Cosmological production of H$_2$ before the formation of the first galaxies

Christopher M. Hirata$^1$ and Nikhil Padmanabhan$^2$

$^1$School of Natural Sciences, Institute for Advanced Study, Einstein Drive, Princeton, NJ 08540, USA
$^2$Joseph Henry Laboratories, Department of Physics, Jadwin Hall, Princeton University, Princeton, NJ 08544, USA

ABSTRACT

Previous calculations of the pregalactic chemistry have found that a small amount of H$_2$, $x[{	ext{H}_2}] \equiv n[{	ext{H}_2}]/n[{	ext{H}}] \approx 2.6 \times 10^{-6}$, is produced catalytically through the H$^-$, H$_2^+$, and HeH$^+$ mechanisms. We revisit this standard calculation taking into account the effects of the nonthermal radiation background produced by cosmic hydrogen recombination, which is particularly effective at destroying H$^-$ via photodetachment. We also take into consideration the non-equilibrium level populations of H$_2^+$, which occur since transitions among the rotational-vibrational levels are slow compared to photodissociation. The new calculation predicts a final H$_2$ abundance of $x[{	ext{H}_2}] \approx 6 \times 10^{-7}$ for the standard cosmology. This production is due almost entirely to the H$^-$ mechanism, with $\sim 1$ per cent coming from HeH$^+$ and $\sim 0.004$ per cent from H$_2^+$. We evaluate the heating of the diffuse pregalactic gas from the chemical reactions that produce H$_2$ and from rotational transitions in H$_2$, and find them to be negligible.

Key words: cosmology: theory – intergalactic medium – molecular processes.

1 INTRODUCTION

One of the key problems in cosmology is to understand the physical and chemical state of the baryonic matter in the Universe. At high redshift, the baryonic matter was fully ionized and co-existed with a thermalized radiation field (the cosmic microwave background, or CMB). By redshift $z \sim 10^4$, the Universe had expanded and cooled to $\sim 3000$ K, at which point the ionized nuclei and free electrons of the primordial plasma combined to form neutral atoms. This cosmic recombination was first studied theoretically by Peebles (1968) and Zeldovich et al. (1968). The observations of the acoustic peaks in the CMB $T_T$ and $T_E$ power spectra [Lee et al. 2001; Netterfield et al. 2002; Halverson et al. 2003; Kogut et al. 2003; Page et al. 2006; Hinshaw et al. 2006] provide direct evidence that cosmic recombination happened, and that it occurred over a narrow range in redshift, in accordance with predictions.

As the Universe continued to expand and cool, the formation of molecules became thermodynamically favourable. Since hydrogen is most abundant, one would expect the most abundant molecule to be H$_2$. However, unlike atomic recombination, which occurs shortly after it becomes thermodynamically favourable and proceeds nearly to completion (e.g. Seager et al. 2000), cosmological formation of molecules is slow and freezes out with a final abundance, $x[{	ext{H}_2}] \equiv n[{	ext{H}_2}]/n[{	ext{H}}] \ll 1$.

Despite their small abundance, molecules in the early universe have been investigated for several reasons. The first is that the primordial gas, mainly of hydrogen and helium atoms, lacks the low-lying excitations necessary for cooling and therefore star formation at low temperatures. On the other hand, molecules (which possess low-lying rotational excitations) could provide the cooling necessary to form the first stars (Saslaw & Zipoy 1967). However, recent calculations indicate that the primordial H$_2$ abundance is far too small for this, and that the only H$_2$ important for cooling of early haloes is formed in collapsed haloes (e.g. Tegmark et al. 1997). A second reason for studying H$_2$ production is that the heating of the gas, either via rotational transitions induced by the CMB or the chemical energy released by formation of the molecules, could affect the temperature of the pregalactic gas. Here even a small effect could be important for proposals to study the absorption of the CMB by pregalactic gas in the H i 21-cm line (Loeb & Zaldarriaga 2004). Finally, there is the (perhaps academic) motivation to understand the composition of the primordial gas as part of elucidating the standard cosmological model.

The first calculation of the primordial H$_2$ abundance was by Saslaw & Zipoy (1967). Noting that the direct radiative association of two H atoms is forbidden, they proposed that H$_2$ molecules could be built up using H$_2^+$ as
energy levels and transitions of the H$_2^+$ ion is recapitulated in Appendix A.

In this paper, we have assumed a primordial helium abundance of $Y_P = 0.24$, and a flat ΛCDM cosmology with parameters from Soldat et al. (2005): $\Omega_0 = 0.0462$, $\Omega_m = 0.281$, and $H_0 = 71.0 \text{ km s}^{-1} \text{ Mpc}^{-1}$. The number density $n$ will refer to the total proper density of hydrogen nuclei in all forms (ionized, atomic, and molecular), although in the regime of interest here it is mostly atomic. The notation $x_i$ (or $x[i]$ for H$_2^+$, H$_2$, and HeH$^+$) will denote the number density of species $i$ relative to the total number density of hydrogen nuclei in all chemical forms (e.g. $x[H_2] = n[H_2]/n = 1/2$ if all hydrogen is molecular).

2 THE REACTIONS

Due to the lack of a dipole moment, it is forbidden for two H atoms to combine radiatively to form H$_2$. Therefore cosmological H$_2$ production proceeds through two main mechanisms catalyzed by charged particles (Saslaw & Zipoy 1967; Peebles & Dick 1968; Hirasawa 1969). The H$^-$ mechanism begins with radiative attachment to form H$^-$,

$$\text{H} + e^- \leftrightarrow \text{H}^- + \gamma, \quad (1)$$

and is completed when the associative detachment reaction

$$\text{H}^- + \text{H} \rightarrow \text{H}_2 + e^-. \quad (2)$$

A minor reaction that can use up H$^-$ ions is mutual neutralization,

$$\text{H}^- + \text{H}^+ \rightarrow 2\text{H}. \quad (3)$$

An alternative mechanism is via H$_2^+$, in which the catalyst is a proton rather than an electron,

$$\text{H} + \text{H}^+ \leftrightarrow \text{H}^+_2 + \gamma. \quad (4)$$

The H$_2^+$ ion can then be converted to H$_2$ via the reaction

$$\text{H}^+_2 + \text{H} \rightarrow \text{H}_2 + \text{H}^+. \quad (5)$$

It is also possible for H$_2^+$ to be destroyed by dissociative recombination,

$$\text{H}_2^+ + e^- \rightarrow 2\text{H}. \quad (6)$$

A third route is via the HeH$^+$ mechanism. This is unimportant in the "standard" calculation, but given that we are revising the H$^-$ and H$_2^+$ rates downward it is only prudent to include it. It begins with the production of HeH$^+$ by radiative association,

$$\text{He} + \text{H}^+ \leftrightarrow \text{HeH}^+ + \gamma. \quad (7)$$

This ion could either be photodissociated (reverse of Eq. (4)), but it could also form H$_2^+$ by the reaction

$$\text{HeH}^+ + \text{H} \leftrightarrow \text{He} + \text{H}_2^+. \quad (8)$$

The H$_2^+$ ion then participates in the usual sequence of reactions, Eqs. (4)–(6).
peaking at $z \sim 260$ for the H$^+$ mechanism and $z \sim 90$ for the H$^-$ mechanism (e.g. Lepp et al. 2002).

Once formed, the H$_2$ molecule can be destroyed by UV photodissociation (Stecher & Williams 1967; Aberall et al. 1992; Haßner et al. 1996b). Photoexcitation of H$_2$ from the ground $X^1Σ_g^+$ electronic state to either $B^1Σ_u^+$ (Lyman band absorption) or $C^1Π_u$ (Werner band absorption), is usually followed by radiative decay back to the $X^1Σ_g^+$ electronic state. However, it is possible that this process leaves the H$_2$ molecule in an unbound vibrational state, resulting in its dissociation into two H atoms (a table of probabilities can be found in e.g. Dalgarno & Stephens 1970). Of course, this relies on the existence of UV radiation in the Lyman and Werner bands, which have minimum energies of 11.2 and 12.3 eV respectively. During the postrecombination era, these energies are 2–3 orders of magnitude larger than $kT_{\text{CMB}} \sim 0.2$ eV, and so the photodissociation of H$_2$ plays a negligible role in determining the pregalactic H$_2$ abundance. The presence of the spectral distortion does not change this situation since the distortion extends only up to 10.2 eV (the H Lyman energy). It is only after the first astrophysical sources turn on that intergalactic H$_2$ can be destroyed.

