REVISITING THE EFFECT OF H$_2$, HD AND LIH MOLECULES
IN THE COOLING OF PRIMORDIAL GAS.

JOAQUIN P. PRIETO$^1$, LEOPOLDO INFANTE$^1$, RAUL JIMENEZ$^2$

ABSTRACT

We use a non-equilibrium chemical network to revisit and study the effect of H$_2$, HD and LiH molecular cooling on a primordial element of gas. We paid special attention in the variation of HD abundance. We solve both the thermal and chemical equations for a gas element with an initial temperature $T = 1000K$ and a gas number density in the range $n_{tot} = 1 - 10^5cm^{-3}$. These are typical properties of the first halos which formed stars. At low densities, $n_{tot} < 10^2cm^{-3}$, the gas reaches temperatures $\sim 100K$ and the main coolant is H$_2$, but at higher densities, $n_{tot} > 10^2cm^{-3}$, the HD molecule dominates the gas temperature evolution and the gas reaches temperatures well below 100K. The effect of LiH is negligible in all cases. We studied the effect of HD abundance on the gas cooling. The HD abundance was set initially to be in the range $n_{H_2}/n_H = 10^{-7} - 10^{-5}$. The simulations show that at $n_{tot} > 10^2cm^{-3}$ the HD cooling dominates the temperature evolution for HD abundances greater than $10^{-6}n_H$. This number decrease at higher densities. Furthermore, we studied the effect of electrons and ionized particules on the gas temperature. We followed the gas temperature evolution with $n_{H_2}/n_H = 10^{-4} - 10^{-2}$. The gas temperature reached lower values at high ionization degree because electrons, H$^+$ and D$^+$ are catalizers in the formation paths of the H$_2$ and HD molecules. Finally, we studied the effect of an OB star, with $T_{eff} = 4 \times 10^4K$, would have on gas cooling. It is very difficult for a gas with $n_{tot}$ in the range between $1 - 100cm^{-3}$ to drop its temperature if the star is at a distance less than 100pc.

Subject headings: cosmology: early universe - cosmology: theory - galaxies: intergalactic medium - atomic processes

1. INTRODUCTION

In a $\Lambda$CDM Universe, the first luminous objects were formed due to fall-in of gas inside the dark matter potential wells (for a review see Barkana & Loeb (2001)). In order to let the fall-in of gas inside the dark matter potential wells, the gas thermal energy should have been radiated away by some physical mechanism. Since the primordial molecular clouds would have zero metallicity, the collisional excitation of the existing molecules is the most plausible mechanism for the cooling of baryonic matter in this environment because the collisional excitation of both H and He atoms are inefficient at temperatures lower than 8000K, which is higher than the temperature of star formation clouds.

Tegmark et al. (1997) showed that the first luminous objects may have formed at $z \sim 30$ inside a $10^6M_\odot$ halo ($T_{vir}$ $\sim 1000K$), which have recently been confirmed by O'Shea & Norman (2007) and Cao et al. (2007). Tegmark et al. (1997) also showed that the stars formed in this environment could be as massive as $\sim 100M_\odot$ (Abel et al. 2002).

After the recombination era, the most abundant molecule in the Universe is molecular hydrogen H$_2$. Despite of its low primordial abundance, $\sim 10^{-3} - 10^{-4}n_H$ (Palla et al. 1989), this molecule has a fundamental role in the gas cooling at temperatures less than 8000K. The first authors to highlight the role of H$_2$ in this context were Saslaw & Zipoy (1967) and Peebles & Dicke (1968). Saslaw & Zipoy (1967) showed the importance of the charge transfer reaction between H$_2^+$ and H to form H$_2$, and Peebles & Dicke (1968) suggested a mechanism to form H$_2$ from H$^-$. The H$_2$ molecule forms by the H$^-$ and H$_2^+$ channels mainly. The reactions

$$H + H^+ \rightarrow H_2^+ + \gamma$$

$$H + e \rightarrow H^- + \gamma$$

are followed by

$$H_2^+ + H \rightarrow H_2 + H^+. \quad (3)$$

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

Due to its zero dipolar moment only quadrupole rotational transitions are allowed, $J \rightarrow J \pm 2$, where $J$ is the quantum number for angular momentum; Abgrall et al. (1982). Furthermore, due to its small moment of inertia (the smallest one between all molecules) the energy gap between its rotational quantum states, $\Delta E$, is large compared with other molecules ($\Delta E_{J=1,J=2} \approx 1/I$, where $I$ is the moment of inertia). The smallest energy gap is $\Delta E_{J=0} \approx 500K$. With this energy difference it is very difficult to reach temperatures below $\sim 100K$, (see Palla (1999) and references therein).

