Non-thermal photons and H$_2$ formation in the early Universe

C. M. Coppola$^{1,2,3}$ *, D. Galli$^3$, F. Palla$^3$, S. Longo$^{2,3,4}$, J. Chluba$^5$

1 Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT
2 Università degli Studi di Bari, Dipartimento di Chimica, Via Orabona 4, I-70126, Bari, Italy
3 INAF- Osservatorio Astrofisico di Arcetri, Largo E. Fermi 5, I-50125 Firenze, Italy
4 IMIP-CNR, Section of Bari, via Amendola 122/D, I-70126 Bari, Italy
5 Johns Hopkins University, Bloomberg Center 435, 3400 N. Charles St., Baltimore, MD 21218

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ABSTRACT

The cosmological recombination of H and He at $z \approx 10^3$ and the formation of H$_2$ during the dark ages produce a non-thermal photon excess in the Wien tail of the cosmic microwave background (CMB) blackbody spectrum. Here we compute the effect of these photons on the H$^-$ photodetachment and H$_2^+$ photodissociation processes. We discuss the implications for the chemical evolution of the Universe in the post-recombination epoch, emphasizing how important a detailed account of the full vibrational manifold of H$_2$ and H$_3^+$ in the chemical network is. We find that the final abundances of H$_2$, H$_2^+$, H$_3^+$ and HD are significantly smaller than in previous calculations that neglected the effect of non-thermal photons. The suppression is mainly caused by extra hydrogen recombination photons and could affect the formation rate of first stars. We provide simple analytical approximations for the relevant rate coefficients and briefly discuss the additional effect of dark matter annihilation on the considered reaction rates.

Key words: molecular processes; cosmology: early Universe.

1 INTRODUCTION

In the era of precision cosmology, the determination of the chemical composition of the early Universe requires an accurate evaluation of the reaction rates of the main chemical processes involved. A detailed chemical-kinetic model for the evolution of the homogeneously expanding Universe in the post-recombination epoch is also needed to follow the collapse of primordial clouds and hence to study the formation of the first-generation stars (Tegmark et al. 1995; Abel et al. 2002; Bromm et al. 2002). In particular, H$_2$ represents a “key” element because of its abundance and coolant properties. For this reason the line emissions associated with molecular hydrogen could in principle give informations about the matter distribution during the phase of pre-reionization of the Universe (e.g., Ciardi & Ferrara 2003; Kong et al. 2012). Over the past years continuous improvements have been made to the modeling of the early Universe chemistry under non-equilibrium conditions. For example, Coppola et al. (2011, hereafter C11), Longo et al. (2011) and Coppola et al. (2012) demonstrated the importance of taking into account the complete internal states of chemical partners in a chemical network for the primordial gas, as well as all non-equilibrium processes occurring at high redshift $z$.

In this paper we compute the abundance of the main chemical species (such as H$_2$, H$_2^+$, H$^-$, HD and H$_3^+$), including the effect of non-thermal photons due to cosmological recombination of H and He (see Sunyaev & Chluba 2009, for overview), and the radiative cascade following the formation of H$_2$. The non-thermal photons appear as an excess in the Wien tail of the CMB blackbody spectrum and thus significantly affect the H$^-$ photodetachment and H$_2^+$ photodissociation processes during the dark ages. As we show here, the main effect is caused by the extra H$_1$ recombination photons released at $z \lesssim 100$, limiting the formation of H$_2$, H$_2^+$, H$_3^+$ and HD. We also estimate the effect of extra ionizations from annihilating dark matter particles on the H$^-$ photodetachment rate, finding a sensitivity of the early Universe chemistry to this process (see Appendix B).
The paper is organized as follows: in Sections 2, 3 we describe the computational methods, providing expressions for the spectral distortion of the CMB introduced by emission processes occurring in past epochs of the expanding Universe. The distortion spectra resulting from primordial atomic recombination and non-equilibrium H$_2$ radiative cascade are then used to evaluate non-thermal reaction rates for photo-processes involving the main “catalytic” species for H$_2$ formation (H$_2^+$ and H$^-$). In Section 3 we describe the time-dependent kinetics and summarize the reaction rates and cosmological parameters introduced. The resulting fractional abundances of several atomic and molecular species adopting the updated rate coefficients of Coppola et al. (2011) are discussed in Section 3.