The cosmological production of H$_2$ can be followed by keeping track of the abundances of the relevant species: H, He, H$^+$, e$^-$, H$_2^+$, HeH$^+$, and H$_2$. The evolution of H, He, H$^+$, and e$^-$ has been investigated in the context of the cosmic recombination, and is essentially unaffected by the rates of the catalytic reactions Eqs. (1–5) due to the small cosmic recombination, and is essentially unaffected by the rates of the catalytic reactions Eqs. (1–5) due to the small

$$k_3(T_m) = 4 \times 10^{-8} \left( \frac{T_m}{300} \right)^{-0.5} \text{ cm}^3 \text{s}^{-1},$$

where the matter temperature, $T_m$, is in Kelvin. (The stimulated radiative attachment can be neglected in comparison with the spontaneous rate because the energy of the emitted photon is always at least the H$^-$ binding energy, or $>0.754$ eV; this is much greater than $kBT_{\text{CMB}}$ in the redshift range of interest.) There is some uncertainty in the associative detachment rate $k_2$ and the mutual neutralization rate $k_1$, which we will discuss in Section III. The ratio of H$^-$ destruction rate to the Hubble rate is always at least $k_{2\alpha}/H \approx 3500[(1+z)/10]^{1.3} \gg 1$, so we may treat $x[H^-]$ by the steady-state approximation,

$$x[H^-] = \frac{k_1{x}_e{x}_H}{k_2{x}_H + k_{-1} + k_3[x][H^+]y},$$

The production rate for H$_2$ via H$^-$ is then,

$$S_+ = \frac{k_1{x}_e{x}_H}{k_2{x}_H + k_{-1} + k_3[x][H^+]y}.$$  

The photodetachment rate $k_{-1}$ depends on the details of the radiation field and can be broken into thermal (blackbody CMB) and nonthermal (spectral distortion) parts:

$$k_{-1} = k_{-1}^{(th)}(T_{\text{CMB}}) + k_{-1}^{(nt)}.$$  

The rate from the thermal photons can be computed via the principle of detailed balance,

$$k_{-1}^{(th)}(T_{\text{CMB}}) = 4 \left( \frac{m_e k_B T_{\text{CMB}}}{2\pi h^2} \right)^{3/2} e^{-\Delta E/T_{\text{CMB}}},$$

where $\Delta E$ is the photodetachment threshold energy. Note that $T_{\text{CMB}}$ is used here instead of $T_m$ since photodetachment depends only on the properties of the radiation field.

In the standard calculation the thermal rates are used, i.e. $k_{-1} = k_{-1}^{(th)}$. The nonthermal contribution to the photodetachment rate is

$$k_{-1}^{(nt)}(x) = n_c \int_{B(H^-)/h}^{\infty} \sigma_v(x) \frac{d\nu}{\nu},$$

where $\sigma_v(x)$ is the number of distortion photons per H atom per logarithmic range in frequency, and $\sigma_v(x)$ is the photodetachment cross section, for which we use the fit by Tegmark et al. (1997),

$$\sigma = 3.486 \times 10^{-16} \frac{(x - 1)^{3/2}}{x^{3.11}},$$

where $x = \nu/(kB(H^-))$. The variable $\nu(x)$ is related to the phase space density $f(\nu)$ of photons by

$$f(\nu) = \frac{1}{e^{\nu/k_BT_{\text{CMB}}} - 1} + \left( \frac{m_e}{8\pi^3} \right)^{3/2} \sigma(v),$$

where the first term denotes the thermal CMB contribution, and the latter term is the spectral distortion. The spectral distortion dominates at high frequencies, $\nu/(kB_T_{\text{CMB}}) > 30$.

The spectral distortion $f(\nu)$ is calculated as in Switzer & Hirata (2003); the H $2s \rightarrow 1s$ two-photon decay and Lyman-$\alpha$ resonance escape rates were obtained from Recfast and integrated as described in Section II.
of Switzer & Hirata (2003). We note that a recent computation by Wong et al. (2003) find an additional distortion due to He $^2P^o_0 \rightarrow 1^1S_0$ two-photon decays and escape from the $^2P^o_0 \rightarrow 1^1S_0$ resonance. As can be seen from Fig. 3 of Wong et al. (2003), the He $^1$ distortion contributes significantly to the photon spectrum at short wavelengths $\lambda < 1400(1 + z)^{-1/3}$ $\mu$m, and could be a significant contribution to H$^-$ or H$_2^+$ destruction rates. However, these photons are in the H I Lyman continuum ($\lambda < 912$ Å) at $z \sim 1500$, when the universe is already optically thick ($\tau \sim 10^7$) due to H I photoionization. Thus we do not expect the high-energy spectral distortion from He $^1$ recombination to survive and have not included it in our analysis.

4 THE H$_2^+$ MECHANISM

The H$_2^+$ mechanism is more complicated to analyze than the H$^-$ mechanism because unlike H$^-$, the H$_2^+$ ion has many bound states. One must therefore determine the populations of each H$_2^+$ level, taking into account the radiative association rates to each level, the radiative and collisional rates for changing the rotational and vibrational quantum numbers, and the destruction rates by photodissociation and charge transfer. We start with an overview of the physics of the H$_2^+$ ion, and describe the full reaction network that describes the ion. Finally, we show how the relevant physics can be captured by a "two-level" approximation; this provides a computationally simpler approach to the H$_2^+$ mechanism.

The H$_2^+$ ion is diatomic, and can be described by specifying the electronic state, a rotational quantum number $N$ describing the total orbital angular momentum, and a vibrational quantum number $v$ equal to the number of radial nodes. The electronic states of interest to us are the ground state $1s\pi_g$ ($X^2Sigma^+_g$) and the first excited state $2\sigma_u$ ($A^2Sigma^+_u$); higher states are not accessible at the temperatures under consideration. We ignore the spin-orbit coupling and hyperfine structure since their energy splittings are small compared to $k_BT_{\text{min}}$, or $k_BT_{\text{CM}}$. Thus the degeneracy of a given rotational-vibrational level is $g_{\text{nuc}} = 2(2N + 1)g_{\text{nuc}}$, where the 2 comes from the electron spin. The nuclear degeneracy is forced by proton wave function antisymmetry considerations to be $g_{\text{nuc}} = 1/4$ for spatially symmetric states and $g_{\text{nuc}} = 3/4$ for spatially antisymmetric states. Almost all of the bound states of H$_2^+$ are in the $1s\sigma_g$ ground electronic state, which has an attractive potential with a minimum energy of $E_{\text{min}} = -2.79$ eV at an internuclear separation $R = 1.06$ Å. The next-lowest electronic state $2\pi_g$ is repulsive (except for a weak attractive region at large distance due to the polarizability of H).

The radiative association reaction (Eq. 3) begins with an H(1s) atom and H$^+$ ion approaching each other. This initial electronic state is a superposition of the $1s\sigma_g$ and $2\sigma_u$ states of H$_2^+$. Because of dipole selection rules, the system can only produce an H$_2^+$ ($1s\sigma_g$) ion from the $2\sigma_u$ initial electronic state. This state is repulsive, so at low initial energies the wave function is confined to large intermolecular separation $R$. Wave function overlap considerations then imply that radiative transitions to highly excited H$_2^+$ ($1s\sigma_g$) states is preferred, since these states have significant wave functions at large $R$. Conversely, direct radiative association to the ground state ($N = v = 0$) is suppressed. This state of H$_2^+$ can be populated by radiative transitions from excited states, but the inversion symmetry of the H$_2^+$ ion implies that these must be electric quadrupole transitions, hence they are slow, compared to destruction of H$_2^+$. This circumstance results in level populations of H$_2^+$ that are very far from LTE. The non-LTE distribution, with higher-energy levels overpopulated relative to the Boltzmann distribution, results in photodissociation cross sections that are significantly higher than the commonly used LTE cross sections of Cerro & Hirata (2003) and Stancl (1994).