The HD molecule forms through D$^+$ and D channel mainly (see Dalgarno et al. (1973); Galli & Palla (2002))

$$D^+ + H_2 \rightarrow H^+ + HD, \quad (5)$$

$$D + H_2 \rightarrow H + HD. \quad (6)$$

1 Departamento de Astronomía y Astrofísica, Pontificia Universidad Católica de Chile, Santiago, Chile; jpprieto@astro.puc.cl, infante@astro.puc.cl
2 ICREA & Institute of Space Sciences (CSIC-IEEC), Campus UAB, Bellaterra 08193, Spain; raulj@astro.princeton.edu
**HD** has a moment of inertia greater than the **H₂** one. Furthermore, it has a finite dipolar moment which allows internal dipolar transitions (transitions of the kind \( J \rightarrow J \pm 1 \)) and internal transition rates greater than in **H₂**.\(^1\)\(^2\)\(^3\) Due to its small moment of inertia, the differences between its energy states are smaller than the energy differences of the **H₂** molecule. All these properties make the **HD** molecule an efficient coolant at low temperatures, below \( \sim 1000 \mathrm{K} \), (see Nagakura & Omukai (2005), Ripamonti (2007), McGreer & Bryan (2008), Palla (1999) and references therein). The \( \text{LiH} \) molecule is formed mainly by radiative association of \( \text{Li} \) and \( H \) and associative detachment of \( \text{Li}^- \) and \( H^- \) (Stancil et al. 1996):

\[
\text{Li} + H \rightarrow \text{LiH} + \gamma , \quad (7)
\]

\[
\text{Li}^- + H \rightarrow \text{LiH} + e^- . \quad (8)
\]

Moreover, this molecule have both a dipolar moment and a moment of inertia larger than the ones of the **HD** molecule. These characteristics could make the \( \text{LiH} \) molecule an efficient cooler at low temperatures, but the cooling functions depend on the number density of the specie, so if the abundance of \( \text{LiH} \) is too low as expected in primordial environments (Stancil et al. 1996) its cooling effect will be negligible. For a review of \( \text{Li} \) chemistry see Bodo (2001) and Bodo et al. (2003).

In the work of Galli & Palla (1998) the effect of **HD** and **LiH** was included on the gas cooling. To calculate the photo-destruction rate coefficient, for photoionizion, photodetachment, and photodissociation, they assumed detailed balance with CMB photons. But, to study the effect of the first stars on the primordial gas we need the cross section for each photo-destruction process, in the spirit of (Glover & Jappsen 2007). These cross sections are described below. Our current work includes the photo-destruction cross sections of both \( \text{Li} \) and \( \text{Li}^- \) and the photodisociation of \( \text{LiH} \) (in its rovibrational ground state) in contrast to previous work.

We improve over recent works (Glover & Jappsen 2007, Glover & Abel 2008) that have studied primordial cooling by exploring the effect of the **HD** abundance and the inclusion of a stellar radiation field. This paper is organized as follows. In §2 we describe both the thermal and chemical model required to follow the evolution of the gas temperature. In §3 we present results and discussion. It includes the gas temperature evolution as a function of gas density and molecular coolers; the gas temperature evolution as a function of **HD** abundance; the temperature evolution as a function of the ionization degree and finally we show the effect of a star radiation field on the gas temperature. In §4 we present the conclusions.

## 2. THERMAL AND CHEMICAL MODEL

As argued above, in a realistic cooling model of primordial gas, it is mandatory to include the molecular coolers. The main molecular coolers at low temperatures are **H₂**, **HD** and **LiH**. In addition to the previous molecules, the model should include the main species created in the primordial nucleosynthesis. Our model includes 21 species: \( H, H^+, H^- , H_2, H_2^+, H_2^-, H_e, H_e^+, He^{++}, HeH^+, D, D^+, HD, HD^+, HD_2D^+, Li, Li^+, Li^-, LiH, LiH^+ \) and \( e^- \). The reactions considered for these species are described in table 1, 2 and 3. This table does not include the formation of **H₂** by three body reaction because this reaction is not relevant at densities studied in this work. The cooling processes (see table 3) considered in this work are:

- **Collisional ionization**: the gas loses energy by ionization of the different species in the environment.
- **Recombination**: the gas loses energy by free electrons capture.
- **Collisional excitation**: the gas loses energy when collisional excited electrons move to the unexcited states.
- **Bremsstrahlung**: loss of energy due to the radiation emitted by accelerated electrons.
- **Compton cooling**: interchange of energy between free electrons and CMB radiation.

