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Models of the gas–grain interaction – deuterium chemistry

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Summary. We have extended chemical models of a dense quiescent cloud, including accretion, and a hot molecular core to include deuterium chemistry, both in the gas phase and on the surface of dust grains. For the dense cloud model we find that as accretion begins to dominate the chemistry, and atoms and molecules leave the gas phase, the destruction rate of many radicals is reduced. As a result their abundances increase sharply before decreasing as they too accrete on to the dust. This is particularly the case for deuterated species. We suggest that if observations of a cloud, such as TMC-1, reveal a high abundance of OD, for example, this would indicate that accretion was dominating the chemistry in that region. Further analysis may lead to some conclusions concerning the present discussion about the exact mode of dissociative recombination. In the model of a hot molecular core we are able to explain the enhanced abundances of NH_2D and HDO, and the high deuterium fractionation observed by including grain surfaces reactions involving deuterium atoms.

1 Introduction

For many years it has widely been accepted that the most important interstellar molecule, H_2, can be formed rapidly enough in the ISM only via reactions involving hydrogen atoms on the surface of dust grains (Hollenbach & Salpeter 1971). Similarly, it has been recognized that in cold clouds, when heavier gas phase atoms and molecules collide with the grains, they will stick to those grains and so form an icy mantle. In the absence of an efficient desorption mechanism total depletion from the gas phase will occur on a time-scale comparable to expected cloud lifetimes (Iglesias 1977).

A comprehensive time-dependent model of a dense cloud, including accretion and an efficient desorption mechanism, has been presented by d'Hendecourt, Allamandola & Greenberg (1985). More recently Brown & Charnley (1988, in preparation, hereafter Paper II), applied a model of the gas–grain interaction specifically to the dense, quiescent cloud TMC-1. They demonstrated that an efficient desorption mechanism is not necessary to match the results of a chemical model, which includes accretion, with observations. Their best fit occurred at a model time of 1.3 Myr, consistent with estimates for the age of the region (Cohen & Kuhi 1979).

By excluding a continually acting, efficient desorption mechanism, support is given to the view that dynamic events, such as star formation, shocks and supernovae flashes, are responsible for returning grain mantle material to the gas phase. To promote this idea, Brown, Charnley & Millar (1988, hereafter Paper I), have modelled a hot molecular core. Such a region shows enhanced gas phase abundances of NH_3, HDO and CH_3OH; Pauls *et al.* (1983) suggest this may be due to evaporated mantle material.

In their model, Brown *et al.* (1988) followed the chemical evolution of a cold cloud in a free-fall collapse, and included accretion and grain surface reactions involving hydrogen atoms. The collapse is assumed to be halted by the formation of a nearby star, and the grains are heated by some mechanism associated with the star causing the mantles to evaporate and return processed material back to the gas phase.

Brown *et al.* concluded that species such as NH_3 could be formed in sufficiently large quantities on grain surfaces to explain the observations, and that other species could have their peak, cold cloud abundances 'frozen' into the mantle material due to accretion. The absence of ions during the hot core phase allows these abundances to remain high for times in excess of 10^4 yr.

However, the model did not include deuterium-bearing species and so was unable to explain one essential feature of hot molecular cores. These regions show a level of deuterium fractionation (Henkel *et al.* 1987; Walmsley *et al.* 1987) that cannot be explained in terms of gas phase chemistry, at the temperatures deduced from observations (100–200 K) (Henkel *et al.* 1987; Hermsen *et al.* 1985; Menten *et al.* 1988).

In this paper we extend the models of Papers I and II to include deuterium chemistry, both in the gas phase and on grain surfaces. A more detailed description of the gas phase chemistry involving deuterium in dense clouds has been presented by Brown & Rice (1986) and by Millar, Bennett & Herbst (1989); here we are more concerned with the effects of including accretion and surface chemistry.

Deuterium, being light, is expected to quantum tunnel through surface potential barriers in a manner similar to that of hydrogen atoms (Leitch-Devlin & Williams 1984), and thus its high surface mobility will enable it to undergo reactions with heavier species resident on the grains. Tielens (1983) has studied the role of deuterium in surface chemistry but incorporated the results into a time-independent model. The very nature of accretion suggests that a time dependent treatment is necessary, as both the gas phase and mantle composition vary as a function of time.

