PART IV

THEORETICAL MODELING APPROACHES

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The Diffuse Interstellar Bands
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Carbon Interstellar Chemistry: Theory versus Observations

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Abstract. To study the interstellar chemical composition and interpret molecular observations, astrochemists have built chemical models over the years. Those models compute the composition of the gas and the icy mantles of interstellar grains taking in account a large number of processes, such as chemical reactions in the gas-phase, interactions with grain surfaces (sticking and evaporation) and chemical reactions at the surface of the grains. Those models rely on a number of parameters (physical parameters of the medium and intrinsic chemical parameters such as rate coefficients), which are estimated with an associated uncertainty. From a chemical point of view, those uncertainties are mainly due to an incomplete knowledge of the efficiency of the processes in the interstellar conditions. Many studies in the recent and past years have been undertaken to improve this knowledge, either using experimental or theoretical results in physico-chemistry.

Keywords. Astrochemistry, Chemical modeling, ISM, PAHs

1. Introduction to interstellar chemistry and chemical models

The interstellar medium (ISM) is composed of gas and dust at different densities and temperatures, and that are exposed to various levels of UV, X-ray and cosmic-ray irradiation levels. Fig. 1 shows the different types of environments of the ISM and the chemical processes that govern the chemical composition. In this proceeding, I will briefly describe here those processes and the chemical models that are used to study astrochemistry. For complete review on this topic, I refer to Wakelam *et al.* (2010a). In the diffuse medium, the density is low and the gas and dust is exposed to the UV photons produced by surrounding massive stars. As a consequence, photo-processes (dissociations and ionizations) dominates the chemistry and the gas is mostly composed of atoms at different levels of ionizations. Grains are mostly composed of refractory material and only the formation of H_2 on the grains is assumed to be efficient. In dense clouds, the only source of ionization is the interaction of gas-phase molecules with high energy particles of the cosmic-rays since the UV photons are absorbed by the dust at the border of the clouds. The cosmic-ray particles can dissociate and ionize the molecules and the atoms but the main effect is the ionization of H_2 and He. The ionization of H_2 is the first step for the formation of molecules in those clouds. Cationic molecular hydrogen reacts with H_2 to form H_3^+ and follows a sequence of ion-molecular reactions that allows the formation of many molecules. The ionization of H_2 by cosmic-rays produces high energy electrons that excite again H_2 by collision. The desexcitation of the H_2 then produces UV photons, which dissociate and ionize the molecules in the gas and at the surface of the grains inside cold dense clouds. This process is known as the Prasad & Tarafdar mechanism (Prasad & Tarafdar 1983). In addition to these processes, bimolecular reactions

