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Infra-red Molecular Line Emission from Grain Surfaces in Dense Clouds

L. J. Allamandola and C. A. Norman

Laboratory Astrophysics, Huygens Laboratorium, Wassenaarseweg 78, 2300 RA Leiden, The Netherlands

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Summary. We examine the possibility of observing the radiative decay of the lowest vibrational state of a number of interstellar molecules embedded in grains that have been vibrationally excited by either photon absorption in the visible to ultraviolet range and subsequent relaxation, radical reactions, or molecule-grain collisions. Data from recent laboratory experiments indicate that in low temperature solids the transfer of energy from vibrational modes into lattice phonons can be inefficient. The predominant mode of decay may then be radiative and we list a number of molecules which may be observable in future infra-red experiments.

Key words: interstellar grains — infra-red astronomy — molecular lines

I. Introduction

Recent laboratory experiments—(Allamandola et al., 1977, Dubost et al., 1976, Legay, 1977; plus references) have shown that the excited vibrational states of a number of simple molecules embedded in a low temperature matrix do not quickly decay into low-lying phonon modes of the matrix but tend to relax more slowly, permitting radiative decay in certain cases. These results have an interesting application in the case of interstellar dust clouds that we shall examine here. We consider three possible mechanisms of vibrational excitation occurring within the complex mantle of interstellar dust grains: A) visible or ultraviolet photon absorption and subsequent relaxation leaving the molecule vibrationally excited in the ground electronic state; B) radical reactions that form electronically excited molecules that will also relax to vibrationally excited ground state molecules; and C) collisions between interstellar grains and molecules which can, in some circumstances, excite the lowest lying vibrational state of some typical interstellar molecules. We then examine the possibility that these vibrationally excited molecules radiatively decay rather than decay into the phonon modes of the grain. We give a list of molecules that are candidates for observation in future infra-red experiments.

Send offprint requests to: L. J. Allamandola

II. Excitation Mechanism

We shall consider the three excitation mechanisms listed above in turn.

A) Visible-Ultraviolet Absorption

When a molecule is electronically excited by a visible or ultraviolet (V – UV) photon it can undergo a large number of processes of which the most important are dissociation, fluorescence, phosphorescence, internal conversion and intersystem crossing (Calvert and Pitts, 1966). These processes ultimately leave the majority of molecules vibrationally excited in the ground electronic state.

We shall assume that of all the UV photons (~1000 –3000 Å) hitting grains within a cloud a fraction $\alpha^{\rm ph}$ of these photons are absorbed by internal states of molecules located in the mantle of the grains. A typical effective collision rate $R^{\rm ph}_{\rm coll}$, between photons and grains is

$$R^{\rm ph}_{\rm coll} = \alpha^{\rm ph}\, n_{\rm ph}\, \sigma_{\rm d}\, c\, n_{\rm d}\, e^{-\tau} \tag{1}$$

$$= \alpha^{\rm ph}\, e^{-\tau}\, \xi\, n_{\rm H}\, n_{\rm ph}\, \sigma_{\rm d}\, c \tag{2}$$

which can be evaluated using:

$$R^{\rm ph}_{\rm coll} = 3\,10^{-11} \left(\frac{\alpha^{\rm ph}}{10^{-1}}\right) \left(\exp\left(-\frac{\tau}{1}\right)\right) \left(\frac{n_{\rm ph}}{10^{-2}\ {\rm cm}^{-3}}\right) \cdot \left(\frac{\sigma_d}{10^{-9}\ {\rm cm}^2}\right) \left(\frac{\xi}{10^{-12}}\right) \left(\frac{n_{\rm H}}{10^3\ {\rm cm}^{-3}}\right) {\rm cm}^{-3}\ {\rm s}^{-1} \tag{3}$$

Where $n_{\rm H}$ is the molecular hydrogen density in the cloud, $n_{\rm ph}$ is the photon number density outside the cloud, τ is a mean optical depth of the region we are considering internal to the cloud, σ_d is the geometrical cross section

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Table 1*. Vibrational lifetime for some simple species trapped in low temperature matrices

