Hunt for Molecules
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MOLECULAR ECHOGRAPHY OF THE EARLY UNIVERSE

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Abstract. Molecules are found in a large variety of astrophysical environnements. They are now widely used as diagnostic probes of the physical conditions in which they occur, and the diversity of molecular frameworks has helped to stimulate interest in different chemical processes. The chemistry of the early Universe is the chemistry of the light elements and their respective isotopic forms. The chemical evolution of the Universe must leave its imprints on the Cosmic Microwave Background (CMB) through resonant scattering of CMB photons by atoms, ions and molecules. In this lecture, the main steps of the chemical evolution of the Universe -the light and heavy element formation as well as the ionization history and the metallicity evolution- are reviewed and briefly discussed.

1 Introduction

Big bang nucleosynthesis (BBN) theory predicts the abundances of the elements produced during the first three minutes after the big bang. Let us briefly recall that the standard model (SBBN) predicts the abundances of

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the light elements, deuterium, helium (^{3}He and ^{4}He) and lithium (^{7}Li) while some departures from the standard model - for example the inhomogenuous model (IBBN) - can also produce heavier elements.

1.1 SBBN

The theoretical description of SBBN requires only a few basic assumptions:

- global expansion is governed by General Relativity,
- particles interactions are governed by the Standard Model of particles physics,
- distributions of particles are governed by stastistical physics and the knowledge of a dozen of nuclei cross sections.

The model has one parameter only: $\rho_{\rm b}$ the density of baryons or η, the baryon-to-photon ratio, see Sarkar (1996) and Signore & Puy (1999). Here, let us only recall the main steps.

At its very beginning (T >>10^{10} K), the Universe was a hot, expanding plasma, with most of its energy in radiation and relativistic particles. In particular, there were electrons, positrons, neutrinos $(\nu_{\rm e}, \nu_\mu, \nu_\tau)$, antineutrinos $(\overline{\nu}_{\rm e}, \overline{\nu}_\mu, \overline{\nu}_\tau)$ and photons. Nucleons were outnumbered while there were no composite nuclei. Weak processes, such as:

$$\nu + n \longmapsto p + e^- \tag{1.1}$$

maintained the ratio of neutrons to protons at its thermal equilibrium value:

$$\frac{N_{\rm n}}{N_p} \sim 1 \ . \tag{1.2}$$

At t ~ 1 sec, T ~ 10^{10} K,the weak processes became non effective, and:

$$\frac{N_{\rm n}}{N_p} \sim \frac{1}{6} \ . \tag{1.3}$$

Decreasing temperatures and densities slowed processes and maintained nuclear statistical equilibrium; therefore, one can calculate the amounts of the newly formed nuclei : D, ^{3}He ,^{3}H and ^{4}He.

After 5 minutes, most protons remained free, most neutrons were in ^{4}He nuclei and much smaller yields of D, ^{3}He and ^{7}Li were synthesized. Low density, Coulomb barriers and the lack of stable elements at A = 5 and A = 8 worked against the formation of larger nuclei. A priori, in SBBN, the elemental composition of the Universe remained unchanged until the formation of the first stars, several billion years later.

Until recently, comparison between the predicted and observationally determined light element abundances provided a general test of concordance and could be used to determine the baryon content in the Universe. Cyburt (2004) shows, in particular, that there is no value of baryon density for which any abundance observations agree well ! Treating all observations equally, Cyburt introduces the notion of *marginal concordance* with a baryon-to-photon ratio such as:

$$\eta_{10} = 10^{10}\,\eta \,\leq\, 7 \tag{1.4}$$

He also considers the two D values from Kirkman (2003) and finds the corresponding ranges:

$$5.93 \,\leq\, \eta_{10} \,\leq\, 6.62 \quad \text{and} \quad 5.93 \,\leq\, \eta_{10} \,\leq\, 6.47 \tag{1.5}$$

But measurements of the CMB anisotropies now supplant BBN as the premier baryometer. In particular, the results from WMAP, see Spergel et al. (2003), lead to:

$$5.89 \,\leq\, \eta_{10} \,\leq\, 6.39 \quad \text{and} \quad 0.0215 \,\leq\, \Omega_{\mathrm{b}}\, h^2 \,\leq\, 0.0233\;. \tag{1.6}$$