2 EFFECT OF NON-HERMAL PHOTONS

Every radiative transition from an upper atomic level $i$ to a lower level $j$ is associated with the emission of a photon, causing a spectral distortion $I_{ij}(\nu)$. Assuming a very narrow emission-profile, the observing frequency $\nu$ at some redshift $z < z_{\text{em}}$, is related to the rest frame frequency, $\nu_{ij}$, of the transition $i \rightarrow j$ by $\nu = \nu_{ij}(1 + z)/(1 + z_{\text{em}})$. For this reason, the redshift at which the transition happens is labelled as $z_{\text{em}}$. The spectral distortion produced by the emission process at $z_{\text{em}}$ and observed at redshift $z < z_{\text{em}}$ can be written as (e.g., see Rubiño-Martín et al. 2006):

$$I_{ij}^e(\nu) = \frac{\hbar c}{4\pi} \frac{\Delta R_{ij}(z_{\text{em}})(1 + z)^3}{R(z_{\text{em}})(1 + z_{\text{em}})^3}$$

where $R(z) = H_0[\Omega_b(1 + z)^4 + \Omega_m(1 + z)^3 + \Omega_k(1 + z)^2 + \Omega_{\Lambda}z^{3/2}]$ is the Hubble function and $\Delta R_{ij}$ is related to the level populations, $N_i$ and $N_j$ of the $i$th and $j$th levels by:

$$\Delta R_{ij} = p_{ij}A_{ij}N_i \frac{e^{h\nu_{ij}/k_B T_\nu}}{e^{h\nu_{ij}/k_B T_\nu} - 1} \left[ 1 - \frac{g_i N_i}{g_j N_j} e^{-h\nu_{ij}/k_B T_\nu} \right]$$

where $p_{ij}$ is the Sobolev-escape probability, $g_i$ and $g_j$ the degeneracy of upper and lower levels, respectively (both factors are equal to one in the case of transitions occurring among the vibrational manifolds), $A_{ij}$ is the Einstein coefficient of the transition and $T_\nu = 2.726 (1 + z_{\text{em}}) K$ (Fixsen et al. 1996, Fixsen 2004).

To evaluate the contribution of spectral distortions to the reaction rate of a photo-reaction at a given redshift $z$, the integration over the actual photon distribution should be carried out:

$$k_{nh}(z) = 4\pi \int_0^{\infty} \frac{\sigma(\nu)}{\nu} B_\nu(\nu) \left[ I_{ij}^e(\nu) + \sum_{i,j} I_{ij}^e(\nu) \right] d\nu.$$  \hspace{1cm} (3)

Here $\sigma(\nu)$ is the cross section of the photo-reaction as a function of frequency, $B_\nu(\nu)$ the Planck distribution at $T_\nu$ corresponding to the redshift $z$ at which the reaction rate is calculated, and $I_{ij}^e(\nu)$ the spectral distortion.

Several physical and chemical processes can modify the pure blackbody shape of the CMB (see Chluba & Sunyaev 2012, for some example related to early energy release); in the present calculations, we consider the primordial recombination of H and He and the non-equilibrium radiative cascade of H$_2$ as sources of distortion photons. For the former, the outputs of CosmoRec (Chluba & Thomas 2011) are used to evaluate the non-thermal photon contribution. For the latter, the values of $A_{ij}$ were calculated as in C11 averaging over the initial rotational levels and summing over the final ones the rovibrationally resolved Einstein coefficients computed by Wohllweiz et al. 1998; the non-equilibrium level populations calculated in C11 at several $z$ have been used, following the treatment of Coppola et al. 2012.

