The Role of H_2D^+ in the Deuteration of Interstellar Molecules

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Collisions between H_3^+ and HD in molecular clouds lead to the fractionation of deuterium in H_2D^+ at temperatures below 20 K. In this article, we describe the chemistry of H_2D^+ and discuss how variations in temperature and elemental abundances affect the level of fractionation in H_2D^+ and other species. We describe how accretion of gas-phase molecules on to cold dust grains enhances the deuteration in several molecules including doubly-deuterated molecules. We show that the ion-neutral drift velocities attained in slow Alfvén waves can destroy H_2D^+ in non-thermal reactions. As a result, the degree of fractionation can be reduced and we discuss observational consequences of such a model for the dark dust cloud TMC-1.

Keywords: interstellar, astrochemistry, deuterium

1. Introduction

Deuterium is made in the first 1000 seconds of the Universe according to conventional models of the Big Bang, with an abundance relative to hydrogen, D/H, which depends sensitively on the baryon density (Schramm & Turner 1988). If the baryon density is low, the D/H ratio is predicted to be much larger than that observed in the local interstellar medium, 1.5 10^{-5}, whereas if it is large, deuterium fuses to form helium in the early Universe and the D/H ratio should be very small. Since the baryon density is an important parameter in determining whether the Universe is open or closed, an accurate determination of D/H in as large a volume of the Universe as possible is very important for cosmology. If the D/H ratio can be shown to imply a baryon density less than the critical value needed to close the Universe, it would be a strong indicator that dark matter must be non-baryonic in a closed Universe.

Non-cosmological sources for deuterium have been proposed. In particular, spallation reactions, i.e. photodisintegration of larger nuclei, have been suggested but are unlikely to be significant on a global scale; in addition they tend to produce an overabundance of lithium (Mullan & Linsky 1998). Although it is difficult to produce deuterium in any non-cosmological processes, deuterium is easy to destroy when it is incorporated into stars, a process known as astration. Hence local, i.e. galactic, determinations of the D/H ratio are always a lower limit to the cosmological ratio.

Direct measurements of D/H can be made through ultraviolet (UV) absorption line studies of atomic D and H in diffuse interstellar clouds and give an average ratio of $(1.5 \pm 0.1)\ 10^{-5}$ (Linsky *et al.* 1995). The fact that interstellar dust grains absorb UV photons efficiently means that these measurements are restricted to objects within about 1 kpc ($3\ 10^{19}$ m) from the Sun (Linsky *et al.* 1995). More recently, there have been attempts made to determine D/H from observations toward distant quasars in which the UV lines are red-shifted into the visible portion of the spectrum. Songaila *et al.* (1994) have claimed that D/H is (1.9-2.4) 10^{-4} towards the quasar 0014+813 at a redshift of 3.32. However, the large number of H atom absorption lines towards distant objects make the identification of weak D absorption lines very difficult. Most workers prefer a value about 10 times smaller (see Tytler *et al.* 1996).

In interstellar molecular clouds, deuterium is in the form of HD and both HD and H_2 are observable only under certain conditions. In diffuse clouds containing some molecular component, although not a dominant one, the abundance ratio of HD to H_2 is about 10^{-6} (Spitzer *et al.* 1973), consistent with an underlying D/H ratio of $1.5\ 10^{-5}$, when the different formation and destruction rates for these molecules are considered. More recently, observations of the pure rotational transitions of HD using the *Infrared Space Observatory* have given ratios relative to H_2 of $(2.0 \pm 0.6)\ 10^{-5}$ (Wright *et al.* 1999) and $(9.0 \pm 3.5)\ 10^{-6}$ (Bertoldi *et al.* 1999) in Orion. In molecular clouds, we expect $HD/H_2 \sim 2D/H$. The fact that these ratios are slightly less than the value of D/H inferred for diffuse clouds might imply that astration has destroyed some primordial deuterium in this molecular cloud, an active star-forming region.

To date, over a dozen molecules containing deuterium have been detected through rotational line emission in molecular clouds. These molecules have abundance ratios relative to their hydrogen analogues which are often enhanced by factors of 100 to 1000 above the cosmic ratio; enhancements in excess of 10000 have been detected. Table 1 summarizes the molecular D/H abundance ratios for a number of molecular clouds in the Galaxy.

