

## Model Calculations of the Molecular Composition of Interstellar Grain Mantles

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**Summary.** The chemical composition of mantles accreting on interstellar grains has been calculated numerically with a chemical reaction scheme which comprises gas phase as well as grain surface reactions. The equilibrium abundances of the molecules in the gas are calculated using gas phase reactions except for H<sub>2</sub> formation. The composition of the growing grain mantle is determined on the basis of the relative accretion rates of the gas phase molecules and diffusion controlled surface reactions.

The results show that in most circumstances grain mantles consist of the molecules H<sub>2</sub>O, H<sub>2</sub>CO, N<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and NH<sub>3</sub>. The relative concentrations of these species depend strongly on the physical conditions in the gas. The formation of H<sub>2</sub> on grain surfaces is examined in detail. We conclude that it proceeds through hydrogen abstraction from molecules like H<sub>2</sub>CO, H<sub>2</sub>S, N<sub>2</sub>H<sub>2</sub>, and N<sub>2</sub>H<sub>4</sub>. In essence these molecules act as enhanced binding sites for H atoms.

The infrared characteristics of the calculated grain mantles are discussed with an emphasis on the observed 3250 cm<sup>-1</sup> "ice" band. Grain mantles accreted at a density of 10<sup>3</sup>–10<sup>4</sup> cm<sup>-3</sup> contain large concentrations of H<sub>2</sub>O (~60%) and produce a broad 3250 cm<sup>-1</sup> "ice" band. It is suggested that the low frequency wing on this feature observed in interstellar spectra is due to absorption by H<sub>2</sub>CO, H<sub>2</sub>O<sub>2</sub>, and NH<sub>3</sub> hydrogen bonded to H<sub>2</sub>O.

**Key words:** dust – infrared – interstellar matter – molecular clouds – molecules

### 1. Introduction

The first detection of interstellar extinction provided definite evidence for the existence of interstellar dust (Trumpler, 1930). Since then, the composition of the grains has been a key question. Among the proposed grain materials are a "dirty ice" mixture, graphite and silicates (van de Hulst, 1949; Cayrel and Schatzman, 1954; Hoyle and Wickramasinghe, 1962; Kamijō, 1963). The dust in the first model consists of a solid mixture ("ice") of CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O with embedded impurities containing other elements all in proportion to their elemental abundance (van de Hulst, 1949).

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Infrared spectroscopy is an important tool for the study of interstellar dust particles. Firstly dust particles emit most of their radiation in the infrared. Secondly interstellar infrared spectra, which have become available during the last decade, contain direct information on the molecular composition of grains.

Infrared observations have shown, for example, that solid particles form in the outflow of late-type stars (Gillett et al., 1968). Late type variable stars commonly show infrared excess radiation above that expected from a cool stellar photosphere at the temperature indicated by the optical spectra (Merrill, 1977). The excess emission of carbon-rich stars is due to an, as yet, unidentified grain material. A minor fraction of the emitting dust around these stars consists of silicon carbide (Forrest et al., 1981). The excess emission of oxygen-rich stars is dominated by a 1030 cm<sup>-1</sup> and 570 cm<sup>-1</sup> emission or absorption feature (Merrill, 1977). These features have also been detected in the infrared spectra of many other objects. They are normally attributed to the stretching and bending vibrations in silicate materials. However no laboratory spectrum has been able to reproduce the shape of both features satisfactorily.

Spectrometric observations of several sources associated with molecular cloud material reveal an absorption feature around 3250 cm<sup>-1</sup>. This feature is generally identified with the stretching vibration of H<sub>2</sub>O ice in grain mantles (Merrill et al., 1976).

Some doubt on the identification of the "ice" band with H<sub>2</sub>O ice has risen since the detailed shape of the interstellar 3250 cm<sup>-1</sup> band cannot be explained by pure H<sub>2</sub>O ice I<sub>c</sub> (Mukai et al., 1978). However, recent laboratory spectra of amorphous solid water, H<sub>2</sub>O (as), at 77 K (Léger et al., 1979) and 10 K (Hagen et al., 1981) have been successful in explaining the observed width. Furthermore we have shown elsewhere that the observed low frequency wing on this feature is due to absorption by mixtures of H<sub>2</sub>O with other molecules (Hagen et al., 1982). The identification of the 3250 cm<sup>-1</sup> absorption band with the stretching vibration of H<sub>2</sub>O ice is supported by the recent discovery of a 1670 cm<sup>-1</sup> and a 220 cm<sup>-1</sup> feature corresponding to the bending and transverse optic vibration of H<sub>2</sub>O (Papoulat et al., 1979; Erickson et al., 1981; Puettner et al., 1979; Sofler et al., 1979). The librational vibration of H<sub>2</sub>O is generally not observed (Atkin, 1981). However in H<sub>2</sub>O (as) this absorption feature occurs around 750 cm<sup>-1</sup> and may therefore escape detection because of atmospheric absorption (Hagen and Tielens, 1982; Hagen et al., 1982). The identification of interstellar solid H<sub>2</sub>O can therefore be considered reliable.

Recent spectra of the 2500 cm<sup>-1</sup> to 1250 cm<sup>-1</sup> region show broad absorption lines due to molecules in the solid phase (Puettner et al., 1979; Sofler et al., 1979). Tentative identification

with vibrational modes of specific characteristic groups of molecules in grain mantles have been proposed (Hagen et al., 1980). The volume ratio of H<sub>2</sub>O ice to silicate is highly variable as inferred from the observed ratio of peak optical depths of the 3250 cm<sup>-1</sup> and 1030 cm<sup>-1</sup> features. For stars with molecular cloud material along the line of sight it is about 0.2. For material in the more tenuous interstellar medium the volume of ice appears negligible (Gillett et al., 1975; Merrill et al., 1976).

It is now generally accepted that graphite, silicate and "dirty ice" grains are present in the interstellar medium. However the relative importance of each material is still controversial. A bimodal dust model has been proposed in which large core-mantle particles (radius,  $a \sim 1200 \text{ \AA}$ ) produce the visible extinction and polarization and small bare particles ( $a \sim 100 \text{ \AA}$ ) produce the ultraviolet extinction (Greenberg and Hong, 1974). In this model graphite and silicate particles are formed in stellar atmospheres. The larger ones ( $a \sim 500 \text{ \AA}$ ) accrete a molecular mantle in the interstellar medium. The smaller ones remain bare because of temperature fluctuations (Greenberg and Hong, 1974). In order to explain the absence of the 3250 cm<sup>-1</sup> ice absorption in the tenuous interstellar medium it is assumed that the mantle molecules are photoprocessed into complex molecules which do not show strong absorption in this wavelength region (Greenberg, 1972, 1982). An alternative model for the dust has been proposed in which the grains in the tenuous interstellar medium consist mainly of bare graphite and silicate material (Mathis et al., 1977; Mathis, 1979). Inside dense clouds these grains may temporarily accrete a "dirty ice" mantle. However it is expected that upon returning to the diffuse interstellar medium these mantles are rapidly destroyed due to photodesorption and sputtering in shocks (Barlow, 1978; Draine and Salpeter, 1979).

Previous studies of interstellar chemistry were mainly interested in explaining the observed gas phase molecular abundances. In this article we calculate the composition of interstellar grain mantles under different interstellar conditions as determined by gas phase and surface chemistry. The results will be compared with interstellar infrared observations. This forms part of an ongoing program of the Laboratory Astrophysics group in Leiden to investigate the physical and chemical properties of grain mantles employing laboratory analogs as well as theoretical studies.

The paper is organized as follows. In Sect. 2 the method for the calculation of the chemical composition of grain mantles (gas phase equilibrium and grain surface reactions) is described. In Sect. 3 the results of the calculations are presented. The molecular composition of interstellar grain mantles under different interstellar conditions is discussed in Sect. 4. In Sect. 5 the infrared characteristics of the calculated grain mantles are examined and compared to the observed infrared spectrum of the BN object. Finally in Sect. 6 the main conclusions of our study are summarized. A discussion of laboratory data relevant to surface chemistry is given in Tielens and Hagen (1982, Paper I).

## 2. Method

The infrared observations with which our model calculations of growing mantles are going to be compared are made towards compact objects, such as BN, deeply embedded in giant molecular clouds. The visual extinction towards BN is estimated to be about 50 mag (Gillett et al., 1975; Bedijn et al., 1978; Beckwith et al., 1979). The total visual extinction of the Orion giant molecular

cloud is about 200 mag (Thaddeus et al., 1971). As will be discussed in Sect. 2B(fii) photodesorption of grain mantle molecules is faster than accretion for  $A_v$  less than about 3 mag. For larger visual extinctions a grain mantle will grow. The total density of hydrogen nuclei,  $n_0$ , in giant molecular clouds ranges from about  $10^2 \text{ cm}^{-3}$  to about  $10^6 \text{ cm}^{-3}$ . Observations show that the relative abundance ( $n_i/n_0$ ) of certain molecules, e.g. CO and H<sub>2</sub>CO, is much lower at high densities ( $n_0 > 10^3 \text{ cm}^{-3}$ ) than at intermediate densities ( $n_0 \sim 10^3 \text{ cm}^{-3}$ ). It has been suggested that this is due to the formation of grain mantles in dense regions (Woolten et al., 1980). The accretion rate is proportional to the density. Consequently denser regions in a molecular cloud are expected to have a larger degree of depletion. In our calculations we have limited ourselves to  $A_v > 5 \text{ mag}$  and  $10^3 \text{ cm}^{-3} < n_0 < 10^5 \text{ cm}^{-3}$ . No specific cloud model, relating  $A_v$ , density and depletion in different regions of the cloud is employed. Instead these parameters are varied independently.

The grain temperature is a crucial parameter in modeling grain surface chemistry. Infrared spectra of compact objects deeply embedded inside dense molecular clouds are dominated by the emission of hot (500 K) grains close to these objects. These hot grains form however only a minority of all the grains in a molecular cloud. Theoretical calculations show that most grains ( $\sim 97\%$ ) are at temperatures below 40 K (Leung, 1976). The minimum temperature of an "ice" grain inside a dense molecular cloud, far from possible embedded luminous sources ranges from 6 to 10 K depending on the assumed optical properties (Greenberg, 1971; Leung, 1975). In our model we have adopted a grain temperature of 10 K. The consequences of this assumption will be discussed in Sect. 4.

The chemical composition of the growing grain mantle is the result of a complex interplay of both gas phase and surface reactions. Both types of processes are of importance for the molecular composition of the gas. On the one hand it has been shown that molecular hydrogen is formed on grain surfaces (Hollenbach and Salpeter, 1970, 1971). On the other hand measurements of the deuterated species HD, DCO<sup>+</sup>, and N<sub>2</sub>D<sup>+</sup> suggest that these species, their protonated counterparts and their progenitors are produced by gas phase reactions (Watson, 1973, 1977). For other molecules both gas phase and surface reaction schemes have been proposed (Watson and Salpeter, 1972a, b; Herbst and Klemperer, 1973; Mitchell et al., 1978; Black and Dalgarno, 1976; Prasad and Huntress, 1980; Allen and Robinson, 1977). Because of the large number of free parameters and the uncertainty in the reaction rates involved it is difficult to estimate the importance of the different processes. However at intermediate densities the observed abundances of most of the simple gas phase molecules can be reproduced well by gas phase chemistry without grain processes other than the surface recombination of hydrogen (Black and Dalgarno, 1977; Mitchell et al., 1978; Prasad and Huntress, 1980). It will be shown that the simple species determine the outcome of the grain surface chemistry, because they are most abundant. We will therefore calculate the composition of the gas employing gas phase reactions only (except for H<sub>2</sub> formation). In this way the gas phase and surface reactions are separated. In order to explain the drop in the relative abundance of CO and H<sub>2</sub>CO in the gas phase at high densities depletion on grain surfaces has been invoked (Woolten et al., 1980; de Jong et al., 1980). In effect the abundance of these molecules depends then mainly on the degree of depletion assumed. This progressive depletion of the interstellar gas is incorporated in the calculation by reducing the heavy element abundance used in the determination of the gas phase equilibrium. The composition of the

growing grain mantle is then calculated from relative accretion rates using diffusion controlled surface reactions.

