

Infrared emission spectra of candidate interstellar aromatic molecules

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INTERSTELLAR dust is responsible, through surface reactions, for the creation of molecular hydrogen, the main component of the interstellar clouds in which new stars form. Intermediate between small, gas-phase molecules and dust are the polycyclic aromatic hydrocarbons (PAHs). Such molecules could account for 2–30% of the carbon in the Galaxy¹, and may provide nucleation sites for the formation of carbonaceous dust^{2,3}. Although PAHs have been proposed^{4,5} as the sources of the unidentified infrared emission bands that are observed in the spectra of a variety of interstellar sources^{6–11}, the emission characteristics of such molecules are still poorly understood. Here we report laboratory emission spectra of several representative PAHs, obtained in conditions approximating those of the interstellar medium, and measured over the entire spectral region spanned by the unidentified infrared bands. We find that neutral PAHs of small and moderate size can at best make only a minor contribution to these emission bands. Cations of these molecules, as well as much larger PAHs and their cations, remain viable candidates for the sources of these bands.

The unidentified infrared bands (UIRs) are generally associated with interstellar molecular clouds that are subjected to intense ultraviolet and optical radiation^{6–11}; one such example is the Trapezium region of the Orion Nebula, where the massive young stars (such as θ^1 Orion C) have ionized the surrounding gas cloud from which they formed. The UIRs are also seen towards planetary nebulae, which result when the gas and dust surrounding a newly formed white dwarf star is ionized and heated by the radiation from the white dwarf.

In the PAH model of the UIRs^{4,5}, absorption of ultraviolet light by an isolated PAH is followed by rapid internal energy conversion, relaxing the molecule to the electronic ground state, but leaving it with the energy of the ultraviolet photon (typically 10 eV) distributed among its vibrational modes. In the collisionless interstellar environment, the vibrationally hot molecule is hypothesized to cool by infrared emission at frequencies characteristic of PAH vibrations, giving rise to the UIRs. UIR frequencies and their PAH local-mode assignments are summarized in Table 1.

We have designed a new experiment to test rigorously the PAH hypothesis in the laboratory. Because of the considerable uncertainties associated with modelling the interstellar environment, our approach is to systematically examine each class of PAH molecule that has been proposed as a possible UIR source. Here we report measurements of infrared emission spectra of four unsubstituted PAHs, two methyl substituted PAHs, and two hetero-substituted PAHs (Fig. 1), all with complete

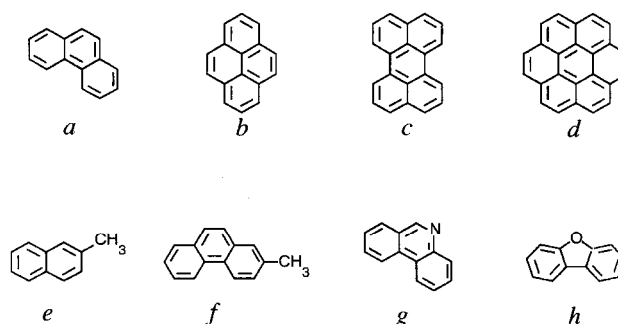


FIG. 1 Chemical structures representing the PAH molecules studied by SPIRES in this work. These include: four unsubstituted PAHs, phenanthrene (a, C₁₄H₁₀), pyrene (b, C₁₆H₁₀), perylene (c, C₂₀H₁₂) and coronene (d, C₂₄H₁₂); two methyl substituted PAHs, 2-methylnaphthalene (e, C₁₁H₁₀), and 2-methylphenanthrene (f, C₁₅H₁₂); and two hetero-substituted PAHs, phenanthridine (g, C₁₃N₃N) and dibenzofuran (h, C₁₂H₈O). Molecules the size of coronene have recently been postulated to account for the 3.3- μ m UIR band²⁰.

coverage of the infrared spectral regions spanned by the UIRs. To obtain such extensive spectral coverage, we use ultraviolet-laser-induced desorption to introduce highly excited gas phase PAHs into a low-infrared-background cryogenic high vacuum chamber. A cryogenic monochromator disperses the infrared emission, and a blocked impurity band solid-state photomultiplier¹² is used to count single infrared photons. Our initial results¹³, in which this single-photon infrared emission spectroscopy (SPIRES) apparatus is described, demonstrate the applicability of this technique to the PAH-UIR problem; monochromator heat leaks limited the spectral coverage in this previous report.

Figure 2 shows SPIRES spectra of the unsubstituted PAHs (Fig. 2a) and substituted PAHs (Fig. 2b) along with the characteristic UIR wavelengths. When comparing laboratory spectra to the UIRs, we note that no single PAH, but rather a family of molecules with similar structure and presumably similar infrared spectra, is postulated to give rise to the UIRs^{14,15}. Bands which appear in a characteristic spectral region but with significant differences in frequency are postulated to combine to produce an apparent continuum, such as the continuum observed in the UIR spectra between 5.5 and 9.5 μ m. But if a conglomerate spectrum is to exhibit relatively narrow bands like the UIR bands at 3.3, 6.2 and 11.2 μ m, then clearly these same narrow

TABLE 1 PAH-UIR hypothesis summary

UIR wavelength (μ m)	3.3	6.2	7.7	8.7	11.2
UIR bandwidth FWHM (cm ⁻¹)	30	30	70 to 200*		30
Characteristic PAH vibrations (see text)	C–H stretch	C–C stretch	C–C stretch	C–H in-plane bend	C–H out-of-plane bend†

Typical peak wavelengths and bandwidths of the primary UIR bands, along the characteristic PAH local-mode vibrations, from Allamandola et al.⁴ unless stated otherwise. Minor UIR features are not tabulated.

* The 7.7- μ m feature is broad and varies from source to source. The 8.7- μ m band is often seen as a shoulder on this feature.

† The wavelength of the 11.2- μ m UIR band is characteristic of C–H out-of-plane bending motions arising from solo C–H bonds on the periphery of the ring. An *ab initio* survey of PAH ion frequencies²⁷ indicates that for large cations with condensed structures, the 11.2- μ m band may also be characteristic of C–H bonds with one adjacent C–H bond (duo C–H) on the periphery of the ring.

