

## NEW EMISSION FEATURES IN THE 11-13 MICRON REGION AND THEIR RELATIONSHIP TO POLYCYCLIC AROMATIC HYDROCARBONS

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### ABSTRACT

If the "11.3  $\mu\text{m}$ " emission feature seen in the spectra of many planetary nebulae, H II regions, and reflection nebulae is due to polycyclic aromatic hydrocarbons (PAHs), then additional features should be present between 11.3 and 13.0  $\mu\text{m}$  (885 and 770  $\text{cm}^{-1}$ ). Moderate-resolution spectra of NGC 7027, HD 44179, IRAS 21282+5050, and BD +30°3639 are presented which show that the "11.3  $\mu\text{m}$ " feature actually peaks at 11.22  $\mu\text{m}$  (891  $\text{cm}^{-1}$ ). The spectra also show evidence for new emission features near 11.9 and 12.7  $\mu\text{m}$  (840 and 787  $\text{cm}^{-1}$ ). These are consistent with an origin from PAHs and can be used to constrain the molecular structure of the family of PAHs responsible for the infrared features. The observed asymmetry of the "11.3  $\mu\text{m}$ " band is consistent with the slight anharmonicity expected in the C—H out-of-plane bending mode in PAHs. Laboratory experiments show that the intensity of this mode relative to the higher frequency modes depends on the extent of molecular "clustering." The observed strengths of the "11.3  $\mu\text{m}$ " interstellar bands relative to the higher frequency bands are most consistent with the features originating from free molecular PAHs. The intensity and profile of the underlying broad structure, however, may well arise from PAH clusters and amorphous carbon particles. Analysis of the 11-13  $\mu\text{m}$  (910-770  $\text{cm}^{-1}$ ) emission suggests that the molecular structures of the most intensely emitting free PAHs vary somewhat between the high-excitation environment in NGC 7027 and the low-excitation but high-flux environment close to HD 44179. Finally, a previously undetected series of regularly spaced features between 10 and 11  $\mu\text{m}$  (1000 and 910  $\text{cm}^{-1}$ ) in the spectrum of HD 44179 suggests that a simple polyatomic hydride is present in the gas phase in this object.

*Subject headings:* infrared: grains — interstellar: grains — line identifications — nebulae: H II regions — nebulae: planetary

### I. INTRODUCTION

Emission features are often seen at roughly 3.3, 6.2, 7.7, 8.6, and 11.3  $\mu\text{m}$  (3030, 1610, 1300, 1160, and 885  $\text{cm}^{-1}$ ) in the spectra of planetary nebulae, H II regions, reflection nebulae, and other objects (Russell, Soifer, and Merrill 1977; Russell, Soifer, and Willner 1977; Sellgren, Werner, and Dinerstein 1983; Aitken and Roche 1982, 1983; Sellgren *et al.* 1985; Cohen *et al.* 1986). These features have been attributed to emission from vibrationally excited polycyclic aromatic hydrocarbons (PAHs) and PAH-related materials (Duley and Williams 1981; Leger and Puget 1984; Allamandola, Tielens, and Barker 1985). A mixture of free molecular PAHs in both neutral and ionized forms, as well as PAH clusters and particles of amorphous carbon (which are built up from PAHs), is thought to be responsible.

Within the framework of the PAH hypothesis, the "11.3  $\mu\text{m}$ " interstellar feature is attributed to out-of-plane bending vibrations of peripheral hydrogen atoms attached to aromatic molecular units. These structures may consist of free molecular PAHs, PAH clusters, or parts of larger amorphous carbon particles. The precise frequency (and perhaps the intensity per H atom) of each C—H out-of-plane bending mode depends on the number of adjacent H atoms on each edge ring (Bellamy 1958). Depending on the molecular geometry, fully hydrogenated aromatic hydrocarbons can have between 1 and 6 H atoms per ring and produce bands in the 11-15  $\mu\text{m}$  (910-670  $\text{cm}^{-1}$ ) range (Fig. 1). The position of the bands fall to progressively longer wavelengths as the number of adjacent hydrogens per ring increases.

The position of the prominent interstellar feature near 11.3  $\mu\text{m}$  (885  $\text{cm}^{-1}$ ) is characteristic of aromatic rings having only nonadjacent peripheral hydrogen atoms, i.e., edge rings with only one hydrogen atom. Based on this, Duley and Williams (1981) initially postulated that the interstellar aromatic material responsible for the interstellar infrared emission features is only partially hydrogenated. Subsequently, the IRAS low-resolution spectrometer (LRS) revealed that an emission "plateau," which rises at about 10.5  $\mu\text{m}$  (950  $\text{cm}^{-1}$ ), underlies the "11.3  $\mu\text{m}$ " feature and extends beyond the telluric window to about 13  $\mu\text{m}$  (770  $\text{cm}^{-1}$ ) (Cohen, Tielens, and Allamandola 1985). Figure 1 illustrates that the extent of this plateau is consistent with PAHs having nonadjacent, as well as two and three adjacent, peripheral H atoms per edge ring, but not four or five. Thus, higher quality spectra in this region should reveal some substructure. Evidence for such structure can be found in previous observations of NGC 7027 (Aitken *et al.* 1979). The observations described here were carried out to search for structure in the 11-13  $\mu\text{m}$  (910-770  $\text{cm}^{-1}$ ) spectra of objects known to produce the interstellar emission bands and thereby test this implication of the PAH hypothesis.