#### A. Gas Phase Chemistry

The gas phase reaction network is adopted from the compilation of Prasad and Huntress (1980). This reaction scheme is based in principle on the ion-molecule scheme of Herbst and Klemperer (1973). We have made minor modifications, mainly by updating reactions with new rate measurements. In total we have 1520 reactions involving 139 species. Only a quarter of these reactions have been studied in the laboratory. The rates and products of the remaining reactions are estimated by analogy with reactions involving chemically similar species. A detailed discussion of the gas phase chemistry is given in Prasad and Huntress (1980).

Because of the large number of reactions and species included in our scheme we have chosen to perform a time-independent calculation of the molecular abundances in dense interstellar clouds. An equilibrium solution is possible since for all the molecules at least one formation and one destruction reaction is included in the network. The assumption of chemical equilibrium is justified for the following reason. The observations with which the model calculations will be compared are made towards compact objects deeply embedded in giant molecular clouds. We expect the chemistry in these clouds to be equilibrated. Time-dependent calculations of interstellar chemistry show that the time required to reach chemical equilibrium in a gas which originally contained only atoms is about  $10^6$  yr at a hydrogen density of  $10^3$  cm<sup>-3</sup> (Langer, 1976; Liszt, 1978). The presence of OB associations in the neighbourhood of giant molecular clouds suggests a dynamical evolution time scale of the cloud of about  $10^7$  yr (Elmegreen and Lada, 1977). This is only a lower limit to the chemical age since giant molecular clouds are most likely formed from smaller, chemically equilibrated, molecular clouds (e.g. see Woodward, 1978 and references therein). The depletion and the density variations occurring during the evolution of a cloud over its  $10^7$  yr lifetime are slow compared to the gas phase reactions which maintain the chemical equilibrium.

The function  $f_i(n)$  gives the change in concentration of a species  $i$  per unit time in terms of the rate constants of its formation and destruction reactions and the set of concentrations,  $\{n_i\}$ , of the species involved in the reactions. At equilibrium  $f_i(n) = 0$  for all species  $i$ , or in vector notation  $\tilde{f}(\tilde{n}) = 0$ , where the vector  $\tilde{n}$  contains the concentrations of all species. The total set of these equations of course dependent. However we also have the charge balance equation and for each chemical element an abundance equation. The complete set of equations can always be reduced to an independent system. This set of non-linear equations is solved iteratively using a Newton-Raphson method. Given an initial trial value for the set of abundances of all species,  $\tilde{n}^{(0)}$ , which do not completely fulfil the set of equations  $\tilde{f}(\tilde{n}) = 0$ , we can calculate an improved estimate,  $\tilde{n}^{(i+1)}$ , by solving the set of equations

$$\tilde{n}^{(i+1)} = \tilde{n}^{(i)} - \frac{\partial \tilde{f}^{-1}}{\partial \tilde{n}} \tilde{f}(\tilde{n}^{(i)}), \quad (1)$$

where  $\frac{\partial \tilde{f}}{\partial \tilde{n}}$  is the Jacobian of the system which is calculated using the current estimate,  $\tilde{n}^{(i)}$ , of the abundances. This procedure is repeated until the desired accuracy is achieved. The system converges rapidly to the equilibrium solution. Typically about 6 iterations are needed to obtain a solution which has a relative accuracy of  $10^{-4}$ . This takes about 1.5 min on our Amdbahl V7B

computer. Most of the numerical effort goes into filling and inverting the  $139 \times 139$  Jacobian matrix. The numerical scheme has been tested by comparing the results with those of Hertel (1976). The two calculations agree within the given accuracy. Free parameters in our calculations are the total hydrogen density,  $n_0 = n_{\text{H}} + 2n_{\text{H}_2}$ ; the relative abundances of the elements  $A_i$ ; the gas kinetic temperature,  $T_0$ ; the cosmic ray ionization parameter,  $\zeta_0$ ; and the available UV flux. 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. Surface Chemistry

##### (i) Surface Binding and Mobility

Our aim is to calculate the chemical composition of a grain mainly as it grows under various conditions in dense clouds. For this it is important to know the evaporation time scales, sticking coefficients and surface mobility of species colliding with a grain. These factors will be discussed for H, H<sub>2</sub>, He, O, C, N and bigger species.

When species in the gas collide with a grain they can be bound to the grain with a strength ranging from the strong chemisorption, ( $\sim 10$  kcal mol<sup>-1</sup>), to the much weaker physical adsorption ( $\sim 2$  kcal mol<sup>-1</sup>). However the stronger chemical binding sites are quickly covered by a few layers of molecules and this will reduce the binding energy quickly to that of the much weaker physical adsorption (Watson and Salpeter, 1972a).

The binding energy of an H<sub>2</sub> molecule to a grain surface is quite uncertain. It has been measured to be about 860 K and 350 K on a H<sub>2</sub>O and CO surface respectively (Lee, 1972). Theoretical evaluation of the binding energy of an H<sub>2</sub> molecule on a perfect H<sub>2</sub>O surface yields about 600 K (Hollenbach and Salpeter, 1970; Govers et al., 1980). Fortunately the precise value of the binding energy of one H<sub>2</sub> molecule to a clean grain surface is not important for the calculations below, because the binding energy of H<sub>2</sub> molecules will decrease with increasing H<sub>2</sub> coverage of the grain surface (Lee, 1972; Govers et al., 1980). As a result H<sub>2</sub> will accrete on a grain surface until the binding energy becomes sufficiently low that thermal evaporation balances accretion. In this way an interstellar grain will be partly covered by an H<sub>2</sub> layer. The surface coverage and the binding energy of H<sub>2</sub> molecules on a grain surface can be determined from the balance of H<sub>2</sub> accretion and evaporation (Govers et al., 1980). The accretion rate is given by

$$R_{\text{acc}} = n(\text{H}_2) \bar{v} \sigma_g \bar{v}, \quad (2)$$

where  $n(\text{H}_2)$  and  $\bar{v}$  are the density and mean velocity of H<sub>2</sub> molecules,  $\sigma_g$  is the grain cross section and a sticking coefficient of unity has been assumed. The thermal evaporation rate is

$$R_{\text{ev}} = N(\text{H}_2) \nu_0 \exp[-E_b/kT], \quad (3)$$

where  $E_b$  and  $N(\text{H}_2)$  are the binding energy and the number of H<sub>2</sub> molecules on the surface,  $T$  is the grain temperature and  $\nu_0$  a characteristic vibration frequency ( $\sim 10^{13}$  s<sup>-1</sup>). Assuming  $n(\text{H}_2) = 10^4$  cm<sup>-3</sup>,  $\sigma_g = 3 \cdot 10^{-10}$  cm<sup>2</sup> and  $\bar{v} = 3 \cdot 10^4$  cm/s (corresponding to a kinetic gas temperature of 10 K) we find  $R_{\text{acc}}(\text{H}_2) = 10^{-1}$  s. Molecular hydrogen will condense on the grain until the binding energy becomes sufficiently low for the thermal evaporation rate to balance the accretion rate. From the experimental results on the binding energy of H<sub>2</sub> as a function of coverage we can estimate that this occurs for a binding energy of about 450 K and a surface coverage of about 20% (Govers et al., 1980; Schutte et al., 1976).



Because of its smaller mass and polarizability the binding energy of an H atom on the surface is lower than for H<sub>2</sub>. Typically  $E_b$  is about 350 K for H. The thermal evaporation timescale for H atoms is then about 2·10<sup>2</sup> s. This is much smaller than the time between H atom-grain collisions in a molecular cloud (10<sup>5</sup> s). This implies that H-atoms can never directly recombine with each other on such a surface. H<sub>2</sub> molecules are however still formed on grain surfaces. As will be shown in Sect. 2B (ii) a hydrogen atom can abstract a hydrogen atom from molecules like H<sub>2</sub>CO, H<sub>2</sub>S, and N<sub>2</sub>H<sub>2</sub> present on the grain surface and form a H<sub>2</sub> molecule.

Because of its low polarizability the binding energy of He atoms on an interstellar grain surface will be low, typically in the range 100–200 K. Its thermal evaporation timescale is therefore less than its accretion timescale. Since it is chemically inactive we have ignored it. For heavier atom and molecules the H<sub>2</sub> layer will not be rigid enough to prevent accretion. In effect these molecules will be bound to the surface underneath the H<sub>2</sub> layer. It is possible to estimate the binding energy of other molecules from their polarizabilities using the measured binding energy of H<sub>2</sub> and H<sub>2</sub>O. For the atoms C, N, and O the binding energy will be about 800 K while for larger molecules, like O<sub>2</sub>, it is about 1500 K (Watson and Salpeter, 1972a). For H<sub>2</sub>O the binding energy is much higher. This is partly due to its strong dipole moment and partly to its ability to form hydrogen bonds. The binding energy of a H<sub>2</sub>O molecule on an ice surface has been calculated to be about 4000 K (Hale et al., 1981).

Theoretical calculations indicate that upon collision between a neutral gas molecule and a grain at 10 K the translational excess energy can be transferred quickly to the molecules in the grain (Hollenbach and Salpeter, 1970). Even for an hydrogen atom colliding with an inert surface the sticking coefficient at 10 K is about unity (Watson, 1976). For heavier species, the larger mass and binding energy improve the likelihood of sticking. We will therefore assume that the sticking coefficient for all neutrals is unity. Grains in dense interstellar clouds will be negatively charged during most of their lifetime due to the larger velocity of electrons as compared to positive ions (Spitzer, 1968). This complicates the sticking for ions considerably because of effects of charge recombination at or near the surface. Consequently the ion sticking coefficient may range from very small to near unity (Watson and Salpeter, 1972a). Another complicating factor is the coulomb interaction. It has been suggested that an excess electron in a grain might be mobile. The coulomb interaction will then enhance the collision cross section by a factor of 10 (Watson and Salpeter, 1972a). In our calculations we will assume that the collision rate of ions is equal to the neutral collision rate. This assumption is of some importance for the gas phase and grain mantle composition. The low abundance of ions in dense interstellar clouds assures a low accretion rate. However the gas phase molecular equilibrium depends strongly on the degree of ionization, which primarily involves the metals. If metal ions accrete and recombine at a high rate on interstellar grain surfaces then the molecular composition of the gas phase may be considerably affected (Umebayashi and Nakano, 1980). However in view of the rather uncertain nature of this process we have ignored it.

The mobility of adsorbed species on the surface depends on the surface structure. The surface potential will vary more or less periodically due to the discrete positions of the mantle molecules. For a particle adsorbed in a potential minimum (site) to move to a neighbouring minimum an energy barrier of about half the binding energy has to be surmounted. The quantum mechanical tunneling time through a rectangular barrier with height  $E$  and

width  $a$  is given by

$$\tau_{\text{tun}} = v_0^{-1} \exp \left[ \frac{2a}{\hbar} (2mE)^{1/2} \right], \quad (4)$$

where  $v_0$  is the characteristic vibration frequency and  $m$  the mass of the tunneling particle (Messiah, 1972). For physically adsorbed H on H<sub>2</sub>O this timescale is  $\tau_{\text{tun}} \simeq 2 \cdot 10^{-10}$  where we have used  $E = 350$  K,  $v_0 = 10^{13} \text{ s}^{-1}$ , and  $a = 1 \text{ \AA}$ .

