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UNVEILING THE EARLIEST STAGE OF STAR FORMATION: THE $H_3{}^+$ DEUTERATION TOOL.

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Abstract. 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_2D^+ molecule, and the low temperature in dark interstellar clouds favors this production. Furthermore, the presence of multiply deuterated species have incited us (Phillips & Vastel 2003) to proceed further and consider the subsequent reaction of H_2D^+ with HD, leading to D_2H^+ (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_2H^+ and $D_3{}^+$ (Roberts, Herbst & Millar 2003) predicted that these molecules should be as abundant as H_2D^+. The first detection of the D_2H^+ was made possible by the recent laboratory measurement by Hirao & Amano (2003) for the frequency of the fundamental line of the para-D_2H^+. In this paper I present observations of H_2D^+ and D_2H^+ towards a sample of dark clouds and prestellar cores and show how the distribution of ortho-H_2D^+ ($1_{1,0}$-$1_{1,1}$) can trace the deuterium factory in prestellar cores. I will also present how future instrumentation will improve our knowledge concerning the deuterium enhancement of $H_3{}^+$.

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 $\sim 1.5 \times 10^{-5}$ (Linsky 2003). 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_2H^+ (Butner et al. 1995; Williams et al. 1998; Caselli et al. 2002; Crapsi et al. 2004, Crapsi et al. 2005; Pagani et al. 2007), H_2CO (Loinard et al. 2001; Bacmann et al. 2003), H_2S (Vastel et al. 2003), HNC (Hirota et al. 2003), CH_3OH (Parise et al. 2004), and NH_3 (Roueff et al. 2000, Tiné et al. 2000). The chemical fractionation process in the gas–phase mainly 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_3OH (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 ∼0.1 (Parise et al. 2002). The high abundance found in the gas phase for the D_2S 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_2D^+:

$$H_3^+ + HD \longleftrightarrow H_2D^+ + H_2 + 230\ \mathrm{K} \tag{1.1}$$

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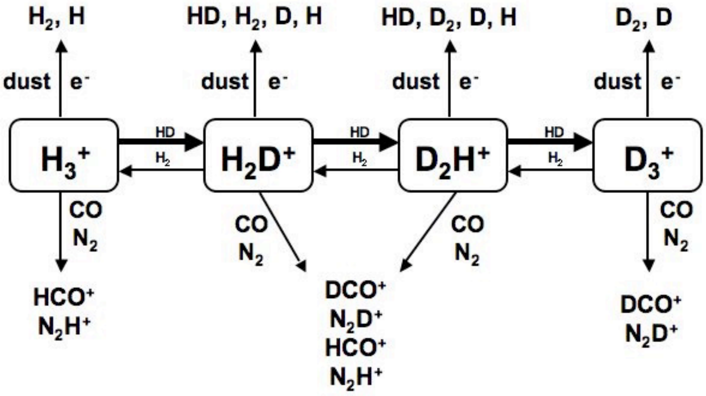

Fig. 1. Main reactions involving the deuterated forms of the H_3^+ molecule. When CO and N_2 are depleted and the fractional ionization is $\leq 10^{-7}$, the reactions with bold arrows are dominant.

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_2D^+ becomes non-negligible. This primary fractionation can then give rise to other fractionations and form D_2H^+ and D_3^+ as first suggested by Phillips & Vastel (2003):

$$H_2D^+ + HD \longleftrightarrow D_2H^+ + H_2 + 180 \text{ K} \tag{1.2}$$

$$D_2H^+ + HD \longleftrightarrow D_3^+ + H_2 + 230 \text{ K} \tag{1.3}$$

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, 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 (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 Roberts et al. 2004; Flower et al. 2004).

2 Observational evidences

We present in the following the recent advances on the deuterium enhancement based on observations of pre-stellar cores and low mass protostars. 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. These objects are cold ($\leq$ 10 K) and dense ($\geq 10^5$ cm^{-3}). They are believed to be on the verge of collapse and therefore are considered as representative of the initial conditions of star formation. As the density increases, gaseous molecules start to freeze out onto dust grains. The disappearance of most molecules (particularly CO as developped in Section 1) triggers an extreme molecular deuteration. In a latter stage, gravitational contraction dominates and the condensation evolves into a low mass protostar surrounded by a thick envelope. Most of the envelope is cold and depleted of heavy molecules, but the innermost regions are heated by the gravitational energy of the central source. Therefore, dust temperature increases and molecules initially trapped onto the dust grains evaporate, enriching the gas-phase chemistry in these regions.
Gas phase species are expected to be depleted at the centers of cold, dark clouds, since they tend to stick onto 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.

