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Letter to the Editor

Infra-red Emission Lines from Molecules in Grain Mantles

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Summary

The hitherto unidentified infra-red emission features in NGC 7027 and other objects are shown to be due to fluorescence from vibrationally excited molecules in grain mantles. Using laboratory data to match the observed spectra, positive identification is made of CH_4, H_2O, NH_3, C_2H_2, H_2O, CO and NO. This provides the most direct evidence for the composition and existence of complex molecular mantles on grains, the first evidence for such luminescence, and positive identification of methane in the interstellar medium.

Keywords: Infra-red lines - interstellar molecules - grains.

I. Introduction.

The middle infra-red spectrum of many infra-red objects contain dozens of emission features which have so far been classed as unidentified. The example with the richest known spectrum is the planetary NGC 7027 (Russell et al, 1977) which forms the basis of this Letter (see Fig. 2). Other spectra containing unidentified features have also been found in many other regions associated with infra-red objects e.g. AGL 3053, AGL 915 (HD 44179), M17 SW, IC 418, BD + 30° 3639, NGC 7538 and NGC 253. All show similar features in the 2 to 14 μm range (Russell, 1977b, Merrill, 1977). The broad profiles of these lines strongly suggest that the emitting molecules are embedded in solids (Hallam, 1972). We assume this is the case and propose to identify these features as due to molecular fluorescence from grains in clouds lying just outside the source. The mechanism of such fluorescence has been previously discussed (Allamandola and Norman, 1978, hereafter referred to as Paper 1).

II. Identification Procedure.

The identification as due to molecular fluorescence from vibrationally excited molecules in grain mantles rests on the following assumptions discussed previously in Paper 1:

1) The grains have a silicate core and a complex molecular mantle (Greenberg et al 1972).

2) Vibrational states of the molecules in the mantle are excited by UV photons or chemical reactions occurring in the mantle or molecule grain collisions.

3) The excited vibrational states can decay radiatively as well as decay into the low lying acoustic phonon modes because of inefficient coupling between the high frequency vibrational modes and the lower lying acoustic or "lattice" phonon modes (and inefficient coupling between the core and mantle modes).

In addition to the above we make use of the fact that, in general, fundamental molecular vibrational modes lie in the spectral range 2.5 to 25 μm. We restrict ourselves to simple molecular species known or likely to be present in the interstellar medium (Townes, 1976), which have been accreted onto grains. Of course, more complicated but less abundant molecules could generate some of these features. However, due to considerations of abundances, and the fact that larger molecules tend to have energetically lower lying fundamental modes which, in principle, may provide an efficient channel for energy release into the acoustic phonon modes we believe that simple species play the dominant spectral role. In addition, the low resolution holding for most of the spectrum taken together with the existence of characteristic fundamentals dictates that one must be careful not to over-interpret such a spectrum.

Since all of these simple characteristic groups normally possess more than one infra-red active fundamental mode of vibration we require that at least all the strongest known infra-red active modes of an assigned species must be evident in the spectrum. Very little data is available concerning the expected relative emission intensities and the structure of the mantle is not known well enough to estimate the efficiency of vibrational energy transfer within the core-mantle grains. Thus our assignments are based solely on frequencies obtained from laboratory measured absorption spectra. Because of this lack of knowledge of emission characteristics we will be unable to make precise abundance determinations. We must also assume that the characteristic line shift and broadening of molecular species embedded in solids is similar for both emission and absorption. The fact that CO in Ar at 10 K emits at 2138 cm^{-1} and absorbs at 2138.6 cm^{-1} supports this assumption (Dubost,

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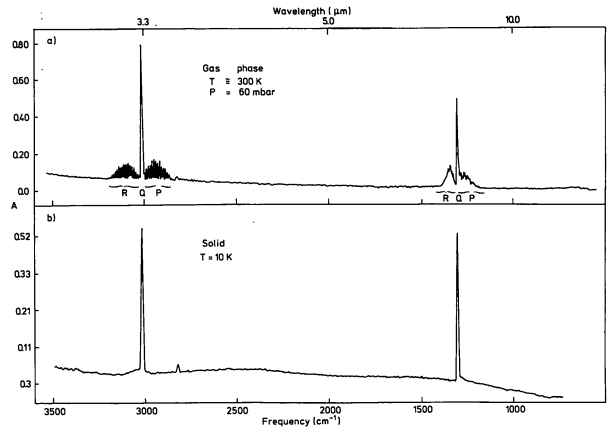

Fig. 1: The infra-red spectrum of (a) gaseous and (b) solid methane.