This estimate depends strongly on the rather unknown lattice size parameter  $a$ . Accurate theoretical studies of quantum mechanical tunneling employing delocalized wavefunctions have been made for atomic and molecular hydrogen on a perfect H<sub>2</sub>O surface (Hollenbach and Salpeter, 1970). In this case the timescale to tunnel to an adjacent potential well is given by

$$\tau \sim 4\hbar/E, \quad (5)$$

where  $\Delta E$  is the width of the lowest energy band. For H and H<sub>2</sub> on an H<sub>2</sub>O surface this timescale has been estimated to be about 10<sup>-12</sup> s. On a perfect grain surface containing  $N$  sites the timescale to scan the whole surface is (Hollenbach and Salpeter, 1970)

$$\tau_s \simeq N^{1/2} \tau. \quad (6)$$

Assuming  $N = 10^6$  and using  $\tau$  from Eq. (5) we find  $\tau_s \simeq 10^{-9}$  s on a perfect H<sub>2</sub>O surface. The surface scanning time on a realistic grain surface will be much longer. It will however still be much smaller than the evaporation time scale of an H atom (2·10<sup>2</sup> s). Consequently an H atom can scan the grain surface many times before it evaporates.

Because the timescale for tunneling depends strongly on the mass of the tunneling particle, species heavier than H can only migrate as a result of thermal hopping. The timescale for this process is given by

$$\tau = v_0^{-1} \exp [E_d/kT]. \quad (7)$$

The barrier against diffusion,  $E_d$ , can be estimated from laboratory experiments employing matrix isolation techniques (Paper I). In this way the classical hopping time scale for atoms from the second period of the periodical system on a H<sub>2</sub>O surface at 10 K has been estimated to be 10<sup>-3</sup> s. For third period atoms this timescale is about 10 s. For molecules this timescale will be very long. The timescale to scan the whole surface is now given by (Paper I):

$$\tau_s = N\tau. \quad (8)$$

Comparing these timescales for scanning the whole surface with the collision timescale of radicals with a grain, about 10<sup>5</sup> s at a density of 10<sup>4</sup> cm<sup>-3</sup>, shows that only H, H<sub>2</sub>, C, N, and O can undergo appreciable migration on a grain surface within an accretion or evaporation timescale. The other species remain trapped in their site. We have therefore selected only reactions of species with the migrating species H, H<sub>2</sub>, C, N, and O. The diffusion of these species ends when they recombine with each other or with a species trapped in a site. We want to emphasize that the adopted grain temperature is crucial for this selection.

At grain temperatures below about 8 K only H atoms and H<sub>2</sub> molecules are expected to be able to scan an H<sub>2</sub>O grain surface. At temperatures above 30 K the hopping time of other species, e.g., H<sub>2</sub>O and NH<sub>3</sub> is also much shorter than the accretion timescale (Paper I).

## (ii) Reaction Network

We have adopted a subset of the surface chemistry reaction network of Allen and Robinson (1977). This reaction scheme contains only reactions with zero activation energy which occur between atoms, radicals and the  $O_2$  molecule. We have excluded reactions involving only nondiffusing species. Statistically insignificant reactions are omitted for simplicity. Reactions for sulphur bearing molecules are added which parallel the reactions of the corresponding oxygen bearing molecules. We have added a number of reactions of atomic oxygen with molecules containing an even number of electrons (non-radicals). These reactions are known to occur at 10 K in solid matrices (Table 1). Other reactions of the heavy atoms C, N, and O are excluded either because they have considerable activation energies or because they are statistically insignificant. Furthermore we have included a number of H addition and abstraction reactions (Table 2). These reactions are known to have considerable activation energies. However we now show that because of its low mass the H atom can tunnel through these barriers and these reactions can occur on interstellar grain surfaces.

Consider a reaction involving a H atom which, in order to react, must overcome an activation barrier,  $E_a$ , much larger than the diffusion barrier,  $E_d$ . The probability  $p$  of tunneling through the activation barrier is given by

$$p = \tau_{t_0} \exp \left[ -\frac{2a}{\hbar} (2mE_a)^{1/2} \right], \quad (9)$$

where the time  $\tau$  that the H-atom spends in a well which is associated with the coreactant is given by Eq. (5). If no radicals are present on the surface then the H-atom will migrate on the surface until it either evaporates or tunnels through an activation barrier and reacts. During one evaporation time the H-atom will enter each site  $n$  times,

$$n = \tau_{ev} / \tau_s, \quad (10)$$

where  $\tau_{ev}$  and  $\tau_s$  are the evaporation and surface scanning time respectively. The probability that a reaction occurs during the  $k^{\text{th}}$  time that a H atom enters the well is given by

$$\phi_k = (1-p)^{k-1} p. \quad (11)$$

And the probability that a reaction occurs within one evaporation timescale is

$$\phi = \sum_{k=1}^n \phi_k = 1 - (1-p)^n \approx np. \quad (12)$$

It should be noted that in this limit  $\phi$  is independent of  $\tau$  and thus independent of the rather uncertain value of the binding energy of H to a grain surface. If the number of coreactants on the surface is  $N_{cor}$  then the probability for a reaction is

$$\phi_{cor} = N_{cor} \phi. \quad (13)$$

Inserting  $\tau_{ev} = 2 \cdot 10^2$  s and  $N = 10^6$  we find  $n \sim 2 \cdot 10^{10}$  from Eqs. (6) and (10). If  $N_{cor} = 1$  then an H atom has a 50% chance of tunneling through an activation barrier of about 4000 K and reacting with that species. If  $N_{cor} = 10^4$  (e.g. 1% surface coverage) then a H atom has a 50% chance of tunneling through an activation barrier of 8000 K and reacting with that species. Consequently the reactions of H listed in Table 2 can be of importance on interstellar grain surfaces. This mechanism is not important for other migrating atoms because of their relatively long surface diffusion and tunneling timescale.

**Table 1.** Reactions with negligible activation energy of atomic oxygen with molecules, containing an even number of electrons, included in the calculations

Reactions	Ref.
$O + CO \rightarrow CO_2$	Fournier et al. (1979), Mohammed et al. (1980)
$O + O_2 \rightarrow O_3$	Paper I
$O + CS \rightarrow OCS$	Paper I
$O + SO \rightarrow SO_2$	Paper I

**Table 2.** Hydrogen addition and abstraction reactions included in the calculations

Reaction	Activation energy (K)	Ref.
$H + CO \rightarrow HCO$	1000	Wang et al. (1973)
$H + H_2CO \rightarrow H_2 + HCO$	1850	Klemm (1979)
$H + O_2 \rightarrow HO_2$	1200	Melius et al. (1979)
$H + H_2O_2 \rightarrow H_2O + OH$	1400	Klemm et al. (1975)
$H + H_2S \rightarrow H_2 + SH$	860	Rommel et al. (1975)
$H + N_2H_4 \rightarrow H_2 + N_2H_3$	650	Francis et al. (1971)
$H + N_2H_2 \rightarrow H_2 + N_2H$	~ 650	Our estimate
$H + O_3 \rightarrow O_2 + OH$	450	Lee et al. (1978)

It has been suggested that reactions of radicals with molecular hydrogen are also of importance, in particular  $H_2 + O \rightarrow H_2O$  (Watson and Salpeter, 1972b). It is expected that this type of reaction has a considerable activation barrier since a molecular bond has to be broken for these reactions to proceed. However because of the large number of  $H_2$  molecules on the surface these reactions may still be of importance. The same kind of analysis applies as discussed above for atomic hydrogen. The limiting timescale for a reaction of a radical with  $H_2$  is now the accretion time of an other radical. For an  $H_2$  surface coverage of 20% and an accretion time of  $10^5$  s reactions with an activation barrier less than about 4500 K can occur. Theoretical calculations of the potential energy surface for the reaction of O plus  $H_2$  give an activation energy of  $\sim 15,000$  K and this reaction can therefore safely be disregarded (Tully, 1980). We consider that the reaction  $H_2 + OH \rightarrow H_2O + H$

is of statistical importance. It has an activation barrier of 2600 K (Schiff, 1973). We have taken this reaction into account.

UV photolysis of grain mantles is expected to change their molecular composition and infrared characteristics. We can estimate the importance of this process in the following way. Assuming no internal UV sources the photolysis rate is given by

$$R_{ph} = \sigma_g \epsilon G_0 f(\tau_{UV}), \quad (14)$$

where  $\epsilon$  is the number of photolysed molecules per incident UV photon and  $f(\tau_{UV})$  is the attenuation factor of the radiation field,  $G_0$ , at a UV optical depth  $\tau_{UV}$ . For our comparison with infrared spectra of interstellar grain mantles we are interested in the efficiency of the photolysis of a grain mantle which consists mainly of  $H_2O$ . We can determine the efficiency of this process from the laboratory experiments on  $H_2O/CO$  mixtures (Hagen, 1982).

Scaling these experiments to the astrophysical situation, e.g. a conversion of 10% H<sub>2</sub>O during the lifetime of a cloud (10<sup>7</sup> yr), yields the following condition on the radiation field

$$f(\tau_{UV}) > 8 \cdot 10^{-4}, \quad (15)$$

where we have assumed  $G_0 = 10^8 \text{ cm}^2 \text{ s}^{-1}$  (Habing, 1968).

The UV intensity inside a molecular cloud depends strongly on the scattering properties of the interstellar dust. The radiation penetrates deeper into the cloud for increasing albedo,  $\omega$ , or mean cosine of the scattering angle,  $g$  (Whitworth, 1975; Sandell and Mattila, 1975; Flannery et al., 1980). Assuming  $\omega = 0.6$  and  $g = 0.7$  (Lillie and Witt, 1976) we find from the accurate radiative transfer calculations of Flannery et al. (1980) that for a visual extinction less than about 7 mag, UV photolysis is important. Due to the presence of young hot stars the UV intensity incident upon a molecular cloud may be much larger than the intensity derived by Habing (1968) for the mean interstellar medium. An O6 star at a distance of 0.5 pc from the cloud surface would increase the limiting magnitude for UV photolysis by about 4 mag. In our calculation we have ignored UV photolysis of grain mantles entirely. Systematic studies of UV photolysis of grain mantles are obviously required and are now underway at the Leiden Astrophysics laboratory. The present calculations are meant to provide a basis for these studies.

### (iii) Molecular Desorption

In the calculation it is assumed that molecules formed on interstellar grain surfaces remain on the grain, except for H<sub>2</sub>. We will now examine six possible mechanisms for the release of molecules from grain mantles into the gas in the absence of heat sources and shocks. It is difficult to estimate the importance of these processes. However since the observed abundances of most of the simple gas phase molecules can be reproduced well by gas phase reactions we have chosen to ignore the influence of the grain processes on the gas phase composition. An exception is made for H<sub>2</sub>, which requires consideration of surface reactions (Hollenbach and Salpeter, 1971).

(1) If a large fraction of the formation energy of newly formed molecules flows into center-of-mass translational motion then a considerable fraction of the newly formed molecules can be ejected into the gas phase. Theoretical calculations of H<sub>2</sub> recombination indicate that this process is important (Hollenbach and Salpeter, 1970; Watson and Salpeter, 1972a; Hunter and Watson, 1978). However, these calculations may have underestimated the transfer of energy to the grain surface. Elsewhere (Paper I) we have argued, on the basis of a critical evaluation of recent matrix isolation studies on energy transfer in low temperature solids (Legay, 1978; Bondybej and Bruns, 1980), that evaporation of newly formed molecules is unlikely. Most of the formation energy will be transferred to neighbouring molecules through multipolar-multipolar interaction, will flow into local rotational modes or will be radiated away. Since only a small amount of energy goes to local center-of-mass translational motion, only a small fraction of all newly formed molecules will evaporate (Paper I).

(2) A fraction of the formation energy will be converted into heat. The resulting temperature rise depends on the size of the grain. If this temperature rise is large enough then this will cause evaporation of all weakly adsorbed species (Allen and Robinson, 1975, 1977; Purcell, 1976). The grain size for which this process becomes important, depends on the amount of energy transferred to the delocalized lattice phonons of the grain, which is unknown.

If all of the formation energy is converted into heat then the limiting grain size is about 50 Å. Grains smaller than this size will not accrete an appreciable grain mantle in molecular clouds. Molecule formation on the surfaces of these grains will therefore contribute to the gas phase composition.

(3) Molecular desorption from small grains can also be caused by the absorption of an UV photon. As in the previously discussed desorption mechanism the resulting temperature rise will cause ejection of all weakly adsorbed species for grains less than about 50 Å in radius (Greenberg and Hong, 1974). This process is not included in the calculations.

