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Non-thermal photons and direct photodissociation of H_2, HD and HeH^+ in the chemistry of the primordial Universe

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ABSTRACT

Non-thermal photons deriving from radiative transitions among the internal ladder of atoms and molecules are an important source of photons in addition to thermal and stellar sources in many astrophysical environments. In the present work the calculation of reaction rates for the direct photodissociation of some molecules relevant in early Universe chemistry is presented; in particular, the calculations include non-thermal photons deriving from the recombination of primordial hydrogen and helium atoms for the cases of H_2, HD and HeH^+. New effects on the fractional abundances of chemical species are investigated and the fits for the HeH^+ photodissociation rates by thermal photons are provided.

Key words: Physical Data and Processes: molecular processes; cosmology: early Universe

1 INTRODUCTION

Photodissociation processes represent important channels to destroy molecules in several astrophysical environments; the mechanisms through which they occur and effect on the chemistry deeply depend on the chemical species involved and on the features of the radiation field these molecules are embedded in. For example, photodissociation due to UV photons produced by the interaction of cosmic-rays with dense interstellar clouds has been reported in the literature (Prasad & Tarafdar 1983; Sternberg, Dalgarno & Lepp 1987; Heays, Bosman & van Dishoeck 2017) and the effects of such UV flux on the chemistry has been described for several chemical species (Gredel, Lepp & Dalgarno 1987; Gredel et al. 1989; Heays et al. 2014). Another example is represented by the X-ray spectra emitted by high-mass young stellar objects (YSOs) that are usually fitted with the emission spectrum of an optically thin thermal plasma (Hofner & Churchwell 1997) and that has been used to describe the chemistry in the envelopes around YSOs (Stäuber et al. 2006). On the other hand, photodissociation can occur following specific dynamical pathways according to the features of the potential energy surfaces describing the possible electronic states of the molecules themselves. In particular, direct photodissociation, predissociation and spontaneous radiative photodissociation are described as the main ways to photodestroy small molecules (e.g. contribution by van Dishoeck in Millar & Williams 1988 and van Dishoeck & Visser 2014); according to the dynamics, different features in the photodissociation cross sections can be observed. Eventually, considering both the radiation field and the dynamics of the photodissociation processes, additional terms can be calculated other than the thermal emission contribution to the reaction rate of photo-processes.

When moving to the early Universe case, non-thermal radiation fields can arise as a result of different mechanisms such as matter/antimatter annihilation, decaying relic/dark matter particles, dissipation of acoustic waves (see e.g. Chluba & Sunyaev 2012), radiative cascade of H_2 (Coppola et al. 2012) among others. They are also called "distortion photons" because of their departure from the Planckian shape of the Cosmic Microwave Background spectrum (hereafter CMB). Among these additional radiation fields, the most relevant for its effect on the chemistry of the primordial Universe and for the level of accuracy with which it has been modelled is represented by the spectrum deriving from the recombination processes of H and He in the so-called epoch of recombination (EoR) (Chluba, Vasil & Dursi 2010; Chluba & Thomas 2011). In fact, because of the adiabatic expansion of the Universe and the effective Compton scattering, the temperature of the matter dropped, allowing for the first bound atomic

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states to form. The effect of non-thermal photons on the early Universe chemistry has been studied in several papers (Hirata & Padmanabhan 2006). In particular Coppola et al. (2013) presented a modified version of the chemistry in the primordial Universe, where the effect of non-thermal photons was investigated on two photodestruction processes that are relevant for the chemistry of H_2, namely the photodissociation of H_2^+ and the photo-detachment of H^-.

In the present work we focus on the effect of non-thermal photons on the photodissociation of the molecular species that are of interest for the primordial Universe. The calculations presented by Coppola et al. (2013) will be here extended to the direct photodissociation of H_2, HD and HeH^+. Although quite simple systems, they represent the key molecular species present in the early Universe chemistry; indeed while H_2 and HD are connected to the cooling of the gas down to few tens of kelvins in the low-metallicity environment present at high redshifts (e.g., Galli & Palla 1998; Lepp, Stancil & Dalgarno 2002; Dalgarno 2005), HeH^+ contributes to the opacity and optical properties of the primordial gas itself (e.g., Schleicher et al. 2008).

This paper is organized as follows: in Section 2 the formalism used for the description and implementation of non-thermal photons in the chemical kinetics is introduced, and the processes investigated are listed. The quantum dynamical features of each channel are described, and references for the used cross sections are provided. In Section 3 the resulting non-thermal rate coefficients are shown and the effects on the chemical kinetics are discussed and reported.

