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THE IR EMISSION FEATURES: EMISSION FROM PAH MOLECULES AND AMORPHOUS
CARBON PARTICLES

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ABSTRACT. PAHs can have several forms in the interstellar medium. To assess the importance of each requires the availability of a collection of high quality, complete mid-IR interstellar emission spectra, a collection of laboratory spectra of PAH samples prepared under realistic conditions and a firm understanding of the microscopic emission mechanism. Given what we currently know about PAHs, the spectroscopic data suggests that there are at least two components which contribute to the interstellar emission spectrum: free molecule sized PAHs producing the narrow features and amorphous carbon particles (which are primarily made up of an irregular "lattice" of PAHs) contributing to the broad underlying components. An exact treatment of the IR fluorescence from highly vibrationally excited large molecules shows that species containing between 20 and 30 carbon atoms are responsible for the narrow features although the spectra match more closely with the spectra of amorphous carbon particles. Since little is known about the spectroscopic properties of free PAHs and PAH clusters, much laboratory work is called for in conjunction with an observational program which focuses on the spatial characteristics of the spectra. In this way the distribution and evolution of carbon from molecule to particle can be traced.

1. INTRODUCTION

To assess the importance of PAHs in astrophysics, one must determine the amount of carbon tied up in these species and understand how they are distributed among the various forms possible. For example, they can be neutral or charged (both positively and negatively); and they can exist as free species, loosely bound in clusters, or tightly bound in amor-

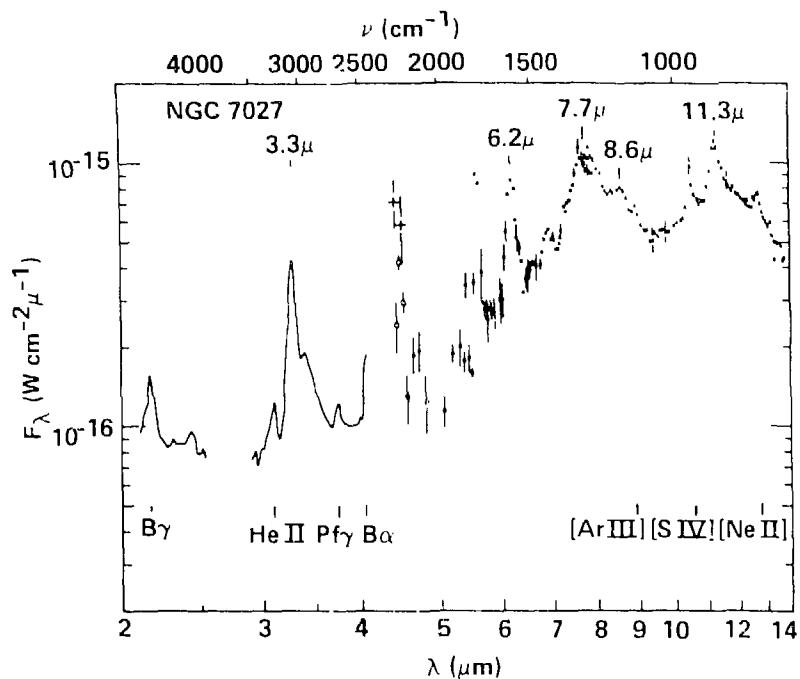


Figure 1. The 2-14 micron spectrum of NGC 7027 shows the emission features superimposed on an intense long wavelength "continuum". (Russell et al., 1977).

taken under conditions which mimic, as closely as possible, the conditions which determine the properties of the interstellar material. The third requirement is a firm understanding of the details of the microscopic excitation-emission mechanism. Given the space limitation, rather than discuss any of these points in detail we will present the overall problem and we will summarize current knowledge and recent results. The state of the observations and theories up to 1983 are reviewed in Willner (1984) and Allamandola (1984).

2. THE SPECTROSCOPIC PROBLEM

2.1. Observational Spectroscopy

Good examples of nearly complete mid-IR spectra of objects which have the emission bands are shown in figures 1,2, and 3 a,b. These figures convincingly illustrate that the spectral variations from one object to the other are significant. Although the 3.3, 3.4, 6.2, "7.7", 8.6 and 11.3 micron bands are present in all of these spectra, important differences are obvious. The 3.3 and 6.2 micron bands are remarkably similar in all objects, having a full width at half-height that is probably characteristic of non-radiative vibrational energy redistribu-

phous carbon particles. To gain this knowledge requires detailed information in three areas which is not presently available. The first is the requirement of a collection of at least 10 to 20 good quality, high signal-to-noise, moderate spectral and spatial resolution, complete mid-IR interstellar emission spectra. The second requirement is the availability of a collection of laboratory spectra of PAHs and PAH clusters

