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On the Middle Infra-red Fluorescence and Absorption of Molecules in Grain Mantles

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Summary. Evidence supporting the assignment of the middle infra-red emission lines present in a number of objects to vibrationally excited grain mantle molecules is presented. The width of the unusually broad features at 6.2 and 11.3 μm are consistent with two broad features of water in the ice form present in the regions studied; the 18 cm^{-1} breadth of the 3.3 μm feature is shown to match that of methane in a solid at 32 ± 7 K and the absence of even rough similarity between the published spectra and the *P* and *R*-like structures expected from gas phase molecules provide the strongest arguments. We propose that the temperature of the grain mantle can be obtained from the breadth of the 3.3 μm methane line. Using a UV pumping model we conclude that, in general, these features originate in a cold fluorescing region associated with a local ultra-violet source. The depth and thickness of this region varies substantially from object to object. This explains why one should not expect a strong correlation between line intensity and, say, visual extinction. Estimates of absorption strengths, with the exception of those for ice bands, are shown to be just below current observational capabilities.

Key words: infra-red astronomy – ultra-violet pumping – interstellar grain mantles

I. Introduction

A wide variety of astrophysical objects exhibit many broad emission features in the middle infra-red which, until recently, have been classified as unidentified (Merrill, 1977). We have assigned a number of these to the fluorescence of vibrationally excited molecules in grain mantles (Allamandola and Norman, 1978a, hereafter Paper I). Three possible excitation mechanisms were considered to occur within the complex mantle of interstellar dust grains: A) visible-ultraviolet photon absorption to an excited electronic state with subsequent relaxation leaving the molecule vibrationally excited in the ground electronic state; B) radical reactions that form electronically excited molecules which can also produce vibrationally excited molecules as in A; and C) collisions between interstellar grains and gas phase molecules which may excite the lowest lying vibrational states. It was found that visible-ultra violet photon absorption was the most generally efficient excitation mechanism (Allamandola and Norman, 1978b, hereafter Paper II, see also erratum in this issue).

In this paper we expand our previous discussion to explain in detail the spectral evidence that supports this model. Most of the objects showing the fluorescence phenomenon are considered. In addition, we demonstrate that it may eventually be feasible to obtain the temperature of the fluorescing grain mantles directly from the width of the methane line with an accuracy of a few degrees. Properties of the fluorescing grain mantles and of their environment are inferred from the strengths and widths of the emission lines. The question of why these features are seen in emission and not absorption is discussed. Using the specific model of UV photon pumping of the fluorescing molecules it is possible to explain the characteristic features of the IR spectra in the objects that have been observed to date. It is shown that even an F star, a relatively weak UV source, may be capable of pumping this fluorescence. Finally we speculate on the possibility that the unidentified diffuse interstellar absorption bands may be due in part to radicals frozen in grain mantles.

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II. Infra-red Emission Features

We discuss the infra-red emission features in terms of their general appearance and characteristics such as line shapes, breadths and positions. The spectrum of the planetary nebula NGC 7027 is used throughout this discussion since it possesses one of the richest and best studied spectra in this region (Russell et al., 1977a; Grasdalen and Joyce, 1976). The contents of this discussion should be applicable to planetaries, galaxies, H II regions and other objects exhibiting these features.

a) Discussion of the Infra-red Emission Features of NGC *7027 as due to Molecules in Grain Mantles*

The features in the spectrum of NGC 7027 which clearly stand out against the odd shaped background are the "silicate-like" absorption at about 10 μm and the striking emission lines (Gillett et al., 1975a, b and Willner et al., 1977). The positions, intensities, and half widths of these lines as measured by hand from the published spectrum of Russell et al., 1977a, are listed in Table 1. From this listing it is clear that 4 out of the 18 measurable linewidths are significantly broader than the resolution element which holds for that particular region of the spectrum. These have been starred in the table.

A number of possible emission mechanisms have been considered for these lines (see for example Russell et al., 1977a, b; Grasdalen and Joyce, 1976). However Merrill (1978) summarized the situation with "The features remain tantalizingly unidentified". More recently Dabrowski and Herzberg (1978a, b) very tentatively identified some of these features as due to the inverse predissociation spectrum of HeH^+. While Black (1970) has done

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Table 1. Wavelength, intensities, linewidths, and instrumental resolution of the features in the spectrum of NGC 7027

line λ(μm)	intensity (10^{-16} W/cm^2 μm^{-1})	linewidth FWHH$^+$(cm^{-1})	resolution[a] (cm^{-1})
2.17		127	69
2.30	0.05		
2.43		102	62
2.92			
3.09	0.7	74	49
3.3*	4.5	118(18)	46(7)
3.4	1.3		
3.77		65	40
4.05			
4.49		50	33
4.65	9.0	59	32
5.23	2.0	61	29
5.39	2.0	23	28
5.61	8.0	29	27
5.90		29	23
6.20*	5.5	62	25
6.98*	1.3	67	22
7.3			
7.7	3.5	} difficult	20
7.8		} to define	19
8.6	1.5	29	17
8.9		16	17
10.5	3.5	15	15
11.3*	6.0	34	13
12.8	1.3	14.7	12

+ FWHH. Full width at half height as approximated by us from the published spectra.

a resolution: 2–4 μm, $\Delta\lambda/\lambda = 0.015$, Merrill et al., 1975. 4–14 μm, $\Delta\lambda/\lambda = 0.015$, Russell et al., 1977a. 3.3 μm high resolution measurement, Grasdalen and Joyce, 1976.

* Features clearly broader than resolution element. 3.3 μm, Grasdalen and Joyce, 1976; 6.20 μm, Russell et al., 1977a; 11.3 μm, Gillett et al., 1973, Gillett et al., 1975b, Aitken and Jones, 1973.