2. Fractionation

The enhanced ratios observed in interstellar molecules are related to the fractionation which occurs in chemical reactions due to the fact that molecular bonds containing deuterium are slightly stronger than those containing hydrogen. The most important reactions in extracting deuterium from its reservoir, HD, involve ions which do not react, or react slowly, with H_2. The three most important fractionation reactions are:

$$\mathrm{H_3^+} + \mathrm{HD} \longrightarrow \mathrm{H_2D^+} + \mathrm{H_2} + \Delta E_1 \tag{2.1}$$

$$\mathrm{CH_3^+} + \mathrm{HD} \longrightarrow \mathrm{CH_2D^+} + \mathrm{H_2} + \Delta E_2 \tag{2.2}$$

$$\mathrm{C_2H_2^+} + \mathrm{HD} \longrightarrow \mathrm{C_2HD^+} + \mathrm{H_2} + \Delta E_3 \tag{2.3}$$

where the reactions are exoergic to the right by amounts equivalent to $\Delta E_1/k \sim 220$ K (Herbst 1982; Smith *et al.* 1982; Sidhu *et al.* 1992), $\Delta E_2/k \sim 375$ K and $\Delta E_3/k \sim 550$ K (Smith *et al.* 1982). Thus, at the low temperatures of cold interstellar clouds, the reverse reactions do not occur despite the overwhelming abundance of H_2, and large fractionations of deuterium in H_2D^+, CH_2D^+, and C_2HD^+ result. Once formed, these ions pass on their enhanced deuterium content in ion-neutral reactions

Table 1. *Observed deuterium fractionation in interstellar clouds*

(This table shows fractionation observed in a number of molecular clouds. OHC, OCR and TMC-1 refer to the Orion Hot Core, Orion Compact Ridge and Taurus Molecular Cloud-1, respectively. Notes: (a) The ratio given is $D_2CO/HDCO$; (b) Observed in gas surrounding core where T $\sim$ 70 K.)

Species	Hot Cores e.g. OHC;	OCR; (T $\sim$ 150-200 K)	Low-mass Cores e.g. IRAS 16293	Cold Clouds e.g. TMC-1 (T = 10 K)
HDO	0.003		$\geq$0.01	
NH_2D	0.003	0.06	0.1	0.01
HDCO		0.14	0.14	0.01
D_2CO^a		0.003	0.25	
CH_3OD		0.03	$\leq$0.1	
CH_2DOH		0.04		
DCN	0.003		0.013	0.02
DNC		0.01	0.03	0.01
CH_2DCN	0.01			
C_2D		0.05^b	0.18	0.01
DCO^+		0.002^b	0.0086	0.02
N_2D^+				0.08
C_3HD				0.1
DC_3N				0.03-0.1
DC_5N				0.01
C_4D				0.004
HDS			0.1	
HDCS				0.02

so that other species are also fractionated. Models can be developed for following the spread of fractionation among the species present in interstellar clouds and observations of molecular D/H ratios can be used to explore the synthetic paths by which the molecules are formed, the interstellar equivalent of a laboratory isotope-labelling experiment.

The ions CH_3^+ and $C_2H_2^+$ undergo slow radiative association with H_2 at low temperatures so that H_3^+ is the most abundant of these three ions. As a result, fractionation involving H_2D^+ is of most importance at low temperatures. However, the relatively small energy barrier to the reverse reaction in (2.1) means that H_2D^+ is rapidly destroyed by H_2 once the temperature reaches 25 K and the fraction of deuterium in H_2D^+ is simply equal to that in HD at higher temperatures. Reaction (2.2) can fractionate CH_2D^+ up to about 60 K and reaction (2.3) fractionate C_2HD^+ up to about 80 K. Above this temperature, significant fractionation cannot occur in gas-phase chemistry via exchange reactions.

