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Three-body recombination of hydrogen in the early Universe

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ABSTRACT

It has been suggested recently that three-body recombination of two protons and an electron might be significant in the formation of atomic hydrogen in the early Universe. We demonstrate that this process is completely negligible in the primordial plasma and that the value of the redshift, at which the transition from ionized to atomic hydrogen occurs, is determined by an equilibrium between the rates of two-body radiative recombination of a proton and an electron and its inverse, namely photoionization of atomic hydrogen.

Key words: astrochemistry – atomic processes – scattering – early Universe.

1 INTRODUCTION

The recombination of hydrogen in the early Universe is an important process that leads subsequently to the formation of H_2, whose role as a coolant – facilitating the gravitational contraction of the first condensations of baryonic material – has been recognized for many years (see e.g. Lepp & Shull 1984; Flower & Pineau des Forêts 2001; Glover & Abel 2008). Studies of the chemistry of the primordial gas (Peebles 1968; Zeldovich et al. 1968; Galli & Palla 1998, 2013) considered that the formation of atomic hydrogen was mediated by the radiative recombination of a proton and an electron,

$$H^+ + e^- \rightarrow H + h\nu \qquad (1)$$

in which a photon of energy $h\nu$ is emitted in order for the atom to form. However, it has been suggested recently (Kereselidze et al. 2019, 2021, 2022) that the three-body reaction

$$H^+ + H^+ + e^- \rightarrow {H_2}^+ + h\nu \rightarrow H^+ + H \qquad (2)$$

in which the intermediate ${H_2}^+$ is formed in an excited electronic state might be a significant contributor to the recombination process in the primordial medium, for redshifts $z \gtrsim 2000$. Although it is not immediately evident that a three-body radiative process should be significant compared with the equivalent two-body reaction, Kereselidze et al. (2019) argued that in the primordial plasma, in which hydrogen is ionized, the mean distance between protons[1] is comparable to the radius of a hydrogen atom in a bound state of high principal quantum number, n, and under these circumstances recombination should be treated as a quasi-molecular process involving ${H_2}^+$.[2]

The classical radius of an H atom is proportional to n^2, where $n \rightarrow \infty$ as the continuum of H is approached, and hence it is always possible – in theory, at least – to find a high-n state of H whose radius is comparable to the mean distance between protons, $\bar{R} \approx [n(H^+)]^{-1/3}$, whatever the value of the proton density, $n(H^+)$; this does not imply that the rate of the three-body reaction (2) is comparable to the rate of the two-body reaction (1). In order to make this comparison, the rate coefficient for the three-body reaction must also be known. In Section 2, this rate coefficient is evaluated and the rates of reactions (1) and (2) are compared. Our concluding remarks are made in Section 3.

2 THE RATE COEFFICIENT FOR THREE-BODY RECOMBINATION

We consider the direct formation of H in the three-body reaction

$$H^+ + H^+ + e^- \rightarrow H^+ + H \qquad (3)$$

in which the excess energy is removed as kinetic energy of a proton; this process is intrinsically faster than the formation of an intermediate molecular ion by radiative stabilization, followed by the formation of the same products, H^+ and H (reaction 2), by the order of $\alpha^{-1} = 137$, where α is the fine structure constant. The rate coefficient for reaction (3) will be denoted by k_f (cm^6 s^{-1}), and that for the reverse reaction

$$H^+ + H \rightarrow H^+ + H^+ + e^- \qquad (4)$$

by k_r (cm^3 s^{-1}). Reaction (4) will be recognized as the ionization of an H atom in a binary collision with a proton.[3] In equilibrium, the rates per unit volume of the forward and reverse reactions are equal:

$$[n(H^+)]^2 n(e^-) k_f = n(H^+) n(H) k_r. \qquad (5)$$

The rate coefficients of the forward and reverse reactions may be related by considering the special case of thermodynamic equilibrium, in which the particle densities are determined by the Saha equation.

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[1] Huang (2022) has since shown that the mean distance between protons shown in fig. 1 of Kereselidze et al. (2019) is an underestimate for $z > 2000$.