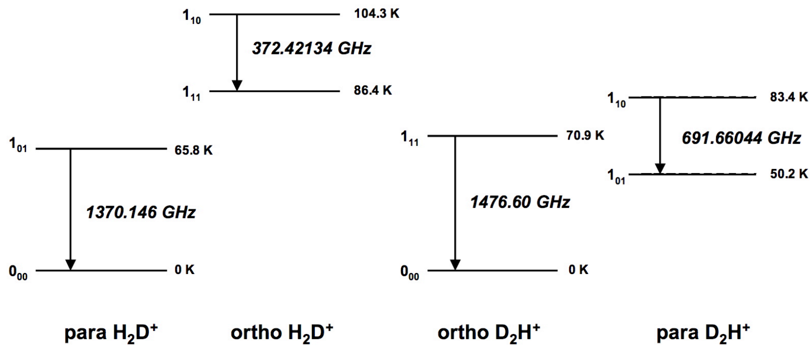

Fig. 2. Diagrams of the lowest energy levels for the H_2D^+ and D_2H^+ molecules.

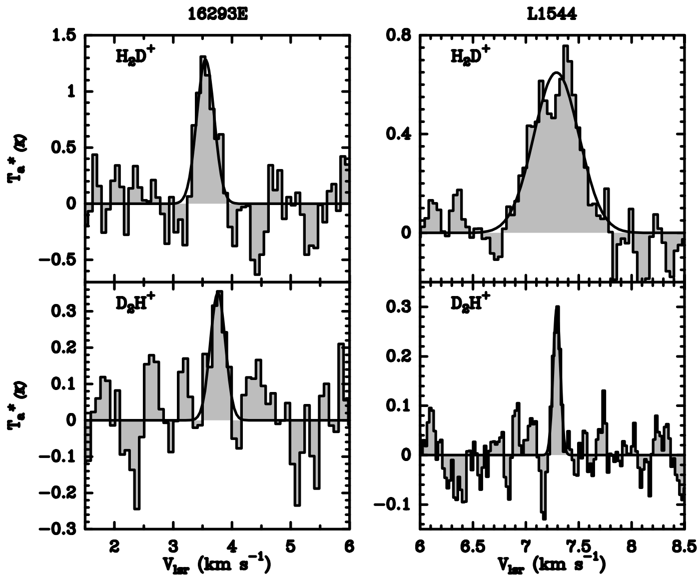

Fig. 3. Spectra of the ortho-H_2D^+ $1_{1,0}$-$1_{1,1}$ and para-D_2H^+ $1_{1,0}$-$1_{0,1}$ transitions towards 16293E (Vastel et al. 2004) and L1544 (Vastel et al. 2006b).

(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.

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 $1_{1,0}$–$1_{1,1}$ transition towards the young stellar object, NGC 1333 IRAS 4A (Stark, van der Tak & van Dishoeck 1999) although with a relatively low signal strength. The strong signal detected by Caselli et al. (2003) in the pre-stellar core L1544 triggered an intense search in many pre-stellar cores known to be CO-depleted and deuterium abundant. Following the H_2D^+ detection by Caselli et al. (2003), another break-through detection has been performed with the first detection of the doubly deuterated hydronium in the 16293E pre-stellar core in Ophiucus (Vastel et al. 2004; see Figure 3). We found that D_2H^+ is as abundant as H_2D^+, which is a remarkable verification of theoretical predictions where all forms of deuterated $H_3{}^+$ have been included. Many H_2D^+ studies have been published within a year, e.g. Vastel et al. (2006a), Hogerheijde et al. (2006), Harju et al. (2006).