To estimate the effect of non-thermal photons on the H$_2$ chemistry, the main formation channels for molecular hydrogen, namely the H$_2^+$ and H$^-$ pathways, should be considered separately. Figure 1 shows the spectrum of the CMB at several redshifts, including the distortion photons produced by the cosmological recombination of H; bottom panel: blackbody plus photons produced by the radiative cascade following the non-equilibrium formation of H$_2$ at the same redshifts. The vertical blue lines represent the thresholds for the processes considered in the present work: from the lowest energy, the threshold for H$^-$ photodetachment (0.754 eV), H$_2^+(\nu = 0)$ and H$_2^+(\nu = 6)$ photodissociation (2.65 eV and 1.247 eV, respectively). The value for the highest vibrational level, H$_2^+(\nu = 18)$, is 0.0029 eV, out of the range of the present figure.

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1 [www.chluba.de/CosmoRec](http://www.chluba.de/CosmoRec)
duced by the cosmological H recombination and the H$_2$ radiative cascade. For the cosmological recombination radiation, only the emission of the Ly-α, Ly-β and Ly-γ lines and the 2s-1s two-photon continuum are shown, with the computation including detailed radiative transfer effects, such as line feedback and two-photon processes. The position of the Ly-α line can be noticed in the upper panel of Fig. 1 while photons above $\sim 10.2$ eV are caused by the Ly-β and Ly-γ transitions. Relative to the Ly-α line these resonances only add a small number of photons in the far Wien tail of the CMB (Chluba & Sunyaev 2007) and thus do not affect the final results for the reaction rates at a significant level. We also omitted the emission caused by transitions among excited states (Rubino-Martín et al. 2006; Chluba & Sunyaev 2008; Chluba, Rubino-Martín & Sunyaev 2007), since these only give rise to a tiny derivation relative to the CMB blackbody spectrum. The reprocessing of helium photons emitted at $z \sim 2000$ was also taken into account for the computation of the distortion (Chluba & Sunyaev 2010), producing a pre-recombination feature in the H I Ly-α recombination spectrum (see also Rubino-Martín et al. 2008).

Helium photons only directly affect the H$_2^+$ and H$^-$ formation rates close to $z \sim 2400$, so that we did not present their contribution to the CMB spectrum separately.

The lower panel of Fig. 1 shows the distortion produced by the radiative cascade following the non-equilibrium formation of H$_2$. At the highest redshift, the largest contribution comes from the most energetic $\sim 4.7$ eV transition between vibrational state $v = 14$ and the vibrational ground level of H$_2$ molecules. At lower redshifts, the high-$v$ transitions become progressively less important because of the expansion of the Universe that shifts them to lower energies. The features present in the spectra produced by molecular radiative cascade lines reflect the presence of many transitions with $\Delta v \gg 1$. As a consequence, the spectra are broader than the ones obtained for the atomic recombination (Fig. 1). As for the cosmological recombination distortion, the photons produced by H$_2$ radiative transitions give rise to an excess in the far Wien tail of the CMB. The extra photons are introduced at late times, during the dark ages, when most of the H$_2$ is forming. In comparison to the recombination radiation it is, however, much smaller and thus only leads to a tiny correction to the reaction rates.

