Acknowledgments: We thank Dr. Marie de Muizon for helpful discussions on the IRAS LRS spectra. J. R. Barker acknowledges partial support from the U.S. Department of Energy, Office of Basic Energy Sciences.

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d'Hendecourt. Meeting held in
February, 1986, Les Houches, Fr.

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THE HYDROGEN COVERAGE OF INTERSTELLAR PAHs

CONF-8602110--2

DE87 003376

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FG02-85ER13442

ABSTRACT. We have calculated the rate at which the CH bond in interstellar PAHs ruptures due to the absorption of a UV photon. The results show that small PAHs (≤25 carbon atoms) are expected to be partially dehydrogenated in regions with intense UV fields, while large PAHs (≥25 carbon atoms) are expected to be completely hydrogenated in those regions. Because estimates of the carbon content of interstellar PAHs lie in the range of 20-50 carbon atoms, dehydrogenation is probably not very important.

Because of the absence of other emission features besides the 11.3μm feature in ground-based 8-13μm spectra, it has been suggested that interstellar PAHs are partially dehydrogenated. However, IRAS 8-22μm spectra of most sources that show strong 7.7 and 11.2μm emission features also show a plateau of emission extending from about 11.3 to 13μm. Like the 11.3μm feature, we attribute this new feature to the CH out-of-plane bending mode in PAHs. This new feature shows that interstellar PAHs are not as dehydrogenated as estimated from ground-based 8-13μm spectra. It also constrains the molecular structure of interstellar PAHs. In particular, it seems that very condensed PAHs, such as coronene and circumcoronene, dominate the interstellar PAH mixture as expected from stability arguments.

1. INTRODUCTION

Emission features at 3.3, 6.2, 7.7, 8.6 and 11.3μm have been discovered in a wide variety of objects all characterized as having copious amounts of UV photons (see the reviews of Aitken (1981) and Willner (1984) and references therein). Spectroscopic analysis of the emission spectrum implicates Polycyclic Aromatic Hydrocarbons (hereafter PAHs) as the carriers (Duly and Williams 1981; Leger and Puget 1984; Allamandola, Tielens and Barker 1985, 1986 herafter ATBa and b). In this interpretation the 6.2 and 7.7μm features are due to the CC stretching vibrations, while the 3.3, 8.6 and 11.3μm features are due to the CH stretching and bending vibrations.

The 11-15μm spectral region, the region of the CH out-of-plane deformation modes in PAHs, can be particularly indicative of the molecular structure of the interstellar PAHs. For an increasing number of adjacent H atoms on an aromatic ring, the position of this vibrational mode shifts to longer wavelengths (Bellamy 1960). The presence of only <u>one</u> interstellar emission band at 11.3μm ground based 8-13μm spectra has been taken to imply that interstellar PAHs are partially dehydrogenated (Duly and Williams 1981). That is, interstellar PAHs are thought to have only isolated H atoms on their aromatic rings. It has been suggested that this partial dehydrogenation of interstellar PAHs results from the large UV flux in the emission regions (Leger and Puget 1984).

We have theoretically investigated the hydrogen loss of interstellar PAHs due to UV photon absorption. From these calculations, it is concluded that the typical interstellar PAH with more than 25 carbon atoms is completely covered with hydrogen (section II). In order to reconcile this apparent difference between (ground-based) observations and theory, we have examined the 8-22μm LRS spectra obtained by the IRAS satellite of all the sources which show the unidentified emission features. These data show the presence of a plateau of emission between 11.3 and 13μm, which has not been recognized in ground-based studies due to telluric absorption (section III). The implications of this emission plateau for the derived hydrogen coverage of interstellar PAHs is discussed in section IV.

2. HYDROGEN LOSS

When a PAH molecule absorbs an UV photon, internal conversion will quickly transform the electronic excitation into vibrational excitation in a lower electronic state. Generally, this internal conversion process is so fast that direct H loss (e.g., through absorption into a dissociative electronic state) is unimportant. The resulting highly vibrationally excited PAH molecule can, however, still lose a hydrogen atom when the number of vibrational quanta located in one CH bond is sufficient to cause rupture (e.g., through excitation into the vibrational continuum of the CH bond). In this section we will calculate the probability for an interstellar PAH to lose a H atom in this way.