The molecular cooling functions are constructed as in Galli & Palla (1998). For both **H₂** and **HD** molecules we adopted the approximate density dependent relation for the cooling functions. For **LiH** we adopted the low density limit cooling function. The molecular cooling functions are quoted as in Puy et al. (1993) at temperatures near \( T_{\text{CMB}} \).

The first stars, by definition, formed in an environment without previous star. But, once population III stars are formed they can photoionize the halos where new stars will form. This process is quantified by the frequency dependent cross section, \( \sigma_A(\nu) \), of the reaction \( A^i + \gamma \rightarrow A^{i+1} + e^- \), where the specie \( A^i \) in the i ionization state moves to \( i+1 \) ionization state due to the interaction with photons.

The presence of a radiation field triggers a photo-destruction rate:

\[
IR_A = 4\pi \int_{\nu_{th}}^{\infty} \sigma_A(\nu) \frac{i(\nu)}{h\nu} d\nu ,
\]

where \( n_A \) is the number density of specie \( A \); \( i(\nu) \) is the specific intensity of radiation in the environment and \( h \) is Planck’s constant. The integral is calculated from the threshold frequency of ionization, \( \nu_{th} \), to infinity.

The heating of the gas due to photoionizations (heat in erg/cm³/s) is given by

\[
\Gamma_A = n_A 4\pi \int_{\nu_{th}}^{\infty} \sigma_A(\nu) \frac{i(\nu)}{h\nu} (h\nu - h\nu_{th}) d\nu ,
\]

where \( h\nu_{th} \) is the threshold energy of ionization. Strictly, in the last two expressions \( i(\nu) \) should be multiplied by \( 1 - e^{-\gamma} \), where \( \gamma = \int \sigma_A(\nu) n_A d\nu \) is the optical depth. Here we assume \( \gamma >> 1 \). For example, **H** photoionization cross section is \( \sim 10^{-18} \mathrm{cm}^2 \). One should remember that for \( d\nu > 1 - 10^{-4} \mathrm{pc} \). We take \( n_H \) in the range \( 1 - 10^4 \mathrm{cm}^{-3} \). This distance is well below the halo scale distance.

The cross sections, the ionization rates and the heating included in this work are mentioned in table 5. With each one of these functions we can calculate both the abundance of all species and the temperature evolution. The abundance of specie \( A \) in the gas evolves following the equation

\[
\frac{\partial n_A}{\partial t} = C_{A,ij} - n_A D_{i,ph} ,
\]
where $C_{A,ij} = \Sigma_{ij} n_i n_j k_{RC,ij}$ is the creation rate of specie $A$ by $i$ and $j$ with $k_{RC,ij}$ the rate coefficient of the reaction and $D_{ph}$ is the destruction rate of specie $A$ by specie $l$, $D_l = \Sigma_i n_i k_{RC,Al}$ or by photoionization $D_{ph} = k_{IR}$. These coupled deferential equations are solved by the backward differencing formula, BDF (Aninos et al. 1997). The gas temperature $T$ changes according to

$$\frac{dT}{dt} = \frac{\gamma - 1}{k_B} \sum_i n_i (\Gamma - \Lambda), \quad (12)$$

where $\gamma$ is the adiabatic gas index; $k_B$ is Boltzmann’s constant; $\Gamma$ is the photoionization heating and $\Lambda$ is the cooling by the processes mentioned before. In the range of both densities and temperatures studied here the gas can cool by molecular de-excitation. This is valid, i.e., for $H_2$ molecule until densities greater than $n \sim 10^8/x_{H_2} \text{cm}^{-3}$, with $x_{H_2}$ the $H_2$ fraction, at higher densities the molecule reach the LTE.