### 2.1 H$_2^+$ channel

Charge transfer between H$_2^+$ and H,

$$H_2^+(v) + H \rightarrow H_2(v') + H^+, \quad (4)$$

represents the dominant formation channel of H$_2$ at high $z$. The reaction (4) is exoergic for all vibrational states, $v$, unlike the charge transfer between H$_2$ and H$^+$ that is endoergic for $v \lesssim 3$, although with low threshold energies (e.g. Krstić & Schultz 1999, Krstić et al. 2002, Krstić 2002, 2003, 2005). For the conditions of the primordial Universe a very efficient collisional way to destroy H$_2^+$ is by dissociative recombination (Motapon et al. 2008; Takagi 2002). Among the photo-processes, the reaction

$$H_2^+(v) + h\nu \rightarrow H + H^+, \quad (5)$$

represents a favourable destruction pathway and it has been the subject of several theoretical quantum chemistry stud-
when only very insignificant amounts of chemical elements have formed. The feedback of helium photons on hydrogen also creates extra features in the Ly-α recombination spectrum that leads to non-monotonic behavior of the H⁻ photodetachment rate at \( z \approx 1800 \). It is also important that at high redshifts (\( z \approx 1300 \)) half of the non-thermal reaction rate is caused by the 2s-1s continuum emission, while in the post-recombination epoch only the H I Ly-α distortion is important. As for \( H^+_2 \) photodissociation, the process of \( H_2 \) radiative cascade remains negligible at all redshifts.

### 3 REACTION RATES AND KINETICS

The chemistry of the early Universe at \( z < 10^3 \) can be described as the kinetics of a H-He plasma in an expanding medium. For this reason, the following time-dependent system of ordinary differential equations (see, e.g. \cite{Galli&Palla1998}) has to be solved:

\[
\frac{dN_i}{dt} = - \sum_j k_{ij} N_j - \sum_j k_{ij} N_j N_j + \sum_n k_{in} N_n + \sum_j \sum_m \tilde{k}_{jm} N_j N_m,
\]

where \( N_i \) is the abundance of the \( i^{th} \) species relative to the total baryonic density, \( k_i \) are the photodestruction rate coefficients of the \( i^{th} \) species via the \( i^{th} \) photoprocess; \( k_{ij} \) are the destruction rate coefficients for the \( i^{th} \) species for collisions with the \( j^{th} \) chemical partner; \( k_m \) are the formation rate coefficients of the \( i^{th} \) species due to the \( m^{th} \) photodestruction process for the \( N_m \) species and \( \tilde{k}_{jm} \) are the formation rate coefficients of the \( i^{th} \) species due to collisions between the \( j^{th} \) and \( m^{th} \) species. Each reaction rate is proportional to the variation of the baryonic density as a function of time

\[
\dot{n_b}(z) = \Omega_b \frac{3H_0^2}{8\pi G\mu m_H}(1+z)^3,
\]

where \( \Omega_b \) is the baryon fraction, \( H_0 = 100h \) km s\(^{-1}\) Mpc\(^{-1}\) is the Hubble constant with \( h = 0.705 \), \( G \) is the gravitational constant, \( m_H \) is the atomic hydrogen mass, and

\[ 0000 \text{ RAS, MNRAS 000, 000--000} \]
\[ \mu = 4/(4 - 3Y_\alpha) \] is the mean atomic weight of the gas, \( Y_\alpha \) denoting the helium fractional abundance by mass. The equations for the radiation and gas temperatures are solved in order to evaluate the specific velocity of each chemical process in the kinetics. For the present calculations, the cosmological parameters from WMAP7 and standard BBN data have been used (Komatsu et al. 2011; Iocco 2012).

For our network, we adopted the rate coefficients summarized in Table 1. The table also provides polynomial fits to the non-thermal contributions to the photodetachment of \( \text{H}^+ \) and photodissociation of \( \text{H}_2^+ \) rates. When applicable, the complete vibrational manifolds of \( \text{H}_2 \) and its cation were used, both in LTE approximation in the entrance channel and as sum of contributions in the exit channel.

