FAST LiH DESTRUCTION IN REACTION WITH H: QUANTUM CALCULATIONS AND ASTROPHYSICAL CONSEQUENCES

S. BOVINO, M. WERNLI, AND F. A. GIANTURCO
Department of Chemistry and CNISM, the University of Rome “Sapienza,” P.le A. Moro 5, 00185 Rome, Italy; fa.gianturco@caspur.it
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ABSTRACT
We present a quantum-mechanical study of the exothermic $^7$LiH reaction with H. Accurate reactive probabilities and rate coefficients are obtained by solving the Schrödinger equation for the motion of the three nuclei on a single Born–Oppenheimer potential energy surface and using a coupled-channel hyperspherical coordinate method. Our new rates indeed confirm earlier, qualitative predictions and some previous theoretical calculations, as discussed in the main text. In the astrophysical domain, we find that the depletion process largely dominates for redshift ($z$) between 400 and 100, a range significant for early universe models. This new result from first-principle calculations leads us to definitively surmise that LiH should be already destroyed when the survival processes become important. Because of this very rapid depletion reaction, the fractional abundance of LiH is found to be drastically reduced, so that it should be very difficult to manage to observe it as an imprinted species in the cosmic background radiation. The present findings appear to settle the question of LiH observability in the early universe. We further report several state-to-state computed reaction rates in the same range of temperatures of interest for the present problem.

Key words: astrochemistry – early universe – ISM: molecules – methods: numerical – molecular processes – scattering

1. INTRODUCTION

The chemistry of the early universe plays an important role in our understanding of the formation of the first chemical objects and on the birth and evolution of galaxies and interstellar clusters. Observations of molecular absorption and emission lines have provided important information about the physical conditions in which molecules are first formed, then excited and destroyed. Lepp et al. (2002) identified 200 reactions considered to contribute to the abundance of 23 atomic and molecular species. Molecular formation in the early universe began when the temperature was low enough that the newly formed atoms could survive for further evolution. In this era, termed as the recombination era, at a redshift around $z = 2500$, the universe was about 100,000 years old and the temperature was about 4000 K. After recombination, the density was still very low and three-body (3B) reactions were still very inefficient: however, it was then that the first molecular species were postulated to be formed through radiative association. In spite of the low fractional abundance which is expected to exist for LiH ($\sim 10^{-10}$–$10^{-19}$), this molecule has nevertheless been considered one of the most likely species to be important in that domain, due to its large permanent dipole moment and the light masses of the involved atoms. Its search has therefore spurred several experimental studies in the recent past (Combes & Wiklind 1998; de Bernardis et al. 1993). Indeed, it was further suggested by Dubrovich (1993) that primordial molecules with large dipole moments might be detectable by their imprint left on the cosmic background radiation (CBR) and arising from the resonant enhancement of the Thomson scattering cross sections which occur at the transition frequencies of the molecules. LiH was thus considered to be very relevant because of the role it may have played as a possible coolant during the late stages of the gravitational collapse of the first cosmological objects, as this very molecule may have survived even H$_2$. In their works, Lepp & Shull (1984), and later Puy et al. (1993) and Palla et al. (1995), concluded that the major formation mechanism of lithium hydride is likely to be via the following radiative association process:

$$\text{Li} + \text{H} \rightarrow \text{LiH} + \nu. \quad (1)$$

The rate coefficients for reaction (1) were later calculated by Dalgarno et al. (1996) and Gianturco & Gori-Giorgi (1997), who also considered the reduction of the abundance of LiH as a consequence of the exchange reaction, the latter being the strongly exothermic channel of the LiH destruction indicated below:

$$\text{LiH} + \text{H} \rightarrow \text{Li} + \text{H}_2. \quad (2)$$

Since the observational detection of LiH is still an ongoing possibility among the options of experimental efforts, the present work intends to clearly and accurately assess the feasibility of such measures vis à vis the outcomes of rigorous computational data. We therefore intend to study the very reaction (2) in the redshift range $1000 < z < 20$ to try to provide a more detailed evaluation of the possible role of this molecule in the early universe evolution. Quantum coupled-channel equations have been solved to first calculate accurate rate coefficients as described in Section 2, while the astrophysical consequences of our results will be detailed in Sections 3 and 4, together with our conclusions.

