

# Extreme Deuteration and Hot Corinos: the Earliest Chemical Signatures of Low-Mass Star Formation

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Low-mass protostars form from condensations inside molecular clouds when gravity overwhelms thermal and magnetic supporting forces. The first phases of the formation of a solar-type star are characterized by dramatic changes not only in the physical structure but also in the chemical composition. Since PPIV (e.g., Langer *et al.*), exciting new developments have occurred in our understanding of the processes driving this chemical evolution. These developments include two new discoveries : 1) extremely enhanced molecular deuteration, which is caused by the freeze-out of heavy-element-bearing molecules onto grain mantles during the Prestellar Core and Class 0 source phases; and 2) hot corinos, which are warm and dense regions at the center of Class 0 source envelopes and which are characterized by a multitude of complex organic molecules. In this chapter we will review these two new topics, and will show how they contribute to our understanding of the first phases of solar-type stars.

## 1. INTRODUCTION

Molecular clouds are the placentas inside which matter evolves from embryos to stars and planetary systems. The material in the molecular cloud feeds the newly forming system. During this formation, the material undergoes several dramatic changes. This chapter focuses on the changes of the chemical composition during the first phases of star formation.

There are several reasons why the study of chemistry in the first phases of star formation is fascinating and important. Among them, two stand out. First, *chemistry is a very powerful diagnostic*, both of the current and the past physical conditions of the forming protostar. Much of this chapter will be spent in illustrating that point in detail. In addition, *chemistry in the first phases of star formation may affect the chemical composition of the objects that will eventually form the planetary system*: planets, comets, and asteroids. In this sense, the study of chemistry during the first phases of star formation is far-reaching. Indeed, one of the major and more fascinating questions linked to the process of the formation of a star and its planetary system, especially if similar to our Solar System, is: *what is the chemical*

*budget acquired during the protostellar phase and inherited by the forming planets?* Answering this question might even shed some light on our own origins. The above ultimate question implies answering several linked questions: what molecules are formed during the protostellar phase? Do molecules exist that are formed prevalently during the protostellar phase, and that are therefore a hallmark of this period? What is their fate? Do they condense onto the grain mantles during the proto-planetary phase? Are they incorporated into planetesimals, which eventually form comets, meteorites and planets? Are these pristine molecules released into nascent planetary atmospheres during early, intense cometary bombardment? And what is the ultimate molecular complexity reached during star formation? In this contribution we will focus on the first questions, those related to the first phase of star formation.

The story starts with the first step towards collapse: the Prestellar Core phase (see the chapters by *Di Francesco et al.* and *Ward-Thompson et al.*). These objects are cold ( $\leq 10$  K) and dense ( $\geq 10^5 \text{ cm}^{-3}$ ) condensations inside molecular clouds. What makes them particularly important is that they are believed to be on the verge of col-

Table 1: Summary of the properties of a sample of Prestellar Cores.  $n_c(\text{H}_2)$  is the central density;  $f_D(\text{CO})$  is the CO depletion factor; the Molecular D/H ratio column contains the observed  $\text{N}_2\text{D}^+/\text{N}_2\text{H}^+$  and/or  $(\text{D}_2\text{CO}/\text{H}_2\text{CO})^{1/2}$  ratio.

Name	$n_c(\text{H}_2)$ ( $10^5 \text{ cm}^{-3}$ )	$f_D(\text{CO})$	Mol. D/H	Ref. <sup>a</sup>
L1521F	3	2.5	0.01	1,2,3
B68	1	3.4	0.03	3,4
L1689B	1	4.5	0.09	3,6,7,8
L183	10	12	0.22	3,9
L1544	14	14	0.23	3,6,10
L694-2	9	11	0.26	3
L429	6	16	0.28	3,6,7
OphD	3	14	0.44	3,6,7
L1709A	1	5.5	0.17	6,7
L1498	1	7.5	0.04	3,5
L1517B	2	9.5	0.06	3,5

<sup>a</sup>REFERENCES: 1- *Tafalla and Santiago* (2004); 2- *Hirota et al.* (2001); 3- *Crapsi et al.* (2005a); 4- *Bergin et al.* (2001); 5- *Tafalla et al.* (2004); 6- *Bacmann et al.* (2002); 7- *Bacmann et al.* (2003); 8- *Redman et al.* (2002); 9- *Pagani et al.* (2005); 10- *Tafalla et al.* (2002).

lapse (*Tafalla et al.*, 1998; *Caselli et al.*, 2002b; *Young et al.*, 2004; *Crapsi et al.*, 2005b), and, in this sense, they are considered to be representative of the initial conditions of star formation. During this phase, matter slowly accumulates towards the center under the gravitational force, which counteracts the thermal and/or magnetic pressure. As the density increases, gaseous molecules start to freeze-out onto the cold dust grains, forming  $\text{H}_2\text{O}$ -dominated ice mantles “dirtied” with several other molecules. The process is so efficient that in the innermost and densest regions of the condensation, heavy-element-bearing molecules are thought to be virtually all frozen out. The low temperatures and the disappearance of most molecules, and particularly of CO, from the gas phase trigger a peculiar chemistry: *an extreme molecular deuteration*.

Once gravitational contraction finally takes over, a protostar is born, consisting of a central object, which eventually will become a star, surrounded by an envelope from which the future star accretes matter. In the beginning, the envelope is so thick that it obscures the central object, and the Spectral Energy Distribution (SED) is totally dominated by the cold outer regions of the envelope, with a temperature lower than  $\sim 30$  K. This phase is represented by so-called Class 0 sources (*André et al.*, 2000). Most of the envelope is cold and depleted of heavy-bearing molecules, frozen onto the grain mantles, exactly as in Prestellar Cores. However, the presence of a central source, powered by gravitational energy, causes the heating of the innermost regions of the envelope. In these regions the dust temperature reaches 100 K, causing the evaporation of the grain mantles formed during the Prestellar-Core phase. The molecules trapped in the ices are injected back into the gas phase, giving rise to a

rich and peculiar chemistry. Complex organic molecules are found in these regions, called *Hot Corinos*.

In this chapter, we will show that extreme deuteration and Hot Corinos are specific signatures of the first phases of low-mass star formation. The chapter is organized as follows. We first briefly describe the physical and chemical structures of Prestellar Cores and Class 0 source (Section 2). We then discuss in detail the deuteration phenomenon (Section 3), Hot Corinos (Section 4), and the chemical models that have been developed to explain these observations (Section 5). The chapter ends with our conclusions.

We conclude this section by listing a few reviews appeared in the literature related to the subjects treated in this chapter. Previous reviews of the chemistry in general are reported in *Herbst* (2005), and during the star formation period in *van Dishoeck and Blake* (1998), *Langer et al.* (2000) and *Caselli* (2006). Reviews of the observations of multiply deuterated molecules as well as the related chemical models can be found in *Roueff and Gerin* (2003), *Cecarelli* (2004a) and *Millar* (2005), and on the Hot Corinos in *Cecarelli* (2004b).

## 2. THE PHYSICAL AND CHEMICAL STRUCTURE IN THE FIRST PHASES OF THE COLAPSE

Since PPIV, our understanding of the physical (temperature and density profiles) and chemical (molecular and atomic abundance profiles) structure of matter in the first phases of low-mass star formation has improved considerably. This is due both to the increased sensitivity of ground-based instruments and to the development of sophisticated models to interpret the data. In this section, we review the observations and their interpretations, which have led to the reconstruction of the gas density, temperature and molecular composition in both Prestellar Cores and Class 0 sources.

### 2.1. Prestellar Cores

Several authors have studied the physical and chemical structure of starless cores; detailed reviews are presented in the chapters by *Di Francesco et al.* and *Ward-Thompson et al.*. Here we briefly recall the basic properties characterizing Prestellar Cores, and discuss some aspects complementary to those presented by the mentioned authors. First, the density profiles of the studied Prestellar Cores are reasonably well represented by Bonnor-Ebert spheres. In practice, the density profile can be approximated by a power law  $r^{-2}$  in the outer regions and a plateau in the center regions of the Prestellar Core. In the following we will refer to the density in the plateau as the “central” density. Typically, the radius of the plateau is 3000-6000 AU (*Crapsi et al.*, 2005a). Figure 1 shows the example of L1544, one of the best studied Prestellar Cores (*Tafalla et al.*, 1998; *Caselli et al.*, 2002b,c), but other Prestellar Cores present basically the same structure (*Alves et al.*, 2001; *Crapsi et al.*, 2005a). In the same figure, the predicted temperature profile is also

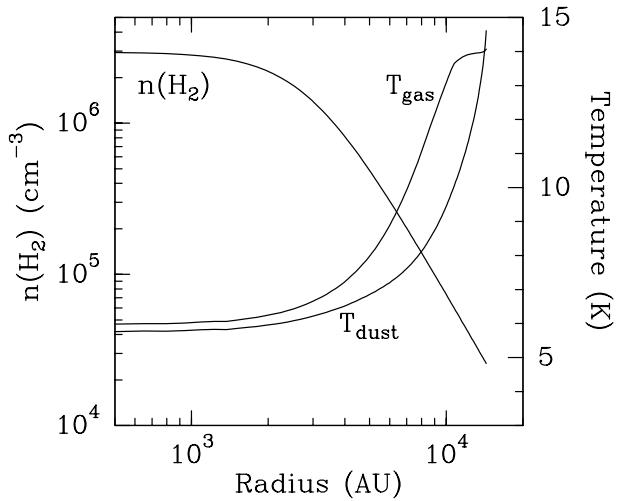


Fig. 1.— The density and temperature profiles derived for the Prestellar Core L1544 (adapted from Crapsi *et al.* in prep.).

