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INFRARED ABSORPTION AND EMISSION CHARACTERISTICS OF INTERSTELLAR PAHs

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ABSTRACT. The mid-infrared interstellar emission spectrum with features at 3050, 1610, 1300, 1150, and 885 cm^{-1} (3.28, 6.2, 7.7, 8.7 and 11.3 microns) is discussed in terms of the Polycyclic Aromatic Hydrocarbon (PAH) hypothesis. This hypothesis is based on the suggestive, but inconclusive comparison between the interstellar emission spectrum with the infrared absorption and Raman spectra of a few PAHs. The fundamental vibrations of PAHs and PAH-like species which determine the IR and Raman properties are discussed. Interstellar IR band emission is due to relaxation from highly vibrationally excited PAHs which have been excited by ultraviolet photons. The excitation/emission process is described in general and the IR fluorescence from one PAH, chrysene, is traced in detail. Generally, there is sufficient energy to populate several vibrational levels in each mode. Molecular vibrational potentials are anharmonic and emission from these higher levels will fall at lower frequencies and produce weak features to the red of the stronger fundamentals. This process is also described and can account for some spectroscopic details of the interstellar emission spectra previously unexplained. Analysis of the interstellar spectrum shows that PAHs containing between 20 and 30 carbon atoms are responsible for the emission.

1. INTRODUCTION

Understanding the origin of the set of interstellar infrared emission bands at 3.28, 6.2, "7.7", 8.6 and 11.3 microns (3050, 1613, 1310, 1160 and 885 cm^{-1}) forms the core of an important problem in interstellar astrophysics. Since their discovery in 1973 by Gillett, Forrest and Merrill, the bands have been found to be associated with a number of stellar objects, planetary nebulae, reflection nebulae, H-II regions and extragalactic sources. As the number and variety of objects discovered to emit these features increased, it became clear that identifying the carrier and elucidating the excitation-emission mechanism were the central issues. These observations also showed that the bands were due to a surprisingly widespread, extremely stable, interstellar constituent (see Willner, 1984 and Allamandola, 1984 for reviews of the observations and theories up to 1983).

While it has been recognized for some time that the emission was most likely pumped by ultraviolet photons, (Allamandola and Norman, 1978), identifying the carrier remained elusive. Although several models have been proposed, until recently none was very satisfactory. In brief, these models are as follows: (1) infrared fluorescence from UV-pumped, vibrationally excited, small molecules (e.g., CH_4, H_2O, NH_3, CO) frozen on 0.1 micron-sized grains at low ($\approx$ 10 K) temperatures (Allamandola and Norman 1978); (2) equilibrium thermal emission from small (0.01 micron) grains at 300 K, coated with an unspecified polymeric material (Dwek et al. 1980); (3) equilibrium thermal emission from characteristic groups on aromatic-like moieties, present at the surface of small carbon grains (Duley and Williams 1981); (4) nonequilibrium thermal emission from very small grains (0.001 micron) of unspecified composition that are temporarily heated to 1000 K by the absorption of a single UV photon (Sellgren 1984; Sellgren, Werner and Dinerstein 1983). There are drawbacks with each model. Model 1 requires a multicomponent mantle that does not change composition under a wide variety of interstellar conditions. Models 2 and 3 require values for the infrared oscillator strength (f) near unity. Typically, f varies from 10^{-5} to 10^{-3} for vibrational transitions. Model 4 relies on the uncertain assumption that a 10 Å-sized species can be treated as if it has bulk thermal and optical properties. Progress towards the hypothesis currently gaining acceptance, that aromatic hydrocarbons may be responsible for the bands, began with the suggestion by Duley and Williams (1981) that they arise from vibrations of characteristic chemical groups attached to the aromatic moities present at the surfaces of small (<0.01 microns) amorphous carbon particles. Leger and Puget (1984) and Allamandola, Tielens and Barker (1985) later proposed that vibrations in individual, molecule sized (0.001 microns) polycyclic aromatic hydrocarbons (PAHs) and PAH-like species were responsible for the bands. As a class these complex, planar, organic molecules which are made up of fused six membered rings (chicken wire-like structure) are extremely stable.

Apart from the overall resemblance of the interstellar IR band spectrum to the vibrational spectrum expected from PAH-like species (see Section 2 below), the results of recent, related observations tend to favor an aromatic hydrocarbon 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 relative IR band intensities among different objects, they are correlated, implying that a single class of chemical species is responsible.

Within the framework of the PAH hypothesis, spectroscopic analysis suggests that there are at least two classes of components which contribute to the total infrared emission spectrum. Free, molecule-sized PAHs produce the narrow features and amorphous carbon particles (which are primarily made up of an irregular "lattice" of interconnected PAHs, see Tielens and Allamandola, elsewhere in this volume) contribute to the broad, underlying component (Allamandola, Tielens and Barker, 1986a; Goebel, 1986.)

In view of the central role PAHs seem to play in determining the IR properties of specific objects as well as of the interstellar medium itself, this chapter will focus on the infrared characteristics of PAHs and the UV-Visible pumped IR emission mechanism.

2. THE VIBRATIONAL SPECTROSCOPY OF PAHs

Although the IR emission 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 1, 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 (1986), 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 suggestive, but inconclusive, 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 Allamandola, Tielens and Barker (1985, 1986b hereafter ATBa,c). Because of the suggestive match, the assumption has been made that PAHs in some form or combination are responsible for the interstellar emission. Only when detailed laboratory spectra for the various free PAHs in their neutral and ionized forms 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 1, the 3.29 micron band is highly characteristic of an aromatic system (Duley and Williams, 1931; Bellamy, 1958). In general, PAHs show a dominant band at about 3.28 microns, 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. 1982a,b, Herzberg, 1968).

Figure 1 shows that the 6.2 micron emission band (which corresponds to a C-C stretching vibration in PAHs) is as characteristic of polycyclic aromatic species as is the 3.3 micron band (LP; Bellamy, 1958).

Perusal of Figure 1 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,c, 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 1, 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. 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 underlying the well-known 11.3 micron band not only relieved some of the difficulty associated with understanding partial hydrogenation in exceedingly H rich environments, but also showed 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. 1986, Cohen, Tielens and Allamandola 1985).

