

LABORATORY AND THEORETICAL RESULTS ON INTERSTELLAR MOLECULE
PRODUCTION BY GRAINS IN MOLECULAR CLOUDS

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ABSTRACT

Laboratory and theoretical studies have been made of the effects of ultraviolet photolysis of interstellar grain mantles. It has been shown that grain photolysis should be important even in dense clouds. A large number of molecules and radicals observed in the interstellar gas appear in the irradiated ices of CO, H₂O, NH₃ and CH₄ which are deposited at 10 K. Energy released during warm-up is seen from visible and infrared luminescence and inferred from vapor pressure enhancement relative to unirradiated samples. Grains are pictured as a source as well as a sink (capture) of molecules. The photolysis of an individual grain provides the stored chemical energy which is sporadically released by relatively mild triggering events (such as low velocity grain-grain collisions in turbulent molecular clouds) to produce the impulsive heating needed to eject or evaporate a portion of the grain mantle. An extremely complex and non-volatile substance possessing the infrared signatures of amino and carboxylic acid groups and having a mass of 514 amu has been produced at a rate corresponding to a mass conversion rate of interstellar grains of between 2% and 20% in 10⁷ years.

1. INTRODUCTION

At the Astrophysics Laboratory of Leiden University we have developed an experimental system which creates for the first time the relevant interstellar analog conditions leading to the formation of a wide range of molecules and their injection into interstellar space as a consequence of the evolution and photoprocessing of grain mantles. The results on ultraviolet produced changes in chemical composition, storage of radicals and vapor pressure enhancement due to the heat released by the combination of reactive species stored in the complex mixtures all lend support to the picture that the interstellar grain mantles are dynamic centers of activity in which gas phase molecules and radicals are modified and regenerated by reactions within the grains.

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B. H. Andrew (ed.), Interstellar Molecules, 355-363.
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We are thus able to demonstrate that the prevailing theories of molecule formation which consider only gas phase and grain surface reactions are not complete because they have not included the role played by the interiors of interstellar dust grains in the formation of molecules.

Experiments in the laboratory are aimed at understanding:

- (1) the photoprocessing of grains,
- (2) grains as a source of molecules up to a very high order of complexity and their injection into the interstellar medium subsequent to photoprocessing,
- (3) grain emission and absorption characteristics from the far infrared to the ultraviolet.

2. PHOTOPROCESSING OF GRAINS

Just as gas phase molecules are photodissociated by photons of sufficient energy, so are molecules imbedded in a solid. A major difference in the solid is that some of the break-up products may more readily recombine (the cage effect) while others (say H) may readily diffuse through the solid and combine with another molecule or with a previously produced radical (see Bass and Broida, 1960, particularly chapter 4; Meyer, 1971; Hallam, 1973). This means that not every "bond-breaking" photon which is absorbed by the grain necessarily produces a net photodissociation. Indicative of the significance of grain mantle photolysis as an important interstellar process is that the time required for the interaction of every molecular bond in the mantle with one high energy photon in an ultraviolet flux of $10^8 \text{ cm}^{-2} \text{ s}^{-1}$ (the mean interstellar field) is only $\sim 200 \text{ yr}$ (Greenberg, 1973). Thus even if the photolysis efficiency per photon is taken to be as small as 10^{-3} (a very conservative estimate), the time required to leave a net 1% of radicals (a rough upper limit, see Jackson, 1959a,b; or see chapter 10 in Bass and Broida, 1960) in the mantle is still only about 1000 yrs which is quite small compared with the mantle life-cycle time ($\sim 10^6$ to 10^7 yr). The photolysis time scale for the deepest molecules in the grain is greater by only about a factor of 10 (Greenberg, 1979).

It may be inferred from earlier calculations (Hagen, Allamandola and Greenberg 1979, hereafter HAG) that grain photolysis is substantial during the $\sim 3 \times 10^8 \text{ yr}$ lifetime of a grain mantle as well as the lifetime ($\sim 10^8 \text{ yrs}$) of a 1 pc cloud whose total visual extinction is about 10 mag.

