

THE CHEMICAL IDENTIFICATION OF GRAIN MANTLES BY INFRARED SPECTROSCOPY

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The composition and physical properties of interstellar grain mantles continues to be an important problem in astrophysics. Part of this importance comes from the fact that grain mantle composition, photochemistry and photophysics are involved in interstellar chemistry (Greenberg et al. 1972, Greenberg, 1979, Greenberg et al. this volume). Because most molecules have a number of fundamental modes of vibration which possess activity between 2.5 and 25 μm (the middle infrared), spectroscopic measurement in this region can provide a direct probe of the molecules making up grain mantles. In addition to molecular composition, under favorable conditions, such measurements can yield molecular abundances, the solid/gas ratio for specific molecules and give an indication of such physical grain properties as temperature and thermal history.

In order to exploit fully the infrared spectrum it must be realised that there are certain spectral characteristics which permit one to distinguish between molecules in low temperature solids, and molecules in the gas phase. Two of the most striking differences are the following: 1) the absence of P and R rotational structure, see Figure 1 (because molecules are no longer free to rotate) and 2) line shifting and broadening which occurs due to interactions within the solid.

The extent to which line broadening and shifting occurs is a sensitive function of the particular molecules involved. While this cannot be quantified on theoretical grounds alone it can be studied empirically (for an example of such an application see the paper by Hagen, Tielens and Greenberg presented at this symposium).

In this paper we discuss the infrared spectra associated with astrophysical objects which show spectral characteristics indicative of molecular mantles.

Objects showing emission.

To the best of our knowledge there are 16 objects which are known to exhibit prominent emission lines. They are listed in Table 1.

Inspection of Table 1 shows that the emission features originate

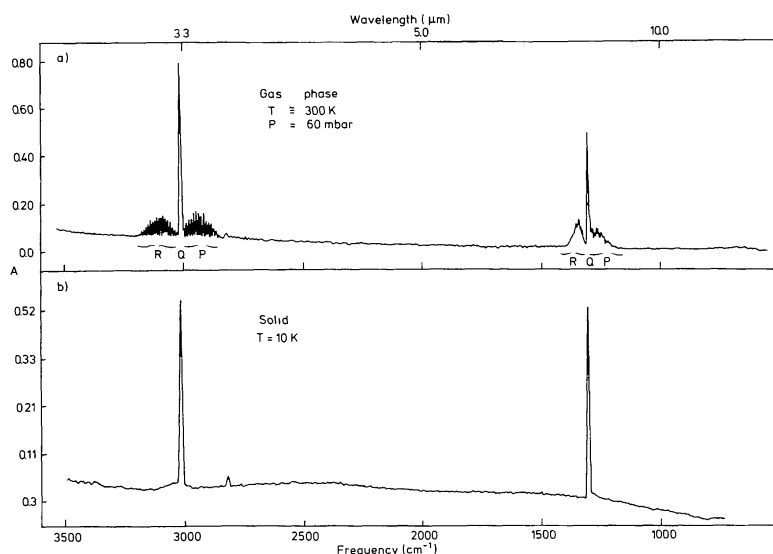


Figure 1. The infrared spectrum of a) gaseous and b) solid methane showing the absence of the P and R branches in the solid.

Table 1. Infrared objects which show prominent emission features.

Object	Type
NGC 7027	High excitation planetary nebula
BD+30°3639	Low excitation planetary nebula
IC 418	Low excitation planetary nebula
Orion	H-II
M17A	H-II
M17B	H-II
NGC 7538	H-II
AGL 3053	H-II
W51-IRS2	Compact H-II
K3-50	Compact H-II
M 82	Galaxy
NGC 253	Galaxy
HD-44179 (AGL 915)	Nebulosity with imbedded source (late B or early A binary)
AFGL 437	Nebulosity with imbedded source
CRL 2132 (MWC 922)	Nebulosity with imbedded source (Early type star)
CRL 2688	Nebulosity with imbedded source (F?)

in objects which contain substantial amounts of dust in proximity to an ultraviolet source.

NGC 7027 will be used for this discussion because it has one of the richest and best studied spectra of all the objects listed. The spectrum is shown in Figure 2.