### 3. RESULTS AND DISCUSSION

We follow the gas temperature for different densities, different $H$D abundances, different ionization conditions and different radiation conditions. The abundances relative to $H$ at the beginning of the evolution are (from Galli & Palla (1998) at $z \approx 10 - 20$): $n_{H^+} = 10^{-4}$, $n_{H^-} = 10^{-12}$, $n_{H+} = 10^{-14}$, $n_{H_2} = 10^{-3}$, $n_{H_2^+} = 10^{-18}$, $n_{D} = 4 \times 10^{-5}$, $n_{D^+} = 0$, $n_{HHD} = 10^{-6}$, $n_{HHD^+} = 10^{-18}$, $n_{H_2D^+} = 10^{-19}$, $n_{H_2D^+} = He^+ = 0$, $n_{HeH^+} = 10^{-12}$, $n_{Li} = Li^+ = 10^{-10}$, $n_{Li^+} = 10^{-23}$, $n_{LiH} = 10^{-21}$ and $n_{LiH^+} = 10^{-18}$. The $H$ and $He$ densities are $\rho_H = 0.75 \rho_{total}$ and $\rho_{He} = 0.24 \rho_{total}$, where $\rho_{total}$ is the total baryonic matter.

In order to know which cooling effect dominates the evolution of gas temperature we considered the main cooling processes independently through their thermal evolution. Figure 2 shows that the cooling of $H_2$, $HD$, $LiH$ - $LiH$ do not appear due to its low value- and the total cooling, $\Lambda$, divided by $n_H n_{H_2}$ for a gas element with $n_{total} = 100 cm^{-3}$ and an $H_2$ abundance of $n_{H_2}/n_H = 10^{-3}$.

$$\frac{\Lambda}{n_H n_{H_2}} \approx \lambda_{H^2} + \left( \frac{n_{HD}}{n_{H_2}} \right) \lambda_{HD} + \left( \frac{n_{LiH}}{n_{H_2}} \right) \lambda_{LiH}. \quad (13)$$

The last expression correspond to the total molecular cooling. Here $\lambda_A = n_H n_{H_2} \lambda_A$ is the cooling due to the excitation of molecule $A$ by an $H$ atom.

This figure shows clearly that in a gas with a number density greater than $n_{total} \approx 10^2 cm^{-3}$ the $H_2D$ cooling is similar to $H_2$ cooling at a temperature $\sim 100K$ when $n_{HHD}$ is greater than $10^{-6} n_{H^+}$. Then, with number densities greater than $\sim 10^2 cm^{-3}$ the $HD$ cooling dominates the thermal evolution and the gas temperature can reach values much lower than the values reached in a gas with lower densities. This behaviour depends strongly on $H$D abundance, which was taken in the range $10^{-5} - 10^{-7}$ relative to $H$. At high densities the gas needs less $HD$ abundance to drop its temperature. Puy & Signore (1998) found that at high densities an temperatures $\sim 200K$ the main molecular cooler is $H_2$. This result was confirmed by Omukai (2000), Uehara & Inutsuka (2000), Flower et al. (2000), Nagakura & Omukai (2005) and Ripamonti (2007) and in a simple way with the results of figure 1 and 2. On the other hand, in order to be an efficient cooler $LiH$ should increase its abundance in about ten order of magnitude due to its low abundance. This increment is too large to be real. The $LiH$ cooling is not important in these cases (see Mizusawa et al. 2005).

Figure 3 shows the gas temperature evolution of an ionized gas. This figure shows that a gas with a large ionization degree could reach lower temperatures than a gas with a small ionization degree, see for example Nagakura & Omukai (2005). This is possible because the formation of the molecular coolers, $H_2$ and $HD$, need $H^+$, $D^+$ and free electrons. The temperature difference between the $n_{H^+}/n_H = 10^{-4}$ and the $n_{H^+}/n_H = 10^{-2}$
case is $\sim 100K$ at $100cm^{-3}$.

Figure 4 shows the effect of an OB star ($R_s = 15R_\odot$ and $T_{\text{eff}} = 4 \times 10^4$) radiation field on the gas temperature at different distances. This figure shows that it is very difficult for an element of gas to drop its temperature if there is an OB star at a distance less than $\sim 100pc$ due to photo-destruction of its cooling molecular agents, Yoshida et al. (2007). In other words if inside a halo of $\sim 10^9M_\odot$ a star is born, it is very difficult for its surrounded gas reach the necessary conditions to form other stars (Oh & Haiman 2003; Omukai & Nishi 1999). The formation of more than one star could be possible if the seed clumps of gas evolve at the same time, without radiation feedback between them.

