PAUL SCHERRER INSTITUT

PSI-PR-99-07
ZU-TH 8/99
February 1999

Primordial Chemistry: an Overview

SW 9907

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Abstract. In the standard Big Bang model, the light elements in the cosmos -hydrogen and helium but also deuterium and lithium- were created in the very early Universe. The main problem is to connect what we can actually observe to day with the standard Big Bang nucleosynthesis predictions essentially because of uncertainties in modeling their evolution since the Big Bang. After a brief review of the primordial nucleosynthesis -predictions and observations of the primordial abundances- we present the preliminary studies of the primordial chemistry: molecular formation and evolution in the early Universe.

I INTRODUCTION

The standard model of the very early Universe is very simple. It is determined by pure physics: expansion is governed by general relativity, particle interactions are governed by the *Standard model* and particle distributions are governed by statistical physics. The model has only one parameter: the ratio η of the number of the baryons n_b to the number of photons:

$$\eta = \frac{n_b}{n_\gamma} \quad \eta_{10} = \frac{\eta}{10^{-10}}. \quad (1)$$

In particular, the predicted abundances of light elements depend only on η (or η_{10}). For more insight into the underlying physics of the standard Big Bang model see the reference books (Kolb & Turner 1990; Padmanabhan 1993 and also Signore & Puy 1999).

The later evolution of the Universe is far from simple: the uniform *plasma* of the early Universe has been converted into the present day Universe through a considerable nuclear and chemical evolution.

In this review, we first recall the very simple predictions of the SBBN (standard Big Bang Nucleosynthesis) model. Then, we will show that the main problem is to connect what we can actually observe to-day with these SBBN predictions. Finally, we present the preliminary studies of the primordial chemistry.

Therefore, section 2 is dedicated to the predictions and the observations of the primordial abundances of the light elements. In section 3 and 4, the formation and evolution of primordial molecules will be introduced. Some conclusions are given in section 5.

II PRIMORDIAL SYNTHESIS

In the early Universe, at $t \sim 1$ sec ($T \sim 10^{10}$ K), neutrons and protons leave the equilibrium curve i.e. for $(n/p)_* \sim 1/6$, neutrons and protons collide to make deuterium:

But as long as $T \geq 10^9$ K (or $t \leq 100$ s) photons have enough energy to photo-dissociate deuterium:

faster than the reactions:

Therefore, until that time, abundances of D , ${}^3\text{He}$, ${}^4\text{He}$ are small. At $T_{\text{nuc}} \sim 10^9$ K, (~ 0.1 MeV), $t_{\text{nuc}} \sim 100$ sec, more complex nuclei can be built:

but also

Let us consider the diagram of the Figure 1, there is a *gap*, there is no stable nucleus with atomic mass 5. To build heavier elements than ${}^4\text{He}$, collisions of rare D , ${}^3\text{H}$, ${}^3\text{He}$ nuclei with ${}^4\text{He}$ are required. But, most of D , ${}^3\text{H}$, ${}^3\text{He}$ nuclei are burned to ${}^4\text{He}$. Therefore, there is very little synthesis of heavier elements.

As the Universe continues to expand and cool, density and temperature decrease: nuclear reactions are more and more rare. At $t \sim 10^3$ sec, the epoch of Big Bang nucleosynthesis is over !

A Predictions of primordial abundance

The two main cosmological parameters on which the predictions depend are: the number of degrees of freedom g (at $T \sim 1$ MeV), and more importantly, the nuclear to photon ratio η . The dependance on η is complicated. The nucleosynthesis process can only be followed in detail by a numerical integration of a large amount of rate equations. The initial computer code due to Wagoner (1973) has been improved and updated by Kawano (1992) and his collaborators (Smith et al. 1993) incorporating new measurements and revised estimates of the nuclear cross sections. This code has been made publicly available by Kawano (1992), and has become the standard code for Big Bang Nucleosynthesis studies. The predictions can be shown graphically in the traditional plot as functions of the nucleon-to-photon ration η . Figure 2 shows the dependence of primordial synthesized light element abundances on η .

Sarkar (1996) and also Hogan (1997) give the following fitting formulas for:

-the predicted fraction of total baryon mass

$$Y_p = 0.235 + 0.012 \ln\left(\frac{\eta_{10}}{2}\right) \left[\left(\frac{\eta_{10}}{2}\right)^{-0.2} + 0.011(1 - \left(\frac{\eta_{10}}{2}\right)^{-0.2}) \pm 0.0006 \right] \quad (2)$$

-the abundance by number of deuterium is

$$\left(\frac{D}{H}\right)_p = 15.6 \times 10^{-5 \pm 0.03} \left[\frac{\eta_{10}}{2}\right]^{-1.6} \quad (3)$$

-the abundance of ${}^7\text{Li}$

$$\left(\frac{{}^7\text{Li}}{H}\right)_p = 1.06 \times 10^{-10} \pm 0.1 \left[\left(\frac{\eta_{10}}{2}\right)^{-2.38} + 0.28 \left(\frac{\eta_{10}}{2}\right)^{2.38} \right] \quad (4)$$

Let us note that the *errors* are due to reaction rate uncertainties. But the major uncertainty in the ${}^4\text{He}$ abundance is due to the experimental uncertainty in the neutron life time. For a detailed report on these uncertainties, see Sarkar 1996 and references therein.

