

# The Formation of Deuterated Molecules in Dense Clouds

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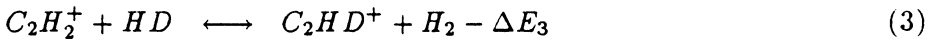
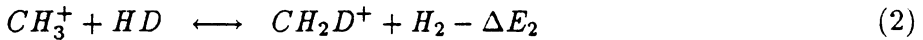
**Abstract.** In this article, I list the deuterated species detected so far, together with an estimate of their abundance ratios relative to their hydrogen bearing parent for a variety of astronomical regions, discuss the basic chemical processes which fractionate deuterium together with some simple estimates of the degree of fractionation which can result from these processes. I then discuss in detail the deuteration of hydrocarbon molecules and show that the effects of chemical reactions which can recycle parent species can appreciably affect estimates of fractionation. Finally I shall discuss how structural effects may inhibit fractionation in the cyanopolynes and related species.

## 1. Introduction

Molecules containing deuterium have been observed in interstellar clouds for many years. Except for the detection of HD in diffuse clouds (Rogerson et al. 1973), all D-bearing species are found in dense molecular clouds having a variety of temperatures ranging from  $\sim 10$  K in cold, dust clouds, to  $\sim 30$ -70 K in giant molecular clouds, to  $\sim 100$ -200 K in hot molecular cores. Table I lists the 14 deuterium-bearing molecules detected in interstellar clouds, together with a rough estimate,  $R$ , of its abundance relative to its hydrogen-bearing form, for a sample of sources. Note that this list excludes  $H_2D^+$  for which Phillips et al. (1985) find one line in one source; this identification, although probably correct, needs confirmation. Since the last Astrochemistry meeting in Goa (Wooten, 1987), there have been detections of  $C_3HD$  (Bell et al., 1986; Gerin et al., 1987),  $C_4D$  (Turner, 1989) and  $D_2CO$  (Turner, 1990), the first doubly-deuterated molecule observed. In general the abundances of deuterated molecules relative to their hydrogenated forms are enhanced, or fractionated, over the HD/ $H_2$  abundance ratio, HD being the reservoir of deuterium in dense clouds. There have also been some significant theoretical advances in this period. In particular, it has been realised that for the hydrocarbon species, it is difficult to decouple the fractionation reactions from the large set which govern the chemistry because several different chemical pathways can contribute to the formation of any particular hydrocarbon. Detailed time-dependent calculations are required and have been carried out by Brown and Rice (1986) and Millar, Bennett and Herbst (1989). Indeed even for a simple species such as  $DCO^+$ , the simple analyses performed by, for example, Watson (1976, 1977), Guélin et al. (1977) and Snyder et al. (1977), do not give the correct ratio at so-called 'early-time' which is thought to give the best agreement with observations (Millar et al..

1989). In addition, it has been recognised that the fractionation observed in hot molecular cores does not result from a high temperature chemistry but must be a relic of a low temperature chemistry involving both gas-phase and grain-surface reactions (Brown and Millar, 1989a,b; Turner, 1990).

The basic reactions which initiate the fractionation of many species involve the abstraction of D atoms from HD:



where  $\Delta E_1$ ,  $\Delta E_2$  and  $\Delta E_3$  are equivalent to about 200 K, 370 K and 550 K, respectively. One can estimate the enhancement factor,  $S$ , that is the factor by which the abundance ratio  $R(XD^+)$  is enhanced over the deuterium abundance ratio in the reservoir,  $R(HD)$  - here  $R(XD) = [XD]/[XH]$ , where the square brackets refer to fractional abundances. At high temperatures,  $\gtrsim 25$  K for  $H_2D^+$ ,  $\gtrsim 60$  K for  $CH_2D^+$  and  $C_2HD^+$ , the enhancement factors decrease exponentially with increasing temperature. The larger abundance of  $H_3^+$  usually ensures that reaction (1) dominates fractionation at very low temperatures, the maximum value of  $S_1$  being  $\sim (1-2) 10^3$ .

In addition to fractionation via HD, the dissociative recombination of  $DCO^+$  leads to an enhancement in the atomic deuterium to atomic hydrogen ratio, and fractionation via reaction of D atoms with species such as  $H_3^+$ ,  $HCO^+$ ,  $N_2H^+$  and  $OH$  may occur (Dalgarno and Lepp, 1984; Croswell and Dalgarno, 1985; Adams and Smith, 1985). The free energies associated with these reactions are much larger than those of reactions (1)-(3) and would imply large enhancement factors at high temperatures. This is not observed for  $N_2D^+$ , for example, indicating that D atoms are not the major reservoir of gas phase deuterium in dense clouds. Even so, appreciable fractionation of OD has been predicted (Croswell and Dalgarno, 1985; Millar et al., 1989; Brown and Millar, 1989a).

