

## The Role of Grains in Interstellar Chemistry

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**ABSTRACT.** Grains affect interstellar chemistry in a variety of ways. Most obviously, they extinguish starlight and thus protect molecules in cloud interiors from photodestruction. The grains themselves contain substantial proportions of particular elements which are therefore less readily available for gas phase reactions and for processing into molecules. Grains in dense clouds are known to accrete molecular mantles which may be further processed; the mantle material is ultimately returned to the gas, either near hot stars or when the clouds are dissipated. Molecular hydrogen, the key to all gas phase chemistry, is undoubtedly formed efficiently on grains, and a plausible mechanism can now be identified. Other molecules, too, form preferentially at surfaces. Finally, the destruction of grains via chemical erosion and by sputtering in shocks provides a substantial molecular contribution to the gas in local regions.

### 1. INTRODUCTION

Apart from their important optical properties, grains have direct effects on interstellar chemistry by acting as sources and sinks for interstellar molecules, and by locking up significant fractions of reactive atoms. In some of the processes, the precise nature of the surface is irrelevant: grains merely provide an inert surface, sufficiently cool for atoms and molecules to stick on collision, and then - possibly - to undergo further processing. Such adsorption leads to the accretion of molecular mantles; these are discussed in Section 2. Specific chemical catalysis may also occur at particular sites on grains of well-determined composition (Section 3). The chemical properties of grains, and their effects in modifying available gas phase abundances, are indicated by studies of interstellar depletions, since it is conventionally assumed that the elements "missing" from the gas phase are present in the grains.

A study of recent depletion determinations (Whittet 1984) suggests that silicates and oxides make up 70% of the grains by mass, and take up 75% of the depleted oxygen. Carbonaceous material must

also be present, although less than has been frequently assumed. The link between carbon grains and the 2200Å extinction feature is weak, since the strength of the feature is apparently anti-correlated with carbon depletion (Millar 1979, Duley 1985). An alternative explanation of the 2200Å feature has been offered (Duley and Najdowsky 1983).

We conclude that the surfaces to be considered for chemical activity in the interstellar medium are silicates, oxides, and carbonaceous grains. The optical properties of such grain populations in comparison to observed properties obviously provide a constraint which must be met. It is likely that this is the case (e.g. Mathis et al 1977, Draine and Lee 1984).

## 2. MOLECULAR MANTLES

There is now clear spectroscopic evidence for the existence of molecular mantles. Lacy et al. (1984) detected features due to solid CO and to solid CN-bearing molecules in dense molecular material associated with compact IR sources. They inferred that a substantial fraction of the available CO had condensed on to grains. Whittet et al (1985) have also detected solid CO in rather less dense ( $n \sim 10^4 \text{ cm}^{-3}$ ) but optically opaque molecular clouds in Taurus. Thus, as predicted by Duley (1974), grain mantles do form if the grain temperature is sufficiently low, and an important component in those mantles is CO. The CN feature observed by Lacy et al. is interpreted by them as evidence of chemical processing on the surface energized by UV irradiation (Greenberg 1982). The Taurus observations, on the other hand, do not show this feature, reinforcing the view that Taurus clouds are quiescent and without embedded sources. Since the fraction of CO in solid form may approach 50%, even in moderately dense clouds, then any discussion of interstellar chemistry must take the mantle molecular content into consideration. Mantle material is clearly present, yet unavailable for gas phase reaction. In particular, the widespread use of CO as a tracer of interstellar gas (e.g. Sanders et al. 1984) needs correction for the mantle CO fraction. This correction helps to reduce the discrepancy between radio and  $\gamma$ -ray measures (Bhat et al 1984) of the interstellar gas content of the Galaxy (cf. Kutner and Leung 1985; Williams 1985).

The "ice" feature at 3.1  $\mu\text{m}$  is also evidence for molecular mantles. Observations (Harris et al. 1978, Whittet and Blades 1980) suggested originally that the ice feature appears only in very heavily obscured objects ( $A_v > 20 \text{ mag}$ ) in which one might expect that a substantial fraction of oxygen had been processed to  $\text{H}_2\text{O}$  in the gas phase. However, later observations (Whittet et al. 1983) have confirmed the presence of the ice feature in relatively low extinction ( $A_v \sim 4 \text{ mag}$ ) clouds in Taurus. In these cool quiescent clouds, most of the oxygen not combined into CO is present as free atoms; very little is expected to be in the form of  $\text{H}_2\text{O}$ . Thus, the detection of substantial ice mantles in these clouds indicates that the surface (s) reaction  $\text{O}_s \rightarrow (\text{H}_2\text{O})_s$  occurs, and that a significant fraction of the product  $\text{H}_2\text{O}$  is retained at the surface (Jones and Williams 1984).