Molecule	T K	ν cm^{-1}	Lattice	Vibrational Relaxation Time s	Radiative Decay Time s
Non-rotators					
CO	8 - 24	2138 - 1937	Ne, Ar	> 0.1	.033
			CO	> .02	
NO	8	1841 - 1701			
			Ar	> .05	.076
C_2^-	14-32	1777	Ar	.002-.02	Forbidden
			Kr	.016-.3	Transition
			Xe	.012-.16	
			N_2	.0008-.008	
Rotators					
OH	4.2	2784	Ne	2.5×10^{-6}	
NH	4.2 - 25	2977	Ar	8×10^{-7}	
NH_3	8	974	Ar	> $.5 \times 10^{-6}$	.066
		970	N_2	1.5×10^{-5}	

* All data except for C_2^- from Legay (1977) and references therein. C_2^- from Allamandola et al. (1977)

of the dust grain and the number density of grains n_d is equal to $\xi\, n_H$.

B) Radical Reactions

Usually, when a radical adds to another species, a new molecule is formed in an excited electronic state. These daughter molecules can then undergo the same processes considered in *A*) above. Thus, in a general sense, the contribution of radical reactions can be considered under dissociation. However, we treat it separately because of the possibility that individual radicals previously formed in the gas phase may stick to the grains. There is also the possibility that in dissociation one photon can form more than one radical which, in turn, can result in multiple reactions; (for example $C_2H_5OH + h\nu \rightarrow C_2H_5 + OH$). The effective radical reaction rate R^{ch} is given by

$$R^{ch} = \eta^{ch}\, \alpha^{ch}\, n_{ph}\, \sigma_d\, n_d, \tag{4}$$

which evaluated becomes:

$$R^{ch} = 3\, 10^{-12} \left(\frac{\eta^{ch}}{1}\right) \left(\frac{\alpha^{ch}}{10^{-2}}\right) \left(\frac{n_{ph}}{10^{-2}\ \mathrm{cm}^{-3}}\right) \left(\frac{\sigma_d}{10^{-9}\ \mathrm{cm}^{+2}}\right) \cdot \left(\frac{\xi}{10^{-12}}\right) \left(\frac{n_H}{10^3\ \mathrm{cm}^{-3}}\right) \mathrm{cm}^{-3}\ \mathrm{s}^{-1} \tag{5}$$

α^{ch} is the efficiency of radical formation by a photon and η^{ch} is the fraction of radicals which ultimately yields molecules in the vibrational states under consideration.

C) Molecule-Grain Collisions

We shall assume that when a molecule hits a grain one can define an efficiency factor α^{coll} which is the fraction of collisions which lead to vibrational excitation of the internal states of the molecule and/or a molecule in the grain. In a typical cloud the amount of collisional energy depends on the collision rate between the molecular species of interest and the grains. The effective collision rate R^{coll}, for a molecular species of mass m_s, number density n_s in a cloud of radius R is

$$R^{coll} = \alpha^{coll}\, \xi\, n_H\, \sigma_d\, n_s\, v_{th,s} \tag{6}$$

where $v_{th,s}$ is the r.m.s. velocity of the molecules. R^{coll} can be written as:

$$R^{coll} = 10^{-13} \left(\frac{\xi}{10^{-12}}\right) \left(\frac{n_H}{10^4\ \mathrm{cm}^{-3}}\right)^2 \left(\frac{\sigma_d}{10^{-9}\ \mathrm{cm}^{+2}}\right) \cdot \left(\frac{v_{th,s}}{10^4\ \mathrm{cm\ s}^{-1}}\right) \left(\frac{x_s}{10^{-4}}\right) \left(\frac{\alpha^{coll}}{1}\right) \mathrm{cm}^{-3}\ \mathrm{s}^{-1} \tag{7}$$

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Table 2. Some simple interstellar molecules+ and their lowest lying fundamental modes of vibration

Molecule	Mode	ν^* cm^{-1}
CO_2	ν_2	667
CH_3CN	ν_7	1124
	ν_4	918
	ν_8	380
H_2CO	ν_6	1167
	ν_5	1280
N_2O	ν_2	589
NO_2	ν_2	750
HCN	ν_2	712
CH_3OH	ν_8	270
NH_3	ν_2	931, 968
H_2C_2	ν_5	729
C_2H_4	ν_4	611
	ν_7	949
CH_4	ν_4	1306
H_2O	ν_2	1595

* All values are gas phase values and taken from Herzberg (1945) or Nakamoto (1963)

\+ CO_2, CH_4, N_2O and NO_2 have not been observed in the interstellar environment; however the observation of similar molecular species strongly suggests the presence of these and others

where x_s is the abundance of species relative to molecular hydrogen. We shall now examine the collisional energy in two distinct cases.

