

Letter to the Editor
Interstellar Grain Explosions: Molecule Cycling Between Gas and Dust

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Summary

In dense molecular clouds all small condensible molecules should have been frozen onto the dust forming mantles. Although these accretion mantles are observed, a significant number of such molecules (CO, H₂O etc.) have also been detected in the gas suggesting that an equilibrium between accretion on and ejection from grains exists. Laboratory evidence for molecule ejection from vacuum ultraviolet photolyzed grain mantle analogs is shown to provide the basic mechanism for this equilibrium.

Keywords: Interstellar Grains, Interstellar Molecules**I. INTRODUCTION.**

Since the discovery of many complex molecules in dense interstellar clouds, a great deal of effort has been spent in trying to understand not only how they are produced, but also how they are maintained in the gas phase. Models based solely on gas phase chemistry utilizing ion-molecule reaction schemes have enjoyed the widest acceptance (Herbst and Klemperer, 1973 ; Prasad and Huntress, 1980). These models, using reaction rates measurable in the laboratory, but disregarding the effects of accretion on the dust, could indeed reproduce the observed abundances of some interstellar molecules. However, when effects of accretion of the condensible molecules and heavy elements on the cold (10K) grains are included, one finds that, in times shorter than the mean lifetimes of molecular clouds, the molecules should have been entirely accreted on the grains forming molecular mantles. Although these accretion mantles have been identified (Hagen et al. 1980), a significant number of molecules have also been detected in the gas. In 1973, Greenberg proposed that an equilibrium between the molecules observed in the gas phase and those accreted on the grains could be maintained by the sporadic release of the chemical energy stored in the grains in the form of frozen radicals which were produced within the mantle itself by the U.V. radiation which penetrates the cloud. A triggering event, such as collisions between grains could heat the grain to a temperature where diffusion of the reactive species should lead to a chain reaction and the evaporation of the mantle. To provide the empirical data required to test this hypothesis, experiments designed to duplicate the relevant physical conditions of interstellar grain mantles have been carried out, the results of which are presented in this letter. The physical constraints required for mantle ejection and possible triggering mechanisms are discussed in connection with the experimental results.

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It is shown that, when equilibrium exists between accretion and evaporation, it is possible to derive a mean fraction f of the condensible species present in the gas. We then apply this to CO and derive the ratio $n_{\text{CO}}/n_{\text{H}_2}$ expected in clouds and discuss the role this process plays in a model cloud.

II. EXPERIMENTAL.

Since the experimental details have been described in detail elsewhere (Hagen et al. 1979), only the relevant aspects will be summarized here. Mixtures of simple gases (CO, CH₄, NH₃ and H₂O) are deposited as a thin film (0.1 - 1.0 μm thickness) onto the surface of an aluminum block cooled to 10K. In view of the high abundance of CO in the ISM and the strong H₂O ice absorption observed in the spectrum of some infrared sources, both CO and H₂O rich mixtures have been used to test the generality of the phenomenon studied. The samples are then photolyzed with vacuum U.V. radiation from an H₂-discharge lamp to simulate the U.V. radiation in space. The chemical evolution and, in particular, the production of frozen radicals is followed by infrared spectroscopy. Upon warm-up, the luminescence originating from the thermally promoted chemical reactions occurring in the sample is recorded, and, simultaneously, the pressure in a calibrated expansion chamber is measured with an ionization gauge. In the laboratory, thermal runaway in the sample is inhibited if the heat conductivity to the substrate is too large. To overcome this difficulty, a thin layer (1 μm) is first deposited and photolyzed. Two additional layers are subsequently deposited and also photolyzed. Radiation effects at the boundary between layers give rise to phonon scattering and reflection, thus reducing thermal transport across the boundary. Consequently, the heat of reaction liberated is confined and results in thermal runaway in the upper layer. In an interstellar grain mantle, the coupling to the surroundings is only by the much more inefficient process of radiation and thermal runaway should always be possible.

