

MAR15-2014-020411

Abstract for an Invited Paper
for the MAR15 Meeting of
the American Physical Society

The correspondence between the infrared vibrational spectra and the underlying hydrogen bonding network in aqueous clusters: caveats and tactics¹

SOTIRIS XANTHEAS, Pacific Northwest National Laboratory

The structural – spectral correspondence relates the observed infrared (IR) vibrational spectra to the underlying molecular structure. In the case of hydrogen bonded clusters the IR “fingerprint” region in the 3,000 – 4,000 cm^{-1} spectral range provides a direct probe of the connectivity and dynamics of the cluster’s hydrogen bonding network. For medium size (n 20) aqueous neutral and ionic clusters, the presence of several closely lying isomers that differ substantially in the oxygen atom network complicates both the sampling of the respective potential energy surfaces as well as the accurate determination of their energy order. Traditionally, a hierarchical procedure based on initial sampling with classical potentials and subsequent refinement with electronic structure methods has been used. We will highlight representative examples for the $(\text{H}_2\text{O})_{20}$, $(\text{H}_2\text{O})_{25}$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{20}$ clusters [1-3] where sampling with classical potentials fails to produce the most stable minima and outline approaches and strategies that are based on a combination of enhanced sampling of configurations in conjunction with electronic structure theory to obtain realistic cluster configurations that are consistent with the measured IR spectra.

[1] S. S. Xantheas, *Can. J. Chem. Eng.* **90**, 843 (2012).

[2] N. Sahu, S. R. Gadre, P. Bandyopadhyay, E. Miliordos and S. S. Xantheas, *J. Chem. Phys.* **141**, 164304 (2014).

[3] C. C. Pradzynski, C. W. Dierking, F. Zurheide, R. M. Forck, T. Zeuch, U. Buck and S. S. Xantheas, *Phys. Chem. Chem. Phys.* **16**, 26691 (2014).

¹Work supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. Pacific Northwest National Laboratory (PNNL) is a multi-program national laboratory operated for DOE by Battelle.