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Tielens, A.G.G.M.

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Surface chemistry of deuterated molecules

A. G. G. M. Tielens

Laboratory Astrophysics Group, Huygens Laboratory, Wassenaarseweg 78, 2300 RA Leiden, The Netherlands

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Summary. The relative concentration of deuterated molecules to their hydrogenated counterparts in grain mantles has been calculated numerically. The chemical reaction scheme used comprises gas phase as well as grain surface reactions.

The results show that the ratio of the concentration of deuterated molecules to their hydrogenated counterparts in a grain mantle is much larger than expected on the basis of the cosmic abundance ratio of D to H. This is mainly due to the large ratio of the concentration of atomic D to H in the gas phase. For formaldehyde the former ratio is even further enhanced by hydrogen abstraction and deuterium addition reactions at the grain surface. The relative concentration of deuterated molecules in a grain mantle depends strongly on the total hydrogen density in the gas phase.

The infrared characteristics of the calculated grain mantles are discussed and observational tests of the model calculations are suggested. Finally the contribution of grain surface chemistry to the concentration of molecules in the gas phase is briefly examined.

Key words: chemical reactions – grains – molecules – abundances, interstellar

1. Introduction

The gas phase of dense molecular clouds contains an unexpectedly large abundance of deuterated molecules such as DCN, DCO⁺, N₂D⁺, and HDCO (Jeffers et al., 1973; Hollis et al., 1976; Snyder et al., 1977; Langer et al., 1979). The abundance of these deuterated species can be enhanced by as much as a factor 10⁴ as compared to the abundance of their hydrogenated counterparts and the cosmic abundance ratio of D to H. This deuterium enrichment is attributed to the lower zero-point energy associated with a molecule in its deuterated form (Solomon and Woolf, 1973).

Gas phase ion-molecule reaction schemes have been proposed for the formation of these deuterated molecules (Watson, 1974, 1976). Assuming a low electron density ($n_e/n_0 \approx 10^{-8}$) these schemes can account for the enhancements observed. If the electron density is indeed this low, magnetic fields cannot sustain the cloud. This has important consequences for star formation (Mestel and Paris, 1979). The fact that gas phase reaction schemes can explain the observed deuterium enhancements has been

Send offprint requests to: A. G. G. M. Tielens, Nasa-Ames Research Center, Moffett Field, CA 94035, USA

claimed as a proof of the validity of those schemes (Watson, 1980). However this claim may be somewhat premature in view of the fact that reactions on grain surfaces and, possibly, in the bulk have not been considered.

We have previously calculated the chemical composition of grain mantles using gas phase and grain surface reactions (Tielens and Hagen, 1982b, hereafter called Paper II). In these calculations deuterium chemistry was ignored altogether because of the relatively low deuterium abundance in the interstellar medium. In this article these calculations have been extended to include reactions involving deuterium in the gas phase and on grain surfaces. Our main aim is to determine the concentration of deuterated molecules relative to their hydrogenated counterparts in grain mantles. The infrared characteristics of these theoretical grain mantles can then be compared with infrared observations through dense interstellar clouds. Such observations may yield insight into the chemistry taking place on grain surfaces. Furthermore some of the molecules comprising the grain mantle can be injected into the gas phase and may influence the concentration of deuterated molecules in the gas phase (see Paper II and references therein for a discussion of possible ejection mechanisms).

This paper is organized as follows. After the method of calculations is briefly summarized in Sect. 2, the results are presented in Sect. 3 and the concentration of deuterated molecules in grain mantles is discussed in Sect. 4. In that section we also examine the infrared spectroscopic characteristics of these grain mantles. Finally we consider the importance of grain surface reactions for gas phase abundances. In Sect. 5 the main conclusions are summarized.

2. Method

The method used to calculate the chemical composition of mantles growing on interstellar grains has been discussed elsewhere (Paper II). It is based on two assumptions: First, that species in the gas phase are in steady state and second, that the composition of the gas phase can be calculated using only gas phase reactions. In the second assumption an exception is made for H₂ which is formed on interstellar grain surfaces (Hollenbach and Salpeter, 1970, 1971). Using these gas phase abundances the relative accretion rates for individual molecules on interstellar grain surfaces are calculated. Finally the composition of the growing grain mantle is determined by including diffusion controlled surface reactions. Probably only H, D, C, N, and O atoms and the H₂ and HD molecules are able to scan the whole grain

Table 1. Gas phase reaction involving deuterated molecules included in the calculations

Reaction	Rate	Ref.
1 D + H ⁺ ⇌ D ⁺ + H + 43 K	10 ⁻⁹	Watson et al. (1978)
2 D ⁺ + H ₂ → H ⁺ + HD	10 ⁻⁹	Fehsenfeld et al. (1973)
3 H ₃ ⁺ + HD ⇌ H ₂ D ⁺ + H ₂ + 178 K	3 · 10 ⁻¹⁰	Huntress and Anicich (1976)
4 H ₂ D ⁺ + CO → DCO ⁺ + H ₂	^a	
5 H ₂ D ⁺ + N ₂ → N ₂ D ⁺ + H ₂	^a	
6 H ₂ D ⁺ + e ⁻ → HD + H	^a	McGowan et al. (1978)
7 → H ₂ + D	^a	McGowan et al. (1978)
8 → H + H + D	^a	McGowan et al. (1978)
9 DCO ⁺ + e ⁻ → CO + D	^a	Mul and McGowan (1979)
10 N ₂ D ⁺ + e ⁻ → N ₂ + D	^a	Mul and McGowan (1979)

^a Rate estimated in analogy to the corresponding reactions involving the hydrogenated counterpart

surface on the same time scale as that for collisions between gas phase radicals and a grain. On this timescale the other heavier atoms and molecules are expected to reside in one site (Tielens and Hagen, 1982a; hereafter called Paper I). We have therefore only selected reactions of species with migrating species. The diffusion of these species ends when they recombine with each other or with a species trapped in a site. The reaction products are assumed to remain on the grain surface.