4.1 Rate equations

The level populations of H$_2^+$ are determined by the solution of a network of production, destruction, and level-changing reactions. Schematically, one may write

$$\frac{dx_i}{dt} = s_i + \sum_j R_{ij} x_j - \sum_j R_{ji} x_i - \gamma_i x_i,$$

where $s_i$ is the rate of production of the $i$th level of H$_2^+$ (in units of ions per H nucleus per second), $R_{ij}$ is the rate for transitions from the $i$th level to the $j$th level, and $\gamma_i$ is the rate for destruction of H$_2^+$ ions in the $i$th level. Note that the level index $i$ encodes both the vibrational and rotational quantum numbers: $i = (v, N)$. We track all 423 bound levels of the ground electronic state, which have quantum numbers ranging up to $v = 19$ and $N = 35$.

The source function of H$_2^+$ comes from the radiative association reaction (Eq. 3) and its rate is given by

$$s_i = \alpha_i x[H^+]^{[1]}x_{\text{HIN}}.$$

The level-changing rates include both radiative and collisional rates, $R_{ij} = R_{ij}^{(rad)} + R_{ij}^{(col)}$. The radiative rates are given by the standard expression

$$R_{ij}^{(rad)} = \left\{ \begin{array}{cc} A_{ij}[1 + f(\nu_{ij})] & E(i) < E(j) \\ A_{ij}f(\nu_{ij})g_i/g_j & E(j) > E(i) \end{array} \right.,$$

where $A_{ij}$ is the Einstein coefficient. In principle there is also a collisional term $R_{ij}^{(col)}$, which could accelerate H$_2$ production by de-activating H$_2^+$ ions into lower energy levels. These lower-energy ions would survive longer since they suffer less photodissociation, and hence have a higher probability of undergoing charge transfer to produce H$_2$. However, it is not possible to produce more H$_2$ molecules by this mechanism than there are de-activating H$_2^+$ ions. We will show in Section 4.2 that even if we assume the Langevin rate for charge transfer H$_2^+$(H,H$^+$)H$_2$, we find that only $\sim 0.005$ per cent of the H$_2$ is produced via the H$_2^+$ mechanism. Thus our conclusions about the final H$_2$ abundance are unaffected except in the highly unlikely circumstance that the de-activation rate coefficient is several orders of magnitude larger than the Langevin rate.

The destruction of H$_2^+$ proceeds by photodissociation (reverse of Eq. 3), charge transfer (Eq. 4), or dissociative recombination (Eq. 5), at a rate $\gamma_i$.

$$\gamma_i = \beta_i + k_{i(\text{ct})} x_{\text{HIN}} + k_{i(\text{dr})} x_{\text{eH}}.$$

The radiative association and dissociation rates $\alpha_i$ and $\beta_i$, and the quadrupole Einstein coefficients $A_{ij}$, are computed in Appendix A. We examine the charge transfer (Section...
42 and dissociative recombination (Section 4.3) reactions in the following sections.

As described in Section 4.3, we neglect \( k_i^{(dr)} \) since it is small during the regime where the \( \text{H}_2^+ \) mechanism is most active; but if it were included, its only possible effect would be to further reduce the already negligible \( \text{H}_2 \) yield from this mechanism.

Eq. (19) possesses a steady-state solution

\[
x = \frac{T}{1} s,
\]

where we have written the level populations as a vector and the matrix \( T \) is given by

\[
T_{ij} = -R_{ij} + \delta_{ij} \left( \gamma_i + \sum_k R_{ki} \right),
\]

which is valid if all the eigenvalues of \( T \) are large (fast) compared to the Hubble time. The \( \text{H}_2 \) production rate via the \( \text{H}_2^+ \) mechanism is then

\[
S_i = n_x \sum_k x_k k_i^{(ct)}.
\]

4.2 Charge transfer

In order to complete our analysis, we need the rate of the charge transfer reaction (Eq. 4) as a function of the matter temperature for each level of the initial-state \( \text{H}_2^+ \) ion. Unfortunately, there are no published computations of the state-resolved rates (Lepp et al. 2002). Most pregalactic chemistry networks have used the value

\[
k_i^{(ct)} = (6.4 \pm 1.2) \times 10^{-10} \text{ cm}^3 \text{s}^{-1}
\]

measured by Krstić et al. (1999) in an ion cyclotron resonance device; however the dependence on the temperature and initial state was not determined. Krstić (2002) has computed cross sections for Eq. 4 and resolved into individual vibrational levels, but was motivated by studies of controlled fusion plasmas and so only extends down to thermal energies (\( \frac{3}{2} k_B T_m = 0.1 \text{ eV} \) at \( z = 300 \)) for some of the levels.

Given that the rate for Eq. 4 has not been measured or calculated accurately for all relevant levels, we have run our calculation for three different cases. In case (A), we use the Krstić et al. (1997) rate coefficient (Eq. 26) for all levels; in case (B) we have used the Langevin rate coefficient, \( k_i^{(ct)} = 2.38 \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \); and in case (C) we have linearly interpolated the values of \( \sigma_v \) and obtained a reaction rate by integrating over a Maxwellian energy distribution,

\[
k_i^{(ct)} = \frac{2}{\sqrt{\pi} (k_B T_m)^{3/2}} \int_0^\infty E^{1/2} e^{-E/k_B T_m} \sigma_v \text{d}E,
\]

where \( E \) is the kinetic energy of the \( \text{H}+\text{H}_2^+ \) system in the centre-of-mass frame and \( \sigma_v \) is the initial relative velocity of \( \text{H} \) and \( \text{H}_2^+ \). For energies less than the lowest tabulated value (0.17 eV in the case of the \( v = 0 \) state) we have assumed \( \sigma_v \) to be constant. This probably overestimates the reaction rate since for most levels \( \sigma_v \) is an increasing function of collision energy.

4.3 Dissociative recombination

It is possible for dissociative recombination (Eq. 3) to reduce the production of \( \text{H}_2 \). In general dissociative recombination can be important if it contributes significantly in Eq. 24, i.e. if

\[
k_i^{(dr)} \gg \frac{\sigma_{\text{H}+\text{H}_2^+}}{x_e} k_i^{(ct)} \approx x_e^{-1} k_i^{(ct)}.
\]

Of the various models we consider, the lowest value of \( k_i^{(ct)} \) occurs for model A, with \( k_i^{(ct)} = 6.4 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \). At \( z < 600 \) where the \( \text{H}_2^+ \) mechanism is most active, we have \( x_e \sim 10^{-3} \) so in order for dissociative recombination to be important, \( k_i^{(dr)} \) would have to be \( \gg 10^{-7} \text{ cm}^3 \text{s}^{-1} \). The tabulated rate coefficients for the first 78 levels of \( \text{H}_2^+ \) are less than this for \( 20 \leq T_m \leq 5000 \text{ K} \) (Schneider et al. 1994); the maximum value in the table is \( 3.1 \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \) at \( T_m = 20 \text{ K} \), and \( 1.3 \times 10^{-7} \text{ cm}^3 \text{s}^{-1} \) for \( T_m \geq 100 \text{ K} \); we therefore neglect dissociative recombination. This may not be a valid approximation at \( z > 600 \) where \( x_e \sim 10^{-3} \), or for the higher excited levels of \( \text{H}_2^+ \) (for which no published rates are available). If dissociative recombination is important in these circumstances, the effect would be to decrease the \( \text{H}_2 \) abundance at \( z > 300 \). There would not be a significant effect at lower redshifts, because at \( z < 300 \) the production of \( \text{H}_2 \) is dominated by the \( \text{H}^- \) and \( \text{HeH}^+ \) mechanisms; \( \text{H}^- \) is unaffected by dissociative recombination, and \( \text{HeH}^+ \) produces \( \text{H}_2 \) in one of the low-lying states for which we have already concluded that dissociative recombination is irrelevant.

