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ABSTRACT

Laboratory investigations of grain mantles are shown to have a direct application to observations of interstellar grains. The experiments have made it possible to show how infrared spectra may be used as a probe not only of the grains as they are but also as they have evolved both chemically and physically. Growth by accretion, ultraviolet photoprocessing, gradual heating, explosions and general effects of grains on interstellar chemistry provide a consistent basis for understanding evolution of grains in terms of interactions with the gas, and ultraviolet radiation in both diffuse and dense regions of space.

1. INTRODUCTION

A typical core-mantle interstellar grain follows a complex evolutionary path involving accretion of atoms and molecules from the gas, surface reactions, solid state photochemical reactions (photoprocessing) and gradual as well as explosive processes of evaporation and desorption. The use of laboratory methods to simulate some of the important physical conditions in space has played a critical role in explaining some of the key observations of dust as it appears in a wide variety of interstellar conditions.

In this paper it will not only be seen that specific experiments can be designed for particular observations but of rather greater importance it will be seen how these results can be encompassed within an integrated whole by putting these results within a suitable theoretical framework of grain evolution. We shall not discuss here the very small particles of the interstellar population.

In the next section I shall briefly summarize and compare the principal interstellar and laboratory parameters. The following sections will be devoted to the ice band, evidence for ultraviolet photochemical processing, radical diffusion in grains and explosions, and finally complex organic residues. The final section will take up time scales for the interstellar processes.

2. INTERSTELLAR AND LABORATORY PARAMETERS

The study of the processes of accretion and photoprocessing of grain mantles is made possible by the creation of laboratory conditions which simulate those relevant to the evolution of grains in interstellar space.

The key components are the low temperature the low pressure and the ultraviolet. The low temperature is achieved by means of a closed cycle helium cryostat within which one gets temperatures as low as 10 K on a "cold finger" which can variously be an aluminum block or a transparent window mounted on a metal ring. Various gases may be controllably allowed to enter the vacuum chamber of the cryostat (pressure down to \(10^{-8}\) torr) via a capillary tube. These gases condense as a clear frost on the cold finger which acts then like the core of the interstellar grains. On one port to the chamber is mounted a source of vacuum ultraviolet radiation which until now has almost exclusively been a microwave stimulated flow hydrogen lamp which has emission peaks at 1216 Å (Ly\(\alpha\)) and about 1600 Å. The normal flux of vacuum UV photons by these lamps is \(\sim 10^{15}\) cm\(^{-2}\) s\(^{-1}\). Through another port (or pair or ports) we may direct the beam of an infrared spectrometer which measures the infrared absorptions in the sample on the cold finger in the range 2.5 \(\mu\)m-25 \(\mu\)m (4000 cm\(^{-1}\) to 400 cm\(^{-1}\)). This is the "finger-print" region for identifying molecules by their stretching, bending and rocking modes of oscillation in a solid. Other measurements made are of pressure, chemiluminescence, mass spectra, and visible absorption. Further descriptive details of the equipment as it existed several years ago may be found elsewhere (Hagen et al. 1979).

A comparison between laboratory and interstellar conditions is seen in Table 1. The most important -- but necessary -- difference is in the time scales for photoprocessing. One hour in the laboratory is equivalent to one thousand years in the diffuse cloud medium and as much as or greater than ten thousand to ten million years in the depths of dense molecular clouds.

The basic mode of operation consists of deposition of mixtures of simple volatile molecules -CH\(_4\), CO, CO\(_2\), O\(_2\), N\(_2\), NH\(_3\), H\(_2\)O, H\(_2\)S-- and simultaneous irradiation as they freeze on the cold finger. Sometimes irradiation is continued after deposition is stopped. We simulate in this way the accretion and photoprocessing of grains in molecular clouds. The principal laboratory sequence and operations are:

1. Infrared absorption spectra of unirradiated pure samples and mixtures at 10\(^{6}\) K. Infrared studies also made of warmed and recooled samples.
2. Infrared spectra following irradiation to detect presence of radicals and new molecules.
3. Infrared spectra of irradiated material following warmup to detect disappearance of frozen radicals and formation of new molecules.
4. Visible absorption spectra of irradiation and warmed up samples.
5. Simultaneous measures of chemiluminescence (visible) and vapor pressure during warmup of irradiated samples.
Table 1. Comparison between laboratory and interstellar conditions