2 FORMULATION OF THE PROBLEM

2.1 Distortion photons and non-thermal rate coefficient

Radiative transitions in any quantum system between higher, i, and lower, j, internal energy levels (or a lower-energy continuum) are associated with the emission of a photon, causing a spectral distortion of specific intensity $\Delta I_{ij}(\nu)$. The observed frequency, ν, of a photon emitted at redshift $z_{\rm em}$ and observed at redshift z is related to its rest frame frequency, ν_{ij} according to $\nu = \nu_{ij}(1+z)/(1+z_{\rm em})$, assuming a narrow line profile. The spectral distortion produced by the emission process at $z_{\rm em}$ and observed at redshift $z < z_{\rm em}$ can be written (e.g., Rubiño-Martín, Chluba & Sunyaev 2008):

$$\Delta I_{ij}^{z}(\nu) = \left(\frac{hc}{4\pi}\right)\frac{\Delta R_{ij}(z_{\rm em})(1+z)^3}{H(z_{\rm em})(1+z_{\rm em})^3} \quad (1)$$

where $H(z) = H_0[\Omega_{\rm r}(1+z)^4+\Omega_{\rm m}(1+z)^3+\Omega_{\rm k}(1+z)^2+\Omega_\Lambda]^{1/2}$ is the Hubble function and ΔR_{ij} is related to the population of the $i^{\rm th}$ and $j^{\rm th}$ levels by:

$$\Delta R_{ij} = p_{ij}A_{ij}N_i\frac{e^{h\nu_{ij}/k_{\rm B}T_{\rm r}}}{e^{h\nu_{ij}/k_{\rm B}T_{\rm r}}-1}\left[1-\frac{g_iN_j}{g_jN_i}e^{-h\nu_{ij}/k_{\rm B}T_{\rm r}}\right], \quad (2)$$

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 pure vibration transitions), A_{ij} is the Einstein coefficient of the transition, and $T_{\rm r} = 2.726\ (1+z_{\rm em})\,{\rm K}$ (Fixsen 2009).

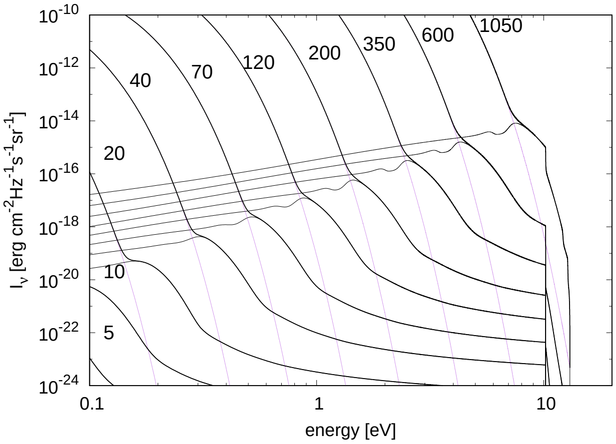

Figure 1. Thermal and non-thermal spectra at different redshift z. Together with the Planck distribution at different radiation temperatures (purple dotted curves, corresponding to the redshift values reported in the figure), the non-thermal contributions are reported. The latter derive both from primordial atomic recombination of H and He and H_2 radiative cascade.

Eventually, the total contribution of spectral distortions to the rate of a reaction with photons at a given redshift, z, can be evaluated by integration over the photon distribution:

$$k_{\rm ph}(z) = 4\pi\int_0^\infty \frac{\sigma(\nu)}{h\nu}\left[B_z(\nu)+\sum_{i\to j}\Delta I_{ij}^{z}(\nu)\right]{\rm d}\nu. \quad (3)$$

In Eq. 3, $\sigma(\nu)$ represents the cross section of the process as a function of frequency, $B_z(\nu)$ is the Planck distribution at $T_{\rm r}$ corresponding to the redshift z at which the reaction rate is calculated. In Fig. 1 the spectra for the non-thermal and thermal photons are reported for different values of the redshift; the calculations performed in this paper have been based on these spectra. Additional details on non-thermal photons distribution can be found in Coppola et al. (2013).

2.2 Molecular species

In the following, a description of the photodissociation processes and molecular species modeled in the present work is given.