(4) Perhaps the most important desorption mechanism for large grains is photodesorption at the edge of the cloud (Watson and Salpeter, 1972a). An important constraint for mantle formation on these grains is therefore that the accretion rate should be larger than the photodesorption rate. The accretion rate is given by

$$R_{ac} = \sigma_g n_i v_i, \quad (16)$$

where  $\sigma_g$  is the cross section of the grain,  $v_i$  and  $n_i$  are the mean velocity and number density of accretable species. The photodesorption rate is given by

$$R_{pd} = \sigma_g Y_{pd} G_0 f(\tau_{UV}), \quad (17)$$

where  $Y_{pd}$  is the photodesorption yield and  $f(\tau_{UV})$  is the attenuation factor of the radiation field at a UV optical depth,  $\tau_{UV}$ . The condition of mantle growth can then be rewritten as

$$f(\tau_{UV}) = n_i v_i / (Y_{pd} G_0). \quad (18)$$

There is considerable debate in the literature on the expected photodesorption yield of molecules physically adsorbed on interstellar grain surfaces (Watson and Salpeter, 1972a; Greenberg, 1973; Barlow, 1978; Drane and Salpeter, 1979). Only a limited amount of experimental data on this subject exists. Greenberg (1973) measured photodesorption yields in the wavelength region 2000 to 2750 Å for a number of molecules physically adsorbed on a quartz window at 77 K. The measured yields lie in the range  $10^{-5}$ – $10^{-7}$ . Unfortunately none of the studied molecules exhibits strong absorption bands in this wavelength region. The high yield of CS<sub>2</sub> ( $10^{-5}$ ) implies that  $\eta$ , the number of desorption per absorption of a photon, is about unity (Greenberg, 1973). For C<sub>6</sub>H<sub>6</sub>, however  $\eta$  is estimated to be only  $3 \cdot 10^{-3}$  (Drane and Salpeter, 1979). Of course the efficiency is expected to be smaller for larger molecules because more internal energy channels are available and it binds to more than one site.

On the basis of these  $\eta$ 's it has been argued that in spectral regions of high absorptivity the photodesorption yield,  $Y_{pd}$  is  $10^{-2}$  (Greenberg, 1973),  $5 \cdot 10^{-3}$  (Barlow, 1978) and  $10^{-5}$  (Drane and Salpeter, 1979). In order to estimate the importance of this process we will adopt  $Y_{pd} = 5 \cdot 10^{-4}$  in the subsequent discussion, corresponding to  $\eta \sim 0.1$ . The above mentioned uncertainty should however be kept in mind. More laboratory data on this subject are highly desirable.

With  $n_i \simeq 10^{-3} n_0$ ,  $v_i \simeq 10^4 \text{ cm/s}$ , and  $G_0 = 10^8 \text{ cm}^2 \text{ s}^{-1}$ , derived from Habing (1968), we find that desorption dominates when

$$f(\tau_{UV}) > 2 \cdot 10^{-4} n_0. \quad (19)$$

Adopting an albedo of 0.6 and a mean cosine of the scattering angle of 0.7 (Lillie and Witt, 1976) for the wavelength region of interest (1000 Å–2000 Å) we find from the accurate radiative transfer calculations for spherical clouds of Flannery et al. (1980)



that at a density,  $n_0$  of  $10^3 \text{ cm}^{-3}$ , the visual extinction corresponding to Eq. (19) is 3 mag. It seems therefore reasonable to assume that for clouds with a total visual extinction of about 6 mag or less mantle growth is inhibited by photodesorption. Thus in diffuse clouds and small dark clouds mantle growth does not occur. In the neighborhood of hot young stars this limiting magnitude will be higher. In this article we will concentrate on mantle growth in regions with  $A_V > 5$  mag.

(5) Photo-chemical processes occurring in the bulk of the grainmantle can lead to rapid evaporation or explosion of the mantle (Greenberg and Yencha, 1973; Greenberg, 1982). The photolysis produces stored radicals. Upon raising the temperature some of these radicals may recombine. The release of the stored chemical energy may lead to rapid evaporation or explosion of parts of the grain. Experiments at the Leiden Astrophysics laboratory (photolysis of mixtures of CO, CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O in various ratios) indicate that this process will occur for radical concentrations as low as a few per mille (d'Hendecourt, 1982), provided that sufficient external triggering takes place (grain-grain collisions form a possible candidate). The ejected material will contribute to the gas phase composition. In these experiments some high molecular mass material remains on the grain. The infrared spectrum of this material shows that most of the sample is evaporated (van de Bult, 1982; see also Greenberg, 1982).

(6) Transient heating by cosmic rays can cause ejection of molecules from grain mantles. A grain is heated by the passage of a cosmic ray and thermal evaporation of surface particles is possible (Watson and Salpeter, 1972a). For a cosmic ray ionization flux  $\xi_0 \sim 10^{-17} \text{ s}^{-1}$  the rate at which molecules bound with an energy of 1000 K to a H<sub>2</sub>O surface can evaporate is estimated to be

$$R_g \approx 10^{-8} \text{ s}^{-1},$$

where a grain size of 1000 Å is assumed (Watson and Salpeter, 1972a). We can compare this rate with the accretion rate [Eq. (16)]. These two rates balance at a molecular density of  $10^{-3} \text{ cm}^{-3}$ . For the bulk composition of the gas phase this process is of no importance and we have neglected it accordingly. However for less abundant molecules which are not easily made by gas phase reactions but readily made on grain surfaces this process and the other listed above may be the dominant source of these molecules in the gas phase (Tielens, 1982).

#### (iv) Numerical Model

We model the chemical evolution of a surface comprising  $N$  sites as follows. One by one species from the gas land on this surface. They are randomly chosen with a change  $P_i$  corresponding to their relative accretion rate

$$P_i = n_i v_i / \left( \sum_j n_j v_j \right), \quad (20)$$

where  $n_i$  and  $v_i$  are the gas phase abundance and mean velocity of species  $i$ . The size of the grain does not enter into this expression since it only determines the absolute timescale of the mantle growth. In total we consider 403 surface reactions between migrating atoms and molecules. The total set of coreactants and reaction products contains 421 different species.

In principle (1) an atom, (2) a radical or (3) a molecule can be chosen from the gas phase. In the first case one of all available surface coreactants which can react without activation energy with the moving atom is chosen randomly with a probability corresponding to its concentration on the surface. Except for

atomic H, if no coreactant is available, the moving atom will remain on the surface until it is selected for reaction. Atomic hydrogen may of course react by tunneling. A reaction is chosen randomly with a chance  $Q_i$  given by

$$Q_i = \phi_{\text{tot}, i} / \sum_j \phi_{\text{tot}, j},$$

where  $\phi_{\text{tot}, i}$  is defined by Eq. (13). If no reaction of this type is possible within the evaporation timescale of H then H will evaporate. In the second case (radical accretion) the radical will react with a moving atom if such an atom is already present on the surface. If no moving atom is available then the impinging radical is trapped at a site where it remains available for reactions with the next migrating atom that lands. The product of a reaction will also remain trapped in the site. In certain circumstances the accretion rate of nondiffusing radicals is larger than the accretion rate of atoms capable of migration. In that case the nondiffusing radicals will remain fixed on the surface until other reactive species attach themselves in sites which contain the original radical. In this way reactions between nondiffusing radicals might also take place. However since this process is only of importance for molecules such as CO and O<sub>2</sub> which do not react with other abundant nondiffusing species we will neglect it. The third case that of a molecule striking the grain surface will result in it being trapped in a site.

The numerical program is based upon a Monte Carlo method. Given the gas phase abundances we calculate the accretion probabilities for each species [Eq. (20)]. A random number generator selects the accreting species and its reaction according to the procedure outlined above. This process is repeated until the desired accuracy is reached. Typically about one million collisions are followed. This takes about 3.5 min on our Amdahl V7B computer. The only input parameters for the surface chemistry calculations are the densities of the gas phase molecules.

### 3. Results

Following the entire procedure outlined above the composition of grain mantles was calculated as they accrete inside dense interstellar clouds using the following free parameters: the total density of hydrogen nuclei,  $n_0$ , the gas temperature,  $T_0$ , the cosmic ray ionization rate,  $\xi_0$ , the radiation field incident on the cloud,  $G_0$ , the visual extinction,  $A_V$ , and the abundances of the elements. All these parameters are necessary to calculate the chemical equilibrium in the gas phase. No additional free parameters are necessary for the surface chemistry calculations. For all of the calculations the cosmic ray ionization rate was fixed on  $10^{-17}$ , the value determined from a detailed analysis of the diffuse cloud  $\zeta$ Oph (Black and Dalgarno, 1976). CO observations of giant molecular clouds have shown that the kinetic temperature is generally 10K, except near regions of recent star formation. We have chosen the gas temperature equal to this value. For the ambient interstellar UV radiation field we have used the values  $G_0 = 10^8 \text{ cm}^{-2} \text{ s}^{-1}$  (deduced from Habing, 1968).

The abundances of the elements are an important parameter in model calculations of interstellar chemistry. In particular the C, N, and O abundances turn out to be crucial for the composition of grain mantles. Unfortunately there is little information on the elemental composition of the interstellar medium. Absorption line studies of diffuse interstellar clouds show that the heavy elements are generally depleted compared to their solar value (Morton, 1974). The depletion pattern changes considerably from region to

**Table 3.** Abundances of the elements relative to hydrogen

Elements	Cosmic	<i>o</i> Per	$\zeta$ Per	$\zeta$ Oph
He	0.1	0.1	0.1	0.1
C	$3.98 \cdot 10^{-4}$	$3.98 \cdot 10^{-4b}$	$2.88 \cdot 10^{-4}$	$1.58 \cdot 10^{-4a}$
N	$1.00 \cdot 10^{-4}$	$3.16 \cdot 10^{-6}$	$5.82 \cdot 10^{-4}$	$6.31 \cdot 10^{-5c}$
O	$6.31 \cdot 10^{-4}$	$5.25 \cdot 10^{-4d}$	$6.31 \cdot 10^{-4d}$	$5.01 \cdot 10^{-4d}$
Na	$2.00 \cdot 10^{-6}$	$2.79 \cdot 10^{-7}$	$8.33 \cdot 10^{-7}$	$2.51 \cdot 10^{-7}$
Mg	$3.16 \cdot 10^{-5}$	$2.32 \cdot 10^{-6}$	$2.88 \cdot 10^{-6}$	$1.00 \cdot 10^{-6}$
Si	$3.16 \cdot 10^{-5}$	$3.35 \cdot 10^{-7}$	$3.43 \cdot 10^{-5}$	$7.94 \cdot 10^{-7}$
S	$1.58 \cdot 10^{-5}$	$1.20 \cdot 10^{-6}$	$1.69 \cdot 10^{-5}$	$7.94 \cdot 10^{-6}$
Fe	$2.51 \cdot 10^{-5}$	$1.36 \cdot 10^{-7}$	$1.58 \cdot 10^{-7}$	$2.51 \cdot 10^{-7}$

If not noted differently: data for  $\zeta$  Oph from Morton (1974), *o* Per from Snow (1976), and  $\zeta$  Per from Snow (1977)

<sup>a</sup> Carbon data from Jenkins and Shaya (1979)

<sup>b</sup> Highly uncertain, Cosmic abundance value adopted

<sup>c</sup> Nitrogen data from Lugger et al. (1978)

<sup>d</sup> Oxygen data from de Boer (1981)

**Table 4.** Composition of the gas phase and grain mantle for  $n_0=10^4 \text{ cm}^{-3}$ ,  $A_0=10 \text{ mag}$ , and  $\delta=1$ . Abundances of the elements are taken from Table 3