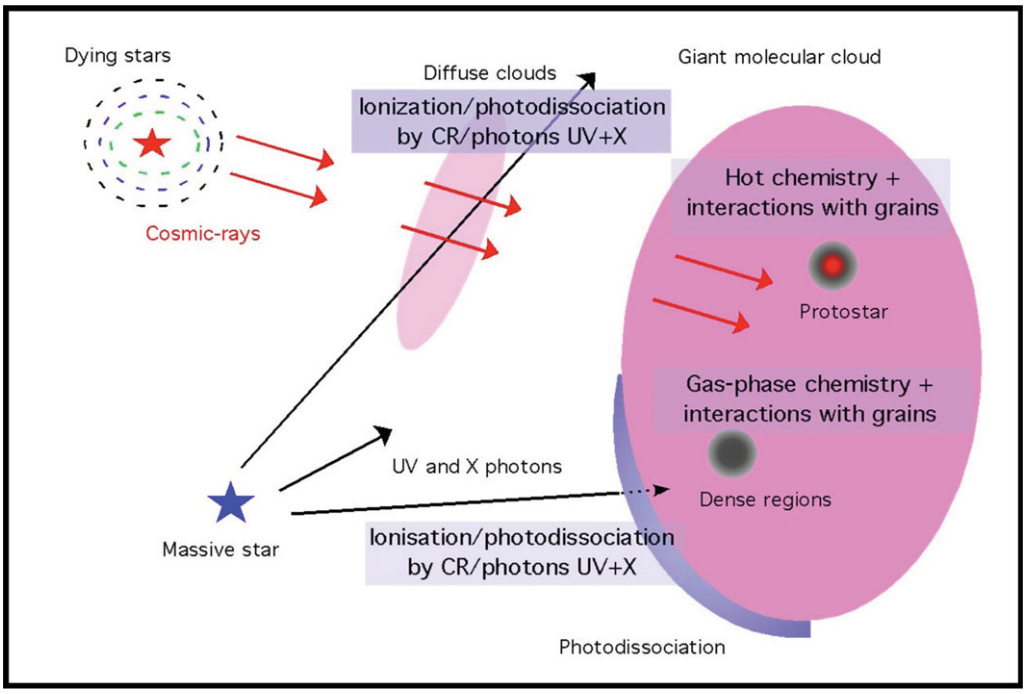

Figure 1. Sketch of the physico-chemical processes at play in the different environments of the interstellar medium (taken from Wakelam *et al.* 2012).

(ion-neutral, neutral-neutral, radiative associations, electronic recombinations) take place in those environments.

In dense environments, interactions between gas-phase species and grain surfaces produce an additional chemistry. When gas-phase species collide with grains, they can undergo van der Walls liaisons with the surfaces (physisorption) and deplete from the gas-phase. Once they are on the surface, they can diffuse and meet each other to react and produce new species. Gas-phase depletions and surface reactions produce an icy mantle at the surface of the grains mostly composed of water (H_2O) and carbon monoxide (CO). Species on the surface are also allowed to go back to the gas-phase by several processes: thermal evaporation (Hasegawa *et al.* 1992), evaporation induced by cosmic-rays (Léger *et al.* 1985) and exothermicity of surface reactions (Garrod *et al.* 2007). The different phases of the interstellar matter are summarized by Fig. 2.

To study the formation and destruction of molecules in the interstellar medium, astrochemists have developed, over the years, chemical models to take in account as much physicochemical processes as possible. Those models solve the kinetic differential equations to compute the species abundances as a function of time in the gas-phase and at the surface of the grains starting from an initial composition and assuming a set of parameters (mostly the physical conditions and the chemical network). We refer to Wakelam *et al.* (2012) for a complete review on chemical modeling. As an example, Fig. 3 shows modeling results for typical dense cloud conditions (a temperature of 10 K and a H total density of 2×10^4 cm^{-3}) starting from atomic gas.

As shown in Wakelam *et al.* (2010b), the two most important parameters for the chemical modeling of dense clouds are the reaction rate coefficients and the elemental abundances. The modeling abundances are strongly sensitive the reaction rate coefficients at early times whereas the uncertainty in the elemental abundances will determine the

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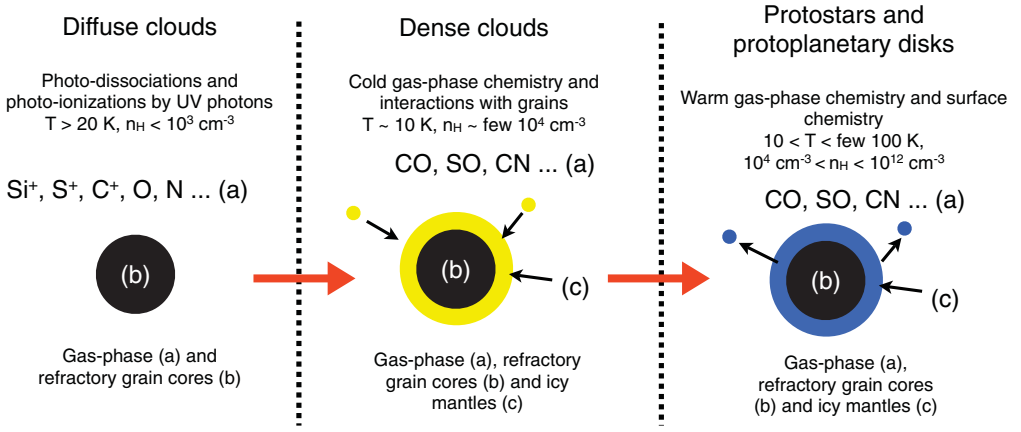

Figure 2. Sketch of the different phases of the interstellar matter depending on the environment. Phase (a) represents the gas (molecules and atoms in the gas-phase), Phase (b) is the core of the grains mostly composed of refractory material and phase (c) is the icy mantle.