In the remainder of this section, the modifications made in the method to include deuterium chemistry are discussed.

A. Deuterium gas phase chemistry

In the gas phase deuterium should mainly be in the form of D or HD. Other deuterated molecules contain only a minor fraction of all of the available deuterium. In Table 1 the reactions which we believe control the D to HD ratio in the gas phase are presented. Note that HD formation on grain surfaces is not included in the calculations of the gas phase abundancies. As will be discussed in Sect. IV.A only a small fraction of all D atoms colliding with a grain will form HD molecules. Most will instead end up in heavier deuterated molecules. With these reactions included a steady state solution is calculated for 1530 reactions involving 145 species. The numerical method used to carry out the calculation for the chemical equilibrium in the gas phase is described in Paper II. The free parameters are: the absolute hydrogen abundance, $n_0 = n_H + 2n_{H_2}$; the relative abundances of the elements; the gas kinetic temperature, T_0 ; the cosmic ray ionization rate, ζ_0 ; and the UV flux available. Assuming no internal UV sources the latter is described by the intensity of the radiation field incident on the cloud, G_0 and the extinction optical depth, A_v .

B. Deuterium surface chemistry

In this section we discuss the binding energy, evaporation time scale, surface mobility and reaction network of deuterium atoms and deuterated molecules on a grain surface. This has already been discussed in Paper II for the other species involved in the calculations.

The binding energy of H, D, H₂, and HD on an interstellar grain surface decreases with increasing H₂ coverage of the surface (Schutte et al., 1976; Govers et al., 1980). The binding energies for these atoms and molecules are therefore determined by the balance between accretion and evaporation of H₂. At a density of 10⁴ cm⁻³ the binding energy and surface coverage of H₂ on a

H₂O surface is estimated to be about 450 K and 20%, respectively (Govers et al., 1980; Paper II). The greater mass of D as compared to H produces a smaller zero-point energy and therefore a larger binding energy. Including this effect the binding energies of H, D, and HD are about 350, 450, and 500 K respectively. These binding energies are quite uncertain. Fortunately the precise value is of no importance for the calculations below. These binding energies imply a thermal evaporation timescale of 3.5 · 10⁶ s for D and of 5 · 10⁸ s for HD, instead of 2 · 10² s and 3.5 · 10⁶ s for H and H₂ respectively. The grain surface residence time for D and HD is thus larger than the time between collisions of gas phase radicals with a grain (~10⁵ s). Assuming that all of the deuterium in the gas phase is in the form of HD, the resulting ratio of HD to H₂ on an interstellar grain surface is about 0.4%.

Because of the larger binding energy of D compared with that of H, the quantum mechanical tunneling time of D to an adjacent site will be longer than that for H. From the detailed analysis of the mobility of H and H₂ on a perfect H₂O surface (Hollenbach and Salpeter, 1970) we estimate this effect to be about a factor of 4. Thus an accreted D atom will scan the whole surface of a grain with a radius of 1000 Å in about 2 · 10⁻⁸ s. This is much faster than the evaporation timescale or the radical-grain collision timescale. Consequently reactions of D with the other atoms and radicals that are on the grain surface should be taken into account in evaluating the surface chemistry.

Reactions involving D and deuterated radicals are included in a fashion completely analogous to their hydrogenated counterparts. Only statistically significant reactions have been taken into account. This selection is based on the gas phase abundance of the precursor.

As in the case of H, reactions between D atoms and molecules with activation barriers can be of importance and are included (see Paper II for further discussion). If no radical is available to react with a newly accreted D atom, then this atom may tunnel through an activation barrier and react with a molecule as it scans the grain surface. The probability of a reaction is given by

$$\phi = N_{\text{cor}} n \tau v_0 \exp \left[- \frac{2a}{\hbar} (2mE_a)^{1/2} \right], \quad (1)$$

where N_{cor} is the number of the coreactants on the grain surface, n is the number of times the deuterium atom enters a particular site during the time between a radical-grain collision, τ is the time it spends in this site, v_0 is a typical vibration frequency, a and E_a are

the width and height of the activation barrier and m is the mass of the deuterium atom (Paper II). Typically the radical-grain collision timescale is about 10^5 s implying $n \approx 5 \cdot 10^{12}$. Inserting $v_0 = 10^{13} \text{ s}^{-1}$, $\tau = 3 \cdot 10^{-11} \text{ s}$, $a = 1 \text{ \AA}$ and $m = 3.2 \cdot 10^{-24} \text{ g}$ and assuming $N_{\text{cor}} = 1$ we find that a D atom has a 50% probability of tunneling (and reacting) through an activation barrier of 4000 K. If $N_{\text{cor}} = 10^4$ (e.g. 1% surface coverage) the D atom has a 50% probability of tunneling through an activation barrier of 6500 K and reacting. Consequently reactions between D atoms and molecules with an activation barrier less than this value must be included in the reaction network.