Anyway, as may be seen in Figure 8, the relative abundances vary considerably with η , so that the SBBN model is an overdetermined system in the sense that fixing one of the primordial abundances fixes η , i.e. leads to predictions of the other nuclides. The SBBN model is a testable theory: consistency demands that the value of η determined by -for instance- the primordial deuterium abundance leads to predictions for ${}^4\text{He}$, ${}^7\text{Li}$, ${}^3\text{He}$ consistent with the observational data. Now, let us consider the observational estimates of the primordial abundances of D , ${}^3\text{He}$, ${}^4\text{He}$ and ${}^7\text{Li}$.

III OBSERVATIONS OF PRIMORDIAL ABUNDANCES

It is a considerable challenge to measure the actual primordial abundances to a comparable level of precision: because of uncertainties in measuring present day abundances, because of uncertainties in modeling the nuclear evolution since the Big Bang. However for each of these nuclei, there is some favorite places to look. The primary references can be found in the overview of the situation for all the isotopes given by Boesgaard & Steigman (1985). Our aim is to provide the participants of the school with the flavor of what is going on. We will begin with a sort of a generic program which must be done for each isotope.

A A Generic Program for obtaining Primordial Abundances

- *Observations*

The program begins with some kind of observations: in general, some atomic or molecular spectral line. Moreover, in the case of D , 3He , one must observe one isotope in the presence of another one, which is $10^4 - 10^5$ times more abundant. Finally, one must observe the different isotopes in different astrophysical sites, because of their very different properties.

- *Conversion of observed lines into abundances*

In general, each isotope is detected by measuring an atomic or a molecular spectral line. One must obtain, from this observed line, an abundance of the isotope i.e. the ratio of the number density of this isotope to the number density of hydrogen.

- *Correction for evolution since the Big Bang*

Except for D , all the isotopes have potential sources which could have increased their abundances since the era of primordial nucleosynthesis. All, except 4He , have significant sinks which could have decreased their abundances since the era of primordial nucleosynthesis. Therefore to arrive at a primordial abundance, one must have:

- a theoretical understanding of all the mechanisms of production and destruction of the isotopes.
- observations of different objects in order that all the free parameters, introduced in step 1, can be determined.

- *The primordial abundances*

One must arrive at a value for each abundance with the required precision. This required precision varies with time and is, in general, just at the level of or slightly beyond current capabilities.

Now, we apply this generic program to each isotope: 7Li , 3He , 4He , D . See the critical review of the observational abundances of light elements in the chapter 4 of Pagel (1997).

B 7Li

- *Observations*

Lithium absorption lines can be easily observed and measured in stars.

- *Conversion of observed lines in abundances*

The observed line gives the stellar photospheric abundance via standard stellar atmospheric technique. The problem arises in relating the observed abundance to the cosmic abundance i.e. the abundance of the star when it formed. For populations I stars, one finds for the abundance (here and now):

$$\left(\frac{Li}{H}\right)_{pop. I} \sim 2 \times 10^{-9}. \quad (5)$$

Spite & Spite (1982) discovered 7Li in population II stars -samples of metal poor halo stars- a quite uniform abundance from star to star, at a level of the Population I value, although their metallicities are down by at least a factor of 100, i.e.

$$\left(\frac{Li}{H}\right)_{pop. II} \sim 10^{-10}. \quad (6)$$

Moreover, observationally ${}^7\text{Li}$ is known to be destroyed by large factors in stellar atmosphere so the fact that very small abundances are observed in some stars could just indicate that those stars have destroyed ${}^7\text{Li}$ which began at a much higher level. In addition, no ${}^7\text{Li}$ depletion is predicted in standard non rotating stellar models, but new recent model with rotation may allow for significant ${}^7\text{Li}$ depletion in Population II stars (Pinsonneault et al. 1992, Charbonnel et al. 1992 and reference therein). It is still an open debate.

- *Evolution*

For many years, it was thought that stars do not produce ${}^7\text{Li}$ in significant amounts during their normal nuclear burning and that the dominant source of ${}^7\text{Li}$ was spallation of nuclei in the interstellar matter by cosmic rays (Walker et al. 1985). It is now thought that there are additional and significative sources of ${}^7\text{Li}$ by novae (Starrfield et al. 1978) and by type II supernovae via the ν -process (Woosley et al. 1990).

- *The primordial abundance*

Spite & Spite (1982) find $(\frac{{}^7\text{Li}}{\text{H}})_{II} \sim 10^{-10}$ in old low metallicity Population II stars. The abundance inferred for younger Population I stars is $(\frac{{}^7\text{Li}}{\text{H}})_I \sim 10^{-9}$. Therefore the Spite's Population II stars seem ideal for estimating the primordial ${}^7\text{Li}$ abundance: $(\frac{{}^7\text{Li}}{\text{H}})_p \sim 10^{-10}$ since it agrees with the SBBN model prediction. To explain, the higher value found in Population I stars, one must consider additional sources such as Supernovae II, novae and cosmic rays.

