Molecular processes in the early Universe

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Abstract. Molecular processes first took place in the Universe in the recombination era as the expanding Universe cooled adiabatically and recombined when the cooling radiation field ran out of photons energetic enough to cause photoionization. The formation of neutral helium heralded the dawn of chemistry as the neutral atoms participated in processes of radiative association to form molecular ions. Dissociative recombination of the molecular ions produced neutral atoms and accelerated the conversion of the ionized plasma into a neutral gas. The subsequent chemistry involved hydrogen, deuterium, helium and lithium created earlier in a brief period of nucleosynthesis. With the continued expansion the Universe became cold and dark and chemistry came to a temporary end until the formation and gravitational collapse of the first distinct cosmological objects. Heavy elements were made, a new source of radiation – starlight – appeared and a richer chemistry was initiated.

1. Introduction

According to the current standard cosmology, the Universe began with the decay of scalar fields into matter and radiation. The effects of the fields were similar to those of a repulsive gravitational force and they drove a brief period of rapid inflation. The quantum fluctuations were stretched into the seeds of later structures built by gravity. At the end of the inflationary period the Universe was intensely hot and dense and filled with energetic radiation. Any composite particle survived only as a transient species to be torn apart immediately by photons or by collisions. Only the fundamental indivisible particles existed. It was an unpromising scenario for the formation of complex structures. From the initial dense hot state the Universe expanded adiabatically and as it did so it cooled and the radiation became less energetic and less intense and the collisions became less violent. In the first second, protons were formed by the combination of quarks and they were not destroyed in the cooler environment. They soon reacted with electrons to form neutrons and a brief period of nucleosynthesis ensued as the temperature fell to a billion degrees. Helium nuclei were created with a fractional abundance by number of about 0.1 together with trace amounts of deuterium and lithium seven nuclei at fractional abundances of $3 \times 10^{-5}$ and $10^{-10}$, respectively. (The fractional abundance of deuterium provides a measure of the baryon density of the Universe.)

The Universe then coasted for about 200,000 years until the temperature had fallen to about 4000 K. At 4000 K the Universe ran out of photons energetic enough to ionize hydrogen. The mean time for photoionization exceeded the Hubble time and the Universe entered the recombination era.

2. Recombination era

The fully ionized plasma that was the Universe before recombination was transformed into a neutral gas with a few relict electrons. The close thermal contact of matter and radiation that had been maintained by Compton scattering of photons and electrons was lost and matter and radiation evolved separately. The Universe became transparent.
Figure 1. Early Universe fractional abundances of positive atomic ions and neutral atoms [1].

The recombination was sequential in the order of the ionization potentials beginning with \( \text{Li}^{3+} \) and ending with \( \text{Li}^+ \). Recombination of lithium \( \text{Li}^+ \) was not completed because by the time photoionization of lithium could no longer occur there were few electrons left with which \( \text{Li}^+ \) could recombine. Figure 1 [1] shows the evolution of the fractional abundances of the positive ions and neutral atoms of \( \text{H} \), \( \text{He} \), \( \text{D} \) and \( \text{Li} \) as functions of the red shift \( z \) for a particular cosmological model. Given the red shift the model determines the time \( t \), the density \( n \) and the radiation temperature \( T \). For a matter dominated Universe \( t = 14 \times 10^9 / (1 + z)^{3/2} \) years, \( n = 10^{-6} (1 + z)^3 \text{ cm}^{-3} \) and \( T = 2.728 (1 + z) \text{ K} \).

At \( z \sim 2500 \), helium was neutral. It was the dawn of chemistry because molecular formation was no longer inhibited by the Coulomb repulsion of the interacting species. The density was 200 \( \text{ cm}^{-3} \) and there was no dust. Molecular formation was necessarily by two-body radiative processes. The hydrogen was still ionized at \( z \sim 2500 \) and it could form the molecular ion \( \text{HeH}^+ \) by radiative association

\[
\text{H}^+ + \text{He} \rightarrow \text{HeH}^+ + \nu. \tag{1}
\]

\( \text{He} \) and \( \text{He}^+ \) also co-existed and some \( \text{He}_2^+ \) was made by

\[
\text{He}^+ + \text{He} \rightarrow \text{He}_2^+ + \nu, \tag{2}
\]
as was a trace of \( \text{LiHe}^+ \) by

\[
\text{Li}^+ + \text{He} \rightarrow \text{LiHe}^+ + \nu. \tag{3}
\]

