H$_2$ AND HD DIRECT PHOTODISSOCIATION IN THE CHEMISTRY OF THE PRIMORDIAL UNIVERSE

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ABSTRACT

In this work, we calculate the thermal contribution to the rate coefficients for the processes of photodissociation of H$_2$ and HD molecules. A comparison between direct and indirect rate coefficients is reported for molecular hydrogen. The rate coefficients are calculated including all vibrational levels of both molecules. Interpolation expressions for all processes are provided as a function of temperature. The resulting total rates for these processes are contextualized by direct numerical calculations based on a standard chemical network for the primordial universe.

Key words: molecular data – molecular processes – radiation mechanisms: thermal

1. INTRODUCTION

Photodissociation processes are important channels in the chemical network of primordial universe chemistry. They are usually grouped in two main classes.

1. Direct photodissociation, which consists in the photon absorption from the ground electronic state of the molecule into the repulsive part of an electronically excited state. It causes immediate dissociation.
2. Indirect processes, when multi-step absorptions take place to cause the dissociation of the molecule.

The indirect process for molecular hydrogen, also called Solomon photodissociation, is usually considered the most relevant. Indeed, especially in astrophysical environments like H I regions, the photons necessary to allow direct photodissociation are absent, due to absorption by atomic hydrogen of photoionizing radiation ($\geqslant$13.6 eV versus $\simeq$14 eV; Spitzer 1948). This process consists of UV-photon absorptions into the electronically and vibrationally excited Lyman (B1 Σ_u^+) and Werner (C1 Π_u) systems followed by fluorescence decay to the vibrational continuum of the ground state.

However, in physical situations present in some astrophysical context, for example in H II regions (e.g., see Glover & Brand 2001; Glover 2007), or in the primordial universe chemistry, the direct photodissociation can represent an efficient dissociation channel, competitive with respect to the Solomon one. In turn, this class of processes could have a significant role in the cooling phenomena occurring therein, as pointed out, e.g., by Bromm & Larson (2004) and Glover (2005) for H$_2$ and Nagakura & Omukai (2005) and Yoshida et al. (2007) for HD. Consequently, it may represent an important aspect in the description of the formation of the first luminous objects.

Concerning the relevance of direct processes in the early universe chemistry, the problem was never explicitly addressed. For an accurate account, the specific rates of these processes must be evaluated taking into account the vibrational distribution of each species. This procedure, which requires the knowledge of the related cross section for each level, is necessary since in some cases the neglect of the changes in the cross sections with the vibrational quantum number can lead to significant corrections as it was recently shown, e.g., for the dissociative attachment process by Capitelli et al. (2007) where the deviations found amounted to several orders of magnitude. In this

work, the direct processes of photodissociation of H$_2$ and HD due to thermal photons are investigated. The absorptions from the ground electronic state Σ_g^+ into the continua of the Lyman (B1 Σ_u^+) and Werner (C1 Π_u) systems are considered. The hypothesis of thermal equilibrium between the different molecular degrees of freedom (electronic, vibrational, and rotational) is assumed. Calculations of the photodissociation rate coefficients are reported as a function of temperature. Analytic fits of the rate coefficients of these processes are provided and the effect of the inclusion of the vibrational states on the results is discussed. The corresponding rates have been consequently determined by inserting our data in a chemical network describing the chemistry of the early universe.

2. COMPUTATIONAL METHODS

The continuous absorption process rate coefficient (Black & Dalgarno 1977) can be written as

$$k_v(T_r) = c \int_{\varepsilon_{\text{th}}}^{\infty} d\varepsilon f(\varepsilon, T_r)\sigma_v(\varepsilon), \qquad (1)$$

where c, $\sigma_v(\varepsilon)$, ε_{th}, and T_r are the speed of light, the state-to-state photodissociation cross sections, the threshold energy for the process, and the radiation temperature, respectively. $f(\varepsilon, T_r)d\varepsilon$ is the number of photons per energy interval and is related to the Planck distribution $u(\varepsilon, T_r)d\varepsilon$ by the following expression:

$$f(\varepsilon, T_r)d\varepsilon = \frac{8\pi\varepsilon^2}{(hc)^3}\frac{1}{e^{\frac{\varepsilon}{KT_r}}-1}d\varepsilon = \frac{u(\varepsilon, T_r)d\varepsilon}{\varepsilon}, \qquad (2)$$

with h and K representing Planck's constant and Boltzmann's constant, respectively. The total rate coefficient, defined as

$$k_{\text{tot}}(T_g, T_r) = \sum_v \chi_v(T_g)k_v(T_r), \qquad (3)$$

is the rate coefficient of the process of photodissociation due to the contribution of all vibrational levels, with $\chi_v(T_g)$ the vibrational distribution function (vdf) that is a function of the gas temperature T_g. The present rate coefficients depend on temperature only since we are considering a thermal radiation spectrum. Line contributions, which imply an estimate of the recombination rate producing the lines, have been considered

Table 1
Data Extrapolation for High-temperature Range

$H_2(v)$ Lyman	$H_2(v)$ Werner
From $v = 3$ for $v = 9, 10, 11, 12, 13$	From $v = 7$ for $v = 8, 9, 10, 11, 12$

HD(v) Lyman	HD(v) Werner
From $v = 2$ for $v = 0$	From $v = 5$ for $v = 9, 10, 11, 12$
From $v = 5$ for $v = 10, 11, 12, 13, 14$	

by Johnson & Bromm (2007), based on He I recombination line and Hirata & Padmanabhan (2006) on the recombination of H I. The impact of such contributions should be evaluated in specific cases where the distortion photons are included.