We present new 10.1-13.2  $\mu\text{m}$  (990-760  $\text{cm}^{-1}$ ) spectra of four objects, NGC 7027, HD 44179, IRAS 21282+5050, and BD +30°3639. These data build on previously reported work (Sandford *et al.* 1987). The spectra of all the objects show the 11-13  $\mu\text{m}$  plateau and three of them show evidence for superposed substructure. These spectra place strong constraints on the geometries of the PAHs responsible for the infrared emission features. When combined with spectra of comparable

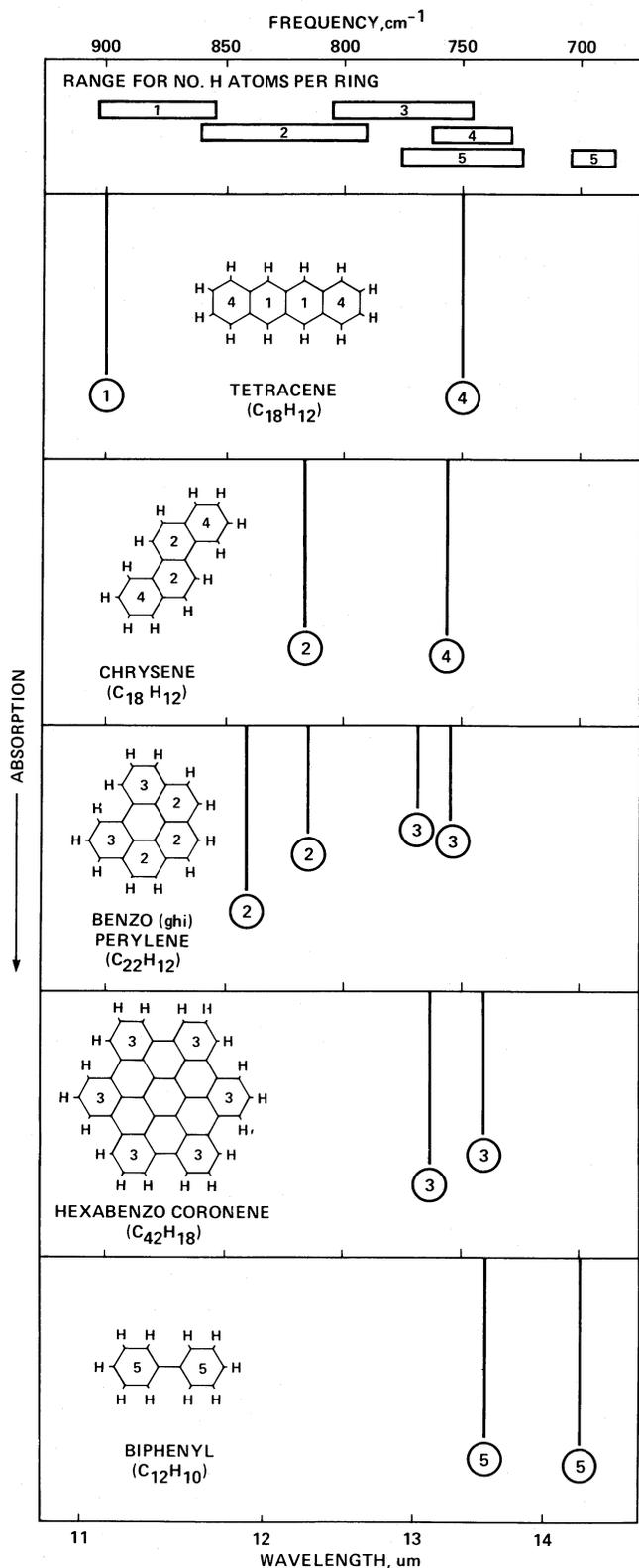


FIG. 1.—Schematic spectra in the 11–15  $\mu\text{m}$  (910–670  $\text{cm}^{-1}$ ) region of a number of PAHs in salt pellets, each having different numbers of hydrogen atoms on their peripheral rings. The number of hydrogen atoms per ring are indicated at the center of each ring and under the corresponding absorption band. The upper portion of the figure indicates the ranges over which different edge structures produce bands. This figure demonstrates that the C–H out-of-plane bending mode of PAHs falls at longer and longer wavelengths as the number of adjacent H atoms per edge ring is increased.

resolution at shorter wavelengths, they can be used to limit the number of possible molecular PAH candidates.

## II. OBSERVATIONS

Spectra were obtained at the NASA/Steward Observatory 60 inch (1.5 m) telescope on Mount Lemmon using a 24-detector, liquid helium cooled, grating spectrometer. The performance and original configuration of this instrument are described by Witteborn and Bregman (1984). This instrument currently incorporates externally selectable apertures and grating tilt angles. The grating has 135 grooves per mm and was used in first-order. Since the detector spacing leaves the spectrum undersampled by a factor of 2–3, each spectrum was repeated at a second grating angle which displaced the spectrum by half a detector width. This procedure provides sampling at 0.03  $\mu\text{m}$  intervals near 12  $\mu\text{m}$  ( $\lambda/\Delta\lambda \sim 400$ ). Each pair of grating settings covers about 1.4  $\mu\text{m}$  and three pairs of settings were required to cover the 10.1 to 13.2  $\mu\text{m}$  range reported here. Each pair of spectra was taken at grating settings that ensured overlap with adjacent pairs.