For the remainder of this paper, we restrict our discussion to clouds having temperatures less than 25 K, where fractionation of H_2D^+ is large. Because the proton affinity of H_2 is so low - only He, O_2 and N among the more abundant species have lower proton affinities - H_2D^+ can transfer a proton or a deuteron in collision with almost all neutral species. By considering the formation and destruction of H_2D^+, we can write the abundance ratio in steady-state as:

$$\frac{[H_2D^+]}{[H_3^+]} = S(T)\frac{[HD]}{[H_2]}$$

where the [M] refers to the number density of species M per unit volume, and the *enhancement factor* S(T) can be written as:

$$S(T) = k_1/(k_{-1} + \alpha f(e) + \Sigma k_M f(M)).$$

Here k_1 and k_{-1} are the forward and reverse rate coefficients of reaction (2.1), with

$$k_{-1} = k_1 \mathrm{e}^{-\Delta \mathrm{E}_1/\mathrm{kT}}$$

α is the dissociative recombination rate coefficient of H_2D^+, $f(e)$ is the electron fractional abundance, i.e., the number density of electrons relative to the number density of H_2, and $f(M)$ the fractional abundance of species M which reacts with H_2D^+ with rate coefficient k_M.

The fractionation resulting from the transfer of a deuteron from H_2D^+ can be exemplified by considering the case of reaction with N_2. Two product channels are possible:

$$H_2D^+ + N_2 \longrightarrow N_2D^+ + H_2 \tag{2.4}$$

$$H_2D^+ + N_2 \longrightarrow N_2H^+ + HD \tag{2.5}$$

where the branching ratios of these are taken to be statistical, i.e., the rate coefficient for (2.4) is taken to be one-half that of (2.5). Since N_2H^+ is formed via

$$H_3^+ + N_2 \longrightarrow N_2H^+ + H_2, \tag{2.6}$$

we can write, on the assumption that the loss rates of N_2H^+ and N_2D^+ are identical:

$$\frac{[N_2D^+]}{[N_2H^+]} = \frac{1}{3}\frac{[H_2D^+]}{[H_3^+]} = \frac{S(T)}{3}\frac{[HD]}{[H_2]}.$$

The expression for $S(T)$ above contains three terms in the denominator which can be related to important cloud parameters. By neglecting the final two terms in the denominator,

$$S(T) = k_1/k_{-1} = \mathrm{e}^{\Delta \mathrm{E}_1/\mathrm{kT}}.$$

Thus, observations of N_2D^+ and N_2H^+ can give an upper limit to the temperature of the gas. If the first and third terms are neglected, one can derive an upper limit for $f(e)$, assuming that α is known. The fractional ionisation is an important parameter in determining the coupling of the magnetic field to the gas. If the ionisation fraction is high, then the ions are coupled to the magnetic field lines as are the neutrals through ion-neutral collisions. For low ionisation, the ions and neutrals decouple and magnetic field support against gravitational collapse can be lost via ambipolar diffusion. Finally, neglect of the first two terms leads to an upper limit for $\Sigma f(M)$ which gives information on the elemental abundances of C, N and O. Likewise the fractional ionisation can be related to the elemental abundances of metals having low ionisation potentials, Mg, Fe, Na, etc., abundances which are otherwise difficult to determine in molecular clouds. If estimates of these parameters can be made from other observations, then fractionation in molecules can be used to determine [HD]/[H_2], and hence the D/H ratio in interstellar clouds. Thus, detailed observations of deuterium-bearing molecules allow one to probe the D/H ratio throughout the volume of our Galaxy and, in the future, to extend this to other galaxies.

3. Chemical kinetic modelling

Detailed models of deuterium fractionation in interstellar clouds have been studied by Brown & Rice (1986), Millar *et al.* (1989), Howe & Millar (1993), Rodgers & Millar (1996) and Willacy & Millar (1998). These models follow the time-dependent fractionation induced by gas-phase chemistry. It is possible that reactions on and in ice mantles on interstellar grains also provide a route to fractionation (Tielens 1983; Brown & Millar 1989; Charnley *et al.* 1997) but it is difficult to make quantitative predictions. However, the large fractionation observed in hot molecular cores, where the gas kinetic temperature of 150 to 300 K preclude gas-phase fractionation, indicates that surfaces do play some part in enhancing molecular D/H ratios. The issue is not entirely clear cut since the grain mantles may simply act as a 'deep freeze' for storing deuterated species formed in the gas at much lower temperatures.

