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POLYCYCLIC AROMATIC HYDROCARBONS AND THE UNIDENTIFIED INFRARED EMISSION BANDS: AUTO EXHAUST ALONG THE MILKY WAY!

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ABSTRACT

We have attributed the unidentified infrared emission features (UIR bands) to a collection of partially hydrogenated, positively charged polycyclic aromatic hydrocarbons (PAHs). This assignment is based on a spectroscopic analysis of the UIR bands. Comparison of the observed interstellar 6.2 and 7.7 μm bands with the laboratory measured Raman spectrum of a collection of carbon-based particulates (auto exhaust) shows a very good agreement, supporting this identification. The infrared emission is due to relaxation from highly vibrationally and electronically excited states. The excitation is probably caused by UV photon absorption.

We have modeled the infrared fluorescence of one particular, highly vibrationally excited PAH (chrysene). In this analysis the species is treated as a molecule rather than bulk material and the non–thermodynamic equilibrium nature of the emission is fully taken into account. From a comparison of the observed ratio of the 3.3 to 11.3 μm UIR bands with the model calculations, the average number of carbon atoms per molecule is estimated to be about 20. The abundance of interstellar PAHs is calculated to be about 2×10^{-7} with respect to hydrogen.

Subject headings: infrared: spectra — interstellar: molecules — laboratory spectra

I. INTRODUCTION

Many celestial objects show a distinctive set of emission features in the infrared, known collectively as the unidentified infrared emission bands (UIR bands). These are usually found together at 3.3, 3.4, 6.2, 7.7, 8.6, and 11.3 μm (Russell, Soifer, and Willner 1977) with weaker features at 5.6 and 6.95 μm (Bregman *et al.* 1983). The relative intensities of the UIR bands vary somewhat (Simpson *et al.* 1984). The bandwidths tend to be independent of source. In addition to the UIR bands, a broad continuum emission in the range 1–5 μm, apparently associated with the bands, was recently discovered in several reflection nebulae (Sellgren *et al.* 1983).

In 1981, Duley and Williams made the perceptive observation that some of the UIR band frequencies are characteristic of large polycyclic aromatic hydrocarbons (PAHs; planar, aromatic, fused ring molecules; e.g., coronene) and they went on to suggest that they are excited via a thermal equilibrium mechanism. Recently, Leger and Puget (1984) modified these ideas by assuming that the excitation mechanism is similar to the single photon excitation process developed by Sellgren (1984). They used, however, a thermal model, appropriate for bulk materials, to calculate the predicted IR emission spectrum for the molecule coronene. In the present work we treat the emitting PAHs as molecules (not as bulk material), using laboratory data, statistical mechanics, and spectroscopic theory to derive their properties and spectrum. The nonequilibrium nature of the excitation and emission processes are considered explicitly, and no assumptions of thermal equilibrium are made.

II. SPECTROSCOPIC IDENTIFICATIONS

We adopt the conclusion of Duley and Williams (1981) that the UIR bands originate from aromatic species that bear fewer hydrogen atoms than the potential number of binding sites, so that the occupancy of adjacent sites is rare. Each C—H bond will then produce relatively simple line emission in the out-of-plane bending region near 11.3 μm plus the normal aromatic C—H stretch near 3.3 μm. The low hydrogen coverage, implied by the observation of only one band near 11 μm, may be a result of the intense UV field in the regions where the UIR bands have been detected. The 3.4 and 3.5 μm bands observed in some objects (Geballe *et al.* 1984; Blades and Whittet 1980) may be due to aliphatic and aldehydic surface functional groups (Duley and Williams 1981). The 8.6 μm UIR band has been assigned to the in-plane C—H bending mode, and the 6.2 μm feature is characteristic of carbon skeletal modes in PAHs (Leger and Puget 1984).