<table>
<thead>
<tr>
<th></th>
<th>Laboratory</th>
<th>Interstellar</th>
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<tbody>
<tr>
<td>Grain mantle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- initial composition</td>
<td>CO, H$_2$O, NH$_3$, CH$_4$.. All condensible species</td>
<td></td>
</tr>
<tr>
<td>- thickness</td>
<td>0.1 µm to 10 µm</td>
<td>~ 0.1 µm</td>
</tr>
<tr>
<td>- temperature</td>
<td>≥ 10 K</td>
<td>≥ 10 K</td>
</tr>
<tr>
<td>Gas: pressure of</td>
<td></td>
<td></td>
</tr>
<tr>
<td>condensable species</td>
<td>3 x 10$^{-8}$ mbar</td>
<td>3n[H] x 10$^{-20}$ mbar</td>
</tr>
<tr>
<td>Ultraviolet flux</td>
<td></td>
<td></td>
</tr>
<tr>
<td>λ &lt; 2000 Å</td>
<td>10$^{15}$ cm$^{-2}$ s$^{-1}$</td>
<td>10$^8$ cm$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>Time scales</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Diffuse clouds</td>
<td>1 hr.</td>
<td>10$^3$ yrs.</td>
</tr>
<tr>
<td>- Molecular clouds</td>
<td>1 hr.</td>
<td>~ 10$^4$ - 10$^7$ yrs.</td>
</tr>
</tbody>
</table>

6. Production of explosion in warmup period by rapid heating of sample on cold finger.
7. Infrared and mass spectrometric studies of complex non-volatile residues remaining after warmup to room temperature.
8. Visible absorption spectra of non-volatile residue.
9. Laser stimulated emission of molecules and radicals.

3. THE ICE BAND

The 3.07 µm OH stretch absorption by solid H$_2$O is by far the dominant infrared feature of interstellar grains outside of the 9.5 µm Si-O stretch of silicates. It is dominant for two reasons: (1) H$_2$O is indeed the most abundant molecule in grain mantles in molecular clouds, (2) Solid H$_2$O has a particularly strong absorption strength.

We have come a long way since the ice band in the BN source was compared with the then only existing data for solid H$_2$O. At that time the beautifully complete table of complex indices of refraction obtained
by Bertie et al (1969) for crystalline ice was applied to calculations of the spectral shape for spherical particles (actually it would have made little difference what shape). These spectra were clearly at variance with the observations.

The matching of the observations has now been accomplished by noting first that one must, in general, consider absorption by mixtures containing varying amounts of H$_2$O, second by noting that the temperature history of the material has significant effects and third that the particle shape may be as important in determining the band shape as the chemical composition and temperature.

Various aspects of the shape effect – elongated vs spherical particles – has been discussed in Greenberg (1972), Greenberg et al. (1983) and Van de Bult et al. (1985). In general, it appears that the measured absorption spectrum in the laboratory is much closer to the absorption spectrum calculated for cylinders than for spherical particles. Since there is every reason to believe that interstellar particles are elongated, as indicated by the interstellar polarization of starlight, this is taken to be a proper representation of reality.

Two examples of ice absorption observations (Whittet et al. 1983) are shown in Fig. 1 (Van de Bult et al. 1985). We note immediately that they are significantly different from each other and from crystalline ice both in shape and in peak position. Using the values of the indices of refraction for pure amorphous ice at 10 K also does not give a good match. However Elias 16 is well represented by a water rich mixture with no more than about 10% NH$_3$ as can be seen in Figure 2 so long as the ice

![Figure 1: Comparison of the observed spectra of HL Tau and Elias 16 normalized to the same optical depth and with straight lines connecting the points. Dashed curve is absorption by crystalline ice (Bertie et al., 1969).](image)
Figure 2: Comparison of absorptions by cylinders having unannealed mantles of H$_2$O:NH$_3$=3:1 (Mixt 2u) with observations of Elias 16. Cylinder compound core = silicate core plus organic refractory mantle; a$_{cc}$=0.12 μm. Ice outer mantle radius: a$_m$= 0.132 μm. Dashed curve is for H$_2$O:NH$_3$=9:1.

is both formed at low temperatures and kept at low temperature. This is characteristic of ice mantles which form in molecular clouds so that Elias 16 which is situated behind the cloud would appear to be sampling an average of molecular cloud grain mantles.

On the other hand the ice band of HL Tau is best given by an ice mixture which has undergone some warmup thus annealing it in a direction away from its more amorphous form (Fig. 3) but not quite to the crystalline phase which occurs at about 130 K. Since HL Tau is indeed suggested to be surrounded by a local cloud of dust which has been heated (Cohen, 1983), the fact that the annealed ice mixture is better than the unannealed one is quite reasonable.
Figure 3: Comparison of absorption by cylinders having annealed mantles of $\text{H}_2\text{O}:\text{NH}_3 = 3:1$ (Mixt 2a) with observations of HL Tau. Cylinder compound cores = silicate core + organic refractory mantle: $a_{\infty} = 0.12 \ \mu \text{m}$. Ice outer mantle radius: $a_m = 0.132 \ \mu \text{m}$. Dashed curve is for $\text{H}_2\text{O}:\text{NH}_3 = 9:1$.