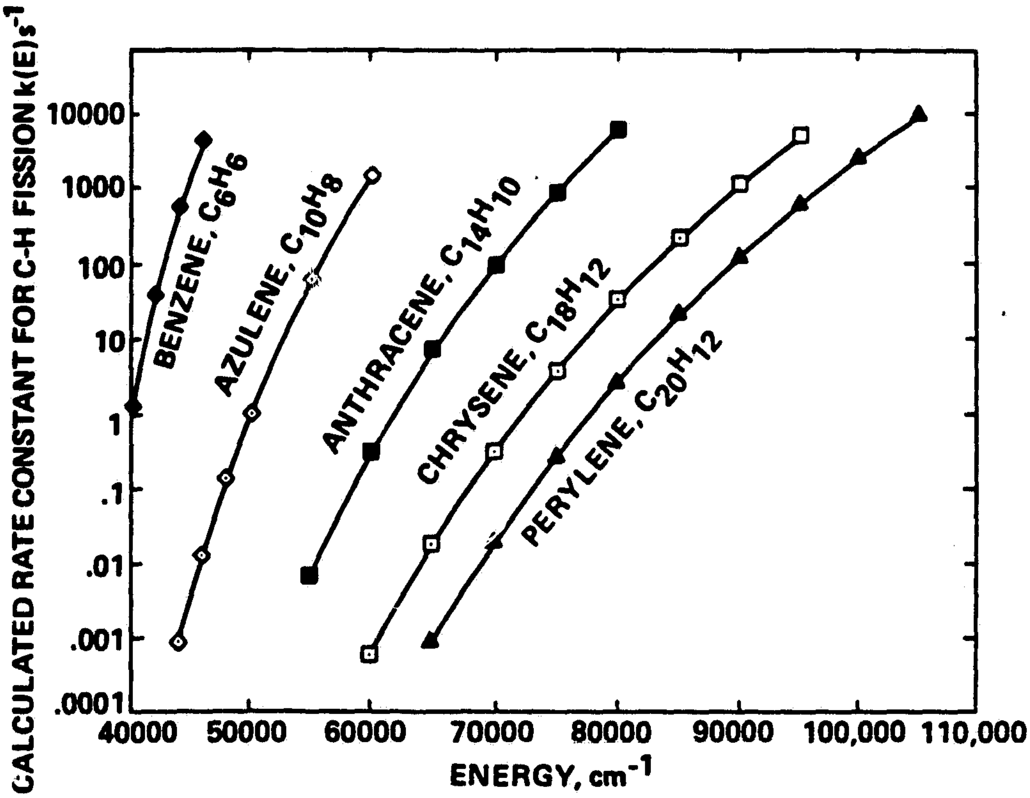

Fig. 1 The rate of CH bond rupture as a function of the vibrational energy content of PAHs calculated using quantum RRK theory (Barker 1983).

Because little is known about the unimolecular reactions of PAHs, we have used the simple quantum RRK statistical theory (see Barker 1983 and references therein), which requires less detailed knowledge of the molecular species and reaction parameters than the RRKM statistical theory. The details of this calculation are discussed elsewhere (ATBb). The results of the calculation for several PAH molecules are shown in figure 1.

For the same internal energy, small molecules lose hydrogen at a higher rate than larger molecules. This is due to the fact that smaller molecules have fewer vibrational modes in which to distribute the energy and, thus, have a higher average excitation per vibrational mode. The probability that enough energy is localized in one CH bond to cause rupture is, therefore, higher. The calculated rate for CH bond rupture has to be compared to that of other loss channels for the vibrational excitation energy. The most important one is infrared fluorescence emission which typically has a rate of about 10 sec^{-1}. Comparison with the calculated results for chrysene ($C_{18}H_{12}$), for example, shows that hydrogen loss will dominate the fluorescent relaxation for this molecule when it has a total vibrational energy content of 80000 cm^{-1} or more (≈10eV; cf., figure 1).

Table I: A comparison of the hydrogen loss rate and the rehydrogenation rate in different interstellar regions.