However, the *lithium problem* opens the way for sceptics to question this value and to ask the following question: could the primordial value be as high or higher than the Population I value ? i.e. ${}^7\text{Li}/\text{H} \sim 10^{-9}$? This would require a large and uniform depletion over a large range of stellar masses. Moreover, it would agree with the predictions of some inhomogeneous Big Bang nucleosynthesis model (see section 5).

Remark: These estimates of the primordial ${}^7\text{Li}$ abundances are done from galactic observations of the lithium resonance doublet line $\lambda 6707$. Let us notice that a very preliminary search for LiH molecules at high redshift has recently been done (de Bernardis et al. 1993, Signore et al. 1994, Puy & Signore 1999). Anyway, lithium is a key element in cosmology.

C ${}^3\text{He}$

- *Observations*

${}^3\text{He}$ is difficult to observe. The only successful technique so far used has been the hyperfine line of ${}^3\text{He}^+$ which is the atomic analog of HI and its hyperfine line the analog of the 21 cm line. It lies at 3.46 cm or 8.66767 GHz. ${}^3\text{He}$ has been detected in galactic HII regions and some planetary nebulae.

- *Evolution and abundance problems*

Arriving at an abundance from the hyperfine line needs many assumptions about the model of the source and about the evolution.

There are many recent developements (see in particular Hogan 1997 and references therein) which argue for caution in using ${}^3\text{He}$ for anything other than a probe of galactic chemical evolution. A growing consensus of opinions favors abandoning ${}^3\text{He}$ as a cosmological probe !

Remark:

Let us only notice that the following constraints:

- Recent solar system measurements by the Ulysses spacecraft lead to (Gloeckler & Geiss 1996):

$$({}^3\text{He}/\text{H})_{ISM} = 2.1^{+0.9}_{-0.8} \times 10^{-5}$$

- From meteorite data (Geiss 1993):

$$({}^3\text{He}/\text{H})_{\text{presolar neb.}} = 1.5^{+0.2}_{-0.3} \times 10^{-5}$$

do not contain primordial information !

D ${}^4\text{He}$

- *Observation*

${}^4\text{He}$ can be observed in galactic and extragalactic HII regions using either optical or radio recombination lines.

- *Conversion of observed lines into abundances*

Deriving an abundance from the observed lines is straightforward. However, corrections must be applied to compensate for excitation effects.

- *The evolution*

In stars, most of the hydrogen is converted into ^4He which is converted into heavier elements. Then, an excess of ^4He returns to the interstellar medium. Finally, one must account for an helium enrichment (Steigman et al. 1989).

- *The primordial abundance*

A widely adopted technique is to measure the abundance of another element, such as C, O, N in several regions. Then, one extrapolates to zero metallicity to estimate the primordial value. There are many recent independent analyses (Hogan 1997, Pagel 1997, Olive et al. 1997), with a debate over the systematic uncertainties in the observationally inferred Y_p and on the controversial object IZw 18 (the most metal deficient object of the sample). Based on 62 extragalactic, low metallicity HII regions, Olive et al. (1997) estimate:

$$\text{either } Y_p = 0.234 \pm 0.002(\text{stat.}) \pm 0.005(\text{syst.}) \text{ with IZw18} \quad (7)$$

$$\text{or } Y_p = 0.237 \pm 0.003(\text{stat.}) \pm 0.005(\text{syst.}) \text{ without IZw18.} \quad (8)$$

Based on another extragalactic sample which partially overlaps with that of Olive et al. (1997), Izotov and Thuan (1998) claim:

$$Y_p = 0.244 \pm 0.002$$

partly because they deduce a high Y_p for IZw18.

Disagreement aside, the two values do not contradict each other given the systematic uncertainty ~ 0.005 of the estimates. We can get a conservative upper limit $Y_p^{\text{max}} < 0.25$.

E D

- *Observations*

α) The deuterated molecules such as HD, CH_3O in the atmospheres of Jovian planets and Titan. But, deuterium has undergone strong fractionation.

β) UV transitions of HD and DI (Lyman series) caused by diffuse clouds on the line of sight to hot stars observed with the COPERNICUS and IUE satellites and now by the Hubble Space Telescope.

γ) The hyperfine line of DI at 91.6 cm which is very weak and difficult to observe.

δ) The deuterated molecules ($DCN, DCH^+, HCO^+ \dots$) from microwave transitions in molecular clouds.

- *Conversion of observed lines in abundances*

α) To derive the abundances from the deuterated molecules in the Jovian planets, one must do many corrections to account for isotopic fractionation by chemical reactions and physical processes during the formation of the planets and for radiative transfer effects in their atmosphere (see in particular Encrenaz 1999 and references therein).

β) There was some controversy about the reality of some *deuterium features* obtained in particular by the COPERNICUS satellite (Vidal-Madjar et al. 1983, Steigman 1988). The nearby star Capella has Lyman- α in emission with interstellar absorption component supposed that have been more recently observed and analysed using the Hubble Space Telescope, but there could be some minor variations in the D/H ratio along different lines of sight (Linsky et al. 1993, 1995, Vidal-madjar et al. 1998).

γ) It seems that searches for DI hyperfine structure line transition at 91.6 cm has been unsuccessful.