The spectra shown in Figure 1 serve to illustrate several additional points. For a free, highly symmetric PAH (e.g., coronene) with an inversion center of symmetry, 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 for free, less symmetric PAHs, or PAHs in clusters or amorphous carbon particles) the IR and Raman spectra 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 2, ATBa), and thus point out the striking similarity between the interstellar emission bands and the vibrational spectra of a mixture of PAHs (amorphous carbon is made up of PAH subunits cross linked in an irregular fashion, see, Tielens and Allamandola, elsewhere in this volume. For comparison, Figure 3 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

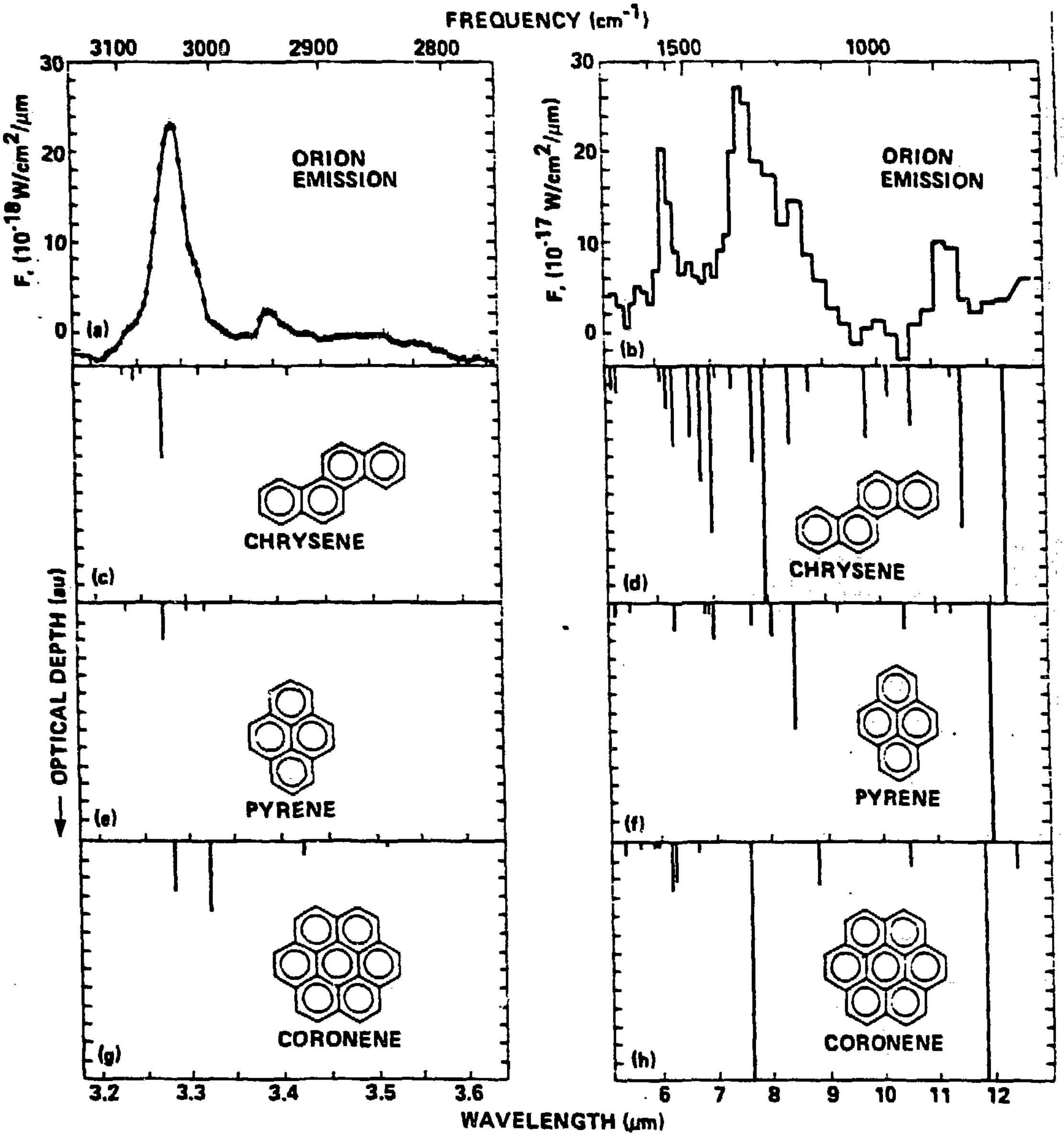

Figure 1. The 3-13 micron emission spectrum from the Orion Bar compared with the absorption spectra of the PAHs chrysene, pyrene and coronene suspended in KBr pellets. (Orion, Bregman et al. 1986; Chrysene, Cyvin et al. 1982a; Pyrene, Cyvin et al. 1979; Coronene, Bakke et al. 1979; Cyvin et al. 1982b). Taken from ATB,c.

component starting at about 3.15 microns, extending to about 3.65 microns, and peaking near 3.41 microns). Figure 4 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 2,3 and 4 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 blended contribution from overtone and combination bands, highly vibrationally excited molecules emit from vibrational levels higher than V=1. Emission from these higher levels, shifted for anharmonicity, contributes significantly to the emission features superimposed on the 3.4 micron plateau and many of the other components of the interstellar spectrum (see section 3.2, Barker et al. 1986 and ATBa,c). The recent discovery of specific bands in this plateau (de Muizon, et al. 1986) supports this explanation of the plateau in terms of overlapping individual lines.

As shown in Figures 2 and 3, the infrared signature of amorphous carbon soots and chars resembles the interstellar IR band spectrum rather 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 elsewhere (ATBb, Goebel, 1986). 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 effect which produce line shifting, broadening and intensity changes (Allamandola 1984), Thus, the infrared spectroscopic properties of small amorphous carbon particles will be largely determined

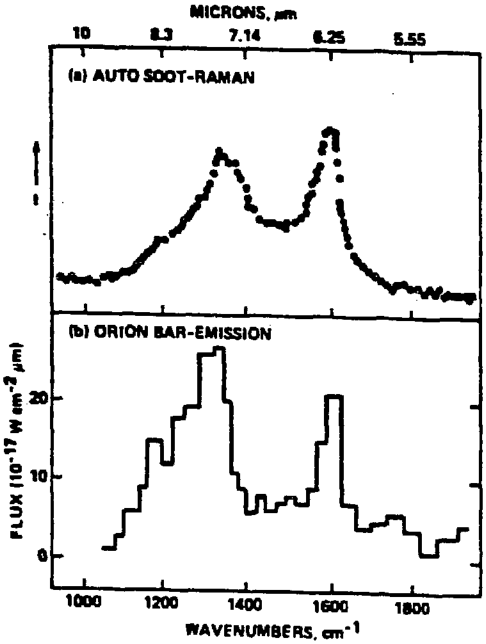

Figure 2. Comparison of the 5 to 10 micron Raman spectrum of auto soot (a form of amorphous carbon) with the emission from Orion (soot spectrum, adapted from Rosen and Novakov 1978; Orion, Bregman et al. 1984, 1986). Taken from ATBa.