Inspection of Figure 2 shows that, superimposed on the peculiar background continuum, there are many prominent emission lines. Those indicated by a dotted line are significantly broader than the resolution

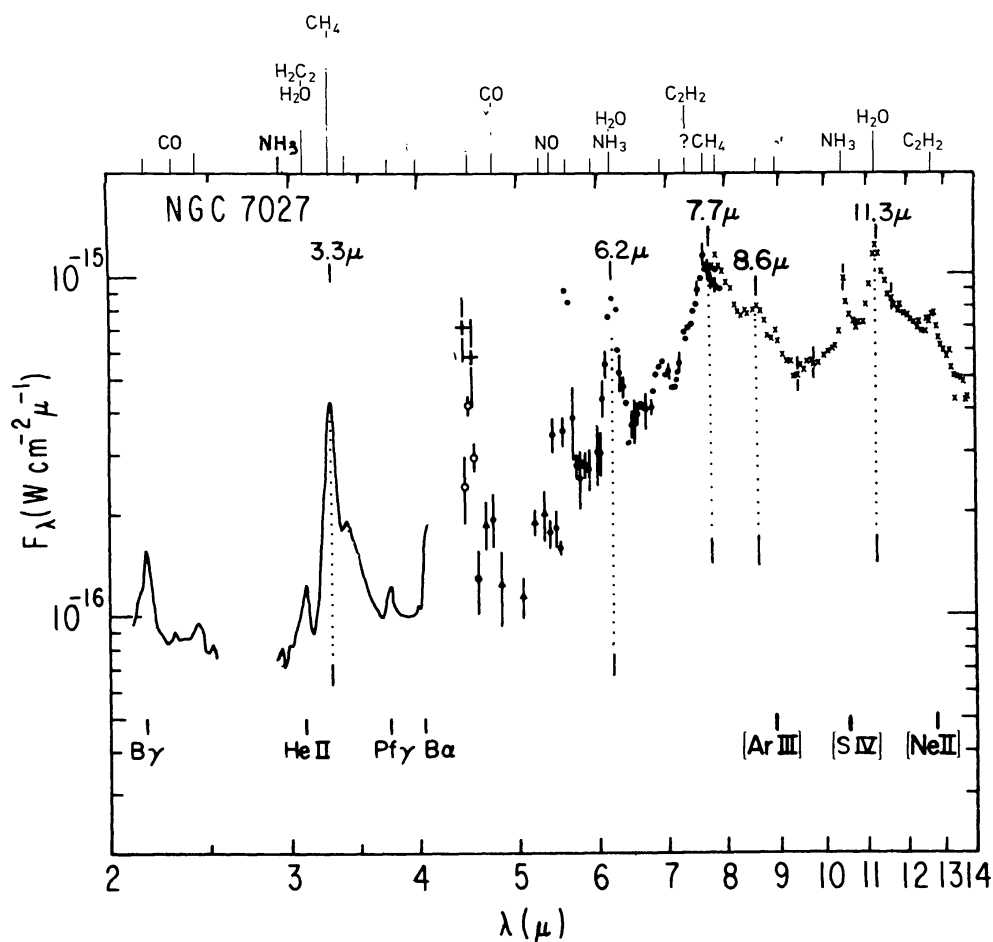


Figure 2. 2-14 μm spectrum of NGC 7027. The top horizontal axis shows the Class I assignments from Allamandola and Norman, 1978 and the dotted lines indicate the features which are broader than the spectral resolution. The spectrum is reprinted from a letter of Russell, Soifer and Willner (1977) which appeared in the *Astrophysical Journal*, University of Chicago Press.

of the spectrometer. Another relevant aspect of these lines is the complete lack of P and R branch-like structure. The broad lines and the absence of evidence for rotation indicate that these features originate from molecules in grain mantles. We have assigned a number of these emission lines in NGC 7027 to molecules in grain mantles based on the comparison of those lines to absorption lines obtained from molecules in low temperature solids (Allamandola and Norman (1978), Allamandola, Greenberg and Norman (1979)).