We thus picture a typical grain mantle as spending a major part of its lifetime consisting of a mixture of complex and simple molecules with embedded frozen radicals for which the stored energy may occasionally be released so completely as to totally evaporate the material (see Fig. 1).

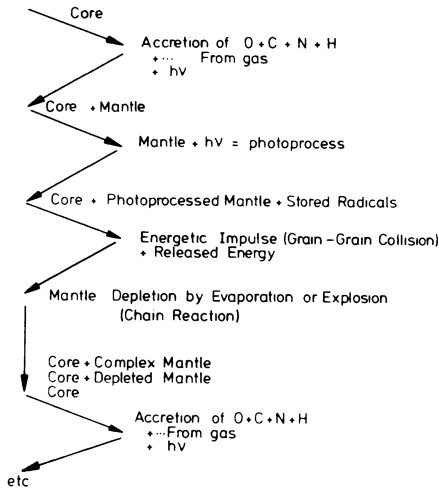


Fig. 1. Schematic of chemical evolution of a grain mantle. Grain mantle cycle time $\approx 10^7$ years.

More frequently there may be reactions which produce local hot spots in a mantle, some of which eject some surface molecules, but many will merely lead to local modifying of the molecular composition. It is interesting to note that any of the stored radicals located at or near the surface of the grain provide the possibility for chemical interaction with accreting atoms and molecules which should be included in a consideration of the growth as well as the chemical composition of grains.

Since all of the time scales in space are impossibly long for laboratory measurements we have scaled the laboratory photoprocessing as shown schematically in Table 1.

TABLE 1

Comparison between laboratory and interstellar conditions

	Lab	ISM
"Initial" composition	(simple molecules) CO, H ₂ O, NH ₃ , CH ₄ ...	All interstellar condensible species
Mantle { Thickness	$\geq 0.1 \mu\text{m}$	$\sim 0.15 \mu\text{m}$
Temperature	$\gtrsim 10 \text{ K}$	$\gtrsim 10 \text{ K}$
Pressure of condensibles	$8 \times 10^{-8} \text{ mbar}$	$3 \times 10^{-17} \text{ mbar}$
Gas { Number of condensible species	$2.4 \times 10^9 \text{ cm}^{-3}$	$1 \text{ cm}^{-3} (n_{\text{H}} = 10^3 \text{ cm}^{-3})$
Ultra-violet { $\phi_{\text{uv}} \equiv \text{Flux } (E > 6 \text{ eV}, \lambda < 2000 \text{ \AA})$	$10^{15} \text{ cm}^{-2} \text{ s}^{-1}$	$10^8 \text{ cm}^{-2} \text{ s}^{-1}$
Equivalent time scales	1 hr	10^3 yr

3. LABORATORY RESULTS

We summarize here a few results which bear on key phases in the life of a grain mantle (see HAG for instrumental details).

3.1 Photoproduction of molecules and radicals at 10 K

A series of infrared absorption spectra of a laboratory sample taken before and after several periods of irradiation is shown in Figure 2.

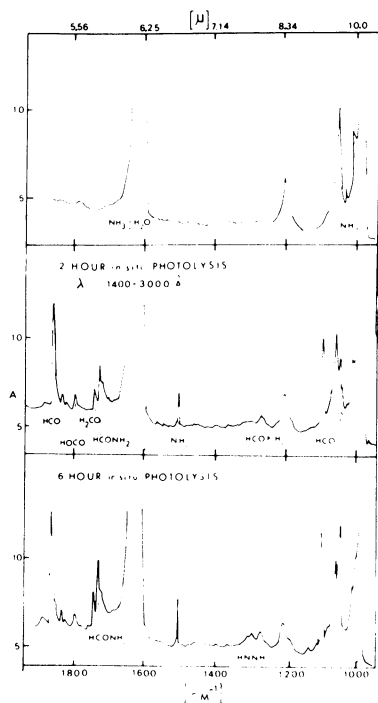


Fig. 2. Infrared absorption spectra of a molecular mixture $\text{CO}:\text{NH}_3:\text{H}_2\text{O}:\text{CO}_2$ (50:1:1:0.09) at 10 K. Upper, before irradiation; middle, after 2 hrs irradiation; lower, after 6 hrs irradiation.