δ) The quantitative interpretation of the molecular line observed in the interstellar molecular clouds is very complicated by various fractionation effects. While these observations are very interesting for the interstellar chemistry, they cannot bring any information on the primordial D/H ratio

- *Corrections for evolution*

It is the simplest element of the four: no one has found a way to produce D at a level approaching that of the Big Bang nucleosynthesis. Moreover D is a fragile nucleus: it is converted into ^3He inside any star. Hence,

the abundance of D can only have gone down since the Big Bang ! The highest observed D abundance is a lower limit to its primordial value.

- *On the primordial abundance of D from galactic measurements*

From galactic measurements (Linsky et al. 1995, Vidal Madjar et al. 1998), from Hubble Space Telescope HST-GHRS observations in direction of Capella, one can say:

$$\left(\frac{D}{H}\right)_p \geq 1.6 \pm 0.1 \times 10^{-5} \quad (9)$$

But: *although this is a lower limit to the primordial abundance, we do not know the history of the galaxy well enough to reconstruct the primordial D from galactic observations.*

The most promising technique is to estimate the $(D/H)_p$ ratio from quasar absorption lines.

- *Primordial D from quasar absorber observations*

Recently, observations of intervening systems at high redshifts, with low metallicities have been performed. Hogan (1997) has presented eight plausible detections of extragalactic deuterium abundance from Keck data with quite contradictory estimates of the D/H ratio: a high value at about

$$D/H \sim 2 \times 10^{-4}$$

others with a low value at about

$$D/H \sim 3 \times 10^{-5}$$

However, Hogan (1998) and Burtler & Tytler (1998) give the recent apparent convergence towards the lower value of D/H , i.e.:

$$\left(\frac{D}{H}\right)_p \sim 3.4 \pm 0.3 \times 10^{-5} \quad (10)$$

More accurate measurements of the (D/H) ratio at high redshift are needed.

- Remark: There is no Galactic conflict with a high primordial deuterium abundance since chemical evolution can destroy D by a factor of 10 or more.

Before discussing the comparison between predicted and observed primordial abundances, let us briefly present some recent developments in Big Bang nucleosynthesis.

IV CONCLUSIONS ON THE SBBN MODEL

We have reviewed the synthesis of the light elements in the context of the standard Big Bang Cosmology and we have compared the predicted abundances of D , ${}^3\text{He}$, ${}^4\text{He}$ and ${}^7\text{Li}$ (see also figure 3) with the current observational data.

If one adopts a very conservative view, one can say that there is *concordance* between predictions and measurements for all the three elements: D , ${}^4\text{He}$, ${}^7\text{Li}$ (primordial abundance of ${}^3\text{He}$ is not measurable). The spread of published results reflects our *ignorance* and/or *systematic errors*. The basic conclusions of SBBN on baryon density are remarkably robust, i.e.

$$0.01 \leq \Omega_b h^2 \leq 0.025 \quad (11)$$

$$\text{or } \Omega_b h^2 \sim 0.015 \quad (12)$$

If our goal is more ambitions -i.e. a test of the SBBN model and a precise measurement of Ω_b or η - there is a potential problem (the so-called SBBN crisis !). In effect there is some inconsistency between the observed value $Y_p \sim 0.234 \pm 0.002 \pm 0.005$ and the low observed $D/H = 3.4 \pm 0.3 \times 10^{-5}$ which involves a collapse of the Ω_b band -in figure 9- towards the high Ω_b side with $\Omega_b h^2 \sim 0.002 \pm 0.005$ and therefore a high value for the central primordial ${}^4\text{He}$ mass fraction (~ 0.245). Our conclusion therefore is: more ${}^4\text{He}$ and D observations at *high redshifts* are needed !

V CHEMISTRY DURING THE EXPANSION

After the short period of nucleosynthesis, the main elements of the Universe are such that:

$$H(\sim 76\%), \quad {}^4\text{He}(\sim 23\%)$$

$$D/H(\sim 10^{-5}), \quad {}^3\text{He}/H(\sim 10^{-5})$$

$${}^7\text{Li}/H(\sim 10^{-10})$$

As the Universe expands and cools, different routes lead to molecular formation.

A Cosmological recombination

Recombination of the primeval plasma in the expanding Universe has been investigated by many authors from the pioneer works of Peebles (1968) and Matsuda (1969). More recently Bernshstein et al. (1977), Dubrovich (1975) then Dubrovich & Stolyarov (1995) studied spectral disturbances of the planck CMBR spectrum due to recombination of the matter.

We have seen in Signore & Puy (1999) that nucleosynthesis provides mainly light elements such as H , D , He and Li .

- *Helium recombination*

Helium ${}^4\text{He}$ is the first element to recombine. The helium recombination occurs in two steps:

- at $z \sim 6000$ where the first electron recombines and singly ionized HeIII :

- then at $z \sim 2700$, HeII recombines into a neutral state, with the sequence:

The conditions for the helium recombination are such that both cases essentially occur in accordance with the Saha equation (discussed in more detail in the next section for hydrogen recombination). Dubrovich & Stolyarov (1997) shown that these two phases of helium recombination give an amplitude of the disturbances of the CMBR spectrum, $\Delta T/T$, which can reach 10^{-6} for the first recombination and 3×10^{-7} for the second (the decrease in the degree of ionization during the recombination of matter gives rise to a recombination photon).