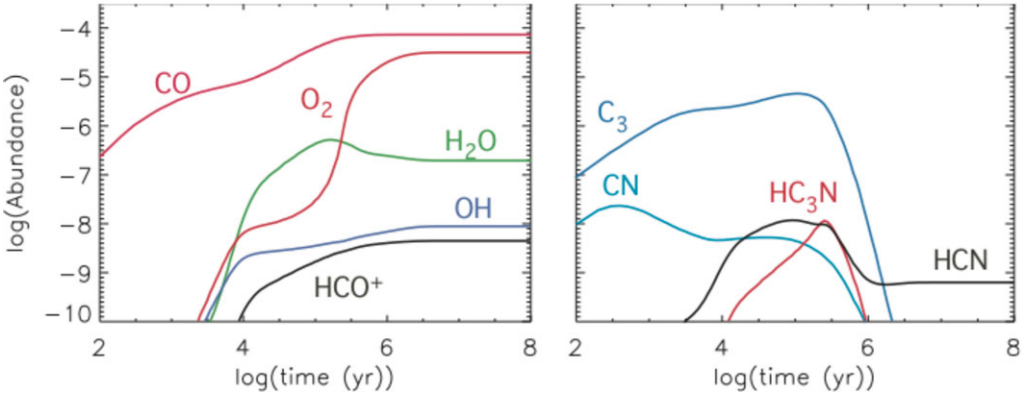

Figure 3. Molecular abundances predicted by a pure gas-phase chemical model for typical dense cloud conditions as a function of time (taken from Wakelam *et al.* 2012).

uncertainty in the model predictions at times later than a few 10^5 yr. The uncertainty in the elemental abundances is caused by the fact that we have no modeling of the chemical evolution of the interstellar material through the entire sequence of formation of dense clouds from the diffuse medium. It has been observed for many years now that depletion of atoms occurs in the diffuse medium. The observations of atomic lines in the visible and UV wavelength show a variation of the total atomic abundance in the gas-phase with the line of sight. This observed depletion seem to increase with the mean density in the line of sight (see Snow & McCall 2006, Jenkins 2009, Whittet 2010). The observations of atomic lines can only go up to a few 10 cm^{-3} in density. If one uses the observed gas-phase atomic abundances in the less diffuse medium as elemental abundances for dense cloud conditions, he/she will overproduce most of the molecular species observed in dense clouds:

- Diffuse O abundances → overproduces O_2 (Hincelin *et al.* 2011)
- Diffuse N abundances → overproduces CN, HCN, N_2H^+... (Hily-Blant *et al.* 2010)
- Diffuse S abundances → overproduces CS, SO, H_2S... (Wakelam *et al.* 2004)
- Diffuse Si abundances → overproduces SiO (Ziurys *et al.* 1989)
- Diffuse Cl abundances → overproduces HCl (Schilke *et al.* 1995)

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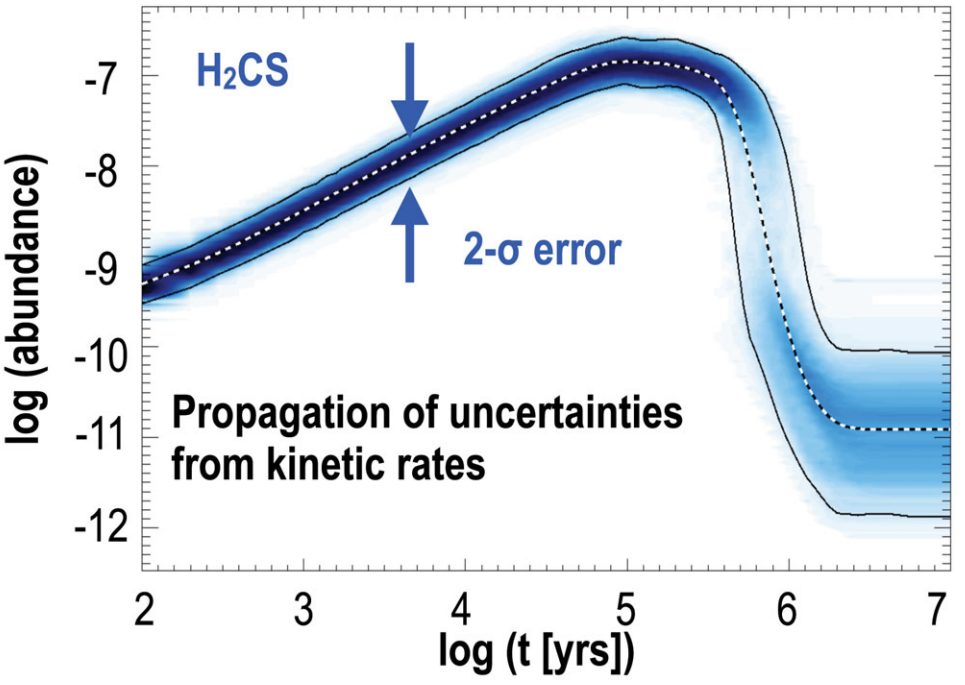