Region	Type	n_H (cm^{-3})	G_o [a]	R_{uv} [b] $[sec^{-1}]$	R_H [c] $[sec^{-1}]$	f_H [d] $C_{18}H_{12}$	f_H [d] $C_{54}H_{18}$	Ref.
Orion Bar	H II Region	10^5	4.4×10^4	2.2×10^{-4}	10^{-4}	3.1×10^{-1}	1.0	1
NGC7027	Planetary Nebula	2×10^5	1.2×10^5	6×10^{-4}	2×10^{-4}	2.5×10^{-1}	1.0	2
NGC7023	Reflection Nebula	10^4	3×10^3	1.5×10^{-5}	10^{-5}	4.0×10^{-1}	1.0	3

Notes:

a) The intensity of the UV field (6-13.6eV) normalized to the average diffuse interstellar radiation field (10^8 cm^{-2} sec^{-1}; Habing 1968).

b) The hydrogen loss rate.

c) The rehydrogenation rate.

d) The fractional hydrogen coverage of chrysene ($C_{18}H_{12}$; $f_{uv} = 0.5$) and circumcoronene ($C_{54}H_{18}$; $f_{uv} = 0.0$).

References:

1) Tielens and Hollenbach 1985b; 2) Ellis and Werner 1986;
3) Castelaz et al. 1986.

The degree of dehydrogenation of interstellar chrysene molecules can now be estimated (assuming no other energy relaxation channels such as electronic fluorescence or ionization), by comparing the rate at which these molecules absorb 10eV photons, R_{uv}, with their collision rate with H atoms, R_H (i.e., the maximum rehydrogenation rate possible). These rates are given by

$$R_{uv} = \sigma_{uv} N_{uv} \tag{1}$$

and

$$R_H = \langle \sigma v \rangle_H n_H \tag{2}$$

where σ_{uv} is the UV photon absorption cross section, N_{uv} is the flux of UV photons with sufficient energy to cause H loss (e.g., $h\nu \geq 10$eV for chrysene), $\langle \sigma v \rangle_H$ is the collision rate coefficient and n_H is the density of H atoms. The UV absorption cross section of PAHs for energies greater than 50000 cm^{-1} (2000Å; 6eV) is not known. We will assume that it is equal to the UV absorption cross section associated with the $\pi \rightarrow \pi^*$ transition, about 10^{-16} cm^2 for chrysene (Birks 1970). This is perhaps on the low side. The UV absorption cross section for coronene, for example, is about 5 x 10^{-16} (Birks 1970). Introducing G_o as the intensity of the UV field in terms of the average diffuse interstellar UV radiation field between 6 and 13.6eV (10^8 cm^{-2} sec^{-1}; Habing 1968) and f_{uv} as the fraction of these photons between 13.6eV and the threshold for H loss by a particular PAH (i.e., 10eV for chrysene) yields for the H loss rate

$$R_{uv} = 10^{-8}\, G_o\, f_{uv} \quad sec^{-1} \tag{3}$$

The collision rate coefficient is about 2 x 10^{-10} cm^3/sec, given a geometrical cross section of 20Å for chrysene and a mean H velocity of 1 km/sec at the gas temperatures of interest (≈100K). This leads to a rehydrogenation rate of

$$R_H = 2 \times 10^{-10}\, n_H \quad sec^{-1} \tag{4}$$

Actually, the collision rate coefficient for interstellar PAHs may be somewhat larger than this. Because of their low ionization potential, most interstellar PAHs will be singly ionized (ATBa). The rate coefficient for collisions of neutral H atoms with ionized PAHs is probably comparable to the Langevin rate (≈10^{-9} cm^3/sec). In our calculations we will assume that the rehydrogenation rate for interstellar PAHs is given by

$$R_H = 10^{-9}\, n_H \quad sec^{-1} \tag{5}$$

Table I lists the UV flux and density in three typical emission regions derived from observations of the OI (63μm) and CII (158μm) fine structure lines. Note that these atomic cooling lines originate from the region where most of the FUV emission is absorbed (Tielens and Hollenbach 1985a), which is also the region where most of the emission in the infrared features originates. Assuming f_{uv} is 0.5 for chrysene, K_{uv} and R_H have been calculated for these regions using these densities and UV fields (table I). The rate for H loss in all three interstellar regions is about a factor of 2 larger than the rehydrogenation rate. In view of the uncertainties in the UV absorption and the collision cross section assumed above, no firm conclusion can be drawn from this comparison. It seems, however, possible that chrysene is partially dehydrogenated in the interstellar medium.