Case I. This case represents the situation in which the grain is effectively stationary and the molecule, possesing kinetic energy corresponding to a temperature between 10 and 100 K, strikes the grain. The energy generated by this collison is absorbed either by the molecule striking the grain or an acceptor molecule in the grain and is given by

$$E_{\text{coll}}=1/2\, m_s\, v_{th,s}^2=kT=8.6\,10^{-3}\left(\frac{T}{100\,\text{K}}\right)\text{eV}. \qquad (8)$$

For 100 K clouds this yields energies on the order of 0.01 eV (70 cm^{-1} for NH_3).

Case II. We now consider clouds or localised regions of clouds in which the grains are accelerated to higher velocities. For example, in order to excite the first vibrational level in ammonia a relative velocity of $1.2\,10^5$ cm s^{-1} is needed. These velocities could be caused by processes such as radiation pressure, cloud collision or loose coupling (ambipolar diffusion) between the neutral gas and the ionized component to which the charged grains are tied.

Thus, if the velocity of the grain with respect to the molecule is of the order of 10^4 cm s^{-1} (Case I), the energy generated upon collision is ~ 70 cm^{-1} which is on the order of lattice phonon modes likely to exist in the grain. This implies that such collisional energies will be absorbed by the grain. However, if the velocity of the grain with respect to the molecule is $\sim 7\,10^4$ cm s^{-1}, then a vibrational mode close to 1000 cm^{-1} may be excited. We have assumed this is the case in constructing Table 4.

III. Radiative Decay and Observable Lines

Until recently it was believed that the vibrational lifetimes of molecules trapped in low temperature solids lay in the pico-second range and that the primary decay channel was into the phonon modes of the lattice. However, it is now known that this decay channel may not be efficient and that, depending on the system and energies involved, the molecule can possess a vibrational lifetime ranging from microseconds to seconds (Legay, 1977). This range encompasses the normal radiative lifetime for molecules possessing allowed infra-red transitions. It appears that the most important feature for deactivation is the presence or lack of a suitable acceptor to take this energy and couple it into the lattice. The smaller the frequency mismatch between acceptor and donor, the more efficient the coupling and the faster the decay. Thus, if only inefficient acceptors are present, a fraction of the molecules possessing allowed low frequency infra-red transitions will radiatively decay before they undergo either phonon or rotational decay. Rotational decay will only dominate for very small molecules. See Table 1 for a partial list of measured lifetimes.

From Table 1 we see that certain vibrationally excited molecules radiatively decay in a solid. These are molecules whose lowest vibrational modes are sufficiently greater than the phonon levels (100 cm^{-1} or less) so that the decay into phonons is inhibited by the frequency mismatch, and which are not sufficiently small to have a rotational decay channel. Note that the molecules which are known to rotate in matrices possess much shorter vibrational lifetimes than do those which have their rotation hindered by the lattice.

Table 2 lists a few simple interstellar molecules and their lowest lying vibrational modes. We note here that, although it has not yet been observed, CO_2 is listed here since it is difficult to imagine that CO is present in such great abundance without the presence of CO_2 ; and it is known that O atoms colliding with CO on a surface combine with little or no activation energy to form CO_2 (White, 1977). Similarly, we include CH_4, N_2O and NO_2.

In Table 3 we have listed some pertinent properties of a few interstellar molecules which, if vibrationally excited and not efficiently coupled to the internal grain modes, are likely to possess sufficiently long vibrational lifetimes to allow them to relax radiatively.