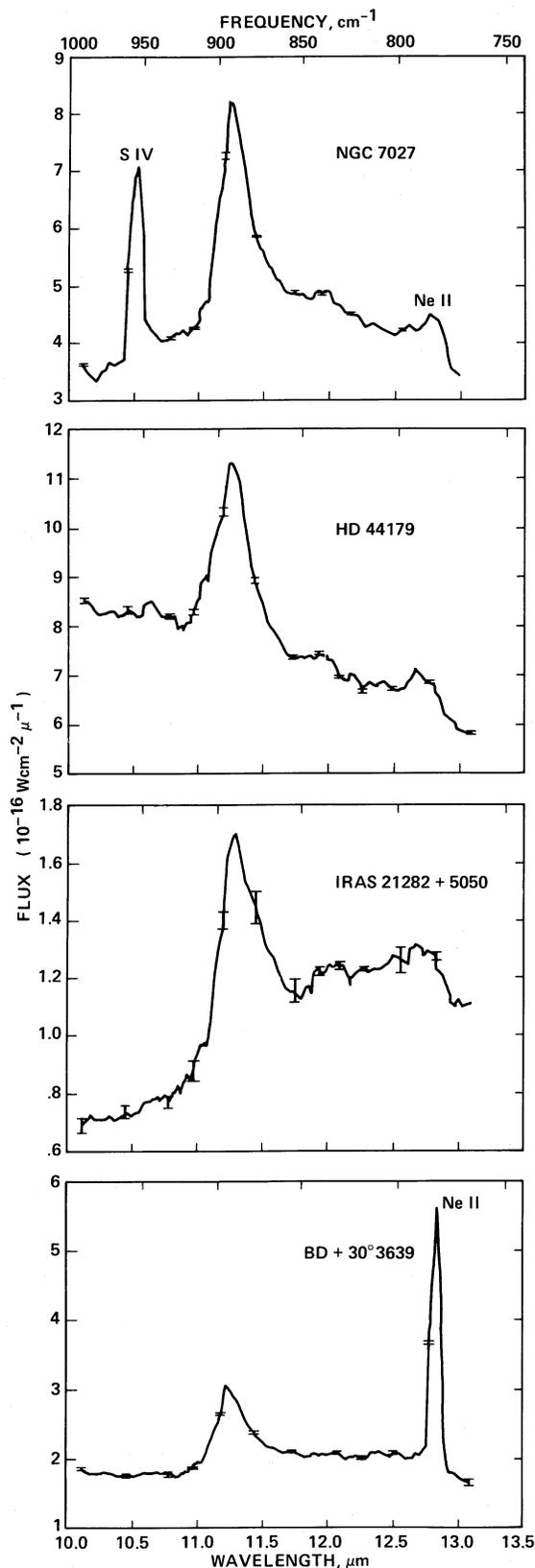
The “slit,” a 1.5 mm diameter, circular aperture, subtended 12" on the sky. It enclosed all of the infrared-bright components of HD 44179, BD +30°3639, and IRAS 21282 + 5050, and most of the infrared-emitting portion of NGC 7027.

Wavelength calibration was achieved by comparison with an ammonia gas cell whose absorption spectrum was obtained each time the grating was moved. Correction for atmospheric absorption was accomplished by comparison with standard stars whose spectra were measured through similar air masses on the same night that the object was observed (usually within an hour). The standard stars were also used to determine the flux at each wavelength. Thus, if we denote the measured (raw) object spectrum by  $F(\lambda)$ , the measured standard spectrum by  $S(\lambda)$ , and the standard star can be characterized by a blackbody  $B(\lambda, T)$  in the 10.1 to 13.2  $\mu\text{m}$  range, then the true spectrum  $G(\lambda)$  is

$$G(\lambda) = \frac{F(\lambda) \times B(\lambda, T)}{S(\lambda)}, \quad (1)$$

where  $T$  is the color temperature of the star near 8.7  $\mu\text{m}$  and  $B(8.7 \mu\text{m}, T)$  is determined from broad-band photometry.

The standard stars used were  $\alpha$  Tau, whose flux at 8.7  $\mu\text{m}$  is  $3.3 \times 10^{-15} \text{ W cm}^{-2} \mu\text{m}^{-1}$ , and  $\alpha$  Her, whose flux at 8.7  $\mu\text{m}$  is  $7.28 \times 10^{-15} \text{ W cm}^{-2} \mu\text{m}^{-1}$ . Both fluxes are based on the magnitudes of Hanner *et al.* (1984) and a 0.0 magnitude flux of  $2.10 \times 10^{-16} \text{ W cm}^{-2} \mu\text{m}^{-1}$  (IRTF Photometry Manual, 1986). Temperatures of 4000 and 3600 K, respectively, were used for these stars. To check the assumptions that these stars are featureless blackbodies in the spectral region of interest, the spectrum of  $\alpha$  Lyr was obtained over the same wavelength range. The  $\alpha$  Lyr spectrum is thought to follow that of a smooth 9650 K blackbody over the 10–13  $\mu\text{m}$  range to within a few percent (Schild, Peterson, and Oke 1971). The ratio of the  $\alpha$  Tau spectrum to that of  $\alpha$  Lyr is flat (since both are in the Rayleigh-Jeans part of the spectrum) and devoid of features (of any width between 0.05 and 2.0  $\mu\text{m}$ ) greater than  $\pm 5\%$  of the continuum between 10 and 12  $\mu\text{m}$  and  $\pm 10\%$  between 12 and 13  $\mu\text{m}$ . The ratio of the  $\alpha$  Tau spectrum to that of  $\alpha$  Her is flat and similarly devoid of features throughout the entire 10–13  $\mu\text{m}$  range to  $\pm 5\%$ . Features attributed to the objects studied in this paper are reported only if they are evident when referenced to two different standard star spectra.



