

Investigations of Water Systems – Ultrafast Two Dimensional Infrared Spectroscopy

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Water is ubiquitous in natural systems. Water's properties are dependent on its three dimensional hydrogen bonding network. The H-bond network undergoes very rapid structural evolution, which is important in many water systems, e.g., solvation of ions. Here the dynamics of bulk water are examined as well as a number of other water systems. The first 2D IR experiments on the water hydroxyl stretch from 2004 are presented and compared to simulations. The detailed nature of the H-bond network dynamics are explicated. To examine more complex water systems, it is shown that the CN stretch of methylthiocyanate can be used as a vibrational probe. The CN stretch has a lifetime of ~30 ps in contrast to the hydroxyl stretch lifetime of 1.8 ps. The increased lifetime makes it possible to investigate slow processes in water systems. Concentrated aqueous solutions of LiCl are discussed. Chemical exchange is observed by the growth of off-diagonal peaks in the 2D IR spectrum. A water can be H-bonded to the nitrogen lone pair or a Li⁺ can be associated with it. The time constants for the interchange of water and Li⁺ associated with the nitrogen lone pair are determined. Then concentrated HCl solutions are studied. Analysis of the chemical exchange data gives the time for the interchange of hydronium cation and water bound to the nitrogen lone pair. Two processes are considered. Either the water and hydronium physically switch places, like water and Li⁺, or a proton is transferred from hydronium to water. It is argued that we are observing proton shuffling, and report the first direct measurement of the time for proton transfer from a hydronium cation to a water molecule. Dynamics of Langmuir monolayers at the air water interface are also investigated. An 18 carbon chain bound to a metal carbonyl group places the metal carbonyl at the air/water interface with the carbonyls in the water surface layer. The challenge of monolayer experiments is the very small number of molecules in a monolayer. A new 2D IR method, which greatly enhances the signal from monolayers, is described. Dynamics of bulk water and water in the surface layer are compared. Distinct water hydrogen bond dynamics are observed in the interfacial layer. Increasing the surface density of the interfacial molecules produces new transient species, "minor structures", which exhibit chemical exchange with the main structural form. Using the ultrafast 2D IR experiments that can take a spectrum in 8 seconds, exceedingly slow dynamics (hours) are shown to exist as the initially prepared air/water monolayer evolves in structure.