4.4 A “two-level” approximation

Although the above discussion completely specifies the solution for the \( \text{H}_2^+ \) channel, it is useful to consider an approximate “two-level” solution. This serves both as a check of the more involved numerical calculations above, as well as highlighting the essential physics behind this channel.

We start by describing the \( \text{H}_2^+ \) channel by the following two level decomposition

- \( \text{H}_2^+ \) forms in an excited state \( \text{H}_2^+(i) \), at a rate \( \alpha_i \),
- \( \text{H}+\text{H}^+ \rightarrow \text{H}_2^+(i) \),

(29)

- The excited ion is then either photodissociated at rate \( \beta_i \),
- \( \text{H}_2^+(i)+\gamma \rightarrow \text{H}+\text{H}^+ \),

(30)

or transitions to aLTE distribution via a quadrupole transition at rate \( R_i \),
- \( \text{H}_2^+(i) \rightarrow \text{H}_2^+ \).

(31)

Note that although this is a two level description, we still consider all energy levels \( i \); they are now however decoupled from each other.

Given Eqs. 24 to 31 we can write out the differential equations describing the time evolution of the abundances of these species. Furthermore, as before, Eqs. 29 and 30 occur significantly faster than the Hubble time, and so, we use the steady-state approximation to eliminate any explicit mention of the \( \text{H}_2^+ \) abundance. This yields the following equation for the \( \text{H}_2^+ \) abundance,
Table 1. The suppressed association rate as a function of redshift, Eq. 34.

| $z$ | $\log_{10} \alpha' \, (\text{cm}^3 \text{s}^{-1})$ | $z$ | $\log_{10} \alpha' \, (\text{cm}^3 \text{s}^{-1})$ |
|-----|---------------------------------|-----|---------------------------------|
| 50  | $-21.8824$                       | 100 | $-22.1948$                       |
| 150 | $-21.9867$                       | 200 | $-21.9676$                       |
| 250 | $-22.0103$                       |     |                                 |

$\frac{dx[H^+]}{dt} = \left( \sum_i \alpha_i R_i \right) n_{H^+} x[H^+] - \beta x[H^+]^2$, (32)

where $\beta$ is now the LTE photodissociation rate (determined by averaging $\beta_i$, as calculated in Appendix A over the Boltzmann distribution of levels at the CMB temperature). Finally, there remains the issue of what to assume for $R_i$; for simplicity, we assume that $R_i$ is the total transition probability to lower levels,

$R_i = \sum_{E_j < E_i} A_{ji} [1 + f(\nu_{ji})]$. (33)

Note that Eq. 34 now resembles the standard $H^+$ calculation with a suppressed radiative association rate,

$\alpha' = \sum_i \alpha_i R_i / (R_i + \beta_i)$. (34)

Note that the error in this approximation could go either direction. This is because, although our nascent $H^+$ ion is likely to be produced in a highly excited state, we do not really know without the full multi-level calculation whether after it emits its first photon the resulting distribution is “more excited” or “less excited” than Boltzmann. We defer a comparison of this approximation with the full calculation until Section 5 and conclude by tabulating the suppressed association rate as a function of redshift (Table 1).

5 THE $\text{HeH}^+$ MECHANISM

The $\text{HeH}^+$ mechanism is really an additional set of reactions that couple to Eqs. 14, 18. Therefore the most straightforward way to include it is to add $\text{HeH}^+$ as an additional “level” in the network of Section 4. Due to its large dipole moment, $\text{HeH}^+$ has very short-lived excited levels (lifetime $\sim 10^{-3}$ s; Roberge & Dalgarno 1982). These lifetimes are short compared to the photodissociation time from these levels or the time between collisions ($\sim 10^8$ s at $z = 300$), so the distribution of level populations is determined entirely by the radiation field. In the absence of a spectral distortion, then, it would be permissible to assume that the level populations of $\text{HeH}^+$ are in LTE at the CMB temperature $T_{\text{CMB}}$.

In reality there is a spectral distortion, however its effect on $\text{HeH}^+$ is negligible. The distortion photons that would affect $\text{HeH}^+$ are those at $E > 1.6(1 + z)/250$ eV, where the distortion is significant compared to the thermal CMB radiation; there is roughly 1 distortion photon in this energy range per H atom. Since the rate coefficient for $H^+$ formation from $\text{HeH}^+$ via Eq. 35 is $9.1 \times 10^{-10}$ cm$^3$ s$^{-1}$ (Karpas et al. 1972), photodissociation of $\text{HeH}^+$ by distortion photons can be significant if the photodissociation cross section averaged over the $\text{HeH}^+$ level and distortion photon energy distributions is $\sigma c \sim 9.1 \times 10^{-10}$ cm$^3$ s$^{-1}$. The cross section for photodissociation from the $v = 0$ level of $\text{HeH}^+$ is always $\sigma c \lesssim 1.5 \times 10^{-12}$ cm$^3$ s$^{-1}$ (Roberge & Dalgarno 1984). The cross section from the higher excited states $v = 7$ and $v = 8$ is $\sigma c \approx 3 \times 10^{-9}$ cm$^3$ s$^{-1}$ near threshold (Saha et al. 1978) and could, in principle, be important, except that the fraction of $\text{HeH}^+$ in these states is $\ll 1$ (they lie 1.56 and 1.62 eV above the ground state, as compared with $k_BT_{\text{CMB}} = 0.07$ eV at $z = 300$). Hence the $\text{HeH}^+$ levels are in LTE at the CMB temperature $T_{\text{CMB}}$ and $\text{HeH}^+$ can be followed as an “effective 1-level” molecular ion.

It is straightforward to write down the additional terms in Eqs. 14, 18 to take into account the $\text{HeH}^+$ contribution. The additional source is due to radiative attachment, $\alpha_{\text{HeH}^+} = \alpha_{\text{HeH}^+} + x[H^+] n_{\text{HeH}^+}$, (35)

where $\alpha_{\text{HeH}^+}$ is the radiative attachment rate coefficient. The destruction term is simply the photodissociation rate, $\gamma_{\text{HeH}^+} = \beta_{\text{HeH}^+}$. (36)

Finally the transition matrix $R$ picks up two additional terms due to Eq. 38. One is the forward reaction term $R_{i,\text{HeH}^+} = \frac{\alpha_{\text{HeH}^+}}{\sum_i \alpha_{\text{HeH}^+}} x[H^+] n_{\text{HeH}^+}$, (37)

where $\alpha_{\text{HeH}^+}$ is the rate coefficient for Eq. 36 and $\sum_i \alpha_{\text{HeH}^+}$ is the branching fraction to the $i$th level of $H^+$. The other is the reverse reaction, which can be obtained by the principle of detailed balance,

$R_{i,\text{HeH}^+} = R_{i,\text{HeH}^+} e^{E(i)/k_BT_{\text{CMB}}} / 2Q(\text{HeH}^+, T_{\text{CMB}})$. (38)

The ratio of reduced masses is $\mu_{\text{HeH}^+,H}/\mu_{\text{HeH}^+,H^+} \approx 5/8$, and the partition function $Q(\text{HeH}^+)$ is obtained at the matter temperature $T_m$ from $\text{Engel et al. 2003}$. The binding energy is $D_0(\text{HeH}^+) = 1.84412$ eV (Zygelman et al. 1998). The factor of 2 comes from the ground state degeneracy of He (He has degeneracy 1). The remaining additional term in the transition matrix is $R_{\text{HeH}^+,\text{HeH}^+} = 0$.

