

# Gas-phase formation of doubly-deuterated species

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**Abstract.** We present the first results from a time-dependent chemical model to include a gas-phase reaction scheme for producing doubly-deuterated species. Under normal conditions the formation of these species is inefficient. However, when the effects of the freeze out of gas phase species onto grains is included in the chemistry we find that the fractionation of both singly and doubly deuterated species is enhanced.

We compare the predictions from our models with recent observations of deuterated molecules in L134N and find that, contrary to previous expectations, we can reproduce the observed levels of fractionation without recourse to an active grain-surface chemistry.

**Key words:** ISM: abundances – ISM: molecules – ISM: clouds – ISM: individual objects: L134N

## 1. Introduction

Deuterated species are an important tool for understanding interstellar chemistry. Deuterium forms slightly stronger bonds than hydrogen at low temperatures ( $< 100$  K) and the abundance of deuterium-bearing molecules can become significantly enhanced over the cosmic D/H ratio of  $\sim 10^{-5}$ . Molecular D/H ratios of the order of  $10^{-2}$  have been observed in cold, dark clouds such as TMC-1.

In contrast, hot molecular cores (HMC's) are clumps of hot, dense gas, usually associated with high mass star formation. The temperatures of these cores (typically 70–150 K) should be high enough to preclude the enhancement of molecular D/H ratios through gas-phase reactions. The ratios which have been measured, however, are generally  $\sim 10^{-3}$  (e.g. Hatchell et al. 1998, 1999), lower than TMC-1, yet still enhanced over cosmic. It is now generally accepted that these ratios have been preserved from an earlier, colder phase of the cloud's history in the ice-mantles of dust grains. Rodgers & Millar (1996) showed that such high D/H ratios could survive for  $\sim 10^4$  yrs after evaporation.

HMC's generally have high abundances of species which do not form efficiently in the gas phase (e.g.  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$ ).

These are thought to be evidence that processing has taken place on the grain surfaces. Since gas-phase chemistry is not expected to produce significant amounts of doubly-deuterated species, observations of enhanced  $[\text{D}_2\text{CO}]/[\text{H}_2\text{CO}]$  ratios in Orion (Turner 1990) and in IRAS 16293 (Ceccarelli et al. 1998; Loinard et al. 2000) have also been taken to be a signature of active grain surface chemistry, though it has remained unclear as to why grain-surface chemistry should produce significant amounts of  $\text{D}_2\text{CO}$ , yet not increase deuterium fractionation, in general, above the levels observed in cold clouds.

This interpretation has become even more questionable following the detection of doubly deuterated ammonia ( $\text{NHD}_2$ ) in the dark cloud L134N by Roueff et al. (2000). Since the temperature in this region is  $\sim 10$  K, too low for efficient evaporation of ice mantles, these molecules are unlikely to be products of an active grain surface chemistry which have been returned to the gas-phase.

The accretion of molecular species onto the surfaces of dust grains, as is expected to occur at the centres of cold, dense clouds, has long been known to increase deuterium fractionation (Brown & Millar 1989; Willacy & Millar 1998). This theoretical expectation has been confirmed by the detection of large  $[\text{DCO}^+]/[\text{HCO}^+]$  ratios in L1544 by Caselli et al. (1999) in clumps in which CO is significantly depleted.

Large enhancements in molecular D/H ratios can, therefore, provide evidence that accretion is occurring. Indeed Roueff et al. considered L134N to be a good candidate for a search for  $\text{NHD}_2$  because mono-deuterated species are so abundant there (e.g.  $[\text{NH}_2\text{D}]/[\text{NH}_3] = 0.1$ ,  $[\text{DCO}^+]/[\text{HCO}^+] = 0.18$ ). Since grain evaporation is unlikely to play any role in the setting of gas-phase fractionation in L134N, we wish to explore the possibility that accretion may increase the abundances of not only the singly deuterated species, but also the doubly deuterated species to observable levels.

Throughout, we adopt the conventions: '[ABC]' means the fractional abundance of molecule ABC; 'fractionation of XD' means  $[\text{XD}]/[\text{XH}]$ .