Figure 4. Prediction of the H_2CS abundance in a protostellar envelop (Wakelam *et al.* 2005). The dashed white line is the mean abundance and the blue envelop the two σ error bar on the abundance.

Modelers usually decrease those atomic abundances (by a factor of a few up to a factor of 1000) to reproduce the dense cloud observations (Graedel *et al.* 1982), Wakelam & Herbst 2008). However, there are many other uncertainties in these chemical modeling, such as the history of the gas and dust in the interstellar medium. The observed depletions in the diffuse medium is a clear indication that there are some physico-chemical processes at play in these environments and that there are chemical species, which contain the missing elements, that still need to be identified. Those species might very well be the carriers of the diffuse interstellar bands. We should develop chemical models of the different types of environments, including the diffuse medium and physical models of the interstellar matter evolution.

2. Comparing observed abundances and chemical model results

The only quantitative method to compare observed abundances and chemical model predictions is to take into account both the uncertainties in the observed and modeled abundances. Despite the fact that many observational studies do not provide error bars on their results, it is much more common to find them than error bars on modeled abundances. It is however possible to study the propagation of the uncertainties in the model parameters to the computed abundances. One source of errors in the models come from uncertainties in the physical conditions, elemental abundances, initial conditions and reaction rate coefficients. Using Monte-Carlo simulations in which the model parameters are randomly varied, error bars on the predicted abundances as a function of time can be estimated. Those methods are explained in Wakelam *et al.* (2006) and Wakelam *et al.* (2010b). Fig. 4 shows an example of such calculation. It represents the abundance of H_2CS in the gas-phase computed by a model for protostellar envelops as a function of

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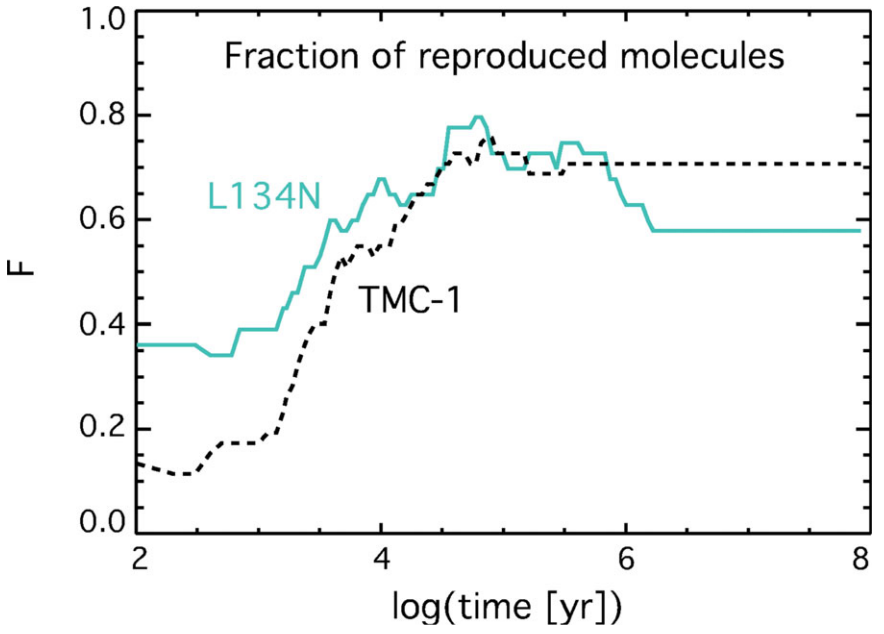