In Section 3 we present the results of incorporating deuterium chemistry into a dense quiescent cloud chemistry, and, in Section 4, into that of a hot molecular core. A complete description of each model can be found in the original papers but a brief review of the salient features appears in the following section, with an emphasis on the factors of particular relevance to deuterium.

2 The basic model

The chemical model has 1322 gas phase reactions involving 107 chemical species based upon the elements of H, D, He, C, N, O and Mg. Initially all species are atomic with the exception of hydrogen and deuterium, which are mostly in their molecular forms, H_2 and HD. The initial relative abundance of atomic hydrogen and deuterium is critical to the grain surface chemistry, as shall be discussed later.

Quantum mechanical calculations by Leitch-Devlin & Williams (1984) show that the time for a hydrogen atom to scan the entire grain surface is very short (~ 10^{-7} s for physisorbed hydrogen on a 0.05 μm grain) compared to the arrival rate, at the surface of an individual grain, of gas phase species X [approximately $10^6/n_x$ s, where n_x is the gas density (cm^{-3}) of X]. The situation is expected to be similar for deuterium. This being so, the factor which determines the reaction pathway for an accreted, immobile, heavy atom or radical is the relative arrival rates of hydrogen and deuterium atoms at the surface, which in turn depends upon their relative gas phase abundances.

As an initial condition we choose 1 per cent of the total hydrogen and 1 per cent of the total deuterium to be atomic. Brown (1988) has shown that, in such dense cloud models, unless more than about 1 per cent of the total hydrogen is atomic initially, reactions between heavier species on the surface become important and the surface chemistry network is more complex (a scenario currently under investigation). However, we note that the D/HD ratio may be somewhat higher than the H/H_2 ratio (Dalgarno & Lepp 1984). Indeed a calculation, neglecting accretion, for a cloud of density 3×10^4 cm^{-3} (see Fig. 1) gives steady state values for the ratios of 8×10^{-2} and 3×10^{-4} respectively. This corresponds to 0.01 per cent of the hydrogen and 7.5 per cent of the deuterium being atomic. For comparison, we include the results in cases where 1 per cent of the hydrogen, and 10 and 75 per cent of the deuterium are initially atomic.

The rate of accretion of a gas phase species, X, on to the dust is given by

$$\lambda_x n_x = S_x n_x v_x \pi a^2 n_g \text{ molecules cm}^{-3}\,\text{s}^{-1},$$

