

Models and observations of deuterated molecules in protostellar cores

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Abstract. Measuring the deuterium fractionation in different molecules can allow one to determine the physical conditions in the gas and to differentiate between gas-phase and grain surface chemical processing. Observations of molecular D/H ratios in different species towards the dense gas surrounding low-mass protostars are presented and are compared with model simulations. These consider gas-phase chemistry, accretion and desorption, and reactions on grain surfaces during the initial stages of core collapse.

Keywords. Astrochemistry, molecular processes, stars: formation, ISM: molecules

1. Introduction

Many different organic species have been detected in regions of both low and high mass star formation. This has led researchers to ask whether the building blocks for life on Earth were formed in the protosolar nebula. Could organic matter on the early Earth even have come from the interstellar medium? Observations of isotopic species can help to determine under what conditions molecules formed and deuterium (^2H) is a particularly useful isotope for this purpose. Although the underlying D/H ratio is $\sim 10^{-5}$, D is preferentially incorporated into molecules at low temperatures. This fractionation is mainly temperature dependent, but can also be affected by density, by electron abundance, and by gas-grain interactions.

The primary fractionation reaction in dark clouds and prestellar cores is H_3^+ reacting with HD (the deuterium reservoir) to give H_2D^+ and H_2 . At temperatures < 25 K, H_2D^+ is not destroyed by H_2 so the $\text{H}_2\text{D}^+/\text{H}_3^+$ ratio becomes enhanced (Millar *et al.* 1989). In dark clouds, H_3^+ and H_2D^+ are primarily destroyed by proton transfer to neutral molecules (e.g., CO, O, N_2) and by dissociative recombination with electrons. Another destruction channel for H_2D^+ is further reaction with HD to form D_2H^+ and D_3^+ , but this is minor compared with destruction by CO *et al.* If a core within the dark cloud begins to contract under gravity, however, the density increases, the temperature and ionisation fraction decrease, and heavier species begin to freeze onto dust grains. In this case the conversion of H_3^+ into its deuterated isotopologues becomes much more efficient and the relative abundances of H_2D^+ , D_2H^+ and D_3^+ can become similar to or even exceed the H_3^+ abundance. This leads to a very efficient transfer of deuterium to other species (see, e.g., Roberts *et al.* 2003, Walmsley *et al.* 2004). This theory is supported by various observational results (Caselli *et al.* 1999, Roueff *et al.* 2000, Vastel *et al.* 2003, Vastel *et al.* 2004, Crapsi *et al.* 2005, etc.).

Different molecules are fractionated via different processes. Simple molecular ions like N_2D^+ and DCO^+ form directly from D_3^+ (and isotopologues) via proton transfer. Neutral hydrogen-bearing species (e.g., H_2O , HCN, NH_3) are deuterated by successive

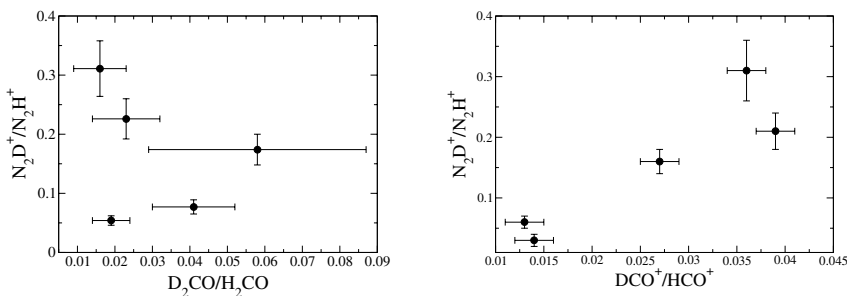


Figure 1. A comparison of the deuterium fractionation in selected species towards 5 low mass protostellar sources: HH211, L1448mms, L1448NW, L1527, and L151 IRS5. LEFT: D_2CO/H_2CO vs N_2D^+/N_2H^+ ; RIGHT: DCO^+/HCO^+ vs N_2D^+/N_2H^+ .

protonation followed by dissociative recombination reactions, but for H_2CO recent theoretical work has shown that this route is inefficient (Osamura *et al.* 2005). Extremely high D_2CO/H_2CO ratios have been observed towards both prestellar and protostellar cores and are increasingly taken to be evidence of active grain surface chemistry and desorption (e.g., Ceccarelli *et al.* 2001, Bacmann *et al.* 2003).