Figure 5. Percentage of molecules, which observed abundances are reproduced by the model, as a function of time in the two dark clouds TMC-1 (CP) and L134N (N) (from Wakelam *et al.* 2006).

time with the 2σ error bar from the Monte-Carlo simulations. Such simulations are time consuming because we need to run thousands of different models to properly cover the uncertainty range. For the moment, they are limited to pure gas-phase models. The main limitation to run those uncertainty calculations for gas-grain models is the definition of the uncertainty in the model parameters. Surface chemistry has a large number of parameters, which uncertainty needs to be defined. For example, binding energies of chemical species to the surface depends on the nature of the surface. In addition, many effects, such as the porosity of the grains, are not treated well enough in those models.

When error bars have been computed for the modeled abundances, it is then possible to study the general agreement of the model predictions with all the species that have been observed in a source. One way of doing that is to look at the times when the individual predicted abundances overlap the observed abundances taking into account both uncertainties. The time for which a maximum number of species is reproduced defines the best agreement of the model. Fig. 5 shows the result of such comparison, which was published in Wakelam *et al.* (2006). For this model, the observed abundances in two dark clouds were considered: TMC-1 (Cyanopolyyne Peak) and L134N (North Peak). Between 20 and 40 species have been observed and the molecular abundances can be find in the literature (see Garrod *et al.* (2007) for a list of observed abundances). Using a pure gas-phase model, we can reproduce between 70 and 80% of these molecules for a cloud age of about 10^5 yr.

3. Importance of PAHs for the formation of large molecules

One direct consequence of the presence of PAHs in clouds is the enhancement of the abundance of many complex organic molecules as shown in Wakelam & Herbst (2008). However, the efficiency of this process depends on the fractional abundance of small PAHs

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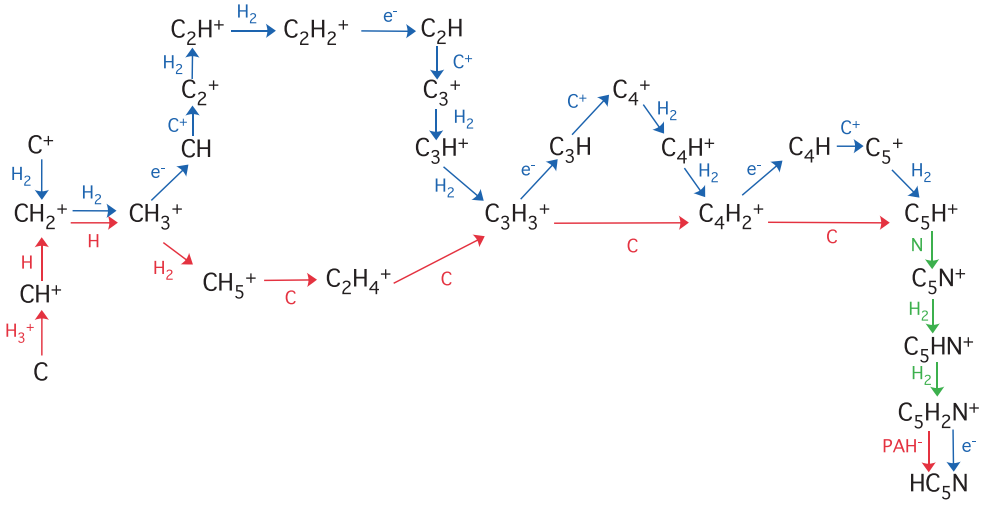

Figure 6. Formation paths of HC_5N under dense cloud conditions in the absence (blue) and presence (red) of PAHs. Green arrows show pathways that are common to the cases with and without PAHs.

that could be present in such environments. In fact, if the abundance of PAHs is larger than the ionization fraction (i.e. a few 10^{-8} compared to the total proton density), PAHs become the main carrier of negative charges. This has two consequences. The first one is that the cross section of PAHs being much larger than that of electrons, the electronic recombination of atomic cations is much more efficient with PAH^- than with electrons. The atomic cations are then much faster neutralized in the presence of PAHs. This opens new chemical paths for the growing of carbon chains as can be seen in Fig 6. In this figure, we show the main reactions leading to the formation of HC_5N in the absence of PAHs (blue arrows) and when PAHs are included in the model (red arrows). It takes much less reactions in the presence of PAHs thanks to reactions with neutral atomic carbon.