## III. DISCUSSION

a) The Bands between 11 and 13  $\mu\text{m}$  and Identifications

The “11.3  $\mu\text{m}$ ” feature is asymmetric in all the spectra. The peak is at  $11.22 \pm 0.1 \mu\text{m}$  ( $891.3 \pm 8 \text{ cm}^{-1}$ ) in all four objects (Fig. 2). The spectra of NGC 7027, HD 44179, and IRAS 21282 + 5050 show evidence for several new emission bands on the 11–13  $\mu\text{m}$  ( $910\text{--}770 \text{ cm}^{-1}$ ) plateau. In addition, the spectrum of HD 44179 shows regular structure between 10 and 11  $\mu\text{m}$  ( $1000$  and  $910 \text{ cm}^{-1}$ ).

In NGC 7027 and HD 44179, there is a broad component between about 11.7 and 12.1  $\mu\text{m}$  ( $855$  and  $826 \text{ cm}^{-1}$ ) and another between 12.5 and 12.9  $\mu\text{m}$  ( $800$  and  $775 \text{ cm}^{-1}$ ). These features are evident in the earlier spectrum of NGC 7027 measured by Aitken *et al.* (1979). In NGC 7027, the long-wavelength limit of the 12.7  $\mu\text{m}$  ( $787 \text{ cm}^{-1}$ ) feature is uncertain due to overlap with the [Ne II] line at 12.8  $\mu\text{m}$  ( $781 \text{ cm}^{-1}$ ). The IRAS LRS spectrum of this object also shows the 12.7  $\mu\text{m}$  feature (Cohen, Tielens, and Allamandola 1985), but the LRS resolution was not sufficient to determine if there is a contribution from [Ne II] at 12.8  $\mu\text{m}$  ( $781 \text{ cm}^{-1}$ ). The 11–13  $\mu\text{m}$  ( $910\text{--}770 \text{ cm}^{-1}$ ) spectrum of IRAS 21282 + 5050 also shows evidence of features near 11.9  $\mu\text{m}$  ( $840 \text{ cm}^{-1}$ ) and 12.7  $\mu\text{m}$  ( $787 \text{ cm}^{-1}$ ). However, the lower signal-to-noise of this spectrum precludes a detailed analysis of these features. Recently, Roche, Aitken, and Smith (1988) have observed the 12.5–12.9  $\mu\text{m}$  ( $800\text{--}775 \text{ cm}^{-1}$ ) feature in Orion. The band is most intense south of the Orion ionization front and appears to be tightly correlated spatially with the “11.3  $\mu\text{m}$ ” feature.

As illustrated in Figures 1 and 3, the 11–15  $\mu\text{m}$  ( $910\text{--}670 \text{ cm}^{-1}$ ) region is diagnostic of the number of peripheral H atoms attached to the edge rings in PAHs. The new interstellar features fall in the range expected for PAHs which have non-adjacent, as well as two and three adjacent, H atoms per edge ring, but not four or five. Thus, the detection of these new interstellar emission features where they would be expected on the basis of the PAH hypothesis strengthens the identification of the interstellar emission bands with PAHs and provides a powerful probe of the molecular geometry of the PAHs responsible.

Bands from different PAHs can blend to some extent, producing a quasi “continuum” which makes quantitative analyses uncertain. Blending may be partially responsible for the relatively smooth, structureless plateau in BD + 30°3639. If a continuum can be defined and removed, it will be possible to make a rough comparison of the emission intensity in each of the bands associated with the hydrogen out-of-plane bending modes corresponding to different edge structures. In the PAH interpretation, the ratio of “above-continuum” flux from about 11.7 to 12.6  $\mu\text{m}$  ( $855\text{--}790 \text{ cm}^{-1}$ ) and from 12.4 to 13.1  $\mu\text{m}$  ( $810\text{--}760 \text{ cm}^{-1}$ ) (not including the [Ne II] contribution) to that from about 10.8 to 11.6  $\mu\text{m}$  ( $925\text{--}860 \text{ cm}^{-1}$ ) is a measure of the ratio of the number of edge rings with two and three

FIG. 2.—The spectra of (a) NGC 7027, (b) HD 44179, (c) IRAS 21282 + 5050, and (d) BD + 30°3639. The reference standard for the spectra in (a), (b), and (c) is  $\alpha$  Tau. The reference standard for the spectrum in (d) is  $\alpha$  Her. The original spectra are oversampled by a factor of 2. In these plots the interleaved data points have been smoothed by averaging three adjacent channels. Representative error bars are shown for every tenth point. They indicate  $\pm 1 \sigma$  for the data prior to smoothing, or  $\pm 1.7 \sigma$  for the smoothed data in this figure. In addition to the emission features discussed in the text, emission at 10.52  $\mu\text{m}$  ( $950.6 \text{ cm}^{-1}$ ) from [S IV] is apparent in NGC 7027 and at 12.78  $\mu\text{m}$  ( $782.5 \text{ cm}^{-1}$ ) from [Ne II] in BD + 30°3639 and NGC 7027.