III. RESULTS.

Upon warm-up, all photolyzed samples give rise to pressure and luminescence behavior similar to that shown in fig. 1 for a CO rich mixture. Without photolysis, no pressure bursts or luminescence are observed. The correlation of light flashes with pressure spikes shows that they are caused by the sudden release of stored chemical energy. The main explosive event consistently occurs at ~ 27 K. Further evidence for chemically driven thermal runaway is provided by infrared studies of the band profile for the ν_2 mode

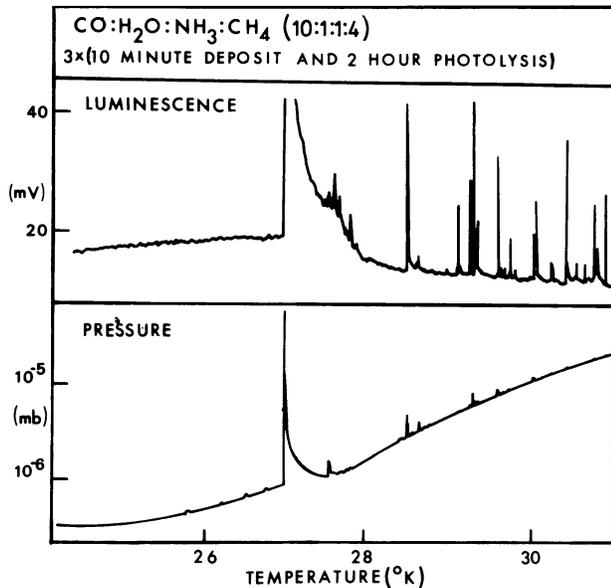


Fig. 1. Typical behavior of luminescence and pressure curves vs temperature in a layered sample.

of NH_3 , which have shown that, although the temperature of the substrate did not exceed 30K, some of the ammonia remaining after explosion was transformed from the amorphous into a metastable form, a transition which normally occurs above 70 K (Sill et.al. 1981).

Differences in the infrared absorption depths for sample molecules before and after explosion, and maximum pressure attained in the expansion chamber are used to deduce the amount of material ejected. Upon explosion, the strength of the infrared absorptions are reduced by 60 %, consistent with the ejected fraction of the sample measured as a pressure burst. Assuming the heat of vaporization to be 8.4 KJ/mol and a typical bond energy of 480 KJ/mol (5 ev), the number of reactions needed to produce the amount of energy required to vaporize the measured quantity of material is calculated. This results in a lower limit of about 10^{-2} for the radical concentration. These data are summarized in table I. Note that 60 % of the sample is ejected because the first layer is thermally coupled to the substrate. In space such an explosive event could release nearly 100 % of the mantle.

Table I. Summary of data related to figure 1.

Number of sample molecules:	$\sim 10^{20}$
Number of incident UV photons:	$\sim 2 \times 10^{19}$
Number of molecules ejected:	$\sim 6 \times 10^{19}$
Required vaporization energy:	$\sim 1 \text{ J}$
Deduced radical concentration:	$\sim 3 \times 10^{-2}$

The ratio R of the number of incident UV photons to the number of molecules in the mantle will determine where this process can take place in interstellar clouds. While, in this set of experiments $R \sim 0.2$, recent saturation experiments have shown that explosive ejection still occurs with ratios possibly as low as 0.1, implying a net radical production efficiency of at least 10 %. Finally it must be emphasized that for relative concentrations of the constituents CO, CH_4 , H_2O and NH_3 as different as (10 : 4 : 2 : 1) and (3 : 2 : 5 : 1), the temperature at which the runaway starts remains surprisingly constant at about 27 K.