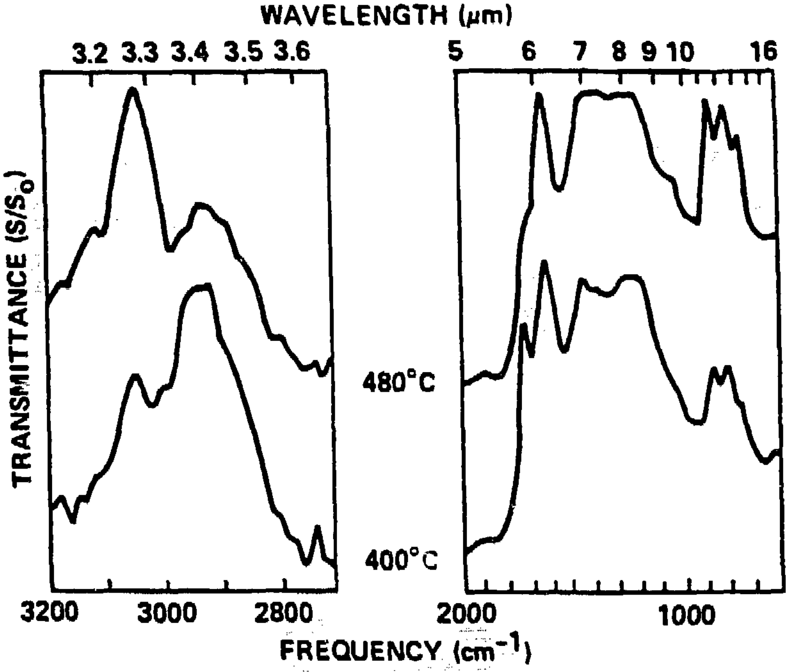

Figure 3. Infrared absorption spectra of chars at 400 and 480°C. Note the similarity between the 480°C char (a form of amorphous carbon) absorption spectrum, with the Raman spectrum of soot. (Char spectra from Mortera and Low 1983). Taken from ATBc.

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/λ law, (see Tielens and Allamandola, this volume) producing the extinction curve reported by Koike et al. (1980) and Borghesi et al. (1983).

Summing up, spectroscopically, a collection of PAH-like species, either in solid form (amorphous carbon grains) or as "free-flying", gas phase molecules, seem to be able to account for the narrow emission features. However, as described in the next section, the intensity of the emission at 3 microns with respect to that at longer wavelengths forces us to conclude that the emission bands originate in molecule sized species.

3. THE EMISSION MECHANISM

The overall excitation-emission mechanism envisioned is as follows. A free PAH, which may be in an ionized or neutral form, absorbs an ultraviolet or visible photon and is excited into an upper electronic state. The PAH quickly converts this electronic energy into vibrational energy. For example, a PAH such as pyrene ($C_{16}H_{10}$) has 72 normal, vibrational modes, each having a specific vibrational frequency lying

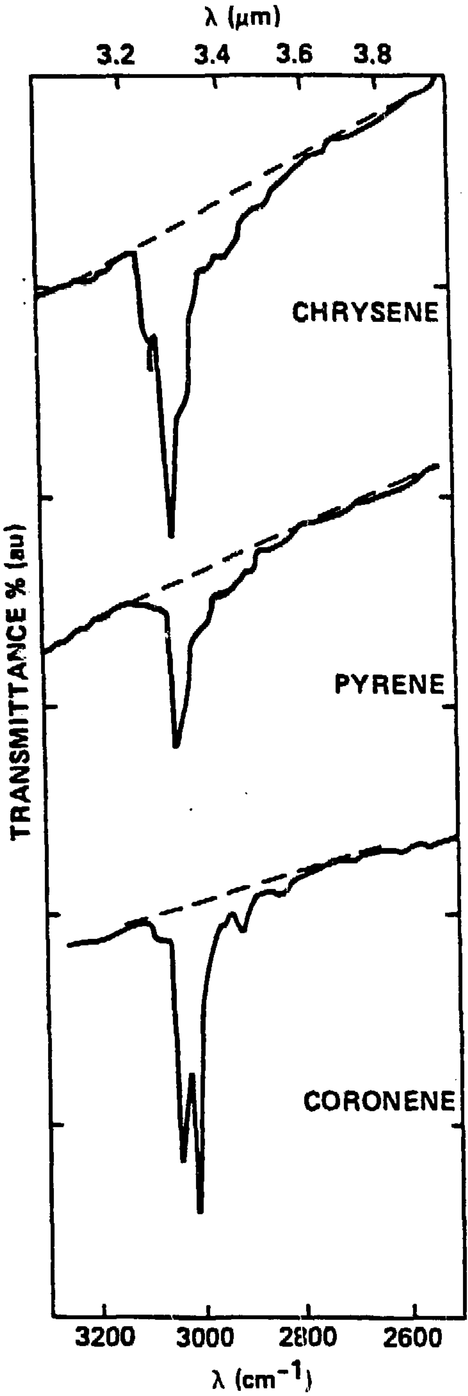

Figure 4. Infrared absorption spectra in the 3.3 micron region of the PAHs chrysene, pyrene and coronene, suspended in KBr. Spectra courtesy of Drs. Cyvin and Klaeboe, University of Trondheim, Norway.

in the 3100-200 cm^{-1} range. Within a few picoseconds of the deposition of the energy in a particular electronic state it will be spread out amongst these modes. Energy transfer from mode to mode occurs on a similar timescale. In the absence of collisions, the only routes for deactivation of the neutral, vibrationally excited molecule are electronic phosphorescence, and fluorescence and infrared vibrational fluorescence (IRF). For ions IRF is the only relaxation mechanism available. It is this relaxation process which is responsible for the interstellar infrared emission bands. The details of this process are described below.

