What Nonlinear−IR Experiments Can Tell You about Water that the IR Spectrum Cannot

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Infrared (IR) spectroscopy is a fundamental technique used to explore structural and dynamical details of molecules. It is ideally suited to probe hydrogen bonded systems because the vibrational frequency of a hydrogen bond donor's A−H bond is extremely sensitive to hydrogen bonding with an acceptor B.[1] The shape and position of the hydroxyl stretch mode of water have been used as evidence for the existence of different species of water as well as qualitative depictions of the integrity of the hydrogen bond network.[2−4] Here, we use nonlinear−IR spectroscopy to investigate the dynamics of four aqueous systems that have very similar absorption spectra. We address the question: to what extent can the dynamics of water vary in systems with very similar absorption spectra?

Hydrogen bonds in water constantly rearrange, dissociating and reforming on a picosecond time scale. Nonlinear−IR spectroscopy has increased our understanding of the water hydrogen bond network dynamics.[5−8] These dynamics can significantly impact fundamental chemical processes, such as electron and proton transfer.[9] The IR spectrum of water has been used by researchers to explore the interaction of water with different chemical moieties, interpreting the observed spectral shifts as an indication of the strength or type of hydrogen bond.[10−13] On the basis of our time-resolved studies, we suggest that augmenting absorption spectra with nonlinear measurements of dynamics can avoid ambiguous interpretations of the relative structure and dynamical behavior of water in different environments.

Here we compare results from absorption and nonlinear−IR experiments probing the OD stretch mode of isotopically mixed water (dilute HOD in H_2O) in four distinct chemical systems. Figure 1 displays the IR spectra of the OD stretch in the systems: anionic Aerosol-OT (AOT) reverse micelles ($w_0 = 10$), a water/tetraethylene glycol dimethyl ether (TEGDE) solution ($w_0 = 7$), a water/acetonitrile solution ($w_0 = 2.3$), and a nonionic reverse micelle nonylphenylpoly(ethylene oxide) (NP; $w_0 = 2$) with the same number of ether oxygens as TEGDE; w_0 is the molar ratio of water to surfactant or to the nonwater species. The w_0 values result in linear−IR absorption spectra with virtually the same peak positions and line widths. Monitoring the local OD stretching mode in HOD eliminates vibrational excitation transport and simplifies the spectra because they do not display any structure, such as multiple peaks. Differences in spectral widths arise predominantly from inhomogeneous broadening contributions.

The similarities of the spectra shown in Figure 1 might be taken to suggest that the hydrogen bond network of bulk water is perturbed similarly in these systems. If the virtually identical spectra indicate the same hydrogen bond network structure, hydrogen bond dynamics would be expected to be the same. However, the four systems are quite different at the molecular level. The distances and angles between hydrogen bond donors and acceptors affect the
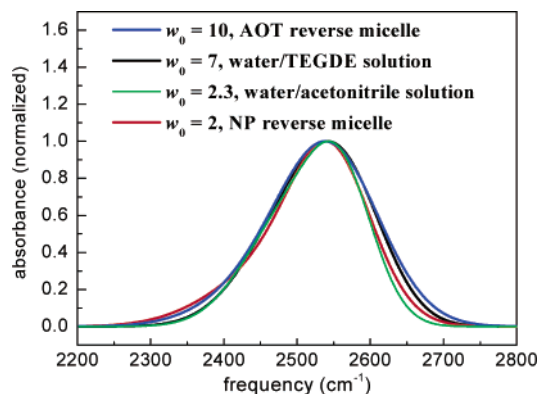

Figure 1. Background subtracted FTIR absorption spectra of the OD stretch mode of 5% HOD in H_2O for different chemical systems. w_0 values denote molar ratios for the solutions. All spectra peak at ∼2540 cm^{-1}.

spectra.[14] The hydrogen bonding interactions between water molecules and headgroups in reverse micelles or nonwater species in the other samples may be quite different and influence the spectra for different reasons. Therefore, despite the concurrence of the spectra, it is not a priori evident that the dynamics will be the same in the various samples. Water molecules involved in various hydrogen bonding arrangements have been discussed for bulk water.[2,3,15] Because all the IR spectra in Figure 1 are blue-shifted relative to bulk water (peak at 2510 cm^{-1}), they are generally believed to report on the presence of fewer and/or weaker hydrogen bonds,[10−13] suggesting equivalent properties in all samples. However, probing these systems' dynamics using nonlinear spectroscopic methods reveals that these similar systems differ significantly.