In Table 2 we present reactions of H and D atoms with molecules and their activation energy. Because of the lack of experimental and theoretical data on the energy barriers involved, we have assumed that D addition and H abstraction by D atoms have the same activation barrier as the corresponding reactions involving H atoms. This is in good agreement with the experiments on H and D abstraction from H_2CO and D_2CO respectively by H and D atoms (McNesby et al., 1960). This assumption is of crucial importance in the deuterium surface chemistry and an accurate determination of these activation barriers is warranted. Because of the mass difference between H and D, deuterium abstraction by H or D atoms from deuterated molecules will have a higher activation barrier than hydrogen abstraction from the corresponding hydrogenated molecules. This energy difference can be estimated from the difference in fundamental vibrational frequencies (e.g. $\Delta E = \frac{1}{2} h \nu_0$). Due to this zero-point energy difference deuterium abstraction from isotopically mixed species is of no importance and consequently they have not been included. The reaction of D with H_2 has an activation barrier of 3900 K (Mitchell and LeRoy, 1973). Since the activation barriers for reactions of D with other molecules abundant on a grain surface (e.g. H_2CO , CO, and O_2 ; see Paper II) are much less, this reaction can be ignored.

Isotopic exchange reactions of the type



are exothermic in the forward direction. However since they are expected to have high activation barriers we have excluded them from our surface chemistry network.

In total 440 reactions between 467 species have been included in the calculations. Since the numerical model has been described in detail elsewhere (Paper II) no further discussion will be given here. The only input parameters for the surface chemistry calculations are the gas phase abundances of the accreting species. These are provided by the gas phase calculations discussed above.

3. Results

The chemical composition of grain mantles as they accrete inside dense molecular clouds is calculated using the procedure discussed in Sect. 2. The following free parameters are involved: the total density of hydrogen nuclei, n_0 ; the gas temperature, T_0 ; the cosmic ray ionization rate, ζ_0 ; the radiation field incident on the cloud, G_0 ; the visual extinction, A_v ; and the abundances of the elements.

In all of the calculations the following free parameters have been fixed at, $T_0 = 10 \text{ K}$; $\zeta_0 = 1.6 \cdot 10^{-17} \text{ s}^{-1}$ (Black and Dalgarno, 1977); $G_0 = 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ (derived from Habing, 1968) and $A_v = 10 \text{ mag}$. For the relative abundances of the elements we have

Table 2. Grain surface reactions involving H or D and possessing an activation barrier

Reaction	Activation energy [K]
$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	1200
$\text{D} + \text{O}_2 \rightarrow \text{DO}_2$	1200
$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$	1400
$\text{D} + \text{H}_2\text{O}_2 \rightarrow \text{HDO} + \text{OH}$	1400
$\text{H} + \text{HDO}_2 \rightarrow \text{H}_2\text{O} + \text{OD}$	1400
$\text{D} + \text{HDO}_2 \rightarrow \text{HDO} + \text{OD}$	1400
$\text{H} + \text{D}_2\text{O}_2 \rightarrow \text{HDO} + \text{OD}$	1400
$\text{D} + \text{D}_2\text{O}_2 \rightarrow \text{D}_2\text{O} + \text{OD}$	1400
$\text{H} + \text{O}_3 \rightarrow \text{O}_2 + \text{OH}$	450
$\text{D} + \text{O}_3 \rightarrow \text{O}_2 + \text{OD}$	450
$\text{H} + \text{CO} \rightarrow \text{HCO}$	1000
$\text{D} + \text{CO} \rightarrow \text{DCO}$	1000
$\text{H} + \text{H}_2\text{CO} \rightarrow \text{HCO} + \text{H}_2$	1850
$\text{D} + \text{H}_2\text{CO} \rightarrow \text{HCO} + \text{HD}$	1850
$\text{H} + \text{HDCO} \rightarrow \text{DCO} + \text{H}_2$	1850
$\text{D} + \text{HDCO} \rightarrow \text{DCO} + \text{HD}$	1850
$\text{H} + \text{D}_2\text{CO} \rightarrow \text{DCO} + \text{HD}$	2350
$\text{D} + \text{D}_2\text{CO} \rightarrow \text{DCO} + \text{D}_2$	2350
$\text{H} + \text{H}_2\text{S} \rightarrow \text{SH} + \text{H}_2$	850
$\text{D} + \text{H}_2\text{S} \rightarrow \text{SH} + \text{HD}$	850
$\text{H} + \text{HDS} \rightarrow \text{SD} + \text{H}_2$	850
$\text{D} + \text{HDS} \rightarrow \text{SD} + \text{HD}$	850
$\text{H} + \text{D}_2\text{S} \rightarrow \text{SD} + \text{HD}$	1350
$\text{D} + \text{D}_2\text{S} \rightarrow \text{SD} + \text{D}_2$	1350

adopted the values observed towards ζ Oph (Morton, 1974; de Boer, 1981; Lugger et al., 1978; Jenkins and Shaya, 1979). The deuterium abundance was set equal to the cosmic abundance value ($1.5 \cdot 10^{-5}$; York and Rogerson, 1976).