Any fraction of the  $H_2O$  product released to the gas phase can be accommodated within present uncertainties of the models and the observations, at least in diffuse clouds (Mann and Williams 1984, 1985).

Associated with the ice feature is a wing which is generally attributed to  $NH_3$  in the ice (Knacke et al. 1982, Leger et al. 1983, Hagen et al. 1983). According to the models (e.g. Watt 1983) gas phase chemistry does not lead to the formation of substantial quantities of ammonia, because  $NH_3$  tends to be further processed to CN-bearing species and also because substantial fractions of N can be tied up in unreactive  $N_2$ . Yet Knacke et al. find that 10–100% of nitrogen is in solid  $NH_3$  in the material towards the BN object. Thus, the reaction  $N_2 \rightarrow (NH_3)_s$  must be occurring on the surface, and a significant fraction of the product  $NH_3$  must be retained there.

If mantled grains are warmed to  $\sim 100K$ , then evaporation is rapid and many molecules may be rapidly injected into the interstellar gas. The source IRc2 appears to be such a situation. It shows a very high abundance of gas phase  $NH_3$  (Pauls et al 1983), containing a high fraction of all available nitrogen. This high fraction is unattainable by gas phase chemistry, and the observation suggests that evaporation of  $NH_3$ -rich mantles has occurred (Wilson et al 1983, Mauersberger et al 1984, Jones and Williams 1984). Observations of HDO in Orion KL (Olofsson 1984) similarly suggest that  $H_2O$  may have a greatly enhanced abundance, containing a substantial fraction of available oxygen. Such an abundance could arise from the evaporation of ice mantles. Menten et al. (1985) have found a similar result for  $CH_3OH$  in W3(OH). The fractional abundance of methanol in this source is about 100 times the expected value, again suggesting that evaporation of - perhaps - processed mantle material has occurred.

### 3. SPECIFIC REACTIONS AT GRAIN SURFACES

#### 3.1. The nature of the surface

In the formation of mantles, the nature of the underlying surface is relatively unimportant, as long as its temperature is sufficiently low for condensation, sticking and (possibly) reaction to occur. These now seem to be reasonably well characterized processes (cf. Leitch-Devlin and Williams 1984, 1985). In this section, we consider two specific types of grain, and discuss reactions which may occur there.

#### 3.2. Molecule formation on amorphous silicates

We now consider particular surfaces: here we are specifically concerned with  $H_2$  formation on amorphous silicates. Although  $H_2$  is fundamental to all gas phase chemistry, no two- or three-body gas phase reaction is sufficiently rapid in the typical interstellar medium, and surface reactions  $2H_3 \rightarrow H_2(\uparrow)$  are involved. The precise mechanism by which this occurs has received some attention (cf. Duley

and Williams 1984a). It is clear that some difficulties occur with physisorbing grains and that weak chemisorption is required. Since the widespread acceptance of the view that a component of the grains is an amorphous silicate or disordered oxide, it is now possible to characterize the expected nature of the surface of such grains in the interstellar medium. Laboratory work suggests that the surface is covered with  $\text{OH}^-$  surface groups of low coordination. The individual vibrational resonances form a surface band whose energy is  $h\nu \approx 0.4$  eV of width  $\Delta E \approx 0.1$  eV. These  $\text{OH}^-$  groups have been identified with the  $\text{H}_2$  formation sites by Duley and Williams. In this picture, the incident H atom interacts with the  $\text{OH}^-$  site, the energy released in the charge-dipole interactions being approximately equal to the surface band energy. Thus, energy transfer from the  $\text{H.OH}^-$  complex to the band is rapid, but the reverse process is unlikely. Rearrangements in the complex can now occur, even if this involves relatively slow H atom tunnelling through a substantial barrier. Such tunnelling gives the rearrangement  $\text{H.OH}^- \rightarrow \text{O}^-\text{H}_2^*$  where the  $\text{H}_2^*$  is vibrationally excited with  $v'' = 4$ . The transfer of one vibrational quantum releases  $\text{H}_2^*$  from the  $\text{O}^-$  site into the gas, with  $v'' = 3$  and a small amount of kinetic energy,  $\sim 0.1$  eV. However, rotational excitation remains low throughout these reactions, and  $J'' = 0, 1$  on release. Subsequent collisions ensure that the molecule is kinetically thermalized, so that after a few collision times the molecule is in the  $v'' = 1$ ,  $J'' < 6$  states, from which it relaxes radiatively. In this view, the formation process itself leads to vibrational and rotational excitation which may contribute to the observed emissions, and to some heating of the gas.