As it is noted by Cyburt (2004), this is a 4% measurement which makes it a sharper probe than any light element currently is. Therefore, one can predict the light element abundances with this baryon density. With this WMAP's baryon density or η one get :

$$\begin{array}{rcl} 0.2480 \leq & Y_p & \leq 0.2490 \\ 2.35\times10^{-5} \leq & D/H & \leq 2.76\times10^{-5} \\ 3.40\times10^{-10} \leq & {}^7Li/H & \leq 5.17\times10^{-10} \end{array} \tag{1.7}$$

Let us remark that if one uses the CMB as the premier cosmic baryometer removing η as a free parameter, one can use SBBN in a new way: either one can gain more information in astrophysics or *new physics* beyond the *Standard Model.* In closing, one can say that the future of SBBN has many possibilities: though all futures will rely on the increased rigor from theory, observations and experiments.

1.2 IBBN

In the framework of SBBN, one can note that there are also traces of ^{6}Li , ^{9}Be , ^{11}B with mass fraction at the level of 10^{-16}-10^{-13} and also of ^{12}C at the level of 5×10^{-15}. But, inhomogeneous Big Bang nucleosynthesis (IBBN) offers a possibility to bridge the mass gaps at A=5 and A=8 via in particular the reaction sequence:

$$^7\mathrm{Li}(\mathrm{n},\gamma) \;\; ^8\mathrm{Li}(\mathrm{n},\alpha) \;\; ^{11}\mathrm{B}(\mathrm{n},\gamma) \;\; ^{12}\mathrm{B}\,(\beta^-)\,^{12}\mathrm{C}\ . \tag{1.8}$$

It is conceivable,though not necessarily probable, that some primordial nuclei with nucleon number A≥12 - are synthesized in scenarios of IBBN, if a small fraction of all cosmic baryons reside in very high density regions at the epoch of BBN. In particular (e.g. Jedamzik et al. 1994), given a baryon-to-photon ratio: $\eta \sim 10^{-4}$ in these high density regions, one can show that:

$$\left[\frac{\mathrm{O}}{\mathrm{C}}\right] \sim 1.3 \quad \text{and} \quad \left[\frac{\mathrm{C}}{\mathrm{Z}_{\mathrm{A}>28}}\right] \sim -1.5 \tag{1.9}$$

most iron group elements are formed. Let us note that the model of Matsuura et al. (2005) produces also very heavy nuclei. Anyway, we need to know whether heavy elements (supposed to be observed at high z) were synthesized in IBBNs or in supermassive stars via supernova explosions (see section 4).

2 Primordial chemistry

Studies on the primordial chemistry (or post-recombination chemistry) have seen a tremendous increase in the litterature. The first chemical networks including primordial molecules (such as H_2, HD and LiH) and ions were carried out by Lepp & Shull (1984), Puy et al. (1993) and more recently by Galli & Palla (1998), Stancil, Lepp & Dalgarno (1998) and Pfenniger & Puy (2003). The development of the primordial chemistry studies owe to Dalgarno an important contribution concerning the calculations of the reaction rates (see Dalgarno & Lepp 1987, Puy et al. 1993, Galli & Palla 1998, and references therein).

In the cosmological context there are no grains which can catalyze the formation of molecular hydrogen, thus any H_2 formed in the uniform background is dissociated by the radiation, until the density is too low to produce it.

Two ways are possible to form H_2 molecules. One concerns the charge transfer:

$$H_2^+ + H \to H_2 + H^+ \tag{2.1}$$

initiated by the radiative association

$$H + H^+ \to H_2^+ + \gamma. \tag{2.2}$$

The second way is relative to H^- by the reactions:

$$H + e^- \to H^- + \gamma \text{ then } H^- + H \to H_2 + e^- \tag{2.3}$$

The photodetachment of H^- and the photodissociation of H_2^+ by the background radiation field restrict the abundance of molecular hydrogen formed at early stages, although the photodestruction of molecular hydrogen is negligible. Its destruction is due to collisional dissociation.
Deuterium chemistry in an early Universe could play an important role in the sense that it could give some explanations on the controversy observations of fractional abundance in high redshift Lyα. Although similar processes contribute to the formation of HD:

$$D^+ + H \to HD^+ + \gamma \text{ then } HD^+ + H \to H^+ + H_2, \tag{2.4}$$

its formation also proceeds through:

$$H^+ + D \to D^+ + H \text{ then } D^+ + H_2 \to H^+ + HD\ . \tag{2.5}$$

The presence of helium in the early Universe gives rise to a rich assembly of molecular processes (see Roberge & Dalgarno 1982) and leads to the formation of HeH^+:

$$He + H^+ \to HeH^+ + \gamma. \tag{2.6}$$

The H_2^+ ions and H_2 produce HeH^+ by the fast reactions

$$H_2^+ + He \to HeH^+ + H \text{ and } H_2 + He^+ \to HeH^+ + H\ . \tag{2.7}$$

The lithium chemistry is initiated by the recombination of lithium, which occured near the redshift $z \sim 450$. The molecular ion LiH^+ is formed by radiative association processes (see Stancil et al. 1996):

$$Li^+ + H \to LiH^+ + \gamma \text{ then } H^+ + Li \to LiH^+ + \gamma \tag{2.8}$$

species	$z = 1000$	$z = 100$	$z = 10$
$[H_2]$	3.25×10^{-12}	3.06×10^{-7}	1.13×10^{-6}
[HD]	2.3×10^{-16}	9.79×10^{-11}	3.67×10^{-10}
$[HeH^+]$	1.43×10^{-22}	7.13×10^{-15}	4.6×10^{-14}
[LiH]	2.04×10^{-49}	1.22×10^{-20}	2.53×10^{-20}

Table 1. Molecular abundances at redshifts $z = 1000$, $z = 100$ and $z = 10$.

which open the way of the formation of the LiH molecules through the exchange reactions

$$LiH^+ + H \rightarrow LiH + H^+, \tag{2.9}$$

which are more rapid than the formation by radiative association of H and Li atoms.

In order to estimate the molecular abundances which depend on the reaction rates[1], it is necessary to know the thermal and dynamical evolution of the medium, see Puy & Pfenniger (2005) for a complete discussion. Fig. 1 shows the evolution of chemical abundances between redshifts $z = 10000$ and $z = 10$. After a transient growth all molecular abundances become almost constant. The final abundances of H_2, HD, HeH^+ and LiH *freeze out* due to the expansion, molecular abundances are presented in Tab. 1 for redshifts $z = 1000$, $z = 100$ and $z = 10$.

3 Primordial objects

Gravitational instability and thermal instability are supposed to be the main processes to form condensations in a dilute gas. In the framework of the gravitational instability theory, each structure started as a tiny local overdensity; nevertheless very little is known about the protoclouds. Fluctuations that survive decoupling are subject to gravitational instabilities if

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[1] the complete chemical network is described in Puy et al. (1993), Galli & Palla (1998), Stancil et al. (1998) and Puy & Pfenniger (2005).

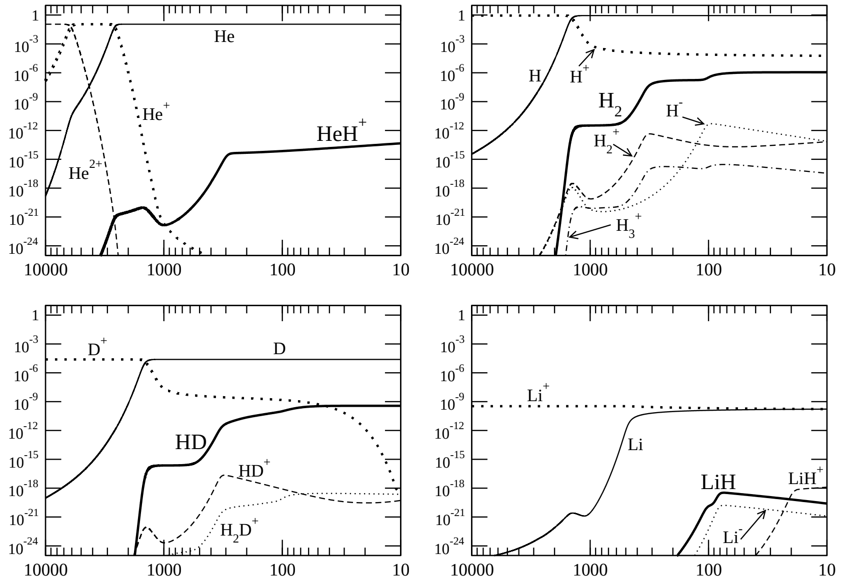

Fig. 1. Evolution of chemical abundances. The ordinates indicate the relative abundances, while the abscissas the redshifts. The frames show the chemistries of He, H, D, and Li respectively (from Puy & Pfenniger 2005).

their sizes are on sufficiently large scale.

