

THE SPACING OF THE INTERSTELLAR 6.2 AND 7.7 MICRON EMISSION FEATURES AS AN INDICATOR OF POLYCYCLIC AROMATIC HYDROCARBON SIZE

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ABSTRACT

A database of astrophysically relevant, infrared spectral measurements on a wide variety of neutral as well as positively and negatively charged polycyclic aromatic hydrocarbons (PAHs), ranging in size from $C_{10}H_8$ through $C_{48}H_{20}$, is now available to extend the interstellar PAH model. Beyond simply indicating general characteristics of the carriers, this collection of data now makes it possible to conduct a more thorough interpretation of the details of the interstellar spectra and thereby derive deeper insights into the nature of the emitting material and conditions in the emission zones. This Letter is the first such implementation of this spectral database. The infrared spectra of PAH cations, the main PAH form in the most energetic emission zones, are usually dominated by a few strong features in the $1650\text{--}1100\text{ cm}^{-1}$ ($6.1\text{--}9.1\text{ }\mu\text{m}$) region that tend to cluster in the vicinity of the interstellar emission bands at 1610 and 1320 cm^{-1} (6.2 and $7.6\text{ }\mu\text{m}$), but with spacings typically somewhat less than that observed in the canonical interstellar spectrum. However, the spectra in the database show that this spacing increases steadily with molecular size. Extrapolation of this trend indicates that PAHs in the 50–80 carbon atom size range are entirely consistent with the observed interstellar spacing. Furthermore, the profile of the 1610 cm^{-1} ($6.2\text{ }\mu\text{m}$) interstellar band indicates that PAHs containing as few as 20 carbon atoms contribute to this feature.

Subject headings: infrared: ISM: lines and bands — ISM: molecules — molecular data

1. INTRODUCTION

The size distribution of the polycyclic aromatic hydrocarbons (PAHs) that contribute to the interstellar mid-infrared emission features is of considerable importance and has been the subject of some debate for more than a decade. This information is crucial since the smallest members of the PAH population dominate the interstellar emission and knowledge of the size range places strong constraints on molecular structures possible. Coupled with studies of relative PAH stabilities and reactivities (see, e.g., Allain, Leach, & Sedlmayr 1996; LePage et al. 1998; Ekern et al. 1998), this size information will give important insight into the precise PAH population in specific regions and will provide an additional probe of the prevailing conditions in those environments. Previous attempts to constrain the size distribution of interstellar PAHs have fallen into three categories. The first attempts were based on purely theoretical analyses, and they concluded that species as small as 20–50 carbon atoms could survive and that these species were representative of the PAHs in the typical mid-infrared emission zones (Leger & Puget 1984; Allamandola, Tielens, & Barker 1985; Omont 1986). Subsequent theoretical analyses were expanded to incorporate observational and experimental data. These studies significantly broadened our perception of the size distribution of interstellar PAHs and indicated that species with as few as 20 C atoms dominate the emission at the shortest wavelengths while those with as many as 200 C atoms dominate the emission at the longest wavelengths (Allamandola, Tielens, & Barker 1989; Jourdain de Muizon, d’Hendecourt, & Geballe 1990; Schutte, Tielens, & Allamandola 1993). Finally, purely experimental measurements have indicated that PAHs with $\leq 30\text{--}40$ C atoms are stable under the conditions in H II regions (Jochims et al. 1994; Jochims, Baumgärtel, & Leach 1999).

Thus, while this body of work as a whole points to a lower limit to the interstellar PAH population between 20 and 50 carbon atoms, the nature of the size distribution is still quite ambiguous, and the typical size of the PAHs contributing most

of the mid-IR emission to any one feature may lie anywhere between roughly 30 and 150 carbon atoms. Adding great uncertainty to *all* of the theoretically based conclusions is the fact that all of the PAH size calculations referred to above were based on the spectral characteristics of *neutral* PAHs, whereas the PAHs dominating the emission in the most energetic sources are *ionized*, possessing intrinsic band intensities that differ significantly from those of neutral PAHs. Fortunately, the early to mid-1990s have brought a renaissance in laboratory studies of PAHs specifically designed to address astrophysical questions such as this. Groundbreaking experimental work at a number of institutions has led to the development of special laboratory techniques for determining the intrinsic infrared properties of PAH molecules and PAH ions under astrophysically relevant conditions (Szczepanski et al. 1995; Hudgins & Sandford 1998; Cook & Saykally 1998; and references therein). Similarly important breakthroughs have been made in the application of high-level ab initio methods for determining the intrinsic infrared properties of isolated PAH molecules and PAH ions (Langhoff 1996; Bauschlicher & Langhoff 1997 and references therein).