4 RESULTS

Using the new rates and the improved rate coefficients reported in C11, we determined the fractional abundances of several atomic and molecular species with the kinetic model described in the previous section. Figure 4 shows the evolution of \( \text{H}_2, \text{H}_2^+, \text{H}_3^+ \) and HD, along with that of \( \text{H}^− \) and \( \text{D}^− \). The main differences with respect to previous studies can be summarized as follows: starting at high redshifts, the abundances are affected by the enhanced \( \text{H}_2 \) destruction channels (\( \text{H}_2/\text{H}^+ \) charge transfer, dissociation via \( \text{H}^+ \) and \( \text{H}^+ \) collisions, photodestruction), \( \text{H}^− \) photodetachment and modified \( \text{H}/\text{H}^− \) associative detachment. The first process results in a reduced fractional abundance of \( \text{H}_2 \) at redshifts \( z \sim 1000 \), where it reaches values roughly one order of magnitude smaller than in previous calculations (e.g. Schleicher et al. 2008). Consequently, the fractional abundances of HD and \( \text{H}_3^+ \) are reduced in the same redshift range. This effect is caused by the inclusion of the entire vibrational manifold, as also found by Capitelli et al. (2007) for the dissociative attachment process of \( \text{H}_2 \) (see Figures 4-6 of C11).

At lower redshifts, the abundances are affected by the combined effect of the enhanced photodetachment of \( \text{H}^− \) and the decrease of the efficiency of associative detachment due to non-thermal photons. This result qualitatively agrees with what was found in the steady-state model by Hirata & Padmanabhan (2006), where however no expression for the non-thermal rate coefficient was given, and here a more detailed treatment for the recombination spectrum is used. The effect of the contribution of non-thermal photons to the photodetachment of \( \text{H}^− \) can be appreciated in Figure 5 (bottom panel) at \( z < 100 \). Although the freeze-out value of \( \text{H}^− \) at low \( z \) remains unchanged, the abundance of \( \text{H}_2 \) is reduced by about 70\% at the epochs when the \( \text{H}^− \) channel is dominant. Importantly, the new evolution reduces the final rise of the \( \text{H}_2 \) abundance at \( z \sim 100 \) that characterized all previous calculations. It is also worth noting that, despite the huge effect of non-thermal photons on the photodissociation of \( \text{H}_2^+ \), its abundance is not significantly affected. This can be understood considering the relatively high threshold energy for the photodissociation process compared to the photodetachment of \( \text{H}^− \) and to the mean thermal energy available. Indeed, the integration over the high frequency part of the distortion spectrum is much more favourable for lower thresholds, as it can be derived from Fig. 1.

5 CONCLUSIONS

We followed the formation and destruction of the main molecules and molecular ions in the early Universe, focusing on the effect of non-thermal photons produced by the recombination of \( \text{H} \) and \( \text{He} \) and by the non-equilibrium formation of \( \text{H}_2 \). We computed the changes in the fractional abundances of \( \text{H}_2, \text{H}^−, \text{H}_3^+, \text{H}_3^+ \) and on deuterated species such as \( \text{D}^− \) and HD. We find that because of high-energy tails in the photon spectra at several \( z \), the efficiency of photodestruction is greatly enhanced, yielding lower fractional elemental abundances than in the standard thermal treatment of the chemical kinetics.

We also showed that the inclusion of vibrational lev-
els in the calculation of reaction rates is critical for their determination at high temperatures when excited levels are more populated. At high $z$, where these conditions apply, the resulting fractional abundances of $H_2$ and $H_3^+$ are reduced by a factor of $\sim 10$. However, if used in other environments where molecular hydrogen is more abundant (e.g. during the collapse of primordial clouds), these new rates are expected to affect more significantly the final molecular abundances.

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**APPENDIX A: FITTING FORMULAE FOR THE RATE COEFFICIENTS**

We fitted the reaction rate coefficients for the photodissociation of $H_2^+$ and the photo detachment of $H^-$ with logarithmic polynomials of the form

$$\log k(T_r) = \sum_n a_n (\log T_r)^n.$$  \hspace{1cm} (A1)

The coefficients of Eq. (A1) are given in Table A1 together with the complete set of reaction rates employed in the kinetic model. The temperature of gas and radiation are indicated by $T_g$ and $T_r$, respectively, and are expressed in K. Natural logarithms are indicated as ln, logarithms to base 10 as log. The results of the fitting formulae are compared to the numerical results in Figures A1-A2.

