Far-Infrared Emission Spectra of Selected Gas-Phase PAHs: Spectroscopic Fingerprints

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The emission spectra of the gaseous polycyclic aromatic hydrocarbons (PAHs) naphthalene, chrysene, and pyrene were recorded in the far-infrared (far-IR) region. The vibrational bands that lie in the far IR are unique for each PAH molecule and allow discrimination among the three PAH molecules. The far-IR PAH spectra, therefore, may prove useful in the assignment of unidentified spectral features from astronomical objects.

An important question in astronomy is the role of the PAH compounds in the chemistry of the interstellar medium. PAH molecules have been identified in meteorites (*1*, *2*) and interplanetary dust particles (3) by mass spectrometry. Several features in the spectra of astronomical objects have also been attributed to neutral or ionized PAHs. One example is the unidentified IR emission bands (UIRs) that are observed in the spectra of objects including planetary nebulae, reflection nebulae, and H II regions (*4*–*7*). It has been hypothesized that the UIRs arise because the PAH molecules absorb ultraviolet (UV) radiation, undergo internal conversion, and then emit radiation in the IR region (*4*–*7*). Indeed, the UIR bands (at 3.3, 6.2, 7.7, 8.7, and 11.3 μm) (*7*) resemble some of the characteristic features in the PAH spectra. Other spectroscopic features, such as the UV absorption feature at 2175 Å and the diffuse interstellar bands, may also arise from the PAHs (*8*, *9*).

Several groups have recorded laboratory spectra of the PAHs in an attempt to assign the unidentified features in astronomical spectra. The interstellar environments that are thought to contain PAHs range from the surfaces of dust grains to the exploding shells of supernovae; this diversity must be approximated by collecting spectra under a variety of experimental conditions. Many investigations have examined the vibrational spectra of the neutral and ionic (*10*–*13*) PAHs isolated in rare gas matrices. The IR and far-IR spectra of solid PAHs have also been studied by embedding the molecules in KBr or CsI pellets (*14*–*16*). Kurtz (*17*) recorded the first gas-phase coronene spectra in the region between 400 and 3500 cm^{-1}. IR absorption spectra of several other gas-phase PAH molecules were obtained by Joblin *et al.* (*18*, *19*) in the same wavelength region. Recently, Saykally and coworkers (*20*) have measured the IR emission spectra of naphthalene, perylene, pyrene, and coronene from 3 to 14 μm (3300 to 700 cm^{-1}) using a new photon-counting technique.

To elucidate the chemistry of the PAHs in the interstellar medium, it is necessary to identify the individual PAH molecules. In principle, it is possible to distinguish among the different types of PAHs on the basis of their spectra. Yet the task is not a trivial one because the PAHs exhibit very similar spectra in the mid-IR, the region that contains most of the normal vibrational modes. The vibrational assignment, however, may be facilitated through theoretical methods. Recently, Langhoff (*21*) calculated the IR spectra of 13 neutral and ionized PAH molecules using density functional theory. The calculations confirmed the previous assignments of the PAH spectra. Furthermore, Langhoff pointed out that the far-IR region, which contains the vibrational frequencies associated with the bending of the aromatic rings, may provide a way to discriminate among the different molecules. Because there were no available far-IR spectra of isolated PAH molecules, Langhoff's work inspired the work reported here.

In order to obtain the spectra of gas-phase PAH molecules, we detected their mid- and far-IR emission and absorption with a Fourier transform spectrometer. The use of thermal emission spectroscopy in addition to the traditional absorption technique is unusual (*22*), but we find emission spectroscopy to be more sensitive, even at long wavelengths. A cell consisting of a stainless-steel tube 120 cm long, sealed with two windows at both ends, was used to contain the samples. The PAH solids were placed near the center of a quartz-lined tube 100 cm long, which was inserted into the sample cell. After evacuation, a commercial furnace was used to heat the central 50-cm portion of the sample cell to produce PAH vapor. The two ends of the sample cell were water-cooled to protect the O-ring seals and to prevent deposition on the end windows. Appropriate optics and detectors were used to cover the spectral range from 50 to 4000 cm^{-1}.