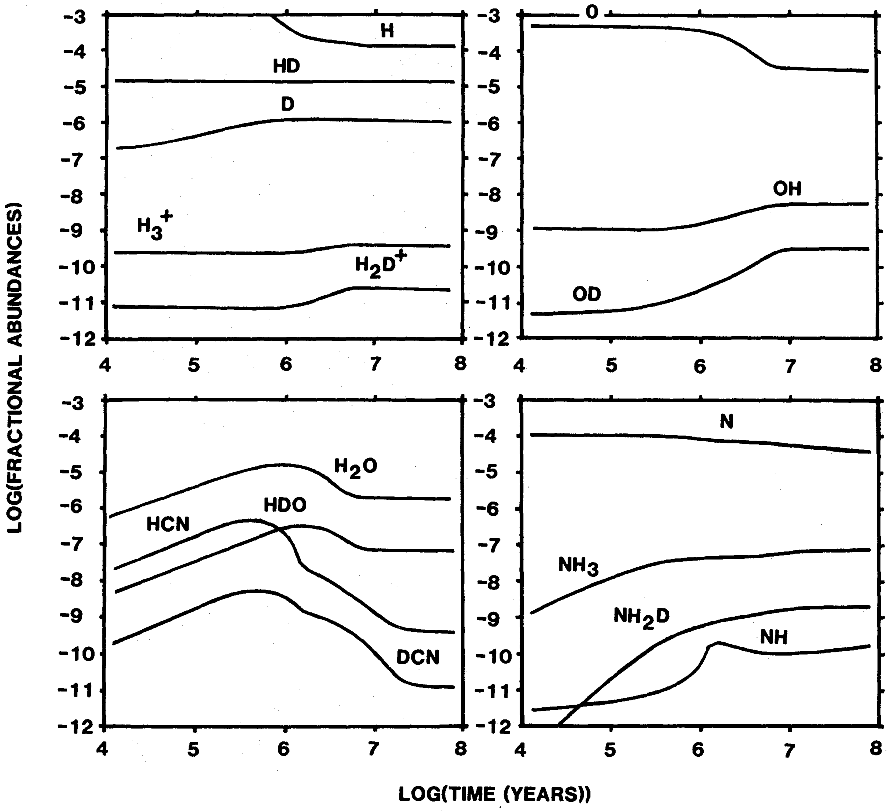

Figure 1. Dense quiescent cloud ignoring accretion. The fractional abundances (relative to H nuclei) of certain species included in the model are shown as a function of time.

where n_x and n_g are the gas phase densities of species X, and the grains respectively, v_x their relative velocity and πa^2 the cross-section for such collisions. S_x is the sticking coefficient believed to be close to, if not equal to, unity for most species (Burke & Hollenbach 1983; Leitch-Devlin & Williams 1985). However, it has been argued [from the formation and destruction rates of H_2 in diffuse clouds (Jura 1974)] that a value of 0.3 is appropriate for H atoms. We adopt values of 0.8 for heavy species (from the work of Paper II) and 0.3 for hydrogen and deuterium. However, we note that if the value for deuterium atoms is greater than that for hydrogen, the result will be a corresponding increase in the deuterium fractionation occurring on the surface.

The parameters common to both the dense quiescent cloud and the hot core models are summarized in Table 1. Only the larger grains are expected to accrete mantles, and although the smaller grains may be sites of molecule formation, they are neglected in this model because of the uncertainties surrounding such processes.

Table 1. Parameters common to both models. Initial fractional abundance of elements (relative to H nuclei) with corresponding depletions (from cosmic) in parentheses.

C	1.86×10^{-4}	(50%)
O	5.41×10^{-4}	(20%)
N	1.15×10^{-4}	(undepleted)
D	1.50×10^{-5}	(")
He	8.51×10^{-2}	(")
Mg	3.50×10^{-7}	(99.98%)

Grain radius = 0.15 μm.
Fractional abundance of grains = 3.5×10^{-13}.
Cosmic ray ionization rate = 1.3×10^{-17} s^{-1}.

3 Dense quiescent cloud

The density of 3×10^4 cm^{-3} and temperature of 10 K are chosen as being typical of a dense cloud. The high visual extinction ($A_v \geqslant 5$ mag) of such regions makes photodestruction unimportant. Gas phase chemistry involving deuterium has been described elsewhere (Brown & Rice 1986; Millar *et al.* 1989) but we reiterate the observation of Watson (1976) and Dalgarno and Lepp (1984) that deuterium fractionation occurs in clouds of such low temperature, chiefly because in the reactions:

$$H_3^+ + HD \Leftrightarrow H_2D^+ + H_2 \qquad (1)$$

$$HCO^+ + D \Leftrightarrow DCO^+ + H \qquad (2)$$

the backward rates are inhibited by barriers of ~230 and 796 K, respectively.

Fig. 1 shows the gas phase fractional abundances of certain species included in the model, as a function of time in the case where accretion on to dust grains is neglected. The case in which accretion is included is shown in Fig. 2. The main result, as can clearly be seen from Fig. 2 is