**APPENDIX B: DARK MATTER (DM) ANNIHILATION**

Dark matter annihilation or decay leads to extra ionizations of hydrogen and helium atoms in the early Universe (Chen & Kamionkowski 2004; Padmanabhan & Finkbeiner 2007, delaying the cosmological recombination process (Peebles et al. 2000) and causing emission of extra recombination photons (Chluba 2010). The additional injection of energy and photons should be taken into account when considering the physical phenomena occurring in the primeval plasma as well as the chemistry. Here we evaluate the effect of extra photons produced by the direct reprocessing of annihilation energy by hydrogen on the rate coefficient of $H^-$ photodetachment. Details on the equations employed and their derivation can be found in Chluba (2010).

The energy release associated with the annihilation of some DM particle $\chi$ with its antiparticle $\bar{\chi}$ depends on the
This implies that the early Universe chemistry is not only sensitive to direct ionizations induced by the annihilation products, but also to the reprocessed energy causing additional ionizations of abundant neutral hydrogen atoms and reemission of Ly-α photons.

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### Table B1. Reaction rates.

| Process | Reaction rates [MKS] | Ref |
|---------|----------------------|-----|
| 1) H + e$^-$ → H$^+$ + hν | $1.4 \times 10^{-24} T^6_k 0.928 e^{-2T_k/16200}$ | GP98 |
| 2) H$^+$ + e$^-$ → H + 2e$^-$ | fit from reference | AAZNZ97 |
| 3) H$^+$ + H → 2H + e$^-$ | fit from reference | AAZNZ97 |
| 4) H$^+$ + H$^+$ → 2H | $1.40 \times 10^{-13} (T_k/300)^{-0.487} e^{T_k/29300}$ | LSD02 |
| 5) H$^+$ + hν → H + e$^-$ thermal | non-thermal: atom. recomb. | this work |
| | | log $k = \sum_{n=0}^{6} b_n (\log T_k)^n$ |
| | | $a_0 = -26.6463$ |
| | | $a_1 = 3.35998$ |
| | | $a_2 = 25.729$ |
| | | $a_3 = -31.6442$ |
| | | $a_4 = 15.9545$ |
| | | $a_5 = -3.60013$ |
| | | $a_6 = 0.298272$ |
| | | $b_0 = 81.12$ |
| | | $b_1 = 139.379$ |
| | | $b_2 = -137.531$ |
| | | $b_3 = 73.0553$ |
| | | $b_4 = -19.4282$ |
| | | $b_5 = 1.99768$ |
| 6) D$^-$ + hν → D + e$^-$ | as fit for reaction (5) | S08 |
| 7) HD$^+$ + hν → D + H$^+$ | (1/2) $\times 1.63 \times 10^7 e^{-32400/T_k}$ | S08 |
| 8) HD$^+$ + hν → D$^+$ + H | (1/2) $\times 1.63 \times 10^7 e^{-32400/T_k}$ | S08 |
| 9) HD$^+$ + hν → H$^+$ + D$^+$ + e$^-$ | 9.0 $\times 10^3 T_k^{1.48} e^{-155000/T_k}$ | S08 |