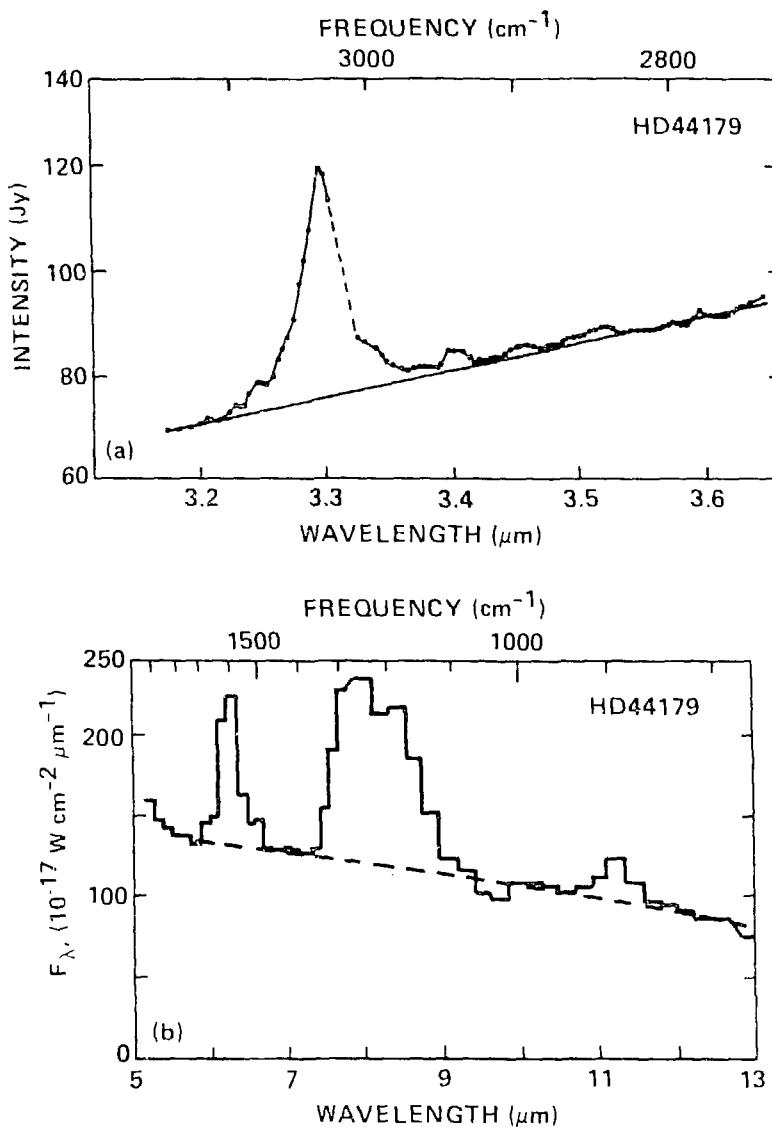


Figure 2. The 3-13 micron spectrum of HD 44179 shows the emission features superimposed on a flat "continuum" (3-4 micron spectrum - Geballe et al., 1985, 5-13 micron spectrum, Cohen et al., 1986).

bution times within individual molecules (Allamandola, Tielens, and Barker, 1985, 1986 - hereafter referred to as ATBa,b) rather than overlap of narrower lines from different PAHs. There are clear variations however, in peak wavelength and profile of the very broad feature generally referred to as the 7.7 micron band. In NGC 7027 and Orion this peaks near 7.7 microns while in HD 44179 the maximum is near 8 microns. The 11.3 micron band also shows some variation, being sharply peaked in NGC 7027 and at position 4 in Orion but broader in HD 44179. Aitken and Roche have spectroscopically studied many objects in the 8 to 13 micron region. Perusal of their spectra show similar behavior for both the 8.6 and 11.3 micron features.

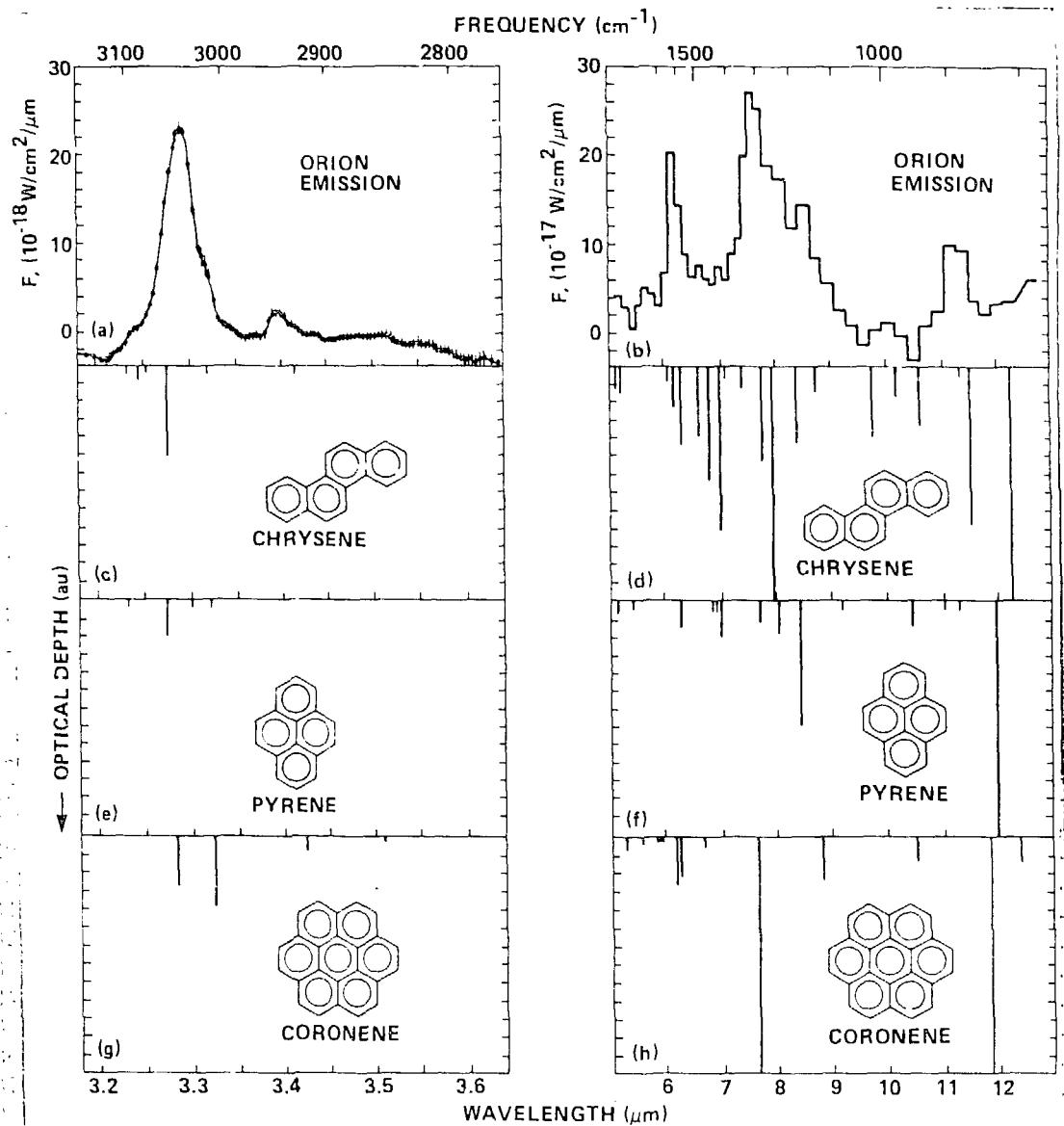


Figure 3. The 3-13 micron emission spectrum from the Orion Bar compared with the absorption spectra of the PAHs chrysene, pyrene and coronene suspended in KBr pellets. The "continuum" emission for the Orion Bar is intermediate between that of NGC 7027 and HD 44179. (Orion, Bregman et al., 1986; Chrysene, Cyvin et al., 1982a; Pyrene, Cyvin et al., 1979; Coronene, Bakke et al., 1979, Cyvin et al., 1982b).

