Abstract. Chemistry plays a particular role in astrophysics. After atomic hydrogen, helium and their ions, the Universe probably contains more mass in molecules than in any other species. Molecule formation in the early, pre-galactic Universe may have had much to do with the formation of galaxies themselves. In this context the possible interaction between primordial molecules and photons of the Cosmic Microwave Background (CMB) is very important through the theoretical perspectives and constraints which could give some information on the theory of the large scale structure formation.

In this paper we recall the more recent progresses on the chemistry of the early Universe, and describe the importance of molecules in the formation phase of proto objects. A special attention is done concerning the case of LiH.

1 Introduction

Molecules are found in a large variety of astronomical environments. They are now widely used as diagnostic probes of the physical conditions in which they occur. The diversity of molecular environments has helped to stimulate interest in a variety of different chemical processes.

According\footnote{1}{see the talk of Signore-Puy in this proceedings and Signore & Puy \cite{ref1}.} to the standard Big Bang cosmology, the space of the Universe expands adiabatically, cooling from an extreme initial temperature and density. Thus at about one second after the Big Bang, the temperature of the Universe remains hot and around $10^{10}$ K. At this stage, the collisions between neutrons and protons can form deuterium, and open the way of the primordial nucleosynthesis through other fusion reactions (see Signore & Puy \cite{ref1} and references
therein). At about 100 sec the nucleosynthesis epoch is over, thus most neutrons are in $^4\text{He}$ nuclei, and most protons remain free while smaller amounts of $^3\text{He}$, $^7\text{Li}$ are synthesized. The low densities, the Coulomb barriers and stability gaps at masses 5 and 8 worked against the formation of heavier elements.

After the nucleosynthesis period atoms form by recombination of these primordial nucleus with free electrons, leading to the thermal decoupling between the matter and the radiation (see Puy-Signore [2]). The radiative recombination processes were then not reversed by photoionization and electron impact ionization, as they had been earlier because the supply of energetic photons and electrons had diminished. The Universe was transformed into a neutral state, apart from the few relict ions and electrons left behind in the expansion.

The chemistry of the early Universe is the chemistry of the elements $\text{H}$, its isotope D, helium and their isotopic forms. 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 CMB (photoionization, photodetachment...). During the last decade, a large litterature has been developped on the chemical networks of the primordial chemistry (Lepp & Shull [3], Puy et al. [4], Stancil et al. [5], Galli & Palla [6], Puy & Signore [7] and [2] for historical description). Thus primordial molecules such as $\text{H}_2$, $\text{HD}$ and $\text{LiH}$ formed.

The existence of a significant abundance of molecules can be crucial on the dynamical evolution of collapsing objects. Because the cloud temperature increases with contraction, a cooling mechanism can be important for the structure formation, by lowering pressure opposing gravity. This is particularly true for the first generations of objects.

Thus, in the first part of this communication, we recall the main and recent results of the molecular influence on the formation of the proto-objects, particularly that of $\text{H}_2$ and $\text{HD}$ molecules. Interactions between primordial molecules and CMB could be important. In the second part, we will recall the potential importance of $\text{LiH}$ molecules on the CMB anisotropies. In particular, the scattering process of CMB photons on $\text{LiH}$ molecules could play an important role and lead to produce secondary anisotropies on the spectrum of CMB. We will conclude this communication on the possible outlooks.

2 Importance of $\text{H}_2$ and $\text{HD}$ for cosmology

As we have seen, early Universe chemistry has been previously investigated by many authors. $\text{H}_2$ and $\text{HD}$ molecules are the most abundant molecules, and could play a non-negligible role on the formation of the first objects of the Universe. These molecules could contribute to cooling function and lead to dynamical influence on the collapse mechanism. Moreover although the abundance of $\text{H}_2$ molecules is rather insensitive to the choice of cosmological model, the abundance of $\text{HD}$ molecules shows large variations.
2.1 $H_2$ MOLECULE

Eddington [8], then Strömgren [9] were the firsts to suggest that $H_2$ might exist in the interstellar space. Herzberg [10] described the quantum mechanics of homonuclear molecules in some details, which opened important theoretical works on $H_2$ in astrophysics. Although the medium is free of grains after the cosmological recombination, the formation of $H_2$ comes into play through the ions $H^-$ and $H_2^+$. In the post-recombination medium the radiation is hotter than the matter. In this context the radiative excitation of the rotational levels, which is here more efficient than the collisional excitation produces a heating -see Puy et al. [4].