1976, Dubost and Charneau, 1976). Another well-known feature of solid state spectra evident in the region of high spectroscopic resolution for NGC 7027 is that the P and R branches which are present only for certain molecules in the gas phase are absent (Grasdalen 1977). This is shown for the methane case in Fig. 1.

III. Assignments.

Using these assumptions, we give in Table I a suggested list of assignments of the features measured in NGC 7027. The absorption spectra of the following molecules agree well within the resolution element for the observed features: H_2O, CH_4, NH_3 and C_2H_2. Less certain but probable identifications are given for H_2CO, NO, CO and N_2O. This uncertainty is made more quantitative by classifying the assignments in terms of a reliability parameter δ, defined as:

$$\delta = \left|\frac{\nu_{observed} - \nu_{assigned}}{\nu_{observed}}\right|,$$ which can be directly compared with instrumental resolution. The assignment reliability categories with their associated identified molecules are defined as follows:

I : $|0 \leq \delta \leq 0.020$ for all lines measurable$|$; H_2O, CH_4, C_2H_2, NH_3, CO, NO

II : $|0 \leq \delta \leq 0.020$ for all but a few lines which have $0.020 < \delta < 0.040|$; H_2CO, HCN, N_2O

III: $|0 \leq \delta \leq 0.02$ for all but a few lines which have $0.02 < \delta < 0.06|$; CH_3NH_2.

A class I identification is a definite assignment, class II likely and class III unlikely. The resolution that holds for small parts of the spectrum presented in Fig. 2 is $\Delta\nu/\nu = 0.010$, but because the resolution is not this good in general, and there is at least an equivalent amount of uncertainty in our evaluation of peak positions solely on the basis of the figure, we have choosen a δ value of 0.02 as the maximum allowable for classification in category I.

We shall now discuss the most reliable assignments in some detail.

1) Water, H_2O. The band shapes present in the spectra observed are consistent with hydrogen bonded water in the solid phase (Bertie et al, 1969, Van Thiel et al, 1957). Independent H_2O molecules have only two strong narrow absorption features in the range of the infra-red under consideration, one at 3700 cm^{-1} (2.7 μm) and the other at 1600 cm^{-1} (6.25 μm); however, hydrogen bonded water in the solid phase displays 1) a large shift of the 3700 cm^{-1} feature to 3300 cm^{-1} with simultaneous absorption enhancement by more than a factor of 10 and substantial broadening, 2) broadening of the 1600 cm^{-1} absorption, and 3) an additional strong broad feature at 850 cm^{-1} (11.8 μm). The extreme broadness of this band allows us to use δ = 0.04 for a Class I assignment in this case. The band may well be centered at the shoulder to the longer wavelength side of the sharp 11.3 μm feature.

2) Methane CH_4. It can be seen from Fig. 1 that solid methane at 10 K exhibits two prominent narrow absorption features in this entire region. The absorption at 3006 cm^{-1} (3.33 μm) corresponds to the C-H stretching motion and the strong feature at 1306 cm^{-1} (7.65 μm) corresponds roughly to an H-C-H bending mode. These two features agree with two strong emission features in the spectrum of NGC 7027. The feature at 3.3 μm is narrow and that at 7.7 μm is broad. Apart from the possibility of other bands blending with the 7.7 μm line we have no obvious explanation for this broadness.

3) Acetylene C_2H_2. The solid spectrum of acetylene posesses two strong absorption bands at 3220 cm^{-1} (3.1 μm) and 765 cm^{-1} (13.1 μm) with a weaker counterpart at 1400 cm^{-1} (7.14 μm). There are features evident in the spectrum of NGC 7027 at all these wavelengths.

4) Ammonia NH_3. Ammonia possesses three moderate to strong infra-red absorptions. All three features have δ values which lie well within our criteria for reliable assignment.

5) Formaldehyde H_2CO. From Table I it can be seen that the assignment in this case is somewhat less reliable. However, the results of Harvey and Ogilvie (1962) show that two of the four bands which do not meet our criteria for class I assignment (2829 and 1715 cm^{-1}) have unusually large uncertainties (± 15 cm^{-1}) as a function of temperature and concentration in the solid in which the H_2CO is embedded, the third (1494 cm^{-1}) is not always present, and the fourth (1250 cm^{-1}) lies to the red of the broad feature centred at 7.7 μm. Thus in the case of interstellar grains, where the composition of the grains is likely to be inhomogeneous, broad lines are expected, and increasing the limits for category II classification to $\delta \leq 0.045$ for the 1494 cm^{-1} feature seems reasonable.