There is also evidence for the presence of broad emission plateaux underneath these emission features. In the 3 micron region there is a broad component extending from about 3.1 to 3.6 microns (Geballe et al., 1985). An equally important plateau is the very broad, roughly

triangularly shaped hump under the 6.2 and 7.7 micron bands which peaks around 8 microns. The 11.3 micron band has also been shown to be part of a broader plateau which extends from about 11 to 13.5 microns (see Tielens et al. elsewhere in this volume and references therein) which is prominent in NGC 7027, evident in Orion, but nearly absent in HD 44179. The behavior of the 8 micron plateau parallels that of the 12 micron plateau; it dominates the mid-IR emission from NGC 7027, seems to be comparable in importance to the bands in Orion at position 4, and it is absent in HD 44179. This broad component is also evident to a lesser degree in the spectra of other objects; see for example the spectra of the reflection nebulae NGC 7023 and NGC 2023 (Sellgren et al., 1985) and several of the planetary nebulae spectra reported in Cohen et al., (1986). This behavior shows that there are two different components contributing to the mid-IR emission, one producing the bands and the other producing the broader features.

Apart from the overall resemblance of the UIR band spectrum to the spectrum expected from PAH-like species, (see Section 2 below, and paper by Leger and references therein, elsewhere in this volume) the results of recent, related observations tend to favor an aromatic origin as well. Cohen et al., (1986) have shown that the fraction of total IR luminosity radiated by the 7.7 micron feature in planetary nebulae is strongly correlated with the nebular C/O ratio. Because the carriers must be produced in these nebulae under harsh conditions, they must be extremely stable and carbon rich, two characteristics completely consistent with the aromatic hydrocarbon hypothesis. Cohen et al. also show that, while there is variation among the UIR band intensities, they are correlated, implying that a single class of chemical species is responsible.

These are the highlights of what we feel are some of the most important aspects of recent infrared observations concerning the PAH problem.

2.2. Laboratory Spectroscopy and the Interstellar Spectra

Although the UIR band spectrum resembles what one might expect from a mixture of PAHs, it does not match in details such as frequency, band profile or relative intensities predicted from the absorption spectra of any known PAH or their mixtures. In Figure 3, the emission spectrum from position 4 in Orion is compared with a schematic version of the absorption spectra of three PAHs: chrysene ($C_{18}H_{12}$), pyrene ($C_{16}H_{10}$) and coronene ($C_{24}H_{12}$). Leger (this volume), shows a similar comparison between the emission spectrum from the reflection nebula NGC 7023 and the absorption spectra of several larger PAHs suspended in KBr pellets. Similar rather suggestive, but uncompelling, comparisons between the interstellar emission spectra with the emission spectrum expected from the PAHs coronene and chrysene can be found in Leger and Puget (1984, hereafter LP) and ATBa,b. These emission spectra are discussed further in the next section.

Because of the suggestive match, the assumption has been made that PAHs in some form or combination are the carriers of the interstellar spectra. Only when detailed laboratory spectra for the various PAHs

become available can precise conclusions be drawn regarding their respective importance. Keeping this qualification in mind, the following general remarks concerning band assignments apply to virtually all PAHs.

As illustrated in Figure 3, the 3.29 micron band is highly characteristic of an aromatic system (Duley and Williams, 1981; Bellamy, 1958), which shows a dominant band, corresponding to a C-H stretch, in addition to a number of weaker bands between 3.1 and 3.6 microns which are overtone and combination bands involving lower frequency fundamentals. (Bellamy, 1958, Cyvin, et al. 1982, Herzberg, 1968).

Figure 3 also shows the 6.2 micron emission feature (which corresponds to a C-C stretching vibration in PAHs) which is as characteristic of polycyclic aromatic species as is the 3.3 micron band (Leger and Puget, 1984; Bellamy, 1958).

Perusal of Figure 3 also shows that the 5 to 10 micron region in PAH spectra is richest in IR active vibrations and the largest density of bands occurs in the 7.2 to 8.5 micron range (ATBa,b, Bellamy, 1958). Unlike the 3.3 and 6.2 micron bands which consistently occur at nearly the same wavelength, independent of the molecule, the precise position of these C-C stretching bands depends on the particular molecular structure. Thus the infrared spectrum of a mixture of PAHs could produce a broad band, possibly with substructure, in this region. Of course the precise peak position and profile would vary somewhat depending on the particular PAH mixture responsible.

The small shoulder at 8.6 microns on the "7.7" micron feature which often appears in the interstellar spectra is assigned to the in-plane aromatic C-H bending mode in PAHs (LP; Bellamy, 1958). As shown in Figure 3, PAHs show several bands close to this position.

The 11.3 micron feature is assigned to the out-of-plane C-H bending vibration (Duley and Williams, 1981; Bellamy, 1958). Because this frequency is so highly characteristic for aromatic species with edge rings which contain only non-adjacent peripheral hydrogen atoms (Bellamy, 1958), Duley and Williams postulated that the aromatic containing material they believed responsible, amorphous carbon particles, was only partially hydrogenated. Figure 3 shows that fully hydrogenated PAHs which contain more than one H atom per edge ring possess several strong bands in the 11-15 micron range. The discovery of the 11-13 micron interstellar emission plateau not only relieves some of the difficulty associated with understanding partial hydrogenation in exceedingly H rich environments, but also shows that edge rings of PAHs responsible for the interstellar emission can have non-adjacent as well as 2 or 3 adjacent peripheral H atoms, but not 4 or 5. (Tielens et al. and references therein, this volume, and Cohen, Tielens and Allamandola, 1985).

The spectra shown in Figure 3 c-h serve to illustrate several additional points. For a free, highly symmetric PAH (e.g., coronene) with an inversion center, the infrared spectrum will appear simple and the Raman and IR active vibrational modes will be mutually exclusive due to the high molecular symmetry. However, if the vibrational force field is not so symmetric (as is the case in free, less symmetric PAHs, or PAHs in clusters or amorphous carbon particles) the IR and Raman spectra

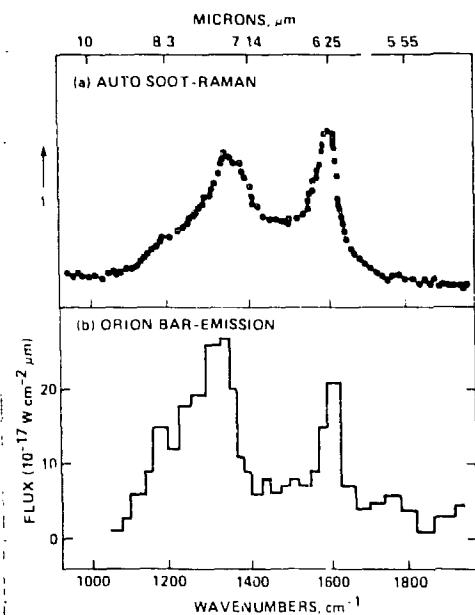


Figure 4. Comparison of the 5 to 10 micron Raman spectrum of auto soot (a form of amorphous carbon) with the emission from Orion (soot spectrum, adapted from Rosen and Novakov, 1984; Orion, Bregman et al., 1984, 1986). Taken from ATBa.

