Deuterium enhancement of monodeuterated species has been recognized for more than 30 years as a result of the chemical fractionation that results from the difference in zero point energies of deuterated and hydrogenated molecules. The key reaction is the deuteron exchange in the reaction between HD, the reservoir of deuterium in dark interstellar clouds, and the H$_3^+$ molecular ion, leading to the production of the H$_2$D$^+$ molecule, and the low temperature in dark interstellar clouds favors this production. Furthermore, the presence of multiply deuterated species have incited our group to proceed further and consider the subsequent reaction of H$_2$D$^+$ with HD, leading to D$_2$H$^+$ (first detected by Vastel et al. 2004), which can further react with HD to produce D$_3^+$. In prestellar cores, where CO was found to be depleted (Bacmann et al. 2003), this production should be increased, as CO would normally destroy H$_3^+$. The first model including D$_2$H$^+$ and D$_3^+$ (Roberts, Herbst & Millar 2003) predicted that these molecules should be as abundant as H$_2$D$^+$ (see contribution by H. Roberts). The first detection of the D$_2$H$^+$ was made possible by the recent laboratory measurement by Hirao & Amano (2003) for the frequency of the fundamental line of the para-D$_2$H$^+$ (see contribution by T. Amano). Here we present observations of H$_2$D$^+$ and D$_2$H$^+$ towards a sample of dark clouds and prestellar cores and show how the distribution of ortho-H$_2$D$^+$ (1$_{1,0}$-1$_{1,1}$) can trace the deuterium factory in prestellar cores. We also present how future instrumentation will improve our knowledge concerning the deuterium enhancement of H$_3^+$. 

**Keywords:** Astrochemistry, Deuterium, Interstellar

1. Introduction

Deuterium bearing species are good probes of the cold phases of molecular clouds prior to star formation and many recent observations point to the fact that their abundance relative to their hydrogenated analogues can be larger, by a factor up to $10^5$, than the solar neighborhood value of $\sim 1.5 \times 10^{-5}$. Therefore the relative abundance of isotopologues does not measure the relative abundances of the isotopes themselves. The deuterium fractionation has been evaluated in prestellar cores and low-mass protostars from observations of HCO$^+$ and N$_2$H$^+$ (Butner et al. 1995; Williams et al. 1998; Caselli et al. 2002; Crapsi et al. 2004, Crapsi et al. 2005), H$_2$CO (Loinard et al. 2001; Bacmann et al. 2003), H$_2$S (Vastel et al. 2003), HNC (Hirota et al. 2003), CH$_3$OH (Parise et al. 2004), and NH$_3$ (Roueff et al. 2000, Tiné et al. 2000). The chemical fractionation process in the gas–phase mainly
Figure 1. Main reactions involving the deuterated forms of the H$_3^+$ molecule. When CO and N$_2$ are depleted and the fractional ionization is $\leq 10^{-7}$, the reactions with bold arrows are dominant.

arises from the difference between the zero-point energies of H$_2$ and HD. Almost incredibly, this can lead to a detectable quantity of triply deuterated molecules like ND$_3$ (Lis et al. 2002; van der Tak et al. 2002) and CD$_3$OH (Parise et al. 2004). Multiply deuterated methanol is thought to be formed mainly on dust grain surfaces (Charnley et al. 1997) in regions where the gas–phase [D]/[H] ratio is enhanced to values larger than $\sim 0.1$ (Parise et al. 2002). The high abundance found in the gas phase for the D$_2$S also seem to favour the grain surface chemistry scenario, when the [D/H] ratio is larger than 0.1 (Vastel et al. 2003). In molecular clouds, hydrogen and deuterium are predominantly in the form of H$_2$ and HD respectively. So the HD/H$_2$ ratio should closely equal the D/H ratio. Since the zero-point energies of HD and H$_2$ differ by $\sim 410$ K, the chemical fractionation will favor the production of HD compared to H$_2$. In the dense, cold regions of the interstellar medium (T $\sim$ 10 K), D will be initially nearly all absorbed into HD. The abundant ion available for interaction is H$_3^+$, which gives H$_2$D$^+$:

$$H_3^+ + HD \leftrightarrow H_2D^+ + H_2 + 230 \text{ K} \quad (1.1)$$

The reverse reaction does not occur efficiently in the cold dense clouds where low–mass stars form, and where the kinetic temperature is always below 30 K, the “critical” temperature above which reaction (1.1) starts to proceed from right to left and limits the deuteration. Therefore, the degree of fractionation of H$_2$D$^+$ becomes non-negligible. This primary fractionation can then give rise to other fractionations and form D$_2$H$^+$ and D$_3^+$ as first suggested by Phillips & Vastel (2003):

$$H_2D^+ + HD \leftrightarrow D_2H^+ + H_2 + 180 \text{ K} \quad (1.2)$$

$$D_2H^+ + HD \leftrightarrow D_3^+ + H_2 + 230 \text{ K} \quad (1.3)$$

We present in Figure 1 the main reactions involving these molecules. Note that the effect of the dissociative recombination of H$_3^+$ is negligible because of the low electron density in such regions. Therefore, the reactions with CO or HD dominate the loss of H$_3^+$.

The dissociation of the deuterated forms of H$_3^+$ is then responsible of the enhancement in the [D]/[H] ratio. One specific parameter can enhance this process: the depletion of neutral species (in particular, the abundant CO) from the gas-phase.
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Figure 2. Diagrams of the lowest energy levels for the $H_2D^+$ and $D_2H^+$ molecules.

(cf. Dalgarno & Lepp 1984). In fact, the removal of species which would normally destroy $H_3^+$ (e.g. CO; Roberts et al. 2000) means that $H_3^+$ is more likely to react with HD and produce $H_2D^+$, $D_2H^+$ and $D_3^+$. The first model including $D_2H^+$ and $D_3^+$ (Roberts et al. 2003) predicted that these molecules should be as abundant as $H_2D^+$ (see also Flower et al. 2004).

Gas phase species are expected to be depleted at the centers of cold, dark clouds, since they tend to stick to the dust grains. A series of recent observations has shown that, in some cases, the abundance of molecules like CO decreases towards the core center of cold ($\leq 10$ K), dense ($\geq 2 \times 10^4$ cm$^{-3}$) clouds. L1544: Caselli et al. (1999); B68: Bergin et al. (2002); Oph D: Bacmann et al. (2003), Crapsi et al. (2005); L1521F: Crapsi et al. (2004); L183 (L134N): Pagani et al. (2005). These decreases in abundance have been interpreted as resulting from the depletion of molecules onto dust grains (see, e.g., Bergin et al. 1997, Charnley et al. 1997). It is now clear that these drops in abundance are typical of the majority of dense cores.

2. Observations

For many years, $H_2D^+$ has been searched for (Phillips et al. 1985; Pagani et al. 1992a; van Dishoeck et al. 1992; Boreiko & Betz 1993), and the advent of new submillimeter receivers led to the detection of the $1_{1,0}-1_{0,1}$ transition towards the young stellar object, NGC 1333 IRAS 4A (Stark, van der Tak & van Dishoeck 1999) although with relatively low signal strength, and in high abundance towards the pre-stellar core L1544 (Caselli et al. 2003). We present in the following the recent advances on the deuterium enhancement based on observations of pre-stellar cores performed at CSO. The pre-stellar stage of star formation may be defined as the phase in which a gravitationally bound core has formed in a molecular cloud, and is evolving towards higher degrees of central condensation, but no central protostellar object yet exists within the core.
Encouraged by laboratory measurements (Hirao & Amano 2003), Vastel et al. (2004) detected the para-D$_2$H$^+$ molecule in its ground transition at 692 GHz. By comparison with their H$_2$D$^+$ observations (see Figure 3), they found that in the prestellar core 16293E, the para-D$_2$H$^+/\text{ortho-H}_2\text{D}^+$ is $\sim 0.75$. Both H$_2$D$^+$ and D$_2$H$^+$ molecules have ortho and para forms, corresponding to the spin states of the protons (for H$_2$D$^+$) or deuterons (for D$_2$H$^+$). In order to compare the modeled abundances with the observations of one spin state only, it is critical to know the ortho–to–para ratio for these two molecules. Under LTE conditions, at temperature $T$, the relative populations of the lowest ortho (1$_{1,1}$) and para (0$_{0,0}$) levels of H$_2$D$^+$ would be:

$$\frac{n(1_{1,1})}{n(0_{0,0})} = 9 \times \exp\left(-\frac{86.4}{T}\right)$$

(2.1)

and the relative populations of the lowest ortho (0$_{0,0}$) and para (1$_{0,1}$) levels of D$_2$H$^+$ would be:

$$\frac{n(1_{0,1})}{n(0_{0,0})} = \frac{9}{6} \times \exp\left(-\frac{50.2}{T}\right)$$