In order to study the effects of ongoing depletion on interstellar grains we have introduced the dimensionless depletion parameter, δ . The gas phase abundances of all of the elements heavier than helium are reduced by this factor with respect to the ζ Oph values. In the gas phase hydrogen and helium are mainly in the molecular (H_2) and atomic (He) form. Therefore they do not accrete appreciably. Deuterium is partly in molecular (HD) and in atomic (D) form. The former does not accrete also on interstellar grain surfaces but atomic deuterium will react on a grain surface. The product molecule will remain on the grain and consequently the deuterium abundance in the gas phase will be reduced. The factor, δ_D , with which the deuterium abundance is reduced is therefore given by

$$\delta_D = [n(\text{HD}) + n(\text{D})\delta] / (n_0 A_D),$$

where $n(\text{HD})$, $n(\text{D})$ and A_D are the number density of HD, D and the initial deuterium abundance. The calculations are started for $\delta = 1$. δ is then reduced in steps of 0.1. The concentration of HD and D needed to calculate δ_D are then taken from the previous step.

In Figs. 1a and b and 2a and b we present the gas phase and grain mantle composition inside dense molecular clouds as a function of n_0 and δ . Table 3 gives the formation rate of (deuterated) molecular hydrogen on grain surfaces as a function of gas phase density, n_0 .

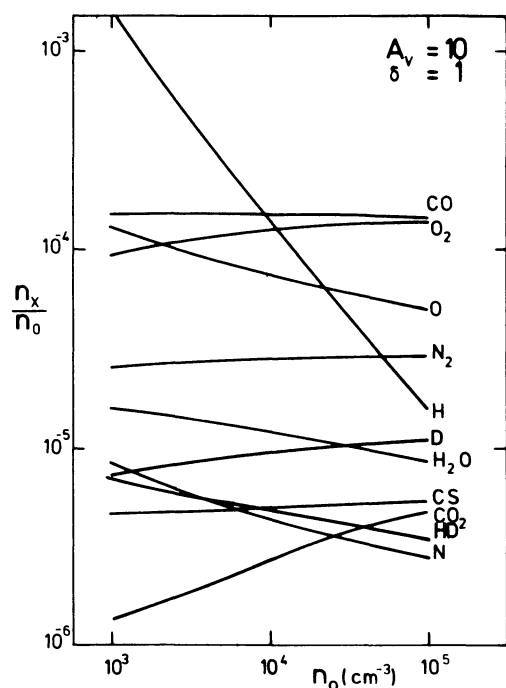


Fig. 1a. The concentration of the most abundant molecules in the gas phase as a function of density

IV. Discussion

A. Deuterated molecules in grain mantles

The amount of deuterated molecules in grain mantles is determined by the concentration of atomic deuterium in the gas phase. The main reactions which influence the gas phase density of D are summarized in Fig. 3. The calculated gas phase concentration of D is generally larger than that of HD because the timescale for HD formation from D is longer than the destruction timescale of HD with H_3^+ . The high DCO^+ abundance in the gas phase is generally believed to result from a low electron abundance (see Fig. 3). In calculating the expected enhancement of DCO^+ it is always tacitly assumed that all of the deuterium is in the form of HD (see for example Watson, 1978). This is incorrect, in particular at the higher densities ($n_0 \gtrsim 10^4 \text{ cm}^{-3}$, see Fig. 1a). This implies that in order to explain the observed enhancement of deuterated species (e.g. DCO^+ and N_2D^+) by ion-molecule gas phase reactions, the electron abundance must be even lower than generally calculated. The abundance of atomic hydrogen is determined by the equilibrium between the formation of H_2 on grain surfaces and its ionization by cosmic rays. Most of the hydrogen in the gas phase is in the form of H_2 . The ratio of D to H in the gas phase is therefore much larger than the elemental abundance ratio.

Because of the relatively low deuterium abundance, the concentration of the most abundant molecules in the gas phase have not altered much in comparison with the values found in the previous calculations. The gas phase consists mainly of H_2 , He, H, CO, O_2 , O, and N_2 (Paper II). The most important surface reactions of carbon, nitrogen and oxygen bearing molecules are summarized in Figs. 4–6.

In the gas phase carbon is mainly in the form of CO (Figs. 1a and 2a). Upon accretion onto a grain surface it forms CO_2 with atomic oxygen and HCO with atomic hydrogen (Fig. 4). The latter

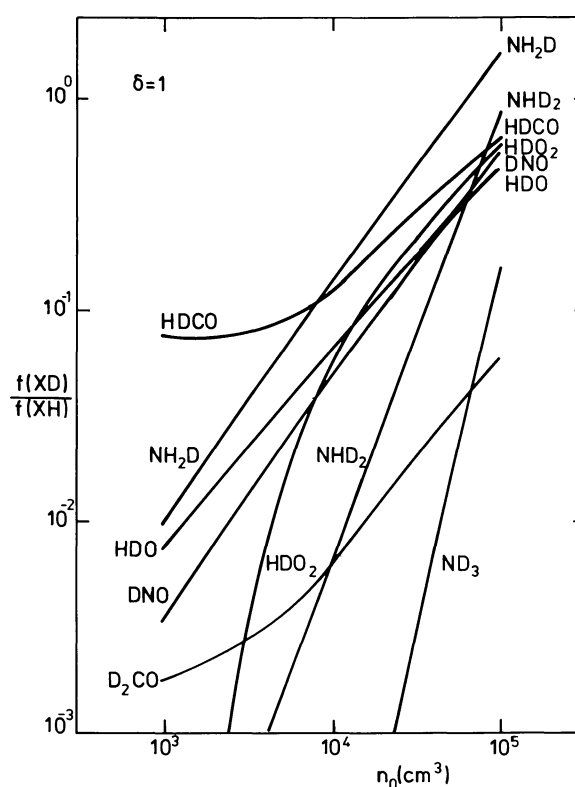


Fig. 1b. The concentration of the most abundant deuterated molecules relative to their hydrogenated counterparts in the grain mantle as a function of density