Table 2. Suggested assignments of the infra-red emission features in the spectrum of NGC 7027

Features λ(μ)	Assignments Previous	Note	Paper I, Class 1
2.17	B_γ	b	
2.30			CO (overtone)
2.43	H_2 Q(1), Q(3)	d	
2.92			NH_3
3.09	? HeII	c	H_2O, C_2H_2
3.30			CH_4
3.40			
3.77	Pf_γ	b	
4.05	B_α	b	
4.49	? {MgIV},{ArVI}	c	
4.65			CO
5.23			
5.39			NO
5.61	? {MgV}	c	
5.90			
6.20			H_2O, NH_3
6.98	{ArII}	c	
7.3			C_2H_2
7.7			CH_4
7.8	{ArV}	a,c	
8.6			
8.9	{ArIII}	a	
10.5	{S IV}	a	NH_3
11.3			H_2O
12.8	{NeII}	a	C_2H_2

a: Gillett et al., 1973; b: Merrill et al., 1975; c: Russell et al., 1977a; d: Treffers et al., 1976.
Paper I: Allamandola and Norman, 1978a.

calculations which show that this, as well as OH, may be present in sufficient concentration to explain the 3.3 μm feature, Flower and Roueff (1978) have found that destruction of HeH^+ by the EUV radiation field is much more rapid than recombination and conclude that "the rate of inverse predissociation, in particular, is much too low to support the recently proposed identifications of HeH^+ in the near infra-red spectrum of NGC 7027".

We shall now present arguments which lead us to believe that a large number of these features arise not from molecules in the gas but rather from molecules within the mantles of interstellar grains which lie in the colder region of clouds away from the exciting source.

The middle infra-red spectral region corresponds energetically to molecular vibrational transitions. The most prominent line, that at 3.3 μm, has been the focus of much attention. The excitation temperature corresponding to radiation at this frequency is of the order of 1000 K, a temperature not easily made consistent with either the central source or surrounding cloud. As pointed out by Russell et al. (1977a) this is consistent with some sort of non-thermal populating mechanism being the origin of this as well as the other prominent features in the spectrum. By far the most likely pumping mechanism is via absorption of ultra-violet photons, as can be inferred from the fact that all the objects known to have emission features shown in Table V apparently have a local ultra-violet source. In Sect. IV we calculate the trend of emission line intensities induced by a local source and show that they fall in the range observed (see Tables 1 and 6). It is difficult to make good abundance estimates based on the measured intensities since the relative line strengths depend on a non-equilibrium fluorescence pumping mechanism. Any abundance calculation would have to include radiative transfer effects as well as detailed energy transfer mechanisms and knowledge of relative quantum efficiencies for the various competing processes such as conversion of UV pumping photons to 1. absorbed acoustic phonons (heat), 2. emitted infra-red photons, 3. emitted UV-visible photons, and 4. reactive molecules. None of these processes are presently understood sufficiently well to warrant a quantitative estimation. In Table 2 are listed the previous assign-

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Table 3. Temperature dependence of methane band linewidths in a) $CH_4:H_2O:CO:NH_3$ (2:1:1:1) and b) pure CH_4

Temperature (K)	Linewidth (cm^{-1}) ν_3(3011 cm^{-1})	ν_4(1299 cm^{-1})
a) Mixture		
12	14	19
19	14	19
27	16	19
38	18	20
30	16	19
∿ 57	?	20
b) Pure CH_4		
12	10	8
16	10	8
20	9	8
30	22	19
45	31	20

ments of the features evident in NGC 7027 as well as our class I assignments (those which are most reliable) from Paper I.

The general appearance of the spectrum, specifically the breadths of key features and lack of resemblance between the features and the *P* and *R* structure which one would expect from excited gas phase molecules (discussed later) lends strong support to the attribution of these features to molecules lying within the mantle of interstellar grains.

Investigation of the low temperature spectroscopic literature shows that while a number of lines which are due to vibrational transitions remain sharp (<0.5 cm^{-1}) a great number are broadened 10–20 cm^{-1} (in some cases more) due to inhomogeneities within the solid environment (Hallam, 1972).

In this light the linewidths presented in Table 1 are especially important. The features in the 2.0–5.23 μm region all appear to be broader than the 0.015 resolution element. Certainly the B_α line should be only as wide as the resolution element (69 cm^{-1}). But, because it appears to be much broader (∼127 cm^{-1}) and because the 3.3 μm feature, when measured under higher resolution conditions, is found to have only an approximately 18 cm^{-1} width instead of the ∼118 cm^{-1} width we are forced to conclude that the linewidths we measure in this region of the spectrum are unreliable. Fortunately, this is not the case for the rest of the spectrum where it is seen that 6 of the 13 lines have widths comparable to the resolution element. Thus as pointed out by the original observers the 6.20, 6.98, and 11.3 μm features are broader than the resolution element, having widths at half height of 62, 67, and 34 cm^{-1} respectively (references in Table 1). The combined 7.7 and 7.8 μm features and the 8.6 μm feature possess linewidths difficult to define. The 6.2 μm and 11.3 μm features were assigned to the broad water ice bands in Paper I, the only molecule in the definite assignment category (when in the ice form) which normally possesses features broader than the 0.015 resolution which holds for nearly the entire spectrum presently available. The remaining broad feature, that at 6.98 μm remains unidentified.

The 3.3 μ feature, which we have assigned to the ν_3 mode of methane has been measured with 7 cm^{-1} resolution by Grasdalen and Joyce. We measure an 18 cm^{-1} linewidth at half height from their spectrum, a width much too great to be explained in terms of a gas phase transition.