The strong 7.7 μm feature is, however, more difficult to assign. Although all PAHs show several bands near 7.7 μm corresponding to carbon skeletal modes, none match the rather broad profile of the observed UIR band (S. J. Cyvin *et al.* 1982 and references therein). However, since the individual peak frequencies of these skeletal modes vary somewhat from molecule to molecule, a collection of many PAHs can provide a match. Laboratory Raman spectra of noncrystalline graphitic

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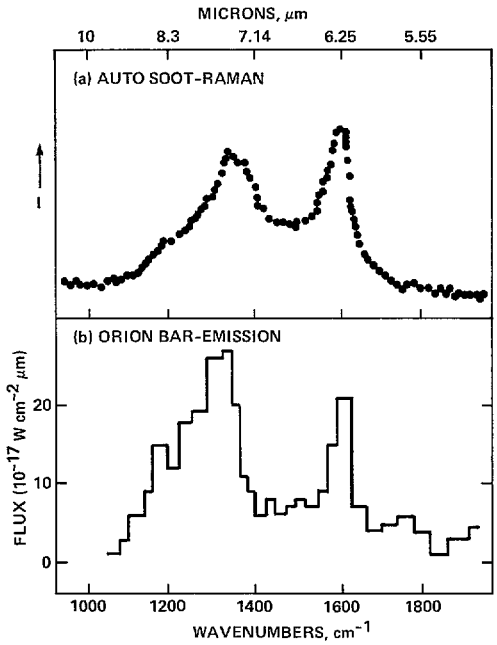

FIG. 1.—(*a*) Raman spectrum from 5 to 10 μm of auto exhaust, adapted from Rosen and Novakov (1978). (*b*) Spectrum from 5 to 10 μm of the Orion bar (Bregman *et al.* 1984).

material, consisting of mixtures of PAHs and graphite, show a band at 6.35 μm and a broader band at 7.5 μm. The strength of the latter feature increases relative to that of the 6.35 μm feature with a decrease in the crystallite size (Tuinstra and Koenig 1973). Assuming one can compare the observed ratio of the interstellar 6.2 and 7.7 μm features with the laboratory data implies an upper limit to the size of the emitting species of about 35 Å (Tuinstra and Koenig 1973).

A particularly striking Raman spectrum from a collection of such molecules (auto exhaust; Rosen and Novakov 1978) is compared in Figure 1 to the UIR bands in the 5–8 μm spectrum of the Orion bar (Bregman *et al.* 1984). The close agreement between the Raman spectrum and the UIR bands is strong circumstantial evidence that they arise from similar groups of species. The agreement between the recently published IR spectra of carbonized material with their Raman spectra shows that the Raman-active and IR-active modes are similar in number and frequency in PAHs (Mortera and Low 1983).

Because of their low ionization potential ($\sim$ 6 eV), the PAHs will probably be singly ionized in the interstellar medium, except in dense clouds. In the IR-emitting regions, the degree of ionization of these PAHs is calculated to be greater than 90% (Allamandola, Tielens, and Barker 1984). It is also likely that the infrared emission originates from electronically excited states (cf. § III). Unfortunately, spectra of ionized, partly hydrogenated, electronically excited PAHs are presently unavailable. Laboratory studies of such species are of great importance for the precise identification of the carriers of the UIR bands.

III. CALCULATED INFRARED FLUORESCENCE INTENSITIES

We attribute the emission in the UIR bands to IR fluorescence from a collection of UV-pumped, vibrationally excited PAHs, although other excitation mechanisms, such as chemical reactions or electron recombination, might also be of importance under some conditions. The IR emission of vibrationally excited PAHs can be treated theoretically in a uniform and relatively simple manner, regardless of the excitation mechanism operative in a particular interstellar environment. As an example, consider UV photon excitation of the "simple" PAH chrysene ($C_{18}H_{12}$), chosen because its IR spectrum is known and superficially resembles the UIR bands, because its UV photophysics is known, and because it is large enough to be representative of the PAHs and small enough to be easily treated theoretically. Although the interstellar case will be more complicated because of the presence of many different chemical species, it is expected that their qualitative behavior will be similar to that of chrysene.