shown. Note the temperature drop in the inner 3000 AU region, confirmed by observations of NH<sub>3</sub> (Crapsi *et al.* in prep.). A similar drop in the dust temperature has been previously observed in other Prestellar Cores (Evans *et al.*, 2001; Pagani *et al.*, 2003, 2004, 2005), as expected from radiative transfer modeling of centrally concentrated and externally heated dense cloud cores (Zucconi *et al.*, 2001). These large central densities and low temperatures are accompanied by the depletion of CO molecules in the central regions, as they condense out onto the grain mantles (Evans *et al.*, 2001; Caselli *et al.*, 1999; Galli *et al.*, 2002). Indeed, if one had to give a short list of properties for the Prestellar Cores they would be large central densities:  $\geq 10^5 \text{ cm}^{-3}$ ; very low central temperatures:  $\leq 10 \text{ K}$ ; depletion of molecular species, including CO; and enhanced molecular deuteration. Table 1 summarizes these properties in a sample of Prestellar Cores. In Figure 2 we show the observed CO depletion factors versus the central densities, where the depletion factor is computed with respect to the standard CO abundance in molecular clouds,  $9.5 \times 10^{-5}$  with respect to H<sub>2</sub> (Frerking *et al.*, 1982). As can easily be seen, there is a clear correlation between the CO depletion factors and the densities. This observationally confirms the basic idea that CO molecules disappear from the gas phase because they freeze-out onto the grains, and that the condensation rate is proportional to the density (see below). Figure 2 also reports theoretical curves, obtained assuming that the CO molecules condense onto the grains at a rate  $k_{\text{freeze}}$  and are released in the gas phase because of the evaporation caused by cosmic rays at a rate  $k_{\text{cr}} = 9.8 \times 10^{-15} \text{ s}^{-1}$  (Hasegawa and Herbst, 1993). The freezing rate can be written as follows:

$$k_{\text{freeze}} = S \langle \pi a_{\text{gr}}^2 v_{\text{CO}} \rangle n_g, \quad (1)$$

where we adopted a sticking coefficient  $S = 1$  (Burke and Hollenbach, 1983), and a mean grain radius of  $a_{\text{gr}}$ .

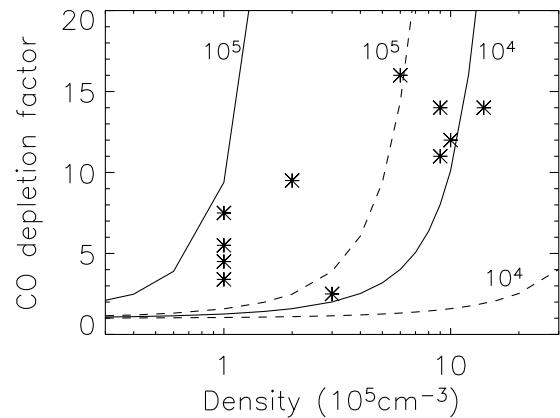


Fig. 2.— CO depletion factor versus the H<sub>2</sub> density. The asterisks represent the observations in the Prestellar Cores quoted in Table 1. The solid lines show the theoretical curves for an age of  $1 \times 10^4$  and  $1 \times 10^5$  yr, respectively, assuming an average grain radius of  $0.1 \mu\text{m}$ . The dashed lines are computed taking an average grain radius of  $0.5 \mu\text{m}$ .

The grain number density  $n_g$  is given by the (mass) dust-to-gas ratio (0.01) multiplied by the gas density, and divided by the grain mass (computed assuming a grain density of  $2.5 \text{ gm cm}^{-3}$ ). The figure shows curves assuming an average grain radius of  $0.1$  (solid lines) and  $0.5 \mu\text{m}$  (dashed lines) respectively. In the first case, which is the typical value assumed in chemical models for the ISM, the denser Prestellar Cores lie around the curve with an age of  $1 \times 10^4$  yr, which is definitively too short an age for these objects, based on several arguments. However, if the average grain radius is larger and equal to  $0.5 \mu\text{m}$ , for example, the observed points lie around the curve at  $1 \times 10^5$  yr, which is a more realistic estimate of the age of these objects. Larger grains would shift the curve even more to larger ages. Note that we used the same value for the cosmic ray evaporation rate, although increasing the grain sizes decreases it because of the larger volume to heat (Bringa and Johnson, 2004; Shen *et al.*, 2004), enhancing the effect. Since the surface  $\pi a_{\text{gr}}^2$  is dominated by the small grains, Figure 2 suggests that the small grains are efficiently removed by coagulation with large grains in the innermost regions of Prestellar Cores (Ossenkopf, 1993; Bianchi *et al.*, 2003; Flower *et al.*, 2005). Other explanations are also possible. For example, the cosmic ray evaporation rate can be enhanced if the ice mantles contain a substantial (1%) fraction of radicals due to UV photolysis (D'Hendecourt *et al.*, 1982, 1986). However, in order to explain Figure 2 the mantle evaporation rate should be increased by more than a factor 30 with respect to the Hasegawa and Herbst (1993) rate. Therefore, our preliminary conclusion is that, most likely, the average sizes of the grains in Prestellar Cores are larger than in the

ISM, and that these objects are older than about  $1 \times 10^5$  yr. It is also interesting noticing that less dense Prestellar Cores point to greater ages and/or smaller average grain sizes. It is not clear at this stage whether this means that those cores will not evolve into denser ones, or whether Prestellar Cores spend more time in this first “low-density” phase than in the “high-density” phase.

## 2.2. Class 0 sources

The physical and chemical structure of the envelopes of Class 0 sources is affected by the presence of a central object, i.e. a heating source, which implies gradients in the density and temperature. This, in turn, implies a gradient in the chemical composition of the gas across the envelope. Two basic methods have been used in the literature to derive the chemical and physical structure of Class 0 envelopes: i) modeling of multi-frequency observations of several molecules, and ii) modeling of the continuum SED and map, coupled with molecular multi-frequency observations. The first method makes use of the intrinsic property that each line from any molecule probes the specific region where the line is excited, namely a region with a specific density and temperature. Using several lines from the same molecule can, therefore, be used to reconstruct the *gas* density and temperature profiles of the envelope. The observations of several molecules are then used to derive the abundance profile of each molecule. Theoretical examples of this method, applied to the problem of collapsing envelopes, are discussed in Ceccarelli *et al.* (2000a), Maret *et al.* (2002a), Ceccarelli *et al.* (2003), and Parise *et al.* (2005b). In these models the density is assumed to follow the evolution of a Singular Isothermal Sphere contracting under the hypothesis of isothermal collapse - the so-called “inside-out” framework, developed by Shu and collaborators (Shu, 1977). In this framework, the density follows a two-slope power law: in the regions not reached by the collapse the density has an  $r^{-2}$  dependence, whereas in the collapsing regions the density follows an  $r^{-3/2}$  law. In addition, in using molecular line observations, one has to also take into account the abundance profile of the molecule used. The simplest profile is that of a single step function, which assumes that the relevant molecule has an almost constant abundance in the cold outer envelope and a jump in the inner region when the grain mantles sublime. Other profiles have been used though, in which the abundance also has a drop in the outer envelope, to take into account the molecular depletion as in Prestellar Cores (Ceccarelli *et al.*, 2001; Schöier *et al.*, 2004; Jørgensen *et al.*, 2004).

The second method uses the dust continuum SED simultaneously with maps to trace the H<sub>2</sub> distribution, and the observations are best-fitted with assumed single power law density distributions (Shirley *et al.*, 2002; Jørgensen *et al.*, 2002; Williams *et al.*, 2005; Young and Evans, 2005). Then, in order to derive the molecular abundance profiles, single-jump and/or drop models are used to interpret multi-frequency observations, as in Schöier *et al.* (2002), Schöier

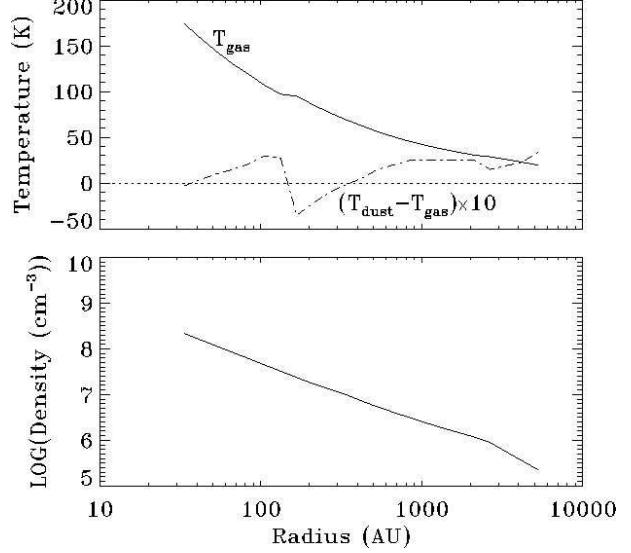


Fig. 3.— The temperature (upper panel) and density (lower panel) profile of the envelope surrounding the Class 0 protostar IRAS16293-2422 (figure from Ceccarelli *et al.* (2000a)).