The formation of methanol in the gas-phase is extremely inefficient under interstellar conditions (Geppert *et al.* 2005). The likely route for CH_3OH production is on the grain surfaces via successive additions of H and D atoms to CO molecules, which also forms formaldehyde as an intermediate product. The surface molecular D/H ratios should reflect the relative abundances of H and D atoms accreting from the gas phase (Brown & Millar 1989, Stantcheva & Herbst 2003). In the prestellar core phase, this atomic D/H ratio is also enhanced due to H_3^+ fractionation (Roberts *et al.* 2003). Once H_2CO and CH_3OH form they may be further fractionated by exchange reactions with atomic D (Watanabe *et al.* 2004, Hidaka *et al.* 2005). Also, exothermic hydrogen abstraction reactions (e.g., $H + H_2CO \rightarrow HCO + H_2$) may enhance deuterium fractionation in the later stages of freeze-out by destroying the non-deuterated formaldehyde (Rodgers & Charnley 2002).

2. Observations and model results

As part of an ongoing project to compare deuterium fractionation in low and high mass star forming regions, DCN, HDCO, D_2CO , N_2D^+ and DCO^+ have been observed using the Arizona Radio Observatory (ARO) 12 m telescope, the 15 m JCMT, and the IRAM 30 m telescope (Roberts *et al.* 2002, Roberts & Millar 2007). The comparison of N_2D^+ with D_2CO is particularly interesting: N_2D^+ traces gas-phase deuteration and depletion, while D_2CO fractionation appears to trace grain surface chemistry followed by evaporation, so one might expect an anti-correlation between the two. N_2D^+/N_2H^+ will increase as the gas evolves from a dark cloud to a prestellar core, then decrease once the protostar forms and begins to heat its environment. Conversely, D_2CO/H_2CO will increase as molecules which formed via low-temperature surface chemistry evaporate.

Figure 1 compares ratios for 5 low-mass protostellar cores (L1527 and L1551 IRS5 in Taurus; L1448mms, L1448NW, and HH211 in Perseus). DCO^+ and N_2D^+ ratios appear to be fairly well correlated (as we expect since they both reflect the H_3^+ fractionation) but the N_2D^+/N_2H^+ ratios in all sources are significantly higher than the DCO^+/HCO^+ ratios. The N_2D^+/N_2H^+ ratios are all >0.05 , which suggests the presence of cold, dense, CO-depleted gas; the DCO^+/HCO^+ ratios are also indicative of cold gas, but not necessarily heavy molecular depletion.

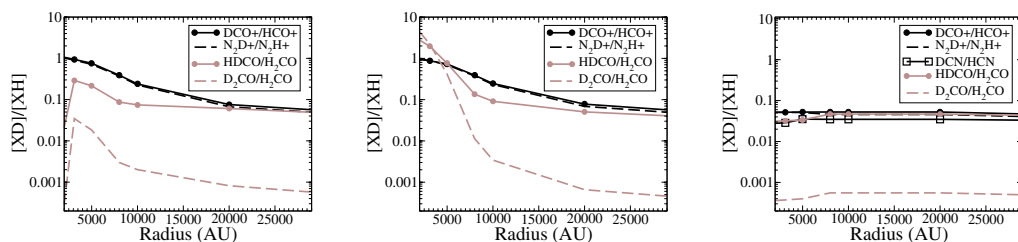


Figure 2. Molecular D/H ratios predicted as a function of radius in a cold core which has collapsed from a constant density to a centrally peaked distribution over 5×10^5 yrs. LEFT: a model containing gas-phase chemistry plus accretion onto grains; CENTRE: as at left, but with non-thermal desorption due to exothermic reactions occurring on the grain surfaces; RIGHT: as at left, but with photo-desorption of CO by cosmic-ray induced photons.

