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The infrared bands of polycyclic aromatic hydrocarbons and the realm of anharmonicity

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Polycyclic aromatic hydrocarbons (PAHs) are the most abundant complex molecules in space. Observations of their aromatic infrared bands (AIBs) show that there is much more information in these IR emissions than can be extracted with current state-of-the-art models. The red shading that is sometimes observed in PAH emission bands is believed to originate from anharmonicity of the vibrational potentials. However, models unavoidably have to use generic laws independent of molecular detail to extract the population of the PAH species as anharmonicity is currently neglected in the calculations of PAH IR emission spectra.

We present an experimental study to tackle the realm of anharmonicity (Maltseva et al. 2015). We performed mass-resolved, high-resolution spectroscopy of cold PAH molecules in the 3-μm CH stretching region. The measured IR spectra show vibrationally resolved bands and, surprisingly, many more strong modes than expected. A measurement of the deuterated counterpart that separates the normal modes from the combination bands demonstrate the anharmonic bands to be Fermi mediated. A combinatorial analysis shows mostly double combination bands of CC stretches to couple to the normal CH stretches and possible involvement of triple combination modes of mostly CH bends. We compare experiment with the harmonic and anharmonic approximations of Gaussian '09 and with an anharmonic approach that includes an advanced Fermi-resonance treatment (Mackie et al. 2015). We demonstrate that anharmonicity and Fermi resonances are essential to predict the molecular reality manifested in high-resolution spectra. The found strong anharmonic behaviour may play a role in the structure and side wings of the 3-μm emission band and thereby provide possible molecular-specific signatures.

REFERENCES

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