4. CONCLUSIONS.

In this work we have developed a model for the temperature evolution of a primordial gas including 21 different chemical species including reaction rates and cross sections available in the literature. We have paid careful attention to explore the space parameter in abundance, specially $HD$, and to include the $LiH$ to study in detail at what abundances the molecular coolants are relevant.
The main results are the following:

1. The HD molecule dominates the gas cooling at temperatures below $\sim 100 - 200K$ in the range of densities $10^2 - 10^4 cm^{-3}$ for HD abundances over $10^{-6}H_2$. The HD effect is more evident at higher densities.

2. The LiH molecule does not have a clear effect on the gas cooling. The gas would need an abundance at least ten orders of magnitude higher to be an efficient cooler, so LiH is ruled out as an important cooler in primordial gas (Mizusawa et al. (2005)).

3. A gas with high ionization degree can drop its temperature more than a neutral gas because both the ionized $H$ and $D$ and electrons are catalyzers in the formation of $H_2$ and HD cooling molecules. These ionization conditions could be presents in post-shock waves zones or relic HII regions, Johnson & Bromm (2006).

4. Is very difficult for a gas to drop its temperature in the presence of an OB star located closer than 100pc. So, in order to form more than one star in a primordial halo the formation of seed clumps should almost be instantaneous, otherwise the radiation feedback of first stars will suppress the star formation conditions (Omukai & Nishi (1999)).

This work, as previous ones, suggests the importance of studying the effect firts stars would have on their surrounding gas in the formation of more than one star within primordial halos (see e.g. Jimenez & Haiman (2006)). For a more accurate study, we need to follow the star formation in a hydrodynamical model, which will we present in forthcoming papers.

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Reactions with H

| Reference | Reaction | Ref |
|-----------|----------|-----|
| RC1A97    | $H + e \rightarrow H^+ + 2e$ | 39  |
| RC2A97    | $H^+ + e \rightarrow H + \gamma$ | 1   |
| RC3GP98   | $H + e \rightarrow H^- + \gamma$ | 40  |
| RC4GP98   | $H + H^- \rightarrow H_2 + e$ | 18  |
| RC5GP98   | $H + H^+ \rightarrow H_2^+ + \gamma$ | 10  |
| RC6GP98   | $H^+_2 + H \rightarrow H_2 + H^+$ | 15  |
| RC7GP98   | $H_2 + H^+ \rightarrow H_3^+ + H$ | 29  |
| RC8GP98   | $H_2 + e \rightarrow 2H + e$ | 35  |
| RC997     | $H + H \rightarrow 3H$ | 20  |
| RC10A97   | $H^- + e \rightarrow H + 2e$ | 39  |
| RC11A97   | $H^- + H \rightarrow 2H + e$ | 1   |
| RC12GP98  | $H^- + H^+ \rightarrow H_2^+ + e$ | 26  |
| RC13GP98  | $H^+_2 + e \rightarrow 2H^+$ | 30  |
| RC14GP98  | $H^+_2 + H^- \rightarrow H_2 + H$ | 7   |
| RC15GP98  | $H^+_2 + H_2 \rightarrow H_3^+ + H$ | 31  |
| RC16GP98  | $H^+_2 + e \rightarrow H_2^+ + H$ | 33  |
| RC17GP98  | $H^+_2 + e \rightarrow H_2 + H$ | 37  |
| RC18GP98  | $H^+_2 + H^- \rightarrow H_2^+ + e$ | 12  |
| RC19GP98  | $H^+_2 + H^- \rightarrow H_2^+ + H$ | 9   |
| RC20GP98  | $H^+_2 + H^- \rightarrow H_2 + H$ | 9   |
| RC21GP98  | $H^+_2 + H^- \rightarrow H_2 + H$ | 9   |