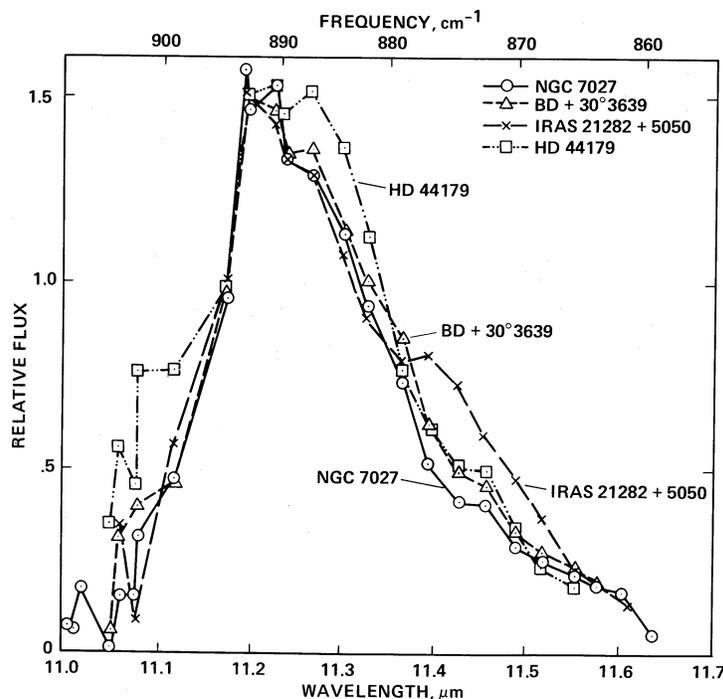


FIG. 4.—Normalized “11.3  $\mu\text{m}$ ” band profiles of NGC 7027, HD 44179, IRAS 21282 + 5050, and BD + 30°3639. The “continuum” under the features has been removed by drawing a straight line from minima near 10.9  $\mu\text{m}$  ( $917\text{ cm}^{-1}$ ) to minima near 11.65  $\mu\text{m}$  ( $858\text{ cm}^{-1}$ ). Note the excess emission in the spectrum of HD 44179 near 11.28  $\mu\text{m}$  ( $887\text{ cm}^{-1}$ ) and the excess emission in the spectrum of IRAS 21282 + 5050 near 11.4  $\mu\text{m}$  ( $877\text{ cm}^{-1}$ ).

of the “11.3  $\mu\text{m}$ ” feature, with a spacing of about  $10\text{ cm}^{-1}$ , may be significant. Additional observations are required to test the existence of these features.

There are indications, however, that the shape of the “11.3  $\mu\text{m}$ ” band is not determined solely by anharmonic effects. Figure 4 shows a plot in which the profiles of the normalized “11.3  $\mu\text{m}$ ” features of NGC 7027, HD 44179, BD + 30°3639, and IRAS 21282 + 5050 are superposed. The profiles were determined by subtracting out the “continuum” under the features. The continuum was estimated by a straight line drawn from minima near 10.9  $\mu\text{m}$  ( $917\text{ cm}^{-1}$ ) to minima near 11.65  $\mu\text{m}$  ( $858\text{ cm}^{-1}$ ). All four objects exhibit a very steep rise between 11.1 to 11.2  $\mu\text{m}$  ( $900$  to  $893\text{ cm}^{-1}$ ), followed by a slower decline between 11.25 and 11.6  $\mu\text{m}$  ( $889$  and  $862\text{ cm}^{-1}$ ). While the general shape of the features is similar in all the objects, there are distinct differences. In particular, HD 44179 shows excess emission near 11.08 and 11.28  $\mu\text{m}$  ( $903$  and  $887\text{ cm}^{-1}$ ) and IRAS 21282 + 5050 shows excess emission near 11.4  $\mu\text{m}$  ( $877\text{ cm}^{-1}$ ). These excesses cannot be explained in terms of anharmonicity. Rather, they imply that these objects contain slightly different populations of PAHs, some of which have fundamental bands at the positions of these excesses. This suggests that observations in other wavelength regions should show similar small differences. Such differences may ultimately place stronger constraints on the molecular structures responsible.

### c) Free Molecular PAHs versus Grains

For the simple aromatic molecules benzene, naphthalene, and anthracene in the gas phase, the intensity ratios of the C—H stretch to the C—H out-of-plane bend range from about 0.8 to 1.2 (Bishop and Cheung 1982; H. Niki, 1985, private communication). However, in the laboratory spectra of larger

PAHs in the solid state, the features due to the C—H out-of-plane bending modes are often far more intense than either the C—C stretching bands or the C—H stretching bands (see, for example, the Aldrich and Sadtler indices; Leger and d’Hendecourt [1987], and Allamandola, Tielens, and Barker [1987]). The C—H out-of-plane bending vibrations also produce the strongest features in the mid-infrared absorption spectra of amorphous carbons (Morterra and Low 1983; Angus, Koidl, and Domitz 1986) and other aromatic-containing solids (Sakata *et al.* 1987). The relative band strengths for these solid PAH samples are in marked contrast to the interstellar emission spectra, in which the “11.3  $\mu\text{m}$ ” band is typically 3–12 times weaker than the broad band near 7.7  $\mu\text{m}$  ( $1300\text{ cm}^{-1}$ ) (Donn, Khanna, and Salisbury 1986; Cohen *et al.* 1986, 1988).

The difference in the strength of the C—H out-of-plane bending mode between PAHs in the gas and solid phases depends upon whether or not the molecules are isolated (Allamandola and Sandford 1988). A PAH in the gas phase is not influenced by neighboring molecules and its spectrum depends solely on the electron distribution within the molecule itself. Samples prepared using the standard salt pellet technique, on the other hand, do not contain truly isolated PAHs. Instead, these samples contain PAH clusters in which each PAH is strongly influenced by its neighbors.