can be very similar. For example, although coronene has 66 C-C modes while chrysene has only 48, the IR spectrum of chrysene is far richer in the C-C stretching region (5-10 microns) because the molecule is less symmetric. It is for these reasons that we legitimately could compare the Raman spectrum of soot in the 6 to 8 micron range with emission from Orion (Figure 4, ATBa), and thus point out the striking similarity between the vibrational spectra of a mixture of PAHs (amorphous carbon is made up of PAH subunits cross linked in an

irregular fashion, see, e.g., Oberlin, 1984, and Marchand, elsewhere in this volume) and the interstellar emission bands (ATBa). For comparison, Figure 5 shows the IR absorption spectrum of a different mixture of aromatic hydrocarbons, known as a char (Mortera and Low, 1983). Note that the char spectrum also shows structure in the 3 micron region which is similar to that shown in many of the interstellar emission spectra (i.e., a dominant 3.3 micron band and a broader, weaker component starting at about 3.15 microns, extending to about 3.65 microns, and peaking near 3.41 microns). Figure 6 shows that spectra of individual PAHs also have similar structure. As mentioned above, the weak absorptions by PAHs in this region are due to overtones and combinations of 5-10 micron fundamentals. The spectra shown in Figures 4,5 and 6 are of PAHs in various solids where the perturbations within the solid broaden the individual bands causing them to overlap and produce a broad component. Free PAHs will show individual bands whose positions and intensities are determined by the molecular structure of each PAH. The interstellar emission component is due to the overlap of individual emission bands which arise from different PAHs. In addition to the weak contribution from overtone and combination bands, highly vibrationally excited molecules emit from vibrational levels greater than $V=1$. Emission from these higher levels, shifted for anharmonicity, contributes significantly to the 3.4 micron plateau and many of the other components of the interstellar spectrum (see Section B, Barker et al., 1986 and ATBa,b). The recent discovery of specific bands in this plateau (de Muizon, this volume) supports this explanation of the plateau in terms of overlapping individual lines.

As shown above in Figures 4 through 6, the infrared signature of amorphous carbon soots and chars resembles the UIR band spectrum rather

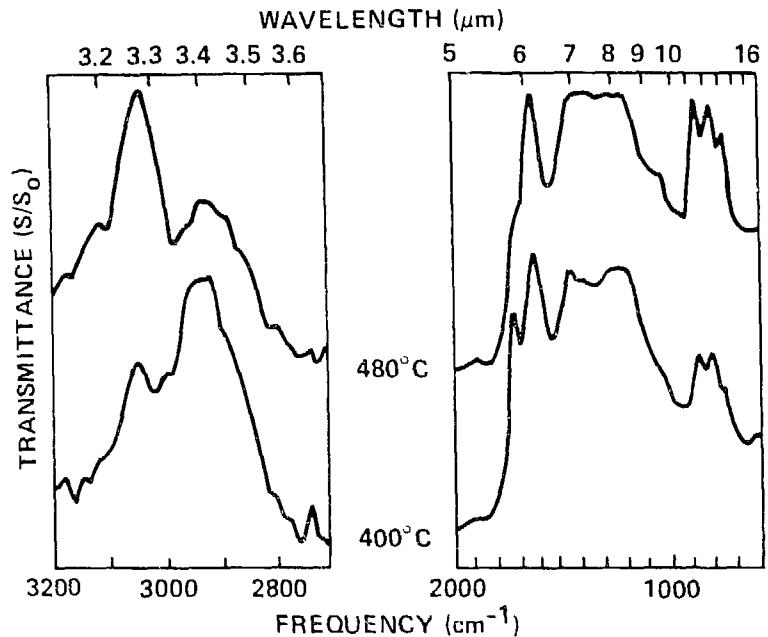


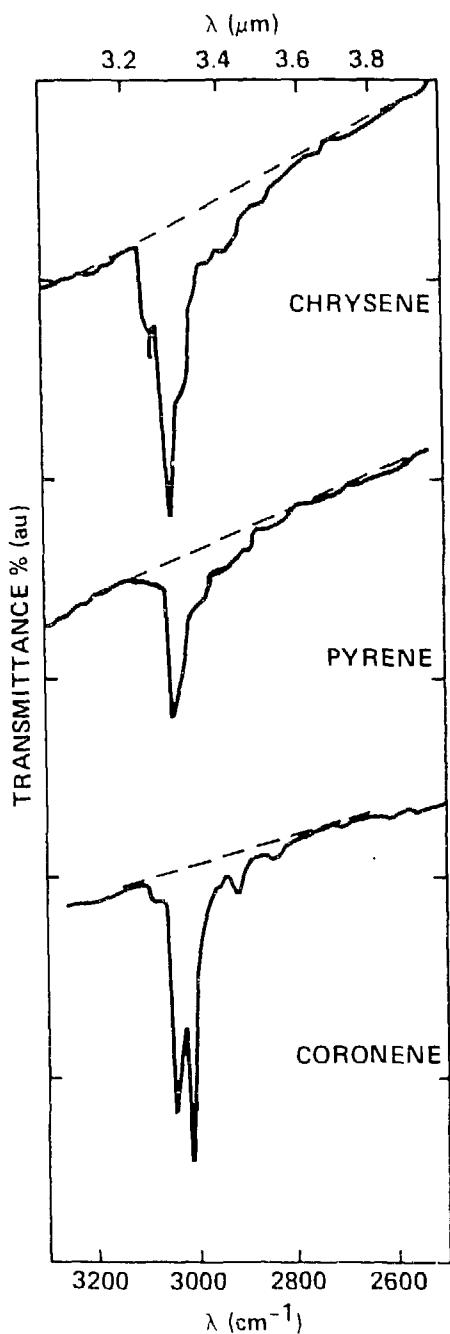
Figure 5. Infrared absorption spectra of chars at 400 and 480°C. Note the similarity between the 480°C char (a form of amorphous carbon) absorption spectrum, the Raman spectrum of soot and the long wavelength continuum in NGC 7027. (Char spectra from Mortera and Low, 1983).

closely. Weak, broad features at roughly 6.2, 7.7, and 11.3 microns are also evident in the extinction

curve of amorphous carbon particles (Koike, Hasegawa and Manabe, 1980, Borghesi et al., 1983). Sakata et al., (1984) have also suggested that the absorption spectrum of the hydrocarbon residue deposited by a methane plasma resembles the interstellar spectrum. The similarities and differences between the interstellar IR emission spectrum and spectra associated with various forms of amorphous carbon are discussed in detail in the papers by Duley, Bussolletti et al., Goebel, and Roessler, elsewhere in this volume. Since amorphous carbon is primarily composed of randomly oriented clusters of PAHs cross-linked and interconnected by saturated and unsaturated hydrocarbon chains, the overall spectral emissivity of small amorphous carbon particles will resemble PAH spectra, with the individual bands blurred out due to the solid state effects which produce the line shifting, broadening and intensity changes discussed by Allamandola (1984). Thus, the infrared spectroscopic properties of small amorphous carbon particles will be largely determined by the properties of the PAHs of which they are made. As the particles get larger, bands will overlap, producing broad features that possibly retain some substructure indicative of the individual PAHs. For still larger particles, bulk properties dominate and the broad components will appear as substructure on a strong continuum which follows a $1/\lambda$ law producing the extinction curve reported by Koike et al. (1980) and Borghesi et al. (1983).