2. THE QUANTUM REACTIVE CALCULATIONS

In the last 20 years, a great deal of effort has been made to calculate accurate rate coefficients for the reaction (2). Stancil et al. (1996) conjectured a temperature-independent rate coefficient of $2 \times 10^{-11}$ cm$^3$ s$^{-1}$ by assuming the absence of an activation barrier and therefore postulated the insignificant role of LiH in erasing primary anisotropies in the CBR field. Dunne et al. (2001), using a quasi-classical dynamics and Defazio et al. (2005), with a real wave-packet method, obtained rate coefficients in a range of temperatures $0 < T < 4000$ K. However, the potential energy surface (PES) used by those
calculations (the one generated by Dunne et al. 2001) presented a rather deep well in the product valley which would cause unphysical trapping and resonance effects in the dynamics within partners which are instead interacting via mainly van der Waals forces. We, therefore, carried out new calculations solving the quantum coupled-channel hyperspherical equations involving a new three-dimensional surface (Wernli et al. 2009) recently calculated and fitted with very good accuracy. The exothermicity of the reaction was estimated to be 2.258 eV, and it now correctly proceeds without a barrier into the exothermic products of Equation (2).

The main improvements introduced by our newly calculated PES for the ground electronic state of reaction (2) have been the correct description of long-range forces among product partners and the elimination of barrier features in the entrance channel of the reagents, as discussed in more detail by Wernli et al. (2009). The reaction probability and rate coefficients were thus calculated and fitted with very good accuracy. The computational parameters in order to yield a confidence level on the final cross sections below 1%. Following earlier suggestions (Padmanaban & Mahapatra 2004) and carefully testing all convergence-controlling parameters in order to yield a confidence level on the final cross sections below 1%. Following earlier suggestions (Zhang & Zhang 1999), we further applied a uniform J-shifting approach to generate the full rate coefficients rest on the reasonable assumption that higher $a_0$ values are chiefly modifying the shape of the transition states through changes of the centrifugal potential of the reaction complex. This is certainly a realistic description of an exothermic reaction that proceeds without a barrier in the entrance channels, as is indeed the case here.

3. RESULTS AND DISCUSSION

To start assessing the outcomes of the quantum calculations described in the previous section, we report in Table 1 the LiH reaction rates, summed over all final states, for the formation of both oH$_2$ and pH$_2$ as product molecules. The range of temperatures covers all the values expected to be relevant for the corresponding range of $z$ of astrophysical interest. Several comments could be made about these results.

1. The rates turn out to be rather large over the whole range of $T$ and to be largely independent of yielding either pH$_2$ or oH$_2$ as products. Most importantly, our new values from accurate ab initio methods turn out to be close to the educated estimates of Stancil et al. (1996), although extending and improving on their temperature dependence. We therefore confirm with the present calculations the likely occurrence of a rapid disappearance of any newly formed LiH because of its reaction with the surrounding hydrogen. This is an important result which now comes exclusively from non-empirical calculations.

2. Above 200 K the rates were obtained by using a functional form $\alpha(T) = aT \times \exp(-bT)$, as suggested by Stancil et al. (1996) in their kinetic model of lithium reaction in the primordial gas. Our calculated parameters are $a = 2.05 \times 10^{-12}$ cm$^3$ s$^{-1}$ K$^{-1}$ and $b = 0.00058$ K for oH$_2$ and $a = 2.18 \times 10^{-12}$ cm$^3$ s$^{-1}$ K$^{-1}$ and $b = 0.00084$ K for pH$_2$. The values employed by Defazio et al. (2005) and by Padmanaban & Mahapatra (2004) were obtained by using the same formula but turned out to be slightly different and to yield different final rates. However, given the fact that they employed a different reaction PES (from Dunne et al. 2001), this result is not surprising.