Figure 5 shows an example of how clustering affects C—H vibration bands in the spectrum of the aromatic molecule naphthalene ( $\text{C}_{10}\text{H}_8$ ). Naphthalene was mixed with argon in the gas phase at a ratio of 1:500. This mixture was deposited onto a 10 K substrate in a vacuum chamber, producing a solid in which the naphthalene molecules were isolated from each other within the argon matrix (top spectrum in Fig. 5). The matrix was then warmed to 25 K at 2 K per minute and

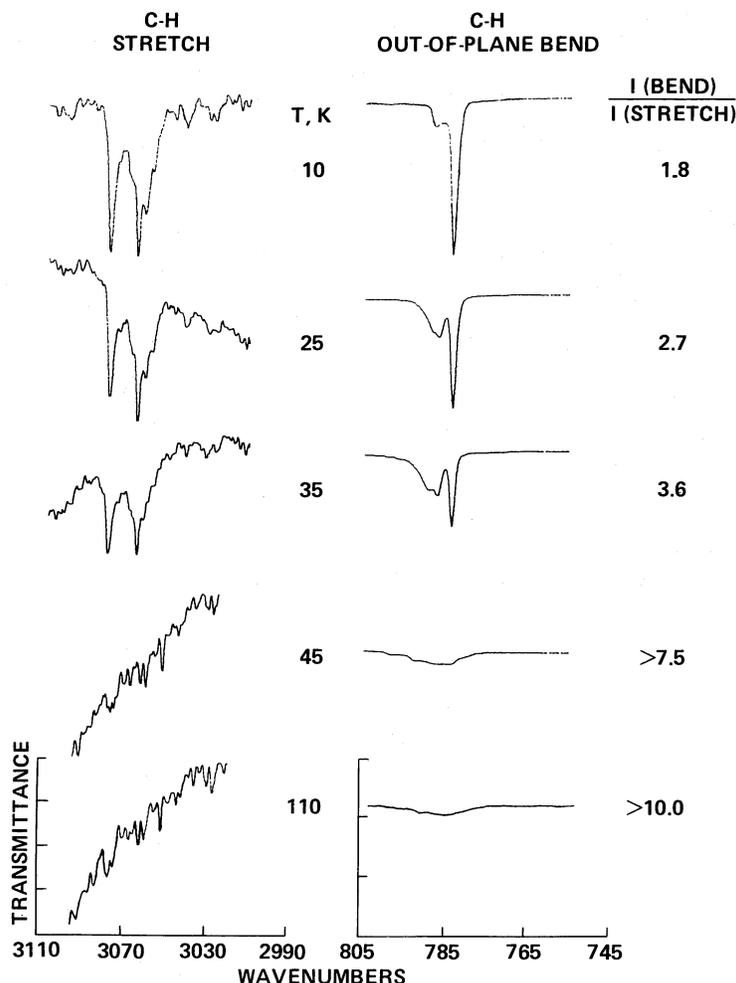


FIG. 5.—Comparison of the absorption strength of the C—H stretch with the C—H out-of-plane bend in the aromatic hydrocarbon naphthalene ( $C_{10}H_8$ ) as a function of molecular clumping. In the top spectrum, the molecules are isolated from one another in an argon matrix at 10 K. Subsequent spectra were taken after the matrix had been warmed to higher temperatures (25, 35, 45, 110 K) and then recooled to 10 K. The warming released more argon than naphthalene and resulted in increased clumping of the naphthalene. The ratio of the integrated band strength of the C—H bending feature to the C—H out-of-plane stretch feature is given after each spectral pair. Note that the strength of the out-of-plane bending mode becomes greatly enhanced as clumping increases. Tick marks on the left vertical axis (C—H stretch) represent 0.5% differences in transmission while those on the right vertical axis (C—H bend) represent 10% differences in transmission.

subsequently recooled to 10 K before taking a second spectrum. This process was repeated for warm-ups to 35, 45, and 110 K. During each warm-up, argon, and to a lesser extent, naphthalene, sublimed away. As the argon evaporated, the average distance between the remaining naphthalene molecules decreased and clustering occurred. The strength of the C—H out-of-plane bending and stretching bands of isolated naphthalene *decreased* as the Ar matrix was warmed (due to clumping and loss of naphthalene). Simultaneously, an intense new band *grew* in the out-of-plane bending region. The new band is blueshifted from the original band and is due to C—H out-of-plane bending vibrations of naphthalene in clusters. A similar effect does not occur for the C—H stretching mode in the  $3.3 \mu\text{m}$  ( $3000 \text{ cm}^{-1}$ ) region. In the case of naphthalene, the cluster-induced enhancement in the out-of-plane bending mode intensity relative to that of the C—H stretching mode exceeds a factor of 5.

We suspect that as the naphthalene molecules stick together, the oscillating, small positive charge associated with the hydrogen atom moving perpendicular to the molecular plane induces an oscillation of the  $\Pi$  electrons in adjacent molecules.

As  $\Pi$  electrons are loosely bound, the dipole change and effective distance over which the dipole oscillates are greatly enhanced and the intensity of the absorption is increased. This effect gives rise to the enhancement of the intensity of the out-of-plane C—H bend. The other C—H vibrations occur in the plane of the molecule and thus presumably do not induce such oscillations in neighboring molecules.