The strongest absorption of chrysene between 2000 and 4000 Å occurs near 2675 Å, connecting the S_0 ground state with the S_3 excited singlet state (Birks 1970). Internal conversion to high vibrational levels in the S_1 state is probably fast ($\sim 10^{-11}$ s) and has a quantum yield near unity. Subsequently nearly 90% of the S_1 molecules undergo rapid (10^{-7} s) intersystem crossing to the lowest chrysene triplet state, about 20,000 cm^{-1} above the ground state (only 12% of the S_1 molecules decay through optical fluorescence). The remaining 17,400 cm^{-1} vibrational excitation in the triplet state will be quickly distributed over all available vibrational modes. Infrared fluorescence ($\leq$ 0.1 s lifetime) from this highly vibrationally excited molecule returns it to the ground vibrational level of the triplet state. Finally, in chrysene, phosphorescence (3 s lifetime) to the ground vibrational level of the ground electronic state will dominate over other possible deactivation channels (for example, intersystem crossing to a highly excited vibrational level of the ground state followed by IR fluorescence to the ground vibrational level). In other molecules, however, the latter process may be more important (Birks 1970). In summary, a UV-pumped, neutral chrysene molecule will show IR fluorescence in the electronically excited triplet state, and about half of the UV photon energy will emerge as IR emission.

To calculate the IR emission spectrum, it is important to realize that the molecule is far from thermodynamic equilibrium. All of the vibrational excitation mechanisms produce nonthermal population distributions that resemble delta functions: the initial, very narrow, low-temperature thermal distribution is displaced upward in energy by an amount governed by the particular excitation mechanism (for example, the photon energy). The population distribution of excited molecules bears, therefore, little resemblance to a high-temperature thermal distribution. Although thermal distributions in some cases can be used to approximate the actual distribution function (by postulating an adjustable "temperature"), the approximation can fail badly when energy-dependent processes are considered, such as infrared fluorescence or chemical reaction (e.g., decomposition). The theoretical expression used to calculate the integrated IR fluorescence band intensity ($\Delta v = 1$ transitions) is derived from quantum statistics and harmonic oscillator vibrational wave functions (Herzberg 1945; Durana and McDonald 1976; Rossi, Pladziewicz, and Barker 1983). The vibrational frequencies of triplet chrysene are unknown, but they are probably similar to those of the ground singlet state. The Einstein coefficients of the triplet state are

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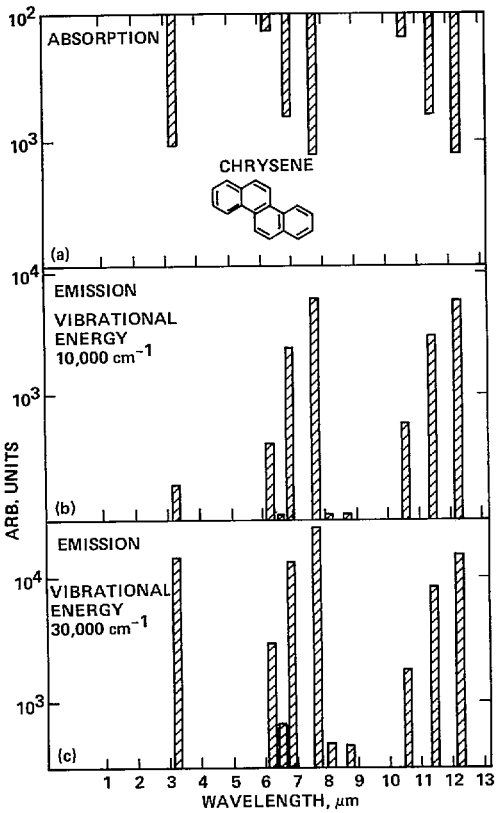