2.2.1 H_2

The photodissociation of H_2 proceeds by two dynamical mechanisms; first, the Solomon process consists of a two-step pathway with bound-bound resonant absorption through the Lyman and Werner bands followed by fluorescent decay into the continuum of the ground electronic state:

$$H_2^{(X;v,j)} + h\nu \to H_2^{(B/C;v',j')} \to H(1s) + H(1s) + h\nu \quad (4)$$

The cross sections show a peculiar peaked behaviour at the energy corresponding to the energies of the emitted photons (e.g., Mentall & Guyon 1977). The Solomon process has been always treated as the main photodestruction channel of H_2 in studies of several environments (Stecher & Williams 1967; Abgrall et al. 1992; Abgrall, Roueff & Drira 2000), including the early Universe case (Galli & Palla 1998; Lepp, Stancil & Dalgarno 2002; Dalgarno 2005). Although reaction 4 represent the main channel though which photodissociation occurs it has been shown that the direct continuum photodissociation process

$$H_2^{(X;v,j)} + h\nu \rightarrow \mathrm{H(1s)} + \mathrm{H(2p)} \qquad (5)$$

can effect the total rate coefficients, for example, in the case of interstellar clouds (Shull 1978) and in the early Universe chemistry (Coppola et al. 2011a). Several authors have calculated the cross sections for process 5 (Allison & Dalgarno 1969; Glass-Maujean 1986; Zucker & Eyler 1986); more recently Gay et al. (2012) provided rovibrationally resolved cross sections. They are available at the website http://www.physast.uga.edu/ugamop/, together with the energy levels. The overall H_2 photoexcitation-emission cross section is highly structured, being a mixture of Doppler-limited line emission and an underlying continuum due to processes (4) and (5), respectively.

2.2.2 HD

HD photodissociation is homologous to the H_2 case. A cross section is calculated by Allison & Dalgarno (1969), though only vibrationally resolved. In the present work, the rotational quantum number of the available cross sections is assumed to be equal to zero.

2.2.3 HeH$^+$

The photodissociation of HeH^+ has been extensively studied both from a theoretical and experimentalist point of view (Loreau et al. 2011; Urbain et al. 2012; Gay et al. 2012), also in the case of excited electronic states (Loreau et al. 2013; Miyake, Gay & Stancil 2011). In this case, the photodissociation is dominated by two processes:

$$\mathrm{HeH}^+(X^1\Sigma^+, v, J) + h\nu \rightarrow \mathrm{He}^+(1s) + \mathrm{H}(1s)(A^1\Sigma^+) \qquad (6)$$

$$\mathrm{HeH}^+(X^1\Sigma+, v, J) + h\nu \rightarrow \mathrm{He}(1s^2) + \mathrm{H}^+(X^1\Sigma^+) \qquad (7)$$

In the following, these are referred to as A ← X and X ← X photodissociation, respectively. As in the case of direct photodissociation of H_2, rovibrationally resolved cross sections and energy levels are available at the website http://www.physast.uga.edu/ugamop/; the details on the calculations can be found in the work by Miyake, Gay & Stancil (2011). These two channels have been previously inserted in chemical networks describing the formation and destruction of primordial molecules (e.g., Galli & Palla 1998; Lepp, Stancil & Dalgarno 2002; Schleicher et al. 2008).

3 RESULTS

The main results concern both photodissociation rates and fractional abundances in the context of early Universe chemistry. In the following the results are described according to the chemical species.