molecule acts as an enhanced binding site for H. H addition and H abstraction by H and D leads to the formation of H_2 and HD. This cycle continues until the HCO molecules is lost by reactions with other migrating atoms, mainly N and D. With the latter HCO forms the deuterated form of formaldehyde, HDCO. Again abstraction and addition by H and D will form H_2 and HD. Because of the difference in zero-point energy HDCO has a much larger activation barrier for deuterium abstraction than for hydrogen abstraction. In effect the conversion from H_2CO to HDCO is therefore irreversible.

The DCO can now cycle many times between HDCO, DCO, and D_2CO until it is lost through reactions of DCO with other migrating atoms, mainly N. As a result of this transformation of formaldehyde to its deuterated forms the relative concentrations of the latter in the grain mantle are even larger than expected on the basis of the enhanced atomic D to H ratio in the gas phase. This particularly true for low densities (Fig. 1b).

In the gas phase nitrogen is mainly in the form of N_2 (see Figs. 1a and 2a), which we assume does not react on interstellar grain surfaces. Atomic nitrogen accreted from the gas phase can form HNO, NH_3 and their deuterated counterparts on the grain surface. Reactions of H and D with nitrogen bearing radicals are completely analogous (Fig. 5) and do not possess activation barriers. The ratio of the concentration of the deuterated molecules to their hydrogenated counterparts reflects therefore the enhanced ratio of atomic D to H in the gas phase.

The oxygen surface chemistry reaction network is quite complicated (Fig. 6). Atomic oxygen can react with the CO molecules already present on the grain surface to form CO_2 . H_2O and its deuterated forms can be formed through an O_3 intermediate or

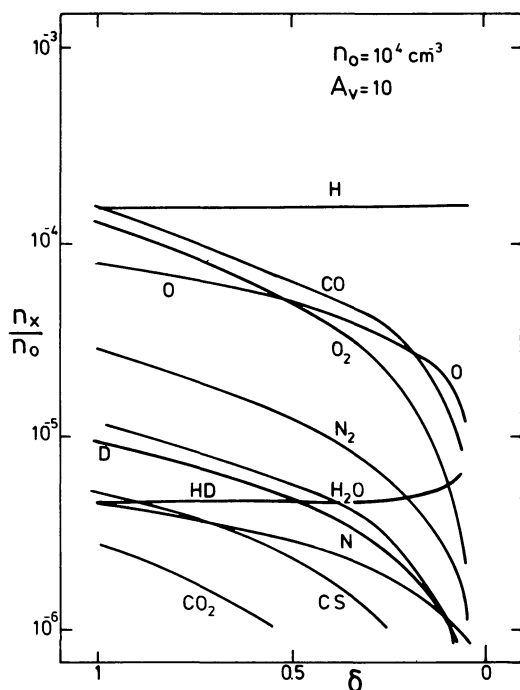


Fig. 2a. The concentration of the most abundant molecules in the gas phase as a function of the depletion parameter δ

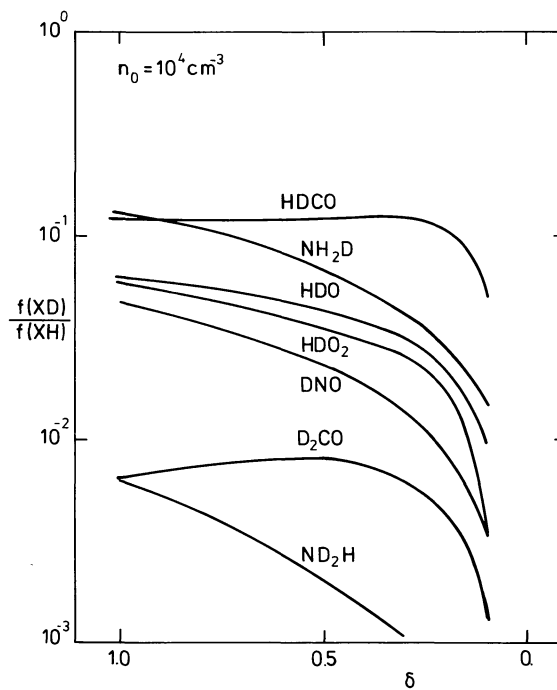


Fig. 2b. The concentration of the most abundant deuterated molecules relative to their hydrogenated counterparts in the grain mantle as a function of the depletion parameter δ

