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An evaluation of the effect of the dissociative attachment of vibrationally excited H₂ on primordial universe chemistry
(Research Note)

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ABSTRACT

Aims. We study the relevance of including vibrational levels of molecular hydrogen in one of the processes taking place in the primordial Universe: the dissociative attachment of H_2.
Methods. We calculated the rate of dissociative attachment of H_2, covering the contribution of all vibrational levels in standard conditions for primordial Universe chemistry. We then compared this rate to the rates of other chemical processes relevant for H_2 balance as a function of z.
Results. It is shown that vibrationally excited levels of molecular hydrogen cannot be neglected in evaluating the rate of dissociative attachment in early Universe conditions and that this process is one of the most relevant channels for destruction of H_2 molecules at $z \approx 10^3$. We also propose a preliminary estimation of the effect of a possible non-equilibrium vibrational distribution on the results.

Key words. molecular processes – cosmology: early Universe

1. Introduction

The H_2 molecule is considered very important in the formation of primordial objects in the post-recombination era. In fact, due to its rotational emission, molecular hydrogen is fundamental for the radiative cooling of interstellar gases, which in turn is essential to the birth of the first matter aggregates (see, for example, Galli & Palla 1998). In this work we focus on the role of vibrationally excited molecular hydrogen in the chemistry of the early Universe. To this aim we estimate the effect of including all vibrational levels v of molecular hydrogen on the evaluation of the rate coefficient of one of the H_2 destruction channels, namely the dissociative attachment:

$$H_2(v) + e^- \rightarrow H + H^-. \tag{1}$$

For the following study, we have considered the primordial Universe as a recombinant hydrogen plasma. Due to the temperatures characterizing the recombination era ($T_g \approx 4000$ K, Dalgarno 2005), we used results from quantum mechanical calculations of wide use in cold plasma physics (Celiberto et al. 2001; Fabrikant et al. 2002). In the calculation of these cross sections an improved version of the resonant scattering model originally developed by Fano (1961) is used. In its application to electron attachment to H_2, it is assumed that a temporary negative molecular ion is formed, which can either ionize, leading to a neutral molecule, or dissociate into an atom and a negative ion. Calculating the wavefunction of the two nuclei in the intermediate molecular ion involves a complex nonlocal potential: earlier calculations like those collected in the database by Janev et al. (1985) are based on a local approximation and can differ substantially from the more accurate ones as shown in preliminary

results by Mundel (1985) and in more detail by Atems & Wadehra (1990) and Fabrikant et al. (2002).

2. Vibrational levels in H₂ dissociative attachment

Till now in the literature concerning molecular kinetics in the primordial Universe, the contribution of vibrationally excited molecules has been considered negligible for all the processes studied, such as the dissociative attachment. In fact, the equilibrium population of excited levels, especially the most excited ones, is very small in the temperature conditions for a large part of the red-shift interval $10\,000 < z < 100$, where molecular kinetics is most important. However, in the case of H_2 dissociative attachment, the relevant cross sections $\sigma_v(\varepsilon)$ increase by orders of magnitude passing from $v = 0$ to higher v (Celiberto et al. 2001; Fabrikant et al. 2002), so that even small concentrations of excited states can strongly affect the global rate. This is given by

$$v = \sum_v k(v) n_e n_{H_2(v)}, \tag{2}$$

where

$$k(v) = \sqrt{\frac{8}{m_e \pi}} \left(\frac{1}{KT}\right)^{3/2} \int_0^\infty d\varepsilon \ \varepsilon \cdot e^{-\frac{\varepsilon}{KT}} \cdot \sigma_v(\varepsilon) \tag{3}$$

and n_e and $n_{H_2}(v)$ represent the electron and molecular hydrogen density, respectively. The latter is calculated as