## 2. The models

Our models are essentially those described in Roberts & Millar (2000, hereafter Paper I), however they now consist of

~300 species (including 120 mono-deuterated and 15 doubly-deuterated species) and ~5550 reactions. We compare results from two different chemical scenarios. Our ‘gas-phase’ model considers a standard gas-phase chemistry, with  $\text{H}_2$  and HD forming on the grain surfaces, while the ‘accretion’ model also includes the possibility that species colliding with grains will freeze onto their surfaces.

The mono-deuterated reaction set is ‘complete’, in the sense that for every reaction containing a hydrogen-bearing molecule there is an analogue reaction containing the equivalent mono-deuterated species. If more than one reaction product contains hydrogen atoms uncertainty arises as to which will be the deuterium bearing product. Due to lack of comprehensive experimental data, the usual approach to this is to assume statistical branching ratios between the various possibilities (Millar et al. 1989; Rodgers & Millar 1996). In most cases we have adopted this method, though there are special cases and caveats, discussed in Paper I. The advantage of generating a complete deuterium chemistry in this way is that it is then possible to compare the models with observations of many deuterated species, however the disadvantage is that it increases the reaction set (and hence the running time of the model) enormously.

In this study we were particularly interested in the fractionation of doubly-deuterated formaldehyde,  $\text{D}_2\text{CO}$ , and doubly deuterated ammonia,  $\text{NHD}_2$ , since these molecules have been observed in the interstellar medium, and, also, doubly deuterated water,  $\text{D}_2\text{O}$ , since its spectrum has been well studied in the laboratory. Therefore, in order to keep the reaction set to a reasonable size, we have included only the species and reactions which we have found important in forming and destroying these molecules.

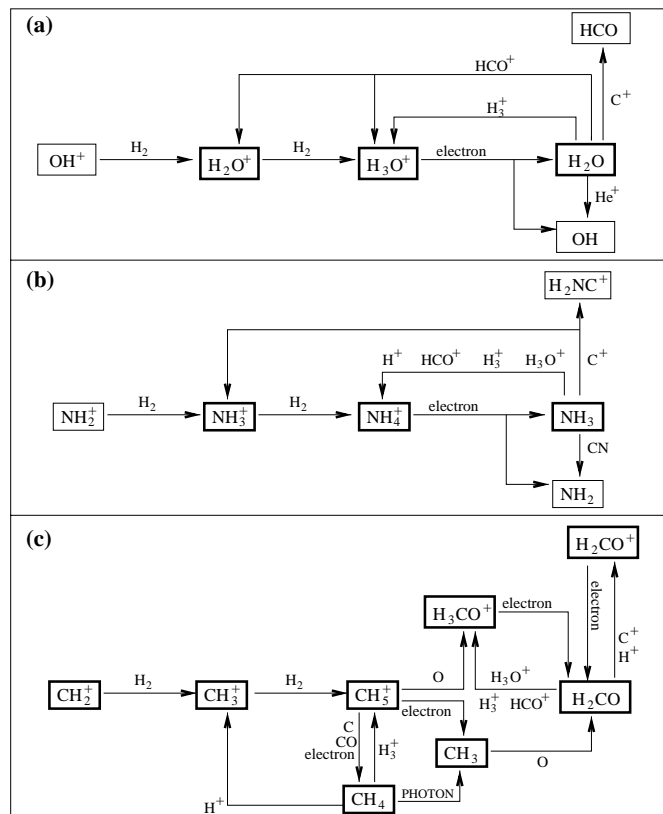
In considering which reactions to include we have examined both the formation routes and the mechanisms for deuteration, the basic reaction networks are illustrated in Figs. 1a–c. As mentioned above, all hydrogen bearing species have a mono-deuterated analogue, and these figures also indicate the species which have doubly-deuterated analogues in the model.

### 3. Results

#### 3.1. The gas-phase model

In order to ensure that we have included all the important reactions, the gas-phase model was run over a wide range of temperatures and densities. Fig. 2 summarises the results from these models for the species of interest. As we expect, the temperature and density dependence of the fractionations of the doubly deuterated species are very similar to their mono-deuterated counterparts.