In the remainder of this paper, we will illustrate fractionation effects by presenting some results from a new time-dependent chemical kinetic model of deuterium chemistry in which we ignore any active effects of grain surface chemistry. The model, which involves some 5300 reactions among 400 species, uses the latest laboratory data on the dissociative recombination of H_3^+ and H_2D^+ and includes the deuterium chemistry of sulphur-bearing molecules for the first time. The detection of doubly-deuterated molecules in hot molecular cores is often taken as evidence of active surface chemistry in such regions. However, the recent detection of NHD_2 (Roueff *et al.* 2000) in L134N, a cold (10 K) quiescent cloud, implies that this species has not been processed through an ice mantle since the physical conditions in L134N make it unlikely that any significant fraction of the mantle can be returned to the gas phase. Doubly-deuterated formaldehyde, D_2CO, has also been detected in cold clouds (Ceccarelli *et al.* 1998) and we have included the gas-phase formation of this species as an example of the chemistry of doubly-deuterated species. We shall see that, under certain conditions, large fractionation in these species can arise in cold clouds.

Our new model (Roberts & Millar, in preparation) has been investigated over a much wider range of density (n = 10^{10}-10^{14} m^{-3}), temperature (T = 10-100 K), and elemental abundances than the models referred to above. In addition, we have included the accretion of molecules on to the dust grains in some calculations, a process which greatly enhances fractionation.

(*a*) *Model results*

Figure 1 shows the steady-state abundance ratio for [DCO^+]/[HCO^+] for elemental abundances appropriate to molecular clouds; that is, depleted below their solar values, as a function of density and temperature. The low-temperature fractionation evident in this figure is due to the reaction of H_2D^+ with CO, which dominates below 20 K. At higher temperatures, the fractionation decreases as H_2D^+ is destroyed by H_2, and the abundance ratio becomes fairly constant.

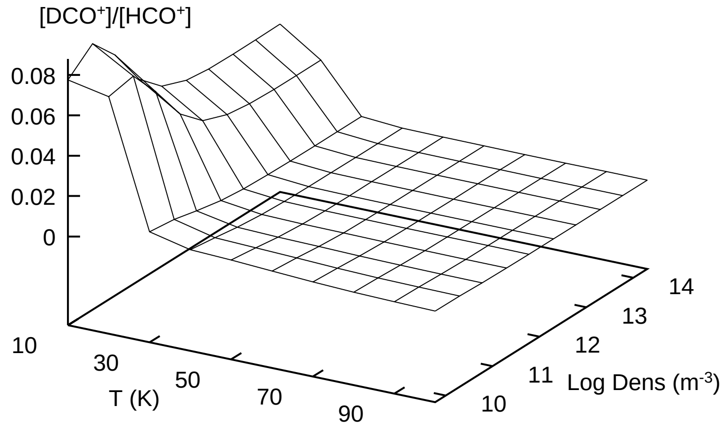

Figure 1. The DCO^+/HCO^+ abundance ratio is shown as a function of density and temperature for elemental abundances appropriate for dark molecular clouds.

Figure 2 shows the effect of increasing the C, N and O elemental abundances by a factor of 3, which has the effect of making the third term in the denominator of the expression for $S(T)$ more important. Hence fractionation by H_2D^+ at low temperatures is reduced. At higher temperatures the abundance ratio shows a complex behaviour, with a value greater than 0.005 over a wide parameter range. At temperatures larger than about 20 K, fractionation in DCO^+ is driven by reaction (2.2) which produces CH_2D^+, followed by reaction with O atoms:

$$CH_2D^+ + O \longrightarrow DCO^+ + H_2. \tag{3.1}$$

For T greater than about 60 K, the fractionation decreases as the reverse of reaction (2.2) reduces the fractionation in CH_2D^+. From these figures, it is noticeable that for $T \sim$ 30-60 K, fractionation in DCO^+ is larger for larger elemental abundances. This is due to the increased abundance of O atoms in the latter model which drives fractionation through reaction (3.1) more efficiently.

As mentioned previously, the electron abundance is sensitive to the abundance of non-reactive metals with low ionisation potentials. Figure 3 shows the results of varying the abundances of these elements in a model with the same C, N and

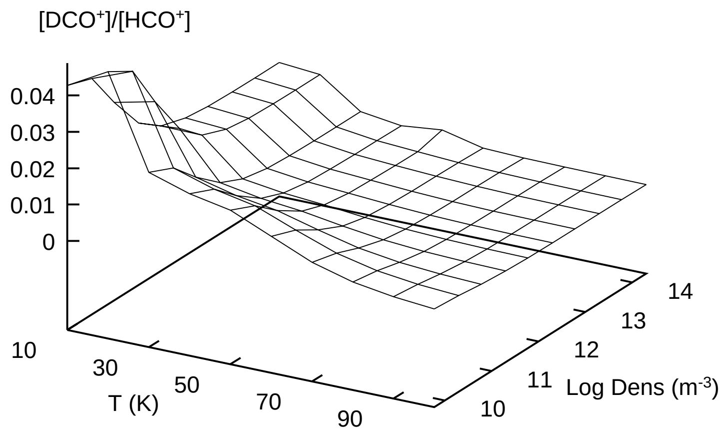

Figure 2. The DCO^+/HCO^+ ratio is shown here for the case where the elemental abundances of C, N, and O have been increased by a factor of three from those used in Figure 1.