*et al.* (2004), Jørgensen *et al.* (2004), and Evans *et al.* (2005). Both methods give approximatively the same structure (temperature and density distribution) when applied to the same object, as in the case of IRAS16293-2422 (Ceccarelli *et al.*, 2000a; Schöier *et al.*, 2002). Figure 3 shows the derived structure of the envelope of this source, obtained by applying the first method to several molecules (Ceccarelli *et al.*, 2000a,b).

Both classes of models predict the existence of regions with dust temperatures larger than 100 K, the sublimation temperature of the grain mantles (Ceccarelli *et al.*, 1996). In these regions, therefore, the components of the grain mantles are injected into the gas phase, and the abundances of the corresponding molecules should increase with respect to the abundance in the cold ( $T_{dust} \leq 100$  K) envelope. Water is the major component of the ice mantles, but unfortunately water lines are not observable from ground-based telescopes. The spectrometer LWS on board ISO provided observations of water lines towards a few Class 0 sources (Ceccarelli *et al.*, 1999), but with relatively poor spatial and spectral resolution, so that the interpretation of the data is not unique. Two interpretations have been advanced. The first one assumes that the water lines originate in the shocks at the interface between the outflows and the envelopes of these sources (Giannini *et al.*, 2001; Nisini *et al.*, 2002). The second one assumes that the water lines originate mostly in the envelope. Based only on the ISO data, it is impossible to discriminate observationally between the two hypotheses. However, if the water line spectra are interpreted as being emitted in the envelope, allowing a jump in the water abundance in the  $T_{dust} \geq 100$  K region, the agreement among the model predictions and the observed line fluxes is rather good (Ceccarelli *et al.*, 2000a;

(Maret *et al.*, 2002b). The observed data are reproduced if the water abundance is  $\sim 3 \times 10^{-7}$  in the outer envelope, and jumps by about a factor 10 in the inner region. In support of this interpretation, the physical structure derived by this analysis is substantially confirmed by observations of other molecules obtained with ground-based telescopes (see below).

Formaldehyde is also an important grain mantle component, and this molecule has the advantage that it has several transitions in the millimeter to sub-millimeter wavelength range observable with ground-based telescopes (Mangum and Wootten, 1993; Ceccarelli *et al.*, 2003). These observations have a much better spatial and spectral resolution than ISO-LWS and provide stronger constraints for the models. A survey of the H<sub>2</sub>CO line emission towards a bit fewer than a dozen Class 0 sources has shown that all the targeted sources, except VLA16293, have a region where the formaldehyde abundance jumps by more than one order of magnitude (Ceccarelli *et al.*, 2000b; Maret *et al.*, 2004). Several of these sources also show jumps in the methanol abundance (Maret *et al.*, 2005). The predicted sizes of the jump regions range from 10 to 150 AU, and are, therefore, comparable to the sizes of the Solar System. The densities are predicted to be larger than  $10^8 \text{ cm}^{-3}$ . However, one should be aware that the above observations have been obtained with *single-dish* telescopes, which, at best, have spatial resolutions corresponding to about 1000 AU in radius. Therefore, both the estimates of the abundances and the warm region sizes suffer from a relatively large uncertainty. Besides, the details of the model adopted in the analysis of the data give rise to additional systematic uncertainties so that the very existence of the H<sub>2</sub>CO abundance jumps is contested by some authors (Schöier *et al.*, 2004; Jørgensen *et al.*, 2005c,a). In addition, the situation is further confused by the presence at small scales of cavities and outflows, which some authors also consider a major component in the line emission attributed to the abundance jumps of the above analysis (Chandler *et al.*, 2005; Jørgensen *et al.*, 2005b).

Finally, several simple molecules (HCO<sup>+</sup>, N<sub>2</sub>H<sup>+</sup>, CS, SO, SO<sub>2</sub>, HCN, HNC, HC<sub>3</sub>N and CN) have been observed in a sample of Class 0 sources (Jørgensen *et al.*, 2004). Given the observed transitions, this study was able to trace the abundance of the observed species in the outer envelope and probe some formation routes, such as for N<sub>2</sub>H<sup>+</sup> and HCO<sup>+</sup>. One remarkable result is the discovery of large regions in the outer envelopes where the molecular abundances are depleted, because of condensation onto grain mantles (Maret *et al.*, 2004; Jørgensen *et al.*, 2005d). However, even more remarkable is the discovery of extreme deuterium fractionation in the Class 0 sources, which will be discussed in Section 3, and which is indeed linked to the molecular depletion.

In summary, from a chemical point of view, the similarity to Prestellar Cores is the most prominent characteristic of the outer envelopes of Class 0 sources. With respect to

molecular depletion and extreme deuteration, they are indeed virtually indistinguishable, suggesting that Prestellar Cores are the likely precursors of Class 0 sources (Maret *et al.*, 2004; Jørgensen *et al.*, 2005c).

### 3. EXTREME DEUTERATION

The previous section has anticipated a major characteristic shared by Prestellar Cores and the envelopes of Class 0 sources: an extreme molecular deuteration. Although the deuterium abundance is  $1.5 \times 10^{-5}$  relative to hydrogen (Linsky, 2003), singly deuterated molecules have been observed in both types of objects with abundances relative to their hydrogenated counterparts between 10% and 50% (Guélin *et al.*, 1977; Loren *et al.*, 1990; van Dishoeck *et al.*, 1995; Tiné *et al.*, 2000; Shah and Wootten, 2001; Roberts *et al.*, 2002; Crapsi *et al.*, 2004, 2005a). Even more extreme, doubly and triply deuterated molecules have been observed (Table 2) with D/H ratios reaching 30% for D<sub>2</sub>CO (Loinard *et al.*, 2002) and 3% for CD<sub>3</sub>OH (Parise *et al.*, 2004). This enhances the molecular D/H ratio by up to 13 orders of magnitude with respect to the elemental D/H ratio. In this section, we review these spectacular observations, which have led to the development of a new class of models for molecular deuteration, described in Section 5. It is worth emphasizing that extreme fractionations have only been observed in *low mass* Prestellar Cores (Section 3.1) and protostars (Section 3.2) so far. Massive protostars do not show the same deuterium enrichment, probably because the chemistry occurs in warmer environments.

#### 3.1. Prestellar Cores

In the last few years, it has become increasingly clear that molecular deuteration reaches extreme values in Prestellar Cores, where multiply deuterated molecules have been detected with ratios larger than 1%. The list of multiply deuterated molecules detected in Prestellar Cores (and Class 0 sources) is reported in Table 2, as well as the typical measured D/H ratio for each species. To the best of our knowledge, two surveys of multiply deuterated molecules – D<sub>2</sub>CO (Bacmann *et al.*, 2003) and ND<sub>3</sub> (Roueff *et al.*, 2005) – have been obtained in (small) samples of Prestellar Cores. Bacmann *et al.* (2003) found that the D<sub>2</sub>CO/H<sub>2</sub>CO ratios correlate with the CO depletion factors, proving observationally the key role of CO depletion in the deuterium enhanced fractionation. This trend is confirmed now by the larger sample of Table 2, as shown in Figure 4: *the larger the CO depletion the larger the molecular D/H ratio* (see also Crapsi *et al.* (2005a)). This is a key point whose importance will be further discussed in Section 5. Another aspect shown in the figure is the similarity of the D/H ratio of the three observed molecules: N<sub>2</sub>H<sup>+</sup>, H<sub>2</sub>CO and NH<sub>3</sub>. Note that the three molecules refer to the D/H ratios of singly, doubly and triply deuterated isotopologues respectively, and the ratios shown in the figure are scaled to account for the number of D atoms. While N<sub>2</sub>H<sup>+</sup> is certainly a gas phase product (formed by the reaction of N<sub>2</sub> with H<sub>3</sub><sup>+</sup>),

Table 2: Summary of the multiply deuterated molecules observed in Prestellar Cores and Class 0 sources. Typical deuterium fractionation ratios are given with respect to the fully hydrogenated counterparts, except for D<sub>2</sub>S and HD<sub>2</sub><sup>+</sup> where the ratio is with respect to the singly deuterated isotopologue. Note that variations among different sources amount to about a factor 3 or so.

Species	Deuterium Fractionation	Ref. <sup>a</sup>
NHD <sub>2</sub>	0.03	1,2,3
ND <sub>3</sub>	0.006	3,4,5
D <sub>2</sub> CO	0.15	6,7,8
D <sub>2</sub> S	0.12	9
HD <sub>2</sub> <sup>+</sup>	1	10
CHD <sub>2</sub> OH	0.06	11,8
CD <sub>3</sub> OH	0.03	12
D <sub>2</sub> CS	0.10	13

<sup>a</sup>REFERENCES: 1- *Roueff et al.* (2000); 2- *Loinard et al.* (2001); 3- *Roueff et al.* (2005) 4- *Lis et al.* (2002); 5- *van der Tak et al.* (2002); 6- *Ceccarelli et al.* (1998); 7- *Bacmann et al.* (2003); 8- *Parise et al.* (2006); 9- *Vastel et al.* (2003); 10- *Vastel et al.* (2004); 11- *Parise et al.* (2002); 12- *Parise et al.* (2004); 13- *Marcelino et al.* (2005).

there is considerable debate on whether formaldehyde and ammonia are formed in the gas phase or on grain surfaces (*Tielens*, 1983; *Ceccarelli et al.*, 2001; *Roueff et al.*, 2005); Section 5). From a purely observational point of view, Figure 4 points to a similar origin for the three molecules, but this is very likely an over-simplification, and maybe just due to the common origin of the molecular deuteration, the molecular ion H<sub>2</sub>D<sup>+</sup> (Section 5).

