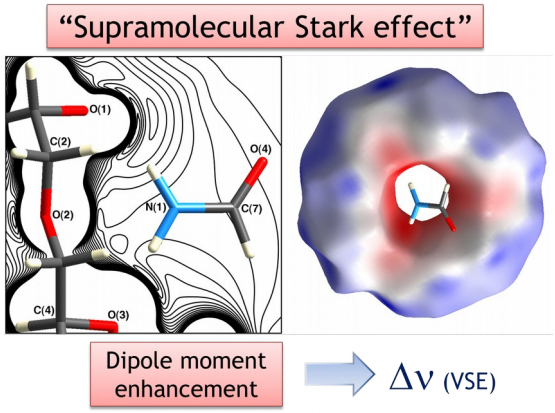
Electric field in supramolecular host-guest complexes from charge density analysis: insights into vibrational stark effect

Sajesh P. Thomas, Rebecca O. Fuller, Alexandre N. Sobolev, Philip A. Schauer, Simon Grabowsky, George A. Koutsantonis and Mark A. Spackman

School of Chemistry and Biochemistry, The University of Western Australia, Crawley, WA 6009

The Vibrational Stark Effect (VSE), the effect of an electric field on the vibrational spectrum, has been utilized extensively to probe the local electric field in the active sites of enzymes [1]. For this reason the electric field induced by a supramolecular host system upon its guest molecules is a topic of special interest due to its implications for various biological processes. Although the host-guest chemistry of clathrates and crown ether complexes is of fundamental importance in supramolecular chemistry, many of these simple systems have yet to be explored in detail using modern techniques [2]. In this context, the results from the experimental charge density analyses of the inclusion complexes of chloro- and fluoroacetonitrile and formamide with 18-crown-6 host molecules will be presented. The charge density models provide estimates of the molecular dipole moment enhancement and the electrostatic contribution associated with the host-guest interactions. Accurate mapping of the electron density using the multipolar model also provides an estimate of the electric field experienced by the guest molecules, and using this field the VSE in the nitrile (-C≡N) and carbonyl (C=O) stretching frequencies of the guest molecules are estimated via quantum chemical calculations on the guest molecules. The results of these calculations indicate notable bond elongation in C≡N and C=O bonds due to the field. The electronic polarization along these covalent bonds induced by the electric field manifests as significant red shifts in vibrational frequencies. These observations are substantiated by FT-IR experiments and thus quantitatively establish the phenomenon that could be termed as the “supramolecular Stark effect” in crystal environment.



1. (a) Park, E. S. and Boxer, S.G. (2002**)** *J. Phys. Chem. B***,** 106:5800-5806. (b) Suydam, I.T., Snow, C.D., Pande, V.S. and Boxer, S.G. (2006) *Science*, 313, 200.

2. Clausen, H.F, Chen, Y.S., Jayatilaka, D., Overgaard, J., Koutsantonis, G.A., Spackman, M.A. and Iversen, B.B. (2011) *J. Phys. Chem. A*, 115, 12962–12972.