| 10) HD$^+$ + hν → HD$^+$ + e$^-$ | 2.9 $\times 10^2 T_k^{1.56} e^{-175000/T_k}$ | S08 |
| 11) D + H$^+$ → D$^+$ + H | 2.06 $\times 10^{-16} T_k^{0.94} e^{-33T_k/40} + 2.03 \times 10^{-15} T_k^{0.332}$ | SA02 |
| 12) D$^+$ + H → D$^+$ + H$^+$ | $10^{-32} [2.259 - 0.6(T_k/10^3)^{0.5} + 0.101(T_k/10^3)^{1.5}$ | SA02 |
| 13) D + H → HD + hν | $-0.01535(T_k/10^3)^{-2} + 5.3 \times 10^{-7}(T_k/10^3)$ | −3 |
| 14) HD$^+$ + H → HD + H$^+$ | 6.4 $\times 10^{-16}$ | D108 |
| 15) D + H$^+$ → HD$^+$ + hν | log $k/10^{-6} = -19.38 - 1.523 \log T_k + 1.118(\log T_k)^2$ | SLD98 |
| | | $-0.1269(\log T_k)^3$ | GP98 |
| 16) D$^+$ + H → HD$^+$ + hν | as fit for reaction (15) | GP98 |
| 17) HD$^+$ + e$^-$ → D$^+$ + H | 7.2 $\times 10^{-14} T_k^{0.5}$ | SLD98 |
| 18) D + e$^-$ → D$^-$ + hν | $3.0 \times 10^{-22} (T_k/300)^{0.95} e^{-T_k/9300}$ | SLD98 |
| 19) D$^+$ + D$^-$ → 2D | $1.96 \times 10^{-13} (T_k/300)^{-0.847} e^{T_k/29300}$ | LSD02 |
| 20) H$^+$ + D$^-$ → D + H$^+$ | $1.61 \times 10^{-13} (T_k/300)^{-0.847} e^{T_k/29300}$ | LSD02 |
| 21) H$^+$ + D → H + D$^+$ | $6.4 \times 10^{-15} (T_k/300)^{0.41}$ | SLD98 |
| 22) D$^+$ + H → D + H$^+$ | $6.4 \times 10^{-15} (T_k/300)^{0.41}$ | SLD98 |
| 23) D$^+$ + H → HD + e$^-$ | $1.5 \times 10^{-15} (T_k/300)^{0.1}$ | SLD98 |
| 24) D + H → HD + e$^-$ | as fit for reaction (22) | S08 |
| 25) H$^+$ + D$^+$ → D + H | $1.61 \times 10^{-13} (T_k/300)^{-0.847} e^{T_k/29300}$ | LSD02 |
| 26) He$^+$ + H → He$^+$ + H$^+$ | 4.0 $\times 10^{-4} T_k^{1.74}$ for $T_k > 10^4$ | S08 |
| | | $1.26 \times 10^{-15} T_k^{1.75} e^{-127500/T_k}$ for $T_k < 10^4$ |
| 27) He$^+$ + H → He + H$^+$ | $1.25 \times 10^{-21} (T_k/300)^{0.25}$ | ZDKL89 |
| 28) He$^+$ + H → HeH$^+$ + hν | $8.0 \times 10^{-26} (T_k/300)^{-0.24} e^{-T_k/4000}$ | SLD98 |
| 29) He$^+$ + H$^+$ + hν → HeH$^+$ + hν | $3.2 \times 10^{-26} T_k^{1.6} e^{-T_k/4000} (1 + 2 \times 10^{-4} T_k^{1.1})(1 + 0.17 T_k^{0.04})^{-1}$ | JSDK95, ZSD98 |
| 30) He$^+$ + H → He$^+$ + hν | $4.16 \times 10^{-22} T_k^{0.37} e^{-T_k/87600}$ | SLD98 |
| 31) He$^+$ + e$^-$ → He + H | $3.0 \times 10^{-14} (T_k/300)^{-0.47}$ | SLD98 |
| 32) HeH$^+$ + hν → He + H$^+$ | $2.20 \times 10^2 e^{-22740/T_k}$ | JSDK95 |
| 33) HeH$^+$ + hν → He + H$^+$ | $7.8 \times 10^3 T_k^{2.2} e^{-240000/T_k}$ | GP98 |

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### Table B2. Reaction rates.