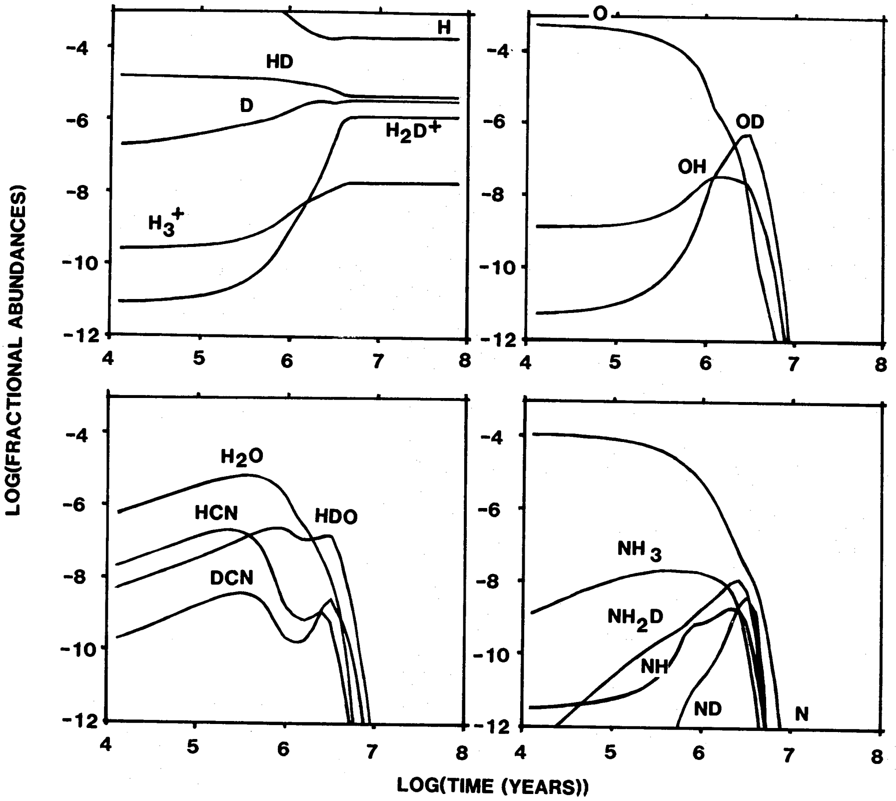

Figure 2. Dense quiescent cloud including accretion.

that as accretion begins to dominate the chemistry, at times $\geqslant 10^6$ yr, the abundance of many radicals (e.g. OD) and deuterated molecules (e.g. DCN), increase sharply, before reaching a peak and then decreasing, as they too accrete on to the dust.

Consider the case of OD. The main gas phase destruction route is via reactions with O, C and N atoms:

$$\mathrm{O+OD \rightarrow O_2+D} \tag{3}$$

$$\mathrm{C+OD \rightarrow CO+D} \tag{4}$$

$$\mathrm{N+OD \rightarrow NO+D.} \tag{5}$$

As accretion dominates the chemistry, these atoms are removed from the gas phase, thereby greatly reducing the destruction rate of OD.

OD is formed from OH which is produced in a series of reactions:

$$\mathrm{H_3^+ + O \rightarrow OH^+ + H_2} \tag{6}$$

$$\mathrm{OH^+ + H_2 \rightarrow H_2O^+ + H} \tag{7}$$

$$\mathrm{H_2O^+ + H_2 \rightarrow H_3O^+ + H} \tag{8}$$

$$\mathrm{H_3O^+ + e \rightarrow OH + H + H,} \tag{9}$$

followed by:

$$\mathrm{D+OH \rightarrow OD+H.} \tag{10}$$

In the initial reaction of the chain (6) the fall in the O atom abundance is compensated for by a corresponding rise in the abundance of H_3^+ (because of the reduction in its own destruction rate as atoms and molecules accrete on to the grains). This leads to an almost unchanged formation rate for OH and consequently OD. Hence, with a decreased destruction rate and an almost unaltered formation rate, the abundance of OD increases, before it eventually condenses on to the dust.

However, we make note here of the recent debate on the products of recombination reactions. For example, in the recombination of H_3O^+:

$$H_3O^+ + e \rightarrow H_2O + H \tag{11}$$

$$H_3O^+ + e \rightarrow OH + H + H \tag{12}$$

we have adopted a 50:50 branching ratio (Prasad & Huntress 1980). However, Bates (1986) has recently argued that such a recombination will always follow the first branch [i.e. reaction (11)]. If this is the case, the peak in the radical abundances may not be so apparent, and instead the abundance of species, such as H_2O, will be more affected. However, there is still much debate concerning the validity of Bates' arguments, and Millar *et al.* (1988) have shown that, even if the reactions (11) and (12) occur in the ratio of 9:1, the OH/H_2O ratio is preserved, particularly at 'early times', the times most relevant to models which do include accretion.