The radiative processes were followed by the non-radiative dissociative recombinations

\[
\text{HeH}^+ + e^- \rightarrow \text{He} + \text{H}, \tag{4}
\]
\[
\text{He}_2^+ + e^- \rightarrow \text{He} + \text{He}, \tag{5}
\]
\[
\text{LiHe}^+ + e^- \rightarrow \text{He} + \text{Li}. \tag{6}
\]

The effect of radiative association and dissociative recombination was an acceleration of the recombination of the Universe. However both hydrogen and lithium were then reionized by the background radiation. Soon though photoionization of hydrogen slowed and neutral hydrogen atoms participated in a chemical reaction

\[
\text{HeH}^+ + \text{H} \rightarrow \text{H}_2^+ + \text{He}. \tag{7}
\]
$H_2^+$ was also formed by direct radiative association

$$H^+ + H \rightarrow H_2^+ + \nu.$$  \hspace{1cm} (8)

The $H_2^+$ was destroyed by dissociative recombination

$$H_2^+ + e^- \rightarrow H + H.$$  \hspace{1cm} (9)

and by photodissociation

$$H_2^+ + \nu \rightarrow H + H^+.$$  \hspace{1cm} (10)

but it could also react with neutral hydrogen atoms

$$H_2^+ + H \rightarrow H_2 + H^+.$$  \hspace{1cm} (11)

to make the neutral molecule $H_2$.

Minor contributions to the formation of $H_2$ came from the radiative association of excited and ground state atoms [2]

$$H + H' \rightarrow H_2 + \nu.$$  \hspace{1cm} (12)

from associative ionization [3]

$$H + H' \rightarrow H_2^+ + e^-.$$  \hspace{1cm} (13)

followed by (11) and by the Raman scattering process [4]

$$H + H + \nu \rightarrow H_2 + \nu'.$$  \hspace{1cm} (14)

but the dominant source of $H_2$ was the associative detachment process

$$H + H^- \rightarrow H_2 + e^-.$$  \hspace{1cm} (15)

The initiating process forming $H^-$ ions was radiative attachment,

$$e^- + H \rightarrow H^- + \nu.$$  \hspace{1cm} (16)

It was not effective until photodetachment had ceased at $z \sim 100$. The amount of $H_2$ that was created was small with a fractional abundance of order $10^{-6}$. Small it was, but significant for the cooling to which it gave rise.

A comprehensive description of the early Universe in the pregalactic era has been assembled and the consequences of different cosmological models have been evaluated [5–7]. Figure 2 reproduces the molecular abundances for one particular model [1].

The kinds of processes that were taken into account are listed in table 1. Figure 2 shows also the predicted abundances of the deuterated molecules HD and $H_2D^+$. The HD molecule is an important coolant. The principal sources of HD are

$$D^+ + H_2 \rightarrow HD + H^+$$  \hspace{1cm} (17)

and

$$D + H_2 \rightarrow HD + H$$  \hspace{1cm} (18)

and the abundance of HD reflects that of $H_2$ at a level of $10^{-9}$.

The $H_2D^+$ molecular ion has a large dipole moment and might be detectable through a process in which erasure of fluctuations in the cosmic background radiation occurs by a resonance scattering process.
that enhances the coupling of radiation and matter [8]. However the density of $H_2D^+$ is much too low, in part because of its destruction by dissociative recombination:

$$H_2D^+ + e^- \rightarrow \begin{cases} H + H + D \\ H_3 + D \\ HD + H \end{cases}$$

(19)

Large differences exist in the abundances of $H_3^+$ and $HD^+$ calculated by Stancil et al. [7] and Galli and Palla [5], some of which stem from different assumptions about the branching ratios of the dissociative recombination (19), but the calculations agree that the abundances are negligible.