The further calculations reported by Table 2 show another interesting facet of the present reaction since we give there the low-$T$ rates obtained for the formation of oH$_2$ starting from different vibrational levels of the LiH molecule; one clearly sees that the initial process of LiH destruction changes when the LiH reacting molecule is internally "hot. Such states could be the result of the occurrence of only partial relaxation of the latter species which is formed during the recombination process indicated by Equation (1). In any event, the order of magnitude of the rates does not vary dramatically when we change the vibrational energy content of the initial molecular partner. The results of the tables are pictorially given by the two panels of Figure 1, where we show on the top panel the temperature dependence of the LiH destruction rates leading to the formation of both pH$_2$ and oH$_2$ and, in the lower panel, the oH$_2$ formation (caused after the LiH destruction) for different vibrational content of the initially formed LiH partner obtained through Equation (1). One sees there that the oH$_2$ formation is the favored process outside a very small $T$-value region, as one should expect to find by nuclear multiplicity consideration. Furthermore, the presence of vibrationally "hot" LiH molecules can cause the depletion rates to become smaller, in favor of the simpler hydrogen exchange reaction.

| Table 1 | Computed Rate Coefficients Summed Over all Final States of the Products |
|---------|-------------------------------------------------------------------|
| $T$ (K) | $\alpha(T)_{\text{ortho}}$ (cm$^3$ s$^{-1}$) | $\alpha(T)_{\text{para}}$ (cm$^3$ s$^{-1}$) |
| 10      | 1.57–11              | 1.71–11              |
| 20      | 4.05–11              | 4.40–11              |
| 40      | 8.14–11              | 8.74–11              |
| 80      | 1.56–10              | 1.61–10              |
| 100     | 1.94–10              | 2.00–10              |
| 200     | 3.65–10              | 3.69–10              |
| 500     | 7.66–10              | 7.16–10              |
| 1000    | 1.14–09              | 9.41–10              |
| 2000    | 1.28–09              | 8.12–10              |
| 4000    | 8.05–10              | 3.03–10              |
| 5000    | 5.64–10              | 1.63–10              |
| 7000    | 2.47–10              | 4.26–11              |
| 8000    | 1.58–10              | 2.10–11              |
| 10000   | 6.20–11              | 4.90–12              |

| Note. The notation 1.57–11 corresponds to $1.57 \times 10^{-11}$. |

| Table 2 | Calculated Rate Coefficients, Summed Over all Final oH$_2$ States, for Different Vibrational Initial States of LiH |
|---------|-------------------------------------------------------------------|
| $T$ (K) | $\alpha(T)_{\nu=0}$ (cm$^3$ s$^{-1}$) | $\alpha(T)_{\nu=2}$ (cm$^3$ s$^{-1}$) | $\alpha(T)_{\nu=4}$ (cm$^3$ s$^{-1}$) |
| 10      | 1.57–11              | 3.33–13              | 6.83–13              |
| 20      | 4.05–11              | 1.48–12              | 2.27–12              |
| 40      | 8.14–11              | 6.28–12              | 4.29–12              |
| 50      | 1.00–10              | 9.88–12              | 9.35–12              |
| 80      | 1.56–10              | 2.47–11              | 2.00–11              |
| 100     | 1.94–10              | 3.72–11              | 2.90–11              |
where it is forming H\textsubscript{2} in vibrational states above
the formation of H\textsubscript{2} (see the
largely remain of the same order of magnitude, although we see
individual H\textsubscript{2}-formation rates change only little by changing
vance for the early universe study, and clearly suggest that the
range of temperatures that also map the redshift values of rele-

tion is important for establishing the differences in the probabil-
molecules in different, final rotovibrational states. This informa-
Only the oH\textsubscript{2} case is being presented. All units are \text{cm}^3 \text{s}^{-1}.

The data of Table 3 additionally present the computed rates
for the depletion reaction (2) leading to the formation of H\textsubscript{2}
molecules in different, final rotovibrational states. This informa-
tion is important for establishing the differences in the probabil-
ities of producing internally excited hydrogen molecules which
in turn can decay by radiative processes. The results cover the
range of temperatures that also map the redshift values of rele-
vance for the early universe study, and clearly suggest that the
individual H\textsubscript{2}-formation rates change only little by changing
the final rotovibrational level of the newly formed molecule: the
examples of Table 3, in fact, indicate a variation of about one
order of magnitude from forming H\textsubscript{2} (ν′ = 0, j′ = 1) to produc-
ing instead H\textsubscript{2} (ν′ = 3, j′ = 9). One should also note that the
H\textsubscript{2}-formation reaction becomes endothermic for the situations
where it is forming H\textsubscript{2} in vibrational states above ν′ = 4 (see
also Wernli et al. 2008).