The formation and growth of new radicals and molecules is clearly demonstrated. The newly formed species which are also known to exist in the interstellar medium are HCO, HNCO, H_2CO , HCONH_2 , and HCOOH. The infrared spectral changes which take place after the sample is warmed up to 40 K and re-cooled (not shown) shows a reduction in absorption by the radicals NH_2 and HCO with simultaneous growth of formaldehyde (H_2CO) and formamide (NH_2HCO). The disappearance of the radicals and the growth of the more stable molecules is expected since mild warming up allows diffusion to take place and permits the unstable species to react to produce stable product molecules.

3.2 Warm-up and energy release

Subsequent to the photolysis of the above mixture the system was allowed to warm up slowly. Almost immediately there appeared a blue-green luminescence apparently produced as the radicals combine. This interpretation is borne out by the fact that the visible absorption spectrum of the HCO radical is gradually reduced during warm-up. The sample was first warmed up to about 27 K then cooled back to 10 K (see Fig. 3). Upon subsequent warm-up there was practically no luminescence

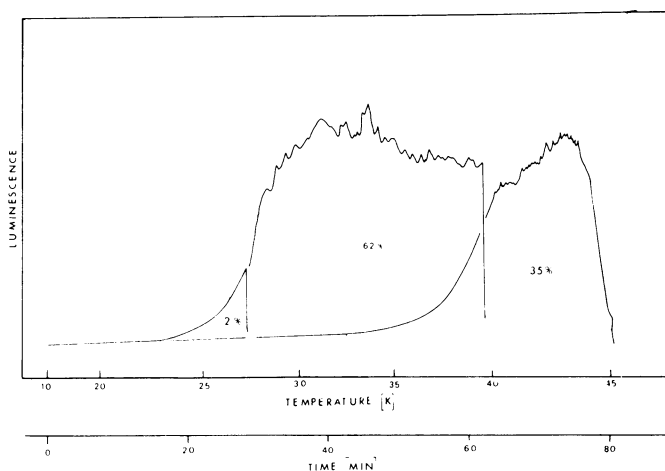


Fig. 3. Luminescence during warm-up of photolyzed mixture $\text{CO}:\text{NH}_2:\text{CO}_2$ (50:1:1:0.09), from 10 K to 45 K with intermediate recooling from 27 K and 40 K.

until the sudden onset at 27 K. The same thing was done up to 40 K with similar results. It appears that only certain frozen radicals are released up to each increase in temperature and that, in cooling and reheating, the radicals which have not been released remain trapped until the appropriate minimum temperature is reached. It is obvious that if the sample had been brought quickly to the temperature of 45 K all the energy seen in Fig. 3 would have been instantaneously released. By implication, since the radical reactions release energy, some of which goes into heating the sample, even a sudden increase to some temperature substantially less than 45 K could also lead to the complete release of stored energy. This is the type of process which we picture as occurring when a slight impulsive heating of an interstellar grain with frozen radicals triggers the release of the stored energy thereby heating the grain further and causing evaporation of the grain. The fact that at least some of the released energy appears as heat has been shown by the fact that the vapor pressure enhancement of various samples increases with the photolysis time (HAG).

The absorption spectrum between 3500 and 10,000 Å has been measured for a number of mixtures. For all cases the region between 4000 and 7000 Å shows the most structure. These absorptions appear only in photolyzed samples. The strong broad absorptions (80 - 100 Å at half height) grow weaker on warm up and are barely detectable at 35 K. It appears that these absorptions are due to HCO (Ewing et al, 1960; Herzberg and Ramsey, 1955; Johns et al, 1963).

3.3 High molecular mass studies

Upon completion of a number of experiments starting with mixtures of NH_3/CO , a yellow non-volatile residue was left on the cold finger. The yellow "stuff" generally appears as a viscous liquid (in one case it seemed to be crystallized) which is water soluble. In one such experiment, 200 µg of the material was recovered from the substrate. This represents a yield of between 0.02% and 0.2% (depending on whether or not we saved all the available residue). Based on the total time of photolysis we infer (see Table 1) that between 2% and 20% of the interstellar dust mantle material is converted into such non-volatile complex molecules in 10^7 years.