LiH has a large dipole moment and LiH might be observable if enough of the primordial lithium is converted to molecular form [8]. Studies of the abundances of LiH and LiH$^+$ [5, 7] now agree that the conversion efficiency is very low. The formation processes are radiative association [9, 10]

$$Li + H \rightarrow LiH + \nu$$

(20)

and the negative ion sequences [7]

$$Li^- + H \rightarrow LiH + e^-$$

(21)

$$Li + H^- \rightarrow LiH + e^-.$$ 

(22)

| Table 1. Atomic and molecular processes in the early Universe |
|-------------------------------------------------------------|
| photoionization                                             | associative detachment |
| radiative recombination                                     | dissociative attachment |
| photodetachment                                             | associative ionization  |
| radiative attachment                                       | excitation transfer    |
| radiative association                                       | dissociative recombination |
| charge transfer                                             | mutual neutralization  |
| proton transfer                                             | photodissociation      |
These processes had to await the recombination of $\text{Li}^+$ to Li [11]. Destruction occurred through [6]

$$\text{LiH} + \text{H} \rightarrow \text{LiH} + \text{H}_2.$$  \hspace{2cm} (23)

It is probably a rapid reaction but even if it is not the abundance of LiH is minute. The delayed recombination of $\text{Li}^+$ allows the formation of LiH$^+$ by radiative association

$$\text{Li}^+ + \text{H} \rightarrow \text{LiH}^+ + \nu$$ \hspace{2cm} (24)

which is then removed by reaction with H and by dissociative recombination

$$\text{LiH}^+ + \text{e}^- \rightarrow \text{Li} + \text{H}$$ \hspace{2cm} (25)

which produces neutral lithium. The predicted abundance of LiH$^+$ exceeds that of LiH but is still very small.

Because the chemistry of the early Universe is driven by radiation there must be some amplification of the reactions by the stimulation due to the background radiation field in which they are embedded [12,13]. Substantial enhancements do occur but their influence on the resulting molecular abundances is limited [7].

After the formation of H$_2$ by the H$^-$ sequence at $z \sim 100$, the decreasing density brought chemistry to a temporary end. The Universe continued its expansion, getting colder and darker. This period after recombination and before the appearance of the first distinct cosmological objects has been called the Dark Ages.

There remain uncertainties in the chemistry. Some of the rate coefficients are little better than arbitrary estimates and potentially significant modifications arise from a detailed study of the role of vibrationally excited H$_2^+$. There may also be modifications in an extended cosmology that takes account of the apparent acceleration of the Universe driven by dark energy. Calculations of molecular abundances that incorporate dark energy by invoking a decaying cosmological constant have been carried out by Hashimoto, Kamikawa and Arai [14]. They conclude that molecular formation would be shifted to an earlier epoch and the limiting abundance of H$_2$ would be doubled.

3. The first cosmological objects

Embedded in the cooling cosmic gas were fluctuations in density of order $10^{-5}$, sufficient that they could grow by gravity to create objects of a size that gravitational collapse could occur. Objects collapse when the gravitational pressure exceeds the thermal pressure. The dissipation of heat as the collapse proceeds is critical in determining the scale size of the collapsing objects. The molecules H$_2$ and HD are efficient coolants compared to the atoms because they can be excited into vibrational and rotational states which can lose energy by radiating. With the increasing density, three body collisions

$$\text{H} + \text{H} + \text{H} \rightarrow \text{H}_2 + \text{H}$$ \hspace{2cm} (26)

$$\text{D} + \text{H} + \text{H} \rightarrow \text{HD} + \text{H}$$ \hspace{2cm} (27)

came to dominate the chemistry [15]. LiH was probably not formed because

$$\text{Li} + \text{H} + \text{H} \rightarrow \text{LiH} + \text{H}$$ \hspace{2cm} (28)

would have been followed by reaction (15).

The enhanced cooling allowed the objects to achieve high densities at which collapse became inevitable. The collapse was mediated by the reactions

$$\text{H} + \text{H} \rightarrow \text{H} + \text{H}^+ + \text{e}^-$$ \hspace{2cm} (29)

$$\text{H} + \text{H} \rightarrow \text{H}_2^+ + \text{e}^-$$ \hspace{2cm} (30)

$$\text{H} + \text{H} \rightarrow \text{H}^+ + \text{H}^-.$$ \hspace{2cm} (31)

Ionization may have occurred more rapidly by first exciting the metastable 2s state of H. The electrons would have destroyed H₂ by electron impact excitation to dissociative states,

\[ \text{H}_2 + e^- \rightarrow \text{H}_2^+(b^3\Sigma_u^+) + e^- \]  

through electron impact ionization

\[ \text{H}_2 + e^- \rightarrow \text{H}_2^+ + 2e^- \] \hspace{1cm} (33)

and dissociative attachment

\[ \text{H}_2 + e^- \rightarrow \text{H} + \text{H}^- \] \hspace{1cm} (34)

