The infrared spectra of very large, compact, highly symmetric, polycyclic aromatic hydrocarbons (PAHs)

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ABSTRACT

The mid-infrared spectra of seven very large PAHs (VLPAHs), with C number ranging from 54 to 130, have been determined computationally using Density Functional Theory (DFT). Trends in the dominant band positions and intensities for the major PAH bands in the 5 to 9 μm region as a function of PAH size, charge (neutral, cation, and anion forms) and geometry are discussed.

The 6.2 μm CC stretching band for these compact VLPAHs is similar to those of the smaller PAHs previously studied and hence support earlier conclusions: astronomical PAHs must incorporate nitrogen to reproduce the class A 6.2 μm PAH band. In contrast, the 7-9 μm CC stretching modes and the CH in-plane vibrations of the largest of the PAH cations and anions considered here produce strong bands close to 7.8 μm and 8.5 μm. This suggests that the astronomical 7.7 μm band complex is produced by a mixture of small and large PAH cations and anions, with small PAHs contributing more to the 7.6 μm component and large PAHs more to the 7.8 μm component. Moreover, Peeters et al. (2002) found a correlation between the peak position of the astronomical 7.8 μm component and the peak of the 8.6 μm band. The similarity in behavior of these two bands in the compact VLPAH spectra suggests that large, cationic and anionic PAHs contribute strongly to the 7.8 and 8.6 μm astronomical features, with the specific peak position and profile reflecting the local PAH cation-to-anion concentration ratio and the relative intensities reflecting PAH size.

Subject headings: Astrochemistry - Infrared : ISM - ISM : molecules - ISM : molecular data - ISM : line and bands - Line : identification - techniques : spectroscopy

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are now thought to be the most plentiful and widespread class of organic compounds in the universe. Their infrared (IR) signature is associated with many different galactic and extragalactic objects and generally dominates their mid-IR emission (e.g. Helou et al. 2000; Uchida et al. 2000; Vermeij et al. 2002; Verstraete et al. 2001; Peeters et al. 2004; Onaka 2004; Bregman & Temi 2005; Brandl et al. 2006; Sellgren et al. 2007; Smith et al. 2007). The spectral details of the PAH features vary between different classes of object and spatially within extended objects (e.g. Joblin et al. 2000; Peeters et al. 2002; van Diedenhoven et al. 2004; Bregman & Temi 2005; Sloan et al. 2005; Compiègne et al. 2007), showing that the details in the emission spectrum depend on, and therefore reflect, the specific PAH molecules present and the conditions within the emission zones.

Most previous work on the IR spectroscopic properties of PAHs focused on species containing about 50 or fewer carbon atoms because large PAHs are not readily available for experimental study and computational techniques for such large systems were not practical. While large PAH accessibility remains limited, computational capabilities have increased and the spectra of large PAHs can be determined with good precision. Here we report and discuss the computational IR spectra of several large, compact, and symmetric PAHs, namely $C_{66}H_{20}$, $C_{78}H_{22}$, $C_{110}H_{26}$, $C_{112}H_{26}$ and $C_{130}H_{28}$. When combined with our previous work on the large PAHs $C_{54}H_{18}$ and $C_{96}H_{24}$ (Bauschlicher & Bakes 2000; Bauschlicher 2002), these spectra provide new insight into the effect of PAH size and structure on their IR spectra. The IR spectra of comparably sized, but less compact and less symmetric, PAHs are discussed in a subsequent paper (Bauschlicher et al. in preparation). These two studies, together with the previous work on nitrogen substitution, substantially deepen our understanding of the PAH populations that contribute to the astronomical spectra.