This Letter focuses on the infrared spectral database generated in the Astrochemistry Laboratory at NASA Ames over the past 7 years (Allamandola, Hudgins, & Sandford 1999 and references therein). This work has employed the matrix isolation technique to measure the infrared spectral properties of 23 neutral, 19 cationic, and three anionic PAHs. The availability of such a systematic compilation now makes possible a more rigorous evaluation of the PAH model and provides the basis for a more detailed analysis of the information contained in the astronomical emission spectra. It is the purpose of this Letter to report a direct, empirical analysis that utilizes band *position* measurements to constrain the size distribution of the PAHs that dominate the emission in the $1650\text{--}1100\text{ cm}^{-1}$ ($6\text{--}9\text{ }\mu\text{m}$) region. This analysis is based on the observed spacing between the interstellar 1610 cm^{-1} ($6.2\text{ }\mu\text{m}$) band and the 1320

cm^{-1} ($7.6 \mu\text{m}$) component of the classical “ $7.7 \mu\text{m}$ ” band (Bregman 1989).

2. RESULTS AND DISCUSSION

The remarkable effect of ionization on the vibrational spectrum of PAH molecules has now been well established both experimentally and theoretically (see, e.g., Szczepanski & Vala 1993; Hudgins, Sandford, & Allamandola 1994; Langhoff 1996). Briefly summarizing, the spectra of *neutral* PAH molecules are dominated by strong aromatic CH stretching and CH out-of-plane wagging features, which fall in the $3150\text{--}2950 \text{ cm}^{-1}$ ($3.2\text{--}3.4 \mu\text{m}$) and $900\text{--}625 \text{ cm}^{-1}$ ($11\text{--}16 \mu\text{m}$) ranges, respectively. The CC stretching and CH in-plane wagging bands, which are found between 1650 and 1100 cm^{-1} ($6\text{--}9 \mu\text{m}$), are much weaker. Upon ionization, however, there is a strong *enhancement* (~ 10 times) of these weak CC stretching and CH in-plane bending features, accompanied by an equally strong *suppression* of the CH stretching features as well as a more modest suppression ($\sim \frac{1}{2}\text{--}\frac{1}{5}$) of the CH out-of-plane bending features. The result is a mid-infrared spectrum whose features are in dramatically better agreement in both *position* and *intensity* with those of the interstellar emission spectrum than that observed previously for the neutral molecules. As a result, comparison of composite spectra produced by mixtures of the small to moderately sized PAH cations ($10\text{--}48$ carbon atoms) are an enormous step forward from the original rough comparisons involving neutral PAHs suspended in salt pellets and solution upon which the PAH hypothesis was founded. Nevertheless, some shortcomings persist, albeit at a much more detailed level than encountered previously. For example, let us consider the comparison between the infrared emission spectrum of the Orion Bar and the absorption spectrum of a PAH cation mixture drawn from the spectral database shown in Figure 1. While the agreement between these two spectra represents an enormous improvement over previous comparisons involving only neutral species or more limited ensembles of ionized PAHs, careful inspection of the positions of the “ 1610 cm^{-1} ” (“ $6.2 \mu\text{m}$ ”) and “ 1320 cm^{-1} ” (“ $7.6 \mu\text{m}$ ”) features reveals that the bands are somewhat “pinched” in the model spectrum relative to the astronomical spectrum. That is, the spacing between the features in the model spectrum (250 cm^{-1}) is somewhat less than that observed in the typical astronomical spectrum ($\approx 300 \text{ cm}^{-1}$). Nevertheless, thanks to the availability of a database large enough to establish trends securely in the spectroscopic properties of PAHs, it is possible to infer much about the nature of the interstellar PAH population from discrepancies such as this.

