Dynamics of Water Molecules in Aqueous Solvation Shells

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We report on the direct measurement of the dynamics of water molecules in the solvation shell of an ion in aqueous solution. The hydrogen-bond dynamics of water molecules solvating a Cl^-, Br^-, or I^- anion is slow compared with neat liquid water, indicating that the aqueous solvation shells of these ions are rigid. This rigidity can play an important role in the overall dynamics of chemical reactions in aqueous solution. The experiments were performed with femtosecond midinfrared nonlinear spectroscopy, because this technique allows the spectral response of the water molecules in the solvation shell to be distinguished clearly from that of the other water molecules in the solution.

The essential role of water in chemical processes is closely connected to the dynamics of the aqueous solvation shells of the reacting molecules. For instance, many reactions only occur after water molecules have been removed from the solvation shells. The structure and dynamics of solvation shells therefore form important subjects of investigation.

A complication in studying aqueous solvation is that the response of the water molecules in the solvation shells cannot easily be distinguished from the response of the molecules in the bulk. For instance, dissolving salt into water leads to a change of the O–H stretch absorption band of the water molecules (*1*, *2*), but this change results both from the presence of additional absorption bands of the solvating water molecules and from a change in the bulk water structure. Furthermore, the cross sections of these absorption components are affected by the strong Coulomb interactions between the dissolved ions and the polarizable water molecules. With linear spectroscopic techniques, these effects cannot be separated. As a result, the O–H stretch absorption band of the solvating water molecules cannot be distinguished, which is unfortunate because, for instance, for water molecules that solvate through a hydrogen bond, the O–H stretch absorption spectrum would give information on the distribution of distances (hydrogen-bond lengths) between the solvating water molecules and the dissolved ion (*3*, *4*).

One way of obtaining highly specific information on solvation structures is by studying small gas-phase clusters consisting of an ion surrounded by a few water molecules (*5–8*). However, it is not clear whether these clusters are really representative of the solvation structures present in bulk water. Specific information on solvation shells can also be obtained by exciting and detecting a dissolved probe molecule (*9*). In this type of experiment, the dynamics of the solvating water molecules are measured through the time-dependent response of the probe molecule. A disadvantage of this technique is that it probes the solvating water molecules indirectly, but, on the other hand, it is the only experimental technique so far that gives information on the dynamics of aqueous solvation shells. Because of the experimental difficulties, most information on the dynamics of aqueous solvation shells originates from molecular dynamics simulations (*10–13*).

Recently, nonlinear spectroscopic techniques that use femtosecond midinfrared laser pulses have been developed that enable a separate measurement of the dynamics of a selected subset of water molecules. With these techniques, the dynamics of neat liquid water [pure liquid H_2O (*14*) and dilute solutions of HDO in D_2O (*14–17*)] and of electrons solvated in water (*18*) have been investigated. Here, we show that nonlinear midinfrared spectroscopy is an ideal technique for studying aqueous solvation shells, because it allows the O–H stretch absorption spectrum of water molecules that solvate through a hydrogen-bond interaction to be separated clearly from the spectral response of the other water molecules. In addition, the technique enables the measurement of the spectral diffusion of the O–H stretch vibrational frequency of the solvating water molecules, providing information on the time scale on which the distance between a solvating water molecule and a dissolved ion/molecule changes.

We performed femtosecond midinfrared pump-probe experiments on the O–H stretch vibration of HDO molecules in an aqueous solution consisting of a low concentration of HDO (0.1 M) in D_2O and different concentrations (1 M, 2 M, 3 M, and 6 M) of KF, NaCl, NaBr, NaI, and $MgCl_2$ (*19*). In the experiment, an intense midinfrared pump pulse excites a substantial fraction of the HDO molecules to the first excited state of the O–H stretch vibration ($\nu_{OH} = 1$). The energy relaxation and spectral relaxation of this excitation are probed with an independently tunable, weak probing pulse that is delayed with respect to the pump pulse. The polarization of the probe pulse is at the magic angle (54.7°) with respect to the polarization of the pumping pulse, to avoid the measurements being affected by the orientational diffusion of the HDO molecules.

