CALCULATED NIR SPECTRA OF NEUTRAL AND CATIONIC PAHS

HENRIK G. KJAERGAARD, KARLEEN A. BROOKING, and TIMOTHY W. ROBINSON , *Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand*.

We have calculated fundamental and overtone CH-stretching vibrational band intensities of polycyclic aromatic hydrocarbons (PAHs) and their corresponding cations. The intensities were determined with a simple anharmonic oscillator local mode model, ab initio dipole moment functions, and scaled ab initio local mode parameters. We have used the self-consistent-field Hartree-Fock theory and the B3LYP density functional theory with the 6-31G(d) and 6-311G(d,p) basis sets. Our calculations are in very good agreement with recent vapor phase overtone spectra of naphthalene both for relative intensity of peaks within a given overtone as well as for the total absolute intensity. We have found that peaks corresponding to non equivalent CH bonds within a given PAH have different intensities, (as observed in the spectra of naphthalene). However, the total intensity for a given overtone region is very similar on a per CH basis for a wide range of PAHs (from benzene to coronene). Significant changes are predicted in the NIR spectra between the neutral and cationic PAHs. The frequencies of the cationic PAHs are shifted higher and the relative intensities of the individual peaks change significantly. A noticeable change in total overtone intensity between a neutral and cationic PAH is also observed. We suggest that these differences should make the NIR region suitable to distinguish between the various forms of PAHs which have been proposed to be present in the interstellar medium.