Mid-IR pump−probe spectroscopy is a nonlinear spectroscopic technique that can measure vibrational energy relaxation and molecular orientational relaxation.[16] Here, two separate polarized mid-IR light pulses (∼60 fs duration) from an optical parametric amplifier pumped by an amplified ultrafast laser system are focused into a sample.[16] The polarized pump pulse excites molecules to the first vibrationally excited state. Due to the anharmonic potential of the OD stretch mode, molecules pumped into the first excited state no longer absorb IR light at the same frequency as the ground state, leading to increased transmission of a probe pulse. The increased transmission decays as population relaxes back to the ground state with vibrational lifetime (T_1). Because the pump pulse excites a subset of water molecules preferentially oriented with respect to its polarization, reorientation of water molecules affects transmission of a polarized probe pulse. Population relaxation and orientational relaxation are separated by measuring the transmission of the probe pulse at two different polarizations relative to the pump pulse.[16]

The population relaxation decays and orientational anisotropy decays displayed in Figure 2a,b differ for the four samples. (Fit
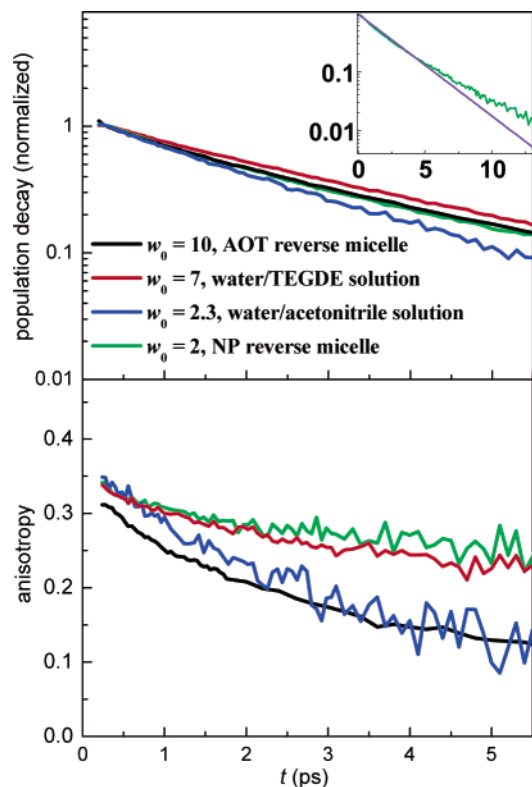
Figure 2. (a) Vibrational lifetime decays of the OD stretch mode of 5% HOD in H_2O for different chemical systems. The inset contains the lifetime decay for the $w_0 = 2$ nonionic reverse micelle along with a single-exponential fit (violet). (b) Anisotropy decays for the same systems. Data are presented for $t > 200$ fs because of a short time nonresonant signal.

values are given in Table S1 of the Supporting Information.) T_1 values obtained from single-exponential fits to the traces in Figure 2a range from 2.1 to 3.0 ps, although all the decays fit better to biexponentials as shown for one of the samples in the inset. The presence of more than one component in the vibrational lifetime decays strongly suggests the existence of more than one ensemble of hydrogen bonding environments. Two distinct subensembles corresponding to two environments have been observed for water in AOT reverse micelles.[16] The orientational anisotropies in Figure 2b also vary substantially. Single-exponential fits through these data reveal decays ranging from ∼5 to 19 ps. The presence of a universal fast vibrational component (<50 fs) leads the anisotropies to extrapolate to smaller values than the theoretical limit of 0.4 at $t = 0$. Complete orientational relaxation of water requires hydrogen bond network randomization (making and breaking of hydrogen bonds). The distribution of hydrogen bonding strengths will affect orientational relaxation as has been suggested for bulk water.[17] Since IR spectra are typically interpreted to report on the strength and degree of hydrogen bonding,[10–13] from Figure 1, the orientational relaxation might be expected to be similar in all of the samples. The data clearly demonstrate otherwise. Furthermore, the model of weakening of the H-bond network associated with a blue shift of the IR spectra relative to bulk water may lead to the conclusion of faster orientational relaxation. Yet all the samples relax more slowly than water, whose orientational decay time is 2.6 ps.[16,18]

The orientational relaxation times of the samples vary substantially. These observations are consistent with the notion that water reorientational motions become hindered when water molecules are interacting with headgroups of reverse micelles and the other systems studied. The different orientational relaxation times indicate that dissimilar environments have diverse affects on the time scale of hydrogen bond rearrangement.

