Surface chemistry of deuterated molecules

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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

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

. 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 $(n_e/n_o \simeq 10^{-8})$ 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

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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.

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

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 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

$\begin{array}{ccc} DCO^{+} + e^{-} \rightarrow CO & + D \\ N_{2}D^{+} + e^{-} \rightarrow N_{2} & + D \end{array}$	\rightarrow H + H + D	\rightarrow H ₂ + D	$H_2D^+ + e^- \rightarrow HD + H$	$H_2D^+ + N_2^- \rightarrow N_2D^+ + H_2^-$		$O^{+} + H_{2} + 178 \text{ K}$	$D^+ + H_2 \rightarrow H^+ + HD$	$D + H^+ \rightleftharpoons D^+ + H + 43 K$	Reaction
<u>α</u> α	£	œ	B	a	a	$3 10^{-10}$	10^{-9}	10^{-9}	Rate
Mul and McGowan (1979) Mul and McGowan (1979)	McGowan et al. (1978)	McGowan et al. (1978)	McGowan et al. (1978)			Huntress and Anicich (1976)	Fehsenfeld et al. (1973)	Watson et al. (1978)	Ref.

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

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.

Deuterium gas phase chemistry

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

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, $\rm H_2$, and HD on an interstellar grain surface decreases with increasing $\rm H_2$ 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 $\rm H_2$. At a density of $10^4 \, \rm cm^{-3}$ the binding energy and surface coverage of $\rm H_2$ 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 510⁸ for HD, instead of 210²s 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

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 210⁻⁸ 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

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

where $N_{\rm cor}$ 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, ν_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 $n \simeq 5 \, 10^{12}$. Inserting $v_0 = 10^{13} \, \text{s}^{-1}$, $\tau = 3 \, 10^{-11} \, \text{s}$, $a = 1 \, \text{Å}$ and $m = 3.2 \, 10^{-24} \, \text{g}$ 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.

of 3900 K (Mitchell and LeRoy, 1973). Since the activation barriers for reactions of D with other molecules abundant on a mixed species is of no importance and consequently they have not been included. The reaction of D with $\rm H_2$ has an activation barrier mental vibrational frequencies (e.g. $\Delta E = \frac{1}{2}hv_0$). Due to this zeroenergy difference can be estimated from the difference in fundaabstraction from the corresponding hydrogenated molecules. molecules will have a higher activation barrier than hydrogen and D, deuterium abstraction by H or D atoms from deuterated chemistry and an accurate determination of these assumption is of crucial importance in the deuterium surface spectively by H and D atoms (McNesby et al., 1960). ments on H and D abstraction from H₂CO and D₂CO involving H atoms. This is in good agreement with the experihave the same activation barrier as the corresponding reactions experimental and theoretical data on the energy barriers involved molecules and their activation energy. Because of the lack of grain surface (e.g. $\rm{H_2CO,CO,}$ and $\rm{O_2}$; see Paper II) are much less point energy difference deuterium abstraction from isotopically barriers is warranted. Because of the mass difference between H we have assumed that D addition and H abstraction by D atoms this reaction can be ignored. In Table 2 we present reactions of H and D atoms with activation

Isotopic exchange reactions of the type

$$HD + XH \rightleftharpoons H_2 + XD$$
 (2)

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.

. Kesults

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, $T_0=10\,\mathrm{K}$; $\zeta_0=1.6\,10^{-17}\,\mathrm{s}^{-1}$ (Black and Dalgarno, 1977); $G_0=10^8\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ (derived from Habing, 1968) and $A_v=10\,\mathrm{mag}$. For the relative abundances of the elements we have

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

Reaction		Activitation energy [K]
↓	HO_2	1200
-	$\overline{\mathrm{DO}_{2}}^{\mathrm{T}}$	1200
$O_2 \rightarrow$	$H_2O + OH$	1400
$+ H_2O_2 \rightarrow$	$\overline{}$	1400
$O_2 \rightarrow$		1400
$+ \text{HDO}_2 \rightarrow$	+	1400
$+ D_2O_2 \rightarrow$	HDO + OD	1400
$+ D_2O_2 \rightarrow$		1400
↓	+	450
+ O ₃ →	$O_2 + OD$	450
+ CO →	HCO	1000
+ CO →	DC0	1000
$+ H_2CO \rightarrow$	$HCO + H_2$	1850
) ↓		1850
+ H	$DCO + H_2$	1850
$D + HDCO \rightarrow J$		1850
$H + D_2CO \rightarrow C$	DCO + HD	2350
+ D		2350
$+ H_2S \rightarrow$		850
$D + H_2S \rightarrow S$		850
$[+ HDS \rightarrow$		850
$+ HDS \rightarrow$	D	850
$1 + D_2S \rightarrow$	SD + HD	1350
$D + D_2S \rightarrow S$	D	1350
:		

adopted the values observed towards COph (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 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 (H₂) 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

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

where $n(\mathrm{HD})$, $n(\mathrm{D})$ 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 .