3.1 The Molecular Emission Process

Figure 5 shows a highly schematic version of the overall excitation - emission processes for a neutral PAH (ATBa,c, see also Jortner, 1986, for a detailed discussion of these processes). Prior to the absorption of a photon, any neutral PAH is in the lowest singlet electronic state, S_o. 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 (S_1,S_2,...). The absorbed energy will quickly redistribute itself within the molecule ($<10^{-12}$s) via internal conversion (IC) ($S_f \leftarrow S_i$; i.e., transfer to a highly vibrationally excited state of the lower lying electronic singlet state) and intersystem crossing (ISC) ($T_f \leftarrow S_i$; i.e transfer to a highly vibrationally excited state of a lower lying electronic triplet state) processes. Note that the latter process leaves the molecules also with a considerable amount of electronic

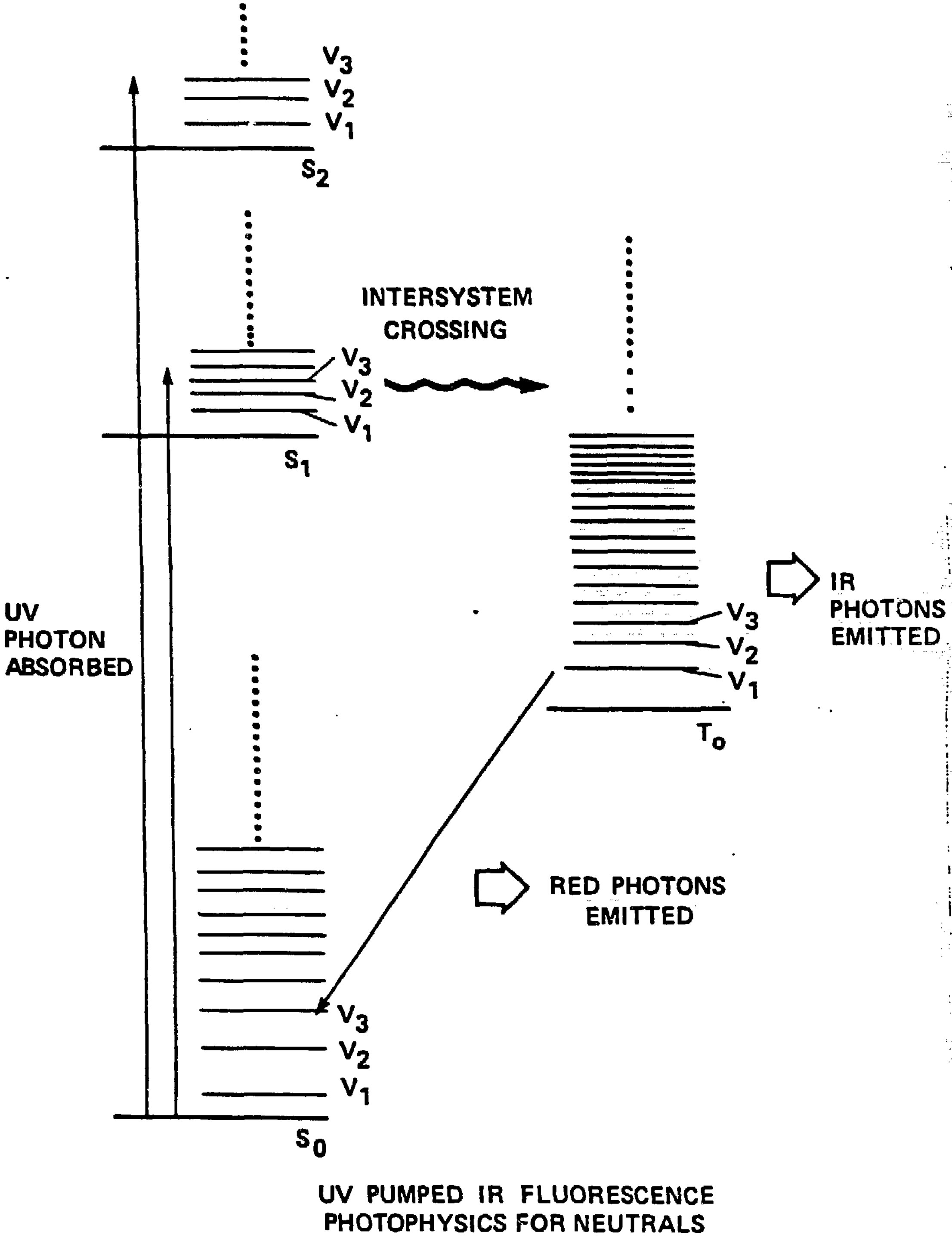

Figure 5. Schematic energy level diagram for a neutral PAH, showing the various radiative and nonradiative excitation and relaxation channels possible. Taken from ATBc.