O abundances as in figure 2, and with $T = 10$ K and $n = 2\ 10^{10}$ m^{-3}. One sees that the $[H_2D^+]/[H_3^+]$ ratio has a weak dependence on $f(e)$ when $f(e)$ is less than $10^{-6.5}$. For this low ionisation level, reactions with neutral species, M, determine the degree of fractionation and the ratio tends to a constant value as $f(e)$ decreases. For models having a larger ionisation level, dissociative recombination of H_2D^+ becomes competitive with the neutral reactions and the abundance ratio decreases approximately as $f^{-0.5}(e)$.

Observations of DCO^+ and HCO^+ have been used to derive the ionisation fraction in molecular clouds, most recently by Caselli *et al.* (1998) and Williams *et al.* (1998), with the latter finding that the average value for $f(e)$ is $10^{-7.1}$ in a sample of around 20 sources.

Another process which can alter the level of fractionation in cold clouds is accretion, that is the freezing out of gas-phase molecules on to the surfaces of dust particles. This process, which occurs on a time scale of $\sim 3\ 10^{15}/\mathrm{n}(\mathrm{m}^{-3})$ years at 10 K, removes species such as CO, H_2O, N_2 and O which destroy H_3^+ and H_2D^+. However, since hydrogen and its isotopes are not frozen out, H_3^+ remains in the gas phase where it is destroyed by HD to form H_2D^+. The result of accretion is an effective decrease in the third term in the denominator of the expression for $[H_2D^+]/[H_3^+]$, which can, as a result, attain a large value. Figure 4 shows the effects of accretion in a model having $n = 2\ 10^{10}$ m^{-3} and $T = 10$ K. In this figure, the

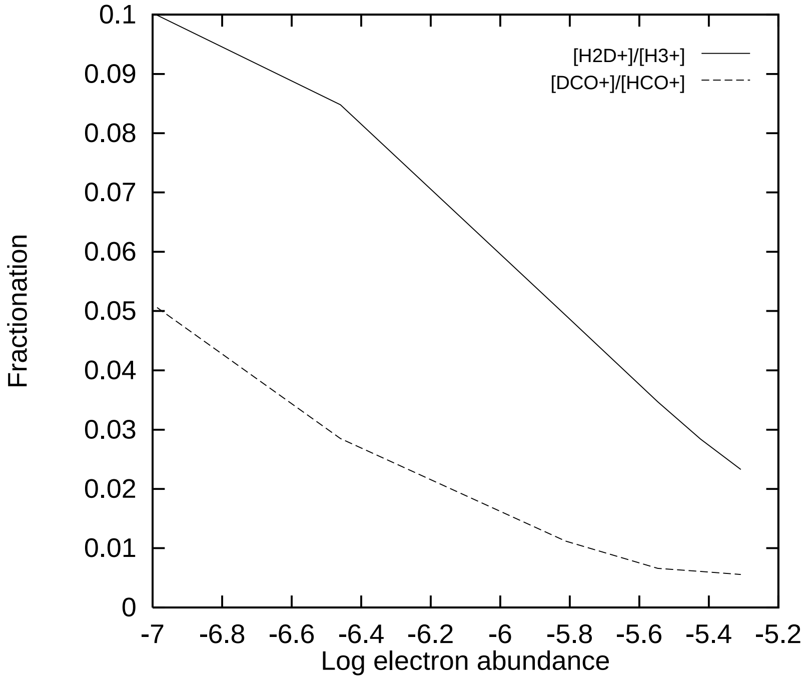

Figure 3. The fractionation in H_2D^+ and DCO^+ is shown as a function of fractional ionisation, calculated using several models as described in the text.

effects of accretion become important after 10^5 years and the $[H_2D^+]/[H_3^+]$ ratio rises from its steady-state value in the absence of accretion, 0.1, to a value greater than 1. The effect of this increase is transferred to other species, for example DCO^+, during the time that accretion is going on. Eventually, the CO is itself completely frozen out on to the grains and both DCO^+ and HCO^+ become undetectable. Figure 4 also includes the fractionation of a doubly-deuterated species, D_2CO, and shows that the ratio of D_2CO to H_2CO can be substantial, i.e., approaching 0.1.

