

Utilization of a Harmonic Oscillator Model to Calculate Franck-Condon Factors of Deprotonated Cyano and Dicyano Benzonitriles

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The diverse molecular structure and reactivity of deprotonated anionic derivatives of cyano and dicyano polyaromatic hydrocarbons (PAHs) play a central role in the field of Biochemistry, combustion chemistry, and Astrochemistry. In this work, we have utilized a harmonic model to calculate the Franck–Condon Factors (FCFs) in the negative ion photoelectron spectra of deprotonated benzonitrile and dicyanobenzonitrile anionic derivatives. The geometry and frequency of the optimized structures of the anion and the neutral radical are calculated using the GAUSSIAN 09 software package while the FC factors are evaluated using PESCAL program. PESCAL utilizes the optimized geometries, normal mode vectors, and normal mode harmonic vibrational frequencies of the anion and neutral states from Gaussian to obtain the vibronic spectra of the neutral radical following photodetachment. 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 adiabatic electron affinity (EA) increase from ~1.9 eV in deprotonated benzonitriles to ~2.5 eV in deprotonated dicyanobenzonitriles. The negative ion photoelectron spectra are dominated by ring distortion vibrational modes as the most dominant vibrational progressions.