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

Andrew L. Mattioda (1); Alessandra Ricca (2); Jonathan Tucker (3) Christiaan Boersma(1); Charles Bauschlicher Jr. (1); Louis J. Allamandola (1)

1. NASA Ames Research Center, Mountain View, CA USA
2. SETI Institute, Mountain View, CA USA
3. Amherst College, Amherst, MA USA

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!

INTRODUCTION

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 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. For round, highly symmetric molecules, such as C_{96}H_{24}, C_{24}H_{24}, etc., out of plane vibrational modes shift as a function of the number of carbon atoms. For example, going from C_{96}H_{24} to C_{24}H_{24}, the drumhead mode shifts by a factor of 4 (C_{96}/C_{24} 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.

PAH fundamental molecular vibrations. The vibrational modes and theoretical spectrum of coronene (C_{24}H_{12}). As you can see, vibrational modes in the Mid-IR consist of subgroups (C-H, C-C, etc.), whereas modes in the FIR involve the entire molecular skeleton.

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.

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). 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).

FIR VIBRATIONAL TRENDS

For round, highly symmetrical molecules, such as C_{96}H_{24}, C_{24}H_{24}, etc., out of plane vibrational modes shift as a function of the number of carbon atoms. For example, going from C_{96}H_{24} to C_{24}H_{24}, the drumhead mode shifts by a factor of 4 (C_{96}/C_{24} 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.

ACKNOWLEDGEMENTS

This research was funded in part by NASA’s Laboratory Astrophysics program, the SETI Institute, NASA Ames Research Center, SETI Institute, Mountain View, CA; Amherst College, Amherst, MA.

REFERENCES