Transient spectra were measured for a solution of 6 M NaI in HDO:D_2O at four different delays after excitation with an intense pump pulse at 3400 cm^{-1} (Fig. 1). This excitation leads to a bleaching of the $v = 0 \rightarrow v = 1$ transition [$\ln(T/T_0) > 0$, with T the transmission of the probe and T_0 the transmission of the probe in absence of the pump] in the frequency region between 3300 and 3600 cm^{-1} and an induced $v = 1 \rightarrow v = 2$ absorption [$\ln(T/T_0) < 0$] at frequencies below 3300 cm^{-1}.

At short delays after the excitation, the maximum of the bleaching is near the central frequency of the pump (vertical dashed line in Fig. 1). The bleaching is substantially nar-

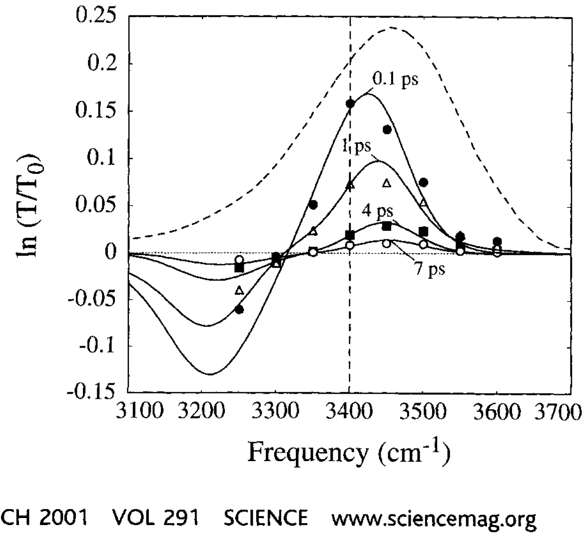

Fig. 1. Transient spectra of an aqueous solution of NaI (6 M) in HDO:D_2O. The spectra were measured at four different delays after excitation of the O–H stretch vibration with an intense pump pulse with a central frequency of 3400 cm^{-1}. The solid curves were calculated with the Brownian oscillator model described in the text in which an additional excited-state absorption term is included to account for the induced absorption observed at frequencies below 3300 cm^{-1} (*19*). The dashed curve represents the linear absorption spectrum.

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rower (≈120 cm^{-1}) than the width of the linear absorption spectrum (≈250 cm^{-1}, dashed curve). The excitation thus leads to a spectral hole in the O–H stretch absorption band; that is, only a subset of the O–H oscillators is excited.

For directional O–H···X hydrogen bonds, the relation between the O–H stretch frequency and the length of the O–H···X hydrogen bond is the same for different types of ionic and molecular systems in the solid and the liquid phase (*3*, *4*). This universal behavior can be explained from the fact that the O–H bond itself is not very sensitive to local electric fields, in contrast to the strongly polarizable O–H···X hydrogen bond. Hence, variations in local electric field strength, for example, as a result of differences in local liquid configuration, affect the O–H stretch frequency mainly by influencing the length of the O–H···X hydrogen bond. As a result, for an O–H···X system, the width of the O–H absorption band is strongly correlated with the width of the distribution in hydrogen-bond lengths, as is observed, for example, for the O–H stretch vibration of HDO dissolved in D$_2$O (*16*, *17*). Hence, the excited spectral hole in the O–H stretch absorption band corresponds to a specific subset of the distribution in hydrogen-bond lengths.

The bleaching signal was measured at different pump and probe frequencies as a function of delay for a solution of 3 M NaI in HDO:D$_2$O (Fig. 2) and for a solution of 1 M NaCl in HDO:D$_2$O (Fig. 3).[4] For all transients, the decay is strongly nonexponential and consists of a rapid decay followed by a much slower decay. All transients can be modeled well as a sum of two exponentials, one with a time constant of 800 femtoseconds (fs) (fast component) and one with a time constant of 3.0 picoseconds (ps) for the NaI solution and 2.3 ps for the NaCl solution (slow component). By tuning the probe pulse through the absorption band, we found that the slow component has the largest amplitude near a frequency of 3500 cm^{-1} for the NaI solution and near a frequency of 3450 cm^{-1} for the NaCl solution.