To compute the $H_2$ production, one must also know $\alpha_{\text{HeH}^+}, \beta_{\text{HeH}^+}, k_{\text{HeH}^+}$, and $\sum_i \alpha_{\text{HeH}^+}$. For $\alpha_{\text{HeH}^+}$, we have used the fit by Galli & Palla (1998) to the results of Roberge & Dalgarno (1982). This rate can in principle be increased by stimulated radiative association. However Zygelman et al. (1998) found that this increases the $\text{HeH}^+$ abundance by $<20$ per cent in the redshift range of interest, and since our analysis does not change the formation and/or destruction mechanisms a similar result would apply to our case. We have thus not included a correction for stimulated radiative association (we will see that the $\text{HeH}^+$ mechanism is not a major source of primordial H$_2$, so a correction of this magnitude in $\text{HeH}^+$ abundance translates into a much smaller correction to the net H$_2$ production). For $\beta_{\text{HeH}^+}$, we have used the principle of detailed balance,

$\beta_{\text{HeH}^+} = \frac{1}{Q(\text{HeH}^+, T_{\text{CMB}})} \left( \frac{\mu_{\text{HeH}^+,H}}{2\pi n^2} \right)^{3/2}$. (39)
\[
ex^{-D_0(\text{HeH}^+)/k_BT_{CMB}\rho_{\text{HeH}}(T_{CMB})}; \tag{39}\]

here \(\mu\) is the reduced mass of \text{He} and \text{H}^+. The rate coefficient \(k\) has been measured by [Karpas et al. 1979] to be \(9.1 \times 10^{-10}\) \text{cm}^3\text{s}^{-1}. For the \(f\), which control the distribution of rotation-vibration levels in the final state of Eq. (4), there do not appear to be any published measurements or calculations. We have thus considered two cases: one in which Eq. (4) populates all energetically available levels with their statistical ratios, and one in which the reaction always leaves \(\text{H}_2^+\) in the ground state of either para-\(\text{H}_2^+(v = 0, N = 0; \text{probability 1/4})\) or ortho-\(\text{H}_2^+(v = 0, N = 1; \text{probability 3/4})\). While the two cases lead to different level populations of \(\text{H}_2^+\), the total abundances \(x[\text{H}_2^+](z)\) and \(x[\text{H}_2](z)\) are unaffected. This is because, for any of the \(\text{H}_2^+\) levels accessible to Eq. (4) at thermal energies, the most probable fate of the \(\text{H}_2^+\) ion is to radiate away its vibrational energy on a timescale of order \(10^7\) s, and then to undergo charge exchange to produce \(\text{H}_2\) on a timescale of order \(10^9\) s. Thus the information about the initial \((v, N)\) distribution of the \(\text{H}_2^+\) is erased. Photodissociation from the low-\(v\) levels of \(\text{H}_2^+\) is strongly suppressed due to lack of wave function overlap, and electric quadrupole excitation to high-\(v\) levels followed by photodissociation is slower than charge transfer; thus photodissociation is not effective at depleting the \(\text{H}_2^+\) produced by Eq. (4). The case where all energetically available levels are populated with their statistical ratios will be used in the rest of this paper.

6 RESULTS: \(\text{H}_2\) ABUNDANCE

We now present the results of integrating the production rate of \(\text{H}_2\) from the three major mechanisms. The total production of \(\text{H}_2\) is obtained by the integral

\[
x[\text{H}_2] = \int (S_- + S_+) \, dt, \tag{40}\]

which is shown in Fig. 1. The production rate per Hubble time \((S_- + S_+) / H\) is shown in Fig. 2. The abundances of the intermediates \(\text{H}^-\), \(\text{H}_2^+\), and \text{HeH}^+, obtained from Eqs. (12, 20), are shown in Fig. 3.

6.1 \(\text{H}^-\)

In our calculation, the final \(\text{H}_2\) abundance is determined essentially entirely by the \(\text{H}^-\) reaction sequence. In accordance with previous calculations, at high redshift \((z \approx 140)\) the \(\text{H}^-\) ion is formed mainly through radiative attachment, and destroyed mainly through photodetachment by thermal CMB photons. Note that this is not quite a Saha-type equilibrium because of the different matter and radiation temperatures. At \(z \approx 127\), the spectral distortion begins to dominate the photon spectrum at energies of \(\sim 1\) eV, where the \(\text{H}^-\) photodetachment cross section peaks. Below this redshift, \(\text{H}^-\) is still produced mainly by radiative attachment, but the destruction mechanism is photodetachment from distortion photons. This situation remains until \(z \approx 67\), when most of the spectral distortion has redshifted to below the \(\text{H}^-\) photodetachment threshold. At this time, the competing photodetachment and associative detachment (Eq. (3) rates are

**Figure 1.** The total abundance of \(\text{H}_2\) as a function of redshift. The thick solid lines shows the new calculation of \(\text{H}_2\) abundance for models A and B (C is indistinguishable from B on the scale of the plot). The thick long-dashed line shows the old calculation, which overestimated \(x[\text{H}_2]\). The thin short-dashed lines show the individual production mechanisms: \(\text{H}^-\), \(\text{H}_2^+/\text{HeH}^+\), and \(\text{H}_2^+\) (without \text{HeH}^+). The triangles indicate the results for \(\text{H}_2^+\) only from the simplified model of Section 4.

**Figure 2.** The production rate of \(\text{H}_2\) via the \(\text{H}^-\), \(\text{H}_2^+\), and \text{HeH}^+ mechanisms, in units of \(\text{H}_2\) molecules per hydrogen nucleus per Hubble time. The thick solid line shows the new calculation of \(\text{H}_2\) rate for models A, while the thick long-dashed line shows the old calculation. The thin short-dashed lines break down the \(\text{H}_2\) production into the individual mechanisms.
Figure 3. The abundances of the intermediates H\(^{-}\), H\(_2\)\(^+\), and HeH\(^+\). The H\(_2\)\(^+\) curve is shown for both models A and B. Note that x[H\(^{-}\)] peaks at z ≈ 62 when H\(_2\) production is also maximized.

The abundances of the intermediates H\(^{-}\), H\(_2\)\(^+\), and HeH\(^+\). The H\(_2\)\(^+\) curve is shown for both models A and B. Note that x[H\(^{-}\)] peaks at z ≈ 62 when H\(_2\) production is also maximized. This is also the era of peak production of H\(_2\); at higher redshifts the H\(^{-}\) ions are destroyed before they can react with H to produce H\(_2\), while at lower redshifts less H\(^{-}\) is produced due to the lower density of the universe and the decrease in reaction rate at low T\(_m\). Ultimately we find that the total amount of H\(_2\) produced via the H\(^{-}\) mechanism, \(\int S_{-}dt\), is only 6 \times 10\(^{-7}\) instead of 2.2 \times 10\(^{-6}\) as found in the standard calculation.

As noted in Section 3, there is some uncertainty in the rate for associative detachment, Eq. (2), argued that the rate coefficient k\(_{2}\) could plausibly be varied between 6.5 \times 10\(^{-10}\) and 5 \times 10\(^{-9}\) cm\(^3\) s\(^{-1}\). We have re-run our analysis using these values and find that the final H\(_2\) abundance varies from x[H\(_2\)] = 4.1 \times 10\(^{-7}\) for the lowest value of k\(_{2}\) to 9.4 \times 10\(^{-7}\) for the highest value. Thus our fiducial estimate of 6 \times 10\(^{-7}\) should be considered uncertain by a factor of \(\sim 1.5\) in either direction.

There is also a large uncertainty in the mutual neutralization rate, with some results (e.g. the experimental work of Moseley et al. 1971) being up to an order of magnitude higher than the fits used here. Using the higher mutual neutralization rate determined by the fit of Moseley et al. (1971), we find that the final H\(_2\) abundance decreases from 6.0 \times 10\(^{-7}\) to 5.7 \times 10\(^{-7}\). Thus the uncertainty in the mutual neutralization rate does not have a significant effect on the final H\(_2\) abundance.