IV. DISCUSSION AND ASTROPHYSICAL IMPLICATIONS.

1) *Triggering mechanism*

In order to trigger the explosive ejection of material from grains in the ISM, the triggering event must raise the temperature of the grain above 27 K for a period of time many orders of magnitude longer than the site hopping time ($\sim 10^{-12}$ sec.) for the diffusing radicals. This puts a severe constraint on the triggering mechanism. Three processes that could conceivably initiate reactions have been considered: U.V. photon -, cosmic ray -, and grain - grain collisions. The first two involve basically the same mechanism: the heat generated by the absorption of a U.V. photon in the grain or the passage of a cosmic ray through it, can raise the temperature in a small volume above the critical value of 27 K. Using a thermal diffusivity for amorphous ice of $10^{-6} \text{ m}^2 \text{ s}^{-1}$ (Smoluchowski, 1981), this temperature will drop by conduction in less than 10^{-11} second. For a radical concentration of 10^{-2} , the probability that two reactants can diffuse and react in 10^{-11} second is negligibly small. This negative conclusion is supported by the observation that, even in long duration photolysis experiments, spontaneous pressure bursts have never been observed, showing that an important constraint on the triggering mechanism is that the critical temperature must be reached in the entire grain. Then, recooling, which proceeds by radiation alone, is long enough (~ 10 sec.) to permit radical diffusion sufficient to generate supercritical grain mantles. Collisions between grains can easily satisfy this requirement provided that they have enough kinetic energy to raise the temperature from 10 to above 27 K. Assuming a heat capacity of $0.1 \text{ J g}^{-1} \text{ K}^{-1}$, a temperature increase of 17 K requires a critical (v_c) collision velocity of only 40 ms^{-1} .

2) *Accretion and photolysis*

Irradiated samples have always shown subthermal molecule ejection when the ratio R, defined in the experimental section, is greater than 0.1. This implies that, when equilibrium exists between the gas and the dust in an interstellar cloud, ejection of molecules triggered by grain-grain collisions will be effective at any point in the cloud as long as the value of R exceeds 0.1. Since the instantaneous value of R determines whether ejection will occur or not, photolysis and collision time scales are of secondary importance in the regime where equilibrium exists. Naturally, as one probes deeper into a dense cloud with no internal U.V. source, R drops and consequently, for $R < 0.1$ accretion must dominate.

3) *Equilibrium between gas and dust*

Assuming equilibrium between accretion of the gas onto grains and evaporation of the mantle following a grain-grain collision, a steady state gas density can be achieved (Greenberg, 1979). Let $n_{\text{O,C,N}}^{\text{A}}$ be the density of all the O, C and N containing condensable species which are available for the recycling process. At any time, a fraction f of these are in the gas, the remaining being in the grains. We have then:

$$n_{\text{O,C,N}}^{\text{A}} = n_{\text{O,C,N}}^{\text{g}} + n_{\text{O,C,N}}^{\text{d}} \quad (1)$$

The rate of depletion of the gas phase constituents, assuming a sticking coefficient of 1, is given by the collision rate between gas and dust:

$$\frac{d}{dt} (n_{\text{O,C,N}}^{\text{g}}) = -f n_{\text{O,C,N}}^{\text{A}} \cdot n_{\text{d}} \sigma_{\text{md}} \langle v_{\text{T}} \rangle \quad (2)$$

where n_{d} is the number density of dust grains, σ_{md} is the molecule-dust collision cross section (πa_{d}^2) with

a_d the dust radius and $\langle v_T \rangle$ is the mean thermal velocity of the gas constituents. The rate of ejection of atoms and molecules is given by the grain-grain collision rate:

$$\frac{d}{dt} (n_{O,C,N}^g)_+ = 2 (1-f) (n_{O,C,N}^A / n_d) n_d^2 \sigma_{dd} \langle v_d \rangle \quad (3)$$

where $(1-f)(n_{O,C,N}^A / n_d)$ is the number of volatiles per mantle, assumed to be totally evaporated, σ_{dd} is the dust-dust collision cross section ($\approx \pi a_d^2$) and $\langle v_d \rangle$ the average relative collision velocity which has to be greater than v_c . Under equilibrium conditions, f can be computed by equating the rates given by eq. (2) and (3):

$$f = \frac{2 \langle v_d \rangle (\sigma_{dd} / \sigma_{md})}{\langle v_T \rangle + 2 \langle v_d \rangle (\sigma_{dd} / \sigma_{md})} \quad (4)$$