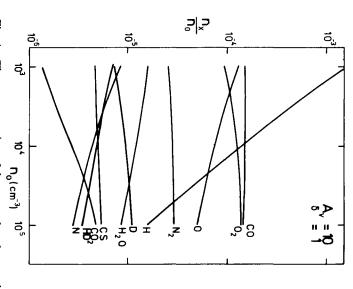


Fig. 1a. The concentration of the most abundant molecules in the gas phase as a function of density

IV. Discussion

A. Deuterated molecules in grain mantles

ratio. in particular at the higher densities $(n_0 \gtrsim 10^4 \, \text{cm}^{-3})$ phase is therefore much larger than the elemental abundance in the gas phase is in the form of H₂. The ratio of D to H in the gas surfaces and its ionization by cosmic rays. Most of the hydrogen termined by the equilibrium between the formation of H_2 on grain generally phase reactions, the electron abundance must be even lower than deuterated species (e.g. DCO+ the form of HD (see for example Watson, 1978). This is incorrect, DCO+ it is always tacitly assumed that all of the deuterium is in timescale for HD formation from D is longer than the destruction timescale of HD with ${\rm H_3^+}$. The high DCO $^+$ abundance in the gas termined by the concentration of atomic deuterium in the This implies that in order to explain the observed enhancement of centration of D is generally larger than that of HD because the phase. The main reactions which influence the gas phase density of The amount of deuterated molecules in is generally believed to result from a low electron abun-(see summarized in Fig. 3. calculated. The abundance of atomic hydrogen is de-Fig. 3). In calculating the expected enhancement of and N₂D⁺) by ion-molecule gas The calculated grain mantles , see Fig. 1a). phase congas

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 , H_2 , H_3 , H_4 , H_5 , H_5 , H_6 , H_7 , H_8 ,

In the gas phase carbon is mainly in the form of CO (Figs. 1a and 2a). Upon accretion onto a grain surface it forms CO₂ with atomic oxygen and HCO with atomic hydrogen (Fig. 4). The latter

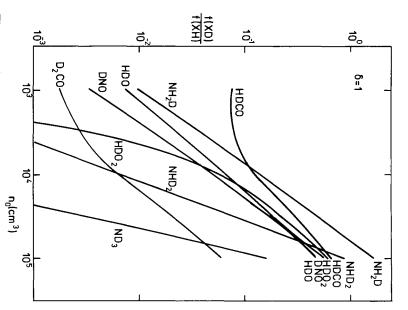


Fig. 1b. The concentration of the most abundant deuterated molecules relative to their hydrogenated counterparts in the grain mantle as a function of density

HDC0 hydrogen abstraction. In effect the conversion from H₂CO to larger activation barrier abstraction and addition by H and D will form H2 with other migrating atoms, mainly N and D. abstraction by H and D leads to the formation of H₂ and HD molecule acts as an enhanced binding site for H. H addition and H HCO forms the deuterated form of formaldehyde, HDCO. Because of the difference in zero-point energy HDCO has a much This cycle continues until the HCO molecules is lost by is therefore irreversible. for deuterium abstraction than With the latter and HD reactions for

The DCO can now cycle many times between HDCO, DCO, and D₂CO 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 N₂ (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, NH₃ 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 CO₂. H₂O and its deuterated forms can be formed through an O₃ intermediate or

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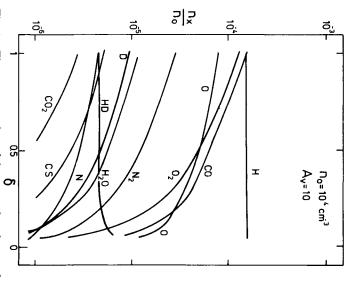
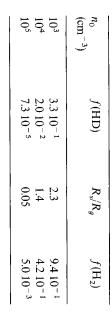


Fig. 2a. The concentration of the most abundant molecules in the gas phase as a function of the depletion parameter δ

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

HX XD XD 10_{:3} ರ್ಮ ಠ್ಠ 5 $n_0 = 10^4 \text{ cm}^3$ HDC0 D_2CO DNO NH₂D ND2H E02 팅 0.5 O

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



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

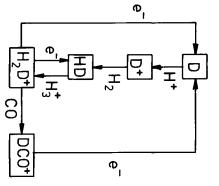


Fig. 3. Schematic representation of the most important reactions involved in the gas phase chemistry of deuterium

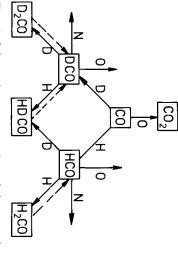


Fig. 4. Schematic representation of the most important surface reactions of carbon bearing molecules

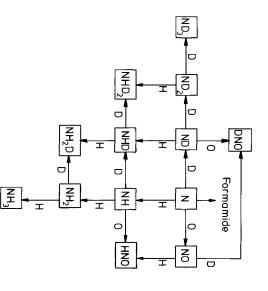


Fig. 5. Schematic representation of the most important surface reactions of nitrogen bearing molecules

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 hydrogenerated 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 10⁵ 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.