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Table 3. Infra-red frequencies, relaxation times and abundances for the molecules considered

Molecule	Mode	ν* cm^{-1}	λ μm	Abundance ($n_H = 10^4$ cm^{-3}) cm^{-3}	Relaxation times in solids when available. (see Table I) s
N_2O	ν_2	(591) 588.8	16.98	~ 10^{-8} (?)	
NO_2	ν_2	(749) 648	15.43	~ 10^{-8} (?)	
CO_2	ν_2	(654) 667 cm^{-1}	14.9	10^{-4} (?)	
HCN	ν_2	(720) 712 cm^{-1}	14.05	10^{-3}	
H_2C_2	ν_5	729	13.71	10^{-4} (?)	
NH_3	ν_2	931 (957)	10.74	10^{-2}	> 5×10^{-7}
		968 (980)	10.33		1.5×10^{-5}
H_2CO	ν_6	(1173) 1167(s)	8.569	10^{-4}	
	ν_5	(1175) 1280(s)	7.813		
CO	ν	(2138) 2150	4.65	1	> 0.1

* Values in parentheses are those observed when the species is in a low temperature solid

We shall now derive estimates of the total intensity in the line in the three distinct cases under consideration. The total luminosity induced by any of these processes in a cloud of radius R is

$$L = h\nu\, R^{(i)}\, \tfrac{4}{3}\pi R^3 \text{ erg s}^{-1} \tag{9}$$

where ν is the frequency of the infra-red line corresponding to the specific low lying vibrational state in question. Of course, $R^{(i)}$ (where (i) = coll, ph, ch) varies from case to case. We have used the fact that the time between the excitation of a particular molecule by photon-grain or molecule-grain collision is very much longer than the radiative decay of the excited vibrational states. The total intensity in the line at a distance d from the source is

$$I = 1/3\, h\nu\, R^{(i)}\, R\left(\frac{R}{d}\right)^2 \text{ erg s}^{-1}\text{ cm}^{-2}. \tag{10}$$

In the case of photon pumping (assuming that only one infra-red photon is produced per ultra violet photon absorbed) using Equation (1) the total intensity can be written as:

$$I^{\rm ph} = 1/3\, h\nu c\, \alpha^{\rm ph}\, n^{\rm ph}\left(\frac{R}{d}\right)^2 (\tau e^{-\tau}) \tag{11}$$

$$= 2\; 10^{-17}\left(\frac{\nu}{1000\text{ cm}^{-1}}\right)\left(\frac{\alpha^{\rm ph} n_{\rm ph}}{10^{-3}\text{ cm}^{-3}}\right) \cdot \left(\frac{R/d}{10^{-2}}\right)^2 \left(\frac{\tau e^{-\tau}}{1}\right) \text{W cm}^{-2} \tag{12}$$

where τ is the optical depth to the UV given by $\tau = n_d\, \tau_d\, R$ and where it has been explicitly assumed that the fluorescing grains are also those that are absorbing the UV. The above formula could be easily modified to include other cases by using $\tau_f\, e^{-\tau_{\rm ex}}$ where τ_f is the optical depth in the fluorescing grains and $\tau_{\rm ex}$ is the mean optical depth giving the total UV extinction.

The expression $\tau e^{-\tau}$ can be assumed to be of order unity not only in the case where $R \approx 1\,(n/10^3\text{ cm}^{-3})^{-1}$ pc, but also in the case of an optically thick cloud irradiated either by an external UV source such as the interstellar radiation field or a shell irradiated by an internal source such as that generated during star formation. In the case of shells, the volume is not $(4/3)\,\pi R^3$ but $4\pi R^2\, \Delta R$ and $\tau = n_d \sigma_d\, \Delta R \approx 1$ where ΔR is the shell thickness. The clouds are always assumed to be optically thin to the middle infra-red. Thus, the intensity of fluorescence is proportional to the product of the pumping UV photon density $n_{\rm ph}$ and the solid angle $(R/d)^2$ subtended by the fluorescing region. Therefore objects of smaller angular size will need larger photon densities, probably inter-

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Table 4. Infra-red line intensity estimates at the top of the atmosphere