Molecule	Cosmic	<i>o</i> Per	$\zeta$ Per	$\zeta$ Oph
Gas phase densities ( $\text{cm}^{-3}$ )				
H	1.41	1.43	1.45	1.48
N	$4.4 \cdot 10^{-1}$	$2.8 \cdot 10^{-2}$	$4.7 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$
O	2.36	1.83	$9.7 \cdot 10^{-1}$	$7.7 \cdot 10^{-1}$
N <sub>2</sub>	$2.8 \cdot 10^{-1}$	$2.0 \cdot 10^{-3}$	$2.6 \cdot 10^{-1}$	$2.8 \cdot 10^{-1}$
O <sub>2</sub>	$6.4 \cdot 10^{-3}$	$4.3 \cdot 10^{-3}$	1.03	1.24
CO	3.55	3.40	2.67	1.51
H <sub>2</sub> O	$1.2 \cdot 10^{-1}$	$1.2 \cdot 10^{-1}$	$1.5 \cdot 10^{-1}$	$1.2 \cdot 10^{-1}$
Mantle composition (mol %) <sup>a</sup>				
N <sub>2</sub>	5.56	$3.7 \cdot 10^{-2}$	4.8	5.4
O <sub>2</sub>	$7.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-3}$	3.2	$7.4 \cdot 10^{-1}$
CO	2.73	$1.3 \cdot 10^{-1}$	2.6	$2.5 \cdot 10^{-1}$
H <sub>2</sub> O	3.90	1.4	30.4	58.4
CO <sub>2</sub>	54.0	62.3	10.5	5.2
H <sub>2</sub> CO	7.3	26.0	33.8	24.7
NH <sub>3</sub>	4.7	$5.0 \cdot 10^{-1}$	$6.0 \cdot 10^{-1}$	$7.0 \cdot 10^{-1}$
CH <sub>4</sub>	1.6	2.3	$3.2 \cdot 10^{-2}$	$4.0 \cdot 10^{-3}$
H <sub>2</sub> O <sub>2</sub>	$4.0 \cdot 10^{-2}$	$4.0 \cdot 10^{-3}$	5.7	2.0

<sup>a</sup> Note that the columns do not add up to 100% due to the presence of many other molecules with a low concentration

region. Typically, Si, Mg, and Fe are depleted by a factor 0.1 to 0.01. They are believed to be locked up in highly refractory grains, like silicates (Field, 1974). A recent analysis of the oxygen abundance reveals that oxygen is only slightly depleted in diffuse interstellar clouds (de Boer, 1979, 1981). The carbon and nitrogen abundances are far more uncertain (Lugger et al., 1978; Jenkins and Shaya, 1979). For most of our calculations we have adopted the values for  $\zeta$  Oph listed in Table 3. We take these values to be representative for those interstellar regions where accretion of grain mantles just begins. Some calculations have also been performed for abundances along the line of sight towards other stars (see Table 3).

Recent observations of dense molecular clouds show that their abundances differ markedly from the abundances in the more

diffuse interstellar clouds (Wooten et al., 1980; Snell, 1980). At higher density the abundances of CO, H<sub>2</sub>CO, and HCO<sup>+</sup> drop considerably. This has been interpreted to be the result of the formation of mantles on grains in dense interstellar clouds (Wooten et al., 1980). We follow de Jong et al. (1980) in mimicking this ongoing depletion by reducing the relative abundances with respect to H of all elements, except He, by the same factor,  $\delta$ . Although species are depleted differently because of difference in mass and, possibly, sticking coefficient we felt that such a refined analysis is beyond the scope of our model.

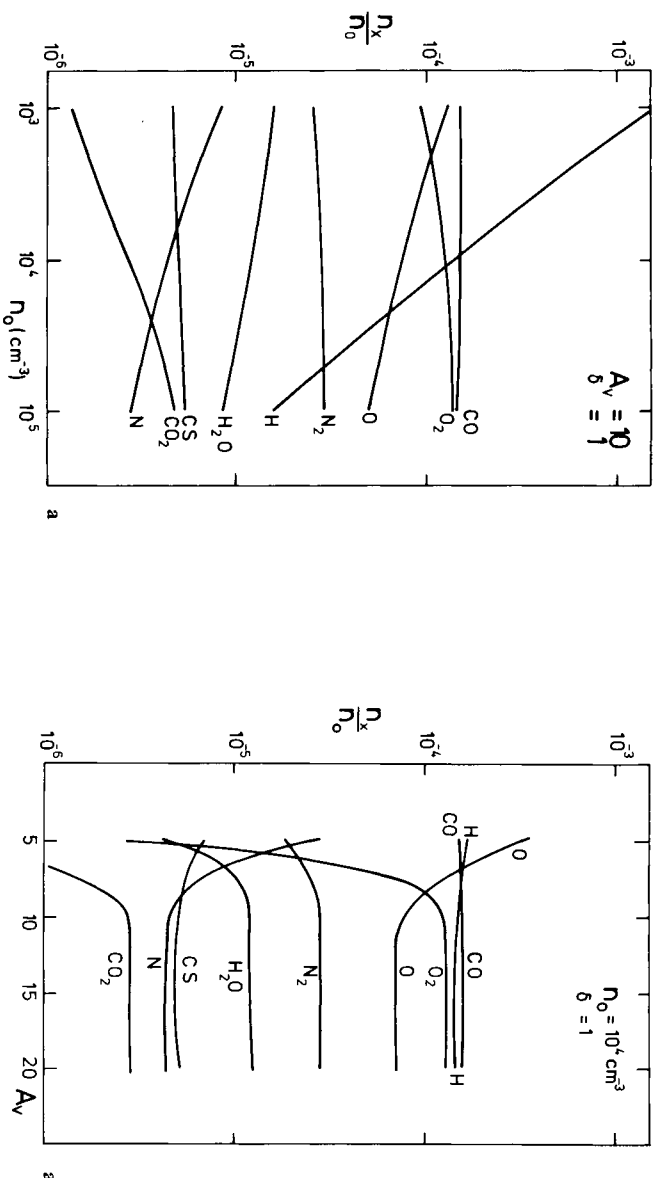
The results of the calculations for the gas phase molecular abundances and the composition of the growing grain mantle as a function of  $n_0$ ,  $A_0$ , and  $\delta$  are given in Figs. 1a and b, 2a and b, and 3a and b. The molecular composition of the gas and of the grain mantles in region with elemental abundances as specified in Table 3 are compared in Table 4.

#### 4. Molecular Composition of Grain Mantles

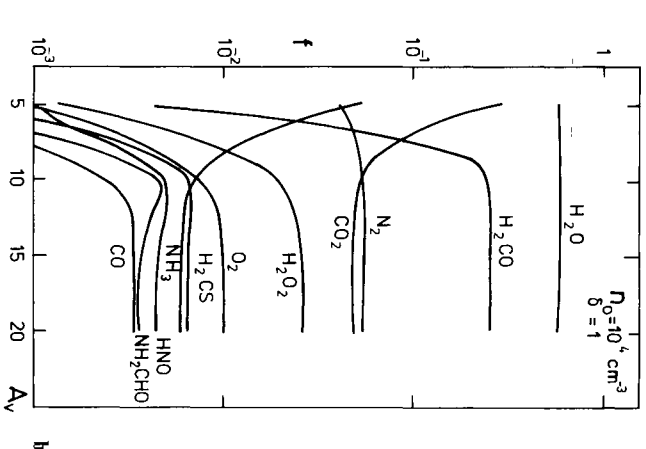
The bulk composition of the grain mantle is determined by the most abundant accreting species. Equilibrium calculations of the gas phase chemistry show that almost all of the carbon in the gas phase is in the form of CO. Nitrogen and the oxygen which is not in CO are either in atomic or molecular (N<sub>2</sub>, O<sub>2</sub>) form depending on the physical conditions (Figs. 1a, 2a, and 3a). Other species are only present as trace constituents of the gas comprising at most a few percent of the total abundance of heavy atoms or molecules. This is in accordance with earlier work on the molecular composition of the gas (Mitchell et al., 1978; Prasad and Huntress, 1980). The ratio of atomic to molecular oxygen is of some importance for the composition of the mantle. The major gas phase reactions involved are summarized in Fig. 4. At high visual extinction atomic oxygen is efficiently converted to molecular oxygen through OH formation and destruction. The O to O<sub>2</sub> ratio is a sensitive function of the metal abundance. In the calculation employing cosmic or *o* Per abundances most of the oxygen is in atomic form (Table 4). This is the result of a decrease in the OH abundance and an increase in the C abundance (cf. Fig. 4). Due to the high metal abundance in the calculation the electron abundance increases and the H<sub>3</sub><sup>+</sup> abundance decreases. Consequently the OH abundance drops. The C abundance increases because of the charge exchange reactions between C<sup>+</sup> and Mg or S. At low visual extinction the O/O<sub>2</sub> equilibrium shifts towards O because of photodissociation of O<sub>2</sub> and OH. With the dust parameters chosen this occurs around 7.5 mag (see Fig. 2a).

In most circumstances the accreting grain mantle consists mainly of H<sub>2</sub>O, H<sub>2</sub>CO, N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, NH<sub>3</sub>, O<sub>2</sub>, and CO in varying concentration. The most important surface reactions for carbon, nitrogen and oxygen bearing molecules are summarized schematically in Figs. 5–7. Carbon accretes mainly in the form of CO. Reactions with O and H atoms form CO<sub>2</sub> and HCO respectively (Fig. 5). The formyl radical can react with H and form formaldehyde. Hydrogen abstraction gives the formyl radical back again. The HCO is lost through reactions with N or O, which results in formamide or formic acid production. The concentration of the latter will be low because of the competitive reactions of O with CO and O<sub>2</sub> which are more abundant on grains than HCO. At high densities  $n_0 \geq 10^5 \text{ cm}^{-3}$ , not enough H and O atoms are present in the gas phase to react with all of the available CO. Consequently high concentrations of CO in the grain mantle should be possible.





**Fig. 1a and b.** The molecular composition of interstellar clouds with  $\zeta$  Oph elemental abundances as a function of density ( $n_0$ ): **a** gas phase ( $n_x/n_0$ ), **b** grain mantle (mole fraction,  $f$ )



**Fig. 2a and b.** The molecular composition of interstellar clouds with  $\zeta$  Oph elemental abundances as a function of visual extinction ( $A_V$ ): **a** gas phase ( $n_x/n_0$ ), **b** grain mantle ( $f$ )

The nitrogen surface chemistry is comparatively simple (Fig. 6). In most circumstances nitrogen in the gas phase is mainly in molecular form ( $\text{N}_2$ ). The accreted  $\text{N}_2$  is chemically inert. Atomic nitrogen is present in large amounts in the gas phase at low visual extinction. It is rapidly saturated by atomic hydrogen to  $\text{NH}_3$ . At low visual extinction atomic oxygen is also abundant in the gas phase. Relatively high concentrations of  $\text{HNO}$  can therefore be expected. Reactions of  $\text{N}$ ,  $\text{NH}$ , and  $\text{NH}_2$  with atomic nitrogen will ultimately result in  $\text{N}_2$ ,  $\text{N}_2\text{H}_2$ , and  $\text{N}_2\text{H}_4$ . Hydrogen abstraction from the last two molecules is possible through tunneling if no

radicals are available on the surface. These molecules act as enhanced binding sites, which results in  $\text{H}_2$  formation through repeated hydrogen addition and abstraction reactions. As discussed before the reactions of  $\text{N}$  with  $\text{HCO}$  ultimately yields formamide.