atoms will form HDO and HDCO (cf. Table 3 and Fig. 1b). CO. This increase is due to the decrease of the collision rate of H the increase in other coreactants for D atoms, notably O_3 , O_2 , and efficiency of the HD formation process drops rapidly, because of densities about one third of all D atoms abstract an H atom from to HD formation is given as a function of gas density. At low fraction, f(HD), of all collisions of D atoms with a grain that lead abstraction from molecules like H₂CO and H₂S (Paper II). HD drogen formation on grain surfaces H₂ is formed by hydrogen importance of this assumption. In our model of molecular hyassumed, for computational simplicity, that the formation of HD In our calculations of the gas phase abundancies we have H₂CO or H₂S. For higher gas densities surfaces on grain surfaces proceeds similarly. In Table 3 the for densities larger than about 10⁴ cm to that of heavier species (cf. can be neglected. We will now asses . Fig. 1a). 4 cm⁻³. m the most D relative the

We can compare the rate at which HD is formed in the gas phase, R_g , to that on grain surfaces, R_g , 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

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

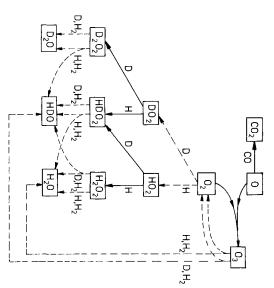


Fig. 6. Schematic representation of the most important surface reactions of oxygen bearing molecules

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

$$\frac{R_s}{R_g} = 710^{-3} n_0 f(\text{HD}).$$

Values for this ratio are given in Table 3. At low densities, $n_0 \lesssim 10^4 \, \mathrm{cm}^{-3}$, 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.

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

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 CO₂ absorption and observations from above the atmosphere are required to search for them.

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the corresponding H₂O modes (e.g. the O-H stretch) or are quite weak (e.g. O-D bending at 1465 cm⁻¹). above the atmosphere are required to search for them. In low density regions ($n_0 < 10^5 \, \mathrm{cm}^{-3}$) the calculated grain mantles consist mainly of $\mathrm{H_2O}$ and $\mathrm{H_2CO}$ while at high densities they consist mainly of CO and $\mathrm{O_2}$. This has important consequences for the infrared spectrum of HDO. The O-D stretch of HDO suspended in $\mathrm{H_2O}$ is shifted to 2450 cm⁻¹ (4.08 µm). At low about 10% of the integrated strength of the 3250 cm⁻¹ band in Pullin, 1979). We expect that the integrated strength of this band is O₂, the O-D stretch in HDO occurs around 2650 cm⁻¹ (3.77 μm) we arrive at an expected equivalent width for the O-D stretch of spectrum of BN is estimated to be about 400 cm⁻¹. Assuming that for isolated molecules. The ratio of the integrated strength of this band to the $3250 \,\mathrm{cm}^{-1}$ O-H stretching band of $\mathrm{H}_2\mathrm{O}$ is about 0.25 concentrations it will have a width of about 75 cm⁻¹. Due to $\mathrm{H_2O}$ (as). The other HDO vibrational modes are either masked by (Tursi and Nixon, 1970; Ayers and Pullin, 1976; Murby and 6 cm⁻¹. In a non-hydrogen bonding environment, such as CO or these grain mantles have been accreted at a density of 10⁴ cm⁻³ 1968). The observed equivalent width of the O-H stretch in the times the HDO/H₂O ratio in the grain mantle (Ikawa and Maeda, complexing with H₂O its intensity is enhanced with respect to that

We now consider the infrared characteristics of HDCO in a grain mantle. In the presence of large amounts of $\rm H_2O$ and other polar molecules, complexing of HDCO with the environment will, as for $\rm H_2CO$, result in broad absorption bands ($\sim 50\,\rm cm^{-1}$; see references in Hagen et al., 1982). In inert matrices the C–D stretching modes occur at 2070 (4.83 µm) and 2180 cm⁻¹ (4.59 µm) (Khoshkoo and Nixon, 1973). In an $\rm H_2O$ matrix these absorptions may be shifted by about $\rm 20\,cm^{-1}$ (Nelander, 1980). In analogy to the gas phase data of $\rm H_2CO$ we expect an integrated strength of these lines of about $\rm 4\,cm^{-1}$ in the spectrum of BN, where we have assumed that these grain mantles have been accreted at a density of $\rm 10^4\,cm^{-3}$. 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 $\rm H_2CO$ vibrational modes (e.g. C–H stretch) or are quite weak (e.g. C–D deformation mode at about $1500\,\rm cm^{-1}$) 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 $\rm H_2$ 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 then 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 \overline{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 $\sigma_g = 3 \cdot 10^{-10} \, \text{cm}^2$, $\overline{v} = 7 \cdot 10^3 \, \text{cm/s}$ and $n_d = 10^{-12} n_0$, assuming ζ Oph abundances we find $R_{ep} = 3 \cdot 10^{-14} \, \text{cm}^{-3} \, \text{s}^{-1}$ for the rate at which H_2 CO molecules evaporate from a grain surface at a density of $10^4 \, \text{cm}^{-3}$ ($f_i = 0.3$).

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 $R_{\rm gas}=4\,10^{-18}\,{\rm cm^{-3}\,s^{-1}}$ at $n_0=10^4\,{\rm cm^{-3}}$. 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 (\sim 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 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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