

Recent Advances in Laboratory Infrared Spectroscopy of Polycyclic Aromatic Hydrocarbons: PAHs in the Far Infrared

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Over 25 years of observations and laboratory work have shown that the mid-IR spectra of a majority of astronomical sources are dominated by emission features near 3.3, 6.2, 7.7, and 11.2 μm , which originate in free polycyclic aromatic hydrocarbon (PAH) molecules. PAHs dominate the mid-IR emission from many galactic and extragalactic objects. As such, this material tracks a wide variety of astronomical processes, making this spectrum a powerful probe of the cosmos

Apart from bands in the mid-IR, PAHs have bands spanning the Far-IR (FIR) and emission from these FIR features should be present in astronomical sources showing the Mid-IR PAH bands. However, with one exception, the FIR spectral characteristics are known only for a few neutral small PAHs trapped in salt pellets or oils at room temperature, data which is not relevant to astrophysics. Furthermore, since most emitting PAHs responsible for the mid-IR astronomical features are ionized, the absence of any experimental or theoretical PAH ion FIR spectra will make it impossible to correctly interpret the FIR data from these objects. In view of the upcoming Herschel space telescope mission and SOFIA's FIR airborne instrumentation, which will pioneer the FIR region, it is now urgent to obtain PAH FIR spectra.

This talk will present an overview recent advances in the laboratory spectroscopy of PAHs, Highlighting the FIR spectroscopy along with some quantum calculations.

PAH FAR IR SPECTROSCOPY!

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INTRODUCTION

! Over 25 years of observations and laboratory work have shown that the mid-IR spectra of a majority of astronomical sources are dominated by emission features near 3.3, 6.2, 7.7, and 11.2 μm , which originate in free polycyclic aromatic hydrocarbon (PAH) molecules. PAHs dominate the mid-IR emission from many galactic and extragalactic objects. As such, this material tracks a wide variety of astronomical processes, making this spectrum a powerful probe of the cosmos!

! Apart from bands in the mid-IR, PAHs have bands spanning the Far-IR (FIR) and emission from these FIR features should be present in astronomical sources showing the Mid-IR PAH bands. Until now the experimental FIR spectral characteristics of PAHs have remained largely unexplored, except a few neutral small PAHs trapped in salt pellets or oils at room temperature. Since most emitting PAHs responsible for the mid-IR astronomical features are ionized, the absence of any experimental or theoretical PAH ion FIR spectra makes it impossible to correctly interpret the FIR data from these objects. In view of the pioneering FIR observations being made by ESA's Herschel Space Observatory and those soon to be made by NASA's Stratospheric Observatory for Infrared Astronomy (SOFIA), it is now urgent to obtain PAH FIR spectra. !

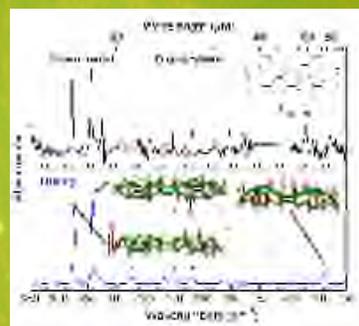
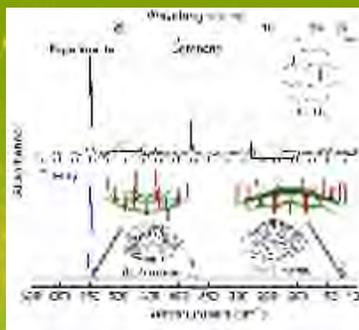
PAH FAR-IR SPECTROSCOPY!

The information contained in the Far IR region is not simply an extension of that contained in the mid-IR bands. PAH vibrations that produce the well-known mid-IR bands include bond stretches and bends. These vibrational frequencies are determined by bond strengths, types of atoms involved etc. and mid-IR spectral studies mainly provide information about chemical subgroups present and chemical classification. However, with increasing wavelengths, other types of fundamental molecular vibrations become important. The modes that produce bands in the FIR involve the deformation of the entire framework of the molecule. These modes are often molecule specific because they arise from the twisting and bending of the entire molecule as a single unit. For PAHs, most of the bands in the FIR are determined by "drumhead" types of vibrations, so called because they resemble the harmonic vibrations of percussion instruments. Since these frequencies depend primarily on the molecule's overall size and shape, they are molecule specific. !



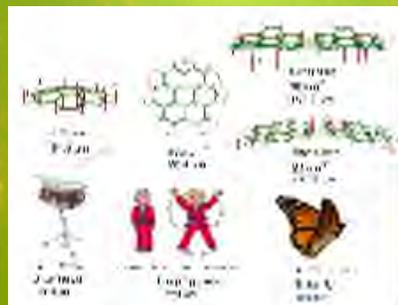
PAH fundamental molecular vibrations. The vibrational modes and theoretical spectrum of coronene ($\text{C}_{24}\text{H}_{12}$). As you can see, vibrational modes in the Mid-IR consist of sub-groups (C-H, C-C, etc.), whereas modes in the FIR involve the entire molecular skeleton.!