It appears that, in regions where eq. (4) applies, the value of f is rather stable within the range of reasonable cloud parameters. Since the kinetic temperature in molecular clouds lies in the range 10 - 50 K, for CO, v_T is between 1 - 2 $\cdot 10^2$ m s⁻¹. The dust velocity on the other hand, is uncertain, and although a theoretical derivation of the dust-dust collision speed in a turbulent medium has been developed, it applies only in the subsonic regime (Völk et al. 1980). A formal extrapolation of this theory using a turbulent gas speed of 10³ m s⁻¹ gives $v_d = 50$ m s⁻¹. Since turbulent gas speeds of 1 - 2 km s⁻¹ are common (Larson, 1981), v_d is likely to be higher than the critical speed of $v_c = 40$ m s⁻¹. Evaluating f using $v_T = 10^2$ m s⁻¹ and either $v_d = v_c$ or $v_d = v_T$ one finds that

$$0.4 < f < 0.7 \quad (5)$$

This suggests that in regions where this process occurs we may expect about 60 % of the available condensibles to be present in the gas, the rest in the mantle. It is perhaps obvious but important to note that, since explosions take place in the mantles which accreted in the cloud itself, the average mantle radius is larger in these regions than in the diffuse cloud medium, consistent with observations. At dust velocities $v_d = 10^2$ m s⁻¹ the time scale for grain-grain collisions is between 10^{4.5} and 10^{5.5} years at densities of 10⁵ and 10⁴ cm⁻³ respectively. These time scales are short enough compared with the mean cloud life time (a few times 10⁷ years) that a steady state between gas and dust will be approached.

In order to estimate the role this process plays in determining the ambient density of condensibles in a molecular cloud, the steady state ratio of CO to H₂ has been calculated. CO has been chosen because of its abundance, detectability and relative stability against photodissociation. Moreover, it is reasonable to assume that the net number of CO molecules remains approximately constant in the recycling process, since if CO combines with other atoms or molecules, most of the product molecules, when ejected are likely to be photodissociated in a relatively short time, revealing the original CO. The CO to H₂ ratio is calculated assuming that 20 % of all the carbon is available for recycling; this number is deduced from the measured depletion of carbon in the diffuse cloud medium (Morton, 1974) and is taken as representative of the total availability of carbon in the gas. Assuming that all this carbon is in CO, we derive $n_{CO}/n_{H_2} \sim 8 \cdot 10^{-5}$ for an f value of 0.6. This compares favorably with the observed values for typical dark clouds (Snell, 1981).

The accretion/explosion process is applicable in all cloud regions where the UV penetration is sufficient to satisfy the necessary and sufficient condition of $R > 0.1$, and triggering is possible. Then eq.

(4) shows that the fraction f and hence, the ratio n_{CO}/n_{H_2} will not change very much provided that the dynamic quantities v_T and v_d do not vary. For inhomogeneous interstellar grains, there exists the possibility that some of the mantle material will be ejected as small solid particles thus affecting the value of f . However such small particles will most likely evaporate as a result of temperature fluctuations due to the absorption of U.V. photons (Greenberg, 1978).

It will now be demonstrated how this process can determine the density of condensibles across a cloud such as L134N. Using the model parameters given by Snell (see table II), the observed properties of such a cloud and $A_{UV} = 2A_V$, R has been computed. Assuming $n_{H_2} = 10^4$ within a central radius of 0.1 pc, R drops below the critical value only for $r < 0.04$ R_{cloud}. Consequently, for some dark clouds, a quasi steady state can exist throughout the whole cloud as generally observed. On the other hand, for central densities of larger than 10⁴, in the absence of internal UV sources, accretion should dominate towards the center. This type of behavior is observed by Wooten et al. (1978) in high density clouds.

Table II. Cloud parameters used to model L134N (from Snell, 1981)

$$\begin{aligned} n_{H_2} &= n_0 R^{-2} ; n_0 = 1.1 \times 10^2 \text{ cm}^{-3} \text{ pc}^{-2}. \\ R_{\text{cloud}} &= 1 \text{ pc} ; T_K = 10 \text{ K} \\ M_{\text{cloud}} &= 100 M_\odot ; A_V \text{ (at center)} = 7 \end{aligned}$$

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