Naphthalene, pyrene, and chrysene solids (97% pure) were obtained from Aldrich and used without further purification. In every experiment, about 30 g of sample was used. The sample was heated slowly up to a maximum of 450°C. Spectra were recorded about every 50°C separately in emission and absorption. Background spectra were also recorded in a similar fashion but without a sample in the cell. The spectral resolution in all cases was 1 cm^{-1}. The integration time for each spectrum varied from 4 to 10 min, and the number of scans co-added ranged from 100 to 200. The final spectra reported here were obtained by dividing the raw spectrum by the background spectrum taken at the same temperature.

Emission and absorption spectra of gas-phase naphthalene, chrysene, and pyrene were obtained over the interval from 50 to 4000 cm^{-1}. In PAH nomenclature, naphthalene is classified as a simple "linear" PAH molecule, chrysene is classified as a typical "nonlinear" PAH molecule, and pyrene is classified as a simple "compact" PAH molecule (*21*). The emission spectrum of pyrene in the region above 400 cm^{-1} is similar to the absorption spectrum reported by Joblin *et al.* (*18*, *19*). We observed several strong bands in the 1700 and 2400 cm^{-1} interval that must be either combination or overtone bands because there are no IR active fundamental transitions in this region. The unambiguous assignment of these vibrational modes is difficult, however, because the number

Table 1. Experimental and theoretical far-IR band positions of naphthalene, pyrene, and chrysene.

Symmetry of molecular vibrational mode	Band positions (cm^{-1}) Experimental*	Theoretical†	Intensity† (km/mol)
	Naphthalene		
b_{3u}	167.0	171.8	1.9
b_{1u}	360.6	357.7	1.3
	Pyrene		
b_{3u}	95.0	98.6	0.5
b_{3u}	214.2	210.0	7.3
b_{2u}	350.0	353.5	1.4
	Chrysene		
a_u	231.5	232.9	4.3

*From this work. †From (*21*) and unpublished data.

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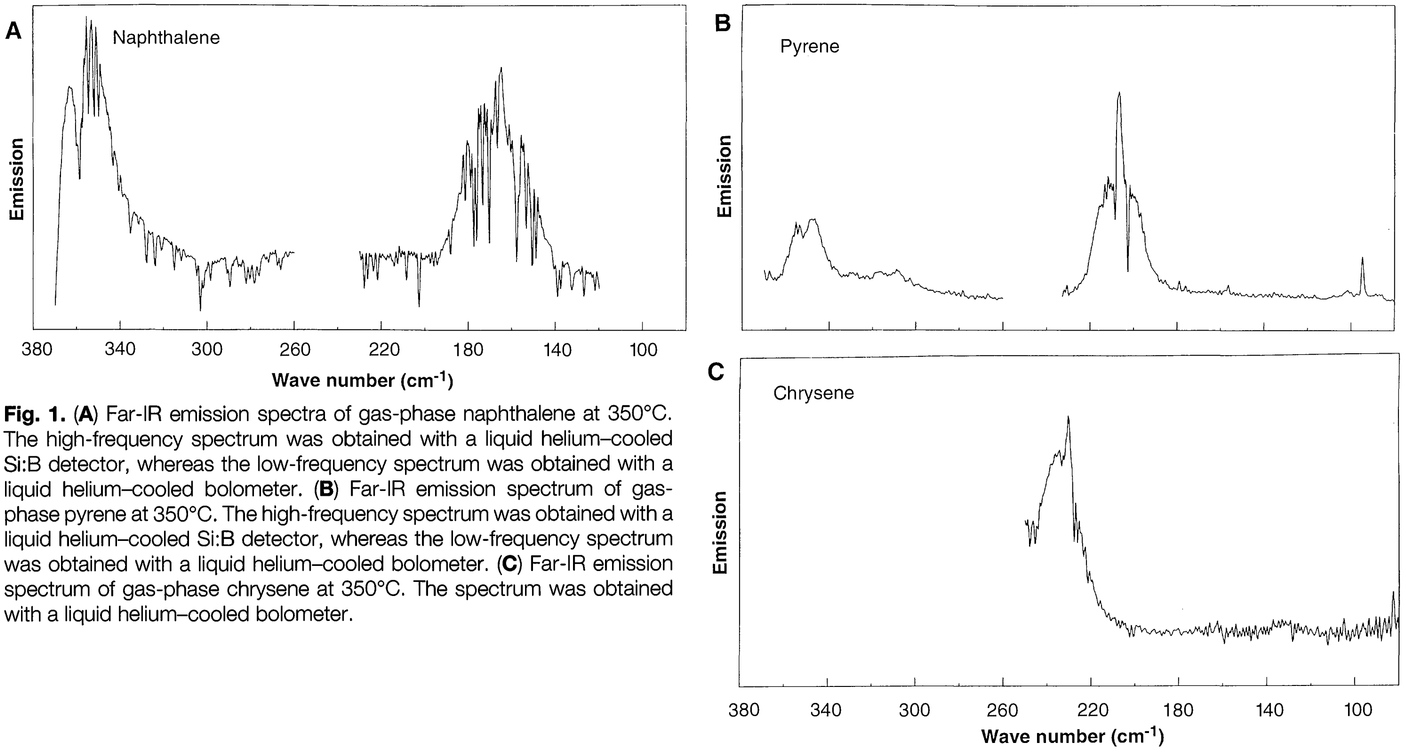