Molecule	Rel.Velocity required to excite transition 10^4 cm s^{-1}	R^{coll} cm^{-3}s^{-1}	I^{coll} W cm^{-2}	R^{ch} cm^{-3}s^{-1}	I^{ch} W cm^{-2}	R^{ph} cm^{-3}s^{-1}	I^{ph} W cm^{-2}
N_2O	6.0	10^{-17}	1.8×10^{-20}	3×10^{-12}	3.9×10^{-17}	3×10^{-11}	3.9×10^{-16}
NO_2	5.9	10^{-17}	1.8×10^{-20}	3×10^{-12}	4.2×10^{-17}	3×10^{-11}	4.2×10^{-16}
CO_2	6.0	10^{-13}	1.8×10^{-16}	3×10^{-12}	4.4×10^{-17}	3×10^{-11}	4.4×10^{-16}
HCN	7.9	10^{-12}	1.8×10^{-15}	3×10^{-12}	4.7×10^{-17}	3×10^{-11}	4.8×10^{-16}
H_2C_2	8.5	10^{-13}	1.8×10^{-16}	3×10^{-12}	4.8×10^{-17}	3×10^{-11}	4.8×10^{-16}
NH_3	12	10^{-11}	1.8×10^{-14}	3×10^{-12}	6.1×10^{-17} 4.4×10^{-17}	3×10^{-11}	6.1×10^{-16} 6.4×10^{-16}
H_2CO	9.6 10	10^{-13}	1.8×10^{-16}	3×10^{-12}	7.7×10^{-17} 8.5×10^{-17}	3×10^{-11} 3×10^{-11}	7.7×10^{-16} 8.5×10^{-16}
CO	13	10^{-9}	1.8×10^{-12}	3×10^{-12}	14.2×10^{-17}	3×10^{-11}	14.2×10^{-16}

nally generated, than, say, nearby dense molecular clouds that could have observable fluorescence induced by the interstellar UV radiation field.

In the case of chemical pumping one finds the intensity takes the form

$$I^{ch}=2\,10^{-18}\left(\frac{\nu}{1000\ \mathrm{cm}^{-1}}\right)\left(\frac{\alpha^{ch}}{10^{-2}}\right)\frac{\eta^{ch}}{1}\cdot\left(\frac{n_{ph}}{10^{-2}\ \mathrm{cm}^{-3}}\right)\left(\frac{R/d}{10^{-2}}\right)^2\mathrm{W\ cm}^{-2}. \quad (13)$$

In the collisional case the analysis is as follows. The total luminosity induced by molecule grain collisions where the energy of the transition $h\nu\approx E_{coll}$ is

$$L=\alpha^{coll}E^{coll}\,R^{coll}\,\tfrac{4}{3}\,\pi R^3\ \mathrm{erg\ s}^{-1}. \quad (14)$$

We have used the fact that the time between collisions is very much greater than the radiative lifetime. The total intensity in the line at a distance d from the source is

$$I=1/3\,\alpha^{coll}\,E^{coll}\,R^{coll}\,R\left(\frac{R}{d}\right)^2\ \mathrm{erg\ s}^{-1}\ \mathrm{cm}^{-2}. \quad (15)$$

The results for specific molecules are given in Table 4 where we have assumed $\eta_H=10^4$ cm^{-3} and $R=1$ pc.

The excitation efficiencies α^{ph}, α^{ch} and η^{ch} are uncertain and vary from molecule to molecule. The values we have used are probably within an order of magnitude of the correct values in most cases. The values adopted are discussed in the Appendix.

IV. Discussion

The molecules listed in Table 4 have been chosen because their lowest lying vibrational fundamental modes possess strong infra-red activity and lie well above the acoustic phonon level, thus promoting the inefficient coupling between the fundamental vibration of the molecule and acoustic phonons of the grain. Using the model presented here we calculate that the intensities of these lines lie close to or above the current 10^{-17} W cm^{-2} detection limit of present day IR telescopes (Wolman et al., 1976). Some interstellar species are relisted in Table 5 with vibrational fundamental wavelengths (corrected for low temperature solid shifts) as observed in absorption, and transparencies at those wavelengths as graded by Allen (1975).