4. The reionization phase

As in stellar collapse, a hot core formed at temperatures where nuclear reactions occurred and some heavy elements like carbon and oxygen were made. A new form of radiation entered the Universe – starlight. All the energy released in the nuclear reactions was released as photons that escaped into the ambient neutral gas. The photons dissociated the molecules and ionized them and the atoms and the Universe was re-ionized. The response of H₂ to the radiation depended on the intensity and distribution with wavelength of the radiation and on the density of the gas. Photodissociation of H₂

\[ \text{H}_2 + \nu \rightarrow \text{H} + \text{H} \] \hspace{1cm} (35)

comprises for wavelengths shorter than 110 nm \[16–18\]. The process is initiated by line absorption and self-shielding enables H₂ to survive if the gas density is high. H₂ can also survive ionization. Indeed the formation can be enhanced because

\[ \text{H}_2 + \nu \rightarrow \text{H}_2^+ + e^- \] \hspace{1cm} (36)

is followed by reactions (11), (16) and (15) producing H₂.

The radiation heats the gas and the hot electrons destroy the H₂ through reactions (32-34). Also effective is the reaction

\[ \text{H}_2(v) + \text{He}^+ \rightarrow \text{He} + \text{H} + \text{H}^+ \] \hspace{1cm} (37)

which is rapid for H₂ in vibrational levels \( v \geq 2 \).

The density distribution of the ionized and neutral gases in the reionization phase and the abundances of heavy elements produced in the collapsing objects and ejected by winds and explosions into the gas are crucial parameters in the evolution of the molecular composition. The chemistry of the recombining plasma has some similarity to that following the passage of a fast dissociative ionizing shock \[19\]. In the warm phase molecular ions are formed by ion-molecule reactions and removed mostly by dissociative recombination. Calculations indicate that the most abundant ions are expected to be H₂⁺, H⁺, HeH⁺, OH⁺ and CH⁺. The most abundant neutral molecules should be OH, CH, H₂O, CH and CO. Negative ion sequences analogous to (16) and (15) will contribute to the formation of OH, CH and CO \[20,21\].

References

[1] Lepp S, Stancil P C and Dalgarno A 2002 \textit{J. Phys.} B 35 R57
[2] Latter N B and Black J H 1991 \textit{Astrophys. J.} 372 161
[3] Rawlings J, Williams D A and Canto J 1968 \textit{MNRAS} 230 695
[4] Federman S R and Frommhold L 1982 \textit{Phys. Rev.} A 25 2012
[5] Galli D and Palla F 1998 \textit{Astron. Astrophys.} 335 403
[6] Stancil P C, Lepp S and Dalgarno A 1996 \textit{Astrophys. J.} 458 401
[7] Stancil P C and Dalgarno A 1998 \textit{Trans. Farad. Soc.} 109 61
[8] Maeli R, Melchiorri F and Tosi D 1994 \textit{Astrophys. J.} 425 372
[9] Dalgarno A, Kirby K and Stancil P C 1996 \textit{Astrophys. J.} 458 397
[10] Lepp S and Shull J M 1984 \textit{Astrophys. J.} 280 465
[11] Dalgarno A and Lepp S 1987 \textit{Astrochemistry} ed S P Tarafdar and M P Varshni (Dordrecht: Reidel) p 109
[12] Stancil P C and Dalgarno A 1997 Astrophys. J. 479 543
[13] Zygelman B, Stancil P C and Dalgarno A 1998 Astrophys. J. 508 151
[14] Hashimoto M, Kannikawa T and Arau K 2003 Astrophys. J. 598 13
[15] Palla F, Salpeter E and Stahler S W 1983 Astrophys. J. 271 532
[16] Solomon P and Wickramasinghe N C 1969 Astrophys. J. 158 449
[17] Stecher T P and Williams D A 1967 Astrophys. J. 149 29
[18] Stephens T L and Dalgarno A 1970 Astrophys. J. 160 L107
[19] Neufeld D A and Dalgarno A 1989 Astrophys. J. 340 869
[20] Dalgarno A and McCray R A 1973 Astrophys. J. 181 95
[21] Harwit M and Spaans M 2003 Astrophys. J. 589 53