We have also studied the case in which the visual extinction is low ($A_v = 3$ mag), and found that the accretion peaks are still clearly apparent, though they are not so pronounced. Increasing the accretion time-scale, by reducing the sticking coefficient, simply leads to the peaks in the radical abundances occurring at a later time.

The increase in the abundance of a radical or a molecule due to the accretion process is greater for deuterium-bearing species, thus increasing the degree of deuterium fractionation. This occurs because the abundance of H_2D^+ rises more sharply than does H_3^+. The abundances of both rise because their destruction rates are reduced, as atoms and molecules leave the gas phase. However, H_3^+ is destroyed, and H_2D^+ formed, in the reaction:

$$H_3^+ + HD \rightarrow H_2D^+ + H_2.$$

As previously mentioned, the reverse route to this reaction is inhibited at low temperatures and this ultimately leads to a higher abundance of H_2D^+ than H_3^+.

The detection of a deuterium bearing radical would be evidence in favour of this model. An unsuccessful search for OD was made by Allen, Cesarsky & Crutcher (1974) towards the galactic centre at a frequency of 310 MHz (corresponding to the $\Delta F = 0$ Λ-doublet transitions of the $^2\Pi_{3/2}$, $J = \frac{3}{2}$ state of OD). We suggest that such a search should be made towards a cloud in the latter stages of its chemical evolution, when accretion is beginning to dominate the chemistry. In Paper II, good agreement with observations of TMC-1 was found at a model time of 1.3×10^6 yr. At that time, this model yields a fractional abundance for OD of 3.6×10^{-8}. If the abundance of OD could be determined from observations it would provide valuable information on continual desorption mechanisms and the mode of dissociative recombination. If accretion is occurring in the absence of an effective desorption mechanism and if the new view of dissociative recombination is valid then high ratios for HDO/H_2O, NH_2D/NH_3, etc. should be observed due to the differential increase in the abundances of H_2D^+ and H_3^+.

In Table 2, the steady-state gas phase abundances of certain species from the model run which excludes accretion, are compared with the final mantle composition from runs which do include accretion and surface chemistry. The mantle is composed of molecules formed in the gas phase and subsequently accreted, as well as molecules formed by reactions on the surface.

It is clear from the table that a large enhancement may arise in the abundance of deuterated molecules, even when reactions with D atoms on the surface are neglected. This arises from the hydrogenation of accreted deuterium-bearing radicals, such as OD, NHD and so on, which have enhanced gas phase abundances just before they accrete, as described above.

Table 2. Results of dense, quiescent cloud model.

	No accretion†	Solid phase abundances			
	$F_D = 0.01$	$F_D = 0.01$★	$F_D = 0.01$	$F_D = 0.10$	$F_D = 0.75$
CH_4	3.5×10^{-8}	9.8×10^{-5} (13.58)	9.8×10^{-5} (13.57)	9.8×10^{-5} (13.56)	9.8×10^{-5} (13.49)
CH_3D	4.1×10^{-9}	7.8×10^{-7} (0.11)	8.7×10^{-7} (0.12)	9.3×10^{-7} (0.13)	1.4×10^{-6} (0.19)
NH_3	8.1×10^{-8}	9.8×10^{-5} (13.59)	9.8×10^{-5} (13.53)	9.8×10^{-5} (13.53)	9.8×10^{-5} (13.50)
NH_2D	2.2×10^{-9}	1.3×10^{-7} (0.02)	5.2×10^{-7} (0.07)	5.5×10^{-7} (0.08)	7.5×10^{-7} (0.10)
H_2O	2.0×10^{-6}	4.2×10^{-4} (57.29)	4.1×10^{-4} (57.22)	4.1×10^{-4} (57.20)	4.1×10^{-4} (57.10)
HDO	6.8×10^{-8}	3.3×10^{-6} (0.46)	3.9×10^{-6} (0.53)	3.9×10^{-6} (0.54)	4.5×10^{-6} (0.62)
Ratios:					
CH_3D/CH_4	0.117	0.008	0.009	0.010	0.014
NH_2D/NH_3	0.027	0.001	0.005	0.006	0.007
HDO/H_2O	0.034	0.008	0.009	0.009	0.011