2. Observations and/or Models

The PAHs considered here are shown in Fig. 1, along with the previously studied coronene ($C_{24}H_{12}$), circumcoronene ($C_{54}H_{18}$), and circumcircumcoronene ($C_{96}H_{24}$) molecules. The spectra for the neutral, cation and anion forms for all these PAHs have been computed. For a detailed discussion of these theoretical spectra, see Bauschlicher et al. (2008).
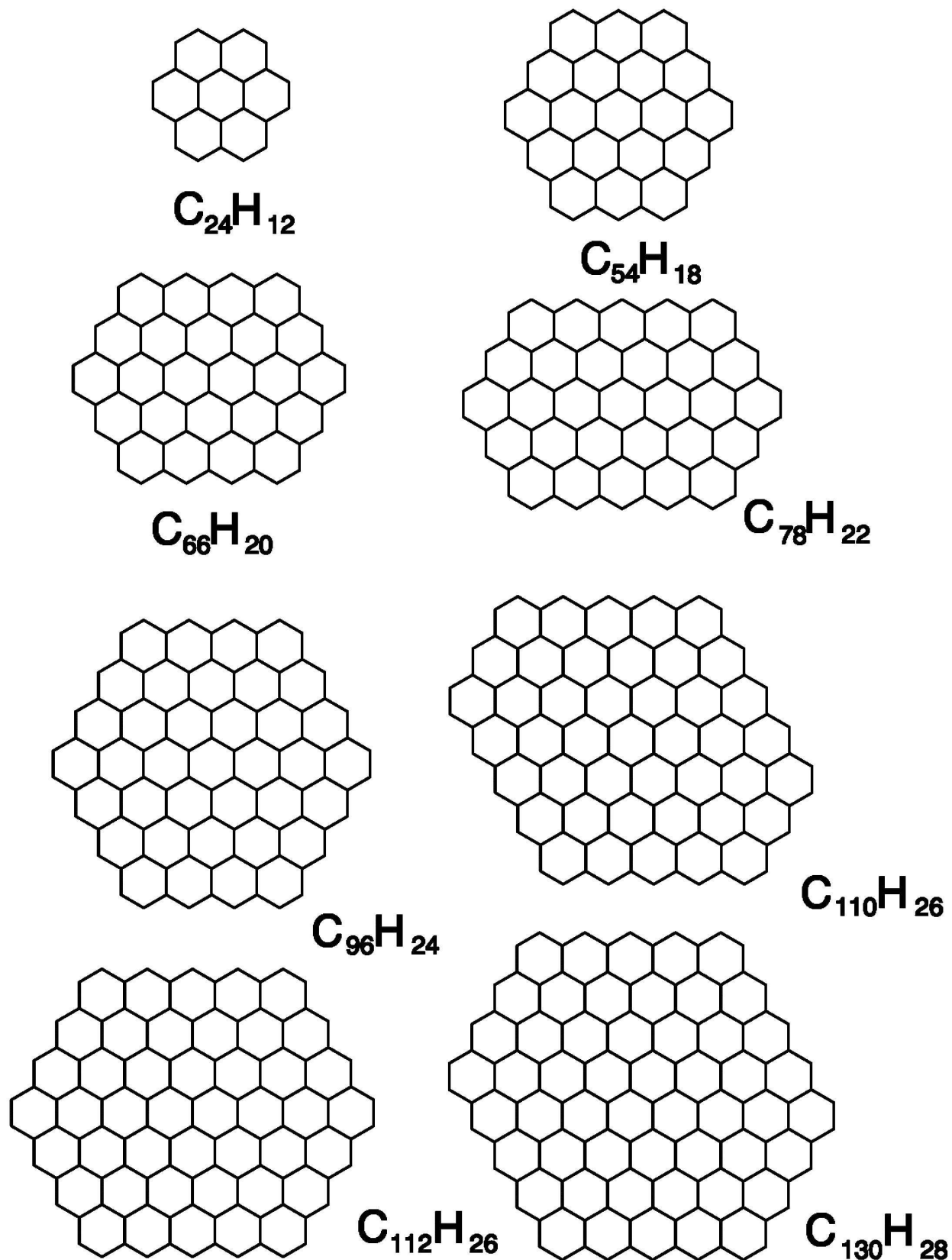
$C_{24}H_{12}$

$C_{54}H_{18}$

$C_{66}H_{20}$

$C_{78}H_{22}$

$C_{96}H_{24}$

$C_{110}H_{26}$

$C_{112}H_{26}$

$C_{130}H_{28}$

Fig. 1.— The structure of the PAHs studied in this paper.

3. Discussion

Consistent with earlier work on smaller PAHs, the intensities of the major features between 5 and 9 μm in these larger PAH cations and anions are enhanced by an order of magnitude or more over those of the neutrals. Therefore, the corresponding spectra of the neutral PAHs will not be considered further.

Fig. 2 compares the emission spectrum from the HII region IRAS 23133+6050 and the Red Rectangle to the average spectrum produced by the large PAHs computed here and an earlier "best fit", average mixture of smaller PAHs (for specifics on the small PAH mixture, see Bauschlicher et al. 2008). The following constraints and conclusions regarding the emitting astronomical PAH population can be drawn from this comparison.

Clearly, the overall agreement between the astronomical emission spectrum and the simple average PAH spectrum lend general support to the PAH model. An excellent fit of the astronomical data with all PAH spectra currently available in the NASA AMES PAH database is given by Cami et al. (these proceedings & in prep.).

The dominant bands in the CC stretching region between 6.1 and 6.4 μm peak slightly redward of 6.3 μm, far to the red of the astronomical 6.2 μm band (i.e. class A, Peeters et al. 2002). Thus, as with small PAHs, the CC stretch in large PAHs comprised of only C and H cannot reproduce the peak position of the astronomical class A 6.2 μm feature, reinforcing our previous suggestion that astronomical PAHs contain nitrogen (PANHs, Peeters et al. 2002; Hudgins et al. 2005).