Lepp & Shull [3] were the firsts to point out this important characteristics, which was confirmed by Puy et al. [4] with a better estimation of the thermal function. In the gravitational collapse the situation is very different [1]; the temperature of CMB is below than the matter inside of the collapse. Thus the thermal balance between matter and radiation leads to produce a molecular cooling function, $H_2$ becoming a good coolant agent of the collapse.

The possibility to observe high redshift systems is mainly associated with the presence of quasars, i.e. strong background sources. Most of our knowledge of the Universe between $z = 1$ and 5 comes from the study of the Lyman-$\alpha$ absorbers in the optical range. In a mini-survey for molecular hydrogen in eight high-redshift damped Lyman-$\alpha$ systems, Petitjean et al. [12] confirmed the presence of $H_2$ in a system toward PKS 1232+082 ($z = 2.3377$). They show that there is no evidence for any correlation between $H_2$ abundance and relatively heavy element depletion into dust grains.

2.2 $HD$ MOLECULE

The role of deuterium was analyzed by Palla et al. [13], then completed by Stancil et al. [5], in the context of the chemical and thermal evolution of the gas component in the post-recombination Universe and more recently by Flower [14]. Puy & Signore [14] revealed that the $HD$ molecule is the main cooling agent, a result which was confirmed later by many authors such as Okumura [15], Uehara & Inutsuka [16] and Flower et al. [17]. Thus $HD$ molecules could have important consequence on the problem of fragmentation of primordial clouds in order to form first structures like massive stars. Searches for a primordial signature of $HD$ is crucial.

One must pointed out that very recently Varshalovich et al. [19] have analyzed the spectrum of the quasar PKS 1232+082 obtained by Petitjean et al. [12]. $HD$ molecular lines have been identified in an absorption system at the redshift $z = 2.3377$, this is the first detection of $HD$ molecules at high redshift.

\footnote{In this case the upper limits on the molecular fraction derived in nine of the systems are in the range $1.2 \times 10^{-7} - 1.6 \times 10^{-5}$.}
The case of LiH

From an initial idea of Zel’dovich, Dubrovich [20] showed that resonant elastic scattering must be considered as the most efficient process in coupling matter and radiation at high redshift. He noted that the cross section for resonant scattering between cosmic microwave background (CMB) photons and molecules is several orders of magnitude larger than that between CMB and electrons; even a modest abundance of primordial molecules would produce significant Thomson scattering.

During an elastic scattering between CMB photons and primordial molecules, a photon is absorbed and reemitted at the same frequency but not in the same direction. This process could have negligible effect because of low abundances of primordial molecules. Dubrovich [21], Maoli et al. [22], Signore et al. [23] showed that this effect could alter the primary spatial distribution of the CMB anisotropies. More precisely resonant scattering of CMB photons on LiH molecules can be particularly efficient for smoothing the primary anisotropies. Maoli et al. [22] pointed out that primordial molecules such as LiH may play significant role in altering the amplitude and power spectrum of CMB anisotropies; the effect depends essentially on the Li abundance and the lithium chemistry. They found that primary CBR anisotropies may be erased or attenuated for angular scales below 10° and frequencies below 50 GHz, if LiH primordial abundance, relative to H, exceed $10^{-10}$. In 1996 Stancil, Lepp and Dalgarno [24] implemented the first complete post-recombination lithium chemistry, and concluded that the final abundance of primordial LiH is below $10^{-18}$, which ruled out this possibility of erasing the primary anisotropies.

Different studies focused on the chemical evolution in primordial clouds by solving a chemical reaction network within idealized collapse models (see Puy & Signore [11], Anninos & Norman [25], Abel et al. [26]). Puy & Signore [15] examined the evolution of primordial molecules in a context of gravitational collapse and showed that primordial molecules could coexist in a collapsing proto-cloud, particularly during the first phase of gravitational collapse. Maoli et al. [27] emphasized the role that elastic resonant scattering through LiH molecules can be produced in this collapsing structure. If the scattering source has a non-zero component of the peculiar velocity along the line of sight, they showed that the elastic scattering is no more isotropic in the observer frame and molecular secondary anisotropies are produced in the CMB spectrum. The angular scale of these secondary anisotropies are therefore directly related to the size of the primordial clouds. Bougleux & Galli [28], then Puy & Signore [29] studied the chemistry of primordial LiH in a collapsing protocloud, from the chemical network of Stancil et al. [24] and the fully quantum mechanical treatment, of the radiative association of the excited Li states, developed by Gianturco & Gori-Giorgi [30]. We concluded that with this chemical network the LiH abundance is closed to $3 \times 10^{-18}$, leading to very low secondary anisotropies in the CMB.