## 2. Deuteration of hydrocarbon molecules

The chemistry of the hydrocarbons have been discussed in detail by many workers. Turner (1989) pointed out that the chemistries of  $C_3H$ ,  $c-C_3H_2$ ,  $C_4H$  and  $HC_3N$  are inter-related, mainly through the  $C_3H_3^+$  ion, and that the fractionation of these ions might be simply related to one another. Consider the formation of  $C_4H$  from  $C_3H_2$ :



where  $f$  is the fraction of the dissociative recombinations of  $C_4H_2^+$  which give  $C_4H$  as a product. The  $C_4D$  molecule may be synthesised from  $C_3HD$  in similar fashion, but with an efficiency reduced by statistical considerations.

If one considers only these formation processes, as Turner (1989) does, then  $R(C_4D) = \frac{1}{6} R(C_3HD)$ . Similarly one can show  $R(DC_3N) = \frac{1}{2} R(C_3HD)$  if  $HC_3N$  is a result of the  $C_3H_3^+ - N$  reaction. This leads to the ratio  $R(C_4D):R(DC_3N):R(C_3HD) = 1:3:6$  whereas the observed ratio in TMC-1 is 1:3.5:18.6 (Turner, 1989), although  $R(C_3HD)$  is very large and uncertain (Bell et al., 1988, Turner, 1989). A more detailed approach is to recognise that proton transfer reactions, involving ions such as  $H_3^+$ ,  $HCO^+$  and  $H_3O^+$ , and charge transfer reactions can destroy deuterated and hydrogenated species at different rates. For example proton transfer reactions with  $C_4H$  lead to destruction of  $C_4H$  only on a fraction  $(1-f)$  of collisions, while the same reactions with  $C_4D$  destroy this species on  $(1-\frac{1}{2}f)$  of collisions. Hence

$$R(C_4D) = \frac{1}{6} \frac{(1-f)}{(1-\frac{1}{2}f)} R(C_3HD).$$

Likewise

$$R(DC_3N) = \frac{1}{2} \frac{(1-f)}{(1-\frac{1}{2}f)} R(C_3HD).$$

If  $f = \frac{4}{5}$  in both reaction (6) and in the recombination of  $HDC_3N^+$  (but see below) we find a ratio  $R(C_4D):R(DC_3N):R(C_3HD) = 1:3:18$ , close to that observed. We can also predict  $R(C_3D)$  on the assumption that  $C_3H$  is formed in the recombination of  $C_3H_3^+$  - note that the reaction  $C_3H^+ + H_2 \rightarrow C_3H_2^+ + H$  is endothermic by  $\sim 550$  K - as

$$R(C_3D) = \frac{1}{2} \frac{(1-f)}{(1-\frac{1}{2}f)} R(C_3HD).$$

Such an analysis is uncertain due to several problems:- (i) we have ignored deuteration from  $H_2D^+$  which is important at low temperatures - although not if  $R(C_3HD)$  is indeed very large, and (ii) we have ignored the effects of the linear and cyclic forms of  $C_3H_3^+$ ,  $C_3H$  and  $C_3H_2$ , which need to be further studied in the laboratory to determine the relevant rate coefficients and branching ratios. Finally the deuteration of the cyanopolyynes is sensitive to the structure of the protonated cyanopolyne ion, a topic we now discuss in detail.

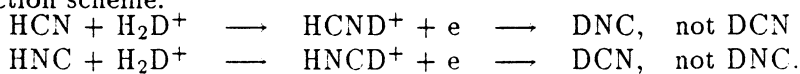
### 3. Deuteration of the cyanopolyynes and of HCN and HNC

Microwave spectroscopy of protonated cyanoacetylene has shown that the most stable state is linear,  $HC_3NH^+$  (Lee and Amano, 1987). Thus deuteration of  $HC_3N$  by ions such as  $H_2D^+$ ,  $N_2D^+$  and  $DCO^+$  may not lead to