Indeed, it has been long believed that the deuterium fractionation is started by the fast ion-neutral reaction H<sub>3</sub><sup>+</sup>+HD leading to H<sub>2</sub>D<sup>+</sup> (Section 5.1). For this reason, H<sub>2</sub>D<sup>+</sup> has long been searched for in regions of massive star formation, where, however, it has never been detected (*van Dishoeck et al.*, 1992; *Pagani et al.*, 1992). The first detection of H<sub>2</sub>D<sup>+</sup> was finally obtained by *Stark et al.* (1999) towards the *low-mass* Class 0 source NGC1333-IRAS4. However, the break-through detection is considered to be that obtained in the Prestellar Core L1544 (*Caselli et al.*, 2003), where the ground ortho-H<sub>2</sub>D<sup>+</sup> line at 372 GHz is ten times brighter than in NGC1333-IRAS4. The observed flux implies an abundance of H<sub>2</sub>D<sup>+</sup> similar to that of electrons, and, therefore, to that of H<sub>3</sub><sup>+</sup>. This was unexpected and unpredicted by the chemical models at the time of the discovery. It is now accepted that the H<sub>2</sub>D<sup>+</sup>/H<sub>3</sub><sup>+</sup> ratio can reach unity in cold gas depleted by heavy-element-bearing molecules, as occurs at the centers of Prestellar Cores (Section 2.1). Actually, in the extreme conditions of the centers of Prestellar Cores, even the doubly deuterated form of H<sub>3</sub><sup>+</sup> has been detected (*Vastel et al.*, 2004). The map of H<sub>2</sub>D<sup>+</sup> emission in L1544 shows that it is very abundant in a zone with diameter  $\sim 6000$  AU (*Vastel et al.*, 2006). This zone coincides with the central density plateau,

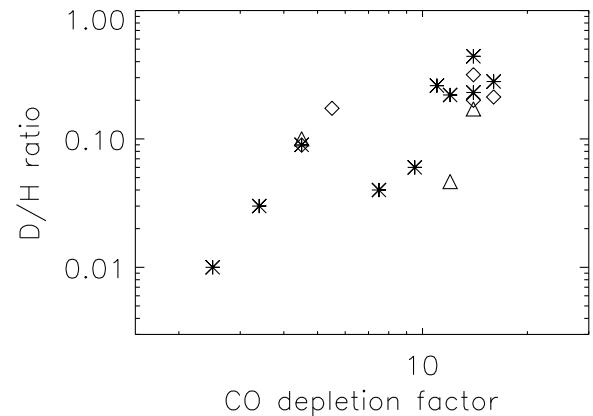


Fig. 4.— The measured N<sub>2</sub>D<sup>+</sup>/N<sub>2</sub>H<sup>+</sup> (stars; from *Crapsi et al.* (2005a)), (D<sub>2</sub>CO/H<sub>2</sub>CO)<sup>1/2</sup> (diamonds; *Bacmann et al.* (2003)) and (ND<sub>3</sub>/NH<sub>3</sub>)<sup>1/3</sup> (triangles; *Roueff et al.* (2005)) in the sample of Prestellar Cores of Table 2, as function of the CO depletion factor.

where CO is highly depleted (*Caselli et al.*, 1999). This further proves the key role played by the freezing of heavy-element-bearing molecules in the enhancement of molecular deuteration. Finally, one has to note that L1544 is not a peculiarity. An on-going project shows that Prestellar Cores are in general strong emitters of the ground ortho-H<sub>2</sub>D<sup>+</sup> line ( $T_{MB} > 0.5$  K; *Caselli et al.*, in prep.).

Thanks to the above observations, the very high diagnostic power of the ground-state ortho-H<sub>2</sub>D<sup>+</sup> line is now realized. This is true not only for chemistry, but also for the study of the evolutionary and dynamical status of Prestellar Cores. For example, the ortho-to-para ratio of H<sub>2</sub>D<sup>+</sup> is predicted to critically depend on the density, temperature and grain sizes (*Flower et al.*, 2005, 2006). Comparing these model predictions with observations, *Vastel et al.* (2006) found that the average grain sizes in L1544 are larger than in the ISM (in agreement with the discussion in Section 2.1). Finally, since very likely most of the heavy-element-bearing molecules are frozen out onto the grain mantles in the centers of the Prestellar Cores, H<sub>2</sub>D<sup>+</sup> is the best, if not the only way to probe those regions. Of particular interest is knowing the kinematical structure and whether and when the collapse starts at the center. *van der Tak et al.* (2005) studied the lines profile of the fundamental ortho-H<sub>2</sub>D<sup>+</sup> line towards L1544 with this scope. They found that the infall likely started at the center of L1544. We predict that similar studies with submillimeter interferometers will be extremely useful to unveil the first instants of collapse.

### 3.2. Class 0 sources

As for Prestellar Cores, recent observations have revealed a zoo of molecules with enhanced deuterium frac-

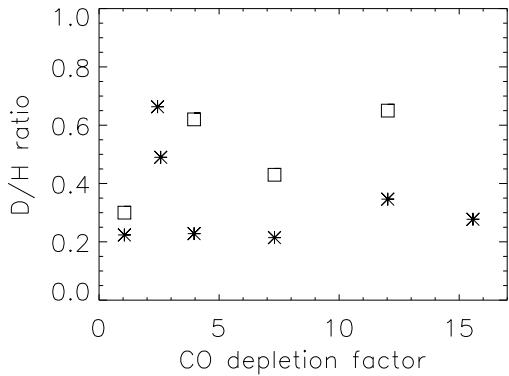


Fig. 5.— The measured  $(D_2CO/H_2CO)^{1/2}$  (stars) and  $CH_2DOH/CH_3OH$  (squares) in a sample of Class 0 sources (Parise *et al.*, 2006) as function of the CO depletion factor.

tionation. Actually, the discovery of abundant  $D_2CO$  in a Class 0 source started the hunt for multiply deuterated molecules. Although doubly deuterated formaldehyde had been detected fifteen years ago in Orion by Turner (1990), the measured abundance ( $\sim 0.2\%$   $H_2CO$ ) did not seem to draw particular attention (probably because Orion has always been considered a peculiar region). The discovery that  $D_2CO$  has an abundance about 5% that of  $H_2CO$  in a low mass protostar, IRAS16293-2422 (Ceccarelli *et al.*, 1998), on the contrary, started a flurry of activity in this field, and initiated the hunt for multiply deuterated molecules. In a few years, the deuterated species quoted in Table 2 were detected.

The best studied Class 0 source is IRAS16293-2422, where multi-frequency observations of singly and doubly deuterated formaldehyde constrain the abundance ratios of these molecules quite well (Loinard *et al.*, 2000) to be  $HDCO/H_2CO = 0.15$  and  $D_2CO/H_2CO = 0.05$ . Besides,  $D_2CO$  is very abundant across the entire envelope, which extends up to a radius of more than 5000 AU (Ceccarelli *et al.*, 2001). Remarkably, the  $D_2CO/H_2CO$  ratio reaches a peak of 0.16 at about 2000 AU from the center. Note that the dust at this distance is warm enough to prevent the condensation of CO, and the gas is too warm,  $\sim 35$  K, to favor the deuterium fractionation in the gas phase (Ceccarelli *et al.*, 2000a; Schöier *et al.*, 2002). In a few words, the two key factors for the enhanced fractionation, cold and CO-depleted gas, are absent in the largest fraction of the IRAS16293-2422 envelope, where  $D_2CO$  is abundant. Therefore, the observed enhanced deuterium fractionation is unlikely to be a present-day product (Ceccarelli *et al.*, 2001). In support of this view, the formaldehyde abundance profile across the IRAS16293-2422 envelope increases by about a factor of ten where the dust temperature exceeds 50 K, suggesting that gaseous formaldehyde is due to the partial, but continuous sublimation of the grain mantles across

the entire envelope. Layered like onions, the components of the mantles sublimate at different distances, corresponding to different dust temperatures. In the regions where the dust temperature is larger than about 25 K, CO-rich mantles sublimate, injecting into the gas phase the CO and the trace molecules trapped in the ice, like formaldehyde. When the dust temperature reaches 50 K the  $H_2CO$ -rich ices sublimate and so on (Ceccarelli *et al.*, 2001). *The observed deuteration is therefore a heritage of the pre-collapse phase* (Section 3.1).

This can also be seen in Figure 5, where the measured D/H ratios of formaldehyde and methanol are reported as function of CO depletion in a sample of Class 0 sources (Parise *et al.*, 2006). Contrary to the Prestellar Cores, there is no clear correlation between the molecular deuteration and the *present* CO depletion. The most plausible explanation is that the deuterated formaldehyde and methanol have been built up during the previous phase and that Class 0 sources are young enough for it not being substantially modified, likely younger than  $\sim 10^5$  yr based on modeling (Charnley *et al.*, 1997). Figure 5 also shows that methanol is systematically more enriched with deuterium than is formaldehyde. This may reflect a different epoch of formation of these two molecules on the ices: the formaldehyde perhaps formed in an earlier stage than methanol, when CO depletion was less severe. Alternatively, present day gas-phase reactions may have changed the initial mantle composition already, or, finally, formaldehyde and methanol follow different routes of formation (gas phase versus grain surface?) (Parise *et al.*, 2006).