The very prominent 3.3 μm emission which we have assigned to the ν_3 mode of methane has been measured with 7 cm^{-1} resolution by Grasdaen and Joyce (1976). We obtain an 18 cm^{-1} line width at half height from

their spectrum. We have measured the temperature dependence of the line width of the 3.3 μm methane line in two different solids, one pure methane and the other a mixture of CH_4 : H_2O : CO : NH_3 : (2:1:1:1). For pure methane the line width remains constant at 10 cm^{-1} up to 20 K, from 20 to 30 K it broadens to about 22 cm^{-1} and at 45 K it is 31 cm^{-1} wide. In the case of the mixture the linewidth is 14 cm^{-1} up to 20 K and undergoes slight broadening upon warm-up to 16 cm^{-1} at about 30 K and 18 cm^{-1} at 38 K. *In addition, the linewidth is a reversible function of the temperature*. Thus using this model of infrared emitting grain mantles and the high resolution measurements of Grasdalen and Joyce one is led to conclude that the grain temperatures lie in the range 25-40 K in the fluorescing regions.

Investigation of the low temperature spectroscopic literature shows that some lines due to vibrational transitions remain sharp ($< 0.5 \text{ cm}^{-1}$) while others undergo substantial broadening (10-20 cm^{-1} is common, and in some extreme cases such as H_2O ice as much as 200 cm^{-1} is possible) (Hallam, 1972). In this light, the features in Figure 2 which are indicated as being broader than the resolution element are extremely important. The width of the emission at 3.3 μm has been discussed as due to CH_4 . The extreme breadth of that at 7.7 μm cannot be due to CH_4 or C_2H_2 transitions alone, nor can that of the 8.6 μm features be due solely to Ar [III]. As pointed out by the original observers the features at 6.2 and 11.3 μm are also broad (Aitken and Jones, 1973; Gillett et al., 1973 and 1975; Russell et al., 1977).

We have assigned these to the broad water ice bands, the only species (with the exception of NH_3) in our Class I assignment category which normally possesses features broader than the 0.015 resolution element which holds for most of the spectrum. The ν_4 mode of NH_3 , which overlaps with ν_2 in H_2O at about 6.2 microns also undergoes extensive broadening when in a multimeric form.

Objects showing absorption lines.

It is also be expected that the infrared spectrum obtained from dark clouds not associated with a local UV source and lying in front of a continuous I.R. source should show absorption due to dust molecules in the cloud. For most molecules these lines should be weak. However, H_2O molecules acquire anomalously large absorption cross sections when they are in the ice form (10 x or more, depending on the crystalline form). This explains why the so-called ice band at 3.1 μm dominates many spectra and may mislead one into thinking that there are no other features in the spectrum which are due to molecules.

In order to study the applicability of infrared absorption spectroscopy to this problem of grain mantle analysis we measure spectra of laboratory prepared samples which are designed to simulate interstellar grain mantles. The spectrum reduced to 30 cm^{-1} resolution, so as to be comparable to that of the other spectra, of an $\text{H}_2\text{O}:\text{CO}:\text{CH}_3\text{OH}:\text{NH}_3$ (6:3:3:2 mixture condensed onto a 10 K substrate is shown in Figure 3-d. This ratio provides an O:C:N ratio of 6:3:1 which was chosen to approximate the cosmic abundance ratio (O:C:N:5.2:3.3:1). The experimental technique