At low visual extinction oxygen will accrete in atomic form (Fig. 2a). It can react with  $\text{H}$  to form  $\text{OH}$  and with  $\text{O}$  to form  $\text{O}_2$ . However since the thermal evaporation timescale of  $\text{H}$  is much less than the accretion timescale of  $\text{O}$  and since coreactants for  $\text{O}$  are always present these reactions are of no importance. Instead it

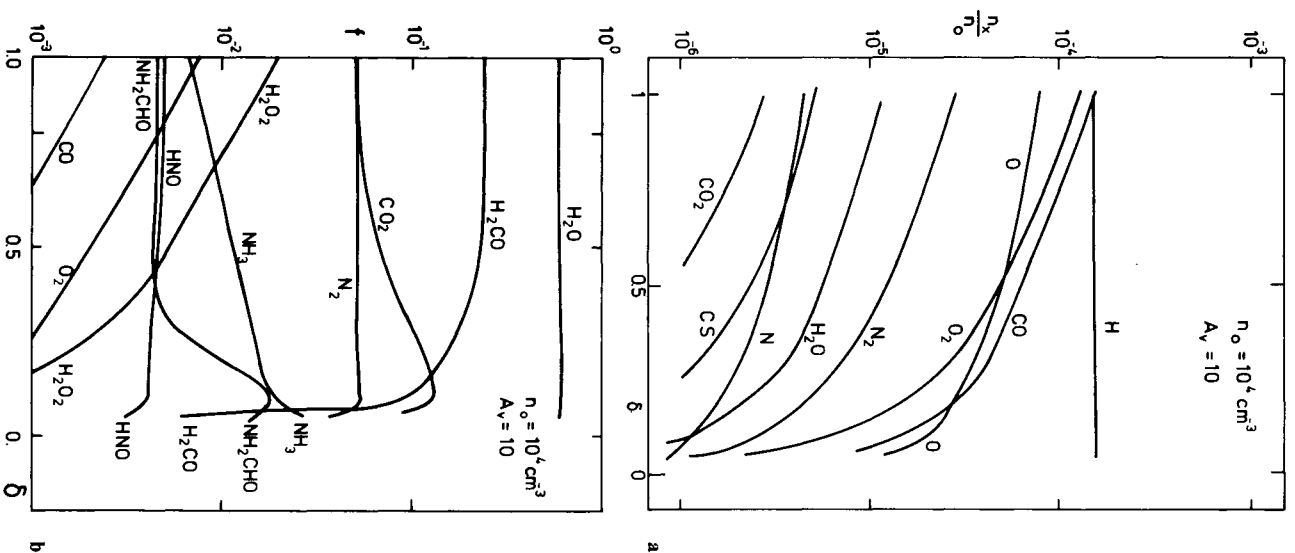


Fig. 3a and b. The molecular composition of interstellar clouds as a function of the depletion parameter ( $\delta$ ).  $\delta = 1$  corresponds to  $\zeta$  Oph abundances in the gas phase,  $\delta = 0$  corresponds to all heavy elements accreted on grain mantles: a gas phase ( $n_x/n_0$ ), b grain mantle ( $f$ )

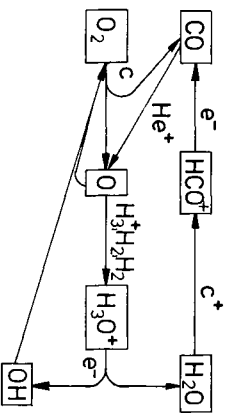


Fig. 4. Schematic representation of the most important gas phase reactions involved in the oxygen chemistry

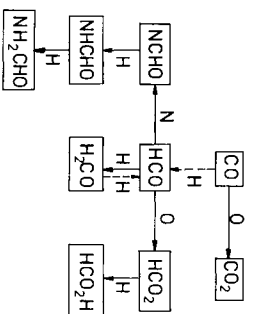


Fig. 5. Schematic representation of the most important grain surface reactions involved in the carbon chemistry. Dashed arrows indicate reactions with activation barriers of H atoms with molecules (see Table 2)

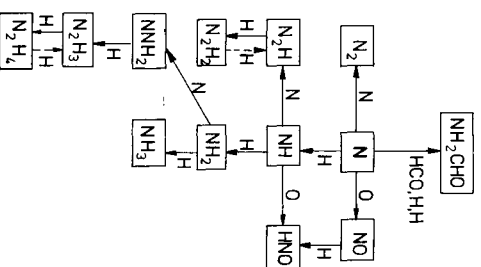


Fig. 6. Schematic representation of the most important grain surface reactions involved in the nitrogen chemistry. Dashed arrows indicate reactions with activation barriers of H atoms and molecules (see Table 2)

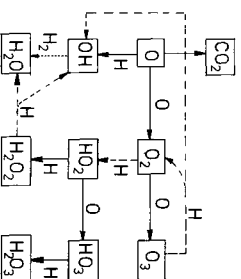


Fig. 7. Schematic representation of the most important grain surface reactions involved in the oxygen chemistry. Dashed arrows indicate reactions with activation barriers of H atoms and molecules (see Table 2). Dotted arrow indicates the reaction  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$

is likely that O reacts with CO and O<sub>2</sub> to form CO<sub>2</sub> and O<sub>3</sub> (Fig. 7). In effect O<sub>2</sub> plays a “catalytic” role in H<sub>2</sub>O formation.

$$\begin{aligned} \text{O}_2 + \text{O} &\rightarrow \text{O}_3 \\ \text{O}_3 + \text{H} &\rightarrow \text{O}_2 + \text{OH} \\ \text{OH} + \text{H}_2 &\rightarrow \text{H}_2\text{O} + \text{H} \\ \text{O} + \text{H}_2 &\rightarrow \text{H}_2\text{O} \end{aligned}$$

In principle the OH in the last step could also react with a migrating atom. However the low barrier for the reaction of OH with  $H_2$  assures that OH is rapidly converted into  $H_2O$  by  $H_2$  present on the grain [see Sect. 2B(ii)]. The net result of these reactions is that the high activation barrier of the reaction  $O + H_2$  to form  $H_2O$  and the low probability of  $O + H + H$  are circumvented.

Molecular oxygen is lost through reactions with H forming  $HO_2$ . In combination with O or H this yields the peroxides  $H_2O_3$  and  $H_2O_2$ . The latter is converted with H to  $H_2O$ . It is clear that in most circumstances a large fraction of the oxygen in the mantle will be locked up in  $H_2O$ . Only at high densities  $n_0 > 10^5 \text{ cm}^{-3}$ , is the oxygen in the mantle in the form of  $O_2$ , due to the low abundance of atomic O and H in the gas phase (Fig. 1).

For ongoing depletion of gas phase molecules on grains (decreasing  $\delta$ ) the gas phase  $O/O_2$  ratio increases, essentially because of the decrease in the electron abundance (see Fig. 3a). The relative  $H_2O$  concentration in the grain mantle does however not change much since both atomic and molecular oxygen are efficiently converted to water when there is an overabundance of atomic H (see Fig. 7). Because of the relative decrease of CO compared to O in the gas phase less formaldehyde and more  $CO_2$  is made on the grain surface (see Fig. 3b). The relative increase in atomic nitrogen in the gas for decreasing  $\delta$  is reflected in the increase of the  $NH_3$  concentration in the grain.

Changing the relative abundances of the elements has a profound influence on the composition of the gas and therefore on the composition of the grain mantle (see Table 4). In particular the  $O_2/O$  ratio in the gas is of extreme importance. Using cosmic abundances or *o*Per abundances yields a very low  $O_2/O$  ratio in the gas. Consequently the  $CO_2$  concentration in the mantle is high while the  $H_2O$  and  $H_2CO$  concentrations are low.

The results of the calculations differ considerably from those of previous work. Since van de Hulst's (1949) classic study, the understanding of the physics and chemistry of the interstellar medium has improved drastically. At that time the interstellar gas was thought to be mostly in atomic form. Consequently saturation of C, N, and O with H was naturally thought to be the dominant process, leading to a mantle composition of mainly  $CH_4$ ,  $NH_3$ , and  $H_2O$  "ices". In our model calculations we incorporate the current knowledge of gas phase chemistry. This leads to considerable changes in the composition of the mantle.  $H_2O$  is, in many circumstances, still the most abundant molecule in the grain mantle, although it results from completely different chemical reactions. Carbon and nitrogen are mostly in the form of  $H_2CO$  or CO and  $N_2$ . As explained above this is due to a complex interplay of gas phase and surface reactions.

Previous studies of molecular hydrogen formation on grain surfaces have assumed that an accreted hydrogen atom remains long enough on the surface for a second hydrogen atom to land. These two hydrogen atoms meet and recombine (Hollenbach and Salpeter, 1970, 1971). As discussed in Sect. 2, when a large fraction of the hydrogen is in molecular form this model has a serious difficulty in that the binding energy of a H atom on an inert surface is less than that of a  $H_2$  molecule. As a consequence, the H atom will not remain long enough on such a surface for a second H atom to land. A somewhat similar problem has been discussed by Hollenbach and Salpeter (1971). They investigated the formation of molecular hydrogen on grain surfaces in a completely atomic hydrogen gas. Since no molecular hydrogen is present in the binding energy of an H atom to a grain surface is high (650 K; Govers et al., 1980). This yields an evaporation timescale of  $10^{15}$  s

at a grain temperature of 10 K. This should be compared to the H-atom grain collision time scale of  $10^5/n_{H_2}$  s. Obviously  $H_2$  formation on grain surfaces is ensured at 10 K. At higher temperatures ( $> 20$  K) however, the evaporation timescale of H atoms is shorter than the H atom grain collision time-scale. To circumvent this problem for molecular hydrogen formation special sites had to be invoked where the H atom is bonded stronger (Hollenbach and Salpeter, 1971). Our calculations show that molecules like  $HCO$ ,  $HS$ ,  $N_2H$ , and  $N_2H_3$  act as enhanced binding sites for H atoms. Atomic hydrogen addition to these molecules followed by hydrogen abstraction yields molecular hydrogen. The activation barrier associated with hydrogen abstraction from these molecules can easily be overcome at 10 K. The timescale for H abstraction from one  $H_2CO$  molecule on a grain surface is only  $10^{-2}$  s [cf. Sect. 2B(ii)]. This is much lower than the H atom evaporation timescale at 10 K or the H atom grain collision timescale in a completely atomic gas. Consequently even in the case envisaged by Hollenbach and Salpeter (1971)  $H_2$  formation on grain surfaces will proceed through H abstraction rather than direct recombination of two H atoms migrating on the grain surface.

At higher temperatures the evaporation timescale of H will be shorter. Consequently the maximum activation barrier which can be overcome at that temperature will be lower. However at 40 K the presence of 0.05%  $H_2CO$  on a grains surface will still ensure  $H_2$  formation. At higher temperatures one might expect that  $H_2$  formation by this process stops because the molecules involved evaporate at about 40–50 K. In general we expect however that even the so-called bare particles will have a few accreted layers of adsorbed molecules on which the bond strength decreases from chemical to physical adsorption. These molecules will not evaporate at these low temperatures because of their increased binding energy. Because only one of these molecules is needed on an interstellar grain surface for molecular hydrogen formation through H abstraction to occur we expect that  $H_2$  formation through H abstraction also takes place at high temperatures, on small grains and in diffuse clouds.

Other studies of surface chemistry have mainly been directed at explaining the observed gas phase molecular abundances by surface reactions alone (Watson and Salpeter, 1972b; Allen and Robinson, 1977; Viala et al., 1979). Our calculations show that gas phase reactions should be included in any model of grain chemistry because they set the scene for the diffusion controlled surface reactions.

We will now discuss the consequences of the adopted grain temperature. At grain temperatures below about 8 K C, N, and O atoms are trapped in the site where they originally landed (Paper I). Consequently reactions between these atoms and radicals or molecules are inhibited. The main difference with our calculations will be that the reaction



does not take place. Instead the oxygen atom will be converted to  $H_2O$  and the CO molecule to  $H_2CO$  resulting in somewhat higher abundances of these molecules than calculated by us.

At sufficiently high grain temperatures molecules will evaporate from the grain mantle. For a pure CO or  $O_2$  matrix the evaporation temperature is in the range 15–20 K (Nakagawa, 1980). Thus for grain temperatures larger than 20 K and  $n_0 > 10^5 \text{ cm}^{-3}$  grain mantles (which are predicted to be primarily composed of CO and  $O_2$ , cf. Fig. 16) are not expected to grow. In fact existing grain mantles with this composition will evaporate above this temperature.