Although our comprehension of the mechanisms leading to molecular deuteration in the ISM has undoubtedly improved in these last few years, there still remain a number of unresolved questions. First, the relative role of gas phase versus grain surface chemistry is uncertain: it is not completely clear yet what molecules and to what extent are formed in the gas phase versus on the grain surfaces. Deuterium fractionation promises to be a key aspect in this issue. Another open question is represented by deuterated water. Searches for solid HDO have so far been in vain, giving some stringent upper limits to the water deuteration:  $\leq 2\%$  (Dartois *et al.*, 2003; Parise *et al.*, 2003), considerably less than the deuteration observed in the other molecules. One possible explanation is that observations of solid  $H_2O$  and HDO may be “contaminated” by the contribution of the molecular cloud in front of the observed protostar (see for example the discussion in Boogert *et al.* (2002)). A more stringent constraint is set by observations of gas-phase HDO in the outer envelope and hot corino, where the icy mantles sublimate. Observations towards IRAS16293-2422 set a stringent constraint to the deuteration of water; in the sublimated ices it is  $\sim 3\%$ , whereas in the cold envelope it is  $\leq 0.2\%$  (Parise *et al.*, 2005a). Therefore, water deuteration seems to follow a different route from formaldehyde, methanol, and the other molecules.

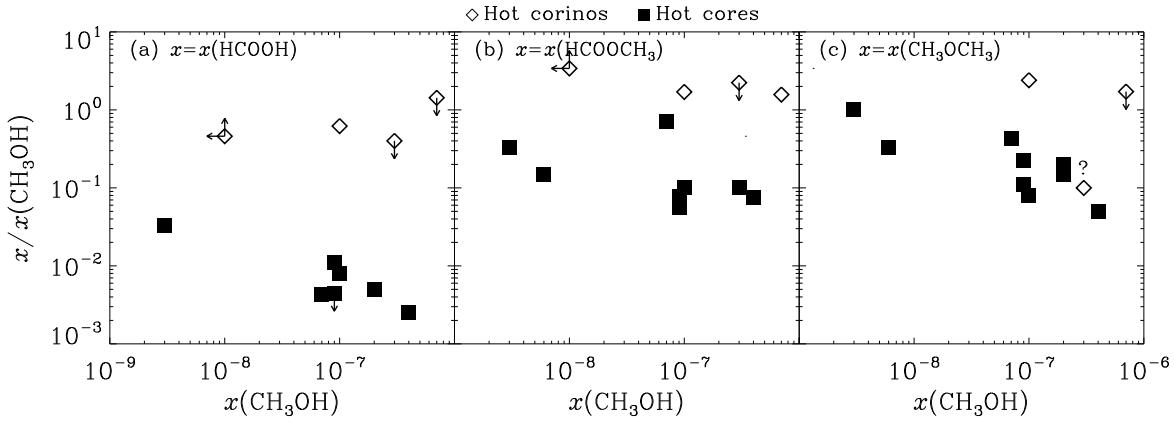


Fig. 6.— Abundance ratios of complex O-bearing molecules to methanol, plotted as a function of the methanol abundance. Diamonds and filled squares represent hot corinos and hot cores respectively (from Bottinelli *et al.* (2006b)).

#### 4. HOT CORINOS

While the outer envelopes of Class 0 sources are so cold that heavy-element-bearing molecules are at least partially frozen onto the grain mantles, the innermost regions are characterized by warm dust, so warm that the mantles sublime totally (Section 2.2). These regions share several aspects of the hot cores, discovered in the 80s around massive protostars (Kurtz *et al.*, 2000). Being “smaller” in size and mass, they have been called *hot corinos* (Ceccarelli, 2004b; Bottinelli *et al.*, 2004b). Based on the analysis discussed in Section 2.2, the radii of the hot corinos are predicted to be around 50 AU (IRAS16293-2422 represents here an exception with a radius of 150 AU), comparable to the sizes of the Solar System. The key question, and the most relevant for the chemical structure of Class 0 sources, is which molecules are found in the hot corinos, and, in particular, whether complex organic molecules are formed, in analogy with massive hot cores. More generally, are the hot corinos a scaled version of the hot cores, or does a peculiar chemistry take place? And, how reliable are the hot corino sizes derived by the analysis of single-dish data?

Once again, the benchmark for these studies has been IRAS16293-2422. In the hot corino of this source, complex organic molecules were detected for the first time (Cazaux *et al.*, 2003), and this hot corino was the first to be imaged (Kuan *et al.*, 2004; Bottinelli *et al.*, 2004b). In practice, all the complex molecules typical of massive hot cores that have been searched for were detected, with abundances similar to if not larger than those measured in hot cores (Cazaux *et al.*, 2003). These species include O and N-bearing molecules such as formic acid, HCOOH, acetaldehyde,  $\text{CH}_3\text{CHO}$ , methyl formate,  $\text{HCOOCH}_3$ , dimethyl ether,  $\text{CH}_3\text{OCH}_3$ , acetic acid,  $\text{CH}_3\text{COOH}$ , methyl cyanide,  $\text{CH}_3\text{CN}$ , ethyl cyanide,  $\text{C}_2\text{H}_5\text{CN}$  and propyne,  $\text{CH}_3\text{CCH}$ . Two years after the first detection in IRAS16293-2422, complex organic molecules were also detected towards the other Class 0 sources NGC1333 IRAS4A and B, and

NGC1333 IRAS2 (Bottinelli *et al.*, 2004a; Jørgensen *et al.*, 2005a; Bottinelli *et al.*, 2006b). The abundances of the O-bearing complex molecules detected in the four hot corinos are shown in Figure 6 as functions of the methanol abundance (Bottinelli *et al.*, 2006b). Note that the abundances have been normalized to the methanol abundance so that they do not depend on the uncertain sizes of the hot corinos. The number of hot corinos where complex organic molecules have been detected is evidently much too small to try to draw firm conclusions based on statistical considerations. Nevertheless, it is obvious that complex organic molecules are rather common in hot corinos. In this respect, the prototypical Class 0 source, IRAS16293-2422, may actually be representative for Class 0 sources. Furthermore, the abundances of HCOOH,  $\text{HCOOCH}_3$  and  $\text{CH}_3\text{OCH}_3$  in hot corinos are comparable to the methanol abundance and to formaldehyde (Bottinelli *et al.*, 2006b), and do not depend appreciably on the source luminosity, nor on the methanol and formaldehyde abundance. If the O-bearing complex molecules are formed in the gas phase from methanol and formaldehyde, as some theories predict (Section 5.3), then they “burn” the majority of their “parent” molecules, and this burned fraction is independent of the amount of  $\text{H}_2\text{CO}$  and/or  $\text{CH}_3\text{OH}$  sublimated from the grain mantles. Alternatively, if the O-bearing complex molecules are synthesized on the grain surfaces, they are an important ice component. So far, however, only HCOOH has been claimed to be found in its solid form (Schutte *et al.*, 1999; Gibb *et al.*, 2000). The other evident message of Figure 6 is that hot corinos are not a simply scaled version of hot cores. The abundance of the O-bearing complex molecules in hot corinos is larger than that in hot cores, by more than a factor of ten: HCOOH is even 100 times more abundant.

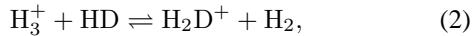
So far, we have focused on results based on single-dish observations. These observations encompass regions of at least 1000 AU, whereas the predicted sizes of the hot corinos do not exceed 150 AU. Recently, interferometric ob-

servations have resolved the emission of complex organic molecules in the hot corinos towards IRAS16293-2422 (Kuan *et al.*, 2004; Bottinelli *et al.*, 2004b; Chandler *et al.*, 2005), NGC1333-IRAS2 (Jørgensen *et al.*, 2005a), and NGC1333-IRAS4B (Bottinelli *et al.*, in prep.). From these data, a few general conclusions can be drawn. First, for IRAS16293-2422 and NGC1333-IRAS4B, the line emission from the complex molecules is concentrated in two spots, centered on the two objects forming in each case a proto-binary system (Wootten, 1989; Looney *et al.*, 2003; Sandell and Knee, 2001; Di Francesco *et al.*, 2001). The full line flux of the observed complex molecules, detected with the single-dish, is recovered in these two spots, which means that all the single dish emission originates in those regions. In addition, there is no sign of outflows in the line emission of complex molecules; the emission is compact and the line profile is relatively narrow. The brightest – and so far only resolved spot – in IRAS16293-2422 has a radius of  $\sim 150$  AU, close to the size expected for warm ( $T > 100$  K) gas (Ceccarelli *et al.*, 2000a). As emphasized above, each of these two objects is indeed a protobinary system. In each case, the two objects in the protobinary have different characteristics; eg., one spot is bright in the continuum but barely detected in the complex molecule line emission, while this is reversed for the other spot. This difference does not necessarily imply that the abundances in the individual spots of these protobinaries are truly different. The spot with the weaker line emission is also unresolved and the line likely optically thick (Bottinelli *et al.*, 2004b). Evidently, high-resolution observations of complex organic molecules are a valuable tool to study the chemistry of the hot corinos, and how it depends on physical conditions, rather than the mantle composition and age, which presumably are the same for the two objects of the binary system.