4. ULTRAVIOLET PHOTOPROCESSING

Although the interstellar medium provides sufficient flux of high energy ultraviolet photons in molecular clouds to modify grain mantles, direct observational evidence for this has only appeared within the past few years. This evidence was contained within the infrared spectral region of 3-5 $\mu \text{m}$ of W33A - a source imbedded within a dust cloud of about 100 magnitudes. It had long been suspected that the absorption feature at about 4.61 $\mu \text{m}$ might be due to CO but it was a bit shifted from its normal position in solid mixtures. The answer to this question was provided by the higher resolution study of Lacy et al (1984) where it then could be seen that along with the CO feature there was an as yet unidentified new feature which, when included at lower resolution, produced a shift to shorter wavelengths. This turned out to be a problem which could be subjected to laboratory analysis. By irradiating a mixture of ices which initially contained CO and NH$_3$ one may observe the immediate appearance of a wing at 4.62 $\mu \text{m}$ (2170 cm$^{-1}$), which distorts the CO feature at 4.67 $\mu \text{m}$ (Fig. 4). It is clearly much smaller than the
Figure 4: Spectra of a water rich mixture (H$_2$O CO:NH$_3$:CH$_4$ = 6:2:1:1). a) unirradiated 10 K; b) photolyzed; c) photolyzed and warmed up to 95 K.
CO absorption, but since CO evaporates at rather low temperatures (in the pure state at about 20 K) all that is required is to warm the sample somewhat. When this is done, the 2170 cm\(^{-1}\) feature attributed to a cyanogen molecule (X=CN) remains constant while the CO decreases. It is not at all difficult to achieve in the laboratory a precise duplication of the W33 "CO feature" (see Fig. 5) and what we conclude is that here, in this molecular cloud, we have directly observed photolysis as well as heating of grain mantles.

The spectrum of W33A contains two additional features, one at 4.9 \(\mu\)m the other a weak one at 3.93 \(\mu\)m which, taken together, provide even further evidence for the photoprocessing of grain mantles. The weak absorption at 3.93 \(\mu\)m is attributed to \(\text{H}_2\text{S}\) so that we have added \(\text{H}_2\text{S}\) to our ice mixtures and gone through the same photoprocessing and annealing as before. The photoprocessing produces the 4.9 \(\mu\)m feature which we identify as carbonyl sulfide, COS. A bonus of these sulfur experiments has been the new insight into the relation between interstellar dust and comets as is discussed by Grim and Greenberg (1986).

Figure 5: Laboratory spectrum of a frozen mixture of simple molecules, including \(\text{H}_2\text{S}, \text{CO}\) and \(\text{NH}_2\), which has been subjected to UV-irradiation at 10 K and then warmed to 85 K. The spectrum of W33A is shown for comparison with its baseline flattened.
5. RADICAL DIFFUSION TIME SCALES IN SPACE

Chemiluminescence and thermoluminescence have been studied as a function of temperature in various ultraviolet irradiated mixtures (Van IJzendoorn, 1985). The trapping and release of radicals stored in the astrophysically relevant mixture $H_2O:CO:NH_3:CH_4 = 5:3:2:1$ has been modeled to provide an estimate of the lifetime of stored radicals in the mantles of interstellar grains over astronomically relevant times.

The warmup-recool cycles (Fig. 6) show that in a temperature interval $\Delta T$ only a small fraction of the radicals with a rather specific activation energy for diffusion, $E_a$, reacts. The intensity of the measured glow curve (Fig. 7) corresponds to the population of traps with activation energies $E_a/k = AT$ where the factor $A$ depends only weakly on the specific diffusion model and may be taken as $A = 20$. Measuring the relevant areas under the glow curve determines the fraction of radicals in several intervals $\Delta(E_a/k) = A\Delta T$ as given in Table 2.

Table 2. Fraction of radicals trapped in various temperature intervals (trap depths).

<table>
<thead>
<tr>
<th>Trap depths, $E_a/k$ (K)</th>
<th>Fraction of trapped radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 400</td>
<td>0.005</td>
</tr>
<tr>
<td>400-600</td>
<td>0.013</td>
</tr>
<tr>
<td>600-800</td>
<td>0.080</td>
</tr>
<tr>
<td>800-900</td>
<td>0.163</td>
</tr>
<tr>
<td>900-1000</td>
<td>0.492</td>
</tr>
<tr>
<td>1000-1100</td>
<td>0.166</td>
</tr>
<tr>
<td>&gt; 1100</td>
<td>0.071</td>
</tr>
</tbody>
</table>

Figure 6: Thermoluminescence glow curves from a photolyzed ice for several warmup-recool cycles. Note that rewarmup does not begin to show luminescence until approximately the temperature at which previous cycle was stopped.
Figure 7: Thermoluminescence glow curve for a previously photolyzed dirty ice mixture (H$_2$O:CO:NH$_3$:CH$_4$ = 5:3:2:1)

The question to be answered is whether chemical energy in the form of frozen free radicals can be stored over time scales ~ 10$^5$ years in molecular clouds (the mean time between grain collisions leading to explosions) without being annealed out.