The search for enhanced fractionation in regions in which accretion is important is still in its infancy but is likely to be a growing area of research due to the development of submillimetre bolometer cameras which can detect and map dust cores in molecular clouds. Caselli *et al.* (1999) have recently found a dust core in the L1544 cloud which appears to have a reduced CO abundance but a $[DCO^+]/[HCO^+]$ abundance ratio around 0.12, a factor of two to three times larger than expected for cold clouds but consistent with chemistry modified by accretion. Similarly, we (Roberts, Little, Phillips and Millar, in preparation) have recently used the JCMT to perform similar observations in the HH 24-26 dark clouds in Orion. These objects show peak CO emissions which are not at the same positions as the dust clumps whereas the HCO^+ and dust peaks coincide. Gibb & Little (1998) have argued that this can be explained by the removal of H_2O to the dust, H_2O being the major destruction route for HCO^+ at high densities. We have recently mapped DCO^+ in these objects and, although the data are still to be reduced fully, we do find

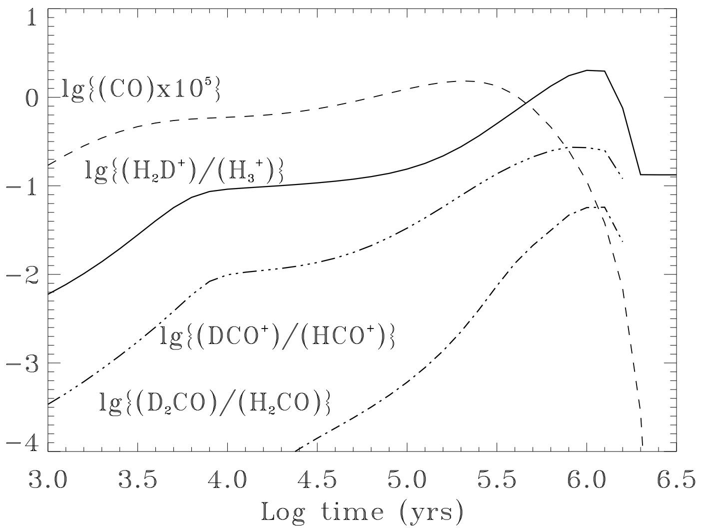

Figure 4. The effects of grain accretion on the fractionation are shown in this figure. The dashed line shows how the CO abundance varies with time, with removal from the gas occurring on a time-scale of about 10^6 years. As CO is accreted on to the dust grains, fractionation ratios can become very large.

indications of enhanced $[DCO^+]/[HCO^+]$ abundance ratios, in agreement with the accretion model.

(*b*) *Non-thermal destruction of* H_2D^+

The small energy barrier to the reverse reaction in (2.1) implies that small non-thermal effects could reduce the fractionation expected in H_2D^+. One non-thermal process occurring in molecular clouds comes through the ion-neutral velocity difference within shear Alfvén waves, may provide the non-thermal line-widths observed in cold clouds. The dissipation time for an Alfvén wave due to ion-neutral damping is, to within 10%, (Charnley 1998):

$$\tau_{in} = 2.65\, 10^{11} n_{10}^{-1} f_{-7}^{-1} \quad \mathrm{sec}$$

where n_{10} is molecular hydrogen density in units of 10^{10} molecules per m^3, and f_{-7} is the fractional ionisation in units of 10^{-7}. Since the Alfvén velocity, v_A, is given by (Zweibel & Josafatsson 1983):

$$v_A = 1.3 B_{100} n_{10}^{-1/2} \quad \mathrm{km\,s^{-1}}$$

where B_{100} is the magnetic field in units of 100 μG, we can define a dissipation length, $L_{in} = v_A \tau_{in}$, over which we may expect non-thermal effects to be important:

$$L_{in} = 3.45\, 10^{14} B_{100} n_{10}^{-3/2} f_{-7}^{-1} \quad \mathrm{m}$$

For typical values in molecular cores, $B_{100} = 1.5$, $n_{10} = 1$, and $f_{-7} = 0.3$, we find $L_{in} = 1.73\ 10^{15}$ m. It is of interest to note that this scale length is similar to that observed for molecular clumps in TMC-1, where Peng *et al.* (1998) find, through interferometer maps of CCS, some 45 clumps of gas with a typical size of $\sim 10^{15}$ m. It may be that the clump size reflects directly chemical activity and evolution in an Alfvén wave, in the sense that the dissipation length of the wave determines a chemical length scale.