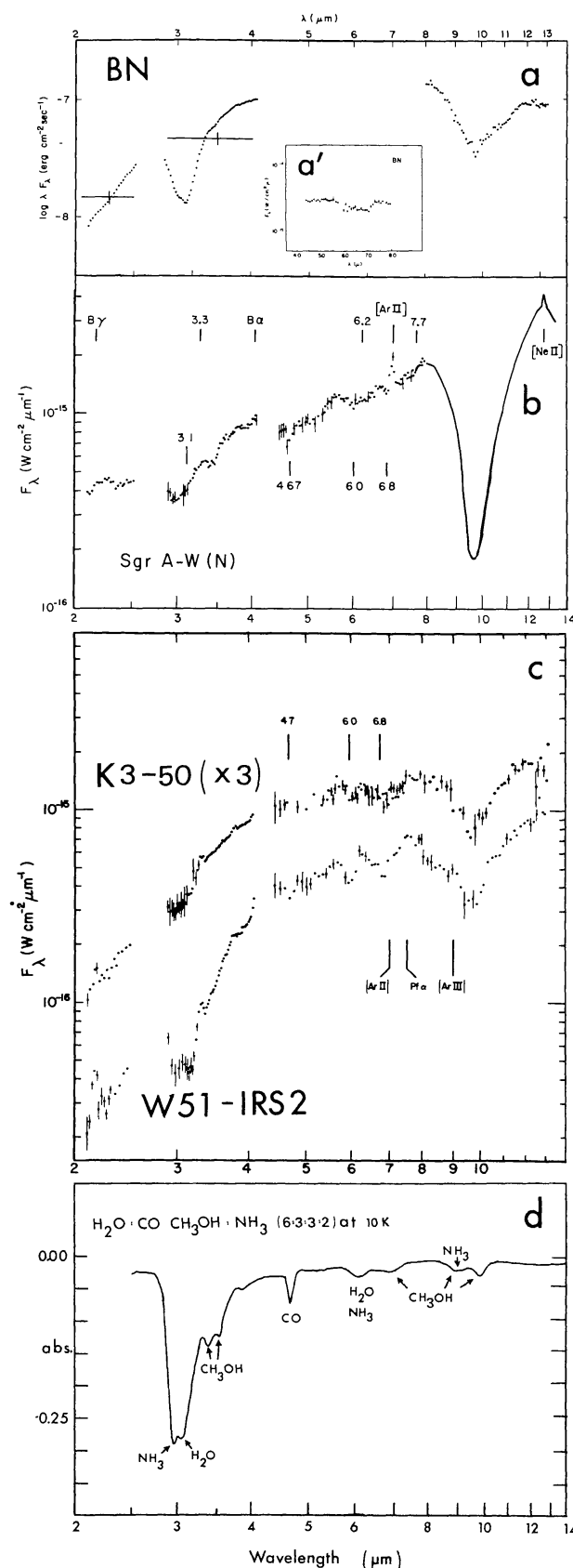


Figure 3. A 2-14 μm spectra of a, a') The BN object reprinted courtesy of Gillet, Jones, Merrill and Stein, 1975 and Russell, Soifer and Puetter, 1977; b) The Galactic Center reprinted from Willner, Russell, Puetter, Soifer and Harvey, 1979; c) K3-50 and W51-IRS2 reprinted from Puetter, Russell, Soifer and Willner, 1979 and; d) The grain mantle analog.

are described by Hagen et al., 1979.

This spectrum is to be compared with the recently published 2-14 μm spectrum of the compact H-II regions W51-IRS2 and K3-50 (Puetter et al., 1979) which are shown in Figure 3C, the galactic center (Willner et al., 1979) shown in Figure 3b and that of the BN object shown in Figure 3a. Examination of this figure shows that the major features of the spectrum obtained in the laboratory agree with those evident in the other astrophysical objects. Unfortunately the spectral and spatial resolution are not yet adequate to determine the extent to which some of the features are contributed to by molecules which are in the solid phase and by molecules which are in the gas phase. However, the general agreement between the laboratory spectrum and those shown in Figure 3 constitutes strong evidence for molecular mantles associated with these objects. The spectra of the individual objects show differences which are apparent even at this low resolution. These differences are probably due to variations in specific and

relative molecular abundances, solid/gas ratios for particular molecules, grain temperatures and thermal history from object to object (Allamandola, Greenberg, Hagen, 1979). This variation stresses the importance of proper exploitation of the infrared spectrum as a diagnostic tool. When better spectra (higher spectral and spatial resolution) are available one can start to unravel the actual photochemistry and photophysics taking place within a particular cloud and better understand the difference between specific clouds.

In this light, objects like W51-IRS2 and K3-50 are especially interesting since they appear to possess both emission and absorption features and may thus represent the transition case from the BN, and related objects which do not show the emission features at all, to the optically visible H II regions, planetary nebulae and diffuse nebulae which show only the emission features.

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DISCUSSION FOLLOWING ALLAMANDOLA

Irvine: Is there not a problem getting a sufficiently high quantum efficiency to produce the fluorescent emission lines by the mechanism you suggest?