The diffusion of radicals leading to their depletion occurs in several steps. The first step is the release of a radical from its trap. The next is diffusion through the matrix. If the fraction of radicals released by a small increase in temperature is small the probability of one diffusing radical meeting another diffusing radical is accordingly small. In this case a radical, once released, either reacts with one in a deeper trap or is itself retrapped without reacting. This latter means that the effective concentration of reactive species is reduced by some factor, $\Omega$.

The diffusion equation for bimolecular reactions derived by Smoluchowski (1917) is

$$-\frac{dX(t)}{dt} = -\frac{dY(t)}{dt} = 4\pi r_o (D_x + D_y) [1 + \frac{r_o}{(\pi(D_x + D_y)t)^{1/2}}] X(t) Y(t) \quad (1)$$

where $D_x$ and $D_y$ are the diffusion coefficients of species $X$ and $Y$; $r_o$ is the reaction distance; $t$ = time.

As discussed above, we may consider $X$ and $Y$ as basically the same species but in different trap depths. Let $Y$ be those which remain trapped while $X$ are those which diffuse. Thus $Y(t) = \text{const} = Y_0$ so that the bimolecular equation is approximated by the monomolecular equation.

$$-\frac{dX(t)}{dt} = 4\pi r_o \Omega Y_0 D [1 + \frac{r_o}{(\pi D t)^{1/2}}] X(t) \quad (2)$$
With an initial radical concentration of 1% or less the relative probability for combining or retrapping of the diffusing radical turns out to be \(-10^{-2}\) so that the factor \(\Omega\) in Eq.(2) is \(-10^{-2}\).

The diffusion coefficient is for \(T > 10\text{ K}\) very closely given by
\[
D = \lambda^2 \frac{kT}{n} \exp \left[-\frac{E_a}{kT}\right]
\]
where \(\lambda\) is the diffusion step distance (Glasstone et al. 1941). The depletion of radicals, \(X\), at a trap energy \(< E_a\) is then given (again approximately) by

\[
X(t) = X_0 e^{-4\pi r_o^2 \Omega Y_0 D t}
\]

where \(r_o = 4 \times 10^{-8}\text{ cm}\) \((r_o = \lambda\), \(Y_0, X_0\) is the number density of radicals trapped at all energies, \(-2 \times 10^{19}\text{ cm}^{-3}\). At \(T = 15\text{ K}\) the time for reduction of the radicals trapped at \(E_a/k < 800\text{ K}\) by a factor of \(e^{-1}\) thus leaving essentially all the remaining \(>90\%\) radicals at higher \(E_a/k\) still trapped is \(-10^6\) years.

This means that the radical concentration once achieved, remains constant — even without further irradiation — for times at least of the order of cloud lifetimes. Although grain–grain collisions which produce temperature increases less than those required for explosion are more frequent than once every \(10^5\) years the total elapsed time of elevated temperature per collision is only the order of seconds so that the integrated effect is entirely negligible.

6. EXPLOSIVE REACTIONS OF STORED RADICALS

At low temperatures, the reactions are controlled by diffusion. However if the temperature is suddenly increased, the rate of radical reactions generates heat faster than it can be conducted away, thus leading to further release of trapped radicals and a runaway explosive chain reaction. This mechanism for depletion for grain mantles appears to be adequate to maintain the gas phase species against depletion on the grains (d'Hendecourt et al., 1982; Greenberg, 1973).

Generally, explosions occur when irradiated ices are raised to temperatures \(>27\text{ K}\). With an initial 1% radical concentration this implies a sudden release of about \(10^{-4}\) molar concentration. The monomolecular diffusion Equation 2 no longer applies because we are in a totally non-linear regime. The released energy at each reaction site is \(-5\text{ eV}\) and is apparently sufficient to generate extra energy fast enough to trigger the chain reaction. In Figure 8 are shown the light flashes and pressure pulses indicating the explosive character. This is to be compared with the glow curve shown in Fig. 7. Color films of the flashes show that they are blue. This color is similar to the overall color of the light emitted in the formation of glyoxal out of two HCO radicals (Van IJzendoorn, 1985) although this is not a proof because no detailed spectra yet exist for the explosive reaction.
Figure 8: Light flashes (above) and simultaneous pressure pulses (below) produced as sample irradiated at 10 K is warmed up. The starting composition was CO:H$_2$O:NH$_3$:CH$_4$ = 10:1:1:4. The sample was deposited over 10 min and exposed to 2 hr of photolysis (in three cycles). Stored chemical energy is released as light and heat when frozen radicals combine in the solid.