For  $n_0 < 10^5 \text{ cm}^{-3}$  the grain mantle composition is predicted to be primarily  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}$ . The evaporation temperature of pure solid  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}$  is 45 and 90 K respectively. In a mixture of  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}$  the evaporation temperature of  $\text{H}_2\text{CO}$  will be higher due to hydrogen bonding between  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}$ . No information is available on the strength of this effect. At any rate grain mantles accreted at  $n_0 < 15^5 \text{ cm}^{-3}$  are not expected to evaporate appreciably until the grain temperature is raised well above 45 K. The  $\text{H}_2\text{O}$  ice itself will not evaporate until 90 K. It should be noted here that the grain temperature has a profound influence on the shape of the O-H stretching band in pure  $\text{H}_2\text{O}$  (as). The halfwidth of this band decreases by about 30% between 10 K and 80 K (Hagen et al., 1981). For mixtures of  $\text{H}_2\text{O}$  and other molecules this effect is less pronounced (Hagen et al., 1982).

For  $n_0 < 10^5 \text{ cm}^{-3}$  grain mantles may still grow for grain temperatures above 20 K, even if the gas phase consists mainly of CO and  $\text{O}_2$ . In the presence of large amounts of  $\text{H}_2\text{O}$  the binding energy of CO and  $\text{O}_2$  will be larger than in a pure CO or  $\text{O}_2$  matrix. These molecules may therefore remain long enough on a grain surface to be saturated by H atoms resulting in  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}$  molecules. We can derive a value for the grain temperature at which mantle growth stops by equating the evaporation rate of CO and  $\text{O}_2$  molecules to the accretion rate of H atoms. This yields

$$T_{\text{max}} = E_b / \ln [2\nu_0 N_{\text{mol}}^{-1}],$$

where  $E_b$  is the binding energy of the molecule,  $N_{\text{mol}}$  the number of CO or  $\text{O}_2$  molecules on the grain surface and  $\tau$  the H atom grain collision timescale. In deriving this formula we have implicitly assumed that all colliding H atoms will saturate CO or  $\text{O}_2$ . Inserting  $E_b = 1500 \text{ K}$ ,  $\nu_0 = 10^{12} \text{ s}^{-1}$ ,  $\tau = 10^5 \text{ s}$ , and  $N_{\text{mol}} = 10^4$  we find  $T_{\text{max}} = 30 \text{ K}$ . Thus even a grain mantle consisting mainly of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{CO}$  will not grow for grain temperatures above 30 K. Grain mantles accreted at grain temperatures between 20 and 30 K may have a composition quite different from our predictions. As noted in Sect. IIB the grain temperature is crucial in selecting the grain surface reaction network. For temperatures above about 20 K atoms from the third period of the periodical system (e.g., S) will be able to scan the grain surface within a radical-grain collision time scale. Consequently reaction between these atoms and radicals should be taken into account above this temperature. This should however, not influence our results dramatically due to the low abundance of these atoms. More important at these grain temperatures are small radicals like OH and NH which might also be able to scan the grain surface. This will alter the grain mantle composition drastically, favoring the production of larger molecules over  $\text{H}_2\text{O}$  and  $\text{H}_2\text{CO}$ .

## 5. Infrared Characteristics of Molecular Grain Mantles

The existence of molecular grain mantles inside dense interstellar clouds is firmly established. Molecules in accretion mantles of interstellar grains will show a number of broad absorption bands (Allamandola et al., 1979). Spectrophotometric observations from 5000 to  $800 \text{ cm}^{-1}$  of many infrared sources associated with molecular cloud material reveal a number of absorption features. Apart from the  $1030 \text{ cm}^{-1}$  absorption band, which is associated with silicates, the strongest of these occurs around  $3250 \text{ cm}^{-1}$ . This feature has generally been identified with the stretching vibration of  $\text{H}_2\text{O}$  ice in grain mantles (Merrill et al., 1976). The depth of this band varies considerably from source to source. For sources with molecular cloud material along the line of sight the

$3250 \text{ cm}^{-1}$  optical depth varies from 0.3 to 1.6. The silicate to ice optical depth ratio varies also and is typically of the order of 0.2 (Merrill et al., 1976). The amount of ice in the more tenuous interstellar medium appears to be negligible (Gilllett et al., 1975; Merrill et al., 1976). However the presence of molecular cloud material along the line of sight is not a sufficient condition for the occurrence of the  $3250 \text{ cm}^{-1}$  absorption feature (Whitert and Blades, 1980).

Recently a number of other broad infrared absorption lines have been detected. These features have been identified with vibrational modes of specific characteristic groups of molecules in grain mantles (Putter et al., 1979; Solfer et al., 1979; Hagen et al., 1980). In this section we will discuss the infrared characteristics of the calculated grain mantles, compare them with existing infrared observations and suggest future observations.

### A. The 4000–2500 $\text{cm}^{-1}$ Region

The varying concentrations of  $\text{H}_2\text{O}$  in the grain mantles calculated above can give rise to the  $3250 \text{ cm}^{-1}$  "ice" band. Because of its ability to form strong hydrogen bonds, the spectrum of  $\text{H}_2\text{O}$  is highly dependent on concentration (Van Thiel et al., 1957; Hagen and Tielens, 1981).

First if the concentration of  $\text{H}_2\text{O}$  is less than a few percent, only isolated molecules (monomers) and dimeric hydrogen bonded aggregates are present in the matrix. The OH-stretching modes then occur around  $3700 \text{ cm}^{-1}$ . The absorption lines are narrow. For larger concentration ( $\sim 10\%$ ) broad absorption bands are present from  $3500$  to  $3000 \text{ cm}^{-1}$  due to the OH-stretch in polymeric groups. Finally for concentrations larger than about 30% the  $3250 \text{ cm}^{-1}$  absorption band characteristic of solid  $\text{H}_2\text{O}$  (as) appears. The width of this feature is comparable to the observed width of the interstellar feature (Léger et al., 1979; Hagen et al., 1981).

The calculations show that for a density of  $10^3$ – $10^4 \text{ cm}^{-3}$  and the  $\zeta$  Oph abundances the concentration of  $\text{H}_2\text{O}$  is about 60% and consequently a broad absorption band centered at  $3250 \text{ cm}^{-1}$  is expected (Fig. 1b). Using the measured strength of this band (Hagen et al., 1981) we derive a  $\text{H}_2\text{O}$  column density of about  $3 \cdot 10^{18} \text{ cm}^{-2}$  towards BN. The silicate column density inferred from the  $1030 \text{ cm}^{-1}$  feature is also  $3 \cdot 10^{18} \text{ cm}^{-2}$  (Gilllett et al., 1975). If we assume that all Si is in the form of silicate and use the cosmic abundances ratio of O to Si, then this implies that only 5% of all condensable oxygen along the line of sight towards BN is in the form of  $\text{H}_2\text{O}$  (as).

The observed  $3250 \text{ cm}^{-1}$  band in BN shows the low frequency wing characteristic of molecular cloud material. It extends to about  $2800 \text{ cm}^{-1}$  (Merrill et al., 1976). Extensive laboratory studies of mixtures of  $\text{H}_2\text{O}$  and other molecules give two possible explanations for this wing (Hagen et al., 1982).

(1) Hydrogen bonding between  $\text{H}_2\text{O}$  and a strong hydrogen accepting base weakens the OH-bond and consequently the absorption shifts to lower frequencies. Candidates for such a base are molecules containing NH and  $\text{NH}_2$  groups. A  $\text{NH}_3/\text{H}_2\text{O}$  ratio of about 0.2 is needed to explain the observed strength of the low frequency wing in the BN spectrum. The  $\text{NH}_3/\text{H}_2\text{O}$  ratio in the calculated grain mantles is generally 0.01. Only at the very edge of the cloud is a higher value attained ( $\sim 0.1$ ). The concentration of other molecules with a NH or  $\text{NH}_2$  group is generally also about 0.01. The low concentration of these molecules is a direct consequence of the gas phase chemistry (cf. Sect. 4).

In the spectrum of BN a small shoulder on the  $3250 \text{ cm}^{-1}$  feature at  $3360 \text{ cm}^{-1}$  is barely visible. In the spectra of other

sources (e.g. W51-IRS2) a second peak can clearly be discerned at this frequency. This shoulder has been attributed to the NH-stretching vibration (Hagen et al., 1980). A concentration of a few percent with respect to H<sub>2</sub>O of molecules with NH groups is needed to explain this feature in BN. This might be somewhat larger than the concentration in the calculated mixtures. However it seems that the observed low frequency wing on the 3250 cm<sup>-1</sup> band in BN is only partly due to complexing of H<sub>2</sub>O with molecules with NH groups. The stronger absorption at 3360 cm<sup>-1</sup> in the spectrum of W51-IRS2 is possible related to the presence of a strong UV source in the H II region. Grain mantles in this region might therefore be more like the calculated ones for  $A_v \approx 5$  mag and contain more NH<sub>3</sub>. The low frequency wing on the 3250 cm<sup>-1</sup> band in the spectrum of this source could therefore result mainly from hydrogen bond interaction between NH<sub>3</sub> and H<sub>2</sub>O. Unfortunately the steepness of the spectrum of W51-IRS2 in this spectral region precludes further analysis of the low frequency wing.

(2) The low frequency wing can also be due to absorption by other molecules. The low resolution presently available would smear out these features into a wing in the interstellar spectra. The only two molecules with an appreciable concentration in the calculated grain mantles which absorb in the frequency region of the low frequency wing are H<sub>2</sub>CO and H<sub>2</sub>O<sub>2</sub>. Comparison of the infrared characteristics of the calculated mixtures with the observations is hampered by the low frequency resolution of the observations and the lack of laboratory spectra of the relevant mixtures.

Formaldehyde has a symmetric and antisymmetric CH-stretching mode in this frequency region (2900–2800 cm<sup>-1</sup>). In the presence of H<sub>2</sub>O it is expected that these lines are broadened considerably and that a shoulder on the 3250 cm<sup>-1</sup> band will appear at 3220 cm<sup>-1</sup> (Hagen et al., 1982). If all of the absorption in the low frequency wing of BN is attributed to the CH-stretching modes of H<sub>2</sub>CO a column density of about 2.10<sup>18</sup> cm<sup>-2</sup> is inferred, using the gas phase data for the strength of these lines (Pugh and Rao, 1976). In view of the uncertainties associated with the effect of the solid state on gas phase cross sections the resulting column density is in reasonable agreement with the H<sub>2</sub>CO/H<sub>2</sub>O ratio in our calculated grain mantle ( $\sim 0.4$ ) and the column density of H<sub>2</sub>O derived above.

Hydrogen peroxide has an overtone of the bending vibration at 2840 cm<sup>-1</sup> which might contribute to the low frequency wing. No reliable estimate for the strength of this band in an amorphous H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture can be made (Hagen et al., 1982).

Summarizing this discussion we can say that grain mantles accreted at a density of 10<sup>3</sup>–10<sup>4</sup> cm<sup>-3</sup> will show a broad 3250 cm<sup>-1</sup> feature due to amorphous solid water H<sub>2</sub>O (as). The presence of other molecules, notably H<sub>2</sub>CO and NH<sub>3</sub>, will produce a low frequency wing on this feature. Moderate resolution interstellar spectra ( $\Delta\lambda/\lambda \sim 3 \cdot 10^{-4}$ ) and laboratory spectra of the relevant mixtures would be helpful in discriminating between the role played by complex formation and that of superposition of different absorption bands. Molecular observations have revealed a gradient in the H<sub>2</sub> density in the Orion molecular cloud. The density in an extended region surrounding BN and KL ranges from 10<sup>3</sup> to 10<sup>6</sup> cm<sup>-3</sup> (Goldsmith et al., 1980). In our model the 3250 cm<sup>-1</sup> “ice” band originates then from the low density region at the outer edge.

A mantle accreted at a density in excess of 10<sup>5</sup> cm<sup>-3</sup> will contain mainly CO and O<sub>2</sub> with some traces of H<sub>2</sub>O. A low concentration of H<sub>2</sub>O also occurs in those mantles accreted in

regions with cosmic abundances or *o*Per abundances. This H<sub>2</sub>O will show up as monomer and dimer lines around 3700 cm<sup>-1</sup>. The integrated strength of these lines ranges from 4% to 25% of the strength of the 3250 cm<sup>-1</sup> band of H<sub>2</sub>O (as) (Hagen et al., 1981, 1982). Unfortunately no interstellar spectra of this wavelength region are available because of atmospheric water vapor absorption. This implies however, that the strength of the observed 3250 cm<sup>-1</sup> “ice” band is not necessarily a good measure of the total amount of solid H<sub>2</sub>O let alone of other mantle material. The presence of high density gas towards Orion warrants a search for these absorption lines.