While a particular PAH cation may, in principle, exhibit features anywhere throughout the $1650\text{--}1100 \text{ cm}^{-1}$ region, it is generally observed that two or three features dominate this region (Hudgins & Allamandola 1995a, 1995b, 1997; Langhoff 1996). Furthermore, these dominant features often fall in the vicinity of the strong interstellar 1610 and 1320 cm^{-1} (6.2 and $7.6 \mu\text{m}$) emission features. As a result, as illustrated in Figure 1, when the spectra of a number of PAH cations are co-added, two dominant features tend to emerge with an appearance very similar to those of the interstellar spectrum. To understand the origin of the aforementioned “pinching,” it is useful to take a step backward and consider the spectra of the individual PAH cations from which these mixtures are derived. To avoid confusion, the following discussion will focus on the subset of molecules in our database for which the assignment of nominal 1610 cm^{-1} and 1320 cm^{-1} features is clear and unambiguous.

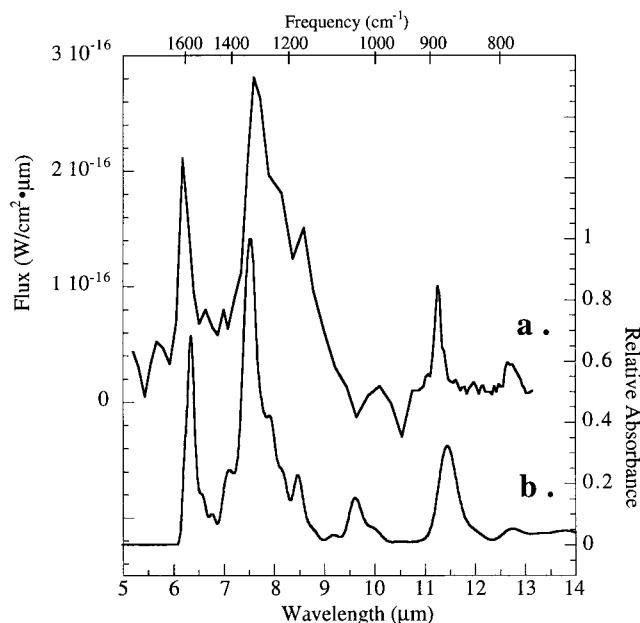


FIG. 1.—Comparison of (a) the infrared emission spectrum of the Orion bar with (b) a composite absorption spectrum generated by co-adding the individual spectra of 11 PAH cations. The individual spectra were calculated using experimentally measured frequencies and intensities and assigning a 30 cm^{-1} FWHM Gaussian band profile, consistent with that expected from the interstellar emitters (Allamandola et al. 1989). The PAH cation mixture consists of 20% benzo[k]fluoranthene⁺ ($\text{C}_{20}\text{H}_{12}^+$) and dicoronylene⁺ ($\text{C}_{48}\text{H}_{20}^+$); 10% coronene⁺ ($\text{C}_{24}\text{H}_{12}^+$), benzo[b]fluoranthene⁺ ($\text{C}_{20}\text{H}_{12}^+$), 9, 10-dihydrobenzo(e)pyrene⁺ ($\text{C}_{20}\text{H}_{14}^+$), and phenanthrene⁺ ($\text{C}_{14}\text{H}_{10}^+$); 5% benzo[ghi]perylene⁺ ($\text{C}_{22}\text{H}_{12}^+$), tetracene⁺, and benz[a]anthracene⁺ (both $\text{C}_{18}\text{H}_{12}^+$); and 2% chrysene⁺ ($\text{C}_{18}\text{H}_{12}^+$) and fluoranthene ($\text{C}_{16}\text{H}_{10}$). The Orion spectrum is reproduced from Bregman et al. (1989).