The general behavior shown by the data of Table 3 is further
presented in a pictorial form by the two panels of Figure 2,
where we show as a function of the temperature and of the
redshift values, the relative behavior of a selection of rates of
H\textsubscript{2} formation into different, final rotovibrational states for
the H\textsubscript{2} molecule. All rates appear to behave very similarly and to
largely remain of the same order of magnitude, although we see
that the production of internally excited species, e.g., see the
formation of H\textsubscript{2} (ν′ = 0, j′ = 11) in the upper panel and of H\textsubscript{2}
(ν′ = 3, j′ = 9) in the lower panel, corresponds to smaller rates.

Hence, the present, state-specific results indeed suggest that the
newly formed H\textsubscript{2} molecules should be preferentially formed in
their ground rotovibrational level, with a reduced probability for
further contributing to radiative emissions.

The relative behavior of the two chief processes, i.e., the
hydrogen exchange reaction (termed here LiH survival) and the
H\textsubscript{2} formation (called the LiH destruction) are reported in Figure 3
over a log–log scale in the main plot, while the
same processes are shown on the temperature and redshift
scales in the inset. The energy dependence clearly indicates
that the H exchange is the dominant process at low collision
energies, as expected because of the steric hindrance created
by the bulkier Li atom to the low-T insertion reaction, while
the destruction of the LiH initially formed is seen to occur for
the majority of the collisional events once the temperature
and the energy) becomes larger than about 300 K. In this
temperature range, as we can see in the inset, z is estimated
(Puy et al. 1993) to be greater than 250. This means that the
destruction process is dominant in the molecular formation
range; we can then assert that, since the fractional abundance

### Table 3

| T (K) | ν′ = 0 | j′ = 1 | j′ = 3 | j′ = 11 | ν′ = 3 | j′ = 3 | j′ = 9 |
|------|--------|--------|--------|--------|--------|--------|--------|
| 10   | 1.13–12| 6.65–13| 3.18–13| 3.85–13| 1.51–12| 1.34–12| 1.34–12|
| 20   | 2.73–12| 1.55–12| 9.73–13| 1.10–12| 2.70–12| 2.65–12| 2.65–12|
| 30   | 3.78–12| 2.15–12| 1.46–12| 1.80–12| 3.44–12| 2.20–12| 2.20–12|
| 50   | 5.31–12| 3.03–12| 2.01–12| 3.01–12| 5.70–12| 3.62–12| 3.62–12|
| 70   | 6.68–12| 3.86–12| 2.30–12| 4.15–12| 9.04–12| 3.85–12| 3.85–12|
| 100  | 8.70–12| 5.21–12| 2.59–12| 5.93–12| 1.80–11| 4.52–12| 4.52–12|
| 120  | 1.05–11| 6.15–12| 2.79–12| 7.15–12| 5.70–12| 4.52–12| 4.52–12|
| 200  | 1.29–11| 7.86–12| 2.48–12| 1.21–11| 3.78–11| 2.73–12| 2.73–12|
| 500  | 1.19–11| 8.33–12| 6.33–13| 3.19–11| 9.45–11| 2.10–13| 2.10–13|
| 1000 | 4.51–12| 3.91–12| 2.81–14| 6.97–11| 1.92–09| 1.27–13| 1.27–13|

Notes: Only the oH\textsubscript{2} case is being presented. All units are \text{cm}^3 \text{s}^{-1}.

![Figure 1](image1.png)

**Figure 1.** Computed quantum reaction rates of LiH destruction. The top panel shows the dependence on the spin state of the final H\textsubscript{2} molecule over a very broad range of T, while the lower panel indicates, at the lower temperatures, the rate dependence on the initial vibrational state of LiH.

![Figure 2](image2.png)

**Figure 2.** Computed rates for H\textsubscript{2}-formation reaction as a function of the temperature and of the redshift values, for different final, rotovibrational states of the H\textsubscript{2} molecule.