Table 3. The formation rate of molecular hydrogen on grain surfaces

n_0 (cm^{-3})	$f(\text{HD})$	R_s/R_g	$f(\text{H}_2)$
10^3	$3.3 \cdot 10^{-1}$	2.3	$9.4 \cdot 10^{-1}$
10^4	$2.0 \cdot 10^{-2}$	1.4	$4.2 \cdot 10^{-1}$
10^5	$7.3 \cdot 10^{-5}$	0.05	$5.0 \cdot 10^{-3}$

through the peroxides. At low densities the pathway initiated by O_3 formation dominates, at high densities the peroxides pathway dominates. O_3 is formed by the surface reaction of O with O_2 . It reacts with H and D ultimately yielding H_2O and HDO respectively. In this reaction pathway the O_2 molecule is reformed again. Therefore, in effect O_2 plays a catalytic role in the formation of water on grain surfaces. The probability for the occurrence of a specific reaction, which has an activation barrier, is given by

$$Q_i = \frac{\phi_i}{\sum_j \phi_j},$$

where the ϕ_i 's are given by Eq. (1) and the summation extends over all possible reactions. We have assumed that the activation barriers for the corresponding reactions of D and H with a given molecule are equal. The resulting ratio of deuterated molecules to their hydrogenated counterparts will, however, differ from the ratio of the accretion rate of D to H. This is due to the difference in mass which enters exponentially into Eq. (1). Reactions with a low activation barrier result in a relatively high yield of deuterated molecules while those with a high activation barrier result in a relatively low yield of deuterated molecules. The exact location of

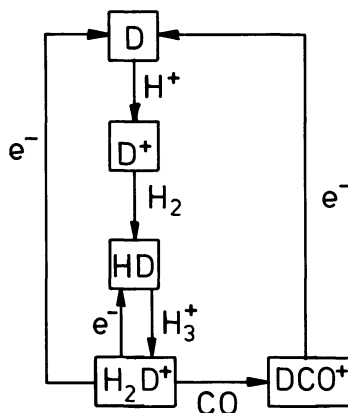


Fig. 3. Schematic representation of the most important reactions involved in the gas phase chemistry of deuterium

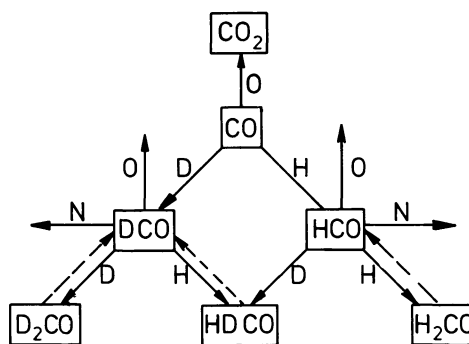


Fig. 4. Schematic representation of the most important surface reactions of carbon bearing molecules

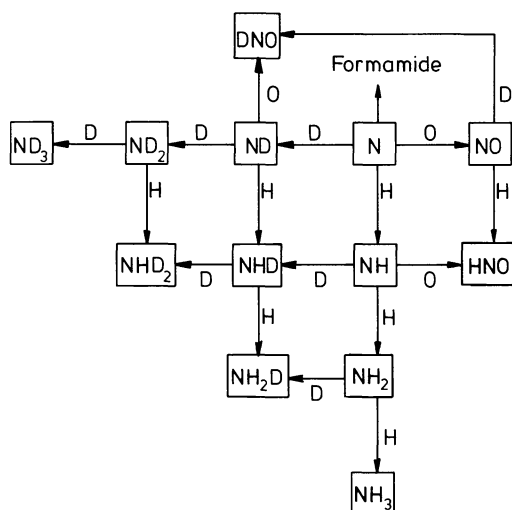


Fig. 5. Schematic representation of the most important surface reactions of nitrogen bearing molecules

the turning point depends, of course, on the relative concentrations of all the coreactants of H and D listed in Table 2. For O_3 this generally gives rise to a HDO/ H_2O ratio larger than expected on the basis of the atomic D/H ratio in the gas phase (see Fig. 1b).

The peroxides pathway for the formation of water starts with H or D addition to O_2 forming the peroxides H_2O_2 , HDO_2 , and D_2O_2 . Reactions of these with H or D finally give H_2O , HDO or D_2O (Fig. 6). The ratio of deuterated water to its hydrogenated form resulting from this pathway is generally slightly lower than expected on the basis of the atomic D to H ratio in the gas phase.

Summarizing we conclude that deuterium enhancements up to a factor 10^5 can be expected for many of the molecules in grain mantles. The concentration of the molecules HDO and HDCO may account for as much as a few percent of all the molecules in the grain mantle. Generally the deuterium enhancement depends strongly on the physical conditions in the gas phase.

In our calculations of the gas phase abundancies we have assumed, for computational simplicity, that the formation of HD on grain surfaces can be neglected. We will now assess the importance of this assumption. In our model of molecular hydrogen formation on grain surfaces H_2 is formed by hydrogen abstraction from molecules like H_2CO and H_2S (Paper II). HD formation on grain surfaces proceeds similarly. In Table 3 the fraction, $f(HD)$, of all collisions of D atoms with a grain that lead to HD formation is given as a function of gas density. At low densities about one third of all D atoms abstract an H atom from HDS, H_2CO or H_2S . For higher gas densities the relative efficiency of the HD formation process drops rapidly, because of the increase in other coreactants for D atoms, notably O_3 , O_2 , and CO. This increase is due to the decrease of the collision rate of H atoms relative to that of heavier species (cf. Fig. 1a). As a consequence, for densities larger than about 10^4 cm^{-3} , most D atoms will form HDO and HDCO (cf. Table 3 and Fig. 1b).