## 5. CHEMICAL MODELS

### 5.1. Molecular deuteration in the gas phase

Although the basic gas-phase mechanism of molecular deuteration in the cold interstellar medium was elucidated almost thirty years ago (Guélin *et al.*, 1977; Watson *et al.*, 1978) and incorporated into detailed models over a decade ago (Millar *et al.*, 1989), it is only recently that an understanding of the effect in star-forming regions has been achieved by astrochemists. Since the reservoir of deuterium lies in the molecule HD, deuteration proceeds by removing deuterium atoms from this molecule onto the many other trace constituents of the gas. The principal mode of transfer at low temperatures has been thought to be the reaction system

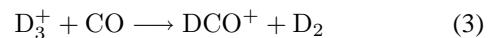


in which the left-to-right reaction is exothermic by approximately 230 K. If no other reactions need be considered to determine the abundance ratio of  $\text{H}_2\text{D}^+$  to  $\text{H}_3^+$ , the slowness of the backwards reaction leads to the stunning prediction that the abundance of the deuterated ion, now referred to as

an isotopologue, can exceed that of  $\text{H}_3^+$ . For cold cores at the standard density of  $10^4 \text{ cm}^{-3}$ , the prediction is in error because  $\text{H}_2\text{D}^+$  reacts quickly with both electrons and heavy species such as CO. The reactions with heavy species serve to spread the enhanced deuteration around so that typical ratios between singly-deuterated isotopologues (e.g.,  $\text{DCO}^+$ ) and normal species (e.g.  $\text{HCO}^+$ ) are predicted to lie in the range 0.01–0.10, in agreement with observation. Two other exchange reactions are of lesser importance: these involve the ions  $\text{CH}_3^+$  and  $\text{C}_2\text{H}_2^+$ . Their deuterium exchange reactions with HD leading to the ions  $\text{CH}_2\text{D}^+$  and  $\text{C}_2\text{HD}^+$  are more exothermic than the  $\text{H}_3^+$  case, so that the backwards reactions are slow up to higher temperatures, and subsequent reactions involving the deuterated ions can maintain deuterium fractionation when  $\text{H}_2\text{D}^+$  is no longer enhanced. Other reactions are also non-negligible, including some involving deuterium atoms (Brown and Millar, 1989).

As the density increases, the picture changes dramatically. Near the center of a cold pre-stellar core, for example, the gas density increases to  $10^{5-6} \text{ cm}^{-3}$  and the time scale for accretion of species onto dust particles becomes so short that most heavy species are strongly depleted onto dust particles. In addition, the fractional ionization in the gas is thought to become quite low if one takes account of gas-grain interactions to deplete the chemically rather inert atomic ion  $\text{H}^+$  (Liszt, 2003). Since seemingly all destruction mechanisms of  $\text{H}_2\text{D}^+$  are slow, a large abundance of  $\text{H}_2\text{D}^+$  does indeed build up, in agreement with observations (Section 3.1). But the story does not end here: in analogy to the reaction above, further reactions with HD convert a significant portion of the  $\text{H}_2\text{D}^+$  to the more deuterated isotopologues  $\text{HD}_2^+$  and even  $\text{D}_3^+$  (Roberts *et al.*, 2003; Walmsley *et al.*, 2004; Ceccarelli and Dominik, 2005). Indeed, simple chemical models of the densest portions show the triply deuterated ion to be the most abundant of the four ions in the series, and possibly the most abundant ion in the gas (Roberts *et al.*, 2003). Figure 7 shows the abundances of the deuterated forms of  $\text{H}_3^+$ ,  $\text{H}^+$  and  $e^-$ , as functions of the CO depletion factor respectively. Since the age and any other parameter is constant, increasing the depletion factor corresponds to increasing the density. For “intermediate” ( $\leq 30$ ) CO depletion factors,  $\text{H}_2\text{D}^+$  is the most abundant deuterated form of  $\text{H}_3^+$ . However, for larger depletions  $\text{D}_3^+$  takes over, and becomes the dominant positive charge carrier. A similar effect leads to the ions  $\text{CD}_3^+$  and  $\text{C}_2\text{D}_2^+$ .

Although a tiny region in the center may be completely devoid of heavy species (Walmsley *et al.*, 2004), such molecules do exist, albeit with depleted abundances, near the center (Bergin *et al.*, 2002; Pagani *et al.*, 2005; Lis *et al.*, 2006). The remaining heavy species will react with all three of the deuterating ions, especially  $\text{D}_3^+$ , leading to highly-deuterated isotopologues such as  $\text{D}_2\text{CO}$  and  $\text{ND}_3$ . Critical here is the high efficiency of  $\text{D}_3^+$  since, unlike the partially deuterated analogs, it can *only* deuterate and not protonate heavy species. Contrast the reaction



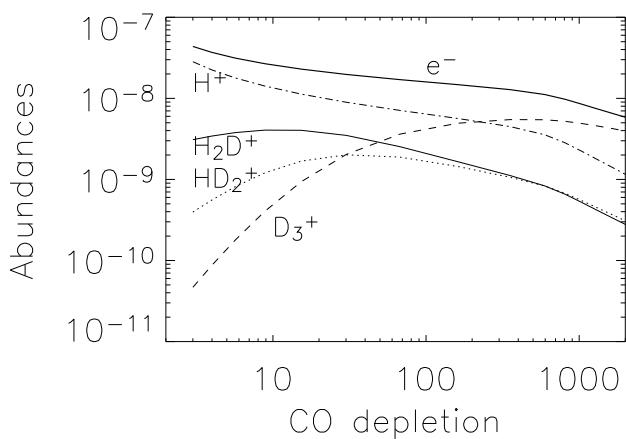
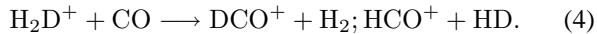


Fig. 7.— Abundance of the deuterated forms of  $\text{H}_3^+$ ,  $\text{H}^+$  and  $e^-$ , as functions of the CO depletion factor: thick solid line  $e^-$ , thin solid line  $\text{H}_2\text{D}^+$ , dashed line  $\text{D}_3^+$ , dotted line  $\text{HD}_2^+$ , and dotted-dashed line  $\text{H}^+$ .

with



In the latter reaction, deuteration occurs on only one of three collisions. The increase in efficiency with  $\text{D}_3^+$  as the deuterating agent is especially important in the formation of multiply deuterated neutral isotopologues, which occurs via a cycle of deuteration followed by dissociative recombination reactions. For example, starting with normal ammonia, deuteration leads to  $\text{NH}_3\text{D}^+$ , followed by dissociative recombination to form  $\text{NH}_2\text{D}$ , followed by deuteration to form  $\text{NH}_2\text{D}_2^+$ , followed by dissociative recombination to form  $\text{NHD}_2$ , etc (Roueff *et al.*, 2005).

Gas-phase chemical models of Prestellar Cores including deuteration range from simple homogeneous treatments relevant to the center of the core (Roberts *et al.*, 2003) to shell models that can be static (Roberts *et al.*, 2004) or in a state of collapse (Aikawa *et al.*, 2003, 2005). Accretion onto grains must be included in all approaches. The collapse can be treated via analytical approaches (Aikawa *et al.*, 2003) or hydrodynamic simulations (Aikawa *et al.*, 2005). The chemistry occurring on grain surfaces can also be included (Aikawa *et al.*, 2003, 2005). A relatively simple static approach by Roberts *et al.* (2004) illustrates the power of the chemical models. In terms of column densities, Roberts *et al.* (2004) obtain a value for  $\text{D}_2\text{CO}$  higher by only a factor of three than that observed by Bacmann *et al.* (2003), and a CO depletion of a factor of 20 compared with the standard value, in good agreement with the observed depletion of 14 (Bacmann *et al.*, 2002) (see also Section 3 and 2). The overall computed  $\text{D}_2\text{CO}/\text{H}_2\text{CO}$  ratio is 0.3, also in good agreement with observation. In general, models with collapse are not in as good agreement with observation because it is not facile to vary the details of the collapse to obtain optimal agreement.

## 5.2. Mantle formation and surface chemistry

As the gas-phase chemistry occurs and mantles accrete in cold sources, a surface chemistry is also active. A proper mathematical treatment of diffusive surface reactions on interstellar grains is not simple. The first such treatments used rate equations analogous to those used for gas-phase processes (Pickles and Williams, 1977), and the method is still the only practical approach to the construction of large gas-grain models (Ruffle and Herbst, 2000). The method is only a rough approximation to reality for a number of reasons, and a variety of more accurate but more complex methods have been advocated. If we imagine grains to be rather smooth surfaces on which binding parameters for adsorbates do not differ strongly from one site to another, there is the problem that only small (fractional) numbers of reactive species such as atomic hydrogen are present on a given grain on average. With such small numbers, it is more reasonable to consider discrete rather than average quantities. Both the discreteness of the problem and the large fluctuations possible from grain to grain then argue for a stochastic approach. Following the pioneering work of Tielens and Hagen (1982), a truly stochastic method was utilized by Charnley (2001) based on Monte Carlo methods, while a master equation approach was advocated by Biham *et al.* (2001) and by Green *et al.* (2001). The latter approach has recently been incorporated into moderately sized gas-grain networks by Biham and Lipshtat (2002), Lipshtat and Biham (2004) and Stantcheva and Herbst (2004).

