

A NEW EMISSION FEATURE IN *IRAS* SPECTRA AND THE POLYCYCLIC AROMATIC HYDROCARBON SPECTRUM

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ABSTRACT

IRAS spectra of those sources which show strong 7.7 and 11.3 μm emission features also show a plateau of emission extending from 11.3 to about 13.0 μm . Like the 11.3 μm feature, we attribute this new feature to the CH out-of-plane bending mode in polycyclic aromatic hydrocarbons (PAHs). Its discovery reinforces the identification of the “unidentified infrared emission features” as emission from PAHs. The wavelength of this new feature suggests that interstellar PAHs are not as partially hydrogenated as hitherto thought. It also constrains their molecular structure.

Subject headings: infrared: spectra — interstellar: grains — interstellar: molecules — molecular processes

I. INTRODUCTION

Emission by aromatic hydrocarbons has successfully provided an explanation for the hitherto unidentified IR emission features at 3.3, 6.2, 7.7, 8.7, and 11.3 μm (Duley and Williams 1981; Leger and Puget 1984; Allamandola, Tielens, and Barker 1985*a*, hereafter ATBa). These emission features dominate the spectrum of many planetary nebulae, H II regions, reflection nebulae, and some external galaxies (Russell, Soifer, and Merrill 1977; Russell, Soifer, and Willner 1977; Sellgren, Werner, and Dinerstein 1983; Aitken and Roche 1982, 1984; Bregman *et al.* 1983; Cohen *et al.* 1986). The spectrum of a collection of polycyclic aromatic hydrocarbons (hereafter PAHs) shows good agreement with the observed interstellar spectra (ATBa) with one crucial exception, namely the 11–15 μm region. Laboratory spectra of PAHs generally show several features between 11 and 15 μm , in contrast to the single 11.3 μm one shown by ground-based (8–13 μm) interstellar spectra. Because this band is characteristic for the CH out-of-plane bending mode of H atoms isolated on aromatic rings (Bellamy 1960), this has been taken to imply that the emitting interstellar aromatic hydrocarbons are only partially hydrogenated (Duley and Williams 1981), despite the great abundance of H. In this *Letter* the presence of interstellar emission features longward of 11 μm , expected from more hydrogenated aromatic rings, is reinvestigated, using the spectra obtained by *IRAS*.

II. THE LRS SPECTRA

The *IRAS* low-resolution spectrometer (LRS) produces short-wavelength (8–13.5 μm) and long-wavelength (11–22.5 μm) 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 ex-

amined all the spectra characterized as having the 11.3 μm band in emission and selected a sample of 20 which show evidence for an emission feature between 11.3 and 15 μm . Objects with strong ionic emission lines have been disregarded because of possible confusion (i.e., the Ne II 12.8 μm 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 1 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 13.72 μm . 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 (11–13.5 μm). 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 15 μm in the long-wavelength spectra of some sources (e.g., P18) is due to the new emission feature at this low resolution.

Besides the 11.3 μm feature all of the selected spectra show good evidence for the presence of the well-known 7.7 and 8.7 μm emission features. The new feature has the appearance of an emission plateau, ending abruptly at about 13.0 μm . This plateau feature is a common characteristic of many of the sources showing the 11.3 μm 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 11.3 μm , and again beyond the plateau until 15.3 μm . Note that the spike in the emission plateau in this source is not due to Ne II emission since its peak wavelength is 13.1 μm . Although all spectra in our sample show the same pattern of emission between 11 and 15