$\text{NH}_2\text{D}$  is primarily fractionated via reactions of  $\text{NH}_3$  with deuterated species such as  $\text{H}_2\text{D}^+$ ,  $\text{DCO}^+$  and  $\text{H}_2\text{DO}^+$  to form  $\text{NH}_3\text{D}^+$  which can then recombine with electrons to give  $\text{NH}_2\text{D}$ .  $\text{NHD}_2$  is fractionated in a similar way, via reaction of  $\text{NH}_2\text{D}$  with the same deuterated molecules.  $\text{HDO}$  and  $\text{D}_2\text{O}$  are also fractionated via similar processes, this time from reactions of  $\text{H}_2\text{O}$  and  $\text{HDO}$  with  $\text{H}_2\text{D}^+$  and  $\text{DCO}^+$ .



**Fig. 1a–c.** The most important chemical pathways involved in forming and destroying **a** water, **b** ammonia and **c** formaldehyde. The heavy boxes indicate those species with a doubly deuterated analogue in the model.

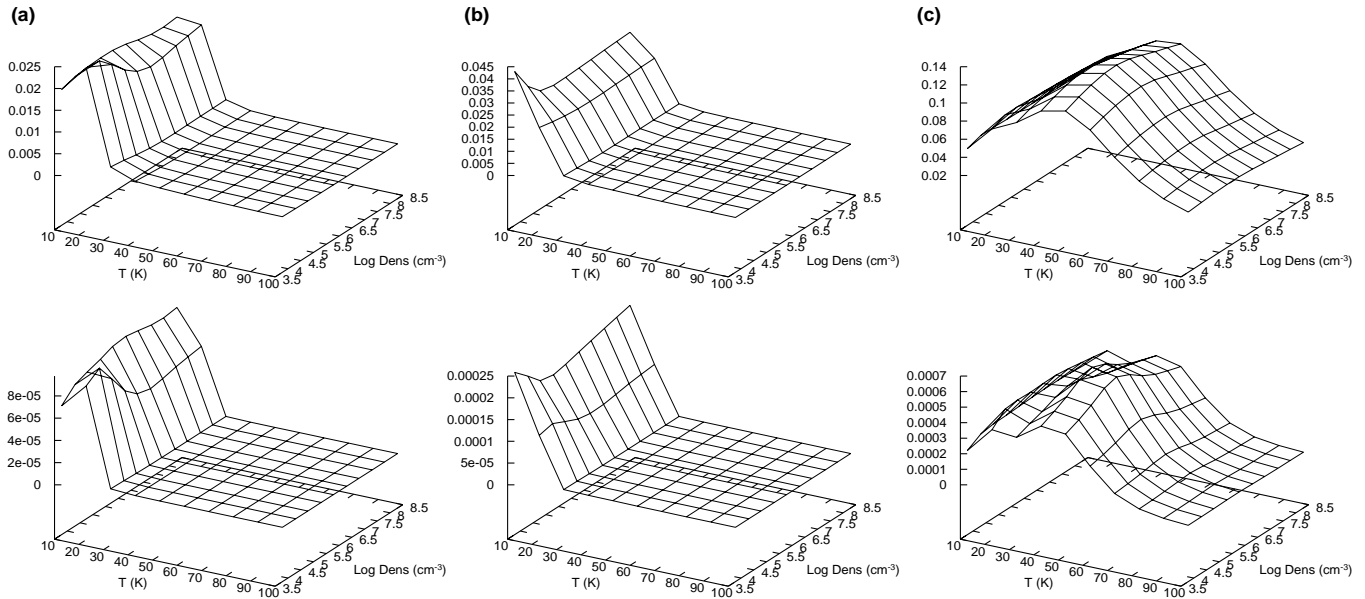
The  $[\text{NH}_2\text{D}]/[\text{NH}_3]$ ,  $[\text{NHD}_2]/[\text{NH}_3]$ ,  $[\text{HDO}]/[\text{H}_2\text{O}]$  and  $[\text{D}_2\text{O}]/[\text{H}_2\text{O}]$  ratios are only enhanced over cosmic values when the temperature is  $< 30$  K, this is due to the fractionation of the precursor ion  $\text{H}_2\text{D}^+$ . The  $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$  ratio is enhanced due to the reaction;