$$n_{H_2}(v) = \chi_v \chi_{H_2} \frac{n_b}{2} \tag{4}$$

where χ_{H_2} is the fractional abundance of H_2 molecule, n_b the baryonic density, and χ_v the *vibrational distribution function*, often indicated with the acronym *vdf*.
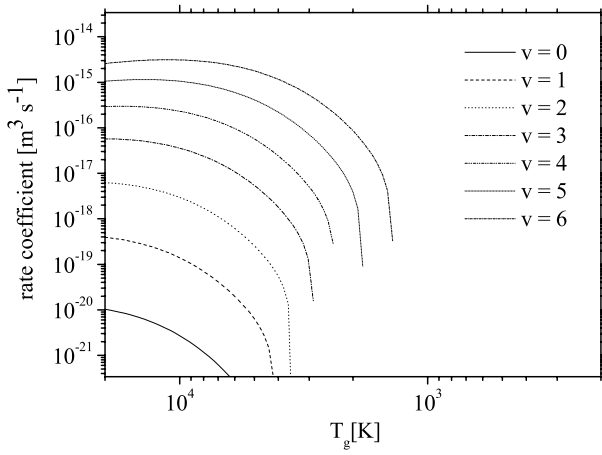
Fig. 1. Rate coefficient trend with T_g for the dissociative attachment process of molecular hydrogen. Vibrational levels are from $v = 0$ to $v = 6$.
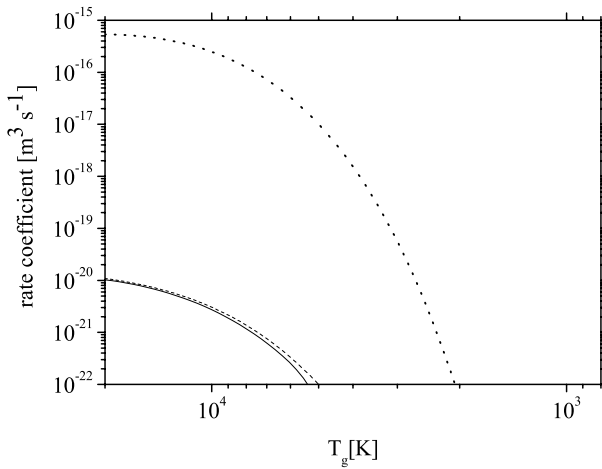

Fig. 2. Comparison between the rate coefficient for the vibrational level $v = 0$ of H_2 (fit by Galli & Palla (1998, dashed line), and the present work (solid line)) in the lower part of the figure, and the total rate coefficient, as defined in Eq. (8), for the dissociative attachment process (dotted line).

The rate coefficients $k(v)$ as a function of the red-shift $1 + z$, which is linked to the gas temperature by the following cosmological relation,

$$T_g = 2.73 \, (1 + z) \text{ K}, \tag{5}$$

are shown in Fig. 1 for the first seven vibrational levels.

The results for $v = 0$ can be compared with those from the article by Galli & Palla (1998), where the dissociative attachment rate coefficient is included as a fit to the experimental data from Schulz & Asundi (1967) for vibrationally cold hydrogen. In the lower part of Fig. 2 we compare our rate coefficient and the one by Galli & Palla (1998), whose analytic expression is given by

$$k_{\text{ref}}(v = 0) = 2.7 \times 10^{-14} T_g^{-1.27} \, e^{-\frac{43000}{T_g}} \text{ m}^3 \text{ s}^{-1}, \tag{6}$$

showing good agreement. To obtain the electronic and H_2 densities, we used the fractional abundances from the literature (Galli & Palla 1998), using the hypothesis of charge neutrality for the fractional abundance of electron (other positive ions have negligible concentrations compared with that of H^+) and the following expression of baryonic density, taken from the same article:

$$n_b = 1.514 \times 10^{-3} \, (1 + z)^3 \text{ m}^{-3}. \tag{7}$$
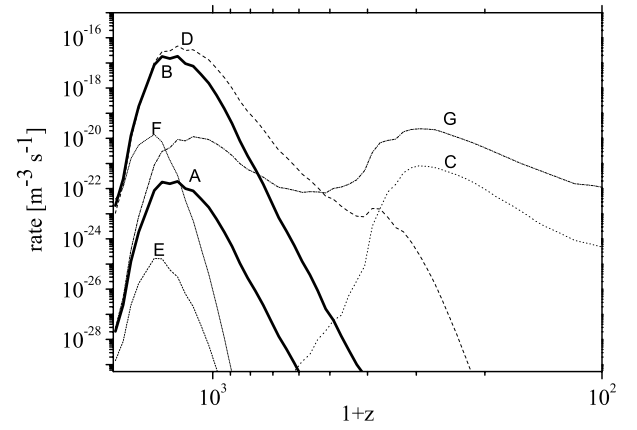
A: dissociative attachment (fit by Galli & Palla, 1998)
B: dissociative attachment (present work)
C: $H_2^+ + H_2 \rightarrow H_3^+ + H$
D: $H_2 + H^+ \rightarrow H_2^+ + H$
E: $H_2 + e^- \rightarrow 2H + e^-$
F: $H_2 + h\nu \rightarrow H_2^+ + e^-$
G: $H_2 + H^+ \rightarrow H_3^+ + h\nu$

Fig. 3. Rates for the destruction processes of molecular hydrogen as a function of $1 + z$.

At this stage we assumed a Boltzmann distribution for the population of vibrational levels, whose energies were taken from Wolniewicz (1983) up to $v_{\text{max}} = 14$, i.e. up to the vibrational level beyond which molecules are assumed to be dissociated. Under these conditions it is possible to calculate the total rate coefficient

$$k_{\text{tot}} = \sum_v k(v) \chi_v \tag{8}$$

as a function of T_g. It is evident that the rate coefficient calculated taking all vibrational levels of H_2 into account in the dissociative attachment process is greater by about five orders of magnitude than that calculated considering only the fundamental vibrational level (see Fig. 2) In the following we report the most significant quantities as functions of $1 + z$, using Eq. (5). In Fig. 3 we show the total rate for the process of dissociative attachment for H_2, as the sum of the contributions of every vibrational level (see Eq. (2)), compared with the dissociative attachment rate obtained with the rate coefficient in Galli & Palla (1998). The effect is relevant and the recalculated dissociative attachment process becomes competitive with respect to the other destruction channels of molecular hydrogen shown in the same figure, whose rate coefficients are the ones in Galli & Palla (1998). It is interesting to note that, in a relatively recent work by Abel et al. (1997), the role of excited states in some channels (in particular the attachment) is assumed to be negligible based on a comparison of collisional and radiative channels; however, such argument cannot be applied to H_2 vibrational excitation, since the related Einstein coefficients are negligibly small compared with typical collision frequencies (dipole forbidden vibrational transition). For future applications we report our calculated rate coefficient in the same analytic form as that given by Galli & Palla (1998):

$$k_{\text{tot}} = 3.67 \times 10^{-5} \times T_g^{-2.28} \, e^{-\frac{47172}{T_g}} \text{ m}^3 \text{ s}^{-1}. \tag{9}$$

The role of vibrationally excited levels can become even more important if chemical non-equilibrium conditions affect the vibrational distribution. In a recombining molecular plasma suprathermal vibrational distribution, tails are often observed due to
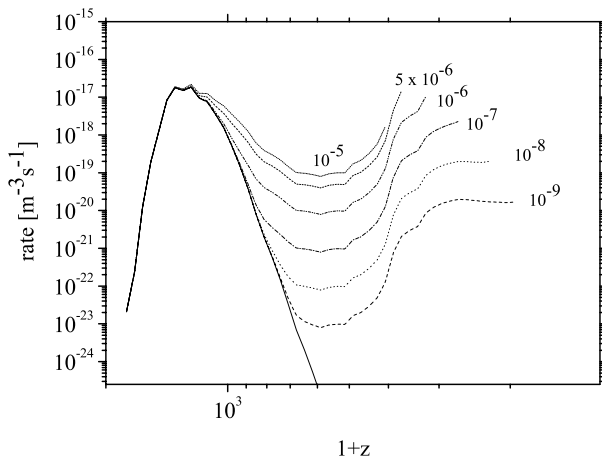
Fig. 4. Comparison between H_2 dissociative attachment rate at equilibrium (Eq. (10) for $\gamma = 0$, solid line) and non-equilibrium (Eq. (10) for the following γ values: 10^{-5}, 5×10^{-6}, 10^{-6}, 10^{-7}, 10^{-8}, and 10^{-9}).