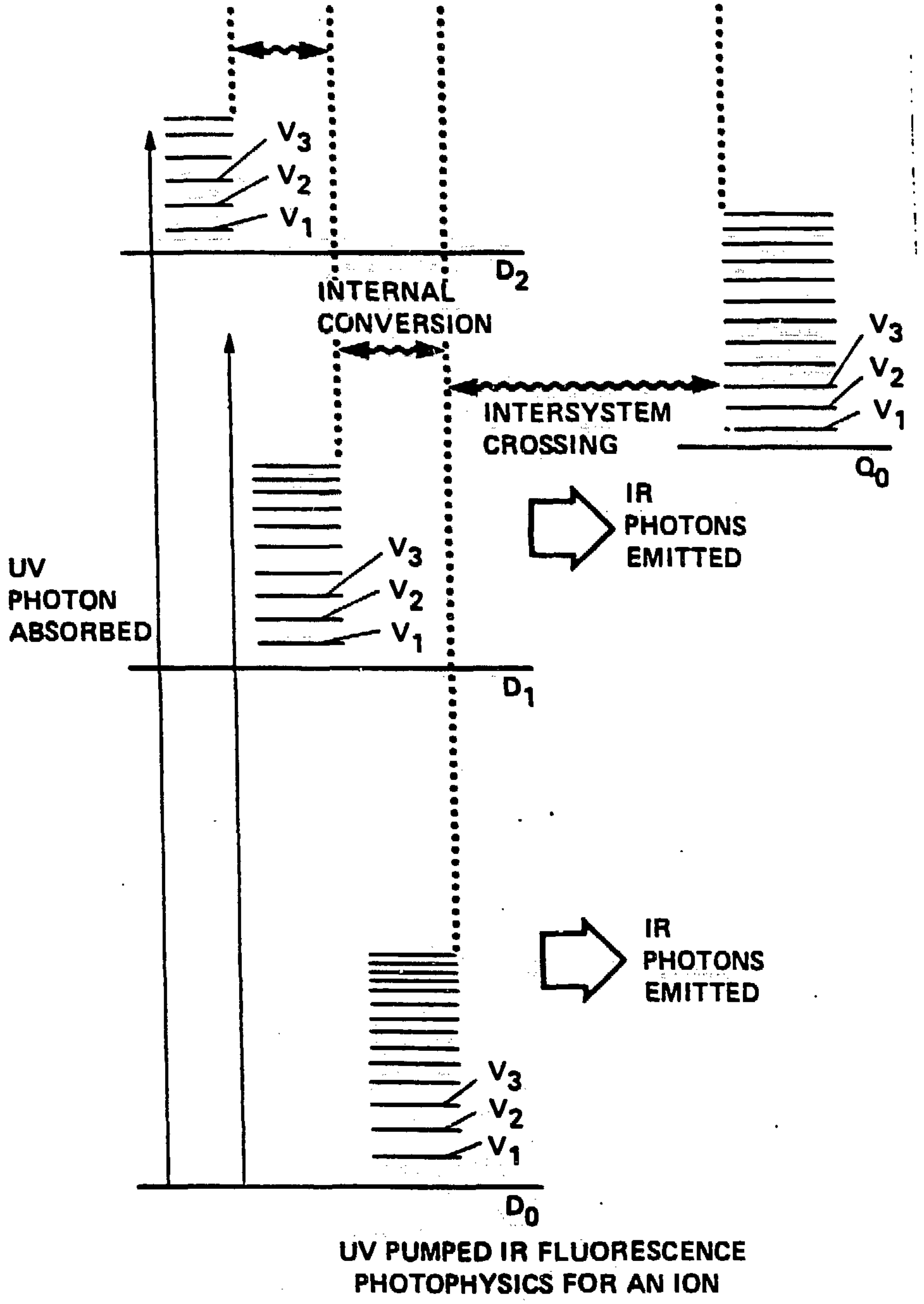

Figure 6. Schematic energy level diagram for an ionized PAH, showing the various radiative and non-radiative excitation and relaxation channels possible. Taken from ATBc.

excitation energy. For chrysene, the strongest absorption corresponds to the $S_3 \leftarrow S_o$ transition which peaks near 2675A. Nearly 90% of these excited molecules undergo rapid ISC to high vibrational levels of the T_o state. Because T_o is lower than S_1 (this is true for virtually all neutral PAHs) and the direct electronic radiative relaxation (phosphorescence) from T_o to S_o occurs very slowly (on the order of several seconds) about 19,400 cm^{-1} of the 37,400 cm^{-1} photon energy 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 ($V_{n-1} \leftarrow V_n$) at the fundamental vibrational frequencies of the T_o state. IRF lifetimes are on the order of a tenth of a second while the phosphorescent lifetime ($S_o \leftarrow T_o$) for chrysene is longer than three seconds.

Figure 6 shows that if the excited PAH is ionized (as we believe to be the case in the 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_o. In the case of an ion, the lowest excited doublet state, D_1, is always lower than Q_o and trapping in the Q_o state, which can only slowly radiatively relax to the ground state, D_o, is not important, (see Leach, 1986, 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_o, where IRF is the only deactivation route.

The calculation is described in detail elsewhere (ATBc; Barker, Allamandola and Tielens, 1986). The feature of this system which distinguishes it from a thermal system is that all molecules which absorb a photon of energy $h\nu$ have the same total energy: in a thermal system each molecule has a different total energy but the ensemble average energy equals $h\nu$. The fractional number of molecules with total vibrational energy E that have v quanta in a particular mode is a ratio equal to the number of ways of distributing the energy while that mode has v quanta excited, divided by the total number of ways to distribute the energy. For energies in excess of a few thousand wavenumbers, the statistical redistribution is completed in less than a few microseconds (Oref and Rabinovitch, 1979, Bondybey, 1984).

The infrared emission spectrum predicted for chrysene is plotted in Figure 7 as a function of vibrational energy content. From Figure 7 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 885 to 3030 cm^{-1} (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 885/3030 cm^{-1} (11.3/3.3 micron) intensity ratio indicates the number of carbon atoms in the smallest emitting species (the most intense emitters).

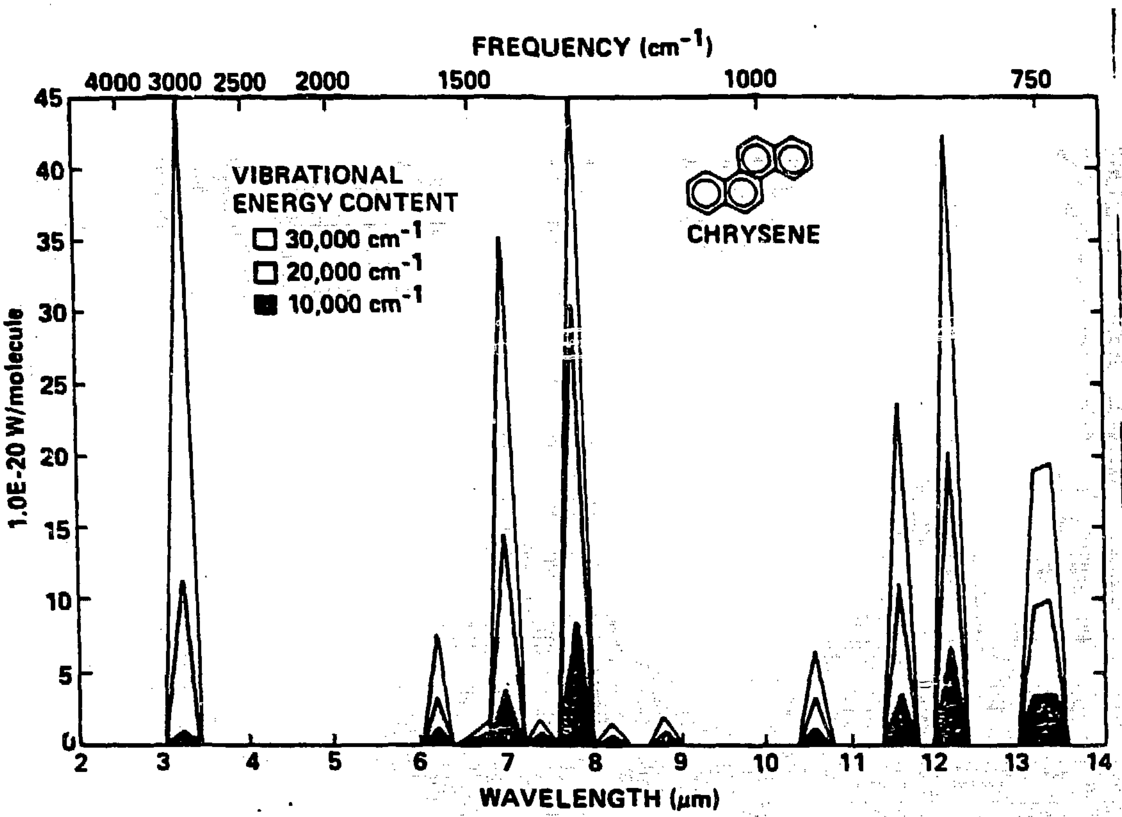

Figure 7. The IR fluorescence spectrum from chrysene as a function of vibrational energy content. Taken from ATBc.