To investigate the origin of the slow component, we varied the concentration and performed experiments on solutions of KF, NaBr, and MgCl$_2$. The amplitude of the slow component scales linearly with the concentration of dissolved salt. At concentrations below 1 M, the slow component remains observable. Changing the nature of the cation has no effect on the experimental observations: Solutions of MgCl$_2$ and NaCl give exactly the same results as long as the concentration of Cl$^-$ is the same. In contrast, the nature of the anion strongly affects the time constant of the slow component. For I$^-$, Br$^-$, Cl$^-$, and F$^-$, we observe time constants of 3.0, 2.7, 2.3, and 0.8 ps, respectively. In view of these observations, the slow component is assigned to water molecules that solvate the anion.

The independence of the experimental observations on the nature of the cation suggests that water molecules that solvate cations have very similar absorption spectra and dynamics as bulk water molecules. Previous work on clusters of Na$^+$ and water molecules showed that for the water molecules that directly surround the Na$^+$ ion, the O–H groups point away from the cation (*20*, *21*) and are expected to form O–H···O hydrogen bonds with bulk water molecules. As a result, the water molecules solvating Na$^+$ show very similar dynamics as the O–H···O oscillators in bulk water and thus contribute to the observed fast component with a T_1 of about 800 fs.

For water molecules solvating a halogenic anion, the O–H groups point toward the anion, leading to the formation of directional O–H···Y$^-$ hydrogen bonds (*1*, *11*, *22*). The lifetime of the O–H···Y$^-$ oscillators, with Y$^-$ = Cl$^-$, Br$^-$, or I$^-$, is surprisingly long compared with the lifetime of O–H···O oscillators. For O–H···F$^-$, the lifetime of the O–H stretch vibration is the same as for the O–H···O oscillator. The increase in lifetime from F$^-$ to I$^-$ can probably be explained from the change in the strength of the O–H···Y$^-$ hydrogen-bond interaction. From F$^-$ to I$^-$, this hydrogen bond becomes weaker and the hydrogen-bond frequency strongly decreases. Both effects will lead to a decrease of the anharmonic interaction between the O–H stretch vibration and the hydrogen bond.

After a few picoseconds, all the excited O–H···O oscillators have relaxed and only excited O–H···Y$^-$ oscillators are observed. Hence, the transient spectra shown in Fig. 1 after 4 and 7 ps are absorption spectra of O–H···I$^-$ oscillators only. This observation demonstrates an important advantage of time-resolved nonlinear spectroscopy over conventional continuous wave spectroscopic techniques: The response of the water molecules that solvate the Cl$^-$, Br$^-$, or I$^-$ can be separated with high selectivity from the response of all other water molecules by simply choosing the appropriate delay-time window.

Analysis of the transients of Figs. 2 and 3 at longer delay times (>3 ps) shows that the final exponential decay depends on the probe frequency. In Fig. 2, the final exponential decay constants are 2.5, 2.7, and 3.1 ps for probe frequencies of 3600, 3550, and 3500 cm^{-1}, respectively. In Fig. 3, the final exponential decay constants are 1.6, 2.0, 2.1, and 2.3 ps for probe frequencies of 3600, 3550, 3500, and 3450 cm^{-1}, respectively. Such a dependence of the exponential decay constant of the O–H···Y$^-$ component on the probe frequency is observed for all aqueous solutions containing Cl$^-$, Br$^-$, or I$^-$ ions and is observed at all concentrations.

The observation of persistently different final exponential decay times can have two different origins. First, the transients may be affected by a slow stochastic modulation of the O-H···Y$^-$ hydrogen bond with a characteristic time scale of about 10 ps. This would mean that the frequency of an excited O-H oscillator changes on the experimental time scale from the frequency at which it was excited to another value within the absorption band. This effect would result in a faster decay of the bleaching when the probe frequency is near the pump frequency and in a slower decay when the pump and probe frequencies are different, as is observed in Figs. 2 and 3. Second, the O–H···Y$^-$ absorption band could show no spectral modulation, but then the vibrational lifetime should be frequency dependent, being shorter at the blue side of the O–H···Y$^-$ absorption band than in the center. In the latter case, the observed decay should depend predominantly on the probe frequency and hardly on the pump frequen-