We can compare the rate at which HD is formed in the gas phase, R_g , to that on grain surfaces, R_s , in the following way. If R_c is the collision rate of D atoms with grains and k_1 the rate constant for reaction 1 in Table 1 then we may write

$$\frac{R_s}{R_g} = \frac{R_c f(HD)}{n(H^+)k_1}.$$

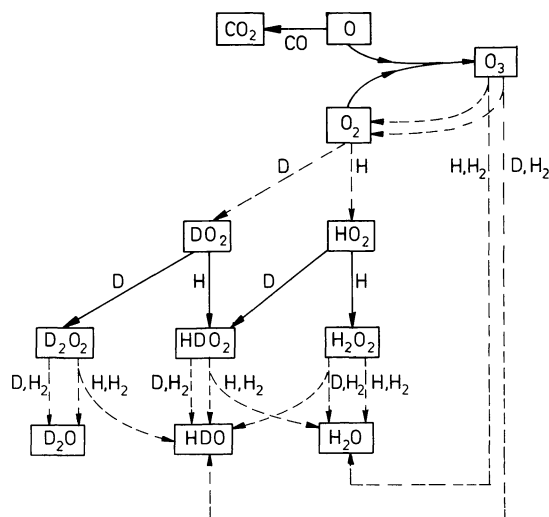


Fig. 6. Schematic representation of the most important surface reactions of oxygen bearing molecules

Inserting $R_c = 7.10^{-18} n_0 \text{ s}^{-1}$ and $n(H^+) = 10^{-6} \text{ cm}^{-3}$ we find

$$\frac{R_s}{R_g} = 7 \cdot 10^{-3} n_0 f(HD).$$

Values for this ratio are given in Table 3. At low densities, $n_0 \lesssim 10^4 \text{ cm}^{-3}$, HD formation on grain surfaces is somewhat more important than HD formation in the gas phase. Obviously we have overestimated the deuterium fractionation of molecules in the grain mantle by about a factor 2 at low densities.

It should be noted that the efficiency of H_2 formation on grain surfaces, $f(H_2)$, is also down at high densities (Table 3). This has not been taken into account in our calculations of the gas phase chemical equilibrium. This has however no serious consequences. The destruction rate of H_2 molecules, mainly by cosmic rays, is small and hydrogen is still mainly in the form of H_2 at those densities. The abundance of atomic H is unchanged since it does not matter whether H atoms form H_2 or heavier molecules on a grain surface.

The concentration of some deuterated molecules (e.g. HDO and HDCO) rests on the assumption that the activation barriers for the reactions between D or H with a given molecule on the grain surface are equal. Experimental testing of this assumption would be extremely important. We have also assumed that isotope exchange reactions of the type (2) have an activation barrier which is high and consequently are of no importance. If this assumption is incorrect then, because these reactions are exothermic in the forward direction and because of the low grain temperatures, essentially every D in an accreted HD molecule should be ultimately bound up in a heavier deuterated molecule. As a result the total concentration of deuterated molecules in the grain mantle will then be higher than in our calculations. Experimental determination of the activation barriers involved in these reactions will be extremely useful.

B. Infrared characteristics

In this section we will discuss the infrared spectroscopic characteristics expected from deuterated molecules in interstellar grain mantles. For a discussion of the infrared characteristics of the other molecules see Paper II. We will concentrate on HDO and HDCO because of their relatively high abundance in the calcu-

lated grain mantles. The O–D stretch in HDO and the C–D stretch in HDCO stand the best chance for detection since they are shifted to a relatively clean region of the interstellar infrared spectrum (2000–2700 cm^{-1}). Unfortunately this spectral region is blocked by atmospheric CO_2 absorption and observations from above the atmosphere are required to search for them.

In low density regions ($n_0 < 10^5 \text{ cm}^{-3}$) the calculated grain mantles consist mainly of H_2O and H_2CO while at high densities they consist mainly of CO and O_2 . This has important consequences for the infrared spectrum of HDO. The O–D stretch of HDO suspended in H_2O is shifted to 2450 cm^{-1} ($4.08 \mu\text{m}$). At low concentrations it will have a width of about 75 cm^{-1} . Due to complexing with H_2O its intensity is enhanced with respect to that for isolated molecules. The ratio of the integrated strength of this band to the 3250 cm^{-1} O–H stretching band of H_2O is about 0.25 times the HDO/ H_2O ratio in the grain mantle (Ikawa and Maeda, 1968). The observed equivalent width of the O–H stretch in the spectrum of BN is estimated to be about 400 cm^{-1} . Assuming that these grain mantles have been accreted at a density of 10^4 cm^{-3} we arrive at an expected equivalent width for the O–D stretch of 6 cm^{-1} . In a non-hydrogen bonding environment, such as CO or O_2 , the O–D stretch in HDO occurs around 2650 cm^{-1} ($3.77 \mu\text{m}$) (Tursi and Nixon, 1970; Ayers and Pullin, 1976; Murby and Pullin, 1979). We expect that the integrated strength of this band is about 10% of the integrated strength of the 3250 cm^{-1} band in H_2O (as). The other HDO vibrational modes are either masked by the corresponding H_2O modes (e.g. the O–H stretch) or are quite weak (e.g. O–D bending at 1465 cm^{-1}).

