Poster Presentation

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Supramolecular Stark Effect in Host-Guest Complexes via Charge Density Analysis

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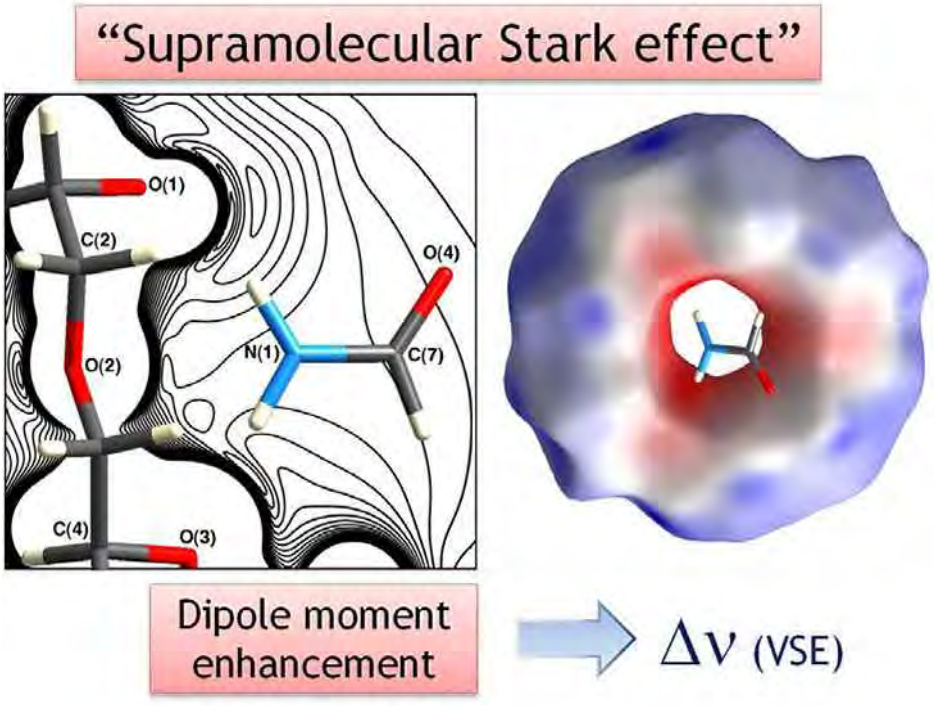
The effect of an electric field on the vibrational spectra, the Vibrational Stark Effect (VSE), has been utilized extensively to probe the local electric field in the active sites of enzymes [1, 2]. For this reason, the electric field and consequent polarization effects induced by a supramolecular host system upon its guest molecules attain special interest due to the implications for various biological processes. Although the host-guest chemistry of crown ether complexes and clathrates is of fundamental importance in supramolecular chemistry, many of these multicomponent systems have yet to be explored in detail using modern techniques [3]. In this direction, the electrostatic features associated with the host-guest interactions in the inclusion complexes of halogenated acetonitriles and formamide with 18-crown-6 host molecules have been analyzed in terms of their experimental charge density distribution. The charge density models provide estimates of the molecular dipole moment enhancements which correlate with the simulated values of dipole moments under electric field. The accurate electron density mapping using the multipole formalism also enable the estimation of the electric field experienced by the guest molecules. The electric field vectors thus obtained were utilized to estimate the vibrational stark effect in the nitrile (-C≡N) and carbonyl (C=O) stretching frequencies of the guest molecules via quantum chemical calculations in gas phase. The results of these calculations indicate remarkable elongation of C≡N and C=O bonds due to the electric fields. The electronic polarization in these covalent bonds induced by the field manifests as notable red shifts in their characteristic vibrational frequencies. These results derived from the charge densities are further supported by FT-IR experiments and thus establish the significance of a phenomenon that could be termed as the “supramolecular Stark effect” in crystal environment.

[1] *E. S. Park and S. G. Boxer J. Phys. Chem. B, 2002, 106, 5800-5806.,* ***[2]*** *I. T. Suydam, C. D. Snow, V. S. Pande, and S. G. Boxer, Science, 2006, 313, 200-204.,* ***[3]*** *H. F. Clausen, Y. S. Chen, D. Jayatilaka, J. Overgaard, G. A. Koutsantonis, M. A. Spackman, and B. B. Iversen, J. Phys. Chem. A, 2011, 115, 12962–12972.*



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