### 6.2 H\(_2\)\(^+\) and HeH\(^+\)

We find that the reactions involving positive ions (Eqs. 8 & 9) do not contribute significantly to the final H\(_2\) abundance. Nevertheless these reactions operate at earlier times than H\(^{-}\) due to the higher binding energy of HeH\(^+\) and H\(_2\)\(^+\) compared to H\(^{-}\), and so they dominate the H\(_2\) production at z > 144. The total amount of H\(_2\) produced by these reactions is \(\int S_{+}dt = 5 \times 10^{-9}\), with almost all of this contributed by HeH\(^+\).

Our computed HeH\(^+\) abundance (see Fig. 3) are very similar to those obtained in previous works (Galli & Palla 1998; Stancil et al. 1998). In contrast, we find much lower H\(_2\)\(^+\) ion abundances (and H\(_2\) production rates via H\(_2\)\(^+\)) than in the standard calculation. This is a consequence of the non-Boltzmann level populations in H\(_2\)\(^+\). An example of these level populations for model A at z = 300 is shown in Fig. 4 (Results are qualitatively similar for model B, with the main quantitative difference being that the lowest-energy states are less populated.) As shown in the figure, the highest-lying levels are nearly in Boltzmann equilibrium since the reaction

\[ \text{H} + \text{H}^+ \leftrightarrow \text{H}_2^+(1s\sigma_g, vN) + \gamma \]  

is fast compared with the electric quadrupole transitions in H\(_2\)\(^+\). (The slight deviation from Boltzmann equilibrium among the high-lying levels in the figure is due to the difference between matter and radiation temperatures.) The populations of the lower-lying levels are determined by a combination of quadrupole radiative cascade rates, sourcing by HeH\(^+\) through Eq. (3), and (at the lowest energies) some quadrupole excitation by the CMB. Note that even in the ground vibrational state (v = 0), the rotational levels of H\(_2\)\(^+\) never come to thermal equilibrium with the CMB because the radiative rates (which may be as long as \(\sim 10^{10}\) s) are slower than the timescale for charge transfer (about \(3 \times 10^8\) s for model A at z = 300).

The overall production of H\(_2\) via the HeH\(^+\)/H\(_2\)\(^+\) mechanisms is found to be x[H\(_2\)] = 4.8 \times 10\(^{-9}\) at z = 20. Of this, only a small fraction (x[H\(_2\)] = 2.6 \times 10\(^{-11}\)) is formed if we artificially turn off HeH\(^+\). (These numbers are for model A, models B and C give numbers that are < 10 per cent higher.) The direct production of H\(_2\)\(^+\) via Eq. (1) only contributes significantly at z > 300 where it is possible to directly produce tightly bound states by radiative association.

The two-level model of Section 6.1 does quite well at reproducing the final H\(_2\) abundance due to H\(_2\)\(^+\) (it yields 2.2 \times 10\(^{-11}\) versus 2.6 \times 10\(^{-11}\) for the full multi-level calculation). It is not quite so good at reproducing the redshift history: at very high redshifts where H\(_2\)\(^+\) can be excited out of the ground state and photodissociated, it underestimates H\(_2\) production because the photodissociation rate of the H\(_2\)\(^+\) ion after it has reached a low-lying level is actually less than the LTE rate.

### 7 HEATING

The principal reason for interest in the molecular abundances in primordial gas is the possible effect on the heating and cooling rates. Before the formation of collapsed structures, the gas is colder than the CMB and hence the effect of molecular transitions is to heat the gas; after collapse the gas is compressed and shock-heated to above the CMB temperature, at which point molecules cool the gas. The latter regime is dominated by H\(_2\) molecules formed in the collapsed gas clouds themselves rather than primordial molecules, and hence it is not considered here. The molecular heating in the pre-collapse regime was first investigated by Pyy et al. (1993), and later by Haiman et al. (1996a), Galli & Palla...
Cosmological production of \( \text{H}_2 \)

7.1 Rotational transitions

In this section we evaluate the heating in the rotational lines of \( \text{H}_2 \). It is found to be negligible, and is much smaller than the direct heating produced by the chemical reactions that generate \( \text{H}_2 \). Determining the rotational line heating requires determining first the level populations and then computing the heating rates by considering all collisional excitations and de-excitations via \( \text{H} \) and \( \text{H}^+ \).

The \( \text{H}_2 \) molecule has two sets of levels with different nuclear spin properties, namely para-\( \text{H}_2 \) (even angular momentum \( J \), and total nuclear spin \( I = 0 \) and ortho-\( \text{H}_2 \) (odd \( J \); \( I = 1 \)). In the high-redshift universe, the timescale for the electric quadrupole radiative transitions that connect \( \text{H}_2 \) levels with the same nuclear spin is fast compared to the timescale for collisions. For example, using the radiative rates of Turner et al. (1977) and the collisional rates described below, we find that the collisional-to-rotational transition rate ratio at \( z = 250 \) is 0.04 for \( J = 0 \); this rate is even less for higher rotational levels or lower redshifts.

Therefore we may treat the \( \text{H}_2 \) molecule as an effective two-level system, tracking separately the abundances of para-\( \text{H}_2 \) and ortho-\( \text{H}_2 \). Within each set of levels (even or odd \( J \)), the populations are assumed to rapidly thermalize to the CMB temperature, \( x[\text{H}_2, J] \propto g_J e^{-E_J/k_B T_{\text{CMB}}} \). Here the degeneracy is \( g_J = (2J + 1)/4 \) for even \( J \) or \( g_J = 3 (2J + 1)/4 \) for odd \( J \). The evolution equation for the fraction \( \mathcal{F} \) of the \( \text{H}_2 \) molecules in the ortho form is

\[
\frac{d\mathcal{F}_{\text{prod}}}{dt} = (\mathcal{F}_{\text{prod}} - \mathcal{F}) \frac{d}{dt} \ln x[\text{H}_2] + \gamma_{p-\text{o}} (1 - \mathcal{F}) - \gamma_{o-\text{p}} \mathcal{F},
\]

where \( \gamma_{p-\text{o}} \) is the para-to-ortho transition rate (in \( s^{-1} \)); and \( \gamma_{o-\text{p}} \) is the ortho-to-para transition rate. The transition rates are

\[
\gamma_{p-\text{o}} = n \left( x[\text{H}^+] \right| \langle \sigma_{p-\text{o}} v \rangle \text{H}_2 + \text{H}^+ + x_{\text{HI}} \langle \sigma_{p-\text{o}} v \rangle \text{H}_2 + \text{HI} \right),
\]

where the averages are taken over both thermal velocity at temperature \( T_m \) and the Boltzmann distribution of \( \text{H}_2 \) rotational levels. A similar equation holds for \( \gamma_{o-\text{p}} \). We have taken the cross sections for \( \text{H}_2 + \text{H}^+ \) from Gerlich (1991). For \( \text{H}_2 + \text{H} \), we have used the fits by Flower (1993), with the correction for reactive scattering by Le Bourlot et al. (1993). Also, since \( \text{H}_2 \) is usually produced in a highly excited rotational state when it forms from \( \text{H}^+ + \text{H} \) (Launay et al. 1991), we have assumed here that \( \mathcal{F}_{\text{prod}} = 3/4 \) as would be suggested by the nuclear spin degeneracy. Once the level populations are established, the heating rate is computed by assuming that an amount of energy \( E_J - E_{J'} \) is added to the translational degrees of freedom of the gas for each collisional \( J \to J' \) transition:

\[
Q_{\text{rot}} = \sum_{J,J'} x[\text{H}_2, J] (E_J - E_{J'}) n \left( x[\text{H}^+] \right| \langle \sigma_{J \to J'} v \rangle \text{H}_2 + \text{H}^+ + x_{\text{HI}} \langle \sigma_{J \to J'} v \rangle \text{H}_2 + \text{HI} \right).
\]

1 The orbital angular momentum \( N \) and the orbital plus electron spin angular momentum \( J \) are identical for the \( \text{H}_2 \) electronic ground state since the term symbol is \( ^3\Sigma^+_u \).