Assuming that the hydrogen loss rate for partially dehydrogenated chrysene is equal to that of completely hydrogenated chrysene, the fractional hydrogen coverage of chrysene, f_H, can be calculated. That is,

$$f_H = n_H/(n_H + 10G_o\ f_{uv}) \qquad (6)$$

Thus, chrysene might lose a considerable fraction of its hydrogen atoms (c.f., table I). These results can be generalized to other PAHs by using the internal energy threshold (i.e., the excition energy for which the H loss rate equals the IR fluorescent rate), appropriate for the specific molecule under consideration. Clearly, small PAH molecules, with a threshold less than 13.6eV, may lose a considerable fraction of their hydrogen atoms.

Large PAH molecules will, however, be completely hydrogenated. For PAH molecules substantially larger than the ones shown in figure 1, the calculated rate constant for CH bond rupture is always much less than the cooling rate due to infrared fluorescence for interstellar vibrational excitation energies less than 13.6eV ($\approx$110000 cm^{-1}; the H atom ionization limit), where we have made the reasonable assumption that the IR fluorescent rate for large PAHs is similar to that of small PAHs. Thus, outside of ionized gas regions, where more energetic UV photons are available, such large PAH molecules will be completely hydrogenated. Note that two photon processes (the absorption of a second UV photon before the first one has been completely radiated away) can cause hydrogen loss for large PAHs. The probability for the occurance of a two photon process is, however, small. For example, for the Orion bar this probability is calculated to be only about 4×10^{-5}, assuming a IR radiative lifetime of 0.1 sec. Even if all two photon processes lead to CH bond rupture, the hydrogen loss rate is only 2×10^{-8} sec^{-1}. This is much less than the rehydrogenation rate (c.f., table I) and, thus, large PAHs will be completely hydrogenated.

Because of the steepness of the CH bond rupture rate with internal vibrational excitation energy, the transition from small, dehydrogenated PAHs to large, completely hydrogenated PAHs is very sharp. From figure 1 it is estimated that this transition occurs for molecules containing about 25 carbon atoms (e.g., coronene ($C_{24}H_{12}$)). Estimates of the number of carbon atoms in interstellar PAHs range from 20 to 50 (Leger and Puget 1984; ATBa,b). It seems, thus, that the majority of the interstellar PAHs should be fully hydrogenated.