The infrared absorption spectrum of the liquid residue is shown in Figure 4. The principal features are readily attributable to amino and carboxylic acid subgroups, but are inconsistent with hydrocarbon or

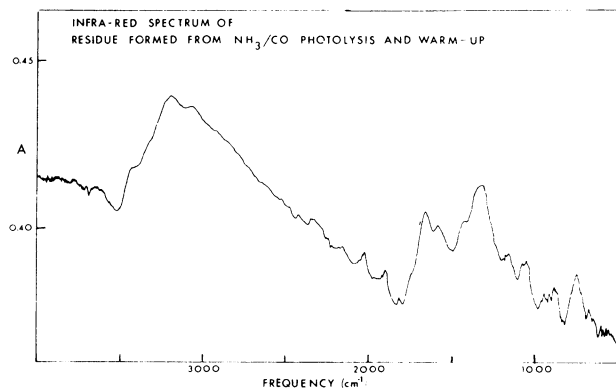


Fig. 4. Infrared spectrum of yellow residue formed from NH_3/CO photolysis and warm-up.

aromatic compounds (Pouchert, 1975). The liquid evaporates between 400 and 500 K (the "crystalline" substance pyrolyzed at 600 K). Both laser and field desorption mass spectrometric techniques yield a mass of 514 amu. Surprisingly this was the only mass. Only the ultimate residue has been studied here. It appears that the more volatile molecules with lower mass numbers must have evaporated. The detection and study of these molecules is now under investigation with an in situ mass spectrometer.

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DISCUSSION FOLLOWING GREENBERG

Snow: You indicated that many molecules likely to exist in grain mantles would absorb photons in the 4.5-5 eV energy range, which coincides with the 2200 Å interstellar extinction feature. Have you measured the ultraviolet spectrum of your simulated grain mantle material, and if so, did a 2200 Å absorption feature appear?

Greenberg: We do not think that the 2200 Å feature can be produced in our mantle materials. It may arise from our non-volatile residue, but a preliminary UV absorption spectrum of this substance did not seem to show it.

Vanden Bout: Your scheme seems to require both high cloud densities for reasonable rates of accretion onto grains, and low cloud densities for reasonable UV fluxes for photolysis. Can you tell us the density of the molecular clouds in which your proposed process operates?

Greenberg: In clouds with n_{H_2} several times 10^4 cm^{-3} there is a rough balance between (1) production of molecules by triggered energy release within previously *adequately* irradiated grain mantles and (2) accretion of molecules on the grains. Without some additional source of energetic photons (over that coming from outside), at higher densities the accretion rate should exceed the production rate, thus leading to a depletion of molecules.

Irvine: The spectrum of comets is due to radicals which, it is usually stated, could not exist for long periods of time in the cometary nucleus. There has been traditionally a problem in time scales if the radicals are produced by photodissociation. Do you think there could be

a significant number of such radicals stored in an icy conglomerate nucleus?

Greenberg: I had thought that the photodissociation production of radicals in comets was not a problem. What is a problem, as I understand it, is the identification of the parent molecules. The latter, by my dust conglomerate model of the comet nucleus, would include *some* radicals stored along with the other molecules, so *some* of the radicals seen would come directly from the comet. What fraction of the total would depend largely on the distance of the comet from the sun at the time of observation - the more distant the comet, the larger would be the number of radicals coming directly from it relative to the number being produced by photodissociation.

Avery: The carbon chain molecules are conspicuous by their absence in the products produced in your grain mantles. Are they being made but not detected, or are they not being made at all?

Greenberg: I cannot preclude the production of chain molecules in our present experiments. However, we will not be able to make a definite statement until we have a means of identifying them by their infrared absorption spectra in a solid matrix. We do know that if we start with some CH_4 in our solid, we can photolyze it to produce C_2H_2 so I believe that we are on the way to producing chain molecules.