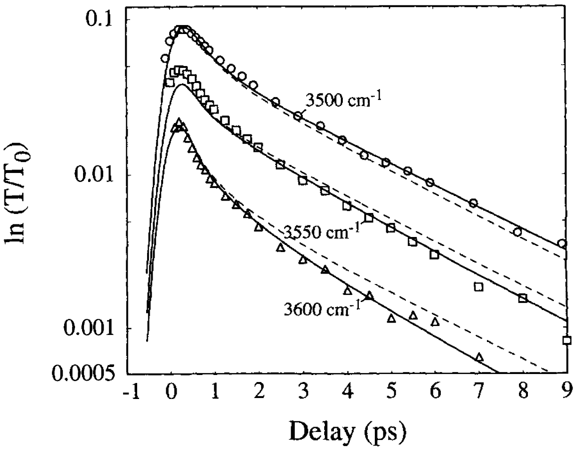

Fig. 2. Transmission changes as a function of delay between pump and probe for a central frequency of the pump of 3575 cm^{-1} and three different probe frequencies, measured for an aqueous solution of NaI (3 M) in HDO:D$_2$O. The solid curves were obtained with the Brownian oscillator model described in the text, with the following parameters: O–H···O oscillator: T_1 = 800 ± 100 fs, τ_c = 500 ± 200 fs, ω_0 = 3420 ± 10 cm^{-1}, and Δ = 119 ± 10 cm^{-1} [corresponding to a full width at half maximum (FWHM) of 280 cm^{-1}]; O–H···I$^-$ oscillator: T_1 = 3.0 ± 0.2 ps, τ_c = 18 ± 5 ps, ω_0 = 3500 ± 10 cm^{-1}, and Δ = 45 ± 5 cm^{-1} (corresponding to a FWHM of 105 cm^{-1}). The dashed curves represent the result of a calculation with τ_c = ∞.

cy. However, we observe that the time constant of the final exponential decay also strongly depends on the pump frequency. For instance, if the pump frequency is below 3500 cm^{-1}, the decay at 3600 cm^{-1} is slower than at 3500 cm^{-1}. This observation rules out the possibility of infinitely slow spectral diffusion. We conclude that the O—H···Y$^-$ hydrogen-bond length is subject to a stochastic modulation process with a characteristic time scale of about 10 ps, which is extremely slow compared with the stochastic modulation of the O—H···O hydrogen bond in neat liquid water, which has a characteristic time constant of only 500 fs (*23*). As a result, the transient spectrum rapidly equilibrates, so that for neat liquid water already after about 1 ps the decay rate becomes independent of the probe frequency.

To determine the correlation time constants of the stochastic modulation of the O—H···O and O—H···Y$^-$ hydrogen bonds, we modeled the data with the Brownian oscillator model (*24*). In this model, the spectral dynamics is described with only two parameters: (i) the correlation time constant τ_c representing the time scale at which the hydrogen-bond length is stochastically modulated and (ii) the width Δ of the Gaussian distribution $e^{-\omega^2/2\Delta^2}$ of O—H stretch frequencies, representing the width of the distribution in hydrogen-bond lengths. It should be noted that there can be additional contributions to the absorption line width that do not express themselves in the distribution in hydrogen-bond lengths. In view of the strong correlation between the O—H stretch frequency and the hydrogen-bond length, these contributions will be small (*3*, *4*). Because of these contributions, Δ can be somewhat smaller than the experimentally observed absorption line width.

For all solutions, we obtained an excellent fit using two Brownian oscillators that represent the O—H···O and O—H···Y$^-$ (with Y$^-$ = Cl$^-$, Br$^-$, I$^-$) components of the absorption spectrum. The transients measured at different probe frequencies were fitted simultaneously to determine the value of τ_c with the highest possible accuracy. For all solutions, the parameters of the O—H···O oscillator correspond very well to the values observed for neat liquid water (*17*). In contrast, the parameters of the O—H···Y$^-$ oscillators strongly differ from those of bulk water. The time constant τ_c of the O—H···Y$^-$ oscillator ranges from 12 to 25 ps, which is 20 to 50 times longer than the value of τ_c (500 fs) of the O—H···O oscillator. The value of τ_c of the O—H···Y$^-$ oscillator depends somewhat on the anion Y$^-$ and on concentration: Increasing the concentration from 1 to 6 M changes τ_c from 18 ± 5 to 25 ± 5 ps for a solution of NaI and from 12 ± 4 to 20 ± 5 ps for a solution of NaCl. For the O—H···Br$^-$ oscillator (*25*), the parameters are similar to those of the O—H···I$^-$ oscillator. For the O—H···F$^-$ oscillator, τ_c could not be determined, because the vibrational lifetime of the water molecules that solvate the F$^-$ ion is too short.