We have measured in our laboratory the temperature dependence of the infra-red spectrum of methane in a sample consisting of an approximately 10.0 μm thick layer of the mixture $CH_4:H_2O:CO:NH_3$(2:1:1:1) deposited on an aluminium substrate at approximately 10 K. Spectral resolution was 1 cm^{-1} and spectra were recorded at various temperatures between 12 and 50 K. The linewidths at half height for this sample and for a similar sample of solid methane are presented in Table 3. Thus we conclude that the width of the 3.3 μm feature in the spectrum of NGC 7027 suggests that, in the fluorescing regions, grain temperatures lie in the range 25–40 K. The lower limit is deduced from the pure CH_4 sample which should possess the minimum linewidth. In addition this behaviour is reversible for samples which undergo repeated thermal cycling as can be seen by the measurements at 27 and 30 K which were taken before and after warm up to 38 K. Note that this reversibility is expected only for molecules which do not possess a permanent dipole moment (such as methane) since those that do can form weakly bound aggregates which cause an irreversible altering of the spectrum. As the data in Table 3 show, even for methane the linewidth is also dependent on the nature of the solid in which it is embedded. The stronger the interaction between the molecules the larger the spectral change since vibrational force constants depend strongly on electron configuration and density. The very strong effects of the hydrogen bond on the one hand [in the case of water the hydrogen stretching mode changes from a sharp line at 3725 cm^{-1} into an extremely broad feature nearly 300 cm^{-1} lower in energy (van Thiel et al., 1957)] and the relatively weak dipole-dipole interaction on the other [in the case of CO its vibration is found to occur at 2136.7 cm^{-1} when a CO-N_2 pair is trapped in an argon matrix and at 2140 cm^{-1} when it is paired with CO_2, NH_3, or H_2O (Dubost, 1976)] show the variability of this effect. Once such an aggregate is formed it will remain because the thermal energies involved at these temperatures are not strong enough to break these bonds. Thus, in the case of molecules which form aggregates the linewidth and position is a type of memory of the thermal history and accretion mechanisms while in the case of non-polar molecules the width and position can yield the temperature directly. As usual however, interpretation of this information must be done with caution since overlapping lines, the photolysis of the material and the presence of very reactive neighbors could produce misleading results. It is impossible to perform this analysis on the other strong CH_4 feature which occurs at 7.8 μm, a difficult region in the spectrum of NGC 7027 because this occurs just in the wing of the broad silicate-like absorption feature [see however the spectrum of HD 4417 (AGL 915) which shows a flat background in the 2–14 μm range with an extremely broad feature at 8 μm]. Without knowing the exact form of the background radiation field it is impossible to deconvolute the 7–9 μm region in a meaningful way.

In Paper I we erroneously attributed the 3.4 μm feature to a weak CH_4 absorption at 2900 cm^{-1}. Methane does not possess a feature at 2900 cm^{-1} but rather a very weak absorption at 3.55 μm (2815 cm^{-1}) as can be seen clearly in Fig. 1, Paper I. However there is no evidence of a feature at this frequency in the spectrum of NGC 7027. Three of our assignments overlap two atomic assignments: that of NH_3 at 10.5 μ overlaps the {S IV} assignment, that of C_2H_2 at 12.8 μm overlaps the {Ne II} assignment and that

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Table 4. Comparison of the strongest matrix-isolated features of the radicals NCO, NH_2, HCO with a few diffuse interstellar bands

Sample	T	Transition	λ (Å)	Possible Diffuse Line Counterpart (Å)
NCO/Ar	(4K)	000←000 $^2\Sigma \leftarrow {}^2\Pi$	4404(a) 4398(b)	4428
NH_2/Kr	(4K)	$0\nu_2 0 \leftarrow 000$ $^2A_1\Pi_\mu \leftarrow {}^2B_1$	6275.33	6269.77
			5684.10	5705
			5149.95	?
			4711.07	4726
HCO/CO	22K	$0,\nu_2 0 \leftarrow 000$ $^2\Sigma^+ \leftarrow {}^2A''$	6695	
			6352	6353.5
			6052	6042
			5789 *	5778.3
			5548	5544.6
			5330	?
			5102	?

* – Strongest feature;
? – There is an unusually large gap in Herbig's list of lines between 4882 Å and 5362 Å.
NCO: (a) McCarthy and Robinson, 1959; (b) Milligan and Jacox, 1967;
NH_2: Robinson and McCarthy, 1959;
HCO: Ewing et al., 1960; Diffuse line wavelengths: Herbig, 1975

of H_2O and C_2H_2 at 3.09 μm overlaps the recent He II suggestion (Russell et al., 1977a). At the resolution of 0.015 which holds for this region, line blending between a narrow 0.1 cm^{-1} wide line, such as that due to the forbidden transition in {Ne II} at 12.8 μm and a broader, say 5 cm^{-1} wide, line due to C_2H_2 is possible. In this light it is clear that the 67 cm^{-1} broad 6.9 μm feature (assigned to the 6.98 μm line of {Ar II}) and the very broad 7.8 μm feature cannot be due solely to {Ar II} and {Ar V} respectively. In addition, note that while the features due to B_γ, Pf_γ and B_α are seen in the spectra of the ionized regions which exhibit the broader features, they are not evident in the other sources (see Table 5). The 10.5 and 12.8 μm features are also seen in most of the objects associated with ionized regions. The nebula HD 44179 shows the 12.8 μm feature and perhaps the 10.5 μm feature thus supporting the possibility of line blending.

Another aspect of the spectrum of NGC 7027 which supports the thesis that the lines originate from molecules frozen into the mantles of interstellar dust grains and not from molecules in the gas phase is the absence of any similarity between these features and the expected *P* and *R* rotational structure associated with gaseous molecules which of course are free to rotate. Since the observed lines correspond to molecules with a high vibrational temperature (on the order of 1000 K) one would also expect a high rotational temperature if they are in the gas. This would naturally give rise to a broad, intense central *Q* band with broader and weaker *P* and *R* branches for perpendicular type bands. Thus if the molecules are gaseous one would expect to observe satellite-like wings to the features which correspond to *P* and *R* branches of, if completely unresolvable, features even broader than those measured. For example in the case of methane the spacing between lines in the *P* and *R* branches is approximately 10 cm^{-1} and even at temperatures much lower than 1000 K, namely at room temperature, the range covered from the low energy end of the *P* branch to the high energy end of the *R* branch is roughly 300 cm^{-1}. For CO, a molecule with a forbidden *Q* branch and a spacing of approximately 4 cm^{-1} this range is about 200 cm^{-1} (for example, see Cole, A.R., 1977). Thus unless there are very unusual excitation and relaxation mechanisms at work in these regions the general features in the spectrum of NGC 7027 and the other objects possessing a similar spectrum are inconsistent with a gas phase molecular origin explanation.

III. Mantle Photochemistry

a) Radical and Molecule Formation

If the picture of a fluorescing mantle pumped primarily by a UV radiation field is valid then it is clear that photochemical processing of the mantle must also be taking place. If the UV flux is sufficiently high, photodissociation will occur during the lifetime of a grain and some of the resultant radicals will interact with their neighbors to form larger molecules (Greenberg et al., 1972; Greenberg, 1973). These processes are known to take place in low temperature matrices which are dilute mixtures of simple gases which are condensed on a cold (4.2–25 K) substrate. Changes in composition resulting from photolysis and temperature variations are studied by a variety of techniques (see, for example: Hallam, 1972; Meyer, 1971). From the earliest work it was evident that reactions in solids at these temperatures were not unusual and new molecules and radicals could be formed.