The  $\text{OH}^-$  sites may also be active in forming other molecules. Low coordination  $\text{OH}^-$  sites are likely to be particularly active chemically, according to the extensive literature on this subject. Interstellar molecule formation at these sites has been thoroughly explored by Duley, Millar and Williams (1978), and Jones, Williams and Duley (1983). The molecules produced at significant rates by such processes are  $\text{OH}_n$ ,  $\text{NH}_n$ , and  $\text{H}_n\text{CO}$ . Laboratory work further indicates that O atoms can be replaced by S atoms in lattices, and this suggests that low coordination  $\text{OH}^-$  sites may become  $\text{SH}^-$  sites in regions of high sulphur depletion. Ion collisions with such grains may produce a wide variety of S-bearing molecules (Duley, Millar and Williams 1980). This suggestion is of renewed interest following the detection of OCS (normally regarded as a tracer of shocks, cf. Hartquist et al. 1980) in the cool quiescent cloud  $\text{TMCl}$  (H.E. Matthews, private communication).

### 3.3. Carbonaceous grains

The detection of 3.3  $\mu\text{m}$  and 11.3  $\mu\text{m}$  emission (e.g. Willner et al. 1979) is evidence of hot ( $\sim 1000\text{K}$ ) carbonaceous material containing aromatic CH groups. Such material could be hydrogenated amorphous carbon (HAC; Duley and Williams 1981, 1983), polycyclic aromatic hydrocarbon (PAH; Leger and Puget 1984, Allamandola et al. 1985) or other molecular material (Hoyle and Wickramasinghe 1979, 1982).

Absorption at 3.4  $\mu\text{m}$ , corresponding to aliphatic hydrocarbon, is seen along low density paths of low excitation. Conversion of unsaturated to saturated material occurs via carbon insertion; the reverse process requires the ejection of  $\text{CH}_n$  groups from grains.

The question of the chemical stability of interstellar carbonaceous material now arises. Laboratory evidence shows that even graphite is reactive with H and O atoms at cryogenic temperatures (Gill et al. 1967, Bar-Nun 1975, Bar-Nun et al 1980a,b) yielding  $\text{CH}_4$  and heavier hydrocarbons, and CO and  $\text{CO}_2$ . These products were retained on the surface, and were released into the gas phase when the surface temperature was raised to  $\sim 100\text{K}$ . The chemical processes involved are all applicable to HAC, PAH and other organic molecules. Thus, carbonaceous grains have a limited life in the interstellar medium, and the chemical destruction mechanism transfers to the gas substantial quantities of hydrocarbons and oxides of carbon.

Finally, if carbonaceous grains are subjected to energetic events, the destruction products can include long chain molecules (polyynes). This process has been suggested (Duley and Williams 1984b) as a source of polyyne material in interstellar regions subjected to shocks. MHD shocks would be particularly suitable for this, since substantial gas-grain velocity differentials occur (Draine et al. 1983, Flower et al. 1985).

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## DISCUSSION

IRVINE: Since there is no direct measurement of the abundance of gas phase water in the Taurus clouds, I don't see why you have to invoke H<sub>2</sub>O production on grains.

WILLIAMS: If one takes the generally accepted density, temperature and age of the Taurus clouds and looks at a variety of time-dependent chemical models of such objects, one finds that no models predict any substantial H<sub>2</sub>O abundance. The oxygen is largely in CO and O atoms. Thus, to produce the H<sub>2</sub>O in mantles, it must be formed by direct reaction on surfaces.