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Our treatment of H₂ cuts off the rotational levels at J_{max} = 9, the highest level for which Gerlich (1990) provides H₂+H⁺ cross sections; but we have found that at z < 400 there is a < 10 per cent change in the heating rate if we cut off the levels at J_{max} = 7 instead.

7.2 Chemical heating

We next consider the chemical heating from each of Eqs. (1) and (5). The first contribution comes from the formation and destruction of H⁺, Eq. (1). The rate of loss of kinetic energy from the forward reaction is k₁E(Tₘ)x_xₜH(n), where E(Tₘ) is the mean energy of the incident electron participating in the reaction. This mean energy is given by multiplying the Maxwell distribution against the radiative association cross section,

$$ \tilde{E} = \frac{\int_0^\infty E^2 \sigma_{ra}(E)e^{-E/k_B T_m} dE}{\int_0^\infty \sigma_{ra}(E)e^{-E/k_B T_m} dE} = k_B T_m \frac{d}{dT_m} \ln \int_0^\infty E \sigma_{ra}(E)e^{-E/k_B T_m} dE = k_B T_m \frac{d}{dT_m} \ln \left( \frac{\sigma_{ra}(T_m)}{T_m} \right),$$

where in the last line we have re-expressed the energy integral in terms of the thermally averaged rate coefficient. By the principle of detailed balance, the average energy of the photodetached electrons from the thermal part of the reverse reaction is given by the same function, E(T_{CMB}). For the electrons that are photodetached by the spectral distortion, the kinetic energy input is hv − B(H⁻). Thus the overall heating term associated with Eq. (1) is

$$ Q_{c1} = - \left( 3 + \frac{d \ln k_1(T_m)}{d \ln T_m} \right) k_B T_m k_1 x_x_{xₜH(n)} + x[H⁻] \left\{ \frac{3}{2} + \frac{d \ln k_1(T_{CMB})}{d \ln T_{CMB}} \right\} k_B T_{CMB} k^{(th)}_{-1} + \int_{B(H⁻)/h}^{\infty} r(ν)σ_{-1}(ν)[hv − B(H⁻)]\frac{dν}{ν}. $$

The second contribution to the heating due to associative detachment, Eq. (2). As noted by Puy et al. (1993), this reaction is exothermic by 3.72 eV; however it is not correct to set the heating term from Eq. (2) equal to 3.72 eV times the reaction rate, because this energy yield is distributed among both the kinetic energy of the ejected electron (which couples to the gas temperature) and the rotational and vibrational degrees of freedom of the H₂ molecule (which are radiated away on timescales of ~10⁶ s, i.e. much shorter than the collision timescale). In order to compute the heating term, one needs to know the mean excitation energy of the final-state H₂ molecule. This can be determined from the (ν, J)-resolved cross sections for associative detachment of H and H⁻, which were computed by Bieniek & Dalgarno (1979) at an initial state energy of 0.0129 eV (which is roughly the initial energy of interest); this yields a mean excitation energy of 2.81 eV. By subtraction we estimate that 0.91 eV of energy is available to heat the gas. Thus we set

$$ Q_{c2} = (0.91 \text{ eV}) k_2 x[H⁻] x_{xₜH(n)}. $$

A third contribution to the heating rate is from mutual neutralization, Eq. (5). The branching fraction for this rate is small, but it is strongly exothermic (12.84 eV) and thus provides a potentially large amount of energy. The final state products are H atoms, which have no rotational or vibrational degrees of freedom. They do however have electronic degrees of freedom; it is energetically possible for the final state to be H(1s)+H(1s) for any 0 ≤ l ≤ n ≤ 4. At low energies, nearly all of the neutralizations go to n = 3 (Fussen & Kubach 1986), so the energy released into translational degrees of freedom is 0.76 eV. The excited H atom decays by emitting H₀, Lyman, and/or 2-photon continuum radiation, none of which can heat the gas. Therefore the mutual neutralization heating term is

$$ Q_{c3} = (0.76 \text{ eV}) k_3 x[H⁻] x_{xₜH(n)}. $$

We also consider the heating and cooling from the H⁺ and HeH⁺ reactions. The contribution from Eq. (1) is obtained by inserting the translational energy E = E(νN) + νhv in the integrals for radiative association (Eq. (47)) and photodissociation (Eq. (56)). The heating from the charge transfer reaction, Eq. (5), depends on the final rotational-vibrational state of the H₂ molecule, which is not resolved in our code. We have assumed that the H₂ is produced in the ground state, which maximizes the heating from this reaction since it implies that the entire energy yield of the reaction is available to heat the gas; however Eq. (3) is not a significant source of chemical energy anyway. The radiative association and dissociation of HeH⁺ (Eq. (5)) was treated using the obvious analogue of Eq. (47), without the spectral distortion since as argued earlier it is unimportant for HeH⁺. The contribution to the heating rate from all of the H⁺ and HeH⁺ reactions is negligible.

7.3 Results

The results are shown in Fig. 6; it is seen that the chemical heating is very small, of the order of 10⁻⁴. The principal source of heating is the H⁻ sequence of reactions, which provide a peak in the heating at z ~ 120 from the photodetachment process, and a second peak at z ~ 70 due to associative detachment. There is even less heating at earlier times, and in any case heating before Compton freeze-out (z ~ 200) will be erased.

We find that the heating due to rotational transitions in H₂ is negligible, in qualitative agreement with the results of Flower & Pineau des Forêts (2004). The fractional heating rate peaks at ~ 3 × 10⁻⁶ at z ~ 50, shortly after the peak in H₂ production rate (there is less H₂ at earlier times, and the decreasing density and temperature suppress collisional rates at later times). The difference from some previous results (e.g. Puy et al. 1993) is due partially to our reduced H₂ abundance but also due to reduced J-changing collision cross sections. In particular, collisions with H⁺ dominate the transfer of rotational energy into translational degrees of freedom. While there remains considerable uncertainty in the potential for the H⁺+H system as noted by several authors (e.g. Galli & Palla 1998; Flower & Pineau des Forêts 2004), we find that the cross sections would have to be increased by a factor of 40 to make rotational heating con-
8 DISCUSSION

We have reconsidered the production of H$_2$ molecules in the pregalactic medium. In contrast to previous studies, we have included the spectral distortion in our analysis, and resolved all 423 rotational-vibrational levels of the H$_2$ ion. We find that in the level-resolved analysis, the H$_2^+$ reaction pathway is greatly suppressed because newly formed H$_2^+$ ions are photodissociated before they can decay to the ground state or undergo charge transfer to become H$_2$ molecules. We also find that the H$^-$ ion is easily destroyed by spectral distortion photons at $z > 70$, so that the production of H$_2$ by this pathway is suppressed relative to the standard calculation. We obtain a final H$_2$ abundance $x_{H_2} = 6 \times 10^{-7}$ assuming standard cosmology.

Unfortunately, the primordial H$_2$ molecules will be very difficult to detect. The main effect of H$_2$ on the thermal history of the gas actually comes from the formation process (via the H$^-$ sequence, Eqs. 112) rather than rotational lines; however the effect is only of the order of $10^{-4}$. In principle the proposed 21-cm tomography of the pre-reionization Universe could reach the sensitivity at which primordial H$_2$ becomes important, since it is sensitive to the temperature of the gas and has many more than $(10^{-4})^{-2} \sim 10^8$ modes. However when assessing the prospects, it should be remembered that the high-redshift 21-cm signal has not yet been detected, and measurements at the $10^{-4}$ level are clearly very far in the future.