We are currently performing ultraviolet photolysis experiments in our laboratories under conditions designed to duplicate, as much as possible, the conditions holding for interstellar mantles (i.e.: a sample of ~0.2 μm thickness, complex composition), to provide better insight into how mantle reactions contribute to the molecules found in the interstellar medium (Greenberg, 1976, 1978). Preliminary results show that, in these complex mixtures, radicals are formed in significant quantities.

b) Diffuse Interstellar Bands

The diffuse interstellar absorption bands have posed an identification problem for over 40 yr. Any acceptable explanation of the diffuse interstellar bands must at least be able to make plausible assignments of the majority of the known features (Herbig, 1975). Some of the lines lie close to the strongest features in the visible region of the spectrum of the matrix isolated radicals NCO, NH_2 and HCO as shown in Table 4. The positions of these features are known to depend strongly on the medium and 10–20 Å shifts in going from one matrix to another are not unusual. The fluorescing grain model with a significant UV pump is additional indirect evidence to support such a model because it strongly argues for low temperature grain mantles with at least some caged molecules and, by implication, free radicals as proposed by Greenberg (1976).

In addition to the question of identification there remain such questions as why an absorption source in a grain whose size is comparable with the wavelength should produce interstellar bands which are only slightly asymmetric in absorption (van de Hulst, 1946) and which show no polarization structure (Greenberg and Hong, 1976). The possibility that an explanation for these observations may be the result of intrinsic compensating line asym-

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Table 5. Infra-red objects which show prominent emission features

Features in NGC 7027	Planetary Nebula		H II Regions							Galaxies		REFL. Nebula	OPTICAL Nebula	Cold IR Source	Early Type Star
λ(μ)	BD +30°3639	IC 418	Orion	M 17A	M 17B	NGC 7538	AGL 3053	W51 - IRS 2	K3 - 50	M 82	NGC 253	AGL 915 HD 44179	AFGL 437	CRL 2688	MWC 922 CRL 2132
2.17	x	x	-	-	-	x	x	x	x	x	-	?	0	?	?
2.30	x	?	-	-	-	?	x	?	?	?	-	?	?	?	?
2.43	x	x	-	-	-	?	x	?	?	?	-	?	?	?	?
2.92	?	?	-	-	-	?	x	?	?	?	-	?	-	?	?
3.09	x	x	x	-	x	?	x	x	?	0	x	?	?	x,?	?
3.30	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
3.40	x	?	x	x	x	?	x	?	?	x	x	?	x,?	?	?
3.77	x	x	x	x	x	?	x	?	x	x	?	?	?	?	?
4.05	-	-	x	x	x	-	x	x	x	x	-	-	?	?	?
4.49	-	-	-	-	-	-	-	-	-	-	-	?	-	-	-
4.65	-	-	-	-	-	-	-	-	-	-	-	?	-	-	-
5.23	-	-	-	-	-	-	-	-	-	-	-	?	-	-	-
5.39	-	-	-	-	-	-	-	-	-	-	-	?	-	-	-
5.61	-	-	-	-	-	-	-	-	-	-	-	?	-	-	-
5.90	-	-	-	-	-	-	-	-	-	-	-	?	-	-	-
6.20	-	-	-	-	-	-	-	-	-	x	-	x	-	-	-
6.98	-	-	-	-	-	-	-	-	-	x	-	0	-	-	-
7.3	-	-	-	-	-	-	-	-	-	?	-	?	-	-	-
7.7	x,?	-	-	-	-	-	x,?	-	-	x	-	x	x,?	-	-
7.8	x,?	-	-	-	-	-	x,?	-	-	x	-	x	x,?	-	-
8.6	x	-	-	-	-	-	x	?	?	x	x	x	x	0	x,?
8.9	0	-	-	-	-	-	?	x	?	0	0	0	?	0	?
10.5	0	-	-	-	-	-	x	x	0	x	x	0	?	0	?
11.3	x	-	-	-	-	-	x	x	x	x	x	x	x	0	x
12.8	x	-	-	-	-	-	x	x	x	x	x	x	?	0	0

x : feature evident.
0 : feature not evident.
? : poor spectral quality.
- : To the best of our knowledge, spectral region not available in the literature as of july 1978.
References: NGC 7027: Gillett et al., 1973; Merrill et al. 1975; Grasdalen and Joyce 1976; Russell et al. 1977a.
BD +30°3639 : Gillett et al. 1973; Russell et al. 1977b.
IC 418, NCC 7538 : Russell et al. 1977b.
Orion, M 17A, M 17B : Grasdalen and Joyce 1976.
AGL 3053 : Merrill 1977.
M 82 : Gillett et al. 1975b; Willner et al. 1977.
NGC 253 : Gillett et al. 1975b; Russell et al. 1977b.
HD 44179 (= AG 915) : Merrill 1977; Russell et al. 1978.
AFGL 437 : Kleinmann et al. 1977.
MWC 922 (=CRL 2132); CRL 2688: Merrill and Stein 1976.
NGC 7538, W51 - IRS 2, K3 - 50: Gillett et al. 1975a and Soifer et al. 1976 (For a better spectrum of NGC 7538 see also Russell et al. 1977b).

metries produced by matrix interaction is being subjected to preliminary theoretical calculations (Tielens, unpublished) but the final answer must await the results of experiments currently underway in our laboratories.

IV. Constraints on the Spatial Distribution of Fluorescing Grains

The amount of fluorescence as induced by ultra-violet flux is clearly dependent on both the quality and quantity of the ultraviolet radiation. For the following discussion we consider a variety of sources of ultraviolet radiation – defined here as having significant flux at wavelength $\lambda < \lambda_0 \simeq 3000$ Å. A number of simplifying assumptions will be used because all we wish to demonstrate here are some of the main features of the problem.