In concluding this section on the spectroscopic aspect of the problem it is important to stress two points:

- 1) Given what is currently known about the spectroscopic properties of PAHs and PAH-like species, free PAHs seem promising candidates to account for the narrower emission components.
- 2) Having said this, there presently seems to be a better match



between the observed IR emission bands and laboratory amorphous carbon particle spectra than with a mixture of the free PAH spectra which we have available. Thus, on the basis of spectroscopic evidence alone, we would conclude that amorphous carbon particles are responsible. However, as described below (and in the article by Leger, this volume), a quantitative assessment of the emission band intensity, in particular that at 3 microns, forces us to conclude that the narrow bands are due to IR fluorescence from molecule sized species. Although this point had been previously raised by a few researchers (see review by Allamandola, 1984) the importance of this aspect of the emission problem was largely unrecognized until quite recently.

3. THE EMISSION MECHANISM

Recently attention was redirected toward the importance of the microscopic details of the emission mechanism. Sellgren, Werner and Dinerstein (1983) discovered the 3.3 micron emission band in reflection nebulae along with a continuum from about 1.25 to 5 microns with a constant color temperature, independent of position in the nebula. The color temperature of the emission was found to be relatively constant across the nebulae even though the pumping photon flux decreased, thus eliminating the possibility of a pumping mechanism in thermal equilibrium. Assuming the emission originated from particles, Sellgren (1984) proposed that thermal fluctuations in very small (10 Å) grains, which were caused by absorption of individual UV photons, could account for the observations. She also noted that the species responsible must be very stable, as two photons would

Figure 6. Infrared absorption spectra in the 3.3 micron region of the PAHs chrysene, pyrene and coronene, suspended in KBr. Spectra courtesy of Drs. Cyvin and Klaeboe, University of Trondheim, Norway.

occasionally be absorbed by these species raising their temperature to over 2000°K. (The two photon event timescale is only about 100⁷ years, while the lifetime of a reflection nebula is on the order of 10⁷ years. If two photon events could destroy the carrier, it would deplete the material in the emission zone.) Although previous results implied the emission is molecular in origin, (in particular the intensity at 3 microns relative to that of the longer wavelength bands,) the observation of a constant color temperature across the nebulae unambiguously pointed out that the emission process is not at thermal equilibrium. The importance of this non thermal-equilibrium, fluorescence process in determining the radiation balance of the interstellar medium also seems responsible for the IR cirrus (discovered by IRAS) and for the very extended 10 micron excess emission associated with reflection nebulae (discovered by Castellaz et al., 1986).

Our philosophy in developing a model to describe the emission process was to do as thorough a calculation as possible on a well understood PAH (chrysene, C₁₈H₁₂), for which most of the intramolecular relaxation processes were well known and which had well characterized vibrational modes. Although the intersystem crossing and internal conversion rates available for chrysene (Birks 1970) were measured in condensed phases and may be different for free gaseous species, the model calculation involved a minimum of speculation.

Figure 7 shows a highly schematic version of the overall excitation - emission process. (See the articles by Jortner and Mukamel elsewhere in this volume for a detailed discussion of these processes.) Prior to the absorption of a photon, any neutral PAH is in the lowest singlet electronic state, S₀. Photons of many energies are incident on the molecule, and of those absorbed, some can ionize the molecule and others can excite it to higher singlet states (S₁, S₂, ...). The absorbed energy will quickly redistribute itself within the molecule (<10⁻¹² s) via internal conversion (IC) (S_f ← S_i) and intersystem crossing (ISC) (T_f ← S_i) processes. For chrysene, the strongest absorption corresponds to the S₃⁰ ← S₀ transition which peaks near 2675A. Nearly 90% of these excited molecules undergo rapid ISC to high vibrational levels of the T state. Because T is lower than S₁ (this is true for virtually all neutral PAHs) and the direct radiative transition (phosphorescence) from T to S₀ occurs very slowly (on the order of several seconds) the energy is trapped in the lowest triplet state, T₀. Thus, a few nanoseconds after the absorption of a 2675A (37,400 cm⁻¹) photon, about 17400 cm⁻¹ is trapped in the triplet state as vibrational energy. The remainder is "stored" by the molecule which is now in the triplet electronic state. This highly vibrationally excited molecule can lose its vibrational energy only by radiating IR photons, primarily by the transitions (V_{n-1}⁰ ← V_n⁰) at the fundamental vibrational frequencies of the T state. This process is known as infrared fluorescence (IRF). IRF lifetimes are on the order of a tenth of a second while the phosphorescent lifetime (S₀ ← T₀) for chrysene is longer than three seconds. Thus, IRF is the major deactivation route, although a small fraction of the excited population will relax via phosphorescent emission of red and near IR photons.