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), napthalene 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

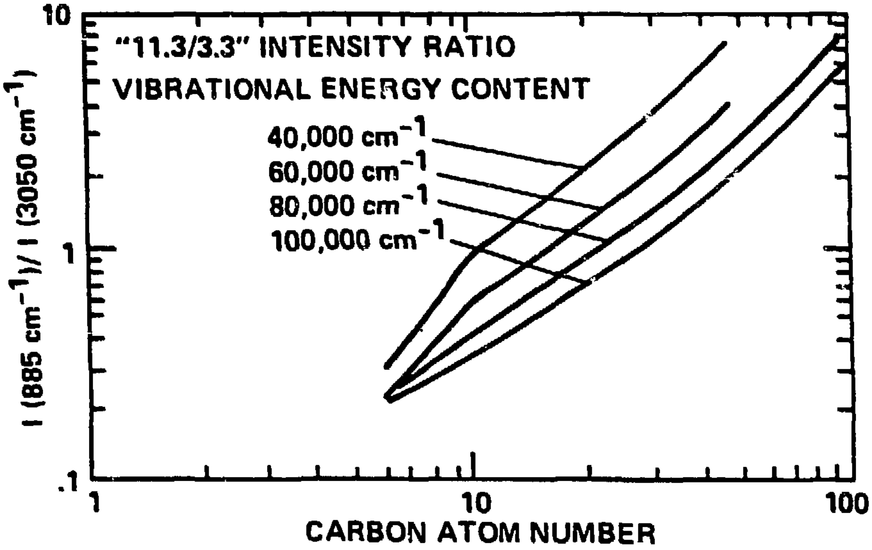

Figure 8. The 11.3 micron/3.3 micron intensity ratio plaotted as a function of carbon atom number and vibrational energy content. The relative fluorescence intensities includes integration over the vibrational cascade. Taken from ATBc.

excitation to some initial energy. For comparison with the emission bands, the calculated decay rates of the IRF emission were used to average the calculated intensities over the entire range of energy up to the initial excitatation 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 8 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 about three, and the ratios observed in other objects range from 2 up to about 4 or 5 (Cohen et al. 1986). If the average emitting species was initially excited to about 80,000 cm^{-1} (1250Å) 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 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, napthalene and anthracene (Niki, 1986). However, if the 11-13 micron modes in the larger emitting PAHs consisting of several fused 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 10 to 30 carbon atoms. As discussed below, 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.

3.2 Molecular Anharmonicity

Introductory descriptions of molecular vibrations and derivations of vibrational frequencies are generally discussed in terms of the harmonic oscillations of two bodies connected with a spring and described by the quantum version of Hookes law where the frequencies are determined by the molecular force field. The force field, which depends on the electron distribution in the molecule, describes the shapes and depths of the potential well which binds the atoms. For example, the frequency range of the aromatic CH stretch is 3100-2900 cm^{-1} (3.23-3.45 microns), while for the in-plane bend it is 1250-1000 cm^{-1} (8-10 microns) and for the out-of-plane bend it is 900 to 555 cm^{-1} (11-18 microns) (see Allamandola 1984, for an introductory level discussion of molecular vibrations; Barrow 1962, for a more detailed treatment; and Herzberg 1968, for an extensive discussion). While virtually all molecular potential wells are anharmonic, the degree of anharmonicity can vary markedly. One of the effects of anharmonicity is to continuously decrease the spacing between the adjacent vibrational states for higher values of v. (In a harmonic oscillator, the spacing between all adjacent levels is constant). Thus, for a given vibration, such as a CH stretch, $\Delta v=1$ transitions between higher v levels will occur at lower frequencies. The extent of anharmonicity depends on the particular vibration involved. For example, the anharmonicity for the IR allowed aromatic CH stretch is rather large, producing a shift on the order of 100 cm^{-1}, while for the C-C stretch and C-H out-of-plane bend it is believed to be less than 10 cm^{-1}. Although data are not available for large PAHs, the anharmonicities for the C-H stretch of the aromatic molecules benzene, C_6H_6; napthalene, $C_{10}H_8$; and anthracene $C_{14}H_{10}$, have been measured (Swofford, Long and Albrecht, 1976; Reddy, Heller and Berry, 1982). The frequencies for the $v=3\rightarrow2$, $2\rightarrow1$ and $1\rightarrow0$ transitions in benzene are 2814 cm^{-1} (3.55 microns), 2925 cm^{-1} (3.42 microns) and 3047 cm^{-1} (3.28 microns) respectively.

If the interstellar IR emission bands originate from highly vibrationally excited molecules, emission from vibrational levels higher than $v=1$ must contribute to the spectrum and anharmonicity effects are expected. In our calculation we have also taken anharmonicity into account.

For chrysene, the calculated emission spectrum for a single C-H stretching vibration is shown in Figure 9a, as a function of vibrational energy content. All other PAHs will exhibit similar spectra, with 100 to 120 cm^{-1} separation between the peaks, but the exact location of the pair depends on the particular molecule. More realistic simulations would include the other C-H vibrational stretch modes, which may have slightly different frequencies, and the effects of the energy-cascade, which we have neglected in preparing Figure 9a. Figure 9 shows there is a remarkable resemblance to the spectra observed from NGC 7027 and S106,