Those molecules are listed in Table 1, together with their sizes, the actual frequencies of their strongest features in this region, and the spacing between those features. Inspection of the data in Table 1 shows that in the majority of cases, the positions of the lower frequency features agree with the canonical 1320 cm^{-1} astronomical position to within 30 cm^{-1} , the natural line width of the individual molecular features. The higher frequency features, on the other hand, typically fall as much as $40\text{--}80 \text{ cm}^{-1}$ lower in frequency than the 1610 cm^{-1} astronomical feature. As a result, as illustrated in Figure 1, when the spectra in the current database are combined, although two dominant features emerge in this region, they exhibit a spacing that is necessarily somewhat smaller than that displayed in the typical astronomical spectrum. Further inspection of the data in Table 1 reveals that the positional discrepancies in the higher frequency bands are not random but are in fact size dependent, with the bands of the largest molecules falling closest to the observed spacing. This trend is illustrated in Figure 2 and quantified in Figure 3. Figure 2 shows a stick diagram of this region of the spectrum for three representative PAH cations from the table (pyrene, $\text{C}_{16}\text{H}_{10}^+$; ovalene, $\text{C}_{32}\text{H}_{14}^+$; and dicoronylene, $\text{C}_{48}\text{H}_{20}^+$). In this representation, the location of each stick reflects the position of an absorption band, while the length of the stick reflects the relative intensity of that band. The approximate full widths at half height (FWHMs) of the canonical interstellar features are indicated by the shaded regions in the diagram. This figure demonstrates the steady increase in the spacing between the most prominent PAH cation bands as molecular size increases. Indeed, for the largest cation in the database (dicoronylene, $\text{C}_{48}\text{H}_{20}^+$), both bands fall squarely within

TABLE 1
EXPERIMENTALLY MEASURED POSITIONS OF THE NOMINAL 1610 AND 1320 cm^{-1} FEATURES FOR SEVERAL EXAMPLES OF PAH CATIONS

PAH	Number of C Atoms	Nominal 1610 cm^{-1} Band Frequency (cm^{-1})	Nominal 1320 cm^{-1} Band Frequency (cm^{-1})	Spacing (cm^{-1})
Naphthalene	10	1524	1218	306
Phenanthrene	14	1566	1275	291
Pyrene	16	1551	1356	195
1, 2-Benzanthracene	18	1539	1332	207
Chrysene	18	1563	1323	240
Benzo(e)pyrene	20	1557	1344	213
Benzo[ghi]perylene	22	1578	1329	249
Coronene	24	1579	1378	201
Ovalene	32	1574	1332	242
Hexabenzocoronene-A	42	1570	1212	358
Dicoronylene	48	1608	1342	266

the envelopes of the interstellar features. This confirms the behavior noted by Langhoff (1996) from theoretical work on a more limited range of PAH sizes (C_{10}H_8 up to $\text{C}_{32}\text{H}_{14}$). This trend indicates that the spacing of the interstellar 6.2 and "7.7" μm features is an independent indicator of the molecular size of the dominant emitting species. Indeed, using the data set presented in Table 1, this relationship is quantified in Figure 3.

Figure 3 shows a plot of the dominant feature positions (*open circles and squares*) as well as their separation (*filled diamonds*), as a function of molecular size. Again, the approximate FWHHs of the interstellar features are indicated by shaded bars near the left-hand axis, while the canonical interstellar spacing is indicated by a shaded bar near the right-hand axis. Linear

fits to these data confirm, as deduced previously from Table 1, that the positions of the nominal 1320 cm^{-1} features tend to fall within the envelope of the interstellar feature and are essentially independent of molecular size. The frequencies of the nominal 1610 cm^{-1} bands, on the other hand, increase steadily with size, approaching that of the interstellar band near the largest end of the molecules in the spectral database. The data points reflecting the frequency difference between these features (*filled diamonds*) also necessarily reflect this trend, and the linear fit to those points can be extrapolated to the region where it intersects the canonical interstellar spacing. Doing so indicates that both the peak position of the 1610 cm^{-1} interstellar band and the overall interstellar feature spacing point to PAHs comprised of 50–80 carbon atoms as the dominant emitters at these frequencies. While this is consistent with the range of the earlier analyses, these results significantly tighten the constraints on the size of the PAH population that dominates the emission.