The second effect of the presence of PAHs is a process of neutralization of the cations less destructive. The recombination of cations with electrons, in most of the cases, produces the destruction of the molecular species into fragments. The dissociative recombination of C_3O^+ for instance produces C_2 and CO. We expect that with PAH^-, the energy released during the reaction is dissipated in the PAH so that the reaction $C_3O^+ + PAH^-$ would lead to a simple neutralization of C_3O. This way, the complex molecules are produced more efficiently. The effect of PAHs on the formation of complex organic molecules are shown in Fig. 7 for a few molecules. For those simulations, PAHs of about 30 carbon atoms (sizes of 4Å) with an abundance of 3×10^{-7} have been assumed.

In order to be more quantitative in those model predictions, better constraints on the abundance and sizes of the PAHs in dense clouds are indeed. In addition, large uncertainties remain for the rate coefficients and products of reactions such as $PAH^- +$ molecular and atomic cations.

4. Summary

To study the chemical composition of the interstellar medium, it is necessary to have a general view of the interstellar cycle and of the physicochemical processes that determine the chemical composition. Elements cannot be studied separately and without taking

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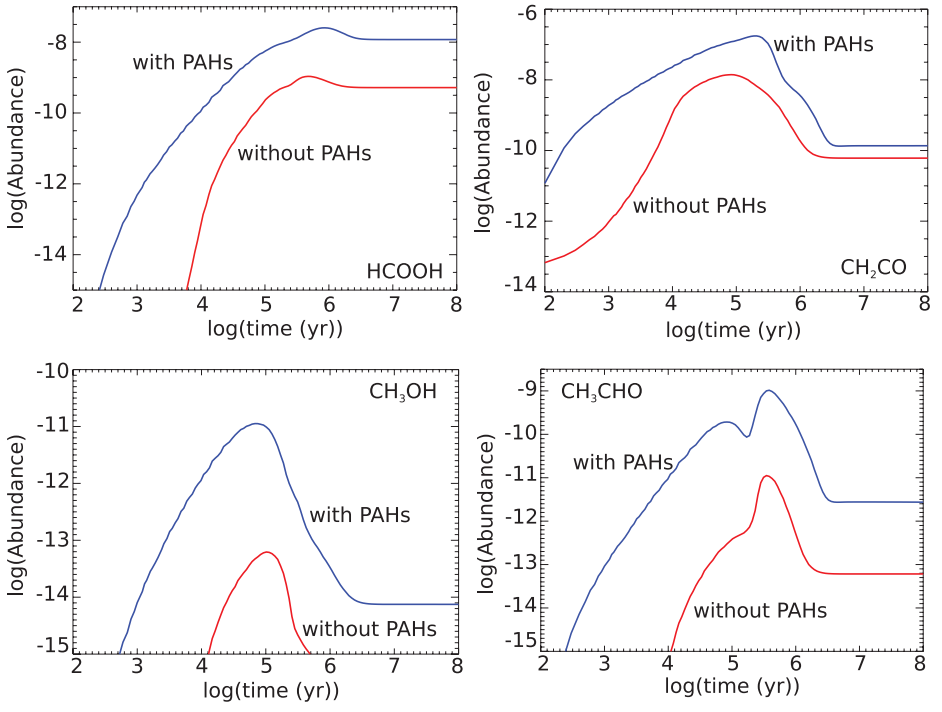

Figure 7. Prediction abundances of some complex organic molecules under dense cloud conditions in the presence and in the absence of PAHs (from Wakelam & Herbst 2008).

into account the general history of the interstellar matter. To solve the problem of the diffuse interstellar bands, one needs to get a global view of the chemical modification of the gas and dust at all stages of the formation of molecular clouds. Even the chemical composition of dense clouds depends on the composition of the diffuse medium they are made of. The depletion of the elements in the diffuse medium remains one of the most important source of uncertainties for the formation of complex organic in denser regions because it determines the amount of the different elements that are available for the gas and ice chemistries. The presence of PAHs in dense clouds could also have an important impact on the formation of those complex molecules.

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