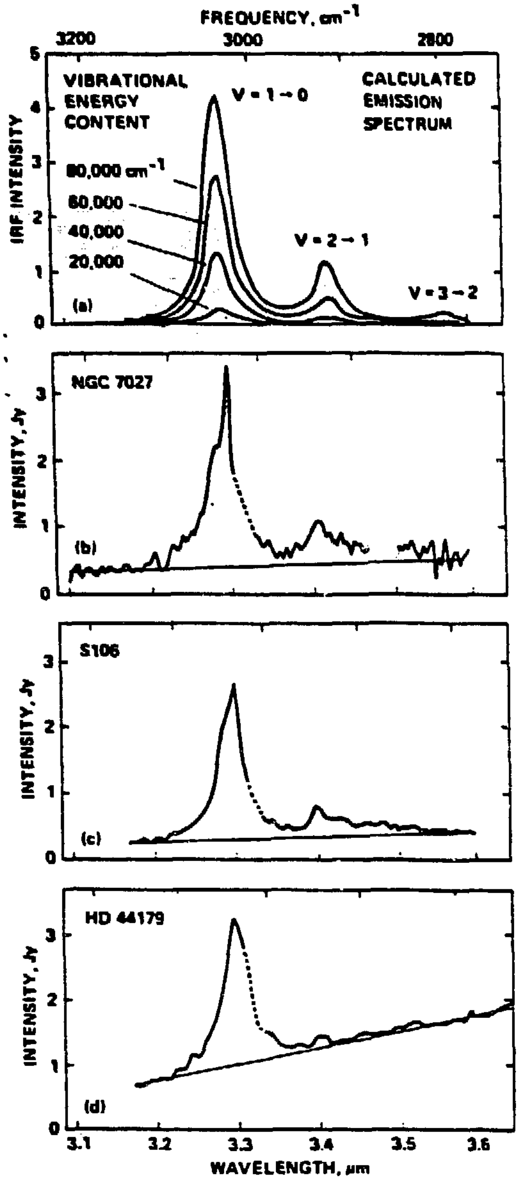

Figure 9. a) The calculated emission spectrum for chrysene in the CH stretching region as a function of vibrational energy content. Anharmonicity is assumed to be 120 cm^{-1}. b), c) and d), the observed emission spectra of NGC 7027, S106 and HD 44179 (Geballe, et al., 1985) showing how emission from higher vibrational levels depends on the availability of energetic photons. In NGC 7027, where the most energetic photons are available, emission from higher levels is important and produces a prominent v=2 1 band, whereas in the relatively benign HD44179, emission from v=2 is barely discernable. S106 is intermediate energetically, and the 3.3/3.4 micron band ratio is intermediate. Taken from Barker, Allamandola and Tielens, 1986.

and possibly from HD44179. Comparison with the observed spectrum shows a distinct satellite peak at exactly the position required. Thus, the peaks observed near 2950 cm^{-1} in various objects provide additional strong support for the PAH hypothesis.

Since the relative importance of the emission from v=2 depends only on the internal energy of the excited molecule, the ratio of intensities from v=1 and v=2 provides a firmer measure of excitation energy and molecular size than is possible by comparing the intensity of the stretching (3050 cm^{-1} 3.3 micron) and out-of-plane bending (885 cm^{-1}, 11.3 micron) modes.

Predictions for the intensity of the v=1 line compared to that for the v=2 line are presented in Figure 10 as functions of molecular size and excitation energy. The effects of the energy-cascade are included in this figure. Inspection of Figure 1 shows that, in Orion the satellite band observed is about ten times less intense than the main band. In Figure 10, a ratio of ten and a maximum excitation energy of 80,000 to 100,000 cm^{-1} are consistent with molecules of about 20-30 carbon atoms, a conclusion in agreement with the range deduced above from the relative intensities of the 885 and 3050 cm^{-1} (11.3 and 3.3

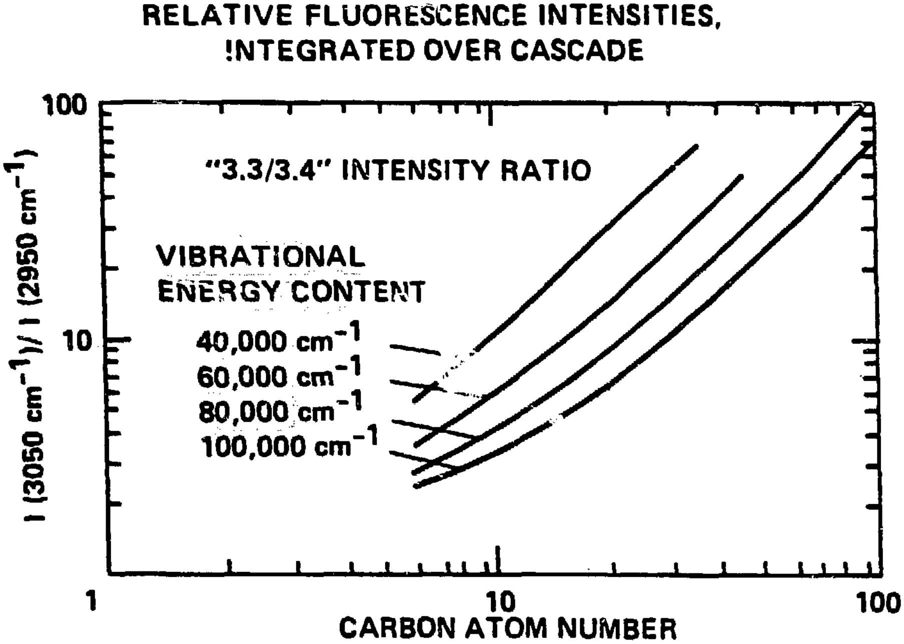

Figure 10. The 3.3 micron/3.4 micron intensity ratio as a function of carbon atom number and vibrational energy content. The relative fluorescence intensities includes integration over the vibrational cascade. Taken from Barker, Allamandola and Tielens, 1986.

micron) bands.

Experimental data are not available concerning the anharmonicties of the other PAH modes. However, molecular force fields are understood well enough to permit an estimation for the out-of-plane CH bend which occurs in the 900 to 500 cm^{-1} range (11-20 microns). Anharmonicity on the order of a few wavenumbers is expected (R. Eggers and J. Pliva, private communication). We have calculated the effects of anharmonicity on the 885 cm^{-1} (11.3 micron) feature assuming an anharmonicity of 5 cm^{-1} and a Lorentzian linewidth of 10 cm^{-1}. The vibrational frequency is much lower than that for the CH stretch (800 compared to 3050 cm^{-1}). Consequently, because the energy is assumed to be distributed statistically among all the modes, emission from considerably higher vibrational states (v levels) is expected to contribute to the band. Although the anharmonicity is only a few wavenumbers it will effectively broaden the band by skewing it to lower frequencies. Thus, as shown in Figure 11, for highly vibrationally excited molecules the band will be rather assymetric. It will also be considerably broader and peaked at slightly lower frequencies than that from molecules containing less vibrational energy.