(rate coefficients from Sidhu et al. 1992), where the energy barrier on the right-hand side prevents destruction of  $\text{H}_2\text{D}^+$  by  $\text{H}_2$ . Other reactions of  $\text{H}_2\text{D}^+$  then transfer this enhancement to species such as  $\text{DCO}^+$  and  $\text{H}_2\text{DO}^+$ . The energy barrier on the right hand side of reaction (1) is relatively small, however, and above  $\sim 25$  K  $\text{H}_2\text{D}^+$  is increasingly destroyed by  $\text{H}_2$ .

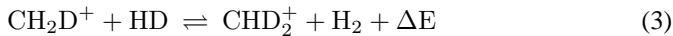
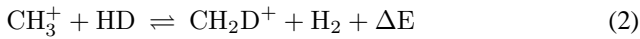
As the  $\text{H}_2\text{D}^+$  ion is such an important precursor of deuterium fractionation in cold clouds it may, at first, appear that its doubly-deuterated analogue,  $\text{HD}_2^+$ , will be equally as important in the production of doubly deuterated species. However, although  $\text{HD}_2^+$  will be present in the gas phase, it primarily reacts via proton/deuteron transfer, which will only form mono-deuterated species. Since it forms from, and has an abundance lower than that of  $\text{H}_2\text{D}^+$ , this is unlikely to contribute significantly to the overall deuterium fractionation.

The fractionation of  $\text{HDCO}$  and  $\text{D}_2\text{CO}$  also reflects that of their precursor ions, in this case,  $\text{CH}_2\text{D}^+$  and  $\text{CHD}_2^+$ , respec-



**Fig. 2a–c.** Steady-state molecular D/H ratios, from our gas-phase model, varying over a temperature range 10–100 K (in intervals of 10 K) and a  $\log_{10}n(\text{H}_2)$  range of  $\sim 3.5$ –8 (in intervals of 0.5); **a**  $[\text{NH}_2\text{D}]/[\text{NH}_3]$  (top),  $[\text{NHD}_2]/[\text{NH}_3]$  (bottom); **b**  $[\text{HDO}]/[\text{H}_2\text{O}]$  (top),  $[\text{D}_2\text{O}]/[\text{H}_2\text{O}]$  (bottom); **c**  $[\text{HDCO}]/[\text{H}_2\text{CO}]$  (top),  $[\text{D}_2\text{CO}]/[\text{H}_2\text{CO}]$  (bottom).

tively, due to reactions (2) and (3);



(rate coefficients from Smith et al. 1982a,b). As the energy barriers on these reactions are somewhat larger than for reaction (1), fractionation is efficient up to  $\sim 70$  K.

### 3.2. The accretion model

As expected, the fractionation ratios from our gas-phase model, for mono-deuterated species reach a few percent at low temperatures and the doubly deuterated species are  $\sim 100$  times less fractionated than that. Thus the detection of doubly deuterated molecules cannot be explained by such a model.

At the centres of cold dense clouds, however, a proportion of species colliding with dust grains are expected to stick, coating each grain in an icy mantle. The removal of these species from the gas-phase has a profound affect on the chemistry, and particularly on the deuterium fractionation, within the cloud. The reason for this is that the removal of species which would normally destroy  $\text{H}_3^+$  (e.g. C, CO,  $\text{N}_2$ , etc.) means that the  $\text{H}_3^+$  is more likely to react with HD and produce  $\text{H}_2\text{D}^+$ . This leads to an increase in the  $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$  ratio, which is passed on to other species for a time, before everything freezes out.