If the excited PAH is ionized (as we believe to be the case in the

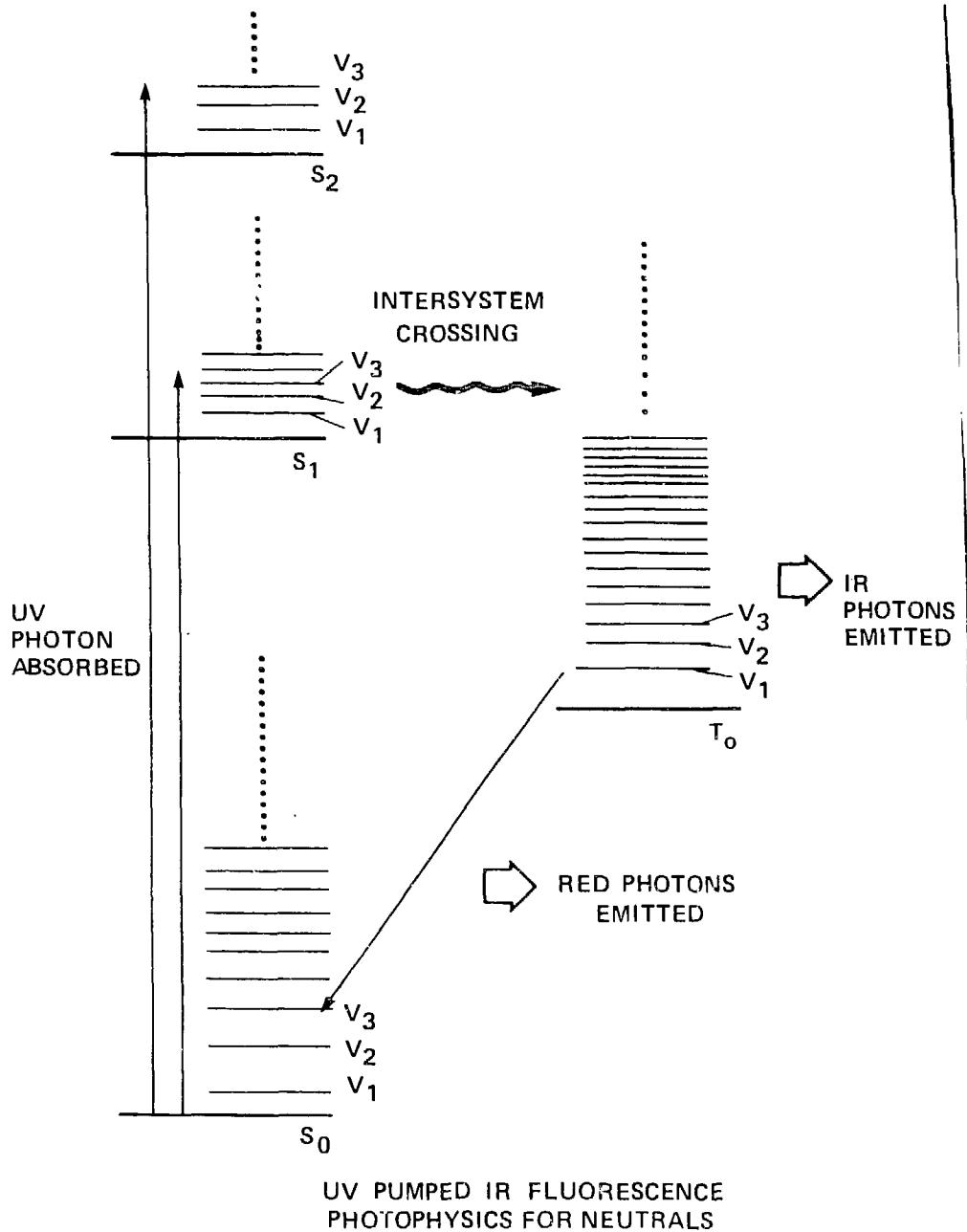


Figure 7. Schematic energy level diagram for a neutral PAH, showing the various radiative and nonradiative excitation and relaxation channels possible. Taken from ATBb.

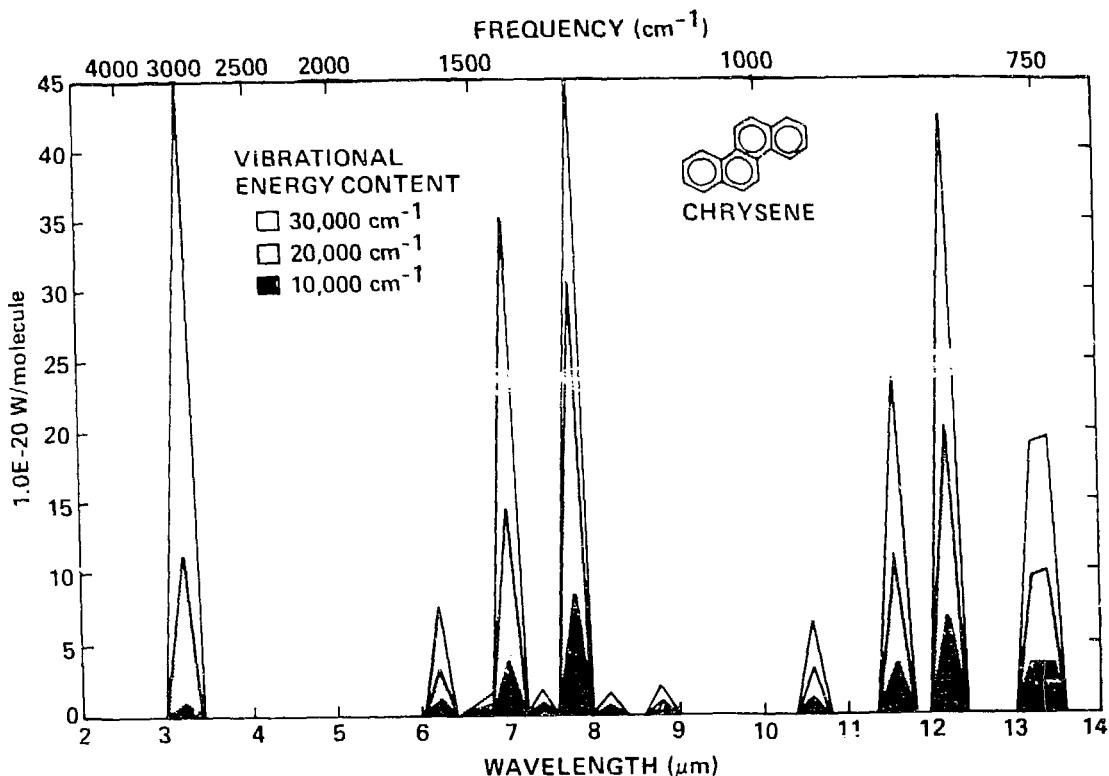


Figure 8. The IR fluorescence spectrum from chrysene as a function of vibrational energy content. Taken from ATBb.

emitting zone), the energy level diagram will be quite different, involving doublet (D) and quartet (Q) states rather than singlets and triplets, with the ground electronic state being a doublet, D_0 . In the case of an ion, the lowest excited doublet state, D_1 , is always lower than Q_0 and trapping in the Q_0 state, which cannot radiatively relax to the ground state, D_0 , is not important. (see the articles by Leach, this volume, for a complete description of this situation.) Thus, for free molecular ions nearly all of the energy is quickly converted to vibrational energy in the ground electronic state, D_0 , where IRF is the only deactivation route.