[2] In fact, the initial state in reaction (2) may be viewed as a proton interacting with a hydrogen atom in a continuum state, not a bound state.

[3] The reverse of reaction (2) is the formation of a pre-dissociating state of ${H_2}^+$ from H^+ and an excited state of H, followed by dissociative photoionization from the pre-dissociating state of ${H_2}^+$.

Then,

$$\frac{n(\mathrm{H})}{n(\mathrm{H}^+)n(\mathrm{e}^-)} = \frac{g(\mathrm{H})}{g(\mathrm{H}^+)g(\mathrm{e}^-)}\left(\frac{h^2 m_{\mathrm{H}}}{2\pi m_{\mathrm{H}^+} m_{\mathrm{e}^-} k_{\mathrm{B}} T}\right)^{3/2} \times \exp\left(\frac{I_n}{k_{\mathrm{B}} T}\right) = \frac{k_{\mathrm{f}}}{k_{\mathrm{r}}}, \quad (6)$$

where g denotes a statistical weight, m the mass, T the temperature, and $I_n > 0$ the ionization energy of level n. Thus, the rate coefficient for the three-body formation of H, k_{f}, may be determined from the rate coefficient for collisional ionization of H by H^+, k_{r}.[4] The ratio of statistical weights in equation (6) is given by

$$\frac{g(\mathrm{H})}{g(\mathrm{H}^+)g(\mathrm{e}^-)} = n^2, \quad (7)$$

where n is the principal quantum number. We note that the same statistical factor of n^2 appears also in the rate of radiative recombination to level n, expressed in terms of the cross-section for photoionization from the same level: see Seaton (1959, equation 1).

The process of ionization of H ($n = 1$) in collisions with H^+ has been studied both experimentally and theoretically, but at higher (keV) energies than are directly relevant here. As shown by Salin (1969) and more recently by Sahoo et al. (1999), the cross-section for reaction (4) has a maximum value $\sigma \approx \pi a_0^2$,[5] the geometric cross-section of H ($n = 1$), for a collision energy $E \approx 50$ keV. We shall adopt a constant $\sigma = a_0^2$, which will certainly overestimate k_{r} and hence k_{f}. Integrating over a Maxwellian velocity distribution, we have

$$k_{\mathrm{r}} = \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \int_{x_1}^{\infty} x \exp(-x)\sigma(x)\mathrm{d}x \quad (8)$$

for ionization from the $n = 1$ ground state of H and where $x = E/k_{\mathrm{B}}T$, $x_1 = I_1/k_{\mathrm{B}}T$, and $\mu = m_{\mathrm{H}^+}m_{\mathrm{H}}/(m_{\mathrm{H}^+} + m_{\mathrm{H}}) \approx m_{\mathrm{H}}/2$ is the reduced mass. If σ is independent of x,

$$k_{\mathrm{r}} = \left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{\frac{1}{2}} \sigma \times \left(1 + \frac{I_1}{k_{\mathrm{B}}T}\right)\exp\left(\frac{-I_1}{k_{\mathrm{B}}T}\right), \quad (9)$$

where $I_1/k_{\mathrm{B}}T \gg 1$ for the redshifts, z, of relevance here. Substituting numerical values of the constants, we obtain $k_{\mathrm{f}} = 3.8 \times 10^{-23} T^{-2}$ cm^6 s^{-1}, which, we recall, is an overestimate of k_{f}.

In order to compare the rates of recombination of hydrogen by the two- and three-body processes, it is necessary to know the density of the third body, H^+. For this purpose, we have used the model of the chemical and thermal evolution of the primordial gas developed by Flower & Pineau des Forêts (2000). This model calculates the radiation and kinetic temperatures of a four-fluid flow, comprising neutral and ionized species, electrons and photons. The time-dependent chemical rate equations for the species densities are solved in parallel with the thermal equations, with full allowance for departures from equilibrium induced by the expansion of the Universe; the model is possibly unique in that it follows simultaneously the evolution of the population densities of individual rovibrational levels of H_2, allowing for collisional and radiative transitions between the levels and, once again, the dynamical effect of the expansion. Full details regarding the equations involved are to be found in section 2 of Flower & Pineau des Forêts (2000). The current version of this code has been updated with respect to the values of cosmological parameters (Lahav & Liddle 2022; see Appendix A) and the chemistry (Faure et al., in preparation).