We now consider the infrared characteristics of HDCO in a grain mantle. In the presence of large amounts of H_2O and other polar molecules, complexing of HDCO with the environment will, as for H_2CO , result in broad absorption bands ($\sim 50 \text{ cm}^{-1}$; see references in Hagen et al., 1982). In inert matrices the C–D stretching modes occur at 2070 ($4.83 \mu\text{m}$) and 2180 cm^{-1} ($4.59 \mu\text{m}$) (Khoshkoo and Nixon, 1973). In an H_2O matrix these absorptions may be shifted by about 20 cm^{-1} (Nelander, 1980). In analogy to the gas phase data of H_2CO we expect an integrated strength of these lines of about 4 cm^{-1} in the spectrum of BN, where we have assumed that these grain mantles have been accreted at a density of 10^4 cm^{-3} . This strength is however quite uncertain since the solid state may affect the absorption cross section of HDCO considerably. Laboratory studies of suitable grain mantle analogs will obviously be very useful. The other HDCO vibrational modes are either masked by the H_2CO vibrational modes (e.g. C–H stretch) or are quite weak (e.g. C–D deformation mode at about 1500 cm^{-1}) and are therefore presently unobservable.

Apart from the O–D stretch in HDO at 2450 cm^{-1} the general prospects of observing infrared absorption lines of deuterated molecules in interstellar grain mantles is low at present. It is, however, expected that, in the near future, with improved frequency resolution, better signal to noise ratio and with observations from above the atmosphere a number of absorption lines of deuterated molecules can be detected. This information is important in furthering our understanding of the physical conditions in dense, interstellar clouds.

C. Deuterated molecules in the gas phase

In these calculations it has been assumed that reactions on the grain surface other than H_2 formation do not influence the gas phase molecular composition. Although this assumption is justified for the most abundant molecules, for those molecules which are more easily made on grain surfaces than in the gas phase,

surface reactions can be of importance (Paper II). This is especially true for formaldehyde and the deuterated molecules. As an example we will consider the contribution of grain surface reactions to the gas abundance of formaldehyde.

The rate at which molecules are ejected from grain surfaces into the gas phase is quite uncertain. In order to estimate the importance of grain surface reactions for the molecular composition of the gas phase we will assume that a fraction α of all molecules which accrete per unit time are finally ejected in the gas phase again. Thus the evaporation rate, R_{ev} , of a given molecule is assumed to be

$$R_{ev} = (nn_g\sigma_g\bar{v})\alpha f_i,$$

where n and \bar{v} are the total gas phase abundance and mean velocity of accreting molecules and n_g and σ_g are the number density and geometrical cross section of the grains and f_i is the relative concentration in the grain mantle of the molecule under consideration. Inserting $\sigma_g = 3 \cdot 10^{-10} \text{ cm}^2$, $\bar{v} = 7 \cdot 10^3 \text{ cm/s}$ and $n_d = 10^{-12} n_0$, assuming ζ_{Oph} abundances we find $R_{ev} = 3 \cdot 10^{-14} \alpha \text{ cm}^{-3} \text{ s}^{-1}$ for the rate at which H_2CO molecules evaporate from a grain surface at a density of 10^4 cm^{-3} ($f_i = 0.3$).

In the gas phase H_2CO is mainly generated by the neutral-neutral reaction between CH_3 and O (Prasad and Huntress, 1980). In our model calculations this reaction has a rate of $R_{\text{gas}} = 4 \cdot 10^{-18} \text{ cm}^{-3} \text{ s}^{-1}$ at $n_0 = 10^4 \text{ cm}^{-3}$. Consequently if α is larger than 10^{-4} grain surface chemistry can be a dominant mechanism for H_2CO formation. It should be noted that the HDCO/ H_2CO ratio resulting from grain surface chemistry (~ 0.1) is in reasonable agreement with the ratio observed in the gas phase (Langer et al., 1979), lending some support to the idea that grain surface chemistry contributes significantly to the formation of H_2CO . Gas phase chemistry might however also be able to explain such a high ratio (Langer et al., 1979; Watson et al., 1975). In view of the uncertainties present in estimating the molecular evaporation rates, further speculation along these lines is not warranted. However we wish to emphasize the fact that the high abundance of some of the deuterated molecules and radicals observed in the gas phase may result from reactions occurring on grain surfaces. A test of the validity of this hypothesis could be made by observing the gas phase as well as the grain mantle composition in the same region.

V. Conclusions

Summarizing we may conclude

- (1) The model for the formation of molecular hydrogen on grain surfaces, proposed in Paper II, predicts a high ratio of atomic D to HD in the gas phase. As a consequence the abundance of deuterated molecules in grain mantles is much larger than expected on the basis of the cosmic abundance ratio of D to H.
- (2) HDCO has a relatively high abundance in grain mantles as compared to other deuterated molecules. This is due to the fact that H abstraction from HDCO has a lower activation barrier than D abstraction.
- (3) The abundance of deuterated molecules in grain mantles is a good indication of the physical conditions in the gas phase.
- (4) Observations of the O–D stretching mode of HDO at 2418 cm^{-1} will be extremely useful for evaluating the importance of deuterium chemistry taking place on grain surfaces.
- (5) A high abundance of deuterated molecules (e.g. HDCO) in the gas phase may be explainable in terms of grain surface reactions.

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