The infrared emission spectrum predicted for chrysene is plotted in Figure 8 as a function of vibrational energy content. From Figures 3 and 8 several conclusions may be reached. Firstly, the IRF spectrum varies dramatically as the vibrational energy is changed and it does not necessarily match the intensity distribution observed in absorption. Secondly, no significant IRF emission is observed from the 3000 cm^{-1} modes (3.3 microns), unless the molecule contains a significant amount of vibrational energy per vibrational mode. Thirdly, the intensities of the 3000 cm^{-1} modes (3.3 microns) relative to the 1000 cm^{-1} modes (10 microns) are directly related to the internal energy of the molecule.

One of the many important consequences of this treatment is that the intensity ratio of the 11.3 to 3.3 micron bands provides a measure of the vibrational energy content of the emitting species if its size is known; conversely, if the energy content of the molecules is known, the size of the emitting species can be estimated. Thus, if one knows the spectrum of the exciting UV field, the 11.3/3.3 intensity ratio indicates the number of carbon atoms in the smallest emitting species (the most intense emitters). Conversely, if one can confine the size of the most intense emitting PAH on the basis of spectroscopic constraints, one can determine the part of the incident radiation field that is most important in pumping the IR bands.

To make this estimate note that for each C-H bond one out-of-plane bending mode and one stretching mode will be present; thus, the number of modes emitting near 885 cm^{-1} (11.3 micron) equals the number of modes emitting near 3000 cm^{-1} (3.3 microns), regardless of the actual number of C-H bonds present in each molecule. Vibrational assignments for benzene (C_6H_6), azulene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$), chrysene ($C_{18}H_{12}$), and perylene ($C_{20}H_{12}$) were used to predict the relative IRF emission intensities due to one C-H stretch mode and due to one C-H out-of-plane mode, assuming they have equal integrated absorption coefficients, as is approximately true in the gas for free molecular benzene (Bishop and Cheung, 1982), naphthalene and anthracene (Niki, 1986).

As an initially vibrationally excited molecule relaxes by infrared emission, it must sequentially emit many infrared photons and undergo an energy cascade before it reaches equilibrium with the low temperatures of the ISM. Thus, the observed interstellar emission bands are due to emission from molecules in all stages of relaxation subsequent to excitation to some initial energy. For comparison with the emission bands, the calculated decay rates of IRF emission were used to average the calculated intensities over the entire range of energy up to the initial excitation level. Ratios of IRF intensities (averaged over the cascade) were calculated for several initial excitation energies. The calculated ratios of IRF intensities are plotted in Figure 9 as a function of the number of carbon atoms in each molecule for several values of initial internal energy.

The observed 11.3/3.3 intensity ratio in Orion is near unity and the ratios observed in other objects range up to about 4 or 5 (Cohen et al., 1986). If the average emitting species was initially excited to about $80,000 \text{ cm}^{-1}$ (1250A) and all of that energy was converted to vibrational energy, it must have 20 to 80 carbon atoms to explain the observed intensity ratios ranging from 1 to 5. At lower excitation energies, even smaller species can explain the observed intensity ratios, but the maximum size is limited by the maximum energy of the photons available (about $80,000 - 100,000 \text{ cm}^{-1}$).

Visual inspection of published IR absorption spectra for PAHs suspended in KBr shows that the integrated absorption strength of the bands in the 11-13 micron range is generally about three to five times more intense than the bands at 3.3 microns. This differs from the near unity values (used in the calculation) observed in the gas phase for benzene, naphthalene and anthracene (Niki, 1986). However, if the 11-13 micron modes in the larger emitting PAHs consisting of several fused

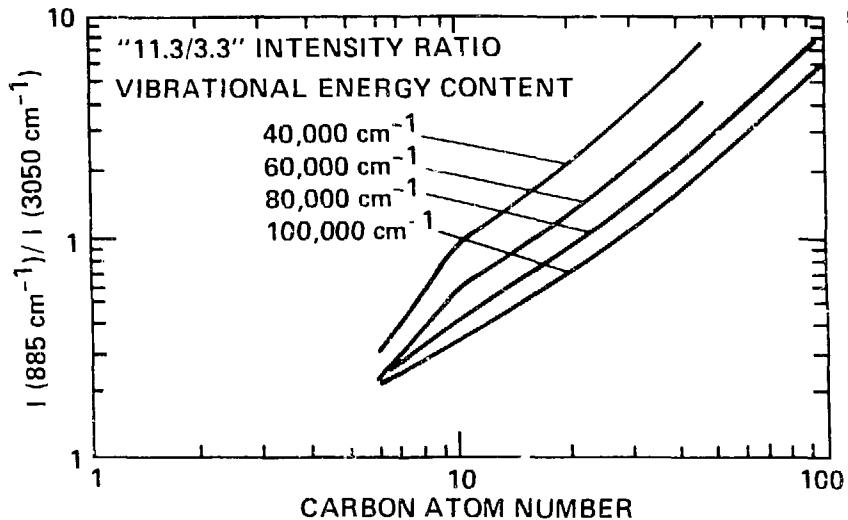


Figure 9. The 11.3 micron/3.3 micron intensity ratio plotted as a function of carbon atom number and vibrational energy content. The relative fluorescence intensities includes integration over the vibrational cascade. Taken from ATBb.

rings has an integrated absorption coefficient three times larger than that of the 3.3 micron mode, the maximum molecular size consistent with the observed intensity ratio range is reduced by a factor of two to three, indicating that the band carriers are species containing about 20 to 30 carbon atoms. This conclusion is in agreement with the number deduced from individual band profiles analyzed by accounting for emission from higher vibrational levels, which are shifted by anharmonicity. Space limitations preclude more than a passing reference to this important point. A detailed discussion is presented in Barker et al., 1986 and ATBb.

In concluding this section on the detailed emission mechanism, we wish to point out that while one can model the emission phenomenon using a thermal model approximation, such approximations are of severely limited validity (ATBa,b; Barker, Allamandola and Tielens, 1986). We stress that the molecular approach permits one to address questions regarding photostability, hydrogen coverage, reactivity, photoisomerization and deuterium fractionation in a completely self-consistent, non-approximate manner in addition to being able to explain the observed emission ratio and account for band profile behavior.

4. THE MULTICOMPONENT NATURE OF THE EMISSION SPECTRUM.

A "dilemma" is presented by 1) the spectroscopic case which suggests amorphous carbon particles in addition to free PAHs as the carrier of the emission, and 2) the energetics which point to molecule sized species containing about 20 carbon atoms. This dilemma is resolved by

realizing that in nearly all cases the aperture sizes used to measure the interstellar spectra encompass a large fraction of the entire emission object. Thus, in many cases, we are collecting photons originating from a zone which includes cold, dense, neutral material as well as highly excited, ionized material close to the pumping star.

