

THREE-DIMENSIONAL WATER NETWORKS SOLVATING AN EXCESS POSITIVE CHARGE: NEW INSIGHTS INTO THE MOLECULAR PHYSICS OF ION HYDRATION

CONRAD T. WOLKE, JOSEPH FOURNIER, *Department of Chemistry, Yale University, New Haven, CT, USA*; GARY H WEDDLE, *Department of Chemistry and Biochemistry, Fairfield University, Fairfield, CT, USA*; EVANGELOS MILIORDOS, SOTIRIS XANTHEAS, *Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA*; MARK JOHNSON, *Department of Chemistry, Yale University, New Haven, CT, USA*.

In a recent effort our group investigated the vibrational mechanics of water using the cage of 20 water molecules surrounding an alkali ion as a paradigm system. The $M^+(H_2O)_{20}$ clusters are well known “magic number” species (for the larger alkali metals) and are thought to form a pentagonal dodecahedral web encapsulating the ion. We are attracted to these systems because they are sufficiently large to display broad OH fundamental envelopes in a manner similar to that found in bulk water, but do so with a relatively small number of structurally distinct, three coordinated sites in a finite assembly that, although challenging, can be analyzed with electronic structure calculations in the context of a “supermolecule”. We show how this arrangement can provide an ideal platform on which to unambiguously identify the spectral signatures of particular binding sites, information that is invoked to explain the bulk (and interface) spectrum of water but cannot be directly measured in bulk water.

Although this behavior is most relevant to simulations of interfacial water, a future direction of this study will be gaining site-specific information for water in an extended two dimensional structure, and the elucidation of the paths of spectral diffusion associated with this arrangement. This unprecedented work will clarify a number of open questions regarding the site-specificity of ground and vibrationally excited state dynamics.