Recently, the ortho-H_2D^+ line has also been mapped in L1544 (Vastel et al. 2006b) and found a strong

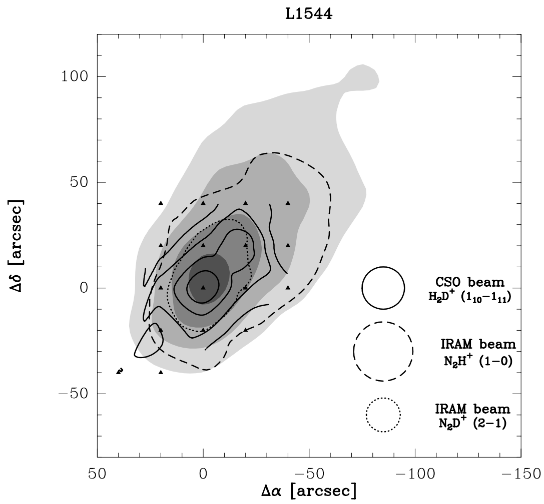

Fig. 4. Integrated intensity maps of H_2D^+ ($1_{1,0}$-$1_{1,1}$), N_2H^+ (1-0) and N_2D^+ (2-1) supperposed on the 1.3 mm continuum emission map of the pre-stellar core L1544. COntour levels are 30, 50, 70 and 90 % of the peak for H_2D^+ and 50% of the peak for N_2H^+ and N_2D^+. The observed positions in H_2D^+ are reported as triangles.

correlation with the CO depletion factor. Figure 4 shows the integrated intensity map of ortho-H_2D^+, together with maps of N_2H^+ (1-0) and N_2D^+ (2-1) and the 1.3 mm continuum emission map. Also, an upper limit on the para-D_2H^+ line has been repported (see Figure 3).

In Figure 5 we present a comparison of the observed ortho-H_2D^+ and para-D_2H^+ lines toward a sample of pre-stellar cores et protostars (Vastel et al. 2004, Vastel et al. 2006a, Vastel et al. 2006b, Caselli et al. *in preparation*) with a model presented in Vastel et al. (2006). The abundances are plotted as a function of CO depletion. Two factors (other than dust temperature) can modify the CO depletion, namely, the age of the condensation (larger ages give larger CO depletions because molecules have more time to freeze out onto the dust grains) and the gas density (the condensation rate is proportional to the gas density). In addition, the cosmic ionization rate regulates the overall ionization degree in the condensation and therefore the H_3^+ isotopomers abundances. Finally, the grain sizes enter both in the CO condensation rate (via the grains area) and in the charge balance, because negatively charged grains recombine with the positively charged molecular ions. In this comparaison, we adopted a cosmic ionization rate of 3 10^{-17} s^{-1}, age of the condensation of 10^5 years and varied the grain size from 0.05, 0.2 and 0.4 μm.

Both H_2D^+ and D_2H^+ molecules have ortho and para forms, corresponding to the spin states of the protons (for H_2D^+) or deuterons (for D_2H^+). 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_2D^+ would be: $\frac{n(1_{1,1})}{n(0_{0,0})} = 9 \times \exp(-\frac{86.4}{T})$ and the relative populations of the lowest ortho ($0_{0,0}$) and para ($1_{0,1}$) levels of D_2H^+ would be $\frac{n(1_{0,1})}{n(0_{0,0})} = \frac{9}{6} \times \exp(-\frac{50.2}{T})$ Therefore, at 8 K, the H_2D^+ ortho–to–para ratio would be $\sim$ 1.8 10^{-4} and the D_2H^+ para–to–ortho ratio would be $\sim$ 2.8 10^{-3}. The ortho form of H_2D^+ 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, the o/p H_2D^+ ratio is not thermalized either. 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 μm, the o/p–H_2D^+ reaches unity and the p/o–D_2H^+ value is about 0.1. Increasing the grain size will decrease the grain surface, leading to a decrease of the H_2 formation rate. Therefore, the H_2 ortho–to–para ratio will obsiously decrease, as well as the H_2D^+ ortho–to–para ratio.

We can directly compare our H_2D^+ observations with the Flower, Pineau des Forets, Walmsley (2004) model, even if their study assumes complete depletion (i.e. that CO abundance should be less than 10^{-6}). Indeed the abundance of both ortho and para spin states of H_2D^+ depends on the ortho and para forms of molecular

