EXPLORING SOLVENT SHAPE AND FUNCTION USING MASS- AND ISOMER-SELECTIVE VIBRATIONAL SPECTROSCOPY

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We illustrate the new types of information than can be obtained through isomer-selective "hole-burning" spectroscopy carried out in the vibrational manifolds of Ar-tagged cluster ions. Three examples of increasing complexity will be presented where the changes in a solute ion are correlated with different morphologies of a surrounding solvent cage. In the first, we discuss the weak coupling limit where different hydration morphologies lead to small distortions of a covalent ion. We then introduce the more interesting case of the hydrated electron, where different shapes of the water network lead to dramatic changes in the extent of delocalization in the diffuse excess electron cloud. We then turn to the most complex case involving hydration of the nitrosonium ion, where different arrangements of the same number of water molecules span the range in behavior from simple solvation to actively causing a chemical reaction. The latter results are particularly interesting as they provide a microscopic, molecular-level picture of the "solvent coordinate" commonly used to describe solvent mediated processes.