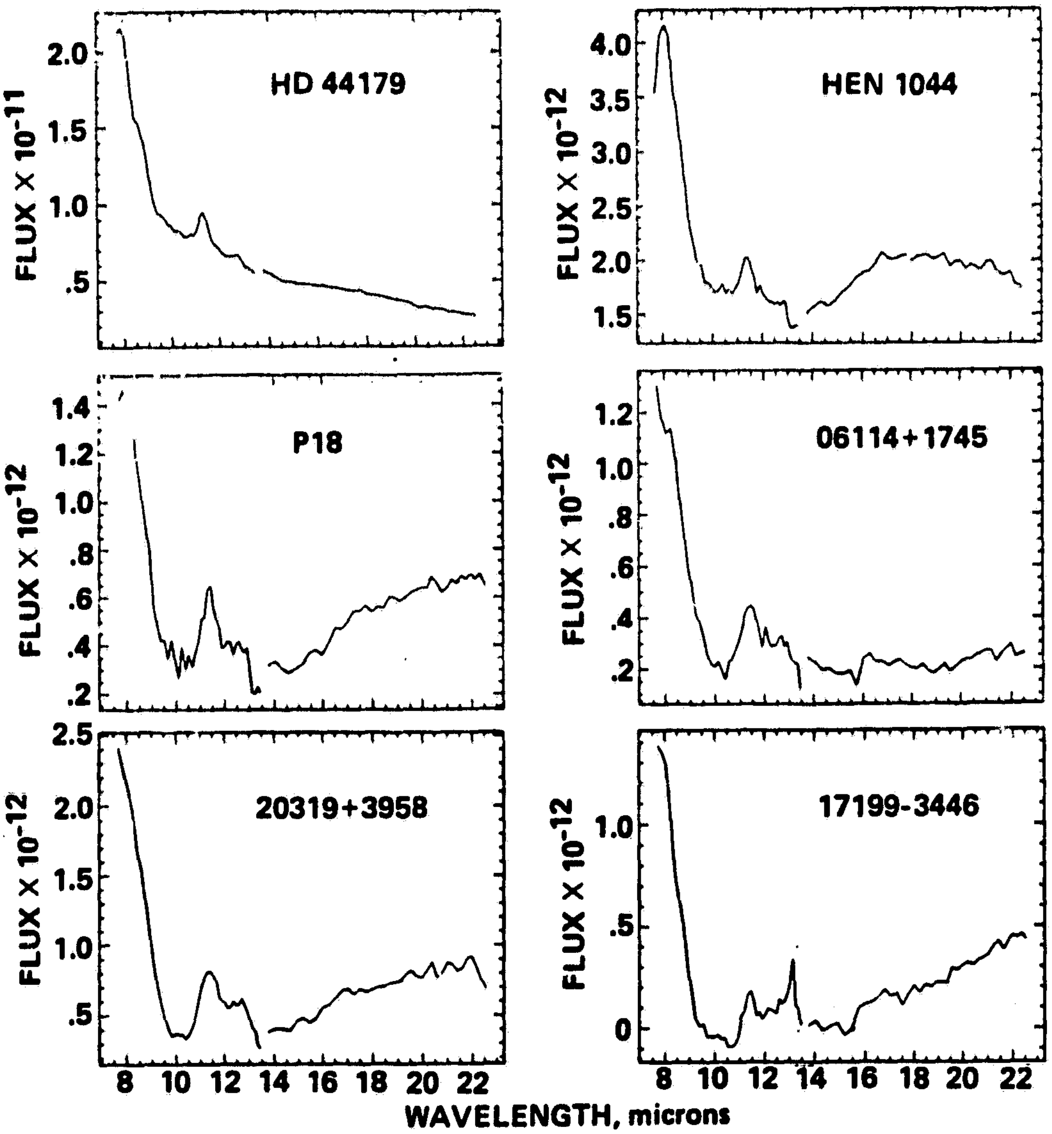

Fig. 2 The LRS spectra of six representative IRAS sources are shown. The short wavelength data span the full useful range from 7.67 to 13.45μm. The long wavelength data are shown from 13.72 to 22.55μm (see text). The 7.7μm feature dominates these spectra. Note also the inflection at 8.7μm which is sometimes visible. The previously known 11.3μm band shows a long wavelength plateau extending to about 13.0μm. Ordinates are flux in $W/m^2/\mu m$.

3. IRAS SPECTRA

Ground-based spectral studies of the CH bending modes in interstellar PAHs are limited to the 8-13μm atmospheric window with considerable uncertainty at the edges, because of atmospheric absorptions. Recently, the Infrared Astronomical Satellite (IRAS) has obtained the first complete interstellar infrared spectra in the 8-22μm region, which contains these important vibrational modes of PAHs. This section examines a set of spectra obtained by this satellite. The details of the analysis are presented elsewhere (Cohen, Tielens and Allamandola 1985).

3.1 The LRS Spectra.

The IRAS low-resolution spectrometer (LRS) has obtained short-wavelength (8-13.5μm) and long-wavelength (11-22.5μm) spectra, each with a resolution ($\lambda/\Delta\lambda$) ranging from 10 at the shortest to 40 at the longest wavelength (De Muizon and Habing 1985). From the LRS data base we have examined all the spectra characterized as having the 11.3μm band in emission and selected a sample of 20 which show evidence for an emission feature between 11.3 and 15μm. Objects with strong ionic emission lines have been disregarded because of possible confusion (i.e., the Ne II 12.8μm line). Inspection of the NGS Palomar Observatory and SRC southern sky photographs indicates that the vast majority of our sample of 20 objects are associated with either very red, or reflection, nebulae.

Figure 2 presents six typical spectra from this sample. Some of these spectra are of well-known sources: the reflection nebulae, P18 and HD 44179, and the WC 10 nucleus of a planetary nebula, Hen 1044 (=He 2-113). Spectra of three sources newly found by IRAS (06114+1745, 17199-3446, and 20319+3958) are also included. To construct these spectra we utilized the full useful range of the short-wavelength LRS spectra and displayed the long-wavelength spectra starting at 13.72μm. Because of the much lower spectral resolution of the long-wavelength IRAS detector we have not used both long- and short-wavelength data in the region of overlap (11-13.5μm). However, the data in the long-wavelength spectra reveal the same structure as the short wavelength spectra, albeit at a degraded resolution. In fact the upturn shortward of 15μm in the long-wavelength spectra of some sources (e.g., P18) is due to the new emission feature at this low resolution.