The ultraviolet radiation sources are represented by black body "stars" of radius R_* and temperature T_* so that the total luminosity is given by

$$L_\nu(R_*) = 4\pi R_*^2 \pi F_\nu(R_*)$$
$$L(R_*) = 4\pi R_*^2 \sigma T_*^4 \text{ erg s}^{-1} \tag{1}$$

where $\pi F_\nu(R_*)$ is the flux at the surface.

The flux of photons with $\lambda < \lambda_0$ is

$$\Phi_{\nu_0}(R_*) = \int_{\nu_0}^{\infty} \frac{L_\nu(R_*)}{h\nu} d\nu$$
$$= 1.52\ 10^{11} \left(\frac{N_{0-\lambda_0}}{N_{0-\infty}}\right) T_*^3 \text{ photons cm}^{-2}\text{ s}^{-1} \tag{2}$$

where $(N_{0-\lambda_0}/N_{0-\infty})$ is the fraction of all photons with $\lambda \leqq \lambda_0$ (see, e.g. Allen, 1973).

In general the radiation field consists not only of the direct stellar radiation but also that which has been converted to L_α. For simplicity we ignore this effect as part of our not taking

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Table 6. Trend of fluorescent intensities induced by various stellar types. The stellar parameters are taken from Allen 1973 unless otherwise specified

Stellar type Main Seq. (V)	$(\frac{R_*}{10\ R_\odot})^2$	$(\frac{T_{eff}}{10{,}000\ K})$	$(\frac{N_{o-\lambda_o}}{N_{o-\infty}})$	$I_\lambda(10^{-14-x}\ \frac{W}{cm^2})$
O5	3.16	4.0	0.803	53.6
B0	0.550	2.8	0.664	2.65
B5	0.145	1.55	0.340	0.61×10^{-1}
A0	0.063	0.99	0.126	0.23×10^{-2}
A5	0.030	0.85	0.067	0.41×10^{-3}
F0	0.018	0.74	0.030	0.86×10^{-4}
Supergiant (I)				
O5 [a]	3.63	4.2	0.817	72.5
B0	4.0	3.0	0.697	24.7
B5 [b]	10.0	1.52	0.329	3.81
A0	16.0	1.2	0.200	1.81
A5 [b]	25.0	0.77	0.043	0.164
F0	40.0	0.70	0.028	0.126

[a] Parameters from Panagia (1973).
[b] Estimated stellar parameters.

proper account of radiative transfer. Thus at a distance r from the source we let the radiation be reduced by the inverse square effect of geometrical dilution and the absorption through the intervening dust. This gives

$$\Phi_{\nu_0}(r) = \bar{W}(r)\Phi_{\nu_0}(R_*) = \left(\frac{R_*}{r}\right)^2 e^{-\bar{\tau}_{u.v.}(r)}\Phi_{\nu_0}(R_*) \text{ photons cm}^{-2}\text{ s}^{-1} \quad (3)$$

where $\bar{\tau}_{u.v.}(r) = \int_{R_*}^{r} d\bar{\tau}_{u.v.}(r)$ is a mean ultraviolet attenuation.

Let the efficiency for conversion of an ultraviolet photon to an infrared fluorescence photon at wavelength λ_M, corresponding to a particular molecule M, be given by α_{λ_M}. Then the rate at which fluorescent photons are emitted per unit volume is

$$R = \alpha_{\lambda_M}\Phi_{\nu_0}(r)\sigma_d n_d \text{ photons s}^{-1}\text{ cm}^{-3}, \quad (4)$$

where σ_d is the ultraviolet cross section of the dust and $n_d(r)$ is the local number density of dust grains.

Consider a cloud of dust in the form of a shell at a distance r and thickness Δr. The total energy emitted by this shell is

$$L_{\nu_M} = \left(\frac{hc}{\lambda_M}\right) R 4\pi r^2 \Delta r \text{ erg s}^{-1}, \quad (5)$$

so that the intensity of radiation at a distance d in the line λ_M is

$$I(\lambda_M) = L_{\nu_M}/4\pi d^2 = (hc/\lambda_M)\left(\frac{r}{d}\right)^2 R\Delta r \text{ erg s}^{-1}\text{ cm}^{-2} \quad (6)$$

which may be written in the form (analogous to Eq. 12 in Paper II)

$$I(\lambda_M) = 1.5\ 10^{-13}\alpha_{\lambda_M}\left(\frac{\lambda_M^{-1}}{1000}\right)\left(\frac{R_*/R_\odot}{10}\right)^2\left(\frac{r}{\text{pc}}\right)^{-2}\left(\frac{N_{0-\lambda_0}}{N_{0-\infty}}\right) \cdot \left(\frac{T_*}{10{,}000}\right)^3\left(\frac{a_d}{10^{-5}}\right)^2\left(\frac{n_H}{10^4}\right)\left(\frac{\Delta r}{\text{pc}}\right)e^{-\bar{\tau}_{u.v.}}\left(\frac{r/d}{10^{-2}}\right)^2 \text{W cm}^{-2} \quad (7)$$

where $R_\odot$ is the solar radius, a_d = mean effective dust radius, n_H = hydrogen density, and λ_M^{-1} is in wave numbers, cm^{-1}. An equivalent form of Eq. (7) may be written as

$$I(\lambda_M) = 1.5\ 10^{-14}\alpha_{\lambda_M}\left(\frac{\lambda_M^{-1}}{1000}\right)\left(\frac{R_*/R_\odot}{10}\right)^2\left(\frac{r}{\text{pc}}\right)^{-2}\left(\frac{N_{0-\lambda_0}}{N_{0-\infty}}\right) \cdot \left(\frac{T_*}{10{,}000}\right)^3 \Delta\bar{\tau}_{u.v.}(r)e^{-\bar{\tau}_{u.v.}}\left(\frac{r/d}{10^{-2}}\right)^2 \text{W cm}^{-2}, \quad (7')$$

where $\Delta\bar{\tau}_{u.v.}(r) = \pi a_d^2 n_d \Delta r$ is the ultraviolet attenuation within the thickness Δr.