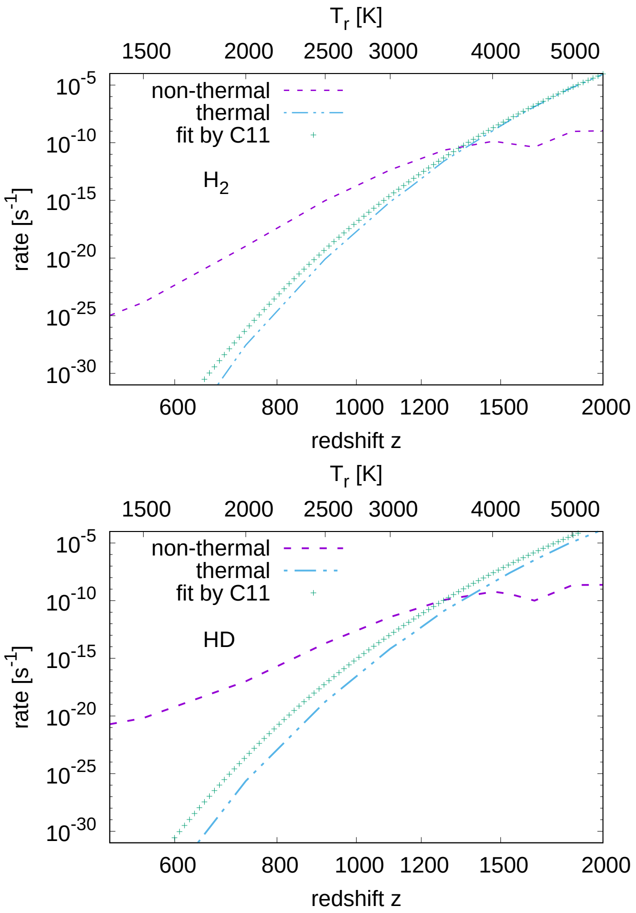

Figure 2. Photodissociation rates as a function of redshift for direct photodissociation of H_2 (top panel) and HD (bottom panel). Both rates calculated adopting a thermal radiation spectrum and non-thermal photons are shown. Comparison with data calculated by Coppola et al. (2011a) (reported as C11 in the key) is provided.

3.1 Reaction rates

3.1.1 H_2 and HD

In Fig. 2, thermal and non-thermal reaction rates for the process of direct photodissociation calculated according to Eq. 3 are shown, for H_2 and HD (top and bottom panels, respectively) as a function of redshift. The presence of extra-photons produced by the primordial recombination of H and He results in the formation of a non-thermal tail in the reaction rate. The value of the redshift at which the crossing-over between non-thermal and the thermal reaction rate appears is $z \sim 1300$; at this z, the radiation temperature is $T_r \sim 3545\ K$. The curves referred to as C11 correspond to the fits provided by Coppola et al. (2011a).

3.1.2 HeH$^+$

In Fig. 3 the reaction rates for direct photodissociation of HeH^+ are shown, separately for the cases of A ← X and X ← X. It is possible to see two important features: firstly, photodissociation rates from thermal photons are quite different from the usually-adopted fits (e.g. Schleicher et al. 2008 (referred to as S08 in the figure) and Galli & Palla

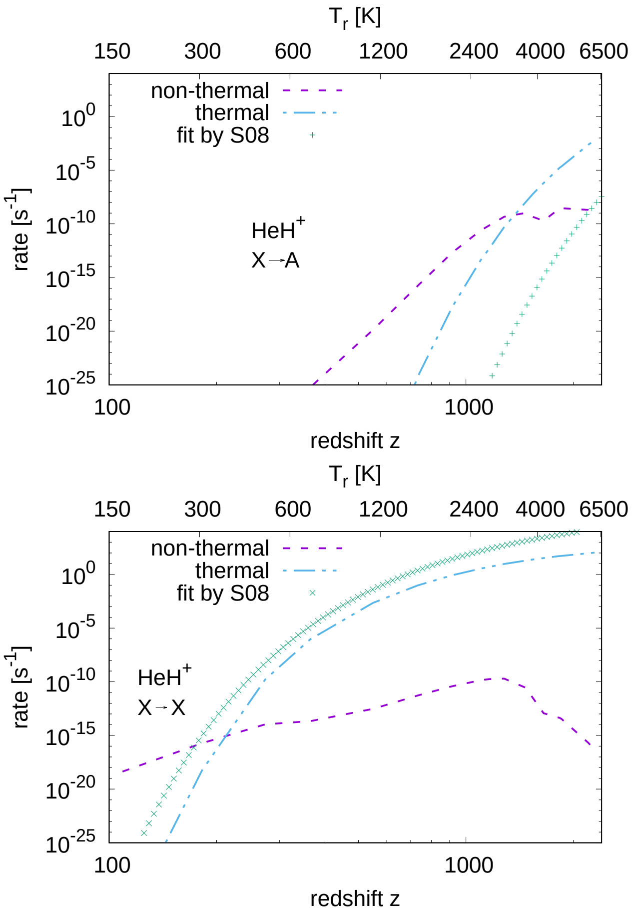

Figure 3. Photodissociation rates for HeH^+: thermal and non-thermal contribution. *Top panel*: transition A←X; *bottom panel*: transition X←X. The blue curve is the thermal contribution calculated in the present work adopting the cross sections by Gay et al. 2012 while the green curve represents the contribution of non-thermal photons to the reaction rate. The crosses represent fits implemented by Schleicher et al. (2008)

1998), which were derived by detailed balance on the data for radiative association of He and H^+ and H and He^+. Secondly, redshift values at which photodissociation rates from non-thermal photons become greater than the thermal contribution are significantly different in the two cases; in the case of the process A ← X this departure happens at $z \sim 1100$ and at $z \sim 200$ for the process X ← X. Then, the radiation temperatures are quite different, respectively $T_r \sim 3000\ K$ and $T_r \sim 550\ K$.