Early studies focused on the chemical evolution and cooling of primordial clouds by solving a chemical reaction network within highly idealized collapse models (see Puy & Signore 1996 and Tegmark et al. 1997).

Further collapse proceeds almost isothermally, and considerable fragmentation occurs. Lepp & Shull (1984) emphasized that the dipole rotational transitions of HD are particularly important at high density and low temperature. Puy & Signore (1997) examined the evolution of primordial molecules in a context of gravitational collapse and showed how the abundances can be modified. The importance of HD molecules was pointed out by Puy & Signore (1998) where they analysed the ratio between the molecular cooling due to HD and that due to H_2, and found that the main cooling agent around

200 K is HD. This result was confirmed by Okumurai (2000), Uehara & Inutsuka (2000) and Flower et al. (2000).

4 Indications on possible metallicity histories of the Universe

We have seen that during the BBN epoch ($t < 5$ minutes), SBBN produces H, He,D, Li while IBBN produces the same elements and small amounts of *metals* (A$\geq$12). Then at the recombination epoch (i.e. t> 7000 years) starts the primordial chemistry of helium, hydrogen, deuterium and lithium.
The natural question is *What about metals ? their production ? their chemistry ?* Let us consider various recent observations:

- There is substantial inventory of metals in the intergalactic medium (IGM) over a wide range of redshift z=1.5 - 5.5, see Songaila (2001), Pettini et al. (2003).
- Studies of quasar absorption spectra have shown the following ionic species in the Ly-α forest: CIII, CIV, OIV, SiIII, SiIV, see Aguirre et al. (2004).

From these observations, there is no apparent evolution of *metals* over the redshifts between z = 1.8 - 4.1. Thus these metals must have been produced before z= 4.
On the other hand, observations of the most distant galaxies and quasars show that even the most distant objects (z = 5 - 6) have chemical abundance at the level of solar, see Freudling et al. (2003). Moreover, the determination of these abundances not only permits to trace the enrichment of the Universe by heavy metals but also gives information on the ionization history of the Universe.
Recent results from WMAP (Kogut et al. 2003), push the reionization redshift as far as z$\leq$20 suggesting a complex ionization history. From these results there is extensive discussion about the nature of reionization and also on the possibility for the Universe being reionized twice. Cen (2003) proposed a scenario in which the Universe was reionized early by Population III stars; but then much of the IGM recombined once these stars were no longer able to form; and the Universe was reionized a second time by the next generation of stars.
For example, in order to quantify the production of elements of this 2-stage model for the ionization history of the Universe, Qian and Wasserburg

(2005) consider: i) for the contribution of Population III stars, the very massive star models of Heger and Woosley (2002) which produced pair-instability SNe; ii) for the contribution at later epoch, the SNII models of Woosley and Weaver (1995).

Finally, in the framework of this 2-stage model for the ionization history of the Universe and in order to predict the possible detections which can be done from Planck HFI, Basu et al. (2004) consider the following atoms and ions as the most important ones: CI, CII, NII, NIII, OI, OIII, SiI, SiII, SI, FeI, FeII and FeIII.

5 Conclusions

With the observations of WMAP, the CMB has become the premier cosmic baryometer and has also given important information on the ionization history of the Universe. The chemical evolution of the Universe, presented here, could certainly have left its imprints through resonant scattering of CMB photons by atoms, ions and molecules. From an initial idea of Zel'dovich, Dubrovich (1977) actually showed that resonant scattering must be considered as the most efficient process in coupling matter and radiation at high redshift. This technique for exploring the dark ages of the Universe has been revisited by the Roma group (de Bernardis et al. 1993, Maoli et al. 1994, Melchiorri & Melchiorri 1994, Signore et al. 1994, and see the lecture of R. Maoli at this conference).

With future CMB observations, new analyses of observational data determining the primordial light element abundances and updated nuclear, atomic, ionic, molecular cross section data, we will be able to perform *precision cosmology* (see discussions in Melchiorri et al. 2003).

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