stars are formed and reionization occurs, thereby invalidating the assumptions at the basis of the chemical network. On the whole, however, we can say that the close competition between efficient formation paths, and nearly as efficient destruction reactions, indicates for the present system a limitation to its final abundances in the redshift region of interest.

The consequences of the interplay between the different conflicting rates discussed above can be seen more clearly in Figure 4 showing the different abundances of various molecular cations on a log–log scale as a function of redshift. Most of the data for species other than LiHe\(^*\) have been presented in earlier
Reactions Considered in the Present Study

| Reaction | Fitted Rate (cm\(^3\) s\(^{-1}\) or s\(^{-1}\)) | Reference |
|----------|-----------------------------------------------|-----------|
| \(p_1\)  | \(\text{Li}^+ + \text{He} \rightarrow \text{LiHe}^+ + h\nu\) (sp.) | \(\log k = -21.87 - 0.204 \log T_g - 0.153(\log T_g)^2 - 0.233(\log T_g)^3 - 0.144(\log T_g)^4 + 0.0148(\log T_g)^5\) | (a) |
| \(p_2\)  | \(\text{Li}^+ + \text{He} \rightarrow \text{LiHe}^+ + h\nu\) (st.) | \(\log(k/T_r) = -22.23 - 0.600 \log T_g - 0.086(\log T_g)^2 - 0.082(\log T_g)^3 + 0.042(\log T_g)^4 - 0.0073(\log T_g)^5\) | (a) |
| \(p_3\)  | \(\text{LiH}^+(v = 0) + \text{He} \rightarrow \text{LiHe}^+ + \text{H}\) | \(k = (5.047 \times 10^{-12} - 2.723 \times 10^{-14} T_g + 7.775 \times 10^{-17} T_g^2 - 1.954 \times 10^{-20} T_g^3) \exp(-441/T_g)\) | (b) |
| \(p_4\)  | \(\text{LiH}^+(v = 1) + \text{He} \rightarrow \text{LiHe}^+ + \text{H}\) | \(\log k = -9.96 - 0.648 \log T_g - 2.743(\log T_g)^2 + 6.092(\log T_g)^3 - 9.297(\log T_g)^4 + 8.397(\log T_g)^5\) \(-4.420(\log T_g)^6 + 1.328(\log T_g)^7 - 0.210(\log T_g)^8 + 0.013(\log T_g)^9\) | (b) |
| \(d_1\)  | \(\text{LiHe}^+ + h\nu \rightarrow \text{Li}^+ + \text{He}\) | \(k = 21 T_r^{0.25} \exp(-5460/T_r)\) | (a) |
| \(d_2\)  | \(\text{LiHe}^+ + e \rightarrow \text{Li} + \text{He}\) | \(\log k = -5.254 - 0.452 \log T_g - 0.791(\log T_g)^2 + 0.463(\log T_g)^3 - 0.076(\log T_g)^4\) | (c) |
| \(d_3\)  | \(\text{LiHe}^+ + \text{H} \rightarrow \text{LiH}^+ + \text{He}\) | \(\log k = 5.780 - 2.274(\log T_g) + 0.154(\log T_g)^2 + 0.0639(\log T_g)^3\) | (a) |

Notes. Fitting expression as function of the gas \((T_g)\) or radiation \((T_r)\) temperatures are accurate to better than 10% in the range \(1 \text{ K} < T_g, T_r < 10^3 \text{ K}\).

References. (a) Bovino et al. 2012; (b) Tacconi et al. 2012; (c) R. Čurík et al. 2012, in preparation.
Figure 4. Computed abundances (number fractions) of molecular cations in the early universe as a function of redshift $z$, obtained from the rates reported in Figure 3.

work, while the evolution of LiHe$^+$ is obtained from the new, accurate quantum calculations of the present study.

Due to the concurrent destruction paths, it is clear from that comparison that, at redshift values between about 20 and 10, the fractional abundance of the LiHe$^+$ ions never increases beyond about $10^{-22}$ number fractions, well below those of HeH$^+$ and LiH$^+$. While the former molecule clearly remains the most interesting candidate for experimental observation, LiH$^+$ is still a borderline case that provides a challenging option while LiHe$^+$ still appears below the sensitivity of current instrumentations.

5. CONCLUSIONS

In the work reported in this paper we have analyzed in greater detail the molecular processes which involve a thus far poorly studied molecular cation, LiHe$^+\left(^1\Sigma^+\right)$, and which deal with its possible formation and destruction in the pregalactic gas through an extensive network of photon-induced and chemically driven processes. In the range of redshifts of interest, we have carried out quantum calculations of chemical formation/destruction reactions which have never been considered before from realistic computational models (see reactions (1)–(3) of Section 2).

Our results clearly show the close competition between production and destruction pathways which turn out to have very similar efficiencies. Hence, the estimated abundances for LiHe$^+$, within $z$ values from about 30 and 10, do not increase as highly as those found for LiH$^+$ and HeH$^+$.

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