Initial fraction of deuterium atomic = F_D. Initial fraction of hydrogen atomic, $F_H = 0.01$ in all calculations. Abundances quoted are relative to H nuclei; figures in parentheses are percentage mantle compositions. †In the case of 'no accretion' abundances are gas phase at steady-state (i.e. $> 10^7$ yr); in all other cases abundances are final mantle components. In the model run marked ★ surface reactions involving deuterium atoms have been neglected.

A larger enhancement in the abundance of the deuterated molecules is obtained, as would be expected, when surface reactions involving deuterium are included. This enhancement is greater for a higher initial fraction of atomic deuterium. However, the degree of fractionation is not particularly sensitive to this choice as the deuterium atom abundance is determined more by the chemistry than by the initial conditions.

4 Hot molecular cores

A study of the gas phase of hot cores provides an insight into both the gas phase and the surface chemistry of a cold, dense cloud. It is believed that the gas phase abundances in hot cores reflect, to a large degree, the grain mantle composition in a cold, dense cloud; the mantles having evaporated as the region's temperature increased. This was borne out in the work of Paper I which successfully explained the enhanced abundances of many species either through the 'freezing' of peak cold cloud abundances, or through formation on grain surfaces.

Further support is given to this idea from the observed abundances of HDO and NH_2D (see Table 4), and the degree of deuterium fractionation. At the temperatures deduced for hot core

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regions, (100–200 K), very little fractionation is expected to occur, because the energy barriers inhibiting the reverse routes of reactions (1) and (2) (see Section 3) may be overcome by the elevated temperature (Millar *et al.* 1989). The observed increase in the abundances of HDO and NH_2D over their typical cold cloud values suggests that they may also be formed on grain surfaces.

In order to investigate this, we have extended the work of Paper I to include deuterium chemistry. We follow both the gas phase and the mantle composition as a cold cloud undergoes an isothermal, free-fall collapse. The collapse is assumed to be halted by the formation of a nearby star. Some mechanism associated with this star then heats the grains and the mantles evaporate, returning processed mantle material back to the gas phase. A more complete description of the model may be found in Paper I but a summary of the important parameters appears in Table 3. Again we choose as an initial condition in the cold cloud, 1 per cent of the hydrogen and 1 per cent of the deuterium to be atomic.

Table 3. Parameters of hot core model.

	Collapse phase	Hot core phase
Kinetic temperature (K)	10	200
Cloud mass ($M_\odot$)	10	10
Cloud radius (pc)	0.33★	0.019
Cloud density (cm^{-3})	3×10^3★	1×10^7
Visual extinction (mag)	1.64★	320

★Indicates parameters which vary as cloud undergoes collapse.

The gas phase fractional abundances of certain species included in the model are shown in Fig. 3. The enhancement, over the cold phase abundances, of species such as H_2O, HDO, NH_3 and NH_2D clearly demonstrates the importance of grain surface reactions.

A comparison with observations of the Orion hot core is made in Table 4. Walmsley *et al.* (1987) derived an abundance ratio for NH_2D/NH_3 of 0.003 from a comparison of column densities. Similarly Henkel *et al.* (1987) have calculated a fractional abundance for HDO of 1.0×10^{-7} (relative to H nuclei). The results of this model are in fair agreement with these observations, indicating that the enhanced abundances of deuterium-bearing molecules in hot cores may be explained in terms of accretion and surface chemistry, followed by the subsequent evaporation of the grain mantles. The calculated hot core abundances may persist for greater than 10^4 yr because of the absence of ions during this phase (discussed in Paper I), and hence the high level of deuterium fractionation is preserved despite the high temperature.