(2.2)

It results that, at 8 K, the H$_2$D$^+$ ortho-to-para ratio would be $\sim 1.8 \times 10^{-4}$ and the D$_2$H$^+$ para-to-ortho ratio would be $\sim 2.8 \times 10^{-3}$. The ortho form of H$_2$D$^+$ is produced mainly in reactions of the para form with ortho-H$_2$ (e.g. Gerlich, Herbst & Roueff 2002). Therefore, its high o/p ratio is attributable to the relatively high ortho-H$_2$ abundance as first noticed by Pagani et al. (1992b). Because the o/p ratio is not thermalized at the low temperature considered here, neither is the o/p H$_2$D$^+$ ratio. This can be illustrated in Flower, Pineau des Forêts, Walmsley (2004) model where, at temperatures lower than 10 K, a hydrogen density of $2 \times 10^6$ cm$^{-3}$ and a grain size of 0.1 $\mu$m, the o/p-H$_2$D$^+$ reaches unity and the p/o-D$_2$H$^+$ value is about 0.1. Consequently the D$_2$H$^+$ abundance should be about 4 times higher than the H$_2$D$^+$ abundance in the 16293E core.

This study supported chemical modelling and the inclusion of multiply deuterated species (Roberts et al. 2003; Walmsley et al. 2004; Roberts et al. 2004; Flower et al. 2005; Aikawa et al. 2005).

(b) L1544

In one of the most heavily CO–depleted prestellar cores, L1544 where $f_D \sim 10$, Caselli et al. (2003) detected a strong ($T_{mb} \sim 1$ K) ortho-H$_2$D$^+$(1$_{01}$-1$_{11}$) line (see Figure 3), and concluded that H$_2$D$^+$ is one of the main molecular ions in the central region of this core. Vastel et al. (submitted) mapped the area around the dust peak position (see Figure 4) and found that the H$_2$D$^+$ distribution closely follow the dust continuum in contrast to the CO molecule that appears to be depleted. Also, the para-D$_2$H$^+$ 1$_{1,0}$–1$_{0,1}$ transition was observed at the dust peak position (see Figure 3). However, the linewidth is about 3 times lower than the expected thermal linewidth for a kinetic temperature of 7 K, as predicted by dust temperature measurement. In absence of a possible explanation for this profile, this observation has been considered as a tentative detection only.

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Figure 3. Spectra of the ortho–H$_2$D$^+$ 1$_1$,$0$–1$_1$,$1$ and para–D$_2$H$^+$ 1$_1$,$0$–1$_0$,$1$ transitions towards 16293E (Vastel et al. 2004) and L1544 (Vastel et al. submitted).

Figure 4. Integrated intensity maps of H$_2$D$^+$ (1$_1$,$0$–1$_1$,$1$), N$_2$H$^+$ (1–0) and N$_2$D$^+$ (2–1) superposed on the 1.3 mm continuum emission map of the pre-stellar core L1544. Contour levels are 30%, 50%, 70% and 90% of the peak for H$_2$D$^+$, and 50% of the peak for N$_2$H$^+$ and N$_2$D$^+$. The observed positions in H$_2$D$^+$ are reported as triangles.

They show the correlation between the ortho-H$_2$D$^+$ abundances at the 0$''$, ± 20$''$ and ± 40$''$ distance from the dust peak and the CO depletion factor, the DCO$^+$/HCO$^+$ ratio and the N$_2$D$^+$/N$_2$H$^+$ ratio (see Figure 5). As intuitively expected, the ortho-H$_2$D$^+$ abundance appears to be well correlated with the CO depletion. Also, the fractionation ratios for the N$_2$H$^+$ and HCO$^+$ molecules increase linearly with the ortho-H$_2$D$^+$ abundance. The surprisingly high confidence level for the correlations between H$_2$D$^+$ and the degree of deuteration in the HCO$^+$ and N$_2$H$^+$ molecules confirms that H$_2$D$^+$ dominates the fractionation of these molecules at low temperatures. Therefore, in the pre-stellar core L1544, D$_2$H$^+$ and D$_3^+$ should not intervene in these fractionations (see Figure 1).