- *Hydrogen recombination*

Due to the binding energy of atomic hydrogen ($I=13.6$ eV), as the Universe continue to cool until $T < 13.6$ eV ($\sim 10^5$ K), the formation of bound atomic structure is energetically favoured. However the high entropy of the Universe delays this process until a temperature of $T_{\text{rec}} \sim 0.3$ eV corresponding to the redshift $z_{\text{rec}} \sim 1300$. Therefore for $T < T_{\text{rec}}$, most of the hydrogen and e^- combine to form neutral atomic hydrogen leaving behind a small fraction ($\sim 10^{-5}$) of free electrons and protons.

The disappearance of free charged particles reduces the scattering cross-section (Thomson scattering). Finally the photons decouple from the rest of the matter; this happens at $T \sim T_{\text{dec}} \sim 0.26$ eV, T_{dec} corresponding to the redshift $z_{\text{dec}} \sim 1100$.

The knowledge of T_{rec} (or z_{rec}) is particularly important because it gives the end of recombination and the beginning of the chemical phase of the Universe when the first molecules are formed, as we will see. T_{rec} , at which hydrogen atoms are formed, can be computed with two assumptions:

- The medium is in thermodynamical equilibrium.
- The recombination proceeds through the electrons and protons combining to form a hydrogen atom in the ground state.

In thermodynamical equilibrium, the number densities are:

$$n_i = g_i \left(\frac{m_i T}{2\pi} \right)^{3/2} \exp \left[\frac{\mu_i - m_i}{T} \right]$$

where the i index means electrons, protons or H atoms. The equilibrium is maintained by the reaction

$$p + e^- \leftrightarrow H + h\nu . \quad (13)$$

The balance of chemical potential gives in this case :

$$\mu_p + \mu_{e^-} = \mu_H$$

because photons in equilibrium have zero chemical potential. The statistical weights are

$$g_p = g_{e^-} = \frac{g_H}{2} = 2$$

and the masses are related by

$$m_H c^2 = (m_e + m_p) c^2 - I .$$

where I is the ionisation potential. The global charge neutrality gives $n_e = n_p$. Let us introduce the ionization fraction x given by

$$x = \frac{n_e}{n_p + n_H} \sim \frac{n_e}{n_{tot}}$$

it follows that

$$\frac{x}{1-x} \sim 3.84 \eta \left(\frac{T}{m_e} \right)^{3/2} \exp \left(\frac{I}{T} \right)$$

with $\eta \sim 2.68 \times 10^{-8} \Omega_b h^2$ (see Danese & de Zotti 1977). Therefore, the Saha equation for the hydrogen recombination can be written as:

$$\frac{x^2}{1-x} = \frac{1}{n_{tot}} \frac{m_e k T}{2\pi h^2} \exp \left(-\frac{I}{T} \right)$$

Thus, if we define T_{rec} as the temperature at which 90 per cent of the electrons have combined with the protons, i.e. $x \sim 0.1$, we obtain the corresponding temperature

$$T_{rec} = T \sim 0.3 \text{ eV}$$

which associate to the redshift

$$z_{rec} \sim 1300$$

This simple description supposes that the recombination process produces hydrogen atom in the ground state.

- *Lithium recombination*

The sequences of lithium recombination are similar to that of the helium recombination:

$$Li^{3+} + e^- \rightarrow Li^{2+} + h\nu$$

$$Li^{2+} + e^- \rightarrow Li^+ + h\nu$$

$$Li^+ + e^- \rightarrow Li + h\nu$$

Nevertheless the ionisation potential of lithium $I = 6.9$ eV is small. Therefore, at the end of the hydrogen recombination, Li atoms are not completely recombined. We will see, in the next section, the importance of this fact on the lithium chemistry.

VI MOLECULAR FORMATION

We have seen that the ions became progressively neutralized in the order of their ionization potentials. At the time neutral helium was formed the hydrogen and lithium are still ionized. With the creation of a neutral species, molecular ions could be formed and initiated the molecular formation.

The chemistry of the early Universe is the chemistry of the elements H and its isotope D , helium and its isotopic forms 4He , 3He and lithium and its isotopic forms 7Li , the ongoing physical reactions are immense after the recombination of hydrogen.

The main processes are collisional (ionization, radiative recombination, attachment...) and radiative due to the presence of the cosmic background radiation (photoionization, photodissociation, photodetachment). The other processes such as collisional excitations are negligible.

The first molecular ions to be formed are HeH^+ and He_2^+ through the radiative association reactions:

The rate coefficients of reactions have been calculated by Roberge & Dalgarno (1982). It is possible at the same time that the molecular ion $LiHe^+$ has been formed through the same process:

Nevertheless the rate of coefficient is not well-known. Dissociative recombinations:

contribute to destroy the molecular ions. These very efficient dissociative recombinations to accelerate the neutralization of H^+ and Li^+ and therefore to limit the relict ionization. Nevertheless the photodestruction processes are particularly efficient at $z \sim 1300$ and after the recombination of hydrogen. The productions of HeH^+ , He_2^+ and $LiHe^+$ are very small. The chemistry of the early Universe is really initiated by the formation of the first molecules: H_2 .