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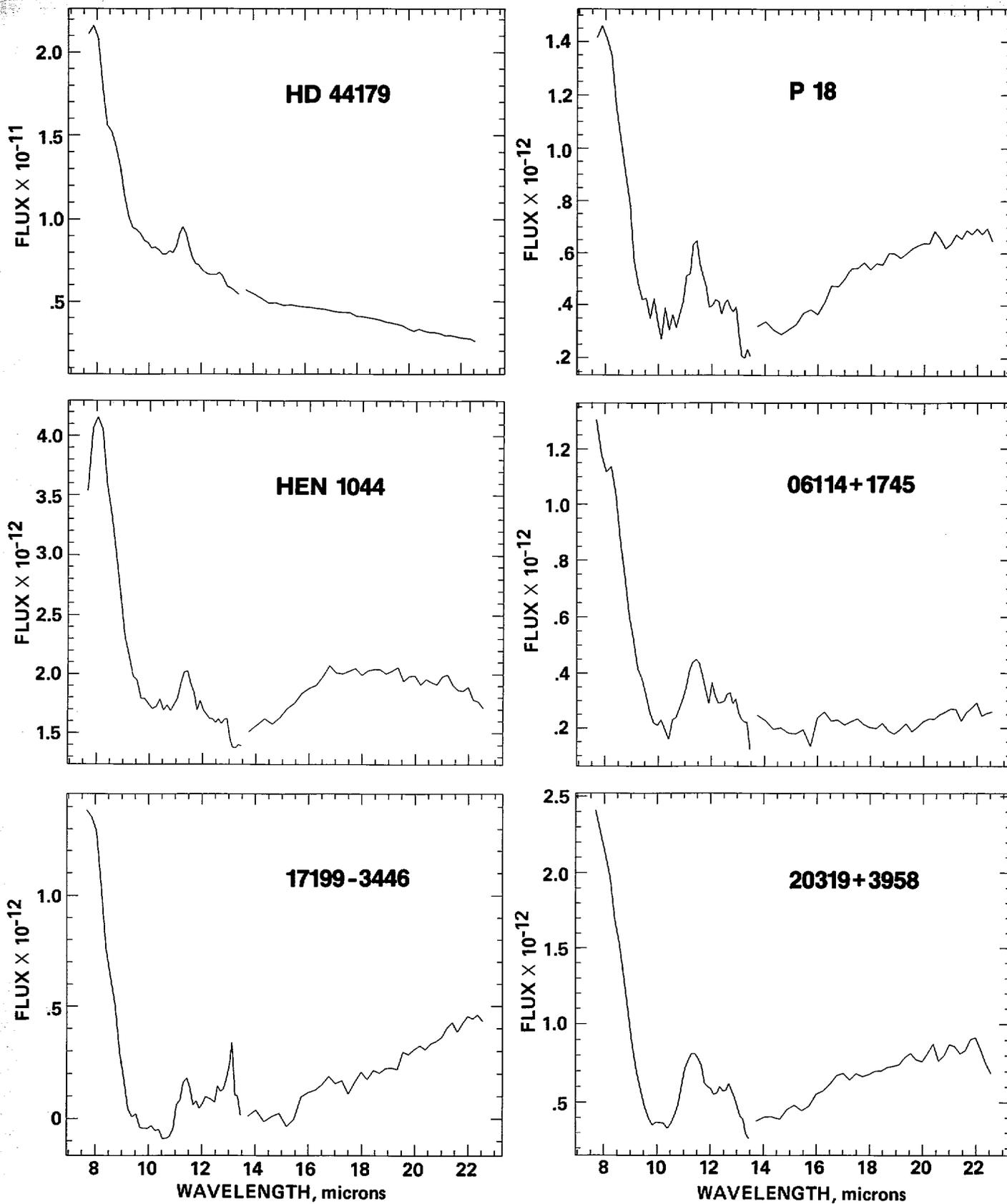


FIG. 1.—The LRS spectra of six representative *IRAS* sources are shown. The short-wavelength data span the full useful range from 7.67 to 13.45 μm . The long-wavelength data are shown from 13.72 to 22.55 μm (see text). The 7.7 μm feature dominates these spectra. Note also the inflection at 8.7 μm which is sometimes visible. The previously known 11.3 μm band shows a long-wavelength plateau extending to about 13.0 μm . Ordinates are flux in $\text{W m}^{-2} \mu\text{m}^{-1}$.

μm , there exist real spectral variations from source to source (e.g., while evident, the new feature is weak in HD 44179).