Aside from H$_2$, there are other molecules with rotational lines such as HD and LiH, which could conceivably have been formed in the early Universe and played a role in the thermal balance. The treatment of these trace molecules is beyond the scope of this paper, but HD in particular may warrant further study as it has been found to be a significant heating source in some past works (e.g. Puy et al. 1998). Since the main route of formation of HD is via the reaction H$_2$(D$^+$,H$^+$)HD (Galli & Palla 1998), any analysis of HD must incorporate the revised H$_2$ calculation presented here.

Finally, one could ask whether the H$_2$ suppression mechanisms discussed here — the spectral distortion and non-equilibrium populations in H$_2^+$ — have a significant effect on H$_2$ cooling of protogalaxies. In the case of the spectral distortion, we have seen that at mean density the photodetachment of H$^-$ becomes unimportant at low redshift, since H$^-$ ions undergo a chemical reaction (usually associative detachment) before being destroyed by radiation. For example, the branching fraction for H$^-$ at mean density to be destroyed by radiation is 0.13 at $z = 40$, 0.09 at $z = 30$, and 0.05 at $z = 20$. In overdense gas clouds at $z < 40$ the collisional reactions are faster and we conclude that the spectral distortion should be negligible. We have tried running our H$_2$ code for overdense conditions at low redshift (e.g. $z = 20$, $\delta_0 = 10^4$, $T = 10^5$ K) and find that the H$_2^+$ levels are still far out of equilibrium, with the lowest levels underpopulated relative to the Boltzmann distribution (at $T_{CMB}$) by many orders of magnitude. However in such clouds H$^-$ is likely to be a more important source of molecules than H$_2^+$ (see e.g. Tegmark et al. 1997). Therefore we do not expect our changes in H$_2^+$ physics to have large consequences for the cooling of the first collapsed objects in the universe.

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Figure 5. The heating rate due to the H$^-$ and H$_2^+$/HeH$^+$ sequences of reactions, and the H$_2$ rotational transitions, for Model A. What is shown is the heating input per Hubble time, $Q/H$, divided by the thermal energy of the gas, $3k_B T_m x_r/2$. The H$^-$ reactions affect the gas temperature at the $\sim 10^{-4}$, and H$_2^+$ reactions have even less influence. The H$_2$ rotational line heating is almost small compared to the chemical reactions.
APPENDIX A: THE H$_2^+$ MOLECULAR ION

The bound states of H$_2^+$ (1s$\sigma_g$) are solved within the Born-Oppenheimer approximation, which for a diatomic molecular ion gives

$$\Psi(r, R) = \chi(r|R) \frac{\Phi(R)}{R} Y_{NM}(R),$$

where $r$ is the electron position, $R$ is the internuclear separation vector, $\chi(r|R)$ is the 1s$\sigma_g$ electronic wavefunction, $\Phi(R)$ is the radial wavefunction, and $R$ is the unit vector in the direction of $R$. The radial wavefunction is a solution to the Schrödinger eigenvalue equation,

$$-\frac{\hbar^2}{2\mu} \Phi''(R) + \left[ V(R) + \frac{\hbar^2(N+1)}{2R^2} \right] \Phi(R) = E\Phi(R),$$

where $E$ is the bound state energy and $\mu$ is the reduced mass of H$_2^+$. The potential $V(R)$ is interpolated from the tabulated values of Bates et al. (1953) and Madsen & Peek (1971). The radiative transitions among the levels of H$_2^+$ (1s$\sigma_g$) are treated according to the method of Bates & Poots (1953), who give the spontaneous rates $A_j$ in terms of the wave functions and the quadrupole moment $M(R)$ of the H$_2^+$ ion. The quadrupole moment is interpolated from the computations of Peek et al. (1978) for $R \leq 12a_0$, and using the asymptotic formula $M(R) \sim R^2/4 - \alpha_0 a_0 R^{-1}$ for $R > 12a_0$ (where $\alpha_0 = 9/2$ is the dipole polarizability of H). The rate for the radiative association reaction (Eq. 4) is required for our calculation. The individual rates to and from each rotational-vibrational level of H$_2^+$ as a function of matter and radiation temperature are not tabulated in the literature, but can be derived using standard methods (e.g. Zygelman & Dalgarno 1990; Stancil et al. 1993). For the dipole radiative dissociation, one solves for the unbound final state Eq. (A2) using the 2$\sigma_a$ potential and the energy normalization (see e.g. Eq. 4 of Zygelman & Dalgarno 1990). Then the radiative dissociation cross section from the vN bound level with energy $E(vN) < 0$ is $\Phi(R)/R$.  

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2 Note that $P(R)$ in Bates & Poots (1953) is equal to our $\Phi(R)/R$. 

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where $\nu$ is the photon energy and

$$\frac{M^2}{\pi^2} = (2N + 1)^{-1} \left[ N \int_0^\infty \Phi(R)D(R)f_{N+1}(R) dR \right]^2 + (N + 1) \left[ \int_0^\infty \Phi(R)D(R)f_{N+1}(R) dR \right]^2 \right].$$  \hfill (A4)

Here $D(R)$ is the dipole matrix element between 1s$\sigma_g$ and 2p$\sigma_u$ states, and $f_{N+1}(R)$ are the unbound wave functions that solve Eq. (A2) with rotational quantum numbers $N \pm 1$ and energy $E(vN) + \nu$. (Only unbound states where $N' = N \pm 1$ contribute due to dipole selection rules.) The dipole moments are interpolated from Bates (1951) and Ramaker & Peek (1973) for $R < 20a_0$; and the large-$R$ asymptotic expression (Ramaker & Peek 1972) is used for $R \geq 20a_0$.

The net radiative dissociation rate, including both thermal and nonthermal contributions to the radiation field, is then given by integrating over all photon frequencies,

$$\beta_{vN} = \frac{8\pi}{c^2} \int_{-E(vN)/h}^\infty \frac{\nu^2 \sigma_{vd}(\nu)}{e^{\nu\hbar/k_B T_{\text{CMB}}} - 1} d\nu + nc \int_{-E(vN)/h}^\infty r(\nu)f_{vd}(\nu) d\nu, \hfill (A5)$$

The spontaneous radiative association cross section is related to the radiative dissociation cross section by phase space factors,

$$\sigma_{r,a,vN}(E) = \frac{\varpi_{H_2^+}^{vN} + \gamma}{\varpi_{H^+}} \sigma_{r,d,vN}[E - E(vN)], \hfill (A6)$$

where $\varpi$ represents the number of quantum states per unit wavenumber $k$ per unit volume for either $H_2^+ (vN) + \gamma$ or $H + H^+$. These are given by

$$\varpi_{H_2^+}^{vN} = 4(2N + 1)g_{\text{nuc}}' \frac{4\pi k_e^2}{(2\pi)^3} \hfill (A7)$$

and

$$\varpi_{H^+} = \frac{2 \times 4\pi k_e^2}{(2\pi)^3} \hfill (A8)$$

where $k_e = 2\pi\nu/c$ is the photon wavenumber and $k_{H^+} = \sqrt{2}\pi E/\hbar$ is the relative wavenumber of $H$ and $H^+$. In addition to the usual factor $(4\pi k^2/(2\pi)^3)$, Eq. (A7) contains a factor of 2 from the electron spin, a factor of 2 from the photon polarization, and the nuclear spin-degeneracy factor $g_{\text{nuc}}'$; Eq. (A8) contains a factor of 2 from the electron spin.

The net radiative association rate coefficient to the $vN$ level is then given by the usual integral of cross section times velocity over the Maxwell-Boltzmann distribution,

$$\alpha_{vN} = \frac{2\sqrt{2}}{(\pi\mu)^{1/2}(k_B T_m)^{1/2}} \times \int_0^\infty E\sigma_{r,a,vN}(E)e^{-E/k_B T_m}[1 + f(\nu)]dE. \hfill (A9)$$

Here $f(\nu)$ is the photon phase space density at frequency $\nu = [E - E(vN)]/\hbar$, and it has been included to take into account stimulated radiative association. The phase space density from spectral distortion photons is $\ll 1$ and can be