6) Additional molecules. There are, in addition, two strong sharp features at 1860 and 2150 cm^{-1} which we have assigned to the diatomic molecules CO (δ=0.006) and NO (δ=0.009). The extremely small δ values associated with these two cases permit a strong assignment although diatomic molecules possess only one fundamental vibrational frequency. The assignment of HCN, N_2O and CH_3NH_2 are perhaps less reliable because they possess some features which lie in a region of poor spectral quality.

IV. Nature of the Solids.

The most striking feature of these spectra is that the silicate absorption feature can also be found in the presence of these

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Table I: Comparison of middle infra-red emission features of NGC 7027 with all medium to strong absorption features of a few simple interstellar molecular species known or likely to be present in the interstellar medium

Observed emission features			Species (frequency, cm^{-1}, δ, line strength)-of some possible assignments grouped by type		
λ(μm)	$\bar{\nu}(cm^{-1})$	$I(10^{-16} W/cm^2 Hz)$	Type I	Type II	Type III
2.17	4610				
2.30	4350	0.05	CO(4280,.016,w-overtone)		
2.43	4120				
2.92	3425		NH_3(3440,004,s)	N_2O(3508, ,s)	
blank	⋮				
3.09	3240	0.7	H_2O(3300,.019,Bd,vs) C_2H_2(3226,.004,vs)	HCN(3287,.015,?)	
3.30	3030	4.5	CH_4(3006,.008,s)	H_2CO(2885,.019,s)	CH_3NH_2(2968,.010,m)
3.40	2940	1.3	CH_4(2900,.014,w)	H_2CO(2829,.038,vs)	CH_3NH_2(2902,.013,m)
3.77	2650			N_2O(2580,.026,s)	CH_3NH_2(2821,.04,m)
4.05	2470			N_2O(2473,.001,m)	
blank	⋮				
				N_2O(2220,.004,m)	
4.49	2228			N_2O(2238,.004,vs)	
:4.65	2150:	9.0	CO(2137,.006,s)	HCN(2097,.025,?)	
:5.23	1910:	2.0			
:5.39	1860:	2.0	NO(1875,.009,s)		
:5.61	1780:	8.0		H_2CO(1715,.037,vs)	
:5.90	1500:				CH_3NH_2(1629,.012,m)
:6.20	1610:	5.5	H_2O(1600,.006,Bd,m) NH_3(1626,.010,m)		CH_3NH_2(1606,.002,m)
6.98	1430	1.3		H_2CO(1494,.045,vs)	CH_3NH_2(1480,.035,m)
7.3	1370		C_2H_2(1390,.015,s)		
7.7	1300	3.5	CH_4(1306,.005,s)		CH_3NH_2(1463,.023,m)
7.8	1280			H_2CO(1250,.023,vs) N_2O(1293,.010,vs)	
8.6	1160	1.5		N_2O(1196, .031,m)	CH_3NH_2(1140,.017,m)
8.9	1120			N_2O(1166,.005,s)	CH_3NH_2(1051,.06,m)
10.3	971	3.5	NH_3(970,.001,vs)		
11.3	885	6.0	H_2O(850,.040,Bd,s)		CH_3NH_2(884,.001,m) CH_3NH_2(858,.031,m)
12.8	781	1.3	C_2H_2(765,.020,vs)		CH_3NH_2(795,.018,vs)

..... →, Poor Spectral Quality Range.
vs,s,m,w signify relative absorption strength of the various lines:
vs, very strong; s, strong; m, medium; w, weak.
References - H_2O: ice, 173K, Bertie et al (1969); H_2O: N_2 matrix, 20K, Van Thiel et al (1957); CH_4: solid, 10K, Hallam (1973) see also Fig. 1; C_2H_2: Polycrystalline film, 63K, Bottger and Eggers (1964); H_2CO, solid, 4K, Harvey and Ogilvie (1962); NH_3: N_2 matrix, 20K, Pimentel et al (1962); NO: N_2 matrix, 20 K, Varetti and Pimentel (1971); CO: Ar matrix, 7K, Dubost (1976); N_2O: solid, 70K, Dows (1957); HCN: N_2 matrix, 20K, Hallam (1973); CH_3NH_2: Ar matrix, 20K, Durig et al (1968).