Since we assume thermal equilibrium, $T_r = T_g = T$. Equation (3) becomes

$$k_{\text{tot}}(T) = \sum_v \chi_v(T) k_v(T). \qquad (4)$$

The photodissociation cross sections $\sigma_v(\varepsilon)$ used to perform the present calculations are taken from Allison & Dalgarno (1969), and were calculated using the standard quantum-mechanical expression involving the dipole moment operator and the wave functions of the initial bound vibrational state and the final continuum one.

A Boltzmann vdf is assumed and the vibrational level energies have been taken from existing data by Wolniewicz (1983). A few cross sections, those reported in Table 1, were lacking of data for the high energy range, as already remarked in the paper by Abel et al. (1997), where interpolated expressions of the available data are provided. In order to overcome this problem, the cross sections were therefore extrapolated at high energy using the trends of comparable processes reported on the same table. This procedure, although necessary in view of the partial lack of data, implies some uncertainties whose impact on the results of chemical networks could be discussed by a procedure similar to that described by Glover et al. (2006) and Glover & Abel (2008).

The rate coefficients calculated in the present work have been introduced in a specific chemical network describing the primordial universe kinetics. The chemical pathways shown by Schleicher et al. (2008) have been considered, in order to evaluate the destruction rates of the chemical species in analysis; the corresponding system of ordinary differential equations has been solved. In the case of H_2, both the direct and indirect photodissociation processes have been considered; for HD, the direct process of photodissociation has been introduced for the first time to the present authors' knowledge.

3. RESULTS AND COMMENTS

In Figure 1, the state-to-state rate coefficients have been reported, respectively, for H_2 and HD. Labels "$v = i$" and "v_{tot}" stand for the contribution calculated considering all the molecules of the gas in the ith state and assuming the Boltzmann distribution among vibrational levels, respectively. The effect of vibrational excitation is not so strong here like that found for the process of dissociative attachment in Capitelli et al. (2007), since the cross sections are not changing so dramatically with the vibrational quantum number, but it is still important. In all cases reported in the figures, the inclusion of the whole manifold of vibrational levels produces results which deviate sensibly from those obtained considering just the cross section
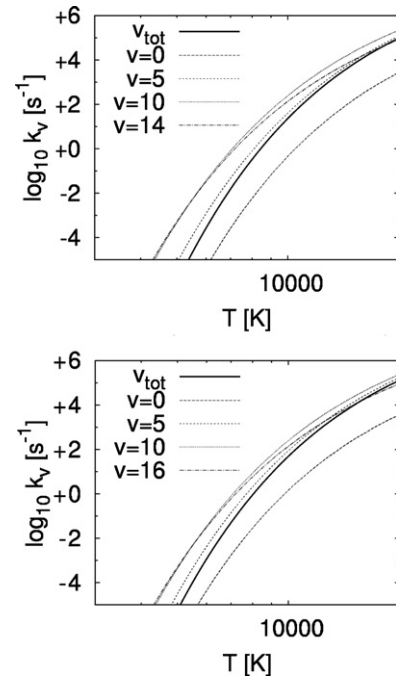

Figure 1. Top panel: H_2 Lyman photodissociation rate coefficients vs. temperature T: the contributions of some vibrational levels ($v = 0, 5, 10, 14$) are shown. They have been calculated in the hypothesis that the fractional abundance of the considered specific vibrational level is equal to 1. The thicker curve represents the total rate coefficient calculated using Equation (3). In the scales used for the plot, the curves corresponding to the Werner and Lyman systems are indistinguishable. Bottom panel: HD Lyman photodissociation rate coefficients vs. gas temperature T: meaning of the symbols and comments as in the top panel.

for $v = 0$ in conjunction with the whole H_2 and HD populations for T_g over $\sim 10^4$ K. At these temperatures the molecules here considered will be almost fully dissociated in most cases, but the accurate determination of the kinetics of the residual molecules in such conditions has a great astrophysical relevance. Our results can be compared with earlier estimates by Shull (1978). In his paper, the author assumes the photon absorption in the range between 912 and 1108 Å (Lyman and Werner bands) and finds $k = 10^{-11} F/F_0$ s^{-1} (where F_0 is the average interstellar background UV-photon flux assumed equal to 3×10^{-4} m^{-2} s^{-1} Hz^{-1}) with a declared error within a factor of two, summing contributions from $v \geqslant 3$, and using the same cross sections as here. A qualitative comparison can be set by fixing, e.g., $T = 10^4$ K, and calculating F as an integrated photon flux from Planck's law. Using the expression above for k, at $\lambda = 912$ Å, the result is $k = 14.8$ s^{-1}. Given the different hypothesis assumed, this is comparable to our result ($k = 32.2$ s^{-1}) at the same temperature.