Table 5 shows that the lines of the molecules with lower frequencies N_2O, NO_2, CO_2, HCN and H_2C_2 occur in regions of either "low" or "no" sky transparency. If the process of collisional excitation is possible, these lower frequency lines are the ones most likely to be observed since they require less kinetic to vibrational energy transfer upon collision. Because of estimated abundance effects the two NO compounds N_2O and NO_2 do not emit enough power to be detected.

Only three lines, the two due to the umbrella mode of ammonia and one due to the out of plane bend in formaldehyde, lie in a "fair" sky transparency region. The ammonia should be the strongest emitter; however, since it falls in the small molecule class, it has a very fast

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Table 5.

Species	Wavelength μm	Wavelength in solid μm	Sky transparency	Solid references
N_2O	16.98	16.92	No window	Meyer (1971)
NO_2	13.33	13.35	No window	Hallam (1973)
CO_2	15.0	15.5	No window	
HCN	14.05	13.88	Low	Hallam (1973)
H_2C_2	13.71	13.15	Low	Bottger and Eggers (1967)
NH_3	10.74	10.45	Fair	Abouaf-Marquin et al. (1970)
NH_3	10.33	10.20	Fair	Abouaf-Marquin et al. (1970)
H_2CO	8.57	8.52	Fair	Harvey and Ogilvie (1962)
H_2CO	7.81	8.51	Low	Harvey and Ogilvie (1962)
CO	4.65	4.68	Rather low	Dubost (1976)
CO_2	4.26	4.29	Rather low	

relaxation rate due to an allowed rotational decay channel in low temperature matrices. This leaves only the formaldehyde line at 8.57 μ a likely candidate for ground based observation.

In general, since all of these lines are weak and 10–50 cm^{-1} wide (0.2–0.5 μm at ~15 μm), instruments with resolution poorer than ~10 cm^{-1} would have difficulty in measuring them. Of course, instruments with resolution better than 10 cm^{-1}, spectral band width on the order of 200 cm^{-1}, and sensitivities on the order of 10^{-17} W cm^{-2}, would be able to detect these lines.

Finally, this entire model assumes a great deal about the properties of the grain mantle. Implicit in all the above is the idea of a core-mantle type of grain with a temperature in the range of 10–50 K and a core radius on the order of 0.05 μm (Greenberg and Hong, 1974). The nature of the mantle is such that it is sufficiently thick to decouple the oscillating dipole excited near the surface from the optical phonons of the "silicate core" presumably consisting of silicon and magnesium "oxides". Since a mantle with a radius of 100 Å should be more than thick enough to do this, currently acceptable mantle thicknesses of the order of 1000 Å or more provide sufficient "insulation" from the core. Of course the mantle itself should be relatively free of suitable acceptors which can efficiently couple the quantum of vibrational energy into the mantle lattice phonon band.

V. Conclusion

We have shown that under plausible conditions a number of the molecules listed in Table 4 may be observable via their infra-red line emission. There are three major constraints on the intensity of the line emission:

(i) We have assumed in evaluating the line intensities in Table 4 that the optical depths of the clouds at frequencies we are considering are of order unity.

(ii) The coefficients α which gave the conversion efficiency to vibrational energy were all estimated. The coefficient α^{coll} is the most uncertain and molecular beam experiments may be able to give an empirical value for α^{coll}; but at the present time the value adopted seems reasonable (see Appendix).

(iii) The experiments referred to in the text show that there is competition between radiative and non-radiative decay channels. In particular, if the solid in which the molecule is embedded has a lattice mode into which the molecular vibrational state can decay, then such radiative transitions will be unlikely.

Observations of such lines would tell us much about the structure of the mantle of the grains in these dense molecular clouds. If the mantle contains species that can act as efficient acceptors (very roughly an acceptor possessing a low lying fundamental that is efficiently coupled to the phonon modes and lying within say 50 Å of the vibrating molecules), then the decay into the acoustic phonon band will dominate the radiative decay and most of this energy will ultimately come out in the far infra-red (250–33 cm^{-1}). However, if the core-mantle picture of a grain is correct and the mantle contains no suitable acceptors, then the picture presented in this paper will be valid and molecular line emission can be expected in the middle infra-red (4000–250 cm^{-1}).