III. INTERPRETATION

In line with the interpretation of the other emission features in these spectra (e.g., 7.7, 8.7, and 11.3 μm), we attribute the newly discovered emission plateau between 11.3 and 13.0 μm to emission by interstellar PAHs. The ground-based and airborne 3–13 μm spectra of several of the objects shown in Figure 1 are dominated by emission features at 3.3, 6.2, 7.7, 8.7, and 11.3 μm . Although the new *IRAS* sources in our sample have not yet been studied shortward of 7.7 μm , the steep rise toward 7.7 μm , and the presence of the 11.3 μm feature strongly suggest the presence of these emission bands in their spectra also.

We have considered several other possibilities for the origin of the new emission plateau: (1) the presence of a deep silicate absorption feature at 10 μm ; (2) thermal emission by silicon carbide grains; (3) line emission by Ne II at 12.8 μm ; and (4) an instrumental effect in the *IRAS* spectrometer. In Figure 2 the structure in the spectrum of P18 is compared to the spectra of GL 490, a source with a deep silicate absorption feature, and to those of GL 2699, an extreme carbon star with a pronounced SiC emission feature. In neither case do the observed spectral features resemble those of P18. An origin of the spectral structure in the 8–13 μm region in silicate absorption had already been ruled out from ground-based observations (Aitken 1981). Ground-based observations have also shown that the shape of the SiC feature is distinctly different from that of the 11.3 μm emission feature (Aitken *et al.* 1979; Cohen 1984) and from the plateau emission. Although a small contribution by SiC is difficult to rule out, we note that SiC, except in circumstellar shells, has never been detected in emission or absorption in the general interstellar medium. We

reject, therefore, SiC emission as the origin of the plateau in reflection nebulae (e.g., P18) and therefore by inference in all of our objects. Ne II emission at 12.8 μm is not expected to be present in reflection nebulae, such as P18. Moreover, the wavelength of the emission plateau that we have identified does not coincide with that of Ne II, nor does the plateau have the structure expected from the overlap of the 11.3 μm band with the Ne II line. Indeed, in a nebula such as BD +30°3639 which does show both, the 12.8 μm Ne II emission line is superposed on this plateau (Russell, Soifer, and Merrill 1977). In retrospect, the plateau emission feature is even apparent in the first 8–13 μm spectrum of NGC 7027 (Gillett, Forrest, and Merrill 1973). Finally, remapping of the prominent 7.7 μm feature could conceivably produce a spectral “alias” near 13 μm . However, both the short- and long-wavelength LRS detectors show similar structure in the 10–15 μm region. If the new emission plateau is due to spectral remapping of some spatial structure (because of its strength, presumably in the 7.7 μm feature), then the long-wavelength detector should not show it, because it is not sensitive to radiation shortward of 11 μm . Moreover, it would be rather diabolical if the spatial structure of all 20 regions is such that it produces a similar spectral feature between 11.3 and 13.0 μm . In summary, we believe that the new feature between 11.3 and 13.0 μm is real and is part of the spectrum of emission features between 3 and 15 μm .