In order to arrive at a rough estimate of the fluorescence intensities for qualitative comparison with those observed we apply Eq. (7) to a variety of stellar type sources. The results are shown in Table 6 where we have used as base values of our parameters: $\alpha_{\lambda_M} = 10^{-x}$ (where x is expected to be >1 but is yet to be determined experimentally), $r = 1$ pc, $\lambda_M^{-1} = 1000$ cm^{-1}, $e^{-\bar{\tau}_{u.v.}} = 10^{-1}$, $a_d = 1.5\ 10^{-5}$ cm, $n_H = 10^4$ cm^{-3}, $(r/d) = 10^{-2}$, $\Delta r = 0.1$ pc. The combination a_d, n_H, Δr leads to $\Delta\bar{\tau}_{u.v.} \simeq 2.2$.

The general range of fluorescent intensities observed to date is 10^{-16}–10^{-18} w cm^{-2}. An examination of Table 6 shows that a local ultraviolet source appears to be needed to provide such intensities if α_{λ_M} is as small as 10^{-2}–10^{-4}.

The particular object NGC 7027 has not been included in Table 6 because its central source is not known. However the very high surface brightness of the nebula clearly implies a very high temperature ultraviolet radiation source. Temperatures as high as 100000–200000 K for the source of NGC 7027 have been suggested, so that it is not surprising to find it to be an excellent fluorescence emitter, since it is also associated with substantial quantities of local low temperature dust (Merrill et al., 1975).

It is interesting to note that among the objects shown in Table 5 there is one (CRL 2688) which has been identified as a shell F star. Although this might appear at first glance to be too cool a source to provide the ultraviolet pump, we see in Table 6 that there may still be a sufficient number of ultraviolet photons present in its spectrum to produce some infra-red fluorescence if it is an F supergiant. The fact that CRL 2688 shows emission features only in the higher energy region of the spectrum is consistent with this picture because if the fluorescence is only marginally pumped one would expect to see the infra-red emission lines only from the higher energy modes since these should be less efficiently coupled to the lattice and thus most likely to radiate (see Paper II and below).

A direct linear relationship, as apparently implied by the simple relation, Eq. (7), is going to be strongly modified by the temperature of the grains. For a given photon energy the fluorescence per grain is proportional to the conversion efficiency factor, α. The value of α depends critically on the degree of coupling of the molecule with the lattice and its phonons whose spectrum and density depends on the grain composition and temperature. At 50–100 K, this coupling is expected to be significant and, in addition, the diffusion of radicals and molecules in the system is appreciable (Pimentel, 1960). At such temperatures the lifetime

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of the excited molecules is not sufficient to permit infra-red radiation. For various reasons, therefore, we expect that above a critical temperature, T_c, the ultra-violet pumping conversion efficiency, α, should fall rapidly for most, if not all molecules in the grain mantle. There is evidence that α is already decreasing at temperatures lower than T_c (Legay, 1977) but the final drop is expected to be even more rapid. We thus anticipate that very close to the ultra-violet source the infra-red fluorescence is small because the grain temperature is too high but that as the distance increases the fluorescence will increase once the temperature drops below the critical temperature. In an intermediate region of subcritical grain temperature the ultra-violet flux is presumed still to be sufficient to produce an observable infra-red flux. Subsequently, because of the ultra-violet attenuation by absorption in the intervening dust grains the fluorescence again decreases even though the grain temperature is low. There is then only a limited region around an ultra-violet source from which fluorescence is possible. This is, of course, a very idealised picture because usually the interstellar material is clumpy and irregular around a source so that we might also imagine localized peaks in the fluorescence. Thus high spatial resolution infra-red observations of these emission lines could provide new information on such localized physical properties as grain temperature, grain density and ultraviolet flux.

Laboratory experiments are currently in progress to obtain constraints on the region where the proposed fluorescence mechanisms can work.

V. Specific Astrophysical Objects

a) Requirements for the Observation of Molecular Lines in Emission

Since the spectral region 3–13 μm is only now being pioneered, complete spectra are not available for a wide variety of sources. To the best of our knowledge, while many infra-red objects have been studied in parts of the middle infra-red only 15 are known to exhibit the unidentified features. These objects are compared in Table 5.

The preceding discussion shows that the fluorescing regions of these objects are required to have the following general characteristics:

(i) adequate UV photon density

(ii) a region of cold dust at $T < T_c$ exhibiting low infra-red extinction at 10 μm and high ultra-violet extinction at 1000–2000 Å.

The planetary nebulae NGC 7027, BD+30°3639, and IC 418 all have sufficient UV continua. NGC 6572 has been studied only in the 8–13 μm region (Gillett et al., 1973) however the spectral quality is too poor to decide if features are present or not.

Similar arguments of high UV flux apply to the galaxies M 82 and NGC 253 which probably contain all of the other types of objects listed in Table 5. The four objects, AFGL 437 (a cluster of young stars embedded in an optical nebulosity), HD 44179 (the peculiar object studied by Cohen et al., "The Rectangle" which seems to have an associated blue star that can provide the UV pump), CRL 2688 (an optically thick, cold infra-red source) and CRL 2132 (=MWC 922, a highly reddened early-type star), are also sources of the emission features.

The set of H II regions Orion, M 17 A and B, and AGL 3053 all have a high UV excitation region capable of pumping an external shell of cold dust and show strong features in the 3 μm region. Unfortunately only the spectrum in the 10 μm region has been published for AGL 3053 which is seen to have a clearly discernible 11.3 μm feature. This set is to be contrasted with another set of H II regions K 3–50, W 51–IRS 1, W 51–IRS 2, and NGC 7538 which barely exhibit some of the features in the 8–13 μm and 2–4 μm range.

The spectra in the 3 and 10 μm region of a number of objects associated with molecular clouds which predominantly show the 3.07 and 9.7 μm ice and silicate features in absorption have been reported by Merrill et al. (1976). These objects are CRL 490, NGC 2024 No. 1, and No. 2, NGC 2264 IR, the previously reported BN source in Orion (Gillett and Forrest and references therein), CRL 2591 (Merrill and Soifer, 1974) and H_2O 610+18 (Pipher and Soifer, 1976).

It is interesting to note that there is an apparent sequence of objects with increasingly strong emission features. The BN and related objects do not show these features; the compact H II regions K–350, W 51–IRS 1+2, and NGC 7538 barely exhibit the phenomenon; the optically visible H II regions, planetaries and nebulosities have the strongest emission features.