In this paper we have restricted ourselves to molecular lines observed from molecules embedded in grains but we also expect that gas phase molecules will also have these infra-red lines excited by chemical reaction and UV absorption. The lines in the grains can be identified as such because they will be broadened and slightly shifted (Hallam, 1973).

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Appendix: Excitation Efficiencies

We shall now give the reasons for our choice of the excitation efficiencies used in the text.

1. α^{ph}—The fraction of photons hitting the grain which are absorbed by molecules in the grain is taken to be 0.1. Using Beer's law and the absorption spectrum of ammonia, the fraction of 80,000 cm^{-1} (1250 Å) photons absorbed in a 200 Å thick mantle of solid ammonia is calculated to be 0.44. The fraction of light absorbed by the molecules considered lies in the range 0.5–0.9. The extinction coefficients used are taken from Robbins (1974 and 1975). A factor which could significantly enhance α^{ph} is the anticipated production of more than one IR photon per pumping UV photon. However, to compensate for uncertainties in mantle composition, thickness and density which would tend to lower these

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values, we choose $\alpha^{ph}=0.1$, a value that may be somewhat pessimistic.

2. α^{ch}—The combined efficiency of radical formation by photons and stabilisation in the grain is taken to be one tenth of the 10% of the incident UV flux we consider absorbed by the mantle. This number may appear pessimistic in view of the fact that, in the gas phase photolysis of water "... the primary quantum yield of hydrogen atom formation is near unity", and in the case of NH_3 "The quantum yield of NH_3 disappearance at 1849 Å may approach unity at low pressure"—Calvert and Pitts (1966 pp. 200, 204). Since we are dealing with photochemical processes occurring in a low temperature solid, the site in which a molecule rests can act as rigid cage adding a steep repulsive term to the interatomic potential for separations greater than the site radius. This can drastically reduce the quantum efficiency for dissociation (Bass and Broida, 1960; Hallam 1973 and Meyer, 1971).

3. η^{ch}—We have chosen the fraction of radicals which ultimately yield molecules in a vibrationally excited state to be unity. Radicals react with little or no activation energy (Meyer, 1971 p. 21). Since radicals formed in the mantle will frequently encounter hydrogen atoms during the lifetime of the grain, each radical will have ample opportunity to react. That these radical reactions occurring in low temperature solids do indeed lead to vibrationally excited molecules in the ground state can be seen from the recent work of Long and Pimentel (1977), Smardzewski and Lin (1977) and Fournier, Lalo, Deson and Vermeil (1977). In these experiments atoms (radicals) such as S, C and O are condensed with molecular reaction partners such as O_2, H_2S and CO in an inert matrix at approximately 10 K. As the sample is slowly warmed a few degrees (allowing limited migration to take place), UV – VIS emission is observed which originates in the upper electronic state of the product molecules formed from the reaction of the radicals and molecules. The fine structure of this emission clearly shows that most of the molecules are left vibrationally excited in the ground electronic state.

4. α^{coll}—The fraction of energy generated by a molecule-grain collision which is absorbed by a vibrational state of the molecule is taken to be unity. The molecular beam experiment of Jones, Wendell and Koski (1977) shows that, as the relative velocity of gaseous reactants is increased, increasingly higher vibrational levels are efficiently populated. Although it is not possible to obtain a quantitative efficiency from this experiment, the spectra presented clearly show that as higher vibrational levels are populated their emission intensity is equal to or greater than the $v=0$ intensity. This implies that at least half of the molecules formed in the more energetic collisions are born in the appropriately higher vibrational level suggesting that the conversion of kinetic to vibrational energy is quite efficient in this case. Since the sticking coefficients for these molecules should be on the order of 0.8 we have somewhat optimistically chosen $\alpha^{coll}=1$.

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Note added in proof: Using the results of this paper, we have identified lines of H_2O, CH_4, NH_3 and other simple molecules in the infra-red spectrum of NGC 7027 (Allamandola and Norman 1978, *Astron. Astrophys.* **63**, 23).

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