To add to the complexity of the problem, interstellar surfaces are likely to be irregular, porous, and even amorphous, so that binding sites for adsorbates are likely to be diverse, including some that contain much deeper wells than others. A new extension of the Monte Carlo method for irregular grains with silicate, carbonaceous and icy surfaces has been introduced by Chang *et al.* (2005) and Cuppen and Herbst (2005) for the specific case of the formation of hydrogen molecules. Here, the fraction of binding sites with deep potential wells totally changes the character of the problem since numerous H atoms are present over wide temperature ranges on each grain. Whether or not an approach of this complexity can be extended to large models is unclear. A simpler approach to different binding sites is the physisorption-chemisorption model of Cazaux and Tielens (2004), where only two types of binding sites are considered for H atoms, shallow and deep. In this approximation, rate equations can be used to a reasonable degree of accuracy.

At later stages, the surface chemistry includes deuteration via atomic deuterium, which is produced in the gas by dissociative recombination of deuterated ions; viz.,  $\text{D}_3^+ + e^- \longrightarrow \text{D} + \text{D} + \text{D}$ , and can lead in very dense regions to an abundance of atomic deuterium nearly equal to the abundance of atomic hydrogen (Roberts *et al.*, 2003, 2004). The H and D atoms land on grains and, because of their rapid diffusion and high surface reactivity, both hydrogenate and deuterate heavy atoms

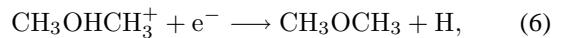
and reactive molecules to form more saturated forms via sequential reactions. For example, the formation of water ice can occur by the addition of two hydrogen atoms to an oxygen atom that lands on a grain surface:  $O + H \rightarrow OH$ ;  $OH + H \rightarrow H_2O$ . or can start from OH, which can be formed on grain surfaces by successive reactions involving  $O_2$  and  $O_3$  (Tielens and Hagen, 1982). Note that even if the gaseous  $O_2$  is low, an appreciable abundance of  $O_2$  can built up on the surface through reactions of O plus O, or  $O_2$  can be formed in the reaction of  $O_3$  with H. There is even laboratory evidence that hydrogenation of CO into formaldehyde ( $H_2CO$ ) and methanol ( $CH_3OH$ ) occurs (Watanabe *et al.*, 2003; Hidaka *et al.*, 2004):  $CO \rightarrow HCO \rightarrow H_2CO \rightarrow H_3CO \rightarrow CH_3OH$ , although two of the hydrogenation reactions possess small activation energy barriers. Following a similar path, not only  $H_2CO$  and  $CH_3OH$  are formed but also their deuterated isotopologues (Charnley *et al.*, 1997). It is interesting to note that there is currently no viable formation mechanism for methanol in the gas phase, so that all methanol detected in the gas has its genesis on grain surfaces. This statement is true even for the small amount of methanol detected in cold sources. Here surface formation is followed by inefficient desorption. The results of a number of models – which differ in the sophistication of the gas-grain interaction, their assumptions on initial conditions including gas-phase abundances, and the chemical routes included – have been reported in the literature (Tielens and Hagen, 1982; Hasegawa *et al.*, 1992; Aikawa *et al.*, 2003; Stantcheva and Herbst, 2003; Aikawa *et al.*, 2005). Deuteration on cold surfaces was first explored by Tielens (1983) and later studied by Brown and Millar (1989), Charnley *et al.* (1997), Caselli *et al.* (2002a), and Stantcheva and Herbst (2003) among others. The basic picture adopted by astrochemists is that D atoms can deuterate atoms and radicals in a similar manner to the reactions of H atoms. If we, for example, consider the competing deuteration and hydrogenation processes starting with surface CO, all of the different isotopologues and isotopomers of methanol can be produced:  $CH_3OD$ ,  $CH_2DOH$ ,  $CH_2DOD$ ,  $CHD_2OH$ ,  $CHD_2OD$ ,  $CD_3OH$ , and  $CD_3OD$  (Charnley *et al.*, 1997). Their relative abundances on grain surfaces depend on the flux ratio between H and D atoms landing on the grains. That the deuteration is more complex than envisioned by astrochemists, however, is shown by some recent experimental evidence provided by Nagaoka *et al.* (2005) where it seems that even normal methanol can be deuterated by reactions with atomic D on grain surfaces.

All model calculations confirm that ices are produced by surface reactions, and that these ices are, at least on average, dominated by water, as observed. The large amount of CO ice detected by observers is probably mainly the result of accretion from the gas, where this molecule is produced copiously. The production of surface methanol occurs once there is sufficient CO to be hydrogenated. The production of the other very abundant surface species – carbon dioxide ( $CO_2$ ) – is not well understood.

### 5.3. Mantle evaporation and complex organic molecule formation

A variety of processes can return ice mantle species to the gas phase, even during the cold prestellar core phase. The most important one here is cosmic ray driven desorption where an Fe-cosmic-ray ( $E \sim 10 - 100$  MeV/nucleon) temporarily heats the grain to a high enough temperature that some mantle species evaporate (Leger, 1983; Leger *et al.*, 1985). By itself, this process will only return weakly bound species (eg., CO,  $N_2$ ) to the gas phase. However, this process becomes very effective, even for more tightly bound species such as  $H_2O$ , if the ices contain chemical energy in the form of stored radicals produced by UV photolysis (D'Hendecourt *et al.*, 1982, 1986; Tielens, 2005). It should be emphasized that the thermal shock driven into the grain by the penetrating cosmic ray can also “lift” off a small quantity of larger species (Johnson *et al.*, 1991).

As the protostellar stage commences and temperatures begin to increase, the “dirty” grain mantles will be lost partially or totally via evaporation in a rather complex process stemming from the heterogeneous nature of the mantles (Viti *et al.*, 2004). Nearer to the bipolar outflows associated with protostellar regions, shock waves can also lead to the removal of the mantles. In particular, heating of ice mantles will lead to evaporation and an injection into the warm dense gas of large quantities of grain surface produced species such as water, methanol, and formaldehyde. Reactions among these simple molecules can then lead to more complex species (Millar *et al.*, 1991; Charnley *et al.*, 1992; Caselli *et al.*, 1993; Rodgers and Charnley, 2003; Nomura and Millar, 2004). The process begins with the production of  $H_3^+$  via cosmic ray bombardment of  $H_2$ , followed by the reaction of  $H_2^+$  and  $H_2$ . This triatomic species, possibly through some intermediaries, transfers its proton to methanol. It has long been believed that the resulting protonated methanol,  $CH_3OH_2^+$ , will rapidly undergo alkyl cation transfer reactions with other species. With  $CH_3OH$  and  $H_2CO$ , this might lead to the formation of dimethyl ether and methyl formate, which are abundant complex molecules in hot corinos (Section 4). However, the above reactions advocated to produce methyl formate do not occur, based on laboratory experiments (Horn *et al.*, 2004). A more successful synthesis seems to be the one leading to dimethyl ether:



but it is to be noted that experimental measurements of the neutral products of dissociative recombination reactions show that two-body products such as shown here are often minor channels. Eventually, these complex species are destroyed on a timescale of  $10^{4-5}$  yr, depending on the temperature and density of the gas, to reform CO. Indeed, if the chemistry were understood well enough, abundances of these species have the potential to be a chemical “clock”, timing the formation of the central object, which has heated

up and evaporated the ices. Other determinants of age are abundance ratios of sulfur-bearing species, although the use of these indicators requires sophisticated modeling of both the chemical and the physical structure of the studied object (Wakelam *et al.*, 2004, 2005). The need for such a sophisticated approach arises because the abundance ratios of sulfur-bearing species, used as clocks, turn out to also be dependent on initial abundances following evaporation as well as on physical conditions.

Deuterium fractionation in the ices arises mainly from reactions involving deuterium atoms accreted from the highly fractionated gas. Such fractionation occurs in the abundant surface species ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ) acting as signposts of a cold prestellar-core history in which gaseous D atoms are abundant. When these species are returned to the gas, the fractionation becomes more apparent. Although it is sometimes difficult to disentangle purely gas-phase fractionation from surface fractionation followed by evaporation, fractionation in gaseous molecules formed mainly on surfaces (e.g., methanol) is due at least initially to surface reactions. This fractionation will also be passed on to daughter products such as dimethyl ether and methyl formate via gas-phase processes. Thus, the deuterium fractionation can be used as a tracer of the chemical routes involved in the formation of complex molecules in hot cores. Indeed, the fractionation pattern of dimethyl ether and methyl formate should reflect directly that of methanol and formaldehyde. Eventually, reactions in the warm dense gas of the hot core will reset this deuterium fractionation to that appropriate for the gas temperature (Charnley *et al.*, 1997). This chemical kinetic evolution may run differently for different species or even for different chemical groups in one species. Specifically, for the fractionation pattern of methanol, it has been suggested that protonation of methanol isotopomers followed by dissociative electron recombination reforming methanol will preferentially remove the deuteration from the OH group but not affect the  $\text{CH}_3$  group (Osamura *et al.*, 2004). The analysis may be incorrect, however, because the most recent storage ring experiments (Geppert *et al.*, 2004) show that protonated and deuterated methanol ions undergo dissociative recombination reactions that lead to virtually no neutral methanol or its isotopologues at all. If all of the gas-phase isotopologues of methanol are depleted at the same rate, then the abundance ratios are indeed determined by the surface chemistry during the previous cooler eon.