It appears that the objects which do *not* show the features have low UV photon fluxes within the cloud due to a high value of A_v (implying high ultra-violet extinction) and consequently cannot excite the fluorescence. Given such a UV model it is clear there should be some anti-correlation between fluorescence and $E(B-V) \approx \frac{1}{3} A_v$. However if a collisional pumping mechanism were responsible, one would expect a correlation. It is probably significant that there appears to be an anti-correlation and this argues against collisional pumping playing the major role.

b) Requirements for the Observation of Molecular Lines in Absorption

On the basis of the core mantle model of interstellar grains we anticipate that the infra-red spectra obtained from dark clouds lying in front of a continuum infra-red source with an intensity of $\sim 10^{-15}$ W cm^{-2} (at Earth's atmosphere), and which are not near a UV source will be rich in molecular absorption lines which however may be very weak.

It is only because of the anomalously strong H_2O absorption *per molecule* as produced by small ice aggregates that H_2O is readily detectable. Even very small aggregates produce an absorption enhancement by a factor of 12 (Van Thiel et al., 1957). The following comparison between absorptions for CH_4 and bulk H_2O shows that this effect can be much stronger.

The absorption cross section of the C-H stretching mode of CH_4 at 3.3 μm is

$$\sigma_{CH_4}(3.3\ \mu\text{m}) = 4\ 10^{-21}\ \text{cm}^2,$$

as deduced from Pugh and Rao, 1976.

For an isolated H_2O molecule the cross section of the O-H stretching mode at 2.66 μm is $2\ 10^{-21}$ cm^2. However, because water is a strongly polar molecule it tends to form aggregates. These aggregates are characteristic of bulk ice for which the maximum absorption is shifted to $\lambda = 3.07$ μm where the complex index of refraction is $m = 1.375 - 0.815\,i$ (dielectric constants $\varepsilon_1 = 1.23$, $\varepsilon_2 = 2.24$, Bertie et al., 1969).

The absorption cross section for a volume V of such aggregated ice molecules is given by (for spheres)

$$C_{abs} = \frac{18.4\pi}{\lambda} V \left\{ \frac{\varepsilon_2}{(\varepsilon_1+2)^2+\varepsilon_2^2} \right\}$$
$$= 2.67\ 10^4\ V\ \text{cm}^2.$$

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Using a density of $s=1$ for ice and therefore $\frac{6.02}{18}10^{23}$ molecules cm^{-3} we get

$$\sigma^{\mathrm{Bulk}}_{H_2O}(3.07\ \mu m)=8\ 10^{-19}\ cm^2$$
$$\simeq 2\ 10^2 \sigma_{CH_4}(3.3\ \mu m).$$

Thus, even in the BN object, where the 3.07 absorption is about 1 mag, the absorption by an equal amount of CH_4 would be only about $0^m.005$ which is scarcely observable (see the spectrum in Gillett and Forrest, 1973). A similar statement can be made for any of the other molecules and radicals one would presume to exist in the grain mantles with the possible exception of the polar molecule NH_3. This however exhibits only about half of the strong intensity enhancement in the X-H stretching region as does H_2O (Pimentel et al., 1962) and this combined with the fact that the N:O abundance ratio is about 1/6 makes it likely that an NH_3 absorption would be substantially less than one tenth of the H_2O absorption.

Finally it must be noted that the strength of the 3.07 μm band cannot be used to provide quantitative evidence for the presence or absence of grain mantles because it depends on the answers to three questions which are not yet completely known: 1. How much of the oxygen is bound as H_2O, 2. How much of the H_2O exists in the monomeric, dimeric or higher polymeric forms, 3. How does the absorption coefficient of polymeric H_2O in complex grain mantles compare with that of pure ice as measured by Bertie et al.? With regard to 1. it is clear that processes such as photolysis and solid state reactions obviously lead to other oxygen containing molecules than H_2O; e.g. CO, H_2CO, SiO, HNCO etc. in grain mantles. Question 2. has been discussed above where we point out that the absorption coefficient per H_2O molecule depends very strongly on the degree of aggregation. Although we do not have a complete answer to question three we have experimentally demonstrated that even in an unphotolyzed complex mantle material the absorption coefficient for the 3.07 μm H_2O feature is generally reduced relative to that of Bertie et al. by a factor of two or greater.

VI. Suggested Observations and Laboratory Experiments

1. High spectral and spatial resolution IR observations over a wide frequency range to include all fundamentals of assigned, and possibly assigned, molecules and radicals (2–40 μm).
2. Laboratory experiments on infra-red fluorescence in solids so that one has information on *emission* as well as *absorption*.
3. An observational search for these lines in absorption.
4. An observational search for spectral features unambiguously associated with radicals which should be present in grains.
5. Quantum efficiency measurements of fluorescence versus photolysis of CH_4, H_2O, H_2CO, NH_3 etc. in low temperature solids.

VII. Conclusions

After examination of the spectra available in the current literature we have presented supporting evidence for our concept of the infra-red fluorescence of molecules in grain mantles as explaining some of the unidentified infra-red emission lines. The strongest and most reliable assignments from Paper I taken together with the 12 previous gas phase atomic assignments account for 21 out of the 25 features listed in Table 2. The general appearance of the spectrum especially the unusually broad features at 6.2 and 11.3 μm which are consistent with water in the ice form, the width of the 3.3 μm feature which is consistent with methane embedded in a solid lying in the range from 25–40 K and the absence of even rough similarity between the spectrum and *P* and *R*-like structure expected from excited gas phase molecules provide the strongest arguments.

Furthermore, we have proposed that the temperature of the grain mantles can be obtained directly from the line profiles of the methane lines; the first direct observation of this important parameter. Using a specific model of UV pumping of the fluorescence we have been able to give some reasons for the occurrence or non-occurrence of the features in many objects. It has been shown that in a number of instances where anti-correlation between visual extinction and line intensity is weak there is a natural explanation in our model of a cold fluorescing shell embedded in a much thicker dust region. A recent 8–13 μm map of Orion supports our model (Aitken et al., 1979).