The largest PAH cations and anions considered have strong bands close to 7.7 μm, the position of the strongest astronomical emission feature. The strong feature produced by the cations and anions overlap to a large extent, but the average anion peak falls about 0.1 μm to the red of the average cation peak. As can be seen in Fig. 2, these data suggest that the astronomical 7.7 μm band is produced by overlapping bands from a mixture of small and large PAH cations and anions, with small PAHs contributing more to the 7.6 μm component and large PAHs more to the 7.8 μm component. This implies that the variation in the peak position of the 7.8 μm feature and hence class B profiles (Peeters et al. 2002) may be related to the variation in relative amounts of large PAH cations and anions since negatively charged large PAHs emit at slightly longer wavelengths than do the PAH cations. This is also consistent with the spatial variation of the 7.8 μm component in the reflection nebula NGC 2023 (Bregman & Temi 2005).

A band near 8.6 μm grows in strength and shifts slightly to the red as PAH size increases for both anions and cations. Note that small PAHs do not show emission at these wavelengths and hence the astronomical 8.6 μm band arises exclusively from large compact PAHs. The
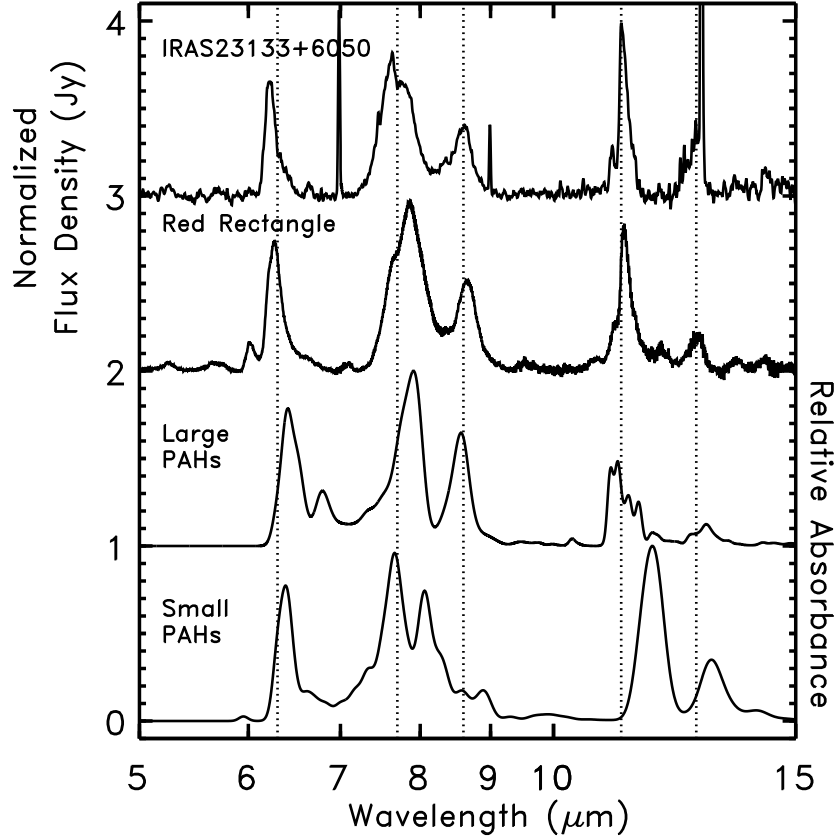
Fig. 2.— Astronomical PAH emission spectra from 5 to 15 μm compared with the spectra of PAH mixtures. Shown are the continuum subtracted ISO-SWS spectrum of IRAS23133+6050 representing class A PAH profiles **(top)**; the continuum subtracted ISO-SWS spectrum of the Red Rectangle, representing class B PAH profiles **(second)**; the average spectrum of the large symmetric PAH cations, neutrals and anions considered here **(third)**; and the composite absorption spectrum generated by co-adding the individual spectra of 11 PAHs, reproduced from Peeters et al. (2002, see text for composition) **(bottom)**. A redshift of 15 cm^{-1}, intrinsic to the emission process, has been applied to the positions of the large and small PAH spectra. To guide the eye, dotted vertical lines are also shown at 6.2, 7.7, 8.6, 11.2 and 12.7 μm.

bands from both the large PAH anions and cations overlap, with the anions contributing more strongly at slightly longer wavelengths. Peeters et al. (2002) found a correlation between the peak position of the astronomical 7.7 μm feature and that of the 8.6 μm band. The inability of small PAHs to reproduce this correlation suggests that the astronomical 7.8 μm component and the 8.6 μm feature originate primarily in large, cationic and anionic PAHs, with the specific peak position and profile reflecting the particular cation to anion concentration ratio in any given object.

For more details regarding the spectroscopy and astrophysical applications of large compact and large irregular PAHs, see Bauschlicher et al. (2008 & in prep.) respectively.

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