## 6. CONCLUSIONS: CLOSED AND OPEN QUESTIONS

In this contribution, we have summarized new insights into the physical and chemical composition and evolution of Prestellar Cores and Class 0 low-mass Protostars. In particular,

1. On the physical structure, Prestellar Cores can be described by the density distribution of a Bonnor-Ebert sphere, whereas Class 0 sources are consistent with the Shu

“inside-out” recipe.

2. At the center of Prestellar Core condensations, densities are so high and temperatures so low that possibly all heavy-element-bearing molecules freeze out onto the dust grains, forming mantles of ices. We discussed the possibility that small grains coagulate into larger grains during this phase.

3. A similar molecular depletion is observed in large regions of the outer envelopes of Class 0 sources. These regions are indistinguishable from Prestellar Cores on this basis, arguing that the latter are precursors of Class 0 sources.

4. The molecular depletion is accompanied by a dramatic enhancement of the molecular deuteration, observed in both Prestellar Cores and Class 0 sources. In the innermost regions of Prestellar Cores, the only observable molecules may be  $\text{H}_2\text{D}^+$  and  $\text{HD}_2^+$ , which are likely as abundant as  $\text{H}_3^+$  or even more so.

5. In Class 0 sources, many multiply deuterated molecules have been observed. Even triply deuterated molecules have been detected, with abundances enhanced by up to 13 orders of magnitude with respect to the D/H elemental abundance.

6. Triggered by the observations of multiply deuterated molecules in Prestellar Cores and Class 0 sources, a new class of models for deuteration has been developed in the last few years. These models predict that the low temperatures coupled with the disappearance of heavy-element-bearing molecules from the gas phase cause the formation of abundant  $\text{H}_2\text{D}^+$ ,  $\text{HD}_2^+$  and  $\text{D}_3^+$ , which are extremely efficient in passing their deuterium atoms on to other molecules. In extreme conditions,  $\text{D}_3^+$  is predicted to be the most abundant molecular ion in the gas, surpassing by orders of magnitude the number density of  $\text{H}_3^+$ .

7. During the cold phases of low-mass star formation, grain mantles are formed, consisting mainly of water ice, but with many other molecules in quantities that can be important. Extreme molecular deuteration is a clear hallmark of this phase and is recorded in the mantles. Hydrogenated molecules, like formaldehyde and methanol, are also believed to be formed on the grain surfaces during the cold pre-collapse phase.

8. Class 0 envelopes consist of two chemically distinct regions: the outer envelopes and the inner regions, called hot corinos. The border between the two is where the dust temperature reaches the sublimation temperature of the grain ices. This has a major impact on the gas chemistry. In the hot corinos, the chemistry is dominated by the evaporation of the mantles, built up during the pre-collapse phase. Once the mantle components are in the gas phase, they undergo successive reactions leading to the formation of many complex organic molecules, similar to those observed in the hot cores.

Although important progress has been achieved in these last few years, it has also been accompanied by the rise of numerous new questions. For example, while molecular depletion is now an accepted “fact”, it is still not to-

tally clear whether in the innermost regions of the Prestellar Cores the density increases so much that not even a trace of heavy-element species remains in the gas phase. Also, it still remains unclear when and exactly how the collapse starts. It is clear now that observations of heavy-element-bearing molecules may not be the best way to proceed. In contrast, as we now realize, the ground-state transition of ortho-H<sub>2</sub>D<sup>+</sup> (and, to a lesser extent, para-HD<sub>2</sub><sup>+</sup>) provides a new and exciting probe with which to search for the long-sought collapse in the innermost regions of Prestellar Cores (*van der Tak et al.*, 2005). However, in order to fully exploit this new diagnostic, we have to first fully understand the ortho-para ratio of H<sub>2</sub>D<sup>+</sup> (*Flower et al.*, 2006), which is not measured at all so far. It is also clear that models for the Prestellar Core phase have improved dramatically with the inclusion of the extreme depletions of the gas phase and the formation of the multiply deuterated forms of H<sub>3</sub><sup>+</sup>. However, these models still struggle to reproduce the extreme observed deuteration, especially that of formaldehyde and methanol. While this is likely due to grain surface chemistry, it remains the case that, unless there is an enhancement in the reactivity of D over H, the gas landing on the grain surfaces at the moment of the mantle formation must have an atomic D/H ratio higher than accounted for by the current gas phase chemistry models. We also have little knowledge as to whether the prediction that D<sub>3</sub><sup>+</sup> is the most abundant molecular ion in extreme conditions is correct. The coming years will likely see many of these questions answered, with the advent of the satellite *Herschel* and, foremost, the interferometer ALMA.

If many questions remain about the cold pre-collapse phase, even more questions are unanswered for the protostellar phase, and many have likely not even been asked. For example, the very nature of the hot corinos is still very much debated. Several authors question how much of the observed warm gas, with complex organic molecules, is due to the interaction of an outflow with the inner envelope (*Chandler et al.*, 2005). Another possibility invoked is that this warm gas enriched with complex organic molecules resides in a disk-like atmosphere (*Jørgensen et al.*, 2005a). The reality is indeed that very few observations have resolved hot corinos; actually, in just one source has this so far occurred (*Kuan et al.*, 2004; *Bottinelli et al.*, 2004b). Until more sensitive observations are available with SMA and ALMA, the question will remain open for debate. Another open question regards the chemistry leading to the observed molecular complexity in hot corinos. No clear observations are able so far to distinguish the roles of gas phase and grain surface chemistry in the formation of formic acid or methyl formate, just to mention two molecules frequently detected. The answer to this question will likely need not only more and more sensitive observations towards the hot corinos, but also laboratory experiments coupled with modeling in order to elucidate the role of the grains in the story. Last, but not least, we suspect that we are just viewing the tip of the iceberg: what is still hidden from our eyes? What is the ultimate molecular complexity reached during the hot corino

phase? Do biotic molecules form? Do they play a role in the trigger and/or diffusion of life in the Universe (see the chapter by *Gaidos & Selsis*)?

Finally, many more questions exist regarding the fate of the molecules formed through the pre-stellar and protostellar phases. It is likely that some condense again onto the grain mantles during the phase of the proto-planetary disk, at least in the outer zones of the disk that are shielded by FUV photons (see the chapters by *Bergin et al.*, *Dutrey et al.* and *Dullemond et al.*). The same grains are likely to coagulate into larger aggregates, which are the bricks from which the planets eventually form (see the chapters by *Dominik et al.* and *Wadhwa et al.*). How much of the mantle formed in the Prestellar Core phase is preserved? Do the molecules, and particularly the complex organic molecules formed during the hot corino phase, freeze-out onto the new mantles without other alterations? Or what kind of alterations do they undergo? How pristine is the material forming the comets, asteroids and planets?

To reconstruct the full story, we need many more pieces of the puzzle. One strong motivation for pursuing the story of protoplanetary disks is that their aftermath may have been part of the history of our own Solar System. The water of the oceans is an emblematic example. The ratio between HDO and H<sub>2</sub>O (known as SMOW) is  $\sim 10^{-4}$  (*De Witt et al.*, 1980), fully ten times larger than the D/H elemental abundance of the Solar Nebula (*Geiss*, 1993). The origin of the oceans has been long debated and new theories keep coming. The deuterium enhancement is in line with the theory that much of the ocean water comes from the bombardment of the early Earth by comets (*Owen and Bar-Nun*, 1995), for comets show a similarly enhanced HDO/H<sub>2</sub>O ratio (*Meier et al.*, 1998; *Bockeleé-Morvan et al.*, 1998). Other possibilities include water brought by smaller bodies of the Solar System (meteorites and asteroids) (*Raymond et al.*, 2004; *Gomes et al.*, 2005). These bodies, as well as comets, have the imprint of the pre-collapse/protostellar phase in their ices (see the chapters by *Jewitt et al.*, *Wooden et al.* and *Alexander et al.*). Regarding deuterium fractionation, the question remains as to what extent the enhanced HDO/H<sub>2</sub>O ratio is a legacy from the protostellar/protoplanetary phase and to what extent it has been modified by subsequent chemistry. And in addition to water, what other molecules were inherited by the early Earth and how did they arrive? As with other molecular indicators, how much of the terrestrial HDO/H<sub>2</sub>O ratio is a legacy depends on how it evolved during the various phases of the earth's formation. So far, we have constraints on the evolution of deuterium fractionation from the pre-collapse, protostellar, and proto-planetary phases for only two molecules, HCO<sup>+</sup> and H<sub>2</sub>O, and in the outer zones of the disk only, which may not necessarily be connected with cometary formation. The case of DCO<sup>+</sup>/HCO<sup>+</sup>, representing deuteration in the gas phase, seems to keep a rather constant value, around 10% (*van Dishoeck et al.*, 2003). The HDO/H<sub>2</sub>O ratio, very likely a product of the grain mantles, seems to remain quite similar too, at a level of  $\sim 1\%$ , with just a rel-

atively small decrease in the proto-planetary phase (*Ceccarelli et al.*, 2005; *Dominik et al.*, 2005). Evidently, this information alone is far too little to resolve the problem of the oceanic origin, but shows how important the study of chemistry in the prestellar and protostellar phases of star formation is and how much it will eventually aid our understanding of later phases up through the present eon. The coming decade will likely see many of these questions answered with the advent of the satellite Herschel and the submillimeter interferometer ALMA.

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