In the case of HDO,  $\text{NH}_2\text{D}$ , HDCO and their doubly deuterated analogues the enhancement comes from the constant cycling between these species and their protonated ion counterparts (see Fig. 1). As the protonated ions are formed via reaction both with  $\text{H}_2\text{D}^+$ , and with species fractionated directly via deuteron transfer from  $\text{H}_2\text{D}^+$  ( $\text{DCO}^+$ ,  $\text{H}_2\text{DO}^+$ ), there is a high probab-

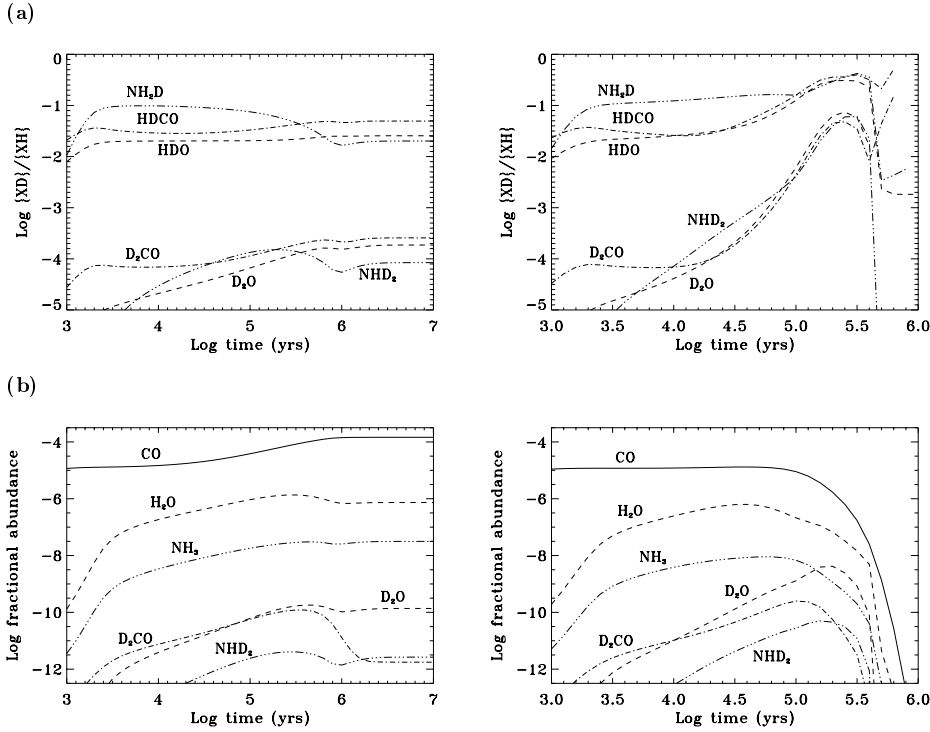
ility for the deuterium to end up incorporated into both the singly and doubly deuterated molecules.

Fig. 3a compares the molecular D/H ratios from both our models, and shows the dramatic increase in fractionation that results from the inclusion of accretion. With accretion, the fractionation of the doubly deuterated species reaches  $\sim 0.02$  after  $10^5$  yrs. Fig. 3b shows the effect that accretion has on the fractional abundances of selected molecules. The abundances of the doubly deuterated species rise significantly as species such as CO and  $\text{NH}_3$  begin to freeze out. We predict that  $[\text{D}_2\text{O}]$  will rise to  $\sim 4 \times 10^{-9}$ , so it may be worthwhile looking for this molecule in the ISM. Possible transitions accessible from the ground are the  $1_{10}\text{-}1_{01}$  line at 316.8 GHz and the  $2_{02}\text{-}1_{11}$  line at 468.2 GHz.

## 4. Comparison with observations

In Table 1 we compare the predictions of our models with the most recent observational determinations by Tiné et al. (2000) and Roueff et al. (2000), which has the advantage of utilising a consistent treatment of the data. As expected, the pure gas-phase chemistry does not produce high enough molecular D/H ratios, even for a simple system such as  $\text{DCO}^+/\text{HCO}^+$  the observed ratio is 4–10 times larger than the model prediction. Our accretion model, on the other hand, produces very good agreement after about  $10^5$  yrs, both with the observed deuterium fractionation and with the observed abundances relative to CO. In all cases the agreement is within a factor of three and for most molecules it is within a factor of two.