Fig. 1. (**A**) Far-IR emission spectra of gas-phase naphthalene at 350°C. The high-frequency spectrum was obtained with a liquid helium–cooled Si:B detector, whereas the low-frequency spectrum was obtained with a liquid helium–cooled bolometer. (**B**) Far-IR emission spectrum of gas-phase pyrene at 350°C. The high-frequency spectrum was obtained with a liquid helium–cooled Si:B detector, whereas the low-frequency spectrum was obtained with a liquid helium–cooled bolometer. (**C**) Far-IR emission spectrum of gas-phase chrysene at 350°C. The spectrum was obtained with a liquid helium–cooled bolometer.

of IR active modes is large for even a small PAH molecule such as naphthalene. In addition, in the region from 400 to 1700 cm^{-1}, where fundamental bands dominate, numerous combination and overtone bands are present. The general similarity between the mid-IR spectra of different PAHs and the spectral complexity makes it difficult to differentiate between individual types of PAHs.

Each PAH molecule, in contrast, has a relatively simple and characteristic spectrum in the region below 400 cm^{-1}. The far-IR bands provide a unique fingerprint for each type of PAH. Figure 1 shows several emission spectra of naphthalene, pyrene, and chrysene. Although the pure rotational lines of water are present in the spectra as an impurity, the profiles of the PAH bands can still be recognized. The effect of increasing temperature on the band position is less obvious, but a red shift of the bands was noticed (*18, 19*). Because the number of low-frequency IR active modes is small, the far-IR spectra (Fig. 1) are less congested than the mid-IR spectra. Table 1 lists the far-IR bands of naphthalene, pyrene, and chrysene that were measured in these experiments.

The agreement between the measured band positions and those calculated by Langhoff (*21*) is remarkably good. All of the relatively strong modes below 400 cm^{-1} that were reported by Langhoff were located in our experiments (*21*). We found that the far-IR spectra of PAH molecules, though relatively weak, may provide a region where the different members of the PAH family can be uniquely identified. The far-IR spectra reported here may help to test the PAH hypothesis for the origin of the unidentified IR emission bands as well as for other unassigned features in the spectra of astronomical objects. Although the Earth's atmosphere is opaque in the far-IR region, observations are possible with satellite-based IR spectrometers such as the Infrared Space Observatory (ISO) (launched in late 1995) and the proposed Space Infrared Telescope Facility (SIRTF) platform, which have orbits above the Earth's atmosphere (*23*). Observations will also be possible from high-flying aircraft platforms such as the Stratospheric Observatory for Infrared Astronomy (SOFIA), which will commence operations in the early part of the next century.

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