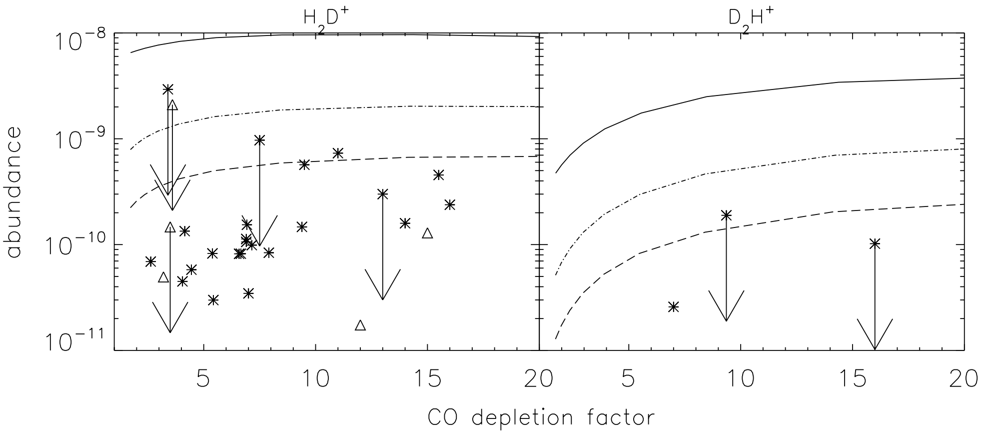

Fig. 5. Variation of the H_2D^+ and D_2H^+ abundances for the model (solid line) as a function of CO depletion. The stars (pre-stellar cores) and triangles (protostars) represent the observed abundances of ortho-H_2D^+ and para-D_2H^+, whereas the lines show the modeled abundance of the ortho+para states (see text). Hence, we expect the observed values to lie below the modeled ones.

hydrogen (through the proton-exchanging reaction of H_3^+ with H_2 followed by reaction 1) which does not vary as a function of depletion. On the contrary, the abundance of both para and ortho forms of D_2H^+ is determined by reactions with HD (produced on the grain surfaces) and will therefore depends on the core depletion. The Flower et al. model predicts H_2D^+ ortho–to–para ratios larger than the maximum value of 0.3 we observed for a temperature of 8 K and a H_2 density of 2×10^6 cm^{-3} (Pineau des Forets, *private communication*) spanning ranges up to 0.4 μm of the grain radius. As a consequence, since the H_2D^+ ortho–to–para ratio decreases as a function of the grain radius, it is likely that this should be larger than 0.2 μm for most of these observations. Depletion of small grains would be consistent with grain coagulation since ice condensation is not enough to increase the grain radius.
A detailed analysis of the 10 starless cores and 6 cores with stars presented in Figure 5 is performed by Caselli et al. *in preparation.*

3 Perspectives

Table 1 lists the telescopes and interferometers that can be used for the study of H_2D^+ chemistry in prestellar, proto-planetary disks and protostars. The observational constraints are strong, since observations at 692 GHz are difficult even on Mauna Kea (4200 m) with CSO and JCMT. The situation on the ground will improve with the advent of ALMA and APEX at 5000 m elevation in Chili. The access to the high frequency 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 and compare with theory. Probably, D_3^+ cannot be observed, because enhanced D_3^+ abundance implies very cold and very dense regions. Since it is a symmetric molecule, it does not have rotational transitions and does have its bending modes in the near-infrared. Therefore, these transitions will only be observable in absorption against a strong near-infrared continuum. Recently Cernicharo et al. (2007) claimed the first FIR detection of H_2D^+ in the line of sight toward SgrB2. Its line of sight crosses the Galactic spiral arms several times where most of the material resides. This detection would open a new playground for the deuterium chemistry studies. However, H_2D^+ and D_2H^+ are so far the only direct tracers of cold, dense phases of molecular clouds prior to star formation.

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

Name	Aperture	Available	H_2D^+ $1_{1,0}$–$1_{1,1}$ (372.4 GHz)	H_2D^+ $1_{0,1}$–$0_{0,0}$ (1.37 THz)	D_2H^+ $1_{1,0}$–$1_{0,1}$ (691.7 GHz)	D_2H^+ $1_{1,1}$–$0_{0,0}$ (1.48 THz)
CSO	10.4 m	Y	Y	N	Y	N
JCMT	15 m	Y	HARP B	N	Y	N
SOFIA	2.5 m	2009?	N	Casimir GREAT (CONDOR)	Casimir	Casimir GREAT (CONDOR)
Herschel (HIFI)	3.5 m	2008	N	N	Y	Y
ALMA	50 × 12 m	2010	Y	N	Y	N
APEX	12 m	Y	Y	CONDOR	Y	CONDOR

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