• Formation of H_2

The study of molecular formation in the post-recombination epoch has grown considerably in recent years. Since the work of Saslaw & Zipoy (1967), this subject has been reviewed by Lepp & Shull (1984), Dalgarno & Lepp (1987), Black (1988), Puy et al. (1993) and Galli & Palla (1998). Different routes lead to H_2 formation, each initiated by slow radiative process:

and

the photodetachment of H^-

and the photodissociation of H_2^+ :

by the background radiation field restrict the abundance of molecular hydrogen formed at the early stages. The photodissociation cross section are referenced in Puy et al. (1993). Note that the photodestruction of molecular hydrogen is found to be negligible. The temperature of the background radiation is too small ($T_r < 3000$ K) to drop the threshold of H_2 destruction. Radiative association (H_2 formation in interstellar medium):

which must be done via adsorption on grains is impossible in the post-recombination medium due to the non-existence of grains at high redshifts.

- *Formation of HD*

Although similar processes contribute to the formation of HD , its formation proceeds mainly through:

and its destruction is efficient through the photodissociations:

In addition the HD molecule has a permanent dipole moment and can be also formed by radiative association:

but this formation is very slow. The formation of HD may also be enhanced by the radiative association reactions:

followed by

- *Formation of LiH*

The situation is very different concerning LiH molecules. Lepp & Shull (1984) suggested that the formation was provided by the only radiative association:

Knowing that the ionization potential of $Li(I)$ is shorter than that of hydrogen, Dalgarno & Lepp (1987) suggested the existence of Li^+ ions after the recombination of hydrogen. Stancil et al. (1996) developed a model of primordial lithium chemistry in the early Universe.

Following these authors, one can say that LiH molecules are formed mainly through the exchange reaction:

and the associative detachment:

These reactions are coupled with the following destruction reactions:

and exchange reactions:

Nevertheless, many rates of reactions are not well-known and just estimated. Therefore *LiH* chemistry is not yet complete. Recently Gianturco & Gori-Giorgi (1996) have carried out a fully quantum mechanical treatment of the reaction:

They have found that the radiative association of *LiH* molecule starting from lithium atoms that are electronically excited, *Li(2p)*, is much more efficient than the one starting from lithium atoms in their ground state, *Li(2s)*. The rate coefficients of this reaction is six orders of magnitude greater than that of the reaction $Li + H \rightarrow LiH + h\nu$ as was pointed out by Lepp & Shull (1984).

On the other hand, to obtain, at these redshifts, the first electronic excitation of lithium atoms;

photons, with $\lambda \sim 0.69 \mu\text{m}$ or $E_\nu \sim 1.75 \text{ eV}$, are needed. Since the de-excitation of lithium atoms through spontaneous emission:

occurs in times of the order of 10^{-6} sec ; a bath of such photons would have maintained lithium atoms in the first electronically excited state *Li(2p)*. Gori-Giorgi argues that (private communication) if this background of photons is a black-body ($\lambda \sim 0.69 \mu\text{m}$, $T \sim 3020 \text{ K}$) the abundances of lithium atoms would have been such as :

$$Li(2p) \sim 10^{-3} Li(2s)$$

because the constant rate of the reaction $Li(2p) + H(1s) \rightarrow LiH + h\nu$ is 10^6 greater than that of the reaction $Li + H \rightarrow LiH + h\nu$, the final *LiH* abundance is more important. Moreover one must also note that photons (with $\lambda \leq 0.5 \mu\text{m}$, $E_\nu \geq 2.5 \text{ eV}$) could destroy *LiH* through photodissociation. Therefore Gori-Giorgi concludes that the best opportunity for obtaining a high abundance would be the existence of a background of photons such as:

$$0.5 \leq \lambda \leq 0.69 \mu\text{m}$$

$$1.7 \text{ eV} \leq E_\nu \leq 2.25 \text{ eV}.$$

What are the possible scenarios which could have led to a background of photons ? The existence of particle decay could be a plausible scenario (see discussions in Signore & Puy 1999). Nevertheless, here we will not consider the electronic excitation of lithium atoms.

VII EVOLUTION

Although primordial gas is a *simple mixture* of hydrogen, deuterium, helium and lithium, we have a large possibility of reactions.

The numerical integration of the coupled chemical equations is an initial value problem for stiff differential equations.

For a classical reaction $A + B \rightarrow C$, in order to calculate the abundance n_C , one must solve the equation

$$\frac{dn_C}{dt} = kn_A n_B$$

where n_A , n_B , n_C are the number densities of species A , B , C , k the reaction rate and t the time. Since the reaction rates depend on temperature, the temperature and density evolution equations must be solved simultaneously, which needs in turn the simultaneous determination of molecular cooling and heating rates.

A Thermal molecular functions

Below 3000 K, only rotational levels of the molecules can be excited (the first vibrational energy level of H_2 is excited for $T < 6000$ K).