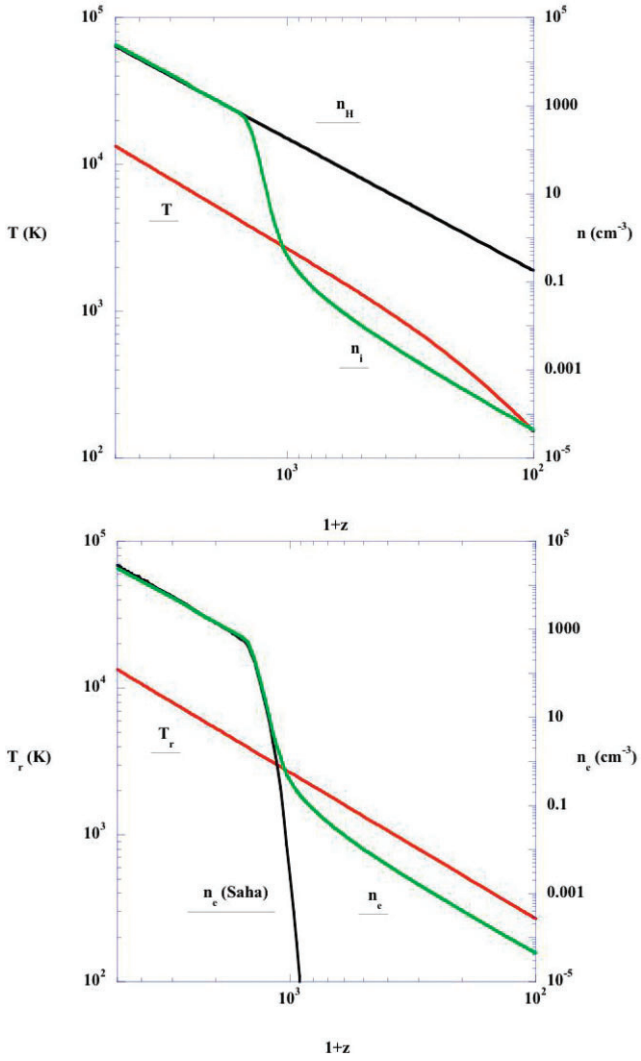

Figure 1. Upper panel: the variations of the kinetic temperature, T, and of the ion density, n_{i}, and the total density, $n_{\mathrm{H}} \equiv n(\mathrm{H}) + n(\mathrm{H}^+)$, around the epoch of H-recombination in the primordial gas, at redshift $z \approx 1000$. Lower panel: the variations of the radiation temperature, T_{r}, and of the electron density, n_{e}, for the same epoch. The electron density predicted by the Saha equation (equation 6) is also shown.

In the upper panel of Fig. 1 are plotted the kinetic temperature[6] and the density of the primordial gas, from $z = 5000$ until after recombination has occurred, at $z \approx 1000$. It may be seen that, during the epoch prior to recombination, $T \gtrsim 3 \times 10^3$ K and $n(\mathrm{H}^+) \lesssim 3 \times 10^4$ cm^{-3}, and hence $k_{\mathrm{f}} n(\mathrm{H}^+) \lesssim 10^{-25}$ cm^3 s^{-1}. On the other hand, the rate coefficient for two-body radiative recombination, reaction (1), is of the order of 10^{-13} cm^3 s^{-1} for 10^4 K $\gtrsim T \gtrsim$

[4]Flower & Harris (2007) applied an analogous procedure to determine the rate coefficient for the formation of H_2 from three H atoms. It should perhaps be emphasized that the relation (6) between the rate coefficients for the forward and reverse reactions is perfectly general, applying also under conditions in which thermodynamic equilibrium is not attained.

[5]$a_0 = 0.5292 \times 10^{-8}$ cm is the Bohr radius.

[6]The differences between the kinetic temperatures of the neutral and charged species are insignificant.