7. ORGANIC REFRACTORY RESIDUES

One of the puzzles about interstellar grains back in the 60's was how to account for the fact that there were regions where no H$_2$O was observed even though the grain sizes were such as to require substantial mantles. It was first postulated that the H$_2$O could have been photolyzed away leaving the OH radical whose absorption, at ~ 2.7 μm, was not observable because of atmospheric absorption by water vapor. The difficulty with this explanation was that the first experiments in 1970 by Yencha and Greenberg on the ultraviolet processing of water rich mixtures never showed an adequate reduction in the H$_2$O in reasonable times. However upon warmup of the photolyzed mixtures there always remained residues of complex organic molecules and herein seemed to lie the possibility of a suitable explanation (Greenberg et al., 1972). Suppose such residues were created in space, we could then envisage mantles which, although they contained the organics O + C + N, did not possess an ice band.

The direct evidence for organic residues in space was finally exhibited in the observation of a 3.4 μm feature seen towards objects in the galactic center. The first such observation was of SgrA W (Willner et al., 1979) and since then, better observations of this feature taken
with higher resolution have confirmed its presence in a number of different galactic center sources. Laboratory produced residues have been successful in recreating the essential shape of the 3.4 μm feature (see Fig. 9) which consists of contributions from the C-H stretch in CH₂.

![Graph showing infrared absorption spectra of several organic refractory residues and the galactic center sources IRS7 and Sgr AW. 1) Residue of CH₄, 2) Residue of CO:H₂O:CH₄:NH₃ = 2:2:1:2, 3) Residue of CO:H₂O:NH₃ = 5:5:1, a) IRS7, b) Sgr AW.]

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and CH$_3$ groups in complex organic molecules. The details of the full spectrum, including the very broad absorption peaked somewhat shortward of 3 μm and therefore not due to the kinds of ice observed in molecular clouds are a subject of further investigation. It is expected that the residue itself contributes to a part of this but in such long lines of sight as towards the galactic center there could be contributions also by grains which have some icy mantles on top of the organic refractory mantles.

This may be seen in Fig. 10 where several galactic center sources are seen to exhibit quite different "3 μm" absorption strengths relative to the 3.4 μm strength (Willner and Pipher, 1982).

![Figure 10: Spectra of galactic center sources corrected for interstellar extinction. Note the variety of absorptions peaked at about 3 μm evidently not due to normal H$_2$O.](image)

The spectral correspondence between the laboratory residue and the galactic center is supported quantitatively by the measured strength of the laboratory 3.4 μm feature (Agarwal et al., 1985). If one models the interstellar grains in diffuse clouds by silicate cores plus organic refractory mantles, the thickness of the mantles required to produce the observed visual extinction defines the volume of organic refractory material. This volume in turn defines a total 3.4 μm absorption given the measured absorptivity of the organic refractory. Using the laboratory 3.4 μm strength one may show that the calculated and observed values of A(3.4)/A(V) are both about 0.05 if one assumes a visual extinction of 40 magnitudes and a mean particle radius of a $\approx$ 0.15 μm.

The volume of organic refractory (otherwise known as "yellow stuff" because of its color) is directly obtained by comparing the 3.4 μm
optical depth to the galactic center of 0.22 with the absorptivity of our laboratory residue.

\[ \tau_{G,C}^{(3.4)} \text{obs} = 0.22 = \tau_{G,C}^{(3.4)} \text{calc} = Y_{O,R} \times O.R. \times \frac{[C(3.4)]}{m_{O,R}} \text{lab} \]  

(3)

where \( Y_{O,R} \) = line of sight volume density of the organic residue mantles; \( s_{O,R} \) = mass density of residue \( = 1.4 \text{ g cm}^{-3} \);

\( [C(3.4)/m_{O,R} \text{lab}] = \text{O.R. absorption per unit mass at 3.4 \mu m = 440 cm}^2 \text{ g}^{-1} \). Substituting these values in Equation 4 we get

\[ Y_{O,R} = 3.57 \times 10^{-4} \text{ cm m.o.s. mass} = 5 \times 10^{-4} \text{ g cm}^{-2} \]  

(4)

which gives a mean mass density \( \rho_{O,R} = 2 \times 10^{-26} \text{ g cm}^{-3} \) towards the galactic center.