Besides the 11.3μm feature all of the selected spectra show good evidence for the presence of the well-known 7.7 and 8.7μm emission features. The new feature has the appearance of an emission plateau, ending abruptly at about 13.0μm. This plateau feature is a common characteristic of many of the sources showing the 11.3μm feature, but not of spectra of other objects. The spectrum of 17199-3446 is particularly striking because there is essentially no flux at all between the emission features at 7.7 and 11.3μm, and again beyond the plateau until 15.3μm. Note that the spike in the emission plateau in this source is present in only one of the three IRAS spectra of this source and, in fact, is probably not real (de Muizon, private communication). Although all spectra in our sample show the same pattern of emission between 11 and 15μm, there exist real spectral variations from source to source (e.g., while evident, the new feature

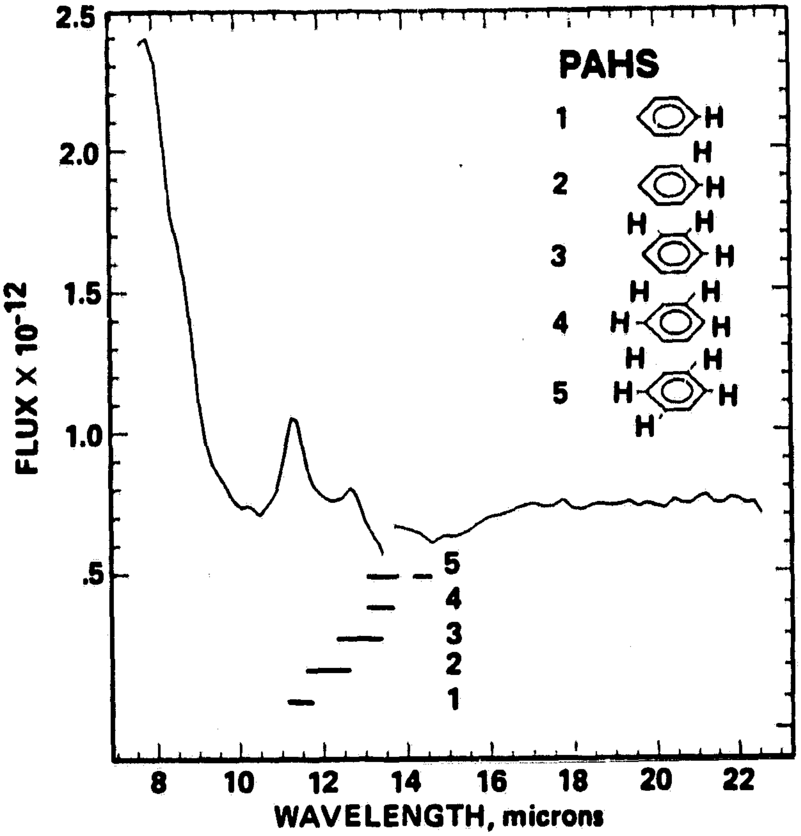

Fig. 3 The average spectrum of the sources in our sample (see text). The horizontal bars in the 11-15μm range indicate the absorption range for isolated, 2, 3, 4 and 5 adjacent hydrogens on an aromatic ring.

is weak in HD 44179).

The average of the 20 spectra (Fig. 3) shows the new emission plateau between 11.3 and 13.0μm. Note that the peak wavelength of the secondary feature at 12.7μm is largely determined by the brightest source (HD 44179) and is therefore presumably not associated with Ne II emission.

3.2 Interpretation

In line with the interpretation of the other emission features in these spectra (e.g., 7.7,8.7, and 11.3μm), we attribute the newly discovered emission plateau between 11.3 and 13.0μm to emission by interstellar PAHs. The ground-based and airborne 3-13μm spectra of several of the objects shown in Figure 2 are dominated by emission features at 3.3, 6.2, 7.7, 8.7, and 11.3μm. Although the new IRAS sources in our sample have not yet been studied shortward of 7.7μm, the steep rise toward 7.7μm and the presence of the 11.3μm feature strongly suggest the