Reactions with He

| Reference | Reaction | Ref |
|-----------|----------|-----|
| RC21A98  | $He + e \rightarrow He^+ + 2e$ | 14  |
| RC22GP98r | $He^+ + e \rightarrow He + \gamma$ | 4   |
| RC23A97  | $He^+ + e \rightarrow He + \gamma$ | 5   |
| RC24GP98 | $He^+ + e \rightarrow He^+ + \gamma$ | 39  |
| RC25GP98 | $He + H^+ \rightarrow He^+ + H$ | 16  |
| RC26GP98 | $He^+ + H \rightarrow He + H^+$ | 42  |
| RC27GP98 | $He + H^+ \rightarrow HeH^+ + \gamma$ | 27  |
| RC28GP98 | $He + H^+ \rightarrow HeH^+ + \gamma$ | 27, 16 |
| RC29GP98 | $He + H^+_2 \rightarrow HeH^+_2 + H$ | 6   |
| RC30GP98 | $He + H^+_2 \rightarrow HeH^+_2 + H$ | 6   |
| RC31GP98 | $He + H^+_2 \rightarrow HeH^+_2 + H$ | 6   |
| RC32GP98 | $He + H^+_2 \rightarrow HeH^+_2 + H$ | 42  |
| RC33GP98 | $He + H^+_2 \rightarrow HeH^+_2 + H$ | 15  |
| RC34GP98 | $He + H^+_2 \rightarrow HeH^+_2 + H$ | 41  |

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- (31) Shavitt (1999)
- (32) Shavitt (1999)
- (33) Stancil et al. (1995)
- (34) Tobie & Tennyson (1999)
- (35) Strombolin et al. (1996)
- (36) Sunfren et al. (1994)
- (37) Theard & Huntress (1973)
- (38) Verner & Ferland (1996)
- (39) Wishart (1979)
- (40) Yousif & Mitchell (1989)
- (41) Ziegler et al. (1989)
TABLE 2
RATE COEFFICIENTS FOR CHEMICAL REACTIONS.

| Reaction (cm$^3$/s) | reaction | ref |
|----------------------|----------|-----|
| Reactions with D     |          |     |
| RC34AG17             | $D + e \rightarrow D^+ + 2e$ | 14  |
| RC35GP98             | $D^+ + e \rightarrow D + \gamma$ | 1   |
| RC36GP98             | $D + H^+ \rightarrow D^+ + H$ | 28  |
| RC37GP98             | $D^+ + H \rightarrow D + H^+$ | 28  |
| RC38GP98             | $D + H \rightarrow HD + \gamma$ | 19  |
| RC39GP98             | $D + H_2 \rightarrow HD + HD$ | 21  |
| RC40GP98             | $HD^+ + H \rightarrow HD + H^+$ | 15  |
| RC41GP98             | $D^+ + H_2 \rightarrow H_2D^+ + H$ | 11  |
| RC42GP98             | $HD + H \rightarrow H_2D + D$ | 32  |
| RC43GP98             | $HD + H^+ \rightarrow H_2D^+ + D$ | 22  |
| RC44GP98             | $HD + H_2 \rightarrow H_2D^+ + H$ | 3   |
| RC45GP98             | $D^+ + H \rightarrow HD^+ + \gamma$ | 10  |
| RC46GP98             | $D^+ + H \rightarrow HD^+ + \gamma$ | 10  |
| RC47GP98             | $HD^+ + e \rightarrow H + D$ | 36  |
| RC48GP98             | $HD^+ + H_2 \rightarrow H_2D^+ + H$ | 38  |
| RC49GP98             | $HD + H_2 \rightarrow H_2D^+ + D$ | 3   |
| RC50GP98             | $H_2D^+ + e \rightarrow 2H + D$ | 8, 17|
| RC52GP98             | $H_2D^+ + e \rightarrow HD + D$ | 8, 17|
| RC53GP98             | $H_2D^+ + e \rightarrow HD + H$ | 8, 17|
| RC54GP98             | $H_2D^+ + H \rightarrow H_2^+ + HD$ | 9, 22, 13|
| RC55GP98             | $H_2D^+ + H \rightarrow H_2^+ + D$ | 3   |
| RC76GA08             | $H + H + HD \rightarrow H_2D + H$ | 9   |
| RC76GA08             | $H + H \rightarrow D + H + H$ | 9   |
| RC76GA08             | $H + HD \rightarrow HD + HD$ | 9   |