The $80''$ beam of the ARO 12 m telescope equates to 10000 AU at the distance of the Taurus Molecular Cloud (15000 AU at Perseus), so it makes sense that the observations are probing the cold envelopes which have yet to be disrupted by the central protostar. Unfortunately, there are not enough sources to make a convincing case for anti-correlation between N_2D^+ and D_2CO . It is interesting, though, that the $\text{D}_2\text{CO}/\text{H}_2\text{CO}$ ratios appear to be 0.01–0.06 even in this cold, gas. Of course, the observations are averaging over the whole protostar-core-envelope system, so is the enhanced D_2CO fractionation tracing warmer gas close to the protostar?

Maret *et al.* (2004) carried out a multiline survey of formaldehyde and methanol towards a sample of low-mass protostellar cores which overlaps with ours. Using radiative transfer modelling, they found evidence for significant increases in species abundances close to the protostars where the gas temperature exceeds 50 K. The radii of these warmer regions, though, were only ~ 100 AU. This is clearly too small for our observations to be sensitive to, even if the density of a warm core is several orders of magnitude larger than the extended envelope. As it does not appear that ion-molecule chemistry and accretion can significantly enhance $\text{D}_2\text{CO}/\text{H}_2\text{CO}$ ratios, the high fractionation seen in the envelopes is evidence that grain-surface chemistry can affect the gas-phase deuteration, even at low temperatures.

Figure 2 shows predicted molecular D/H ratios in a cold, collapsing envelope. The model includes both gas-phase and grain surface reactions. The model is based on that presented in Roberts *et al.* (2004), but with updated reaction rates based on the latest release of the UMIST database for astrochemistry, RATE06 (www.udfa.net). The rate of accretion of molecules onto grains is governed by the density, which increases from 10^4 cm^{-3} at the outer radius to 10^6 cm^{-3} at the inner radius. The temperature is 10 K throughout, so thermal desorption is inefficient except for very light species (H, He, H_2). The figure compares the effect of different non-thermal desorption mechanisms on the deuterium chemistry.

The left-hand plot of Figure 2 shows results when only thermal desorption is used. The fractionation of the singly deuterated species increases from \sim a few $\times 10^{-2}$ in the outer envelope to >0.1 at 5000 AU. There is no difference between the N_2D^+ and DCO^+ fractionation and $\text{D}_2\text{CO}/\text{H}_2\text{CO}$ ratios at 10000 AU is significantly lower than observed. The central plot shows the effect of desorption due to reactions on the grain surfaces. The bulk of the energy released by an exothermic reaction will be dissipated in the grain, but there is a possibility that some of the reaction products will desorb. This has been modelled in detail by Garrod *et al.* (2007) using classical unimolecular rate theory.

Here the simple assumption is that 1% of the product species are returned to the gas phase. It is clear that this has a large effect on HDCO and D₂CO fractionation, so that the D₂CO/H₂CO ratios are even higher than the observations at radii ≤ 6000 AU. This method, therefore, returns enough deuterated formaldehyde to the gas-phase to enhance beam averaged column densities. It does not, however, affect fractionation of the molecular ions. The right-hand plot shows the effect of including CO photo-desorption. The visual extinction in the models is high enough that direct photo-desorption is inefficient, but there is a cosmic ray induced photon field even in the high density regions. Using rates derived from experiments by Öberg *et al.* (2007), this mechanism significantly increases the amount of CO in the gas-phase. As Figure 2 shows, this drastically reduces the deuterium fractionation at smaller radii for all species, because CO destroys D₃⁺ and isotopologues. Direct cosmic-ray desorption is not yet included, but if it is efficient enough, it could further reduce the gas-phase fractionation.

Roberts *et al.* (2007) presented a more comprehensive comparison of the effects of non-thermal desorption mechanisms in dark clouds, constraining the efficiency of the methods by a comparison with the observed CO depletion, but one can only determine a lower limit on this quantity. Molecular D/H ratios are very sensitive to the overall level of molecular depletion and, as shown above, different species are affected by different desorption mechanisms. A comparison of the effects of different desorption mechanisms on deuterium fractionation in prestellar cores is now underway, particularly looking for mechanisms which can explain both the enhanced D₂CO/H₂CO ratios and the difference between N₂D⁺ and DCO⁺.