DC<sub>3</sub>N as has previously thought. That is the reaction H<sub>2</sub>D<sup>+</sup> + HC<sub>3</sub>N leads to linear HC<sub>3</sub>ND<sup>+</sup>. If we now assume that in the dissociative recombination of HC<sub>3</sub>ND<sup>+</sup> the D-atom cannot be rearranged sufficiently to bond to the carbon atom at the other end, then the deuterium in DC<sub>3</sub>N, and by extension, DC<sub>5</sub>N, DC<sub>7</sub>N, etc, cannot arise from deuteron transfer, but in the formation process itself. It is also worth noting that if HC<sub>3</sub>NH<sup>+</sup> and HC<sub>3</sub>ND<sup>+</sup> are the correct structures, then reactions of H<sub>3</sub><sup>+</sup>, HCO<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, etc. will recycle HC<sub>3</sub>N and DC<sub>3</sub>N at the same rate, so that R(DC<sub>3</sub>N) =  $\frac{1}{2}$  R(C<sub>3</sub>HD) independent of f, the fraction recycled.

The actual value expected depends on various assumptions concerning the formation of the formaldehyde-type ions H<sub>2</sub>C<sub>3</sub>N<sup>+</sup> and HDC<sub>3</sub>N<sup>+</sup> from the reactions of C<sub>3</sub>H<sub>3</sub><sup>+</sup> and C<sub>3</sub>H<sub>2</sub>D<sup>+</sup> with N atoms. In order to see the effects of including the various isotopomers of HC<sub>3</sub>N and HC<sub>3</sub>NH<sup>+</sup>, D A Howe and I have adapted the model of Millar et al. (1989) using the so-called 'old' dissociative recombination branching ratios and calculated the pseudo-time-dependent behaviour of abundances and fractionation ratios for conditions typical of TMC-1 and of the Orion ridge clouds. For our purposes, we shall concentrate on the TMC-1 model, for which R(DC<sub>3</sub>N) falls from 1.9 10<sup>-2</sup> in the model of Millar et al. (1989) to 4.3 10<sup>-3</sup> at early time, compared with an observed value of (1.5 ± 0.5) 10<sup>-2</sup> (Suzuki, 1987). At steady-state, the values of R(DC<sub>3</sub>N) are larger, but the absolute abundances of HC<sub>3</sub>N and DC<sub>3</sub>N are much less than those observed.

Like HC<sub>3</sub>NH<sup>+</sup>, the HCNH<sup>+</sup> ion is linear and H<sub>2</sub>D<sup>+</sup> and related ions may also not be efficient in synthesising DCN from HCN and DNC from HNC. If the deuterium atom cannot move during dissociative recombination, then the possibility arises that HCN is related to DNC and HNC to DCN, by the reaction scheme:



Other products are possible, of course. It is possible that because HCND<sup>+</sup> and HNC D<sup>+</sup> are much smaller than the cyanopolyne ions, rearrangement of the D atoms could occur.

Detailed calculations on this suggestion are needed but are complicated by the presence of H<sub>2</sub>NC<sup>+</sup> formed in the reaction of C<sup>+</sup> with NH<sub>3</sub> (Allen, Goddard, and Schaefer 1980), and the lack of reliable branching ratios in the dissociative recombinations of HCNH<sup>+</sup> and H<sub>2</sub>NC<sup>+</sup> with electrons.

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TABLE I

Deuterium-bearing molecules detected in interstellar clouds. For each species we give an estimate, R, of its abundance relative to its hydrogen-bearing form, for a sample of sources. HD is detected in diffuse clouds with an abundance ratio HD/H<sub>2</sub> ~ 10<sup>-6</sup>.

Molecule	TMC-1 <sup>a</sup>	Orion <sup>b</sup>	Orion Hot Core <sup>c</sup>
HDO			>.002
DCO <sup>+</sup>	.015	.002	
N <sub>2</sub> D <sup>+</sup>	<.045		
DCN	.023	.02	.005
DNC	.015	.01	
C <sub>2</sub> D	.01	.045	
NH <sub>2</sub> D	<.02		.003
HDCO	.015	.02	.14
c-C <sub>3</sub> HD	.08		
C <sub>4</sub> D	.004		
DC <sub>3</sub> N	.015		
DC <sub>5</sub> N	.013		
CH <sub>3</sub> OD			.03
D <sub>2</sub> CO			.02

<sup>a</sup>TMC-1 is a dark cloud with kinetic temperature ~ 10 K. <sup>b</sup>Orion is a giant molecular cloud with kinetic temperature ~ 50-70 K. <sup>c</sup>Orion Hot Core is close to a site of star formation and has kinetic temperature ~ 200 K.