Nevertheless a precise analysis of the chemical network shows that most of reaction rates are quite uncertain. For example the reaction rate of the main
reaction which dissociates the $\text{LiH}$ molecules:

$$\text{LiH} + H \rightarrow \text{Li} + \text{H}_2$$  \hspace{1cm} (1)

is constant and independent of the temperature and of the density!

4 Outlook

Although astrochemical observations started in the visible, they are dominated by the radio and above all by millimetre and sub-millimetre observations. Tentative of direct searches of primordial molecules were developed this last decade, but the results were not at the level of efforts of teams of observers (see for example De Bernardis et al. [31], Signore et al. [32], Combes & Wiklind [33]). Recently Papadopoulos et al. [34] revealed the discovery of large amounts of low-excitation molecular gas at redshift $z \sim 3.91$. Shibai et al. [35] investigated the observability of hydrogen molecules in absorption. They argued that the absorption efficiency of the hydrogen molecules become comparable with or larger than that of the dust grains in the metal-poor condition expected in the early Universe. Thus the absorption measurement of the hydrogen molecules could be an important technique to explore the primordial gas clouds that are contracting into first-generation objects.

The HERSCHEL satellite [36] could prove the origins of structure and the chemistry at the early interprotostructure medium and furnish a spectral atlas for molecules (see Encrenaz et al. [37]). A submillimetre spectra of protoclouids of gas could offer important constraints on the critical chemistry, on dynamics, on the heating and the cooling processes that occur in the primordial gas before and during gravitational collapse of protostructure. The research of primordial lines with HERSCHEL [36] could open an important new field of cosmology: the cosmochemistry.

Theory is essential for many aspects of astrochemistry (or cosmochemistry). Chemical models require chemical rates and these are not always available from experimentalists. The calculations of the minimum energy pathway and dynamical calculations are crucial. This last point is particularly important for lithium chemistry. Recently Zaldarriaga & Loeb [38] explored the imprint of the resonant 6708 Å line opacity of neutral lithium on the temperature anisotropies of the CMB at observed wavelengths of 250-350 µm. They showed that the standard CMB anisotropies would be significantly modified in this wavelength band. The primordial chemistry and particularly $\text{LiH}$ could give same conclusions and important consequences on the temperature and polarization anisotropies.

Very recently LoSecco et al. [39] argued that extragalactic cold molecular clouds could lead to a significant absorption on the CMB. They speculate that the use of very high resolution spectrometers on large aperture telescopes might facilitate a 1-2 order of magnitude improvements in the CMB temperature measurements at high redshifts. Such accurate observations would enable us to constrain the anisotropy, inhomegeneity of the Universe and the proto-chemistry.

We have seen the possibility of fragmentation of proto-clouds by the cooling due
to \( H_2 \) and \( HD \) molecules. This process could lead to the formation of primordial massive stars, which could be a possible source of contamination in heavier elements at early epochs. Then, the gravitational collapse of following objects (galaxies...) could be strongly influenced by the existence of heavier elements such as \( CO \), \( CI \) or \( HCN \).

Chakrabarti & Chakrabarti \cite{40} showed that a significant amount of adenine, a DNA base, may be produced during molecular collapse, through the \( HCN \) addition. Recently Sorrell \cite{41} outlines a theoretical model for the chemical manufacture of interstellar amino acids and sugars. This chemistry model explains the existence of both the amino acid glycine and the sugar glycolaldehyde; this last component was recently detected in millimetre-wave rotational transition emission from the star-forming cloud Sagittarius B2 \cite{42}. The formation of DNA bases could happen in the early history of the Universe. Pre-biotic molecules could have contaminated the first objects and planets from the beginning \cite{43}.

We are living in a golden age of astronomy, new observations with instruments such as NGST \cite{44}, PLANCK \cite{45} and HERSCHEL \cite{36}, will push forward the frontiers of our ignorance. As Herbst wrote: *Astrochemistry may not tell us much about the first three minutes, but ultimately it should tell us our place in the Universe.*

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