REFERENCES — (1) Abel et al. [1997]; (2) Adams & Smith [1981]; (3) Adams & Smith [1985]; (4) Aldrovandi & Pequignot [1973]; (5) AMDB [1989]; (6) Black [1979]; (7) Dalgarno & Lepp [1987]; (8) Datz et al. [1985]; (9) Florer & Harris [2001]; (10) Gain & Palla [1998]; (11) Gerlich [1982]; (12) Gerlich & Hornung [1992]; (13) Herbst [1983]; (14) Inami et al. [1987]; (15) Karpas et al. [1979]; (16) Kirmia et al. [1996]; (17) Larsson et al. [1996]; (18) Lainey et al. [1991]; (19) Lepp & Skiff [1984]; (20) MacLow & Skiff [1986]; (21) Meier et al. [1994]; (22) Millar et al. [1982]; (23) Orienti [1994]; (24) Pear & Haydon [1994]; (25) Peterson et al. [1994]; (26) Poulet et al. [1978]; (27) Roberge & Dalgarno [1982]; (28) Savin [1992]; (29) Savin et al. [1994]; (30) Schneider et al. [1994]; (31) Schutz & Asundi [1967]; (32) Shavitt [1989]; (33) Sibthorpe & Tennyson [1999]; (34) Stancil et al. [1993]; (35) Streid et al. [1996]; (36) Sundstrom et al. [1994]; (37) Heard & Huntress [1975]; (38) Verner & Ferland [1996]; (39) Wishart [1979]; (40) Yonsei & Mitchell [1989]; (41) Yonsei & Mitchell [1989]; (42) Zigman et al. [1989].

TABLE 3
RATE COEFFICIENTS FOR CHEMICAL REACTIONS.

| Reaction (cm$^3$/s) | reaction | ref |
|----------------------|----------|-----|
| Reactions with Li    |          |     |
| RC56GP98             | $Li^+ + e \rightarrow Li + \gamma$ | 8   |
| RC57GP98             | $Li^+ + H^- \rightarrow Li + H$ | 4   |
| RC58GP98             | $Li^+ + H^+ \rightarrow Li + H$ | 4   |
| RC59GP98             | $Li + e \rightarrow Li + \gamma$ | 5   |
| RC60GP98             | $Li + H^+ \rightarrow Li + H$ | 2   |
| RC61GP98             | $Li + H^+ \rightarrow Li + H + \gamma$ | 6   |
| RC62GP98             | $Li + H^- \rightarrow LiH + e$ | 7   |
| RC63GP98             | $Li^+ + H + \rightarrow Li + H + e$ | 7   |
| RC64GP98             | $LiH^+ + H \rightarrow LiH + H^+$ | 7   |
| RC65GP98             | $LiH + H^+ \rightarrow LiH^+ + H$ | 7   |
| RC66GP98             | $LiH + H \rightarrow Li + H_2$ | 7   |
| RC67GP98             | $Li + H \rightarrow LiH^+ + \gamma$ | 1   |
| RC68GP98             | $Li + H^+ \rightarrow LiH^+ + \gamma$ | 1   |
| RC69GP98             | $LiH + H^+ \rightarrow LiH^+ + H$ | 7   |
| RC70GP98             | $LiH^+ + H \rightarrow Li + H_2$ | 7   |
| RC71GP98             | $LiH + H \rightarrow LiH + H$ | 3   |
| RC72GP98             | $Li + H + H \rightarrow LiH + H$ | 3   |
| RC73GP98             | $Li + H + H \rightarrow LiH + H$ | 3   |

REFERENCES — (1) Dalgarno et al. [1996]; (2) Kimura et al. [1994]; (3) Mizusawa et al. [2005]; (4) Pear & Haydon [1994]; (5) Ramsbottom et al. [1994]; (6) Stancil & Zigman [1996]; (7) Stancil et al. [1996]; (8) Verner & Ferland [1996].
TABLE 4
COOLING PROCESSES.