the fact that recombination supplies chemical energy so that molecules are produced in excited vibrational states. Such a process leads to a vibrational distribution that could be represented by a superposition of a Boltzmann distribution at low temperature, which accounts for the large quantity of molecular density and mean energy, and a thermalization curve connected with the lifetime of a molecule in the vibrational level v during its degradation towards thermal energies. Such recombination tails have been found by rigorous calculations of different gas systems (N_2, O_2) (Armenise & Capitelli 2005). While these calculations are not yet available for hydrogen, we observe that the supra-thermal tails found for other gases can be roughly represented by a slowly decreasing function of v, such as $1/(1 + v)$. Provisionally, we assume here, for a first parametric study of this effect, the following expression for the vdf:

$$\chi_v \propto \text{Boltzmann} + \gamma \cdot \frac{1}{(1 + v)}, \qquad \sum_v \chi_v = 1 \qquad (10)$$

where the parameter γ measures the relative relevance of the supra-thermal tail with respect to the Boltzmann distribution. The value of this parameter should be established in future studies that will take into account the various atomic and molecular processes on the ground of this kind of non-equilibrium. In this work, however, γ is a non-equilibrium parameter, which we will keep as low as needed for having a negligible total energy contribution by the tail, to show that even if we are in this situation, the effect on the dissociative attachment is not negligible. The temperature T of the Boltzmann contribution has been adjusted in order to obtain the same mean energy of the equilibrium distribution at the same z; nonetheless, given the above described conditions, the needed correction to the temperature is very small. In Fig. 4 the dissociative attachment rate versus $1 + z$ for the γ values indicated in the corresponding caption is reported. The effect of the supra-thermal vibrational tail on the kinetics of the dissociative attachment is

very relevant. Again, this effect is due to the strong increase in the dissociative attachment cross sections with the vibrational level v.

Similar effects may be also produced by a temperature separation between degrees of freedom (not discussed much in the literature but quite possible after the separation of the radiation and gas temperatures, T_r and T_g), together with anharmonic vibrational kinetics of the H_2 molecules (Capitelli 1986).

3. Conclusions

In this work we have discussed the relevance of the H_2 vibrational levels in the recombination era of the Universe. We provided the dissociative attachment rate coefficient of molecular hydrogen, calculated considering all the contributions deriving from the 15 vibrational levels of the ground electronic state as not negligible. Our result was compared with Galli & Palla (1998). In this way we have stressed a difference of five orders of magnitude, emphasizing that the contribution of vibrational levels in the computation of the dissociative attachment rate for molecular hydrogen cannot be neglected. We have shown that a possible supra-thermal non-equilibrium tail in the vibrational distribution could have a very strong effect on dissociative attachment rate due to atomic recombination.

On the grounds of these considerations and preliminary evaluations, we can say that future works on molecular kinetics in the primordial Universe should estimate the potentially non-equilibrium distribution of vibrational H_2 states and, probably, of other molecules that are more important than H_2 in the energetic coupling between radiation and matter, such as HD. These future studies should be based on an authentic vibrational non-equilibrium kinetics, built on a *vibrational master equation* and a rigorous critical evaluation of the available data for the cross sections and the rate coefficients of every individual vibrational, probably roto-vibrational, state of the cosmologically relevant molecules.

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