3.2 Fractional abundances

The calculated direct photodissociation rates calculated by considering both thermal and non-thermal emission with the available cross sections have been implemented in a time-dependent chemical network (e.g. Galli & Palla 1998, Coppola et al. 2011b, Longo et al. 2011, Galli & Palla 2013). The presence of non-thermal photons does not significantly affect the fractional abundances of the chemical species of interest; this result is qualitatively expected from comparing the values at which the departure from thermal to non-thermal features occurs and the maxima in the cross sections.

A significant deviation follows from the introduction of the direct process of photodissociation for H_2 and HD (in addition to the Solomon processes) at high values of redshift, where differences up to four orders of magnitude can be appreciated (see Fig. 4). Although significant, this result does not effect the successive phases of chemical evolution, that are mainly controlled by formation processes occurring at lower redshifts (H_2^+ channel followed by the H^- one).

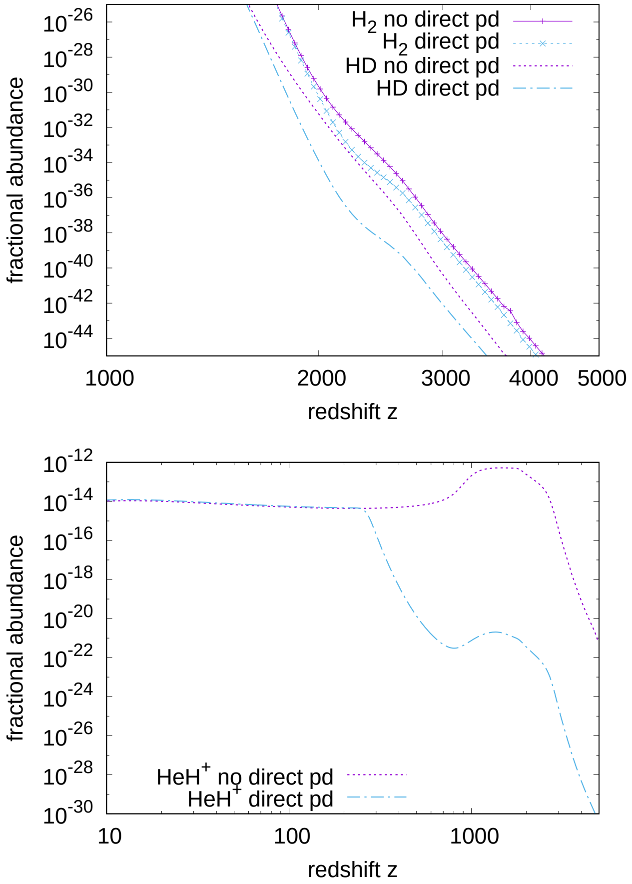

Figure 4. Fractional abundances with and without the contribution of direct photodissociation; *top panel:* H_2 and HD, *bottom panel:* HeH^+.

4 CONCLUSIONS

In the present work the effect of non-thermal photons on the direct photodissociation of three molecules in the context of early Universe chemistry has been investigated. There is no effect on molecular abundances at low redshifts, but some large changes occur at higher z. Such effects agree with estimates performed by taking into account on one hand the thresholds for these chemical processes and, on the other hand, the radiation temperature at which they are expected to become significant. In the case of H_2 and HD, for example, the energy threshold is quite high; consequently, the direct photodissociation is expected to play a role at high values of z, as confirmed by the present simulations. Moreover, the contribution to the photodissociation rates from thermal and non-thermal photons has been provided, showing the ranges at which each term dominates. Updated fits for the direct photodissociation rates of HeH^+ as a function of radiation temperature are provide in Appendix A.

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APPENDIX A: FITS

The calculations reported in this paper concerning HeH^+ have been performed using the cross sections of Miyake, Gay & Stancil (2011). For convenience, we provide an empirical form of the thermal rates, both for the transition A ← X and X ← X to the analytical expression:

$$\mathrm{k}(T_r) = a\ T_r^b\ \exp(-c/T_r). \tag{A1}$$

The values of the parameters in both cases are reported in Tab. A1.

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Table A1. HeH^+ direct photodissociation reaction rates: updated fits for the thermal contribution as a function of T_r

	Thermal [s^{-1}]
$HeH^+(X^1\Sigma^+, v, J) + h\nu \rightarrow He^+(1s)+H(1s)(A^1\Sigma^+)$	
	a = 273518 b = 0.623525 c = 144044 [K]
$HeH^+(X^1\Sigma+, v, J) + h\nu \rightarrow He(1s^2) + H^+(X^1\Sigma^+)$	
	a = 2.03097 $\times 10^8$ b = -1.20281 c = 24735 [K]