

# 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 Galaxy<sup>1</sup>, and may provide nucleation sites for the formation of carbonaceous dust<sup>2,3</sup>. Although PAHs have been proposed<sup>4,5</sup> as the sources of the unidentified infrared emission bands that are observed in the spectra of a variety of interstellar sources<sup>6–11</sup>, 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<sup>6–11</sup>; one such example is the Trapezium region of the Orion Nebula, where the massive young stars (such as  $\theta^1$  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<sup>4,5</sup>, 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

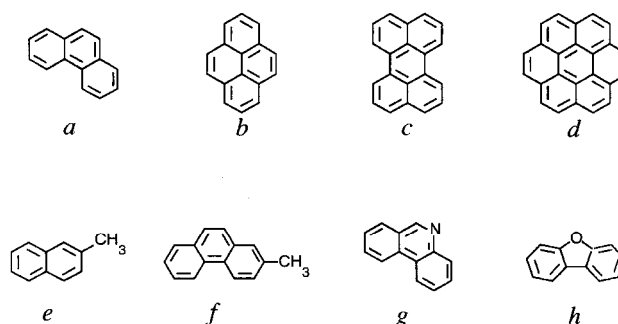


FIG. 1 Chemical structures representing the PAH molecules studied by SPIRES in this work. These include: four unsubstituted PAHs, phenanthrene (a, C<sub>14</sub>H<sub>10</sub>), pyrene (b, C<sub>16</sub>H<sub>10</sub>), perylene (c, C<sub>20</sub>H<sub>12</sub>) and coronene (d, C<sub>24</sub>H<sub>12</sub>); two methyl substituted PAHs, 2-methylnaphthalene (e, C<sub>11</sub>H<sub>10</sub>), and 2-methylphenanthrene (f, C<sub>15</sub>H<sub>12</sub>); and two hetero-substituted PAHs, phenanthridine (g, C<sub>13</sub>N<sub>3</sub>N) and dibenzofuran (h, C<sub>12</sub>H<sub>8</sub>O). Molecules the size of coronene have recently been postulated to account for the 3.3- $\mu$ m UIR band<sup>20</sup>.

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 photomultiplier<sup>12</sup> is used to count single infrared photons. Our initial results<sup>13</sup>, 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<sup>14,15</sup>. 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  $\mu$ m. But if a conglomerate spectrum is to exhibit relatively narrow bands like the UIR bands at 3.3, 6.2 and 11.2  $\mu$ m, then clearly these same narrow

TABLE 1 PAH-UIR hypothesis summary

UIR wavelength ( $\mu$ m)	3.3	6.2	7.7	8.7	11.2
UIR bandwidth FWHM (cm <sup>-1</sup> )	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.<sup>4</sup> unless stated otherwise. Minor UIR features are not tabulated.

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

† The wavelength of the 11.2- $\mu$ 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 frequencies<sup>27</sup> indicates that for large cations with condensed structures, the 11.2- $\mu$ 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.

## LETTERS TO NATURE

bands must appear consistently in the individual molecular emission spectra. This is not observed in our laboratory spectra for bands arising primarily from C–C stretching and C–H out-of-plane bending vibrations. This constitutes strong evidence that the molecules studied here cannot be major sources of the UIRs.

The 3.3- $\mu\text{m}$  bands observed in our spectra do show a remarkable invariance in frequency among the different PAHs studied, and yield consistent and significant red shifts relative to the bands measured in cryogenic matrix absorption experiments ( $\sim 25\text{ cm}^{-1}$ ). Emission features with similar lineshapes and exhibiting systematic red shifts with increasing internal energy content have been observed in previous ultraviolet laser excitation experiments<sup>13,16,17</sup>, as well as in high-temperature equilibrium gas cell experiments<sup>18–20</sup>, and have been attributed to unresolvable sequence bands which are characteristic of highly vibrationally excited molecules<sup>13,17</sup>. Similar red shifts are observed for the other bands in the spectra, although the effect is not as pronounced. As the red shifts and band broadening due to high internal energy content can only be determined empirically, experimental measurements of molecules under astrophysical conditions are essential to test the PAH-UIR hypothesis. Such measurements are also needed to provide an adequate basis for modelling the

emission spectra which one expects to observe for other molecules, such as PAH ions, for which only matrix data presently exist.

Although relative intensities reported here are only semi-quantitative, gross differences clearly exist between the intensity patterns of the SPIRES spectra and the UIRs. The 6.2- and 7.7- $\mu\text{m}$  UIR bands, assigned primarily to C–C stretches, are strong when compared to 3.3- $\mu\text{m}$  C–H stretches and 11.2- $\mu\text{m}$  C–H out-of-plane bends; our laboratory PAH spectra exhibit the opposite result. The intensity differences reported here indicate that, whereas neutral PAHs such as those included in this study could account for the majority of the UIR emission observed in the 3.3- $\mu\text{m}$  band and the minor 3.4- $\mu\text{m}$  band, they could account for less than 10% of the emission observed in the other UIR bands.