The basic effect of the Alfvén wave on fractionation is to provide kinetic energy, via ion-neutral drift, to all ion-neutral reactions, including that between H_2D^+ and H_2. We can define an effective temperature for these non-thermal reactions as:

$$T_{eff} = T_n + \frac{m_{in} v_{in}^2}{3k}$$

where v_{in} is the ion-neutral drift speed and m_{in} is the reduced mass of the collision partners. Figure 5 shows the variation of v_{in} in a typical Alfvén wave, together with the effective temperature for the $H_2D^+ + H_2$ reaction. One sees that the effective temperature can be as large as 25 K in the wave, which has the result of decreasing the $[H_2D^+]/[H_3^+]$ abundance ratio. In figure 6, we show the abundance variations in $[H_2D^+]/[H_3^+]$, $[N_2D^+]/[N_2H^+]$ and $[DCO^+]/[HCO^+]$. The reduction in the first ratio is large, a factor of 7 to 8, and slightly less, a factor of 3 to 4 for the other two ratios.

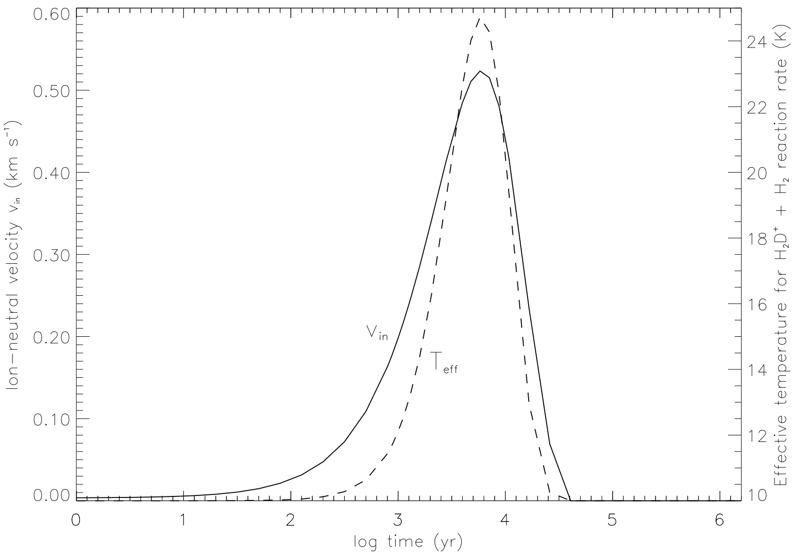

Figure 5. The ion-neutral drift speed and the effective temperature for the reactive collision between H_2 and H_2D^+ are shown as a function of time in the wave.

This ion-neutral drift also affects grain dynamics since the dust particles carry charge. In particular, collisions among the dust particles can release ice mantles to the gas with subsequent alterations to the gas-phase chemistry. Markwick *et al.* (2000) have shown that such a model can account quantitatively for the gradients in molecular abundances observed along the TMC-1 ridge (Pratap *et al.* 1997). The return of ice mantle material also affects the deuterium chemistry and figure 7 shows the variation in fractionation which results in such models. Here the initial decrease in fractionation is caused by the sudden release of material, mostly H_2O, from the grains which results in the destruction of H_2D^+ followed, at about 10^4 years, by the effects of ion-neutral drift as discussed above. The deep well evident in the $[H_2D^+]/[H_3^+]$ ratio effectively delineates the region in which the effective temperature is larger than about 20 K. Finally, for times longer than about 3 10^5 years, the effect of the Alfvén wave becomes negligible and the fractionation ratios reset to their original values. It is interesting to note that the effects of mantle evaporation are not evident in the fractionation at long times. This occurs because the H_2O injected in to the gas is processed via ion-neutral reactions into O_2 which, since it does not react with H_3^+ and H_2D^+, does not influence the degree of fractionation.