This behavior of the out-of-plane C—H bending mode places an important constraint on the nature of the carrier of the interstellar emission bands. The intensity of the interstellar  $3.28 \mu\text{m}$  ( $3050 \text{ cm}^{-1}$ ) emission band relative to the intensities of the longer wavelength bands implies that the emitters are molecules rather than particles (Leger and Puget 1984; Allamandola, Tielens, and Barker 1985). It has also been speculated that individual PAHs in clusters, or PAH structural units in amorphous carbon particles, if they are sufficiently decoupled from their neighbors, might behave as free species (Allamandola 1987; Duley 1987, 1988). However, since clustering can produce an enhancement of at least a factor of 5 in the out-of-plane bending mode, PAH-units inside larger grains cannot be responsible for the interstellar emission features

unless they are isolated in such a manner that less than about 1/10 of all their peripheral H atoms interact with neighboring aromatics. It is conceivable that such isolation could be achieved by bridging the aromatics with aliphatic chains, but the absence of dominant  $3.4 \mu\text{m}$  ( $2940 \text{ cm}^{-1}$ ) aliphatic features in the interstellar spectra argues against this possibility. Thus, the low intensity of the " $11.3 \mu\text{m}$ " band relative to the other bands in the interstellar spectra strongly suggests that free PAHs are responsible for the narrow infrared emission features.

Nonetheless, clustering of PAHs probably occurs to varying degrees in many environments, and amorphous carbon particles of some sort must certainly be present in many objects. PAH clusters would be expected to show enhanced emission between 11 and  $13 \mu\text{m}$  ( $910$  and  $770 \text{ cm}^{-1}$ ) relative to the other emission bands arising from the same clusters. These emission bands would be much broader than the features due to free molecular PAHs (see Fig. 5) and would overlap more completely, producing a pseudo "continuum." Indeed, the relatively featureless plateau seen in most emission objects between 11 and  $13 \mu\text{m}$  ( $910$  and  $770 \text{ cm}^{-1}$ ) may contain a substantial contribution from the C—H out-of-plane bending mode of PAHs in clusters or amorphous carbon particles. This plateau is often comparable to or more intense than the plateau under the  $6.2$  and  $7.7 \mu\text{m}$  ( $1610$  and  $1300 \text{ cm}^{-1}$ ) bands which is also thought to be due to amorphous carbon particles (Bregman *et al.* 1988). The large broad emission bump centered near  $12.4 \mu\text{m}$  ( $806 \text{ cm}^{-1}$ ) in the spectrum of IRAS 21282 + 5050 (Fig. 2c) may well have an important contribution from PAH clusters and amorphous carbon grains.

#### d) New Bands in the HD 44179 Spectra between 10 and 11 Microns

The spectrum of HD 44179 (Fig. 2b) is unique in that it clearly shows a regular series of emission bands (or absorption bands) extending from about 10 to  $11 \mu\text{m}$  ( $1000$ – $910 \text{ cm}^{-1}$ ). The pattern and spacing are suggestive of rovibrational (i.e., simultaneous rotational and vibrational) transitions of a relatively simple gas-phase molecule. The observed band separation of  $12$ – $15 \text{ cm}^{-1}$  is quite large and suggests simple hydrides are responsible. However, no diatomic hydrides have fundamental vibration bands near  $10 \mu\text{m}$  ( $1000 \text{ cm}^{-1}$ ), implying that the features must be due to the bending mode vibration of a polyatomic hydride. Possible candidates include simple

hydrides (neutral or ionized) containing three or more atoms such as  $\text{SiH}_2$ ,  $\text{SiH}_3$ ,  $\text{SiH}_4$ ,  $\text{NH}_2^+$ ,  $\text{NH}_3$ ,  $\text{CH}_2$ ,  $\text{C}_2\text{H}$ , etc. While there is presently no evidence that the molecule responsible for these features contains carbon, it is interesting to consider the possibility that we may be seeing either the building blocks from which PAHs are made or the molecular fragments resulting from their destruction. Unfortunately, the present data do not allow us to uniquely identify the species responsible. Further observations at even higher resolution will be required before a positive identification can be made.

#### IV. CONCLUSIONS

Moderate-resolution spectra of NGC 7027, HD 44179, BD + 30°3639, and IRAS 21282 + 5050 show evidence for several emission features between 10.5 and  $13.0 \mu\text{m}$  ( $950$ – $770 \text{ cm}^{-1}$ ) which are consistent with emission from free molecular PAHs. The positions of these new features constrain the type of molecular structures responsible and confirm earlier conclusions that most of the infrared emission originates in PAHs containing nonadjacent, doubly adjacent, and triply adjacent peripheral H atoms. The asymmetric profile of the " $11.3 \mu\text{m}$ " band (which peaks near  $11.2 \mu\text{m}$ ,  $893 \text{ cm}^{-1}$ ) is consistent with the slight anharmonicity expected in the out-of-plane bending mode of PAHs. While the  $11$ – $13 \mu\text{m}$  ( $910$ – $770 \text{ cm}^{-1}$ ) spectra suggest that the structures of the most intensely emitting PAHs do not vary much in these very different objects, some variations are evident. These variations imply that different objects contain slightly different populations of PAHs. The precise positions of the new peaks show that symmetric, highly compact PAHs dominate the interstellar emission. These are the most stable PAHs.