Such intensity differences between neutral PAHs and the UIRs have been noted before<sup>19</sup>, and thus constitute a general argument against these molecules being major UIR sources. Recent attention has consequently been turned to ionized PAHs. Matrix absorption spectra of PAH cations<sup>21–25</sup> produce a promising trend of bands shifting towards the 7.7- $\mu\text{m}$  and 11.2- $\mu\text{m}$  features, as well as band intensity ratios more closely resembling the UIRs. Models predict that PAHs are largely ionized in many regions where the UIRs are generated<sup>4,26</sup>. Because of the substantial

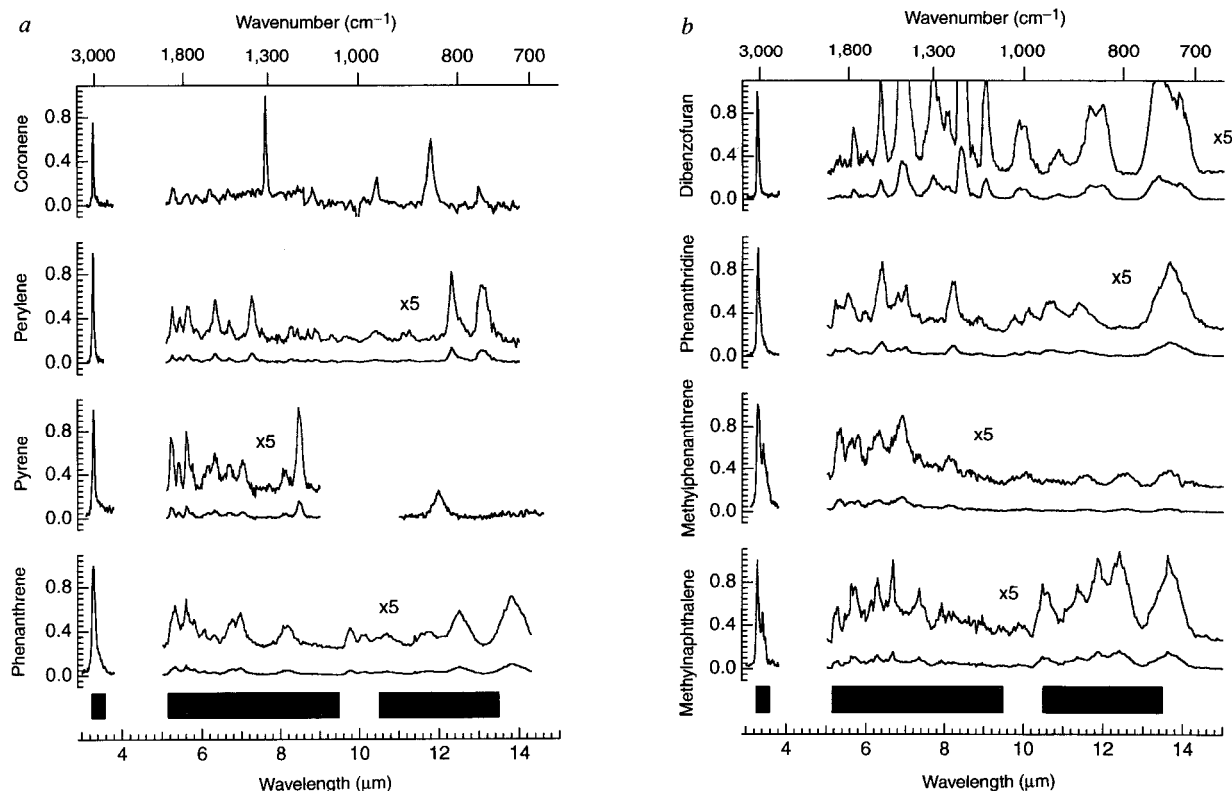


FIG. 2 Infrared emission spectra of the unsubstituted PAHs (a) and substituted PAHs (b) depicted in Fig. 1, measured by SPIRES under conditions approximating the interstellar environment. The bars on the bottom of the spectra represent the wavelengths at which UIR bands are observed. The dark bands correspond to wavelengths at which distinct peaks are observed, and the light-grey bands correspond to wavelengths where associated continuum emission is observed. For pyrene, perylene and coronene, a 150 groove  $\text{mm}^{-1}$  grating was used for the spectra between 3 and 4  $\mu\text{m}$ ; between 5 and 14  $\mu\text{m}$  a 75 groove  $\text{mm}^{-1}$  grating was used. For phenanthrene and the substituted PAHs, a 50 groove  $\text{mm}^{-1}$  grating was used between 10 and 15  $\mu\text{m}$ . The spectra were corrected for the estimated instrument response functions. Difficulties associated with calibration using a variable-temperature cryogenic black-body source include

limited detector dynamic range and stray light from the ruled gratings, which lead to estimated uncertainties of a factor of ten with regard to relative band intensities. The spectra from the multiple gratings were combined, and the relative intensities were converted from photon flux to power and normalized to the most intense peak in each individual spectrum. A vibrational temperature can be estimated by using the SPIRES frequencies in conjunction with the pyrene and coronene red-shift measurements of Joblin and co-workers<sup>19</sup>, which assume a linear dependence of peak position on temperature. Temperatures are calculated for each band and the result is averaged. This calculation yields vibrational temperatures of 1,019 K and 814 K for pyrene and coronene, respectively. In our previous report<sup>13</sup>, we used a similar approach to estimate the internal energy of laser-desorbed naphthalene to be  $\sim 30,000\text{ cm}^{-1}$ .

differences in ion infrared band strengths with respect to the neutrals<sup>27</sup>, only a small excess of ions would be necessary to reproduce the UIRs, so long as these ions consistently exhibit strong features at 6.2 and 11.2  $\mu\text{m}$ , and exhibit a lack of strong features at other non-UIR wavelengths. Hence it appears essential to extend the laboratory experiments described here to ionized PAHs to assess definitively the PAH hypothesis. We note that the general mechanism proposed for production of the UIRs (ultraviolet absorption followed by internal conversion and infrared emission)<sup>4,5</sup> is quite strongly supported by our measurements, as well as by earlier measurements of ultraviolet-laser-excited PAHs<sup>13,16,17,28,29</sup> in the 3- $\mu\text{m}$  region.  $\square$

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