In addition to providing insight into the size of the dominant emitters, the spectral database can also be used to infer information concerning PAH size distribution. The 1610 cm^{-1} band often exhibits a red wing (Cohen et al. 1989; Roelfsma et al. 1996; Beintema et al. 1996) and is superposed on a weaker

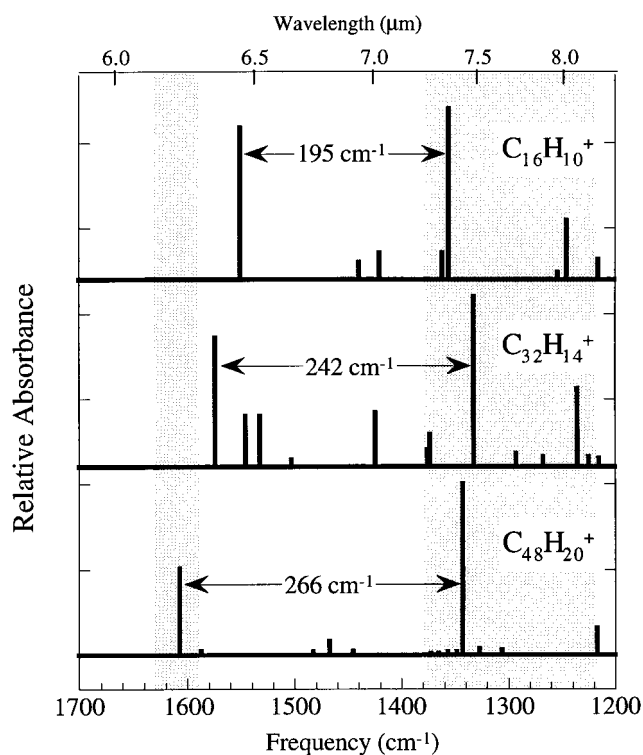


FIG. 2.—A schematic comparison of the absorption spectra of the cations of the PAHs pyrene ($\text{C}_{16}\text{H}_{10}^+$), ovalene ($\text{C}_{32}\text{H}_{14}^+$), and dicoronylene ($\text{C}_{48}\text{H}_{20}^+$) illustrating the evolution of the spacing of the dominant features in the 1700–1200 cm^{-1} region as a function of molecular size. The data for the ovalene cation are taken from Langhoff (1996).

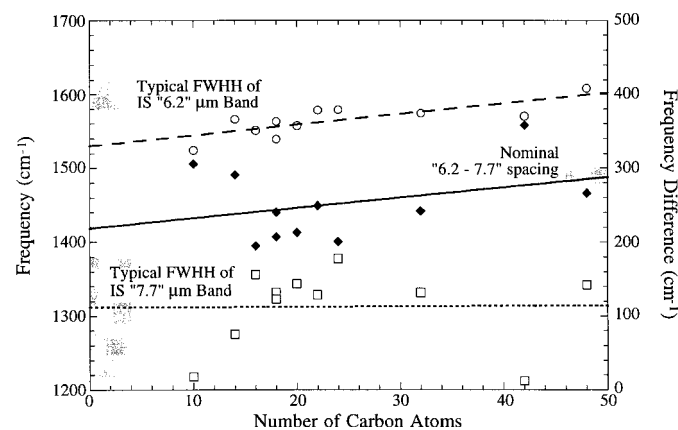


FIG. 3.—A plot of the positions of the dominant PAH features in the 1700–1200 cm^{-1} region (*open symbols, left-hand axis*) and the spacing of those features (*filled symbols, right-hand axis*) as a function of molecular size. The typical FWHHs of the canonical 1610 cm^{-1} (6.2 μm) and 1310 cm^{-1} (7.7 μm) interstellar features are indicated by shaded regions along the left-hand axis, while the canonical interstellar spacing is indicated by the shaded region along the right-hand axis. The lines represent the best linear fits to the various data sets.

pedestal (Cohen et al. 1986, 1989). A natural explanation for this within the framework of the PAH model is that the profile is determined by the superposition of the individual molecular bands that fall in this region. Thus, given the spectral trend discussed above, the low-frequency limit of the interstellar band, typically around 1515 cm^{-1} ($6.6\text{ }\mu\text{m}$), should be indicative of the smallest molecules contributing to this feature. The situation with the high-frequency limit is less clear, since the database is incomplete and the steady rise in the nominal 1610 cm^{-1} band position does not cover the observed cutoff. However, based on vibrational spectroscopic principles, this increase should not continue ad infinitum but, rather, should at some point roll off, and the band position should remain more or less constant with further increases in molecular size.