The production rate of the O.R. in the laboratory when scaled to determine the production rate in molecular clouds gives (Schutte and Greenberg, 1986) \( \frac{d \rho_{O,R}}{dt} = 1.5 \times 10^{-41} \text{ g cm}^{-3} \text{ s}^{-1} \). The time required to produce the above observed density is \( \approx 4 \times 10^7 \text{ yrs} \). This is of the order of molecular cloud lifetimes and shows that the O.R. grain mantles are produced at a rate which can maintain them against destruction as will be seen in the next section on general grain evolution.

A number of the physical properties of organic refractory grain mantles have been studied. It has been shown that they have significant absorption starting in the visible and increasing to strong values in the ultraviolet. This is important in grain modelling of the extinction and scattering (Chewicki, 1985). Chemical analyses and mass spectroscopy have been reported (Greenberg, 1983; Agarwal et al. 1985) which show that the organic refractory material consists largely of molecules of prebiotic character.

8. GRAIN MANTLE EVOLUTION IN MOLECULAR CLOUDS

The interplay between the atoms and molecules in the gas and in the grains is a complex one. Because the mean temperature of the grains is of the order of 10 K, all condensable species stick after collision at thermal speeds. If this were to continue unchecked and if there were no way to return the accreted atoms and molecules to the gas, the grains would freeze out the gas in a relatively short time. The depletion of the gas by accretion occurs at the rate.

\[ \frac{d n_G}{dt} = n_G v_G n_d A_d \]  

(5)

where \( n_G \) is the number of gas phase condensable atoms per cm\(^3\), \( v_G \) = gas
velocity, \( n_d \) = number of core-mantle grains per \( \text{cm}^3 \), \( A_d \) = area per grain. Using \( v_G = 10^4 \text{ cm s}^{-1} \), \( n_d = 10^{-8} \text{ cm}^{-3} (n_H = 10^4 \text{ cm}^{-3}) \), one derives an e-fold depletion time scale of

\[
\tau_{\text{dep}} < 10^6 \text{ yr}
\]  

which is comparable with or shorter than the \( 10^6-10^7 \text{ yr} \) characteristic of individual cloud life times, the value \( 10^6 \) being on the short side and \( 10^7 \) years being the mean time between cloud - cloud collisions.

The most likely mechanism for returning accreted volatile mantles to the gas within molecular clouds seems to be the explosion of grain mantles resulting from the sudden release of stored energy in the form of free radicals produced by ultraviolet radiation of the grains (d'Hendecourt et al., 1982). A scheme for including this in the total time dependent chemistry of clouds has been developed (d'Hendecourt et al., 1985). The gas phase ion-molecule reactions are considered along with accretion and grain surface reactions leading to gradual formation of grain mantles which are sporadically triggered to explode by grain-grain collisions induced by cloud turbulence or by occasional impacts of heavy cosmic ray ions (Léger et al., 1985). The time dependence of the composition of both the gas and grain mantles is followed starting with various initial conditions of cloud density and ultraviolet flux spanning a wide range of possibilities.

We present here a small sample of the results. In Figs. 11a, 11b, 11c, we present the time dependence of the gas and mantle components for what we call the standard case defined by density \( n_H = 2 \times 10^4 \text{ cm}^{-3} \), and \( U_{\text{V}} \), flux given by an attenuation of the mean diffuse cloud field by \( e^{-2A_{\text{V}}} \), where \( A_{\text{V}} \) is the visual extinction. We note several important results for the grain mantle:

1) At early times the grain mantle is dominated by H\(_2\)O + CH\(_3\) + NH\(_3\), more or less as given by Van de Hulst (1949) in his dirty ice grain model.

2) At intermediate times (\( 10^5-10^7 \text{ yr} \)) the mantle is dominated by H\(_2\)O or, eventually CO, (if we exclude the effect of photoprocessing which leads to CO\(_2\) as seen in Figure 4).

3) At longer times H\(_2\)O + CO\(_2\) remain the dominant constituents with no significant amount of CH\(_3\) or NH\(_3\).

For lower gas densities and extinctions (\( n_H = 2 \times 10^3 \text{ cm}^{-3} A_{\text{V}} = 2 \)) the results are similar but for greatly reduced U.V. and increased density (\( n_H = 10^5 \text{ cm}^{-3} A_{\text{V}} = 8 \)) the grain mantle ultimately, after \( t > 5 \times 10^7 \text{ yr} \) loses almost all its H\(_2\)O, the oxygen becoming locked up in the O\(_2\) molecule.

Although grain mantle photolysis is used to account for the storing of radicals and consequent explosions, it has not here been considered in terms of chemical changes within the mantle. This will produce some changes from the results reported here and will be taken up in the future.

One very general statement which can be made is that the gas and mantle compositions are not at all the same. For example the H\(_2\)O abundance in the solid phase is almost always considerably larger than in the gas phase, with ratios > 10 and as high as \( 10^2-10^4 \) being common;
Figure 11a: Time evolution of the abundances of the molecular components of the gas in a cloud with density $n_H = 2 \times 10^4 \text{cm}^{-3}$ and extinction $A_V = 4$ magnitudes.