FIG. 2.—Bar diagram representation of mid-IR spectra of chrysene. (*a*) Absorption spectrum. Band strengths have been approximated by summing over the individual relative line strengths, listed by Cyvin *et al.* (1982), which are encompassed within each bar. The values 1, 5, 25, 125, and 625 have been arbitrarily assigned to each of their levels of relative intensities vw, w, m, s, and vs, respectively. (*b*) and (*c*) The calculated emission spectrum of chrysene. The vibrational energy content of the triplet state of chrysene is 10,000 and 30,000 cm^{-1}, respectively (see text).

assumed to be similar to those of the singlet state which can be estimated from the measured IR spectrum (B. N. Cyvin *et al.* 1982; see Fig. 2*a*).

The results obtained for chrysene are presented in Figures 2*b* and 2*c* for two levels of vibrational excitation of the triplet state. Some general conclusions can be reached. First, the IR fluorescence emission spectrum varies dramatically as the vibrational energy is changed, and it resembles the observed UIR bands at excitations above 20,000 cm^{-1}. Second, the relative IR fluorescence emission intensities bear only superficial resemblance to the relative integrated absorption strengths from which they were derived. Third, no significant 3.3 μm fluorescence will be observed unless the molecule contains a substantial amount of vibrational excitation.

The latter conclusion can be used to derive an estimate of the size of the emitting species. For a fixed excitation energy, the strength of the 3.3 μm band decreases relative to that of the lower frequency modes when the number of atoms in the molecules (e.g., the number of vibrational modes) increases. This is because it is less likely for a high-frequency mode to be excited as the average energy per oscillator decreases. Of course, the relative intensities of the different modes also depend on the densities of states and strengths of the different modes. We note, however, that one out-of-plane bending mode and one stretching mode will be present for each C—H bond. Thus the number of modes emitting near 11.3 μm equals the number of modes near 3.3 μm, regardless of the actual number of C—H bonds present in each molecule. Furthermore, since both modes are of comparable integrated absorption strength in both benzene and coronene, we presume that this is true for PAHs in general (S. J. Cyvin, private communication). Assuming that the excitation is dominated by the strong UV absorption bands around 2500 Å and that about half of the absorbed energy will wind up in vibrational excitation, as is the case for chrysene, model calculations yield an average number of carbon atoms in the interstellar PAHs of about 20 (Allamandola, Tielens, and Barker 1984). If all of the absorbed UV photon energy goes into vibrational excitation, then the number of carbon atoms is about 50.

Leger and Puget (1984) obtained a lower limit to the number of carbon atoms in the emitting species of about 50 atoms, based on an analysis of the stability of PAHs in terms of thermal desorption from a solid. Although their approach is appropriate for sublimation of bulk materials in thermal equilibrium, it fails in the case of the nonthermal photochemical decomposition of molecules. Recall that the energy distribution function in the excited molecule is unlike that of a high-temperature thermal distribution function. In this respect, it is worth pointing out that the carbon skeleton of PAHs, in particular those with rings fused together, is very stable (Clar 1972). Absorption of photons with energies greater than about 6 eV can produce stable ions, induce the loss of an H atom, or rearrange the skeleton to a more stable form. However, little or no fragmentation of the carbon skeleton is expected (Turro 1978).

The observed 30–50 cm^{-1} widths and line shapes of the narrowest bands at 3.3, 6.2, and 11.3 μm are consistent with emission from highly vibrationally excited species and do not necessarily imply a solid state origin. Anharmonicity will not significantly contribute to the width, because the emission is dominated by the 1–0 transition (Allamandola, Tielens, and Barker 1984). The width may be partly due to the blending of lines from different PAHs, as is the case for the 7.7 μm feature. The intrinsic line width from any given molecule reflects the effects of coupling among many levels (Jortner, Rice, and Hochstrassen 1969) and indicates the rate of intramolecular energy transfer among the vibrational modes. Laboratory measured intrinsic line widths for similar species suggest that blending is not responsible for the width of the narrower interstellar features (Oref and Rabinovitch 1979).

