

Anharmonicity and the IR Spectra of PAHs

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It is widely accepted that polycyclic aromatic hydrocarbons (PAHs) are ubiquitous throughout the galaxy. The vibrational frequencies of PAH molecules in the infrared (IR) have been shown to be an excellent fingerprint for their existence and for assessing the physical conditions of the astrophysical environment in which they are observed. The Ames PAH database is now used routinely by astronomers to understand the specific PAH features, enabling them to determine the importance of ionized PAHs, nitrogen-containing PAHs (PANHs) etc. for a specific object. While the laboratory spectra and theoretical calculations that make up the PAH database have been enormously useful, it is becoming clear that future space telescopes will be high-resolution and thus there is a need for high-resolution gas-phase experiments and theoretical calculations that explicitly include anharmonic effects. In this presentation, studies from the last five years that focused on explicitly computing anharmonic spectroscopic constants and vibrational spectra for various PAH molecules will be discussed. A brief overview of the theoretical approach will be discussed including the best electronic structure method to use and the use of vibrational second-order perturbation theory (VPT2) to compute the anharmonic spectroscopic constants and vibrational spectra, and the importance of resonances, especially in the C-H stretching region. Other details to be mentioned are an improved method for distributing the IR intensity across the bands of a polyad resonance, and the importance of anharmonic IR intensities, especially in regions of the spectrum where no fundamental bands occur. Where available, comparison to recent experiments will be discussed as well.

Finally, astronomers observe PAH molecules in emission, so our approach to compute anharmonic temperature-dependent spectra, including the evolution of resonances, and then to use a library of these temperature-dependent spectra to compute a cascade emission spectrum will be discussed as well. Results from these calculations will be discussed and compared with experiment where available. The details of our work can be found in Refs. [1-3], and references therein.

References

- [1] C. J. Mackie, T. Chen, A. Candian, T. J. Lee, and A. G. G. M. Tielens, *J. Chem. Phys.* 2018, **149**, 134302.
- [2] E. Maltseva, C. J. Mackie, A. Candian, A. Petrignani, X. Huang, T. J. Lee, A. G. G. M. Tielens, J. Oomens, and W. J. Buma, *Astron. Astrophys.* 2018, **610**, A65.
- [3] C. J. Mackie, A. Candian, X. Huang, E. Maltseva, A. Petrignani, J. Oomens, W. J. Buma, T. J. Lee, and A. G. G. M. Tielens, *Phys. Chem. Chem. Phys.* 2018, **20**, 1189.