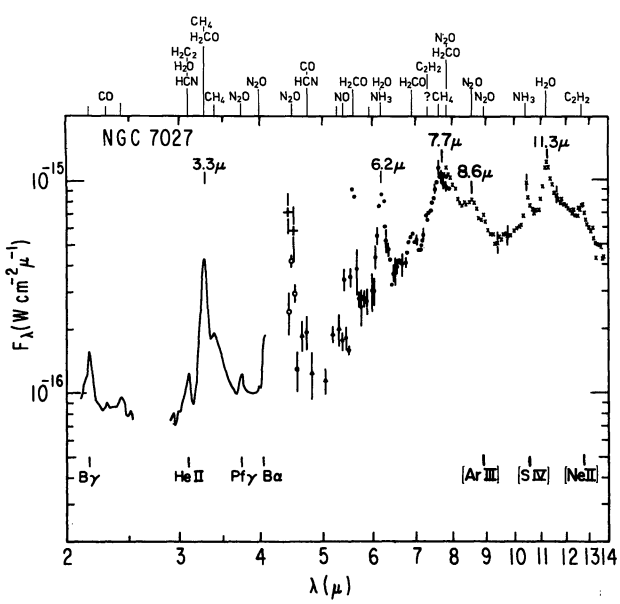

Fig. 2: 2 - 14 μm spectrum of NGC 7027 reprinted by kind permission from a letter of Russell, R.W., Soifer, B.T. and Willner, S.P. (1977a) which appeared in the Astrophysical Journal, University of Chicago press. Our assignments of the various features are noted across the top horizontal axis.

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emission lines. One can clearly see the presence of the silicate feature in absorption in Fig. 2. This is consistent with the picture of the core-mantle structure of an interstellar grain (assuming the emission and absorption come from the same place) where the fluorescence originates in the mantle which is energetically decoupled from the core which gives rise to the silicate absorption band (Paper 1).

Conclusions

We have suggested a new explanation for the emission features common to a number of infra-red sources and prevalent in the infra-red spectrum of NGC 7027 from 2 - 14 μm. These are assigned as molecular emission features originating in the complex mantle of grains - not intimately associated with the hot exciting source but deriving from the colder region outside the source. We have made positive identifications of CH_4, H_2O, C_2H_2, NH_3, H_2CO, CO and NO.

Our assignments of the 3.3 μm, 3.4 μm and 7.7 μm feature as due to methane, CH_4, is the first direct evidence for the presence of this molecule in the interstellar medium. This is also the first observation of molecular fluorescence from solids in the interstellar medium and thus provides a powerful tool to probe into the nature of interstellar grains.

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References

Allamandola, L.J. and Norman, C.A. 1978, Astronomy and Astrophysics, in press.

Bertie, J.E., Labbé , H.J. and Whalley, E. 1969, J. Chem. Phys. 50, 4501.

Bottger, G.L. and Eggers, D.F. 1967, J. Chem. Phys. 40, 2010.

Dows, D.A. 1957, J. Chem. Phys. 26, 745.

Dubost, H., 1976, J. Chem. Phys. 12, 139.

Dubost, H. and Charneau, R. 1976, Chem. Phys. 12, 407.

Durig, J.D., Bush, S.F. and Baglin, F.C. 1968, J. Chem. Phys. 49, 2106.

Grasdalen, G.L. and Joyce, R.R. 1976, Ap. J. 205, L 11.

Greenberg, J.M., Yencha, A.J., Corbett, J.W. and Frisch, H.L. 1972, Liège symposium, Mem. Soc. Roy. Liège III, 425.

Hallam, H.E. (Ed.) 1972, Vibrational Spectroscopy of Trapped Species. John Wiley and Sons, New York.

Harvey, K.B. and Ogilvie, J.F. 1962, Can. J. of Chem. 40, 85.

Herzberg, G. 1945, Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules, D. van Nostrand and Co., Toronto.

Merrill, K.M., 1977, Infrared Observations of Late Typestars, I.A.U. symposium 42.

Pimentel, G.C., Bulanin, M.O. and Van Thiel, M., 1962, J. Chem. Phys. 36, 500.

Russell, R.W., Soifer, B.T. and Willner, S.P. 1977a, Ap. J. 217, L 149.

Russell, R.W., Soifer, B.T. and Merrill, K.M. 1977b, Ap. J. 213, 66.

Townes, C.H. 1976, Liège Symposium on Interstellar Molecules, Mem. Soc. Roy, Liège IX, 453.

Van Thiel, M., Becker, E.D., Pimentel, G.C. 1957, J. Chem. Phys. 27, 486.

Varetti, E.L. and Pimentel, G.C. 1971. J. Chem. Phys. 55. 3813.

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