To understand the behavior of these features, it is necessary to consider the nature of PAH vibrational modes in the $1400\text{--}1200\text{ cm}^{-1}$ ($7.1\text{--}8.3\text{ }\mu\text{m}$) and 1600 cm^{-1} ($6.2\text{ }\mu\text{m}$) regions and their relationship to molecular structure. PAH spectral features that fall in the $1400\text{--}1200\text{ cm}^{-1}$ ($7.1\text{--}8.3\text{ }\mu\text{m}$) region arise from vibrations involving coupled CC stretching and CH in-plane bending motions within the molecule. As a result, these features are sensitive both to the peripheral geometry (i.e., the "edge" structure) of the molecule, which defines the force fields that govern CH bond motion, as well as to the extent of its carbon skeleton, which defines the force fields experienced by the CC bonds. Thus, significant variations in the positions of features in this region are expected, even between PAH isomers, simply on the basis of differences in their edge structures. Vibrational modes in the 1600 cm^{-1} region, on the other hand, arise from pure CC stretching motions within the carbon skeleton of the PAH. The data in Table 1 confirm that these features are indeed sensitive to the size of the carbon skeleton but are relatively insensitive to edge structure. That notwithstanding, the further removed a particular portion of the carbon skeleton is from the edge of the molecule where growth occurs, the smaller the effect on the internal force field that determines its vibrational frequencies. Thus, as molecule size increases, an ever increasing *fraction* of the total carbon skeleton of the molecule will be unperturbed by a particular modification to the carbon skeleton. As the relative impact of increasing molecular size diminishes, so too will the spectral alterations, which are caused by that increase, diminish. For small PAHs, the addition of even a single ring constitutes a significant modification to the carbon skeleton and strongly influences the pure CC stretching vibrational frequencies. On the other hand, in the macroscopic limit, the properties of very large PAH molecules must approach those of (effectively infinite) graphitic sheets, whose spectral properties are not at all altered by further microscopic alterations in size.

Consequently, based on the data presented in Table 1, we

conclude that species as small as naphthalene (C_{10}H_8) contribute very little to the envelope of the interstellar 1610 cm^{-1} feature. On the other hand, species containing 20 carbon atoms *are* important since they would emit near 1560 cm^{-1} ($6.4\text{ }\mu\text{m}$), a position in the interstellar spectra that in many cases exhibits roughly half the intensity of the peak (see, e.g., Roelfsma et al. 1996). It is worth noting that another possible contributor to the red wing on the $6.2\text{ }\mu\text{m}$ feature is anharmonic hot-band emission (Barker, Allamandola, & Tielens 1987; Cohen et al. 1989). However, the most recent analyses of hot-band emission suggest that while this is a natural consequence of the PAH model, it appears that it is not a major player in determining band profiles and producing satellite features in other portions of the spectrum (Schutte et al. 1993; Joblin et al. 1996; Sloan et al. 1997).

3. CONCLUSIONS

The studies of PAH cations discussed here show that the infrared spectra of these species are characteristically dominated by a few strong features in the $1650\text{--}1100\text{ cm}^{-1}$ ($6.1\text{--}9.1\text{ }\mu\text{m}$) region that tend to cluster in the general vicinity of the interstellar infrared emission bands at 1610 cm^{-1} ($6.2\text{ }\mu\text{m}$) and 1320 cm^{-1} ($7.6\text{ }\mu\text{m}$). While the positions of the nominal 1320 cm^{-1} features in the PAH cation spectra are in good agreement with the position of the interstellar emission band, their corresponding nominal 1610 cm^{-1} features are actually observed to fall some $40\text{--}80\text{ cm}^{-1}$ below the position of the interstellar feature, resulting in a modest but significant pinching of the two features in model spectra. However, the frequencies of the nominal 1610 cm^{-1} PAH cation features are found to increase steadily with molecular size. Extrapolation of this trend indicates that PAHs in the $50\text{--}80$ carbon atom size range are consistent with the spacing of the interstellar features and dominate the emission in these bands. Furthermore, the profile of the typical 1610 cm^{-1} interstellar emission band traces the PAH size distribution and can be used to extract information concerning that distribution. Specifically, the data indicate that PAHs as small as 20 carbon atoms provide measurable contributions to the interstellar emission.

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