Figure 11b: Same as Fig. 11a for the grain mantle.

Figure 11c: Relative fractions of the major volatile components of the grain mantles in a cloud with $n_H = 2 \times 10^4 \text{cm}^{-3}$ and extinction $A_V = 4$ magnitudes.
i.e., water does not appear on grains as a result of accretion of water molecules from the gas but is rather made on the grains.

Although the H₂O abundance in grain mantles has sometimes been stated to be small even in molecular clouds we see that throughout a substantial portion of a cloud's duration the H₂O fraction in the accreted mantle should be quite large. In very young clouds (t ≤ 10⁵ years) a characteristic fraction of H₂O is > 60%. In Figure 11c, 12 and 13 are shown the time variation of the H₂O fraction for the three basic cases treated. Since a mean time scale for cloud-cloud collisions is ~ 10⁷ years we take this to be a canonical mean cut-off time for unperturbed cloud chemistry. In no case is the predicted H₂O concentration < 50% for t < 10⁷ years so that one should find large amounts of solid H₂O in molecular cloud grains. This is indeed confirmed by observations as shown in Section 3.

The theoretically predicted drop in the H₂O mantle fraction in dense clouds for t > 10⁷ years is probably prevented from occurring because such clouds are likely to have much shorter lifetimes. The free-fall lifetime of a cloud with \( n_H = 10^5 \text{ cm}^{-3} \) is \( t = 4 \times 10^5 n_H^{-2} \text{yrs} = 10^5 \text{yrs} \) which is a lower limit to the cloud lifetime, so it is not likely to remain static for 100 times this value even if maintained by magnetic fields.

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**Figure 12:** Relative fractions of the major volatile components of the grain mantles in a cloud with \( n_H = 2 \times 10^5 \text{ cm}^{-3} \) and \( A_V = 2 \) magnitudes.

**Figure 13:** Relative fractions of the grain mantles in a cloud with \( n_H = 10^5 \text{ cm}^{-3} \) and extinction \( A_V = 8 \) magnitudes.
9. GENERAL GRAIN EVOLUTION

The evolutionary picture of dust which is emerging is a cyclic one in which the particles find themselves alternately in diffuse clouds and in molecular clouds. A small silicate core captured within a molecular cloud gradually builds up an inner mantle of organic refractory material which has been produced by photoprocessing of the volatile ices. Within the dense clouds critical densities lead to star formation and subsequent ejection of some of the cloud material back into the surrounding space. Much of this material finding itself in a very tenuous low density environment expands to the diffuse cloud phase. Dust particles in the diffuse medium are subjected to numerous destructive processes which rapidly erode the outer volatile mantles away and, in fact, erode part of the organic refractory material. It is important to note that without their organic refractory mantles the silicate cores could not survive. The rate of destruction of pure silicate grain leads to a maximum lifetime of $t_{\text{Sil}} \approx 4 \times 10^8$ yrs which (Draine and Salpeter, 1979) converts to a mass loss rate of $\frac{d m_{\text{Sil}}}{dt} = -5 \times 10^{-43}$ g cm$^{-3}$ s$^{-1}$. Assuming a mass loss rate from M stars of $\dot{M}_{\text{star}} = 7 \times 10^{-7}$ g cm$^{-3}$ s$^{-1}$ and a full cosmic abundance silicate production leads to a production rate for silicates of $\frac{d m_{\text{Sil}}}{dt} < 10^{-45}$ g cm$^{-3}$ s$^{-1}$ which is 100 times lower than the destruction rate. On the other hand, the production rate of the O.R. of $\frac{d m_{\text{OR}}}{dt} = 10^{-41}$ g cm$^{-3}$ s$^{-1}$ is adequate to replenish the mantle material lost in the diffuse cloud phase even if the O.R. is somewhat less tough than the silicates. Therefore silicate core-organic refractory mantle grains survive the diffuse cloud phase to reenter the molecular cloud phase.

