DFT Studies of the Electronic Transitions of PAHs and Their Implications for the 2175Å Interstellar Extinction Bump

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The 2175 Å extinction bump is the most pronounced spectroscopic feature on the interstellar extinction curve. In recent years, it is often attributed to polycyclic aromatic hydrocarbon (PAH) molecules. To evaluate this attribution, we perform a systematic, computational study of the electronic transitions of over 40 PAH molecules in their anionic, neutral, cationic, and di-cationic charge states. We use density functional theory (DFT) to obtain their optimized geometries on ground state, and time-dependent DFT (TD-DFT) to calculate their electronic absorption spectra. The frequency-space implementation based on linear combinations of localized orbitals are adopted to obtain independent information for each state. Such calculations are quite computationally expensive, especially as the number of electronic transitions increases. The method used here gives the best compromise between computer time and accuracy to evaluate the band positions and strengths of the electronic transitions of PAHs near the 2175 Å extinction bump. It is found that the weighted sum of the absorption spectra of these PAH species closely resembles the 2175 Å interstellar extinction bump. We discuss the dependence of the computed bump strength on charge states. Using a real-time propagation scheme, we also compute the absorption spectra of PAHs up to 60 eV and compare them with the ultraviolet (UV) interstellar extinction curve, including the extinction bump and the far-UV rise.