Negative Ion Photoelectron Spectroscopy of Polyaromatic Anions: Radical Vibrational Structure and Gas-Phase Acidity Determination

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As one of the most abundant forms of carbon in the universe, polyaromatic hydrocarbons (PAH) play a central role in the field of Biochemistry and Astrochemistry. In this work, we present a Franck–Condon analysis of the vibrational structure resulting from the negative ion photoelectron spectra (PES) of naphthalene and anthracene anions as a prototype for analysis of negative ion PES systems containing a rigid, ring structure. The Franck–Condon (FC) factors of the anion PES are simulated using the PESCAL program. PESCAL obtains the FC factors using molecular geometry, normal mode vectors, and normal mode harmonic vibrational frequencies of the anion and neutral states. The geometric and frequency optimized structures of the anion and the neutral radical are calculated using the GAUSSIAN 09 software package. The FC simulations are based on a harmonic oscillator approximation model that utilizes the Duschinsky rotation between the normal mode vectors of the anion and neutral. The calculated adiabatic electron affinity is utilized in the negative ion thermochemical cycle to determine gas-phase acidity values of neutral molecules.