This variation in behavior has been observed. Aitken and Roche (1983) have measured the interstellar 11.3 micron band at several positions in NGC 7027. In the central, ionized region where the most energetic photons are available, the band is substantially broader and markedly more assymetric than the band originating in the outer neutral

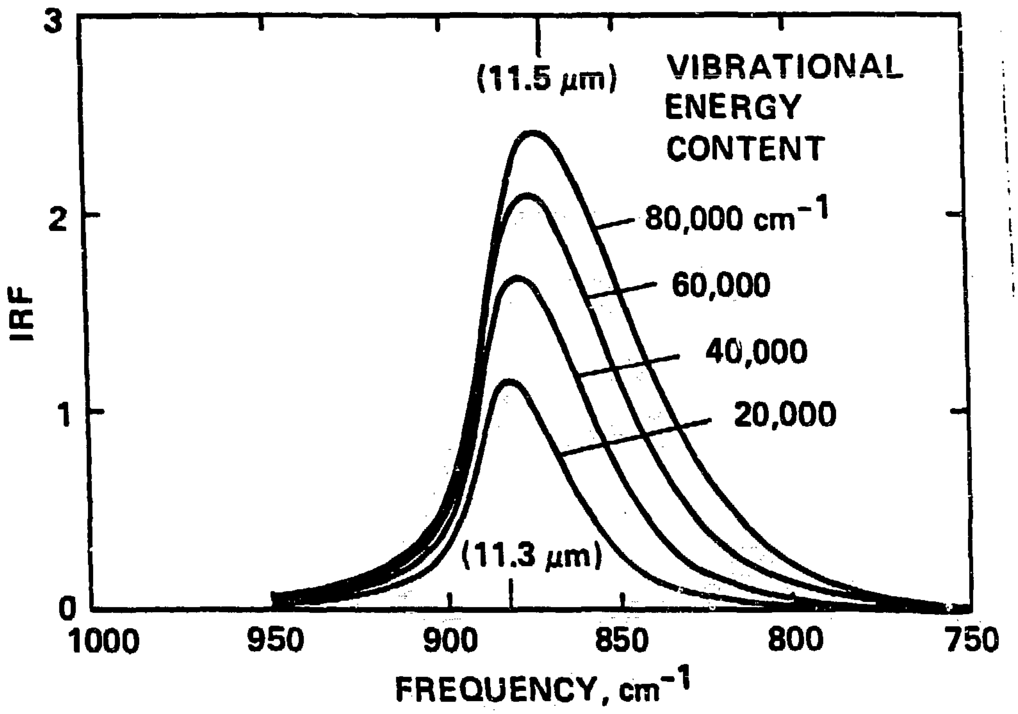

Figure 11. The calculated emission spectrum in the CH out-of-plane bending region as a function of vibrational energy content. Anharmonicity is assumed to be 5 cm^{-1}, natural linewidth 10 cm^{-1} and v=1 0 at 880 cm^{-1}. Taken from Barker, Allamandola and Tielens, 1986.

zone, where far less energetic photons are available. Until a more quantitative measure of the anharmonicity for these lower frequency modes is available, one cannot determine the size of the emitting species responsible as precisely as the analysis of the 3050 cm^{-1}.2930 cm^{-1} (3.3 micron/3.4 micron) band intensity ratio allows. Within the framework of the assumptions made here (anharmonicity 5 = cm^{-1}, Lorentzian width 10 = cm^{-1}), the size of the emitting species, assuming 100,000 cm^{-1} of vibrational energy, is again in the 20-30 carbon atom range.

In concluding this section on the emission process, 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 (ATB,c; Barker, Allamandola and Tielens, 1986). We stress that in addition to being able to explain the observed variations in emission ratio and account for band profile behavior, the molecular approach permits one to address questions regarding photostability, hydrogen coverage, reactivity, photoisomerization and deuterium fractionation in a completely self-consistent, more rigorous, general manner.

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4. REFERENCES

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

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. and Norman, C. A. (1978), Astro. Ap. 66, 129.

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. (1968a, ATBb), Chapter in *Polycyclic Aromatic Hydrocarbons and Astrophysics*, eds. Leger, A. and d'Hendecourt, L. B. (D. Reidel Publishing Co., Dordrecht).

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

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

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

Barrow, G. M., 1962, *Introduction to Molecular Spectroscopy*. (McGraw Hill, New York).

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

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

Bondybey, V. (1984), Ann. Rev. Phys. Chem. 35, 591.

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. (1984) NASA/ASP Symposium, Airborne Astronomy, NASA/Ames Research Center (NASA CP 2353).

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

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. (1986) Ap. J., 302, 737.

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, 379, 1359.

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

de Muizon, M., Geballe, T. R., d'Hendecourt, L. B., and Bass, F., (1986) Ap. J. Lett., 306, L105.

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

Dwek, E., Sellgren, K., Soifer, B. T. and Werner, M. W., 1980, Ap. J. 238, 140.

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

Gillett, F. C., Forrest, W. J., and Merrill, K. M., 1973, Apt. J. 183, 87.

Goebel, J. (1986) Chapter in Polycyclic Aromatic Hydrocarbons and Astrophysics, eds. Leger, A. and d'Hendecourt, L. B. (D. Reidel Publishing Co., Dordrecht).

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

Jortner, J. (1986), Chapter in Polycyclic Aromatic Hydrocarbons and Astrophysics, eds. Leger, A. and d'Hendecourt, L. B. (D. Reidel Publishing Co., Dordrecht).

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

Leach, S. (1986), Chapter in Polycyclic Aromatic Hydrocarbons and Astrophysics, eds. Leger, A. and d'Hendecourt, L. B.)D. Reidel Publishing Co., Dordrecht).

Leger, A., (1986), Chapter in Polycyclic Aromatic Hydrocarbons and Astrophysics, eds. Leger, A. and d'Hendecourt, L. B. (D. Reidel Publishing Co., Dordrecht).

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)

Oref, I. and Rabinovitch, B. S. (1979), Acc. Chem. Res. 12, 166.

Reddy, K. V., Heller, D. F. and Berry, M. J. (1982), J. Chem. Phys. 76, 2814.

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

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

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

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

Swofford, R. L., Long, M. E., and Albrecht, A. C. (1976), J. Chem. Phys. 65, 179.

Tielens, A. G. G. M., Allamandola, L. J., Barker, J. R. and Cohen, M. (1986), Chapter in Polycyclic Aromatic Hydrocarbons and Astrophysics, eds. Leger, A. and d'Hendecourt, L. B. (D. Reidel Publishing Co., Dordrecht).

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.