The enhanced molecular D/H ratios are currently the only real evidence that accretion is occurring in L134N, since the observed abundances of CO and  $\text{NH}_3$  do not appear to be reduced from their canonical values in dark clouds. However, as Fig. 3b



**Fig. 3.** The evolution of selected **a** molecular D/H ratios and **b** fractional abundances predicted by our gas-phase (left) and accretion (right) models at 10 K,  $n(\text{H}_2) = 5 \times 10^4 \text{ cm}^{-3}$

**Table 1.** A comparison of abundance ratios measured in L134N (Tin e et al. 2000; Roueff et al. 2000) with predictions from our models at 10 K,  $n(\text{H}_2) = 5 \times 10^4 \text{ cm}^{-3}$

Ratios	Observed	Modelled		
		gas-phase		accretion
		$10^5$ yrs	$10^7$ yrs	$10^5$ yrs
$\text{DCO}^+/\text{HCO}^+$	1.8(-1)	1.6(-2)	4.7(-2)	1.6(-1)
$\text{DCO}^+/\text{CO}$	7.7(-6)	1.1(-7)	2.5(-7)	2.5(-5)
$\text{NH}_2\text{D}/\text{NH}_3$	1.0(-1)	7.5(-2)	2.0(-2)	1.6(-1)
$\text{NH}_2\text{D}/\text{CO}$	1.5(-4)	3.5(-5)	4.4(-6)	1.2(-4)
$\text{N}_2\text{D}^+/\text{N}_2\text{H}^+$	3.5(-1)	2.3(-2)	3.9(-2)	1.8(-1)
$\text{N}_2\text{D}^+/\text{CO}$	3.5(-6)	5.8(-9)	1.1(-8)	2.7(-6)
$\text{NHD}_2/\text{NH}_3$	5.0(-3)	1.3(-4)	8.4(-5)	4.1(-3)
$\text{NHD}_2/\text{CO}$	7.5(-6)	6.3(-8)	1.8(-8)	3.1(-6)

NOTE: a(-b) implies  $a \times 10^{-b}$

shows, in our model, after  $10^5$  yrs, [CO] and [NH<sub>3</sub>] are still at 70 and 75 %, respectively, of their early-time values. So accretion does not have to be very far advanced to have a significant effect on the deuterium chemistry. That is, observations of CO may not necessarily provide good evidence that the gas-grain interaction is significant.

## 5. Discussion

The results from our time-dependent model of interstellar chemistry show that it is not always necessary to invoke an active surface chemistry to produce high abundances of doubly deuterated species. At the centres of cold, dense clouds, where gas-phase species are beginning to freeze out onto dust grains, abundances

of both singly and doubly deuterated molecules can become very large.

We have compared the predictions from our models with observations of one particular cloud, L134N. We find that our accretion model is in good agreement with observed fractionation after  $\sim 10^5$  yrs.

The situation in star forming regions such as Orion and IRAS 16293 is more complicated, since temperatures are uncertain and there is evidence, from the high abundance of species which do not form efficiently in the gas-phase (e.g. H<sub>2</sub>S, H<sub>2</sub>O and SiO) that some processing on grain surfaces has already taken place. However, the observed [HDCO]/[H<sub>2</sub>CO] and [D<sub>2</sub>CO]/[H<sub>2</sub>CO] ratios in these sources can be reproduced by our accretion model at low temperatures, the fractional abundance of D<sub>2</sub>CO reaching  $\sim 5 \times 10^{-11}$ . Thus, these observed ratios could have been set during an earlier, colder phase of the cloud's history and preserved on the dust grains.

This may go some way towards explaining the apparent contradiction in the observed deuterium fractionation in hot cores, such as the Orion Compact Ridge, whereby it has seemed necessary to have a grain-surface chemistry which actively works to fractionate doubly deuterated species, yet which produces no significant enhancement in singly deuterated species over cold cloud values.

This study indicates that the chemistry of doubly deuterated species is likely to be more important than has been previously thought, and should certainly motivate searches for other doubly deuterated molecules.

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