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Discussion

ZIURYS: When determining the $\text{DCO}^+/\text{HCO}^+$ ratio, how do you account for high opacity in HCO^+ ?

ROBERTS: We actually observed H^{13}CO^+ and estimated the HCO^+ column densities based on a constant $^{13}\text{C}/^{12}\text{C}$ ratio.

VAN DISHOECK: But H^{13}CO^+ lines can sometimes also have significant optical depth.

ZIURYS: Yes, with the HCN you could use the hyperfine structure from the nitrogen quadrupole. I just wonder how much uncertainty will be introduced if the H^{13}CO^+ lines had significant optical depth.

ROBERTS: That is an interesting point: if the H^{13}CO^+ lines are not optically thin then we will be underestimating the HCO^+ abundance, making the $\text{DCO}^+/\text{HCO}^+$ ratios in Figure 1 upper limits. This would mean that the difference between N_2D^+ and DCO^+ fractionation is even more pronounced. Actually, I am currently using the radiative transfer code, RATRAN, to model the H^{13}CO^+ line profiles and better determine the HCO^+ abundance.

VAN DISHOECK: I have a question about your ammonia, ND_3 . It wasn't quite clear to me from your conclusion whether you now favor grain surface or gas phase formation, because it has been sort of going back and forth in the literature.

ROBERTS: We believe that deuterated ammonia forms relatively efficiently via both gas-phase and grain surface reactions at low temperatures and high depletions. The relative abundances of the different isotopomers, however, may be different depending on which route dominates (Rodgers & Charnley 2002). I haven't yet compared results for the different desorption mechanisms for every molecule, but they are likely to have different efficiencies with respect to evaporating ammonia and so could alter the gas-phase deuterium fractionation to different degrees. Observations show that ammonia resists depletion in prestellar cores to higher densities than CO, but is this due to a lower binding energy/sticking coefficient for N followed by formation of NH_3 in the gas-phase? Or has NH_3 formed from N frozen onto the grain surfaces and then evaporated via non-thermal desorption? Looking at the deuterium fractionation could distinguish between the two.

MUMMA: Very interesting. I want to ask you to comment on why you would think that if a molecule forms on the grain surface which is hydrogen bonded weakly (the bond energy that has to be dissipated being far larger than this binding strength); why would you not expect this to work all the time so all the products desorb?

ROBERTS: The formation of methanol on the grain surfaces is a multi-step process, so all the products cannot desorb at each step otherwise it would never form. From an observational point of view; the abundances of 'surface formed' species (e.g. water, methanol, hydrogen sulphide) are significantly higher towards warm regions (where shocks and/or thermal desorption have occurred) than towards cold regions (where non-thermal desorption mechanisms operate). Also, water and methanol ice are detected along many lines of sight. These observations all suggest that the bulk of the species which form on the grains remain there until the whole mantle is evaporated. The original calculations using this method (Garrod *et al.* 2007) took into account the rate at which the energy is lost

to the surface, compared to the binding energy of the species onto the grain. My simple assumption, that 1% of the products evaporate, is based on their work and does give a reasonable agreement with observations towards cold, dark clouds.

GARROD: The energy dissipation to the surface is fast, so only a small proportion of the energy released by bond formation is available to desorb the product molecule, so you end up with this approximately one percent fraction.

VAN DISHOECK: That must be different for different molecules.

GARROD: It is, but that is a second order effect. To first order, the results for most reactions are very similar, even taking larger bonding into account.

VAN DISHOECK: I think it's good to remember there probably some other desorption mechanisms which will also operate at that level of efficiency.

ROBERTS: Yes, that's definitely true. I initially looked at desorption due to surface reactions because the species we want to return into the gas phase to improve agreement with observations (CH_3OH , D_2CO , N_2 , and NH_3) are exactly the ones which are formed on the grains. Figure 2 compares the effect on the D/H ratios of this method vs. CO photo-desorption, which has a dramatically different effect on the deuterium fractionation. Future work will look at the effects of combining both methods, along with other mechanisms, like cosmic-ray desorption, which may act to desorb more volatile species.



Helen Roberts presents her talk on deuterated molecules.