The population of the rotational levels is mainly due to collisional excitation and de-excitation with H , H_2 and He on one hand and to radiative processes (absorption from CMBR and spontaneous or induced emission) on the other hand. These processes are fast enough to reach a statistical equilibrium between the energy levels, in which case the population of all levels can be computed using detailed balance equations:

$$\begin{aligned} n_i \sum_{j' \leq i} (k_{ij'}^X n_X + A_{ij'} + B_{ij'} u^{ij'}) + n_i \sum_{j' \geq i} (k_{ij'}^X n_X + B_{ij'} u^{ij'}) \\ = \sum_{j \geq i} (k_{ij}^X n_X + A_{ij} + B_{ij} u^{ij}) n_j + \sum_{j \geq i} (k_{ij}^X n_X + B_{ij} u^{ij}) n_j \end{aligned} \quad (14)$$

where i, j or j' denote the rotational levels of the molecules; n_i is the abundance of the level i , k_{ij}^X is the rate of collision with species X leading to a transition from level i to level j , A_{ij} the radiative transition probability of spontaneous emission, B_{ij} the Einstein coefficient of induced emission and u^{ij} the intensity of the radiation field at frequency ν_{ij} . The population of the rotational levels, which is related to the mean temperature, is computed for the first rotational levels ($J = 0$ to 14) for H_2 , HD and LiH between $z = 1000$ to $z = 5$.

Molecular cooling corresponds to collisional excitation followed by radiative transition. Molecular heating is due to radiative excitation from cosmic background radiation followed by collisional de-excitation. Notice that, although the radiative de-excitation is order of magnitude faster than collisional one (as the excitation rates have the opposite ordering), the full cooling and heating processes must be evaluated.

We introduce the de-excitation collisional probability P_{ji}^c :

$$P_{ji}^c = \frac{n_X k_{ji}^X}{n_X n_j k_{ji}^X + n_j A_{ji} + n_j B_{ji} u^{ji}} \quad (15)$$

and the de-excitation radiative probability P_{ji}^r between the levels i, j :

$$P_{ji}^r = \frac{n_X n_j A_{ji} + n_j B_{ji} u^{ji}}{n_X n_j k_{ji}^X + n_j A_{ji} + n_j B_{ji} u^{ji}} \quad (16)$$

and the energy radiated per unit volume (or molecular cooling) is then:

$$\Lambda_{mol} = \sum_j n_j \sum_i n_X n_i k_{ij}^X P_{ji}^r \epsilon_{ji} \quad (17)$$

and the energy gain from the cosmic background radiation per unit volume (molecular heating):

$$\Gamma_{mol} = \sum_j n_j \sum_i n_i B_{ij} u^{ji} P_{ji}^c \epsilon_{ji} \quad (18)$$

where ϵ_{ji} is the energy difference between levels i and j . The ratio between the cooling and heating is:

$$\eta = \frac{\Lambda_{mol}^j}{\Gamma_{mol}^j} = \exp\left[T_j\left(\frac{1}{T_m} - \frac{1}{T_r}\right)\right] \quad (19)$$

where the temperature T_j corresponds to the energy ϵ_{ji} . In the cosmological context after the decoupling between matter and radiation, the radiation temperature T_r is always greater than matter temperature T_m . Thus, the molecular cooling is lower than the molecular heating, and molecules contribute to transfer energy from the cosmic background radiation to matter, as do Compton interaction.

The relations are used to estimate the cooling and heating fluxes due to the molecules H_2 , HD and LiH . Since H_2 is an homonuclear molecule, radiative transitions within the lowest electronic state involve only quadrupole transitions whose rates are taken from Danby et al. (1987). Collisions rates of the H_2 molecule with H , H_2 and He are the ones used by Abgrall et al. (1982).

HD and LiH molecules have a lower excitation temperature than H_2 (112 K and 21 K respectively). Since both molecules have a dipole moment ($\mu_{HD} = 8.3 \times 10^{-4}$ debye, Abgrall et al. 1982 and $\mu_{LiH} = 5.88$ debye, Wharton et al. 1960), radiative decay is much faster. We take here $10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$ as conventional value for the collision rates of LiH and HD with H .

B Evolution of temperatures and abundances

The adiabatic expansion of radiation is given by:

$$\frac{dT_r}{dt} = -T_r H_o (1+z)^{3/2} \quad \Omega_o = 1 \quad (20)$$

where H_o is the Hubble constant and Ω_o the density parameter. Coupling between matter and radiation via the Thomson diffusion, after the phase of recombination ($z \leq 1000$) in the expanding Universe, leads to a thermal evolution equation:

$$\frac{dT_m}{dt} = -2T_m H_o (1+z) \sqrt{1+\Omega_o z} + \frac{8\sigma_T a_{bb} T_r^4}{m m_e c} x_e (T_r - T_m) \quad (21)$$

where a_{bb} is the black body constant, σ_T the Thomson cross section, x_e the ionisation fraction, m_e the electron mass and c the speed of light (we shall keep further below the radiation temperature equation unchanged since the amount of energy transferred from radiation to matter is found to be small). Once the molecules form, the thermal evolution equation must also take into account a molecular source term. Due to the expansion and to the chemical reactions, the comoving particle density evolves as:

$$\frac{1}{n} \frac{dn}{dt} = -3H_o (1+z) \sqrt{1+\Omega_o z} + \frac{1}{n} \left(\frac{dn}{dt} \right)_{ch} \quad (22)$$