10^3 K, for recombination to the $n = 1$ ground state (cf. Seaton 1959; Flower & Seaton 1969); the rate coefficient for recombination to all excited states is approximately twice that to the ground state. Thus, we deduce that three-body recombination fails by at least 12 orders of magnitude to compete with two-body radiative recombination of hydrogen in the primordial gas. A similarly large disparity exists between the rates of the reverse of reactions (1) and (3), namely photoionization of H by the background (black-body) radiation field and collisional ionization of H by H^+. In other words, reaction (1) and its inverse dominate reaction (3) and its inverse by at least 12 orders of magnitude in the recombining primordial plasma.[7]

Kereselidze et al. (2022) estimated the degree of ionization of the recombining hydrogen gas on the assumption that the Saha equation (equation 6) applies. They then showed that the value of the redshift at which recombination occurs differs from 'standard' models, owing to an increase in the ionization potential, estimated to be 20 per cent, arising in the intermediate H_2^+ complex. In the lower panel of Fig. 1, we compare the electron density computed from the Saha equation with that predicted by the cosmological model.[8] It may be seen from this figure that the Saha equation predicts well the degree of ionization in the pre-recombination gas (cf. Sunyaev & Chluba 2009). However, as we have shown, the validity of the Saha equation relates to an equilibrium between reaction (1) and its inverse, reaction (2) and its inverse being completely negligible. It follows that any effect on the ionization potential, arising from the formation of the H_2^+ complex, will also have negligible consequences.[9]

3 CONCLUDING REMARKS

We have assessed quantitatively the relative contributions of the three-body reaction (2) and the two-body radiative reaction (1) to the recombination of hydrogen in the primordial gas and have shown that the former process is at least 12 orders of magnitude slower than the latter. The degree of ionization in the pre-recombination plasma is represented accurately by the Saha equation; but this is due to an equilibrium between photoionization of H by the background radiation field and radiative recombination of electrons with protons.

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[7]Although this conclusion applies strictly to recombination to the $n = 1$ ground state, we remark that most of the population of a hydrogen atom is in its ground state, under the physical conditions considered here.

[8]Fig. 1 shows that the kinetic and radiation temperatures diverge only after recombination of hydrogen has taken place.

[9]The ionization potential would tend to *decrease* – although only slightly – owing to collisional broadening of the closely spaced high-n energy levels, which lowers the level of the effective continuum.

DATA AVAILABILITY

The data generated by this study are available on request to the author.

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APPENDIX A: COSMOLOGICAL PARAMETERS

The evolution of the scale factor, $a(t) = 1/(1 + z)$, where z is the redshift, is determined by

$$\frac{1}{a}\frac{\mathrm{d}a}{\mathrm{d}t} = H(t), \tag{A1}$$

where we adopt

$$H(t) = H_0 \left(\frac{\Omega_\mathrm{m}}{a^3} + \frac{\Omega_\mathrm{r}}{a^4} + \Omega_\Lambda \right)^{\frac{1}{2}} \tag{A2}$$

with the following values of the parameters: $H_0 = 67.4$ km s^{-1} Mpc^{-1}, $\Omega_\mathrm{m} = 0.315$, $\Omega_\mathrm{r} = 8.3 \times 10^{-5}$, and $\Omega_\Lambda = 0.685$. If Ω_r is neglected, then

$$a(t) = \left[\frac{\Omega_\mathrm{m}}{\Omega_\Lambda} \sinh^2 \left(\frac{t}{t_\Lambda} \right) \right]^{\frac{1}{3}}, \tag{A3}$$

where $t_\Lambda = 2/(3H_0\Omega_\Lambda^{0.5})$; this equation relates the redshift, z, to the evolution time, t.

The present background radiation temperature is $T_\mathrm{r} = 2.726$ K, and $\Omega_\mathrm{b} = 0.0493$.

The above parameters lead to a current ($z = 0$) density $n_\mathrm{H} \equiv n(\mathrm{H}) + n(\mathrm{H}^+) = 1.9 \times 10^{-7}$ cm^{-3}, somewhat higher than the value of 1.4×10^{-7} cm^{-3}, deduced by Kereselidze et al. (2021).

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