

Computational Spectroscopy of Polycyclic Aromatic Hydrocarbons In Support of Laboratory Astrophysics

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are strong candidates for the molecular carriers of the unidentified infrared bands (UIR) and the diffuse interstellar bands (DIBs). In order to test the PAH hypothesis, we have systematically measured the vibronic spectra of a number of jet-cooled neutral and ionized PAHs in the near ultraviolet (UV) to visible spectral ranges using the cavity ring-down spectroscopy. To support this experimental effort, we have carried out theoretical studies of the spectra obtained in our measurements. *Ab initio* and (time-dependent) density functional theory calculations are performed to obtain the geometries, energetics, vibrational frequencies, transition dipole moments, and normal coordinates of these PAH molecules. Franck-Condon (FC) calculations and/or vibronic calculations are then performed using the calculated normal coordinates and vibrational frequencies to simulate the vibronic spectra. It is found that vibronic interactions in these conjugated (electron systems are often strong enough to cause significant deviations from the Born-Oppenheimer (BO) approximation. For vibronic transitions that are well described by the BO approximation, the vibronic band profiles are simulated by calculating the rotational structure of the vibronic transitions. Vibronic oscillator strength factors are calculated in the frame of the FC approximation from the electronic transition dipole moments and the FC factors. This computational effort together with our experimental measurements provides, *for the first time*, powerful tools for comparison with space-based data and, hence, a powerful approach to understand the spectroscopy of interstellar PAH analogs and their contribution to the interstellar extinction, the UIR and the DIBs.

References: [1] Xiaofeng Tan and Farid Salama, *J. Chem. Phys.* **123** (2005) 014312.
[2] Xiaofeng Tan and Farid Salama, *J. Chem. Phys.* **122** (2005) 084318.

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