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References

Aitken, D.K., Roche, P.F., Spenser, P.M., Jones, B.: 1979 (preprint)
Aitken, D.K., Jones, B.: 1973, *Monthly Notices Roy. Astron. Soc.* **165**, 363
Allamandola, L.J., Norman, C.A.: 1978a, *Astron. Astrophys.* **63**, L23, Paper I
Allamandola, L.J., Norman, C.A.: 1978b, *Astron. Astrophys.* **66**, 129, Paper II
Allen, C.W.: 1973, *Astrophysical Quantities*, University of London, The Athlone Press, London
Bertie, J.E., Labbé, H.J., Whalley, E.: 1969, *J. Chem. Phys.* **50**, 4501
Black, J.H.: 1978, *Astrophys. J.* **222**, 125
Cole, A.R.H.: 1977, compiler, I.U.P.A.C. Commission on Molecular Structure and Spectroscopy (Pergamon Press, Oxford)
Dabrowski, I., Herzberg, G.: 1978a, *Mém. Soc. Roy. Sci.*, Liège; 1978b, *Trans. N.Y. Acad. Sci.* **38**, 14
Dubost, H.: 1976, *Chem. Phys.* **12**, 139
Ewing, G.E., Thompson, W.E., Pimentel, G.C.: 1960, *J. Chem. Phys.* **32**, 927
Flower, D.R., Roueff, E.: 1978, *Astron. Astrophys.* (in press)
Gillett, F.C., Forrest, W.J.: 1973, *Astrophys. J.* **179**, 483
Gillett, F.C., Forrest, W.J., Merrill, K.M.: 1973, *Astrophys. J.* **183**, 87
Gillett, F.C., Forrest, W.J., Merrill, K.M., Capps, R.W., Soifer, B.T.: 1975a, *Astrophys. J.* **200**, 609
Gillett, F.C., Kleinmann, D.E., Wright, E.L., Capps, R.W.: 1975b, *Astrophys. J.* **198**, L65
Grasdalen, G.L., Joyce, R.R.: 1976, *Astrophys. J.* **205**, L11
Greenberg, J.M.: 1973, Molecules in the Galactic Environment, Symposium on Interstellar Molecules, Charlottesville, Va., 1971, ed. M.A. Gordon and L.E. Snyder, John Wiley and Sons
Greenberg, J.M.: 1976, *Astrophys. Space Sci.* **39**, 9
Greenberg, J.M.: 1978, Pre-Stellar Interstellar Dust, IAU Colloquium, Tucson, Arizona

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1979A&A....77...66A

Greenberg, J.M., Hong, S.S.: 1976, *Astrophys. Space Sci.* **39**, 31
Greenberg, J.M., Yencha, A.J., Corbett, J.W., Frisch, H.L.: 1972, *Liège Symposium, Mém. Soc. Roy. Liège* III, 425
Hallam, H.E. (Ed.): 1972, Vibrational Spectroscopy of Trapped Species, John Wiley and Sons, New York
Herbig, G.H.: 1975, *Astrophys. J.* **196**, 129
Hulst, H.C. van de: 1946, *Rech. Astron. Obs. Utrecht,* **11**, Part 1
Kleinmann, S.G., Sargent, D.G., Gillett, F.C., Grasdalen, G.L., Joyce, R.R.: 1977, *Astrophys. J.* **215**, L79
Legay, F.: 1977, in *Chemical and Biochemical Applications of Lasers*, ed. C.B. Moore, Acad. Press, p. 43
McCarthy, M., Robinson, G.W.: 1959, *J. Chim. Phys.* **56**, 723
Merrill, K.M.: 1977, Infra-red Observations of Late Type Stars, I.A.U. *Symp.* 42, Ed. R. Kippenhahn, J. Rahe, W. Strohmeier, Schadel Press, Bamberg, p. 446
Merrill, K.M., Russell, R.W., Soifer, B.T.: 1976, *Astrophys. J.* **207**, 763
Merrill, K.M., Soifer, B.T.: 1974, *Astrophys. J.* **189**, L27
Merrill, K.M., Soifer, B.T., Russell, R.W.: 1975, *Astrophys. J.* **200**, L37
Merrill, K.M., Stein, W.A.: 1976, *Publ. Astron. Soc. Pacific* **88**, 874
Meyer, B.: 1971, Low Temperature Spectroscopy, Elsevier Press, New York
Milligan, D.E., Jacox, M.E.: 1967, *J. Chem. Phys.* **47**, 5157
Panagia, N.: 1973, *Astron. J.* **78**, 932
Pimentel, G.C.: 1960, in *Formation and Trapping of Free Radicals*, ed. A.M. Bass and H.P. Broida, Acad. Press, p. 69
Pimentel G.C., Bulanin, M.O., Van Thiel, M.V.: 1962, *J. Chem. Phys.* **36**, 500
Pipher, J.L., Soifer, B.T.: 1976, *Astron. Astrophys.* **46**, 153
Pugh, L.A., Rao, K.N.: 1976, in *Molecular Spectroscopy Modern Research*, Vol. II, ed. K. Rao, Acad. Press, 1976
Robinson, G.W., McCarthy, M.: 1959, *J. Chem. Phys.* **30**, 999
Russell, R.W., Soifer, B.T., Merrill, K.M.: 1977b, *Astrophys. J.* **213**, 66
Russell, R.W., Soifer, B.T., Willner, S.P.: 1977a, *Astrophys. J.* **217**, L149
Russell, R.W., Soifer, B.T., Willner, S.P.: 1978, *Astrophys. J.* **220**, 568
Soifer, B.T., Russell, R.W., Merrill, K.M.: 1976, *Astrophys. J.* **210**, 334
Treffers, R.R., Fink, U., Larson, H.P., Gautier III, T.N.: 1976, *Astrophys. J.* **209**, 793
Van Thiel, M., Becker, E.D., Pimentel, G.C.: 1957, *J. Chem. Phys.* **27**, 486
Willner, S.P., Soifer, B.T., Russell, R.W., Joyce, R.R., Gillett, F.C.: 1977, *Astrophys. J.* **217**, L121

Note added in proof: In Paper I we attributed the 3.4 μm feature to a weak CH_4 absorption at 2900 cm^{-1}. As pointed out in Sect. 2 this is normally not infra-red active, however we find that in mixtures choosen to duplicate the dirty ice mantles infra-red activity is induced in this mode and it is readily seen in absorption.

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