The case of NH<sub>3</sub> is more convincing, perhaps. No models can produce substantial NH<sub>3</sub> abundances (i.e. containing much of the total nitrogen). Thus, where we see that X(NH<sub>3</sub>) is comparable to X(N) either in mantles or in the gas, we may immediately infer that some process other than gas-phase is involved. In the Taurus clouds, one can only conclude that surface reactions produce NH<sub>3</sub> effectively.

D'HENDECOURT: (i) With reference to the HAC or PAH, we have recently detected new IR emission lines at 3.4, 3.5  $\mu\text{m}$ , together with the classical 3.3  $\mu\text{m}$  line and we show in our poster paper that these new bands can be produced by radicals like CH<sub>3</sub>, CH<sub>2</sub>, HCO on the edge of PAH molecules. (ii) The X-CN appearance or non-appearance in astronomical spectra is not necessarily an indicator of the efficiency of UV photolysis processes because it depends somehow on the initial composition of the mixture studied in the laboratory. To me, the CO<sub>2</sub> molecule, which cannot be observed unfortunately, is a good indicator of the photolysis process as it is readily formed in any ice mantle containing CO, H<sub>2</sub>O and/or O<sub>2</sub>. CO<sub>2</sub> is not formed by grain surface reactions alone.

WALMSLEY: As you noted, water ice can be observed in the Taurus clouds at moderate extinction but this does not seem to be true in general and there are many regions where the ice feature is not seen for A<sub>v</sub> smaller than, say, 10 mag. The Taurus clouds are also peculiar in the sense that cyanopolyne formation seems to be efficient at a large number of sites in this region. One wonders whether there is a connection between these two facts. One possibility might be that the prevalence of star formation and its associated features (e.g. bipolar flows, shocks, etc.) is different in different molecular clouds.

LEGER: If 3.3  $\mu\text{m}$  and 3.4  $\mu\text{m}$  features are coming from CH radicals on same carbonaceous material, how do you explain that 3.3  $\mu\text{m}$  dominates when seen in emission and 3.4  $\mu\text{m}$  when in absorption?

WILLIAMS: I consider that in the cooler regions, carbon insertion followed by hydrogenation will tend to convert surface species to e.g. CH<sub>3</sub>. In regions of higher excitation, such species are removed. The most likely next step is the addition of H to form aromatic - CH.

LANGER: There is indirect evidence of a low H<sub>2</sub>O gas phase abundance in clouds. The deuterium enhancement in clouds is limited by the abundance

of neutral species and with the large reaction rate coefficients (as suggested by Smith and Adams) the  $\text{DCO}^+/\text{HCO}^+$  ratios observed in clouds limits  $n(\text{H}_2\text{O})/n(\text{H}_2) < \text{few} \times 10^{-6}$  in many sources.

WILLIAMS: This is an interesting comment which helps to support my view of the formation of ice in the Taurus clouds.

GREENBERG: Why do you not accept the concept of continuous desorption (or ejection) of molecules from grain in molecular clouds? I just don't see how, without the explosions, we can prevent all the gas phase molecules being accreted on the grains in time scales short compared with the cloud lifetime.

WILLIAMS: I don't believe that explosions occur in interstellar grains because - in my view - the required density of radicals in the mantle will not occur there (though it is obviously attained in your laboratory work). Consequently, all molecules will be accreted, as you say, unless some major dynamical event (e.g. star formation) occurs. This picture is now being suggested by various authors (cf. Benson and Myers in "Nearby Molecular Clouds" Toulouse 1984).

GOEL: We now know that molecules are formed in gas phase reactions and also on the surface of grains. Have there been any studies where grains act as catalysts only?

WILLIAMS: Yes, many such calculations have been made. I can give you references. Mantle accretion is a process that occurs more rapidly than other processes in interstellar molecular clouds and will ultimately dominate all other chemical processes. It must be taken into account; i.e. we must describe the physics correctly before building chemical models of greater and greater sophistication. Since molecules are seen in dense clouds, it implies, in my view, that major dynamical events are occurring since clouds are considerably older than the  $\sim 10^5$  years that accretion would imply. Hence our chemical models of molecular clouds must include dynamics. Static clouds are probably inadequate, except perhaps for the very diffuse objects.