Dynamics of Water in AOT Reverse Micelles Probed Using Ultrafast IR Vibrational Echo and Pump-Probe Spectroscopies

IVAN PILETIC, HOWE SIANG TAN, MICHAEL FAYER, Stanford University — Water is used extensively as a solvent in chemistry and is ubiquitous in biological systems. Water’s unique properties are intimately related to its dynamic hydrogen bond network. In addition to the bulk, water is often found in nanoscopic environments. Therefore, it is important to understand the dynamics of water that is nanoscopically confined and to compare it with bulk water dynamics. Nanoscopic pools of water (1.7 – 4.0 nm diameter) in Aerosol-OT reverse micelles were directly probed using ultrafast vibrational echo and pump-probe spectroscopies on the OD hydroxyl stretch mode of water (5% HOD in H2O). The data are compared with experiments conducted on bulk water as well as 6M NaCl solution. Fits of the vibrational echo data demonstrate that the dynamics of water slow down substantially with decreasing reverse micelle size. The fastest dynamics (~50 fs) which reflect local hydrogen bond fluctuations, are similar to bulk water. The longer time scale dynamics are attributed to the dissociation and reformation of hydrogen bonds, and slow significantly (~10 times) as the nanopool size is reduced. Lifetime and anisotropy measurements using pump-probe spectroscopy also display similar size dependences. The vibrational echo and pump-probe data clearly distinguish the dynamics of bulk water and concentrated NaCl solutions from the dynamics of nanoscopic water confined in reverse micelles.

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