| Process | Reaction rates [MKS] | Ref |
|---------|----------------------|-----|
| 34) H^- + H → H_2 + e^- | log k = -14.4 - 0.15(log T_k)^2 - 7.9 \times 10^{-3}(log T_k)^3 | C11 |
| 35) H^+ + H → H_2^+ + hν | log(k/10^{-6}) = -19.38 - 1.523\log T_k + 1.118(\log T_k)^2 - 0.1269(\log T_k)^3 | GP98 |
| 36) H_2^+ + H → H_2 + H^+ | 6.4 \times 10^{-16} | GP98 |
| 37) 2H + H → H^+ + H | 5.5 \times 10^{-35}T_k^{-1} | PS883 |
| 38) H_2 + H^+ → H_2^+ + H | ln k = a_0 + a_1T_k + a_2T_k^{-1} + a_3T_k^2 | C11 |
| 39) H_2^+ + e^- → 2H + e^- | 1.91 \times 10^{-15}T_k^{0.136}e^{-54407.1/T_k} | TT02 |
| 40) H^+ + H → H_2^+ + e^- | 6.9 \times 10^{-15}T_k^{0.35} for T_k < 8000 | GP98 |
| 41) H_2^+ + e^- → 2H | 9.6 \times 10^{-13}T_k^{-0.9} for T_k > 8000 | C11 |
| 42) H_2^+ + H^- → H + H_2 | 5 \times 10^{-12}T_k^{0.5} for T_k < 100 | AAZN97 |
| 43) H_2 + e^- → H + H^- | 3.67 \times 10^{-5}T_k^{2.28}e^{-47172/T_k} | CCDL07 |
| 44) H_2^+ + hν → H + H^+ | | |
| thermal | 1.63 \times 10^7e^{-32490/T_k} | GP98 |
| non-thermal: atom. recomb. | log k = \sum_{n=0}^{5}a_n(\log T_k)^n | this work |
| 45) H_2 + hν → H_2^+ + e^- | 3.06587 \times 10^{9}e^{-18948.1/T_k} | C11 |
| 46) H_2^+ + hν → 2H^+ + e^- | 9 \times 10^{-5}T_k^{0.48} - 33500/T_k | GP98 |
| 47) H_2 + hν → H^- + 2H | ln k = 17.555 + 7.2643 \times 10^{-6}T_k - 1.4194 \times 10^{7}T_k^{-1} | C11 |
| 48) H_2 + H → H + H + H | 1.9535 \times 10^{-10}T_k^{0.93267}e^{-49743/T_k} | C11 |
| 49) D + H_2 → HD + H | 1.69 \times 10^{-16}e^{-4680T_k+198800/T_k^2} for T_k > 200 | GP02 |
| 50) D^+ + H_2 → HD + H^+ | 9 \times 10^{-17}e^{-3876/T_k} for T_k < 200 | GP02 |
| 51) HD + H → H + D + H_2 | 10^{-15}(0.417 + 0.846\log T_k - 0.137(\log T_k)^2) | GP02 |
| 52) HD + H^+ → D^+ + H_2 | 5.25 \times 10^{-17}e^{-4430/T_k+173900/T_k^2} for T_k > 200 | GP02 |
| 53) He + H_2^+ → HeH^+ + H | 3 \times 10^{-16}e^{6717/T_k} | GP98 |
| 54) HeH^+ + H → He + H_2^+ | 4.3489 \times 10^{-16}T_k^{2.110373}e^{-31.5396/T_k} | BTGG11 |
| 55) H^+ + H_2 → H_2^+ + hν | 10^{-18} | GP98 |
| 56) H_3^+ + e^- → H + H_2 | 4.6 \times 10^{-12}T_k^{-0.65} | GP98 |
| 57) H_2^+ + H → H + H^+ + H | ln k = a_0 + a_1T_k + a_2T_k^{-1} + a_3T_k^2 | C11 |
| 58) H_2 + H^+ → H + H + H^+ | ln k = a_0 + a_1T_k + a_2T_k^{-1} + a_3T_k^2 | C11 |
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