The Far-IR spectra of coronene and dicoronylene isolated in a krypton matrix at 20 K are compared with their theoretically calculated spectrum using Density Functional Theory (DFT). Note how the complexity of the FIR spectrum increases in going from coronene to dicoronylene. !



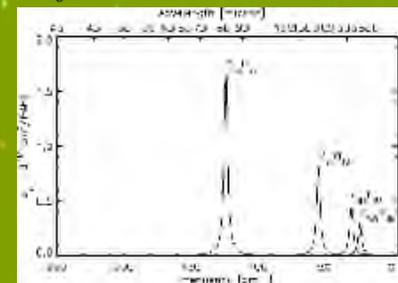
FIR VIBRATIONAL MOTIONS

There are three types of basic vibrational motions exhibited by PAHs in the FIR. These are the drumhead, jumping jack and butterfly modes. Examples of these motions in coronene and dicoronylene are given in the figure below. !



FIR VIBRATIONAL TRENDS

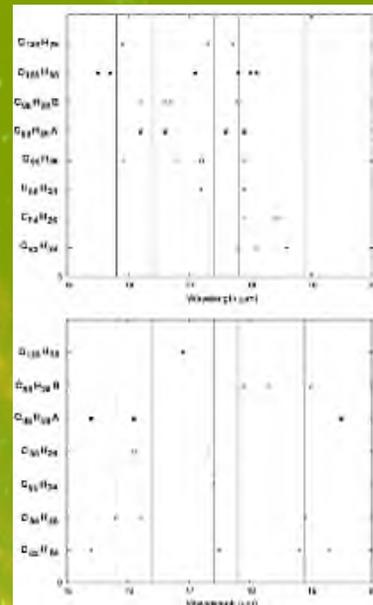
For round, highly symmetric molecules, such as $\text{C}_{24}\text{H}_{12}$, $\text{C}_{36}\text{H}_{24}$, etc., out of plane vibrational modes shift as a function of the number of carbon atoms. For example, going from $\text{C}_{24}\text{H}_{12}$ to $\text{C}_{36}\text{H}_{24}$, the drumhead mode shifts by a factor of 4 (C96/C24 ratio). Using such a shift one can potentially predict the peak position of the drumhead modes for round, highly symmetric PAHs. This is illustrated for the drumhead modes in the figure below.!



THE 15 - 20 mm REGION

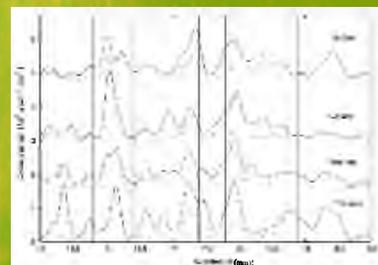
Our research has shown the 15 to 20 mm region to be a transition from the subgroup vibrations typical of the mid-IR to the skeletal motions indicative of the Far-IR. Listed below are some of our findings for this unique region.!

Neutral PAHs



The above plots show the out-of-plane (top) and in-plane (bottom) band positions with intensities greater than 2 kmol^{-1} for the 15-20 mm region for eight large PAHs (see Ricca et al. 2010 for PAH structures). The frequencies have been shifted by 15 cm^{-1} to the red, to account for absorption/emission differences. It is interesting to note that all neutral large PAHs in this investigation exhibited bands around 17.8-18 mm in their out-of-plane vibrational modes. In this respect, the 17.8 mm band is similar to the PAH "fingerprints" in the mid-IR. The vibrational motion responsible for this mode can best be described as a C-H out-of-plane motion combined with a drumhead mode with many nodes. !

Charged PAHs



The figure above shows the sum of all synthetic absorption spectra for pure PAHs (containing only C and H atoms) with more than 50 carbon atoms, in the NASA Ames PAH spectral database. As is easily seen in the figure, PAH charge state greatly impacts this region. The biggest impacts appear around the 16.4 and 17 mm band. However, the figure also reveals that PAH anions exhibit a peak around 19.4 mm. Such information could be useful in determining the ionization state of PAHs in various regions or within an extended object. !

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REFERENCES

- Mattiola, Ricca, Tucker, Bauschlicher & Allamandola, 2009, *AJ*, **137**, 4054!
- Ricca, Bauschlicher, Mattiola, Boersma & Allamandola, 2010, *ApJ*, **709**, 42!
- Boersma, Bauschlicher, Ricca, Mattiola, Peeters, Tielens, Allamandola, 2010, (submitted)!