Structural information can also be inferred from the anisotropy decays. The slow reorientational motion of water in the TEGDE solution indicates that water molecules bind to the ether oxygen atoms. The chemical similarity of TEGDE and the NP surfactant along with the virtually identical IR spectrum might suggest similar hydration of the surfactant polyether chain. However, the 7 waters per 5 ether oxygens in TEDGE is significantly more than the 2 waters per 5 ether oxygens in the NP reverse micelles. This leads to the expectation that the anisotropies would look dramatically different; Figure 2b shows otherwise. Experiments on TEGDE (not shown) with 2 waters per 5 ether oxygens show very slow orientational relaxation. The results for NP demonstrate that the water is pooled rather than binding to the ether oxygens, as it does in the TEGDE solutions.

The structural and dynamical differences among these four systems cannot be discerned from their linear−IR absorption spectra. Substantial differences exist, although the spectra are virtually identical. As a result, higher order vibrational spectroscopies are very useful for unraveling the underlying structural and dynamical properties of water in complex environments.

Supporting Information Available: Experimental details, data analysis, and results. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Henri-Rousseau, O.; Blaise, P. *Adv. Chem. Phys.* **1998**, *103*, 1−186.
(2) Walrafen, G. E. *J. Chem. Phys.* **1968**, *48*, 244−251.
(3) Senior, W. A.; Verrall, R. E. *J. Phys. Chem.* **1969**, *73*, 4242−4249.
(4) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman and Co.: San Francisco, 1960.
(5) Deak, J. C.; Rhea, S. T.; Iwaki, L. K.; Dlott, D. D. *J. Phys. Chem. A* **2000**, *104*, 4866−4875.
(6) Asbury, J. B.; Steinel, T.; Stromberg, C.; Corcelli, S. A.; Lawrence, C. P.; Skinner, J. L.; Fayer, M. D. *J. Phys. Chem. A* **2004**, *108*, 1107−1119.
(7) Fecko, C. J.; Eaves, J. D.; Loparo, J. J.; Tokmakoff, A.; Geissler, P. L. *Science* **2003**, *301*, 1698−1702.
(8) Woutersen, S.; Emmerichs, U.; Nienhuys, H.-K.; Bakker, H. J. *Phys. Rev. Lett.* **1998**, *81*, 1106−1109.
(9) Sumi, H.; Marcus, R. A. *J. Chem. Phys.* **1986**, *84*, 4894−4914.
(10) Onori, G.; Santucci, A. *J. Phys. Chem.* **1993**, *97*, 5430−5434.
(11) Scatena, L. F.; Brown, M. G.; Richmond, G. L. *Science* **2001**, *292*, 908−912.
(12) Stangret, J.; Gampe, T. *J. Phys. Chem. A* **2002**, *106*, 5393−5402.
(13) Nickolov, Z. S.; Ohno, K.; Matsuura, H. *J. Phys. Chem. A* **1999**, *103*, 7544−7551.
(14) Lawrence, C. P.; Skinner, J. L. *Chem. Phys. Lett.* **2003**, *369*, 472−477.
(15) Kropman, M. F.; Bakker, H. J. *Science* **2001**, *291*, 2118−2120.
(16) Piletic, I. R.; Moilanen, D. E.; Spry, D. B.; Levinger, N. E.; Fayer, M. D. *J. Phys. Chem. A* **2006**, *110*, 4985−4999.
(17) Nienhuys, H. K.; van Santen, R. A.; Bakker, H. J. *J. Chem. Phys.* **2000**, *112*, 8487−8494.
(18) Rezus, Y. L. A.; Bakker, H. J. *J. Chem. Phys.* **2005**, *123*, 114502(1)−114502(7).

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