The 3250 cm<sup>-1</sup> “ice” band has not been observed in the tenuous interstellar medium (Gillert et al., 1975; Merrill et al., 1976). It is not expected that mantles grow on grains in these regions because of the high photodesorption yield [Barlow, 1978; Draine and Salpeter, 1979; see also Sect. 2B(ii)]. A mantle might be expected to be present as the result of an earlier denser epoch. Two explanations have been offered for the absence of the 3250 cm<sup>-1</sup> band.

(1) The timescale for the destruction of an H<sub>2</sub>O ice grain mantle by photodesorption and by sputtering in cloud-cloud collisions has been estimated to be in the range 5 · 10<sup>4</sup> to 5 · 10<sup>6</sup> yr (Barlow, 1978; Draine and Salpeter, 1979). This is short compared to dynamical timescales. A strong 3250 cm<sup>-1</sup> ice band is therefore not expected in the diffuse interstellar medium.

(2) It has been suggested that the grain mantles accreted inside dense molecular clouds are photoprocessed into less volatile material (Greenberg et al., 1972; Greenberg, 1982). The resulting material might not show strong molecular absorption bands and escape detection in the infrared. Whether this process can compete with grain mantle destruction mechanisms depends on the relative yields of the processes involved.

#### B. The 2500–1200 cm<sup>-1</sup> Region

Spectra of sources which show the 3250 cm<sup>-1</sup> absorption band generally also show two other solid state absorption bands, in addition to the strong silicate absorption (Willner et al., 1980). These bands occur at 1670 cm<sup>-1</sup> (6.0 μm) and 1475 cm<sup>-1</sup> (6.8 μm) and each has an integrated strength of only about 10% of the 3250 cm<sup>-1</sup> band. These bands have been attributed to bending or deformation modes of OH<sup>-</sup>, NH<sub>3</sub><sup>-</sup>, and CH-group respectively (Pueter et al., 1979; Soifer et al., 1979; Hagen et al., 1980).

The calculated grain mantles will show a band at about 1700 cm<sup>-1</sup> partly due to the bending mode in H<sub>2</sub>O (as) and partly due to the C=O stretch in H<sub>2</sub>CO. If we attribute about 75% of this absorption band in BN to H<sub>2</sub>O and 25% to H<sub>2</sub>CO then we arrive at column densities for these molecules in agreement with the calculated concentration at  $n_0 \approx 10^4$  cm<sup>-3</sup> and with our interpretation of the OH- and CH-stretching region discussed above.

The CH-deformation mode of H<sub>2</sub>CO at 1500 cm<sup>-1</sup> is expected to be too narrow and too weak to explain the 1475 cm<sup>-1</sup> band. A column density of 3 · 10<sup>19</sup> cm<sup>-2</sup> would be needed to explain the observed feature. This is much larger than the value inferred from the low frequency wing on the 3250 cm<sup>-1</sup> band and the 1670 cm<sup>-1</sup> band. Of the other molecules present in the calculated grain mantles only H<sub>2</sub>O<sub>2</sub> shows two absorption bands in the wavelength region. If it is hydrogen bonded to H<sub>2</sub>O the two OH bending modes will occur at 1455 and 1387 cm<sup>-1</sup> (Giguère and Harvey, 1959). No laboratory data on the strength of the features in these kind of mixtures is available. However since the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O ratio is about 0.03 and since the OH-bending mode is

much less intense than OH-stretching mode in  $\text{H}_2\text{O}_2$ , it seems doubtful that the calculated abundance of  $\text{H}_2\text{O}_2$  is sufficient to explain the observed strength of the  $1475\text{ cm}^{-1}$  relative to the  $3250\text{ cm}^{-1}$  band. The  $1475\text{ cm}^{-1}$  band has been identified with  $\text{CH}_2$  and  $\text{CH}_3$  deformation modes (Soifer et al., 1979; Hagen et al., 1980). Besides  $\text{H}_2\text{CO}$  no molecules with  $\text{CH}_2$  or  $\text{CH}_3$  groups are formed with a appreciable abundance in the calculations. This is due to the fact that all carbon in the gas phase is locked up in CO. In grain mantles this leads to  $\text{H}_2\text{CO}$ . The concentration of other  $\text{CH}_2$  or  $\text{CH}_3$  containing molecules, like  $\text{CH}_3\text{OH}$ , in grain mantles is limited to the amount directly accreted from the gas phase. This abundance in the grain mantle is however too small to explain the  $1475\text{ cm}^{-1}$  band. A larger concentration of  $\text{CH}_3\text{OH}$  might result from hydrogen addition to  $\text{H}_2\text{CO}$ . It has been suggested that this reaction occurs in laboratory experiments (Okabe, 1978). However it has not directly been measured. It is therefore not included in the calculations. Laboratory experiments of this reaction will be extremely valuable for our understanding of the composition of interstellar grain mantles.

The fundamental mode of CO in a solid is at  $2138.5\text{ cm}^{-1}$  ( $4.68\text{ }\mu\text{m}$ ) (Dubost, 1975). Its integrated strength is however only 5% (Pugh and Rao, 1976) of the  $3250\text{ cm}^{-1}$  band. A weak absorption line has been detected at this frequency towards some sources which show the  $3250\text{ cm}^{-1}$  "ice" band and it may be present in other spectra (Pueter et al., 1979). Unfortunately the published high resolution spectrum of BN do not extend to  $2138.5\text{ cm}^{-1}$  (Hall et al., 1978). This makes it impossible to determine the relative concentrations of CO in the gas phase and solid state. The total column density of carbon along the line of sight towards BN is about  $4 \cdot 10^{19}\text{ cm}^{-2}$  as inferred from the strength of the  $1030\text{ cm}^{-1}$  silicate feature. High spectral resolution observations around  $2160\text{ cm}^{-1}$  yield a column density of  $1.2 \cdot 10^{19}\text{ cm}^{-2}$  of CO gas at  $100\text{ K}$  (Hall et al., 1978). We estimate that the solid  $\text{H}_2\text{CO}$  column density is about  $2 \cdot 10^{18}\text{ cm}^{-2}$  (see above). Part of the missing carbon might be in the form of solid CO in grain mantles accreted at densities in excess of  $10^4\text{ cm}^{-3}$ . Such high densities are known to be present around BN (Goldsmith et al., 1980). From the gas phase absorption cross section we infer that the integrated strength of the solid CO line is about  $4 \cdot 10^2 f_{\text{CO}}\text{ cm}^{-1}$  where  $f_{\text{CO}}$  is the fraction of the carbon along the line of sight condensed in the form of CO.

The concentration of  $\text{CO}_2$  in the calculated grain mantles is relatively high. For mantles accreted in regions with cosmic abundances or *o* Per abundances  $\text{CO}_2$  is the dominant constituent (Table 4). The fundamental mode of  $\text{CO}_2$  is at  $2349\text{ cm}^{-1}$  ( $4.26\text{ }\mu\text{m}$ ) and has an integrated strength of about one half of the  $3250\text{ cm}^{-1}$  band of  $\text{H}_2\text{O}$  (as) (Pugh and Rao, 1976). If  $f_{\text{CO}_2}$  is the fraction of carbon along the line of sight towards BN condensed in the form of  $\text{CO}_2$  in grain mantles, then the integrated strength of the  $2349\text{ cm}^{-1}$  line is  $3.3 \cdot 10^3 f_{\text{CO}_2}\text{ cm}^{-1}$ . This line is relatively narrow in the solid phase and its strength per resolution element is expected to be therefore much larger than the  $3250\text{ cm}^{-1}$  band. However because of atmospheric absorption this band has not yet been observed. A search for this band could yield important information on the physical conditions in dense interstellar clouds.

The stretching vibration of molecular oxygen occurs around  $1600\text{ cm}^{-1}$ .  $\text{O}_2$  is a homonuclear diatomic and its vibrational mode is therefore normally infrared inactive. However due to perturbations by neighboring molecules it can become infrared active in the solid phase. No information on its strength is available, but it will be very weak.

### C. The $1250\text{--}800\text{ cm}^{-1}$ Region

Many molecules show absorption bands around  $1000\text{ cm}^{-1}$ . Observation of these bands is hindered by the presence of the strong  $1030\text{ cm}^{-1}$  ( $9.7\text{ }\mu\text{m}$ ) silicate absorption band. Often there is some structure present in the observed  $1030\text{ cm}^{-1}$  band. However identification of this structure with modes of specific molecules is not meaningful in view of the low spectral resolution and low signal to noise ratio of the data and the presence of complicated radiative transfer effects.

It has been suggested that the librational modes of  $\text{H}_2\text{O}$  should have been observed in interstellar spectra which show the  $3250\text{ cm}^{-1}$  "ice" feature. It has, however, not been observed despite large variations in the ice to silicate volume ratios (Capps et al., 1978; Aitkin, 1981). On the basis of laboratory spectra of hexagonal crystalline ice  $I_h$  at  $250\text{ K}$  the librational band was expected to occur at about  $850\text{ cm}^{-1}$ . At the low temperatures of interstellar grains ( $10\text{ K}$ ) pure  $\text{H}_2\text{O}$  will however condense in the form of unannealed amorphous solid water  $\text{H}_2\text{O}$  (as). The peak frequency of the librational band in  $\text{H}_2\text{O}$  (as) occurs at  $760\text{ cm}^{-1}$ , not  $850\text{ cm}^{-1}$  (Hagen and Tielens, 1982). Spectra of  $\text{H}_2\text{O}$  in solid mixtures with other molecules also show the librational band at frequencies below  $870\text{ cm}^{-1}$  (Hagen et al., 1982). Consequently detection of this band in the interstellar medium is hampered by atmospheric absorption. In addition, the librational band in  $\text{H}_2\text{O}$  (as) is also much broader and weaker than in  $\text{H}_2\text{O}$   $I_h$ . Taken together this may account for the general absence of this feature in interstellar spectra.

### 6. Conclusions

From the calculations of the chemical composition of grain mantles which accrete in dense molecular clouds we can draw the following conclusions.

1. Both gas phase and surface reactions are important in determining the composition of mantles accreted on interstellar grains.
2. Molecules like  $\text{HCO}$ ,  $\text{HS}$ ,  $\text{N}_2\text{H}$ , and  $\text{N}_2\text{H}_3$  act as enhanced binding sites for molecular hydrogen formation on interstellar grain surfaces.
3. The bulk composition of grain mantles consists of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{CO}$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{NH}_3$  in varying ratios, plus other trace constituents. The exact composition reflect the physical conditions in the gas phase.
4. The observed  $3250\text{ cm}^{-1}$  "ice" band can be explained by mantles accreted at a density of  $n_0 \sim 10^3\text{--}10^4\text{ cm}^{-3}$ . The low frequency wing on this feature is then mainly due to absorption by  $\text{H}_2\text{CO}$ . In some circumstances absorption of  $\text{H}_2\text{O}$  hydrogen bonded to  $\text{NH}_3$  may also contribute appreciably to this wing. Moderate resolution spectra of the  $3250\text{ cm}^{-1}$  band could discriminate between these two possibilities and yield further insight into cloud evolution.
5. The observed  $1670\text{ cm}^{-1}$  band is attributed to absorption by  $\text{H}_2\text{O}$  and  $\text{H}_2\text{CO}$ . The observed  $1475\text{ cm}^{-1}$  band is too strong to be due to absorption by  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}_2$ .
6. Many of the molecules present in the calculated grain mantles have concentrations too low or absorption strengths too small to make them detectable with present day techniques. However it is expected that when the signal to noise ratio and frequency resolution are improved even the weaker interstellar features should become measurable. These observations are expected to yield a wealth of information on the chemical history of the grains and the gas.



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