| Cooling process (erg/cm³ s) | reaction | ref |
|-----------------------------|----------|-----|
| Collisional ionization      |          |     |
| H                           |          |     |
| CI1A                        | $H + e \rightarrow H^+ + 2e$ | 1   |
| CI2A                        | $H^- + e \rightarrow H + 2e$ | 1   |
| CI3A                        | $H^- + H \rightarrow 2H + e$ | 1   |
| He                          |          |     |
| CI4A                        | $He + e \rightarrow He^+ + e$ | 1   |
| CI5A                        | $He^+ + e \rightarrow He^{++} + 2e$ | 1   |
| D                           |          |     |
| CI6A                        | $D + e \rightarrow D^+ + 2e$ | 1   |
| Recombination               |          |     |
| H                           |          |     |
| Rec1A97                     | $H^+ + e \rightarrow H + \gamma$ | 1,2 |
| He                          |          |     |
| Rec4GP98                   |          |     |
| Rec4A97d                   | $He^+ + e \rightarrow He + \gamma$ | 1,2,3 |
| Rec5GP98d                  | $He^{++} + e \rightarrow He^{+} + \gamma$ | 3   |
| D                           |          |     |
| Rec9GP98                   | $D^+ + e \rightarrow D + \gamma$ | 3   |
| Collisional excitation of   |          |     |
| CE1A97                      | $H$ | 2,1 |
| CE2GP98                     | $H_2$ | 3   |
| CE3A97                      | $He$ | 2,1 |
| CE4A97                      | $He^+$ | 2,1 |
| CE5GP98                     | $HD$ | 3   |
| CE6GP98                     | $LiH$ | 3   |
| Bremsstrahlung              |          | 2   |
| Compton cooling             |          | 4   |

References. — (1) Abel et al. (1997); (2) Black (1981); (3) Galli & Palla (1998); (4) Peebles (1971); (5) Verner & Ferland (1996).
| $\sigma_A (\text{cm}^2)$ | $IR_A (\text{s}^{-1})$ | $\Gamma_A (\text{erg/cm}^{-3}\text{s})$ | reaction | ref |
|---------------------------|-------------------------|-------------------------------|---------|----|
| H | $\sigma_H 1G07$ | $IR_H 1G07$ | $H + \gamma \rightarrow H^+ + e$ | 8 |
| | $\sigma_H 2G07$ | $IR_H 2G07$ | $H^- + \gamma \rightarrow H + e$ | 2 |
| | $\sigma_H 3G07$ | $IR_H 3G07$ | $H \rightarrow H + e$ | 2 |
| | $\sigma_H 3G07p$ | $IR_H 3G07p$ | $H_2 + \gamma \rightarrow H^+_2 + e$ | 6 |
| | $\sigma_H 3G07p$ | $IR_H 3G07p$ | $H_2 + \gamma \rightarrow H^+_2 + e$ | 4 |
| | $\sigma_H 4G07$ | $IR_H 4G07$ | $H_2^+ + \gamma \rightarrow H^++H$ | 3 |
| | $\sigma_H 5A97$ | $IR_H 5A97$ | $H_2^+ + \gamma \rightarrow 2H^+ + e$ | 11 |
| | $\sigma_H 6A97$ | $IR_H 6A97$ | $H_2 + \gamma \rightarrow H + H$ | 1 |
| He | $\sigma_{He} 7G07$ | $IR_{He} 7G07$ | $He + \gamma \rightarrow He^+ + e$ | 12 |
| | $\sigma_{He} 8A97$ | $IR_{He} 8A97$ | $He^+ + \gamma \rightarrow He^{++} + e$ | 7 |
| D | $\sigma_D 9G07$ | $IR_D 9G07$ | $D + \gamma \rightarrow D^+ + e$ | 8 |
| | $\sigma_D 10A97$ | $IR_D 10A97$ | $HD^+ + \gamma \rightarrow H + D^+$ | 11 |
| | $\sigma_D 11A97$ | $IR_D 11A97$ | $HD^+ + \gamma \rightarrow H^+ + D$ | 11 |
| Li | $\sigma_{Li} 13RM$ | $IR_{Li} 13RM$ | $Li + \gamma \rightarrow Li^+ + e$ | 10 |
| | $\sigma_{Li} 15Rams$ | $IR_{Li} 15Rams$ | $Li^- + \gamma \rightarrow Li + e$ | 9 |
| | $\sigma_{Li} 16KD$ | $IR_{Li} 16KD$ | $LiH + \gamma \rightarrow Li + H$ | 5 |

**References.** — (1) Abel et al. (1997); (2) de Jong (1972); (3) Dunn (1968); (4) Galli & Palla (1998); (5) Kirby & Dalgarno (1978); (6) O’Neill & Reinhardt (1978); (7) Osterbrock (1974); (8) Osterbrock (1980); (9) Ramsbottom et al. (1994); (10) Reilman & Manson (1979); (11) Shapiro & Kang (1987); (12) Yan et al. (1998).