(the subscript ch denotes the contribution of chemical reactions). We thus obtain:

$$\begin{aligned} \frac{dT_m}{dt} = & -2T_m H_o (1+z) \sqrt{1+\Omega_o z} + \frac{8\sigma_T a_{bb} T_r^4}{3m_e c} x_e (T_r - T_m) \\ & + \frac{2(\Gamma_{mol} - \Lambda_{mol})}{3nk} + \frac{2\Theta_{ch}}{3nk} - \frac{T_m}{n} \left(\frac{dn}{dt} \right)_{ch}, \end{aligned} \quad (23)$$

where $\Gamma_{mol} - \Lambda_{mol}$ is the energy heat-loss function, the term $\left(\frac{dn}{dt} \right)_{ch}$ characterizes the variation of density due to the chemistry. Θ_{ch} is the chemical heating and cooling calculated from the Hess Law:

$$\Theta_{ch} = \sum_i k_i n_i^X n_i^Y \Delta H_i$$

where k_i is the reaction rate of the reaction i , n_i^X and n_i^Y the abundances of species X and Y produced in reaction i and ΔH_i is the enthalpy of the reaction i . These two chemical contributions remain negligible. The initial elemental abundances are given by the standard model of nucleosynthesis (see Signore & Puy 1999).

The integration starts at $z = 1000$ with an electronic abundance of 10^{-1} . We take the following initial values $H/H^+ = D/D^+ = 1/9$.

Relative abundances of H_2 , HD , H^+ , D^+ , HD^+ are shown on Figure (1). H_2 abundance rises through two processes. The first step corresponds to the H_2^+ channel: $HD^+ + H \rightarrow HD + H^+$. In Figure (2), we plot the abundance of LiH , LiH formation becomes effective when the photodestruction decreases ($z \leq 400$).

Note that in Figures (4) and (5), the final abundances of H_2 , HD and LiH are *freeze-out* due to expansion. Collisional reactions are inefficient due to the decrease of the density.

In Figure (6), we compare molecular heating and cooling with the contribution due to the Compton heating. The main source of heating is due to the Compton process. We see that molecular Compton heating is dominant. We find that molecular heating is dominated successively due to H_2 then HD .

VIII CONCLUSIONS

Let us emphasize the importance of two preliminary results:

1) The ability of primordial HD molecules to heat/cool primordial gas when H_2 becomes inefficient:

- during the expansion of the Universe molecules are a net heating source: H_2 molecules dominate the heating at $T > 150$ K while HD molecules dominate at $T < 150$ K.
- during the collapse of protostructures molecules are a net cooling source -see Puy & Signore 1999-

2) The presence of molecules -such as LiH , LiH^+ , which have a large dipole moment -could be of a very great interest in the early Universe. In effect, if their abundance is high enough, they may be detectable through resonance enhanced Thomson scattering of the CMB photons -de Bernardis et al. 1993, Dubrovich 1993, Melchiorri & Melchiorri 1994, Maoli et al. 1994, 1996, Signore et al. 1994, 1997. Supposing a very high rate for the reaction:

-informed by the group of Dalgarno- all these authors have shown that LiH could: i) erase primary CMB anisotropies (at some frequencies) during the expansion of the Universe, ii) induce secondary anisotropies (at some frequencies) if these molecules are condensed into large moving clouds.

Primordial chemistry is a new field in astrophysics. A lot of reactions rates must be calculated or measured in laboratories. Let us only notice that: i) in particular many groups are working on a better treatment of recombination reactions, ii) for example in a near future, a galactic observation of LiH will be done at the CSO (Caltech Submillimeter Observatory, Hawai-USA) in order to confirm or to infirm the lithium chemistry.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Stéphane Charlot, Philippe Jetzer, Lukas Grenacher, Bianca Melchiorri-Olivo and Francesco Melchiorri for valuable discussions on this field. Part of the work of D. Puy has been conducted under the auspices of the *D^r Tomalla Foundation* and Swiss National Science Foundation.

FIGURES CAPTIONS

Figure 1: Reaction network of the SBBN model.

Figure 2: Dependence of the final abundances of primordial synthesized light elements on η (from Sarkar 1996).

Figure 3: SBBN abundance yields versus baryon density Ω_b (from Schramm 1998). The *concordance region* is large due to inclusion of possible systematic errors on Li/H . The width of the curves represents the uncertainty due to input of nuclear physics in the calculation.

Figure 4: Evolution of the primordial abundances after the recombination of hydrogen ($z < 1000$)

Figure 5: Evolution of lithium species after the recombination of hydrogen ($z < 1000$)

Figure 6: Processes of heating in 10^{20} erg cm $^{-3}$ s $^{-1}$. Λ_{adiab} is the adiabatic cooling, Γ_{compt} the Compton heating, Γ_{molec} the molecular heating and Λ_{molec} the molecular cooling.

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- FIGURE 2 -

- FIGURE 3 -

Primordial abundances

- FIGURE 4 -

- FIGURE 5 -

- FIGURE 6 -