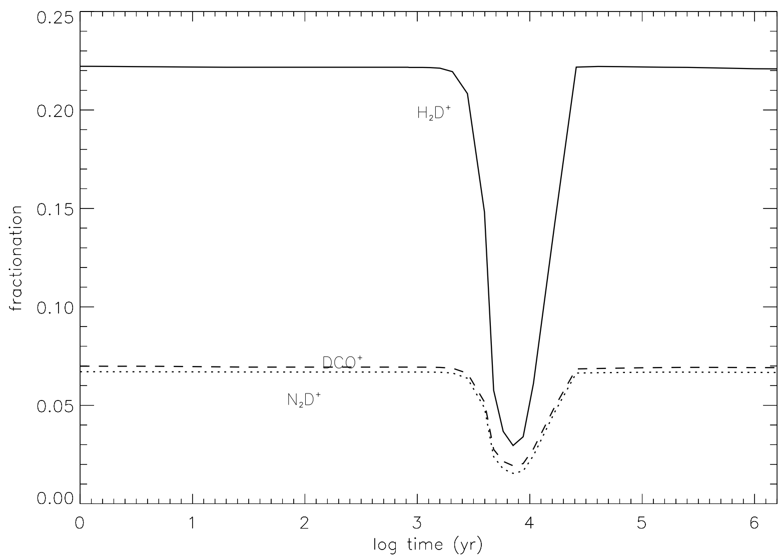

Figure 6. The variation in the abundance ratios of H_2D^+/H_3^+, DCO^+/HCO^+ and N_2D^+/N_2H^+ is shown as a function of time. The rise in effective temperature causes an increase in the destruction of H_2D^+ in the Alfvén wave, an effect which propagates in other ratios.

If Alfvén waves do play a significant role in determining the level of fractionation, then one might expect to find observable effects, including gradients in fractionation ratios and correlations between line-widths and fractionation (Charnley 1998). The former will be the topic of a separate paper (Markwick *et al.*, in preparation). However, it is already evident that some correlations between line-width and frac-

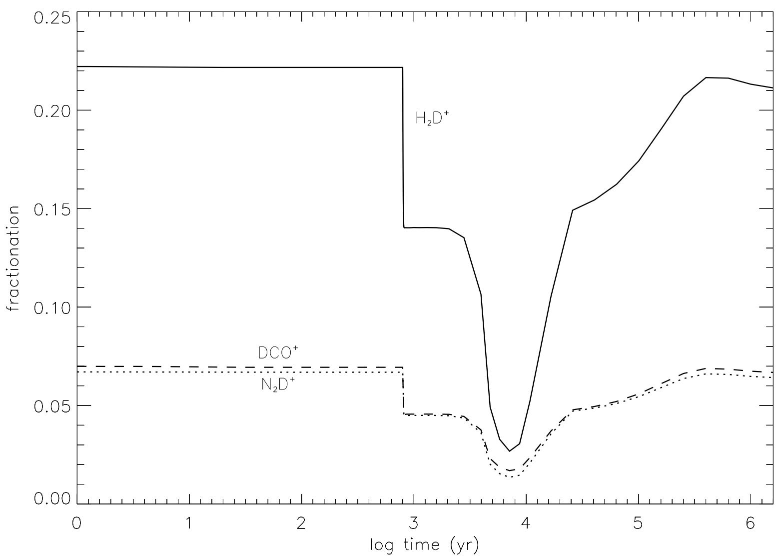

Figure 7. The variation in the abundance ratios of H_2D^+/H_3^+, DCO^+/HCO^+ and N_2D^+/N_2H^+ are shown as a function of time for the case in which the Alfvén wave causes liberation of ice mantles from dust grains. The release of this material causes the sharp decrease in fractionation at around 1000 years. See Markwick *et al.* (2000) for more details about the mantle destruction.

tionation exist. In TMC-1, both C_3HD (Bell *et al.* 1988) and N_2D^+ (Butner & Charnley, in preparation) have fractionation levels which are greatest in material with the narrowest line-widths, exactly as expected in the Alfvén wave model. We note that not all deuterated species will be affected in an identical manner. Species formed from C_2HD^+, which has the largest energy barrier against destruction by H_2, will survive unless the ion-neutral drift speed is large (Charnley 1998).

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