Allamandola: No, because the quantum efficiency, that is the total number of IR photons emitted per UV photon absorbed, can be less than one. We estimated 0.1, a pessimistic value because one UV photon can contain many vibrational quanta. In addition, we have the broad range of possible UV pumping sources, ranging from the very UV-rich O stars to UV-poor F stars, which can excite this fluorescence if the stellar-cloud geometry is favorable. We have calculated that, when all these things are considered, the effective quantum efficiency can be as much as 100 times lower under favorable conditions.

Herzberg: Have any vibrational transitions been observed in emission in a solid matrix in the laboratory? It seems to me that the lifetimes of vibrational transitions are so long (of the order of milliseconds) that relaxation will occur before emission can take place.

Allamandola: Infra-red emission corresponding to vibrational transitions *has* been observed from inert, low temperature solid matrices, although the radiative lifetime is longer than one would expect for non-radiative decay into the lattice. The mechanism we have proposed here is based on this phenomenon also occurring in low temperature molecular mixtures. Experiments by Prof. Legay and his co-workers at the Molecular Photophysics Institute in Orsay are relevant. They irradiate a thin slab of solid CO with a low power CO laser beam tuned to excite the $V'' = 0$ to $V'' = 1$ transition. When the irradiation is terminated they measure emission not only from $V'' = 1$ to $V'' = 0$, but from much higher V'' levels as well, as high as $V'' = 23$, I believe. Here we have an example of infra-red emission corresponding to vibrational relaxation occurring in a solid molecular matrix. We also have some very recent results from our laboratory. Two weeks ago Fred Baas measured, for the first time, vacuum ultraviolet induced infra-red emission from a 10K CO/NH₃ mixture. These are early results, and the signal detected by the cooled InSb detector was quite weak, but evident.

Millar: The 3.1 μ m absorption band does not appear until $A_V \gtrsim 20$ magnitudes. In terms of your grain model, is there a physical reason why this should be so?

Allamandola: The nature of the absorption feature depends critically on the nature of the ice. Unless the history of the mantle is known, it is very dangerous to draw from the observations at 3.1 μ m conclusions regarding the presence or absence of H₂O. The absorption cross section of the OH stretch in the H₂O molecule is a very sensitive function of local environment. This cross section can undergo an enhancement by as much as a factor of 100 as H₂O molecules form larger and larger aggregates. There is also a very significant effect on the position and width of the line. Monomeric water absorbs at about 3700 cm⁻¹ with a 1-10 cm⁻¹ width, complexed "ice" at about 3200 cm⁻¹, with a breadth of 300-400 cm⁻¹.

Willner: There are emission features that occur together as a set in nearly all sources where any of the individual features occurs. These are at 3.3-3.4 μm , 6.2 μm , 7.7 μm , 8.6 μm , and 11.3 μm . Is the 3.4 μm band of CH_4 active or forbidden in your ice samples.

Allamandola: We have found this band to be infra-red active in our complex mixtures. This break-down of "forbiddenness" has something to do with the degree of polarizability of the solid environment. If solid CH_4 is studied, the band *is not* infra-red active, presumably because the lattice is made up of non-polar molecules.

Gilra: Dr. Willner talked about *absorption* features in the previous talk. You have discussed the *emission* features. Since in at least some cases the "dust" producing the emission features is in the same neighbourhood as the dust producing the absorption features, would it be unreasonable to conclude that the dust is the same in the two cases? Some spectral differences between the absorption and emission may be caused by the mode of excitation. For example, the emission spectrum due to molecules in a matrix is somewhat different from the absorption spectrum due to the same molecules in the same matrix.

Willner: The absorption features, with the exception of the silica feature, have never been seen in emission. The emission features have never been seen in absorption, unless the 3.3-3.4 μm feature turns out to be this wing of the 3.1 μm absorption. If we are talking about ices, we would not expect to see 3.1 μm in emission, because a high temperature would be required, and presumably the ice would evaporate.

Allamandola: It is certainly reasonable to expect absorption if there is a continuum IR source behind the cloud. In this respect the compact HII region W51 IRS2 has some spectral features which resemble emission and some which resemble absorption. Whether the emission and absorption positions occur at the same frequency must await confirmation. My guess is that the frequencies will not be very different, based on the CO laser-excited emission frequency which is within one wavenumber of the absorption position, as shown by Dubost. It is an open question whether one can find the conditions in which the *same* grains both emit and absorb.