Laboratory experiments show that the strength of the C—H out-of-plane bending mode relative to the higher frequency modes in PAHs is a strong function of molecular "clustering." The strength of the interstellar " $11.3 \mu\text{m}$ " feature relative to the other observed emission features implies that the "narrow" interstellar features are most likely due to free molecular PAHs.

A series of regular features between 10 and  $11 \mu\text{m}$  ( $1000$  and  $910 \text{ cm}^{-1}$ ) has been found in the spectrum of HD 44179. These features are probably due to rovibrational transitions in a gas phase molecular species. It is not known whether the species is neutral or ionized. The large spacing between features suggests that a simple polyatomic hydride is responsible.

#### REFERENCES

- Aitken, D. K., and Roche, P. F. 1982, *M.N.R.A.S.*, **200**, 217.  
 ———. 1983, *M.N.R.A.S.*, **202**, 1233.  
 Aitken, D. K., Roche, P. F., Spenser, P. M., and Jones, B. 1979, *Ap. J.*, **233**, 925.  
 Allamandola, L. J. 1987, in *Polycyclic Aromatic Hydrocarbons and Astrophysics*, ed. A. Leger, L. B. d'Hendecourt, and N. Boccarda (Dordrecht: Reidel), p. 339.  
 Allamandola, L. J., and Sandford, S. A. 1988, in *Dust in the Universe*, ed. J. Bailey (Dordrecht: Reidel), p. 229.  
 Allamandola, L. J., Tielens, A. G. G. M., and Barker, J. R. 1985, *Ap. J. (Letters)*, **290**, L25.  
 ———. 1987, in *Physical Processes in Interstellar Clouds*, ed. G. E. Morfill and M. Scholer (Dordrecht: Reidel), p. 305.  
 Angus, J. C., Koidl, P., and Domitz, S. 1986, in *Plasma Deposited Thin Films*, ed. J. Mort and F. Jansen (Boca Raton: CRC Press), p. 89.  
 Barker, J. R., Allamandola, L. J., and Tielens, A. G. G. M. 1987, *Ap. J. (Letters)*, **315**, L61.  
 Bellamy, L. J. 1958, *The Infra-Red Spectra of Complex Organic Molecules* (2d ed. Wiley: New York).  
 Bishop, D. M., and Cheung, L. M. 1982, *J. Phys. Chem. Ref. Data*, **11**, 119.  
 Bregman, J. D., Allamandola, L. J., Tielens, A. G. G. M., and Witteborn, F. C. 1988, *Ap. J.*, submitted.  
 Cohen, M., and Jones, B. F. 1987, *Ap. J. (Letters)*, **321**, L151.  
 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., Witteborn, F. C., Wooden, D., and Rank, D. 1986, *Ap. J.*, **302**, 737.  
 Cohen, M., Tielens, A. G. G. M., Bregman, J. D., Witteborn, F. C., Rank, D. M., Allamandola, L. J., Wooden, D., and de Muizon, M. 1988, *Ap. J.*, in press.  
 Crawford, M. K., Tielens, A. G. G. M., and Allamandola, L. J. 1985, *Ap. J. (Letters)*, **293**, L45.  
 Donn, B., Khanna, R. K., and Salisbury, D. 1986, *Bull. A.A.S.*, **18**, 1031.  
 Duley, W. W. 1987, in *Polycyclic Aromatic Hydrocarbons and Astrophysics*, ed. A. Leger, L. B. d'Hendecourt, and N. Boccarda (Dordrecht: Reidel), p. 373.  
 ———. 1988, in *Dust in the Universe*, ed. J. Bailey (Dordrecht: Reidel), p. 297.  
 Duley, W. W., and Williams, D. A. 1981, *M.N.R.A.S.*, **196**, 269.  
 Hanner, M. S., Tokunaga, A. T., Veeder, G. S., and A'Hearn, M. F. 1984, *A.J.*, **89**, 162.  
 IRTF Photometry Manual. 1986, NASA Infrared Telescope Facility.  
 Leger, A., and d'Hendecourt, L. B. 1987, in *Polycyclic Aromatic Hydrocarbons and Astrophysics*, ed. A. Leger, L. B. d'Hendecourt, and N. Boccarda (Dordrecht: Reidel), p. 223.  
 Leger, A., and Puget, J. L. 1984, *Astr. Ap. (Letters)*, **137**, L5.  
 Morterra, C., and Low, M. J. D. 1983, *Carbon*, **21**, 283.

- Roche, P. F., Aitken, D. K., and Smith, C. H. 1988, *M.N.R.A.S.*, submitted.  
Russell, R. W., Soifer, B. T., and Merrill, K. M. 1977, *Ap. J.*, **213**, 66.  
Russell, R. W., Soifer, B. T., and Willner, S. P. 1977, *Ap. J. (Letters)*, **217**, L149.  
Sakata, A., Wada, S., Onaka, T., and Tokunaga, A. T. 1987, *Ap. J. (Letters)*, **320**, L63.  
Sandford, S. A., Witteborn, F. C., Bregman, J. D., Cohen, M., and Allamandola, L. J. 1987, *Bull. A.A.S.*, **19**, 952.  
Schild, R., Peterson, D. M., and Oke, J. B. 1971, *Ap. J.*, **166**, 95.  
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)*, **271**, L13.  
Stein, S. E. 1978, *J. Phys. Chem.*, **82**, 566.  
van der Zwet, G. P., and Allamandola, L. J. 1985, *Astr. Ap.*, **146**, 76.  
Witteborn, F. C., and Bregman, J. D. 1984, *Proc. SPIE*, **509**, 123.

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