The overestimate in the abundance of some species, notably ammonia, is possibly due to the neglect of surface reactions between heavier species (currently under investigation), a larger degree of chemical processing in the gas-phase during the diffuse stage, or a greater initial depletion of the elements than that assumed.

5 Conclusions

(i) As accretion begins to dominate the chemistry in cold, dense clouds, atoms and molecules leave the gas phase and the destruction rates for many radicals, which are destroyed predominantly by atoms, are decreased. The formation rates for these radicals remain almost unchanged because of a rise in the abundance of the ions H_3^+ and H_2D^+ so that the

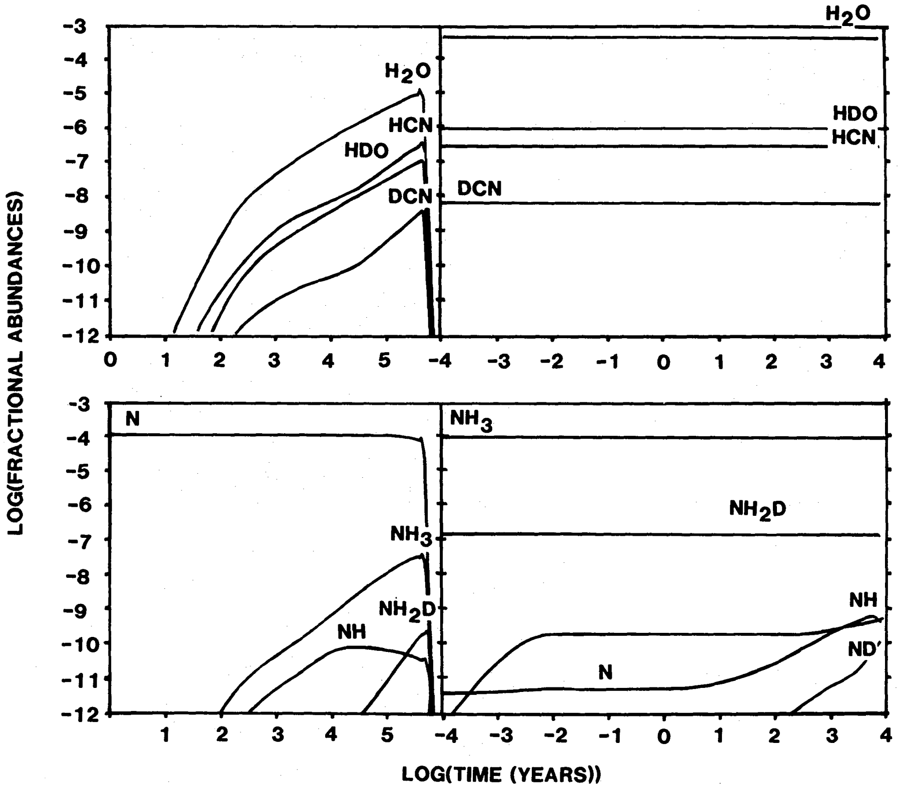

Figure 3. (a) Hot molecular core. The fractional abundances (relative to H nuclei) of certain species included in the model are shown as function of time during the cold, collapse phase (left hand frames) and the hot core phase (right hand frames).