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Figure 5. Variation of the observed ortho-H$_2$D$^+$ as a function of the depletion factor, DCO$^+$/HCO$^+$ ratio and N$_2$D$^+$/N$_2$H$^+$ ratio in the pre-stellar core L1544. The $\chi^2$ parameter and its probability are reported.

(c) L183 (L134N)

Another example is the cold, dark, starless cloud core L183, where we present observations of the ortho-H$_2$D$^+$ (1$_{10}$-1$_{11}$) ground transition (Vastel, Pagani et al. in preparation). We traced the central ridge and the central peak of L183 (defined in Pagani et al. 2003, 2004) together with detailed maps of several transitions of N$_2$H$^+$ and N$_2$D$^+$ obtained at IRAM and at CSO (see Figure 6). N$_2$H$^+$ and N$_2$D$^+$ do not trace the dust peak and thus are depleted in the most inner part of the cloud (Pagani et al. 2005) while H$_2$D$^+$, as expected from theory and other source observations (as in the case of L1544) does peak at the dust peak. Surprisingly, the H$_2$D$^+$ is very extended, spanning 150" in declination and presents a second intensity peak, of similar strength to the main peak, 50" north of it. This second peak has no local dust counterpart.

We also searched for para-D$_2$H$^+$ (1$_{10}$-1$_{01}$) at 692 GHz towards the main dust peak but have found no emission so far. The para-D$_2$H$^+$/ortho-H$_2$D$^+$ ratio is thus lower than 0.4, two times less than in the case of 16293E and at least 2 times less than in the case of L1544.

3. Perspectives

Recently Caselli et al. (in preparation) performed a survey in H$_2$D$^+$ over a sample of prestellar cores, and some protostars. Three quarters of these sources present a
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Figure 6. Integrated intensity maps of $N_2H^+$ (1–0) and $N_2D^+$ (1-0) superposed on the dust emission map of the pre-stellar core L183. Contour levels 90% of the peak for $N_2H^+$ and 85% for $N_2D^+$. The $o$-$H_2D^+$ column densities (squares) and the upper limit on $p$-$D_2H^+$ (diamonds) are reported for $T_{ex} = 7, 8, 9$ K.

Table 1. Current and future facilities for the chemistry of $H_2D^+$ and $D_2H^+$.

| Name            | Aperture | Available | $1_{1,0}-1_{1,1}$ (372.4 GHz) | $1_{0,1}-0_{0,0}$ (1.37 THz) | $1_{1,0}-1_{0,1}$ (691.7 GHz) | $1_{1,1}-0_{0,0}$ (1.48 THz) |
|-----------------|----------|-----------|-------------------------------|------------------------------|-------------------------------|-------------------------------|
| CSO             | 10.4 m   | Y         | Y                            | Y                            | Y                             | N                             |
| JCMT            | 15 m     | Y         | HARP B                       | Y                            | N                             | Y                             |
| SOFIA           | 2.5 m    | 2007      | N                             | Casimir                      | Casimir                       | Casimir                       |
| Herschel (HIFI) | 3.5 m    | 2007      | N                             | Y                            | Y                             | Y                             |
| APEX            | 12 m     | 2005-2006 | Y                             | CONDOR                       | Y                             | CONDOR                        |
| ALMA            | 50 × 12 m | 2010     | Y                             | CONDOR                       | Y                             | N                             |

strong emission (between 0.5 to 1 K in main beam temperature). In dark clouds affected by molecular depletion, the deuterated forms of the molecular ion $H_3^+$ are unique tracers of the core nucleus, the future stellar cradle. Thus, their study becomes fundamental to unveil the initial conditions of the process of star formation (kinematics, physical and chemical structure of pre–stellar cores). Table 1 lists some of the major telescopes and interferometers that can be used for the study of $H_2D^+$ chemistry in prestellar, proto-planetary disks and protostars. Furthermore, the access to the para-$H_2D^+$ and ortho-$D_2H^+$ transitions with new submillimeter receivers on ground based and space telescopes will enable to determine precisely the ortho–to–para ratios for both molecules.

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