The high excitation planetary nebula NGC 7027, which occupies only a few arcseconds of the sky, typifies this situation. Because it is a very intense infrared object, several groups have mapped this object at different wavelengths. On the basis of broad band maps Bentley (1982) concludes that two separate components are responsible for the IR emission. One which carried the features, the other responsible for the continuum as measured at 10 microns. Aitken and Roche (1983) have carried out a very thorough 8-13 micron spectral mapping program of this source which is very informative. Their spectra show interesting spectral variations in the features, not only in going from the ionized to the neutral zone, but also within each zone as well. Most recently, Goebel (1986, and this volume) has shown that there is a remarkable resemblance between the spectrum of hydrogenated amorphous carbon (HAC) and the underlying continuum (not the features) in NGC 7027 and suggested that HAC particles, warmed by the incident photons, were primarily responsible for the broad underlying continuum. High spatial and spectral resolution IR maps of NGC 7027 shows that the emission at 8.2 microns (presumed to be a tracer of the "7.7" micron feature) peaks in a very different location within the nebula than the continuum emission (due to the broad component) as measured at 10 microns (Goebel, 1986). Taken together these results show that emission from both amorphous carbon like particles and free PAHs contribute to the overall infrared emission from NGC 7027 (and presumably in other objects which have sufficient flux to heat small particles).

Our principle conclusion is that progress in this field requires studies which focus on the spatial characteristics of the spectra from these components. It is only in this way that the distribution and evolution of carbon from molecule to particle can be traced. Thus, at this stage of the interstellar IR emission band problem, spectroscopic studies on extended objects are called for. Under the right conditions (where confusion from particle emission can be eliminated) it may be possible to limit the particular PAHs responsible for the features to a handful.

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5. REFERENCES

Aitken, D. K. and Roche, P. F. (1983), *Mon. Not. R. Astr. Soc.* 202, 1233

Aitken, D. K. and Roche, P. F. (1982), *Mon. Not. R. Astr. Soc.* 200, 217

Aitken, D. K., Roche, P. F., Spenser, P. M. and Jones, B. (1979) *Ap. J.*

Allamandola, L. J. (1984), "Absorption and Emission Characteristics of Interstellar Dust" in Galactic and Extragalactic Infrared Spectroscopy, eds. Kessler, M. F. and Philips, J. P. (D. Reidel Publishing Co., Dordrecht), 5.

Allamandola, L. J., Tielens, A. G. G. M. and Barker, J. R. (1985), Ap. J. Letters, 290 L25 (ATBa).

Allamandola, L. J., Tielens, A. G. G. M. and Barker, J. R. (1986), Ap. J., submitted. (ATBb).

Barker, J. R., Allamandola, L. J., and Tielens, A. G. G. M. (1986), Ap. J. (Letters) submitted.

Bakke, A., Cyvin, B. N., Whitmer, J. C., Cyvin, S. J., Gustavsen, J. E., and Klaeboe, P. (1979), Z. Naturforsch 34a, 579.

Bellamy, L. J. 1958, The Infrared Spectra of Complex Organic Molecules, (John Wiley and Sons, 2nd ed. New York)

Bentley, A. F. (1982) Astron. J., 87, 1810.

Birks, J. B. (1970), Photophysics of Aromatic Molecules (London: Wiley-Interscience)

Bishop, D. M. and Cheung, L. M. (1982), J. Phys. Chem. Ref. Data, 11, 119.

Borghesi, A., Bussoletti, E., Colangeli, L., Minafra, A. and Rubini, F., (1983), Infrared Physics 23, 321.

Bregman, J., Allamandola, L. J., Simpson, J., Tielens, A., and Witteborn, F. (1981) NASA/ASP Symposium, Airborne Astronomy, NASA/Ames Research Center (NASA CP 2353).

Bregman, J. et al. 1986) in preparation.

Castellaz, M., Seligson, K. and Werner, M., (1986), Ap. J. (Letters) submitted.

Cohen, M., Tielens, A. G. G. M., and Allamandola, L. J. (1985) Ap. J. (Letters), 299, L93.

Cohen, M., Allamandola, L. J., Tielens, A. G. G. M., Bregman, J., Simpson, J. P., Witteborn, F. C., Wooden, D. and Rank, D. (1985) Ap. J., in press.

Cyvin, S. J., Cyvin, B. N., Brunvoll, J., Whitmer, J. C., Klaeboe, P., and Gustavsen, J. E. (1979), Z. Naturforsch, 34a, 876.

Cyvin, S. J., Cyvin, B. N., Brunvoll J., Whitmer, J. C., and Klaeboe, P. (1982b), Z. Naturforsch, 37a, 1359.

Cyvin, B. N., Klaeboe, P., Whitmer, J. C. and Cyvin, S. J. (1982a), Z. Naturforsch, 37a, 251.

Duley, W. W. and Williams, D. A. (1981) Mon. Not. R. Astro. Soc., 196, 269.

Geballe, T. R., Lacy, J. H., Persson, S. E., McGregor, P. J., and Soifer, B. T. (1985), Ap. J. 292, 500.

Goebel, J. (1986), B. A. A. S., 17, Abstract 52.06, 908.

Herzberg, G. H., (1968), Infrared and Raman Spectra of Polyatomic Molecules, (D. van Nostrand Co., Princeton).

Koike, C., Hasegawa, H., and Manabe, A., (1980), Astrophys. Space Sci. 67, 495

Leger, A., and Puget, J. L. (1984), Astro. Ap. 137, L5. (LP).

Mortera, C., and Low, M. J. D. (1983), Carbon, 21, 283.

Niki, H. (1986), (private communication).

Oberlin, A. (1984), Carbon 22, 521.

Robin, M. (1975), Higher Excited States of Polyatomic Molecules II (Academic Press, N.Y.)

Rosen, H., and Novakov, T., (1978), Atmospheric Environment 12, 923.

Russell, R.W., Soifer, B. T. and Willner, S. P. (1977) Ap. J. (Letters) 217, L149.

Sakata, A., Wada, S., Tanabe, T., and Onaka, T. (1984), Ap. J. (Letters), 287, L51.

Sellgren, K. (1984) Ap. J., 277, 623.

Sellgren, K., Allamandola, L. J., Bregman, J. D., Werner, M. W. and Wooden, D. H., (1985) Ap. J. 299, 416.

Sellgren, K., Werner, M. W., and Dinerstein, H. L. (1983), Ap. J. (Letters) 217, L149.

Willner, S. P. (1984), "Observed Spectral Features of Dust" in Galactic and Extragalactic Infrared Spectroscopy, eds. Kessler, M. F. and Phillips, J. P. (D. Reidel Publishing Co., Dordrecht), 37.

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