The mean star production rate of $1-2 \ M_\odot$ yr$^{-1}$ implies an interstellar medium turnover time of $\sim 5 \times 10^9$ yr so that this is the absolute maximum lifetime of a dust particle no matter how resistant to destruction. If we use a mean molecular cloud-diffuse cloud period of $2 \times 10^8$ yrs (10 years in each) then a typical grain anywhere in space will have undergone at least 20 cycles so that, for example, the typical diffuse cloud dust particle age is $\geq 10^9$ yrs and consists of a mix of particles which have undergone a wide variety of photoprocessing. Note that the organic refractory mantles are subjected to the highest photoprocessing rates in the diffuse cloud phase. This would imply that the organic refractory mantle on a grain is not a homogeneous substance. A result of sequential formation (in the molecular cloud phase) and of intense photoprocessing (in the diffuse cloud phase) would lead to a layering in which the innermost layers have been the most irradiated and the outermost layer is first generation organic refractory. Because of this kind of layering, and the fact that the grains are of various ages leads one to expect average homogeneity of diffuse cloud grains both in size and structure which is observed as a uniformity in the visual extinction curve and a rather structureless 3.4 $\mu$m feature. In other words, diffuse cloud grains represent a steady state average of grains of a multiplicity of chemical and physical histories.
A schematic representation of grains in the various regions of space is shown in Figure 14. In the final stage of cloud condensation we may expect that all remaining (condensable) molecules will have accreted onto the dust. In addition, the very small ($\leq 0.01$ $\mu$m) particles will be collected and trapped within the outer volatile mantle.

Figure 14: Cross section of grains at various stages of evolution.

REFERENCES


DISCUSSION

GLASSGOLD: Have you investigated the explosive reaction on irregular surfaces which might more nearly approximate interstellar grain surfaces than the laboratory cold finger. For example, the grain material might be similar to the open deep structure suggested by the Brownlee particles.

GREENBERG: I am sure that grain mantles are not completely regular. However the comparison with Brownlee particles does not seem appropriate. Brownlee particles are rather large aggregates of particles of ~0.1 μm. As I have written elsewhere, I believe that comets are floppy aggregates of interstellar dust and that comet debris after it loses its volatile components gradually evolves towards more compact interplanetary structures (as theorized by Mukai and Fechtig). These particles, when captured in the earth's upper atmosphere, after having existed in the solar system for 10^4 to 10^5 years, may then be what we call Brownlee particles.
KHAZE: What kind of residue and the list of molecules would you get if electrons and charged particles are deposited on the ices instead of UV photons?

GREENBERG: I suspect that using electrons and protons instead of UV photons would lead to many similar molecules but undoubtedly there would be differences in relative proportions as well as in kind (cf. Agrawal et al. (1985)).

HUEBNER: (i) I assume that the explosive reaction that you observe on heating the deposit on the cold finger is of a chemical nature. Have you identified the gas phase products of this reaction? Are they simpler and possibly revert to the original materials such as H₂O, NH₃, and CH₄? (ii) In the interstellar medium the grains are in a bath of hydrogen, while in your laboratory the cold finger is presumably in a vacuum. Have you repeated the experiments immersing the cold finger in hydrogen?

GREENBERG: (i) We are currently planning an experiment called a double cold finger experiment in which the exploded molecules and radicals from one (heated) cold finger will be collected and triggered in an inert matrix on a neighbouring cold finger. We hope that this will tell us not only the distribution of molecules but also of radicals which come off in the explosion. (ii) No. We have talked about it many times and have always done what we considered more unique experiments. However I agree with you that it would be a very important experiment to do.

IRVINE: A few years ago, you thought you are on the track of the diffuse interstellar bands from these grains. What happened?

GREENBERG: I was afraid someone will raise this question. Fred Bostock identified 4430 band and a few 'others'. The 'others' are right but 4430 is definitely spurious. However, I still believe, that the bands cannot be produced by any kind of solid particles that we can think of. They must be due to some molecules. How and where these molecules are created is still an open question.

P.A. FELDMAN: I would like to follow up on Dr. Irvine's question by asking you to tell us, specifically, why you now believe that the diffuse interstellar bands (DIBs) are not produced by grains but by gas-phase molecules?

GREENBERG: I do not believe that the DIBs are produced by grains for a number of reasons: (1) their shapes are inconsistent with absorption by impurities in grains, (2) their widths are generally too small to be produced by impurities in grains and more important the observed uniformity of both shape and position of a particular DIB is not possible with variability of impurity sites in a matrix, (3) there is no evidence for polarization in the bands, and (4) the differences in the shapes of different bands are not correlated with wavelength as would be expected for impurities in solid particles (cf. Chlewicki et al., Ap.J. June 1986).

D'CUNHA: In your laboratory studies on the photolysis of the mixture
of CO, NH₃ and H₂O, you showed a list of molecules that were left as residue. How did you go about identifying them?
GREENBERG: We have used mass spectroscopy, and gas and liquid chromatography. This has been discussed by Agarwal et al. (1985).

PIRRONELLO: Don't you think that, at least partially, the differences observed in the "signature" of ice in Elias 16 and HL Tau could be due to a slight degree of crystallization which occurred in the ice around HL Tau, a very young T Tau type star characterized by an intense radiation field and a strong wind?
GREENBERG: Yes, in fact, we have indeed attributed the ice band shape in HL Tau to annealing because the ice is still amorphous, and not yet crystalline.