IV. DISCUSSION

The abundance of interstellar PAHs can be estimated from the observed ratio of the flux in all of the UIR bands to the far-IR flux (2%; Dwek *et al.* 1980). This implies that the total FUV cross section of the PAHs is about 2% of that of the dust. Assuming a standard dust-to-gas ratio, the standard dust extinction curve and a UV photon absorption cross section of 10^{-16} cm^2 for the PAHs, yields an abundance of PAHs relative to hydrogen of about 2×10^{-7}. If each PAH contains 20 carbon atoms, about 1% of all the available carbon is in the form of PAHs.

In addition to the emission in the UIR bands, the mysterious IR continuum (Sellgren, Werner, and Dinerstein 1983)

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may also be due to these PAH species. It could be produced by either fluorescence and phosphorescence from the lowest lying electronic states or by emission from the overlapping overtone and combination bands, perhaps with a minor contribution from anharmonicity. Four micron "continuum" emission, 5 times less intense than that at 3.3 μm, has been measured in a PAH (Barker, Rossi, and Pladziewicz 1982).

In addition to the vibrational modes already observed in the UIR bands, twisting and bending motions of planar PAH carbon skeletons emit in the frequency range 600–10 cm^{-1} (16–1000 μm). Unfortunately, detection of these modes in objects showing the UIR bands may be hampered by the strong far-IR continuum due to dust. If these modes are about as strong as the strongest mid-IR band (e.g., 1% of the far-IR dust continuum for the integrated band strength) and their line widths are about 40 cm^{-1}, then their peak intensities will only be about 2% of the intensity of the dust continuum. However, the limited information available indicates that the far-IR bands are much weaker than the mid-IR bands (B. N. Cyvin *et al.* 1982; S. J. Cyvin *et al.* 1982). This will make detection difficult, except under favorable circumstances. A search near 500 cm^{-1} may be warranted in interstellar regions with low dust temperatures (e.g., reflection nebulae far from the illuminating star). It is also possible that emission from these low-frequency modes is related to the far-IR cirrus detected with *IRAS* (Low *et al.* 1984).

The presence of the UIR bands in a variety of objects suggests a ubiquitous presence of PAHs in the interstellar medium. Since the features are seen in planetary nebulae, it is likely that PAHs are formed in the carbon-rich outflow from such objects. In effect they may even be the leftover condensation nuclei, which did not get incorporated into carbon dust grains. These stable molecules are not easily photodissociated, because many alternate channels for energy relaxation are available. Probably their most important destruction mechanism in the interstellar medium is sputtering in fast shocks ($\geq$ 200 km s^{-1}), as is the case for small carbon dust grains.

The ubiquitous presence of PAHs is not in conflict with the nonobservance of ring molecules in molecular clouds at millimeter wavelengths (Myers, Thaddeus, and Linke 1980). The large partition function of each PAH and the presence of a large collection of them will make it very difficult to detect their rotational transitions. The vibrational transitions are less hampered by this effect, because each mode tends to pile up at one frequency. Furthermore, the emission at these fundamentals is pumped by the UV radiation field, rather than by collisions with the gas. This increases the energy reservoir for the vibrational transitions substantially above that of the rotational transitions. Finally, many of the PAHs sought for at millimeter wavelengths contain other atoms besides carbon in the ring. These are generally much less stable than the PAHs considered here.

The existence of interstellar PAHs as an important constituent of the interstellar medium may have observational consequences in other spectral regions, in particular in the visible and UV. The vibronic transitions of ionized PAHs will fall in the visible region of the spectrum (Crawford, Tielens, and Allamandola 1985). Due primarily to the moments of inertia of these molecules, individual rotational lines will blend into band contours (van der Zwet and Allamandola 1985). Many of these profiles resemble the observed shape of some of the diffuse interstellar bands (Herbig 1975).

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