

Energy transfer in single hydrogen-bonded water molecules

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The importance of water in many chemical and biological processes has stimulated the intensive study of the dynamical properties of bulk liquid water. However, the role of water in chemical and biological processes is in most cases played by only a limited number of water molecules in strongly restricted environments. Here we study the properties of water in strong molecular confinement. The studied systems consist of inverse micelles of water and single water molecules (H_2O and HDO) hydrogen-bonded to acetone ($\text{C}_3\text{H}_6\text{O}$). The vibrational dynamics of these systems are measured with nonlinear femtosecond mid-infrared spectroscopy¹⁻⁴. The pulses used in these measurement are tunable between 3 and 4 μm , have a pulse duration of ~ 150 fs, and have a maximum energy of 20 μJ .

We observe that the confinement of liquid water results in a lengthening of the lifetime of the O-H stretch vibrations: $T_1=0.26\pm 0.05$ ps for bulk liquid water, $T_1=0.35\pm 0.05$ ps for an inverse micelle containing ~ 5000 H_2O molecules, $T_1=0.9\pm 0.1$ ps for an inverse micelle containing ~ 5 H_2O molecules, and $T_1=6.3\pm 0.3$ ps for a single H_2O molecule hydrogen-bonded to acetone. We also find that the hydrogen-bond dynamics and orientational dynamics of confined water molecules are ~ 3 times slower than the corresponding dynamics of the molecules in bulk liquid water. This is a surprising result, because the strength of the hydrogen-bond interaction decreases when the number of interacting water molecules is reduced.

In the dominant hydrogen-bonded structure formed by single $\text{H}_2\text{O}/\text{HDO}$ molecules and acetone, only one of the O-H/O-D groups is hydrogen bonded to the C=O group of an acetone molecule. This hydrogen bond breaks and reforms with a characteristic time constant of 1 ± 0.2 ps. These hydrogen-bond dynamics are observed to result in a transfer of vibrational energy between the two O-H groups of the H_2O molecule. The transition state of this energy transfer process is identified as a hydrogen-bonded complex in which the H_2O molecule forms two weak hydrogen bonds to two acetone molecules, and in which the vibrational excitation is delocalized over the molecule. The resonant vibrational energy transfer between the two O-H bonds of the confined water molecule is observed to be completely controlled by the formation and breaking of hydrogen bonds to the embedding acetone molecules. As a result, the resonant energy transfer between the two O-H groups of the H_2O molecule is ~ 20 times slower than in bulk liquid water.

¹ S. Woutersen, U. Emmerichs, and H.J. Bakker, "Femtosecond Mid-Infrared Pump-Probe Spectroscopy of Liquid Water: Evidence for a Two-Component Structure", *Science*, **1997**, 278, 658

² R. Laenen, C. Rauscher, and A. Laubereau, "Dynamics of Local Substructures in Water Observed by Ultrafast Infrared Hole Burning", *Phys. Rev. Lett.*, **1998**, 80, 2622

³ G.M. Gale, G. Gallot, F. Hache, N. Lascoux, S. Bratos, and J.-C. Leicknam, "Femtosecond Dynamics of Hydrogen Bonds in Liquid Water", *Phys. Rev. Lett.*, **1999**, 82, 1068

⁴ J. Stenger, D. Madsen, P. Hamm, E.T.J. Nibbering, and T. Elsaesser, "Ultrafast Vibrational Dephasing of Liquid Water", *Phys. Rev. Lett.*, **2001**, 87, 027401