IV. DISCUSSION

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

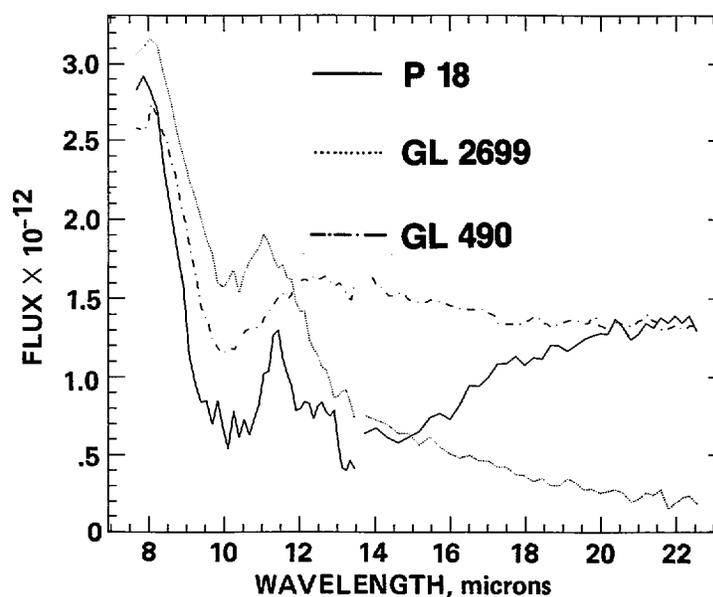


FIG. 2.—The emission spectrum of P18, multiplied by 2 for comparison purposes, is compared with the SiC emission in the extreme carbon star GL 2699 and the deep silicate absorption structure in GL 490. Axes as in Fig. 1.

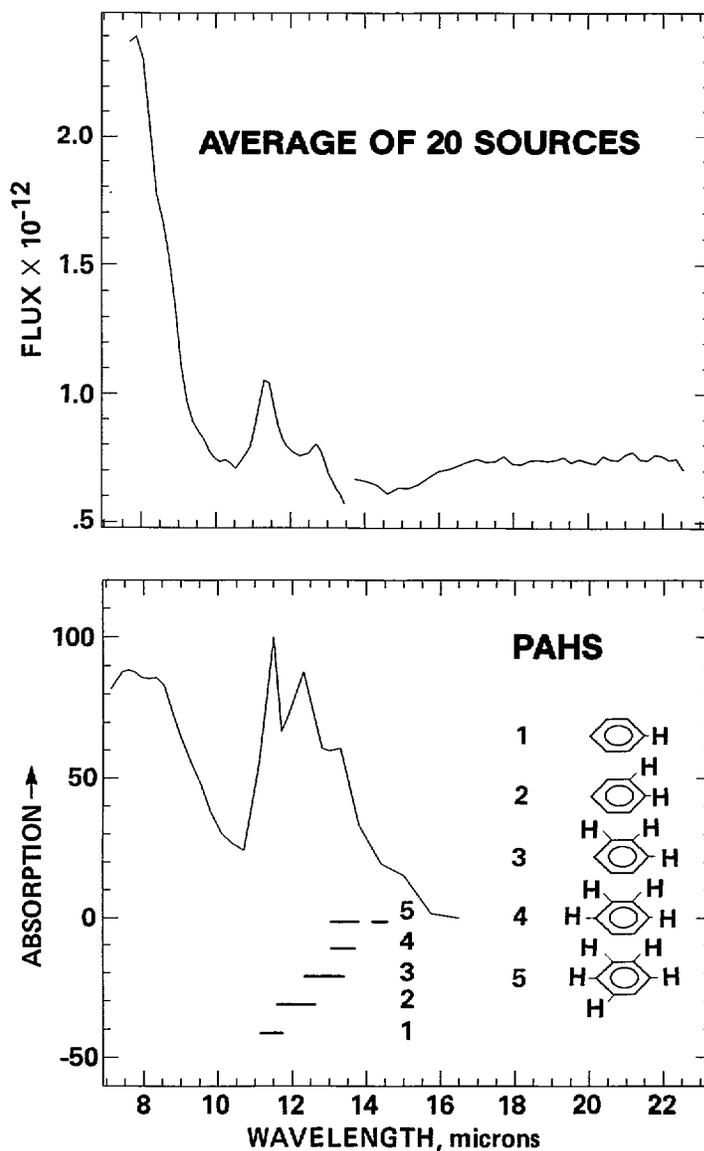


FIG. 3.—(top) The average spectrum of the sources in our samples (see text). Axes as for Fig. 1. (bottom) Absorption spectrum of a collection of PAHs produced by pyrolysis of cellulose (Mortera and Low 1983). Ordinate represents increasing absorption.