![Figure 3](image3.png)

**Figure 3.** Computed hydrogen-exchange reaction (dashed line) and oH\textsubscript{2} formation (solid line) over a large energy range (in the main plot) and over the first 1000 K (in the inset).
is dramatically reduced, the exchange reaction is likely to be negligible. Furthermore, we can assert that the high-temperature processes markedly favor the destruction of any LiH formed during the recombination stage and therefore that no LiH species are expected to significantly survive that stage.

The final Figure 4 reports now the general behavior of the quantum reaction rates for the destruction process as a function of redshift, a quantity which covers the expected range relevant for early universe evolution. One clearly sees once more that the quantum reaction rates for the destruction process as a function of the $z$ values.

![Figure 4. Computed quantum LiH destruction rates, into pH$_2$ formation, as a function of the $z$ values.](image)

4. PRESENT CONCLUSIONS

As is well known by now, the first galaxies and stars were formed from an atomic gas of chiefly H and $^4$He with trace amounts of D, $^3$He, and $^7$Li. Since, there was a clear absence of heavier elements, the necessary radiative cooling kinetics below 8000 K must have been controlled by a small fraction of that gas which was molecular, in order to make the collapse of the primordial clouds more efficient. In the present work, we have therefore revisited the chemistry of the $^7$LiH molecule, expected to be formed via radiative recombination via Equation (1), to now understand from ab initio calculations how likely it would be for it to survive the possible reactions with the very abundant hydrogen gas existing under those conditions. We have carried out quantum calculations of the reactive processes that are allowed at the existing conditions of those clouds and which essentially involve the exothermic channels of reaction (2), i.e., either the hydrogen replacement process LiH$^+$ + H$^+$ $\rightarrow$ LiH$^0$ + H$^+$, that allows the LiH molecule to survive, or the H$_2$-formation processes (into oH$_2$ and pH$_2$) LiH + H $\rightarrow$ Li + o,pH$_2$, which describe the destruction of the initial molecular partner.

The calculations employ a newly obtained PES (Wernli et al. 2009) and carry out a coupled-channel study of the quantum reaction, summing over all possible final states of H$_2$, and further analysing the possible changes due to having the initial LiH molecule formed in some of its excited vibrational levels. The final rates were obtained by employing the uniform $J$-shifting procedure (Zhang & Zhang 1999) and were extended to higher temperatures following the scheme outlined in Section 2. The rates for both events (i.e., H replacement and H$_2$ formation) were thus obtained over a very broad range of redshift values, covering those that pertain to the recombination era.

The present calculations are the first quantum results in regions of astrophysical interest which employ both the "exact" coupled-channel dynamics and the best, thus far, reactive PES obtained from ab initio computations (Wernli et al. 2009). They allow us to make the following points.

1. Over the range of relevant $z$ the destruction reaction dominates over the LiH "survival" of the hydrogen replacement channel (see Figures 3 and 4).
2. To have the initial molecule still excited in any of its internal vibrational states does not modify the above result, although showing an increase of the simple H-replacement rates as $v$ increases (see Figure 1).
3. The analysis of the rates of H$_2$ formation into different rovibrational levels (Figure 2) indicates that such species is preferentially formed into its lower $(v'$, $j'$) states, although the formation of internally "hot" H$_2$ molecules is far from negligible.
4. Formation of either oH$_2$ or pH$_2$ changes the computed rate values very little, thereby not influencing the above findings.
5. The computed rates with the present PES turn out to be larger than the earlier calculations with a less accurate form of reactive interaction (Padmanaban & Mahapatra 2004; Defazio 2005) and similar in size to the earlier, empirical estimates by Stancil et al. (1996). Such accurate findings therefore indicate as being very hard to have and to observe any possible LiH survival under early universe conditions.

In conclusion, the present new data strongly indicate rapid destruction of LiH molecules by exothermic reaction with the ubiquitous hydrogen atom in the clouds, a process very likely to occur at the time of the recombination era. As a consequence, it would be very difficult for such short-lived species to leave their observational imprinting in the CBR. One should also keep in mind that the present, accurate new depletion rates are directly affecting the use of cosmological models for estimating LiH abundances. As a consequence of such new values, the ensuing optical depth of the universe due to elastic Thomson scattering of CBR photons from the present LiH species should be lower, and thus certainly different from that estimated in earlier studies (e.g., Bouleux & Galli 1997) hence settling in the negative the question of possible LiH detection.

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