The large difference in τ_c between bulk liquid water and the aqueous solvation shells of Cl$^-$, Br$^-$, and I$^-$ likely results from differences in structure between bulk liquid water and aqueous solvation shells. For bulk liquid water, the disordered three-dimensional structure allows the simultaneous breaking and formation of hydrogen bonds. As a result, the energy cost of locally breaking a hydrogen bond will be low (and thus τ_c is short), because it can be compensated for by the simultaneous formation of a new hydrogen bond at a different position. For aqueous solvation shells, the removal of a water molecule from the first solvation shell involves a breakdown of the solvation structure, which will have a high associated energy cost that cannot be as easily compensated for as in bulk liquid water. This means that the large τ_c of the solvation shell is not the direct result of the interaction between the ion and the surrounding water but rather results from the mutual interactions of the water molecules in the solvation shell in combination with their well-ordered arrangement around the ion. An interesting observation is that τ_c is somewhat longer for the solvation shells of Br$^-$ and I$^-$ than for the solvation shell of Cl$^-$. This observation indicates that τ_c is probably determined not only by the binding energy of a water molecule in the solvation shell but also by the frequency of the (deformational) vibrations of the solvent cage. Hence, τ_c could be shorter for Cl$^-$ than for Br$^-$ and I$^-$, because the solvation shell of Cl$^-$ is smaller, leading to higher frequency solvent-cage modes.

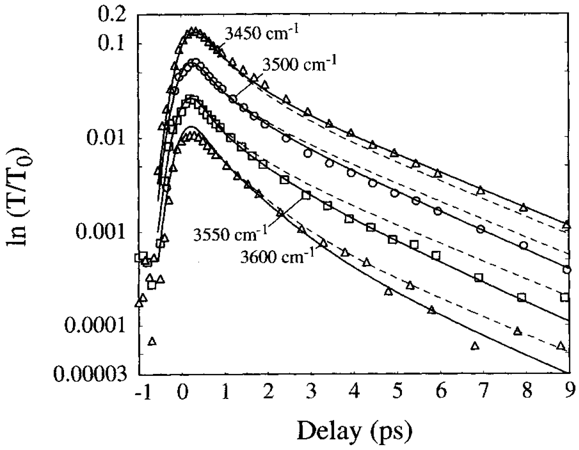

Fig. 3. Transmission changes as a function of delay between pump and probe for a central frequency of the pump of 3525 cm^{-1} and four different probe frequencies, measured for an aqueous solution of NaCl (1 M) in HDO:D$_2$O. The solid curves were calculated with the Brownian oscillator model. For the O—H···O oscillator, the parameters were the same as in Fig. 2; for the O—H···Cl$^-$ oscillator, they were T_1 = 2.3 ± 0.2 ps, τ_c = 12 ± 4 ps, ω_0 = 3450 ± 10 cm^{-1}, and Δ = 69 ± 5 cm^{-1} (corresponding to a FWHM of 160 cm^{-1}). The dashed curves represent a calculation with $\tau_c = \infty$.

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19. The midinfrared pulses are generated through parametric generation and amplification in BBO and KTP crystals. These nonlinear frequency-conversion processes are pumped with the output of a Ti:sapphire regenerative/multipass amplifier (800 nm, 3 mJ, 100 fs, 1 kHz). The generated midinfrared pulses are tunable between 2.7 and 4 μm and have a typical pulse energy of 20 μJ and a pulse duration of about 200 fs. The spectral bandwidths of the pump and probe pulses are 80 and 60 cm^{-1}, respectively.
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