the IR absorption spectrum of a collection of PAHs (Mortera and Low 1983). This mixture of aromatic species has been produced by the vacuum pyrolysis of cellulose (e.g., filter paper) at 600°C. The IR spectra obtained between 400°C and 600°C show the spectroscopic characteristics of a mixture of aromatic species, e.g., the CH stretch at 3.3 μm , the CC stretch at 6.2 μm , a broad band due to CC stretches around 7.7 μm , and the CH deformation modes between 11 and 15 μm . It should be emphasized, however, that the exact production process of the PAH mixture is of little importance. Vacuum pyrolysis, combustion, carbon arcs, or burning will generally produce soot, which is a collection of PAHs (Mortera and Low 1983; Tuinstra and Koenig 1973; Koike, Hasegawa, and Manabe 1980; Borghesi *et al.* 1983; Sakata *et al.* 1984). In essence this is because PAHs are the thermodynamically

most favored hydrocarbons under these conditions, and these are the building blocks for the soot particles. Although different processes may lead to somewhat different mixtures of PAHs, all have similar infrared characteristics.

Direct comparison of the observed interstellar emission spectra with laboratory absorption spectra is a valid procedure in this case. The IR fluorescing modes between 11 and 15 μm are close in energy and, therefore, are insensitive to the total internal excitation energy of the molecules (e.g., the absorbed UV photon energy, ATBa). The overall agreement between the laboratory spectrum and the observed interstellar spectra is quite good, again supporting the identification of the interstellar UIR bands with emission by a collection of PAHs. The bands between 11 and 15 μm (CH bending modes) in the laboratory spectra are more intense relative to that at 7.7 μm

(CC stretching modes) than in the *IRAS* spectra. Possibly, this discrepancy implies that the interstellar PAHs are slightly larger or are less hydrogenated than the laboratory samples. Some caution should, however, be exercised because of possible saturation effects in strong bands with this experimental technique.

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 11.92 μm ; 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 13.6 μm (Sadtler spectrum 15223). Thus, this 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 11.3 μm feature; hence, the suggestion that interstellar aromatic hydrocarbons are only partially hydrogenated (Duley and Williams 1981). The discovery of a plateau of emission longward of 11.3 μm forces a reconsideration of partial hydrogenation. 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. The predominance of such condensed PAHs is also expected from thermodynamic considerations (Crawford, Tielens, and Allamandola 1985). Some caution should, however, be exercised with this conclusion because PAHs with less than 25 carbon atoms can lose H atoms when exposed to a strong UV field (Allamandola, Tielens, and Barker 1985b). Such small (partially hydrogenated) PAHs might perhaps also be able to explain the observed dominance of the 11.3 μm band in the spectra.

Spectral variations between the different sources are of considerable interest. HD 44179 (the Red Rectangle) has a much simpler spectrum than other sources. In particular, the broad feature underneath the 3.4 μm band, the plateau underneath the 6.2 μm band, and the broad emission bump underneath the 7.7 μm feature, which form such a striking aspect of the spectra of other sources (e.g., NGC 7027 and the Orion bar), are notably absent in the spectrum of this source (Geballe *et al.* 1985; Cohen *et al.* 1986). In keeping with this trend, the plateau emission between 11.3 and 13.0 μm is also less pronounced in HD 44179. These spectral variations have been interpreted in terms of compositional variations in the collection of PAHs responsible for the IR emission (Cohen *et al.* 1986). Presumably, smaller PAHs can survive better in the more benign environment of the Red Rectangle than in NGC 7027 or the Orion bar. Because the smallest PAHs present in a region will dominate the emission spectrum, the spectrum of HD 44179 appears simpler than the others (Cohen *et al.* 1986). The weakness of the plateau emission in the Red Rectangle supports this model, if the emitting PAHs in this source contain less than about 25 carbon atoms. These PAHs may then have lost some H atoms, increasing the strength of the 11.3 μm feature relative to the 12–13 μm emitting modes. In contrast, NGC 7027, with the strongest emission plateaux yet detected underneath the 6.2 and 7.7 μm features, also shows the strongest emission plateau between 11.3 and 13.0 μm suggesting that relatively large PAHs also contribute to the spectrum.

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