Thaddeus: It does seem to me that it is a bit of a tease just to compare a list of the molecules that you get in your frost with the molecules that are found in dense pockets of interstellar gas. In that sense your experiment is a variation of the classic Miller-Urey experiment. It has been known for 30 years now that you do get the interstellar molecules out in a number of different ways if you take these simple compounds, put them in a flask, and give it a good kick. The real problem is the time scale of getting the molecules back into the gas, and the quantity of material that you can produce in this way. In spite of what you say, the clouds where we see the big molecules are as black as Satan's snout in many ways. The limit to the rate of production must be the time scale for getting the grain out where the photolysis can take place, then back into this black thing that's as dark as photographer's cloth, then getting the stuff off the grain again.

Greenberg: What we are trying to do is to estimate how much material is ejected by a dust grain when it is hit, and what kinds of molecules are ejected. In a way, it is indeed a bit of a tease to have shown evidence for production in solids of molecules observed in the gas phase in space. On the other hand, it is quite reasonable to expect that these molecules, or at least some combinations of them, will be ejected from the solid provided the right conditions exist to kick them out. I agree that the molecules we see in the solid are not necessarily present in the same relative abundances as those that are dumped off when the solid is evaporated or exploded or whatever. As I have already said in response to Dr. Vanden Bout there must be some mechanism to cause this to happen. One mechanism which I have proposed is that of grain-grain collisions, even at speeds as slow as 0.1 km s^{-1} . This might occur as a result of cloud turbulence, for example. In an earlier paper (Stars and Star System, ed. B. Westerlund, Reidel, 1979, p. 173) I have shown that collision velocities of the order of 0.1 km s^{-1} provide enough of an

increase in grain temperature to trigger reactions among the frozen radicals, which then release enough energy to heat the grain and further cause evaporation of some portion of the grain mantle. I have also estimated that an ultraviolet flux large enough to keep the grains in a state of sufficient excitation may be found even in the greater volume of clouds in which the total visual extinction is as high as 20 and the only ultraviolet radiation is that from the diffuse interstellar medium. The irradiation process is slow but steady while the collision process is sporadic. But statistically the two together may provide a quasi steady state. One can put in reasonable parameters, and end up with reasonable number densities of molecules in these clouds, where the rate of production is related to the rate of ejection from grains, and the rate of destruction is related to the rate of accretion onto grains. Now clearly that explanation leaves out all the gas-phase reactions that are also taking place. It is as bad a solution as considering only gas-phase reactions and ignoring the grain-accretion problem, but at least it gives some upper limits. If the molecules are made from the grains and absorbed also on the grains, then some sort of reasonable rate process has to be attained, and that, presumably, we can investigate in the laboratory.

De Zafra: Do you have any information on rates of free-radical relaxation back to parent molecules? High photo-flux laboratory results could fail to mimic very low-level irradiation processes when relaxation is considered.

Greenberg: We have left an irradiated sample on the cold finger (without warm-up) for as long as 4 or 5 days without seeing any apparent loss of radical concentration. Although a more quantitative experiment will be necessary, I predict that the rate of radical relaxation will be exceedingly low at 10 K. We have considered a more serious question regarding photon flux. It turns out that there is a negligible possibility that a photon will strike a particular molecule while it is in an excited state produced by a previous photon. For a sample of thickness $>0.1 \mu\text{m}$, $\tau \sim (\phi_{\text{UV}} d^3)^{-1} \sim 1000 \text{ s}$ is the time between two photons interacting with the same molecule, where ϕ is the photon flux ($10^{15} \text{ cm}^{-2} \text{ s}^{-1}$), and d is the molecule diameter $\sim 2 \times 10^{-8} \text{ cm}$. Molecular relaxation times are generally many orders of magnitude less than this.

Feldman: Have you used HCN/C₂H₂ mixtures to deposit grain-mantle analogues in any of your experiments? I would be interested to learn what kind of chain and ring molecules are produced.

Greenberg: We have not used HCN/C₂H₂ as initial material.