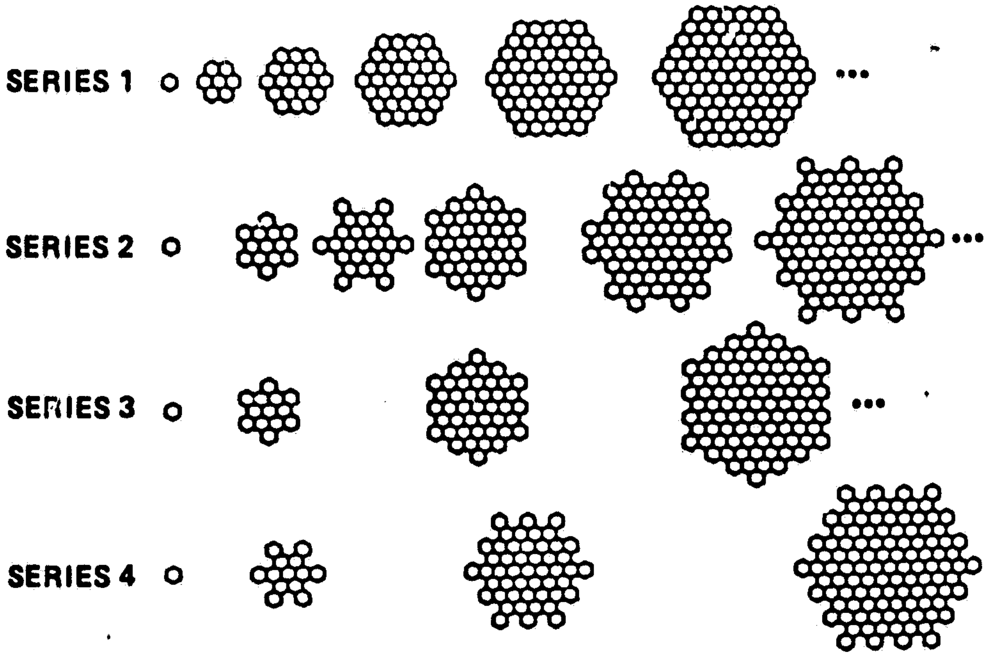

Fig. 4. Homologous series of hexagonally symmetric PAH molecules. In each series except 2, all of the molecules have the same corner structure. Molecules in series 2 have three different corner structures (Stein and Brown 1986). Note that the molecules in series 1 have only isolated and two adjacent hydrogens on their aromatic rings.

presence of these emission bands in their spectra also. Other interpretations of the emission plateau between 11.3 and 13.0μm have been considered and rejected (Cohen, Tielens, and Allamandola 1985).

The absorption frequencies of the CH out-of-plane bending mode are highly characteristic for the number of adjacent H atoms on an aromatic ring (Bellamy 1960). Due to strong coupling between the bending vibrations of adjacent H atoms, the peak frequency of this mode shifts to longer wavelengths when the number of adjacent H atoms increases. This is illustrated in Figure 3 where the range of absorption frequencies for different numbers of adjacent H atoms is indicated by horizontal bars. Large PAHs generally have several absorption bands in this wavelength region, because different rings can have different numbers of adjacent H atoms depending on their location within the molecule. For example, the condensed 10 ring molecule ovalene ($C_{32}H_{14}$) has aromatic rings with one and with two adjacent H atoms. Its spectrum shows, therefore, two absorption bands (at 11.43 and 11.92μm; Sadtler spectrum 28759). In contrast, in the linear five-ring system pentacene ($C_{22}H_{14}$) the end rings have four adjacent hydrogens, while the other rings have isolated nonadjacent H atoms. Its spectrum shows strong bands at about 11.05 and 13.6μm (Sadtler spectrum 15223). Thus, the 11-15µm wavelength region places important constraints on the molecular structure.

It should be stressed that only PAHs with isolated H atoms can give rise to an 11.3µm feature; hence, the suggestion that interstellar aromatic hydrocarbons are only partially hydrogenated (Duly and Williams 1981). The theoretical estimates of the degree of dehydrogenation of interstellar PAHs (see section II) and the discovery of a plateau of emission longward of 11.3µm forces a reconsideration of partial dehydrogenation. The IRAS spectra show that the interstellar PAHs responsible for the emission features are predominantly made up of aromatic rings with isolated, two, and, possibly, three adjacent H atoms. PAHs with four or five adjacent H atoms are excluded. This important clue strongly suggests that pericondensed PAHs such as ovalene ($C_{32}H_{14}$) and circumcoronene ($C_{54}H_{18}$), which have only isolated and two adjacent H atoms, dominate the interstellar PAH mixture.

Finally, the presence of spectral variations among the sources in this sample should be emphasized. Unfortunately, the signal-to-noise in most sources is insufficient to judge the reality of the minor substructure on this newly discovered emission plateau. Yet, some sources differ clearly from the average. The Red Rectangle (HD44179) is one such case (c.f., figure 2). The simplicity of its 11-15µm spectrum parallels that of its 3µm and 5-8µm spectrum (Cohen et al. 1986). The weakness of the 11.3-13.0µm emission plateau in this source is presumably related to its benign conditions, which allows smaller PAHs to survive and dominate the infrared spectrum (Cohen, Tielens and Allamandola 1985; Cohen et al. 1986).