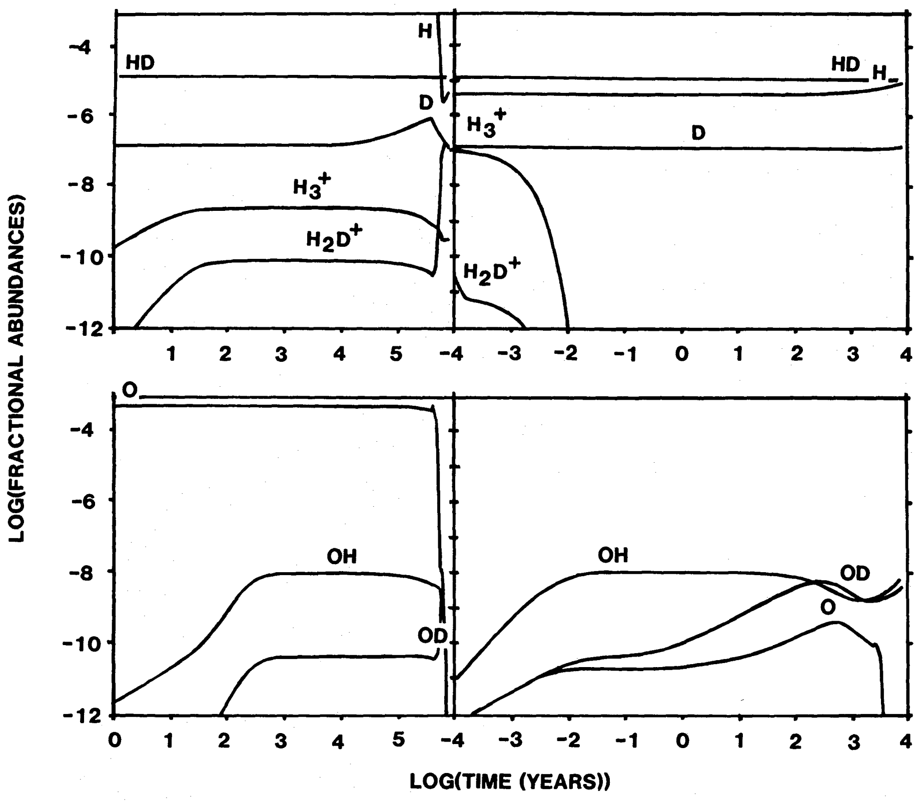

Figure 3. (b) As figure (a).

Table 4. Comparison with observations of the Orion hot core.

	Calculated★ᵃ	Observed★	References
CH_4	9.92×10^{-5}	—	
CH_3D	4.16×10^{-7}	—	
NH_3	1.00×10^{-4}	10^{-5}–10^{-6}	1, 2ᵇ
NH_2D	1.59×10^{-7}	4.5×10^{-9}	2ᵇ
H_2O	4.64×10^{-4}	—	
HDO	1.03×10^{-6}	1.0×10^{-7}	3, 4
Ratios:			
CH_3D/CH_4	0.004	—	
NH_2D/NH_3	0.002	0.003	
HDO/H_2O	0.002	—	

★Abundances relative to H nuclei. ᵃCalculated abundances are at a model time of 10^4 yr in hot core phase. ᵇSource size of 10 arcsec assumed. N(NH_3) calculated using $NH_2D/NH_3=0.003$ (ref. 2). References: (1) Blake *et al.* (1987), (2) Walmsley *et al.* (1987), (3) Henkel *et al.* (1987), (4) Plambeck & Wright (1987).

abundances of these radicals increases sharply before decreasing again as they accrete on to the dust.

(ii) The abundance of H_2D^+ increases more sharply than H_3^+ because H_3^+ is destroyed in reactions with HD, forming H_2D^+, whereas the reverse reaction is inhibited by an energy barrier at 10 K. This leads to a greater deuterium fractionation of those species not yet accreted on to the dust.

(iii) If the standard value for the branching ratios of the dissociative recombination of H_3O^+ holds, then a search of a cloud, for example TMC-1, in its latter stages of chemical evolution, should reveal a high abundance of the OD radical. If the recombination products of H_3O^+ could be determined, observation of OD would provide a good test for the idea that accretion is occurring in such regions, in the absence of a continually acting desorption mechanism.

(iv) The surface hydrogenation of deuterated radicals may produce large enhancements in the solid phase abundances of deuterated water, ammonia and methane.

(v) Including surface rections involving deuterium atoms further enhances the abundance of these deuterated ices. The degree of deuterium fractionation on the surface depends weakly upon the initial gas phase atomic D/atomic H ratio.

(vi) Such surface reactions may account for the enhancements observed in the abundances of HDO and NH_2D in hot cores, adding further support to the idea that grain mantles have been evaporated in such regions.

(vii) A study of the fractionation of more complex species, such as methanol (Mauersberger *et al.* 1988), may provide further insights into the efficiency of surface chemistry in producing large molecules.

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