The resulting destruction rates obtained by the implemented chemical kinetics network are shown in Figure 2; it is evident that, in all cases, the direct photodissociation processes play an important role among the destruction channels of H_2 and HD in the early phases of our universe, competitive to the usually introduced loss channels. In particular, it is evident from Figure 2 that the direct photodissociation rate is comparable with the indirect Solomon one. The significance of the photodissociation process among destruction pathways can also be shown for HD, as reported in the other panel of Figure 2.

Although the addition of these processes does not affect sensibly the mole fraction of H_2 and HD under the present hypothesis, it must be noted that the rate of direct photodissociation of H_2
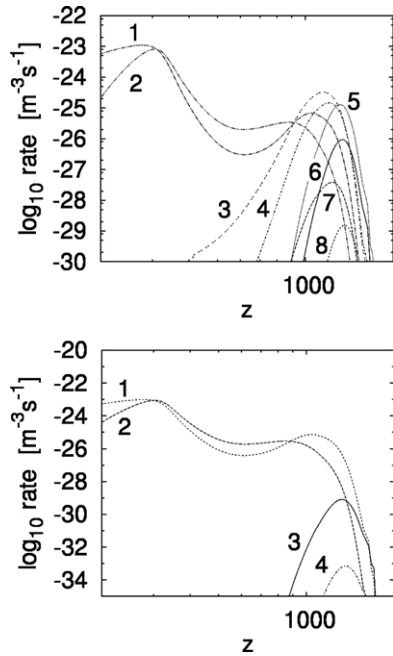
Figure 2. H$_2$ and HD destruction channel rates in the early universe chemistry. For H$_2$, 1.H$_2$ + D$^+$ → HD + H$^+$; 2.H$_2$ + D → HD + H; 3.H$_2$ + H$^+$ → H$_2^+$ + H; 4.H$_2$ + e^- → H$^-$ + H; 5.H$_2$ + γ → 2H (Solomon process); 6.H$_2$ + γ → 2H (direct photodissociation, present work); 7.H$_2$ + e^- → 2H + e^-; 8.H$_2$ + γ → H$_2^+$ + e^-. For HD, 1.HD + H$^+$ → D$^+$ + H$_2$; 2.HD + H → D + H$_2$; 3.HD + γ → H + D (direct photodissociation, present work); 4.HD + γ → HD$^+$ + e^-.

Table 2
Rate Coefficients Fit

Molecule	System	$k_{\rm tot}$ (s^{-1})
H$_2(v)$	Lyman	$1.27 \times 10^8 \times T^{0.084} e^{-\frac{159600}{T}}$
	Werner	$6.46 \times 10^8 \times e^{-\frac{165530}{T}}$
HD(v)	Lyman	$1.19 \times 10^7 \times T^{0.28} e^{-\frac{145310}{T}}$
	Werner	$5.70 \times 10^8 \times e^{-\frac{157380}{T}}$

and HD is constantly much higher than that of the respective photoionizations, two processes included as a rule in chemical networks. Therefore, the processes studied in this paper should be included in any comprehensive rate analysis like that in Stancil et al. (1998, Figures 5– 9), and generally in chemical networks to grant reliability toward changes of model parameters. Moreover, preliminary calculations of the vdf of H$_2$ (Coppola et al. 2010) based on a master equation (Dalgarno 2005; Lepp et al. 2002) suggest that fractional abundance of excited levels can be reduced by introducing the direct photodissociation by about an order of magnitude at $z \simeq 2500$. By using the same model, it is possible to discuss the assumption of thermal equilibrium for the present calculations, while there is some significant deviation between the contribution to the total rate of specific levels compared to LTE (e.g., an order of magnitude for $v = 8$), the total rate is only marginally affected.

For future applications, we report our calculated rate coefficients in Table 2.

4. CONCLUSIONS

In this work, the direct process of photodissociation of molecular hydrogen and HD has been investigated. Calculations of the rate coefficients have been presented, taking into account the entire ensemble of vibrational levels of these molecules. A comparison with existing data on indirect photodissociation rate coefficient has been performed, putting into evidence the significance of the direct process in the temperature range considered (1000–50,000 K).

The competitiveness of the corresponding reaction rate has also been verified through numerical solution of a chemical reaction network for the primeval universe plasma.

The present calculations represent the "equilibrium" contribution to the direct photodissociation rate coefficients. Indeed, both vdf and photon energy distribution have been considered in their thermal shape (Boltzmann and Planck's distributions, respectively). However, non-equilibrium conditions can be considered for either the vdf (Capitelli et al. 2007; Coppola et al. 2010) or the radiation spectrum (Hirata & Padmanabhan 2006). These effects have to be evaluated as an additional contribution to the present rate coefficients, in order to comprehensively model non-equilibrium physical conditions:

$$k_{\rm non-equ} = k_{\rm tot} + k_{\rm non-thermal}. \tag{5}$$

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