IV. DISCUSSION

In building up graphite sheets starting from benzene, different edge structures can be recognized. Figure 4 shows these different edge structures possible in various series of hexagonally symmetric PAHs (Stein and Brown 1986). Disregarding the first member of each series (Benzene), these series are characterized by a different number of adjacent peripheral hydrogen atoms. The IRAS observations suggest that the members of series one dominate the interstellar mixture, with perhaps a small contribution of series three. Series two or four, however, do not seem to contribute substantially to the interstellar mixture. It is our contention that this reflects directly the carbon condensation process in circumstellar shells.

Interstellar PAHs are probably formed in the carbon-rich outflows from planetary nebulae and carbon Miras. Figure 5 illustrates the first steps in the high temperature carbon polymerization route which is thermodynamically most favorable (Stein 1978). Note that this carbon condensation route goes through coronene and, eventually, circumcoronene (i.e., series one in figure 4). Within this scheme, the completely condensed PAHs, in which all aromatic rings are connected to at least two others (e.g., pyrene and coronene), are even more stable relative to the others. Essentially, this is because this structure permits electron delocalization to a larger extent than the less

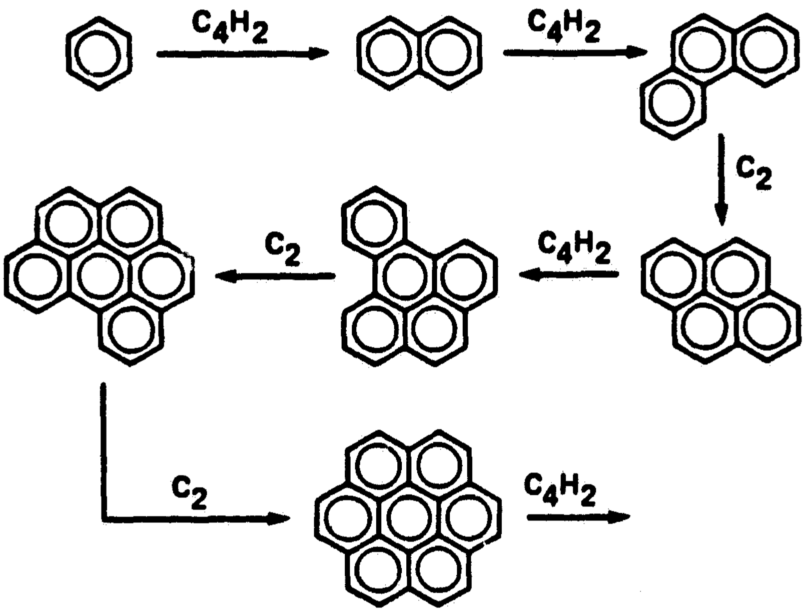

Fig. 5. First six members of the most thermodynamically favorable high-temperature carbon condensation route (Stein 1978). Successive members of this series are formed by adding two or four carbon atoms at a time, the number required to complete an additional fused aromatic ring. Note that C_2 and C_4H_2 refer only to the number and type of atoms added in each step and do not refer to specific chemical species or mechanisms.

condensed forms. These PAHs are, therefore, expected to dominate the mixture of PAHs initially injected into the interstellar medium by carbon stars and planetary nebulae and to survive the longest once in the interstellar medium. For example, the distribution of PAHs injected into the interstellar medium by carbon-rich objects will be further modified by processes in the interstellar medium, such as photodissociation, photoisomerization and sputtering in shocks (Crawford, Tielens, and Allamandola 1985). Again, because of their stability, these processes will favor the very compact PAHs such as pyrene, coronene, ovalene, and circumcoronene. Of course, other geometries will also be present but to a lesser degree, in particular in the harsher environments. In regions with benign conditions, such as the Red Rectangle, one might, however, expect to see emission from these less stable PAHs (as well as from smaller PAHs).

The dominance of these condensed PAHs in the interstellar mixture, as evidenced by the 11-15μm spectra (e.g., the CH out-of-plane deformation modes) may, therefore, merely reflect the role thermodynamic stability plays in the formation and destruction processes of interstellar PAHs.

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