



Love and Fear of Water: Water Dynamics around Charges and Apolar Solutes
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Summary

Water molecules are deceptively simple considering their importance to many (biological) processes. Since a number of decades it has become clear that the interesting properties of water and its role in these processes can be attributed to the ability of water molecules to form up to four hydrogen-bonds. Key aspects to consider in this context are the characteristics of water in the vicinity of electric charges and hydrophobic groups. In this thesis we describe a number of studies on the vibrational relaxation and reorientation dynamics of water molecules in aqueous solutions. These processes take place on a picosecond timescale and have been found to be sensitive probes of the hydrogen-bond network. The experimental technique that we used is polarization resolved femtosecond infrared pump-probe spectroscopy. This technique uses extremely short laser pulses (100 femtoseconds) to excite a molecular vibration in a small subset of the water molecules. The excited molecules have a different absorption spectrum than those in the ground state and this transient absorption difference is probed by a second laser pulse. By varying the waiting time between the pump and probe pulses, the time dependent behavior of the transient absorption differences are obtained. These time dependent data provide information on dynamical parameters of the system like hydrogen-bond dynamics and molecular reorientation. In the following paragraphs we summarize our findings on the structure and dynamics of water in solutions of salts and amphiphilic molecules that we obtained with this technique.

VIBRATIONAL DECAY IN PURE WATER In chapter 5 we demonstrated that the vibrational relaxation time T_1 of the OH stretch vibration in pure liquid water depends on the strength of the local hydrogen-bond interaction. The resonance frequency of weakly hydrogen-bonded OH groups of water is blue-shifted with respect to that of strongly hydrogen-bonded OH groups. By varying the spectrum of the pump pulse we could thus selectively excite a subset of OH groups that donate hydrogen-bonds of a certain strength. We found that the T_1 lifetime shows a smooth transition between $T_1 = 220$ fs for strongly hydrogen-bonded OH groups to $T_1 = 560$ fs for weakly hydrogen-bonded OH groups. These values were found to be consistent with a kinetic model including spectral diffusion, Förster transfer, and vibrational relaxation via energy transfer to the overtone

of the H₂O-bending mode. In addition, we showed that the OH stretch overtone absorption band mainly represents weakly hydrogen-bonded OH groups due to an interference effect of the electrical and mechanical anharmonicities of the OH vibration. After excitation, the overtone decays extremely rapidly to the first excited state. The subsequent decay to the ground state shows the same characteristics as found after direct excitation of weakly hydrogen-bonded OH groups.

JUMP REORIENTATION OF WATER In chapter 6 we studied the reorientation dynamics of water. To avoid certain experimental difficulties, these experiments were performed by exciting the OD stretch vibration of HDO molecules in isotopically diluted water (8% HDO in H₂O) instead of using pure H₂O. After excitation the transient absorption changes were monitored with a probe pulse that is polarized either parallel or perpendicular to the pump polarization. From these two signals, a parameter can be constructed that exclusively represents the reorientation dynamics of the excited OD groups. It was predicted by molecular dynamics simulations that water molecules do not rotate in a diffusive fashion, but rather make small rotational jumps in which a hydrogen-bond is broken and a new hydrogen-bond is formed with another water molecule. We excited a subset of OD groups that donate a very weak hydrogen-bond and have a large probability to be close to a jump. The reorientation dynamics that we obtained were fully consistent with the jump model of reorientation. In addition, we found that for increasing temperatures the rate of jumps increases. From these results we derived that the activation energy of the jumping mechanism is 11 kJ/mol.

SLOW WATER AROUND HYDROPHOBIC GROUPS In chapter 7 we studied the reorientation dynamics of water in a concentrated solution of tetramethylurea (TMU) in isotopically diluted water. TMU contains four methyl groups and has shown to be an ideal model system to study hydrophobic hydration. We found that both the reorientation dynamics and spectral diffusion of water molecules are much slower in the TMU solution than in neat water. Our results show that the translational motion of water molecules around hydrophobic groups is hindered. As a result, it is harder for a water molecule to increase the distance to its hydrogen-bonding partners and to allow a possible new partner to approach. Such a configurational change is needed to enable a reorientational jump. The slow reorientational dynamics thus follow directly from the slower structural diffusion. With increasing temperature we found that both the structural diffusion and the reorientation dynamics speed up, consistent with previous findings that show that the effects of hydrophobes on the dynamics of water strongly decreases at higher temperatures.

COOPERATIVE EFFECTS IN ION HYDRATION In chapters 8 and 9 we studied the reorientation dynamics of water molecules in (halide) salt solutions using a similar experiment as described above. The spectral blue-shift of the OD-stretch resonance frequency of halide bound water molecules enabled us to specifically isolate the response of these water molecules. We found a number of contribu-

tions to the observed dynamics: 1) a wobbling motion with a time constant of 2.0 ± 0.3 ps, 2) a slow motion with a time constant of 9 ± 1 ps that we associate with the rotational diffusion of the water molecule over the anion surface and 3) a component due to the exchange of water molecules inside and outside the anion solvation shell. Anions with a smaller radius interact more strongly with their solvation shell and thus have a larger restricting effect on the wobbling motion. We found that the nature of the cation can limit the freedom of the wobbling motion even further, but only if its surface charge density is sufficiently high. Highly charged anions and cations (or ionic molecular groups) were found to participate in a water complex, in which the solvating water molecules are severely hindered in their reorientation due to the combined effect of the cation and the anion.

COMBINED EFFECTS OF HYDROPHOBES AND IONS Cations of the class of tetra-*n*-alkylammonium (TAA) salts contain hydrophobic groups in the form of four alkyl chains. For such systems the question arises whether the charged nature or the hydrophobic nature is more dominant in the hydration properties. In chapter 10 we studied TAABr salts with various alkyl lengths and thus hydrophobicity using the same analysis techniques as for the halide salts in previous chapters. We find that even for the shortest alkyl chains (Me_4NBr), the reorientation dynamics of the water solvating the cation is slower than in bulk water, consistent with the picture of hydrophobic hydration. In addition, at high concentrations the wobbling component of OD groups hydrogen-bonded to halide ions that we found in previous chapters was found to be severely hindered by the presence of the hydrophobic cations. The cations with long alkyl chains (Et_4NBr , Pr_4NBr , Bu_4NBr) form clusters with bromide ions and water molecules. The water molecules inside these clusters are highly confined, causing the reorientation of OD groups bound to the bromide ions that penetrated such a cluster to become even slower than 30 ps. For Me_4NBr such aggregation effects are not observed, probably because for this ion the repulsive coulomb interaction is strong enough to prevent the formation of large aggregated ion clusters. Continuing on these results, we made a comparison between urea, tetramethylurea, guanidinium chloride and tetramethylguanidinium chloride in chapter 11. In line with previous results we found that methylation of urea and guanidinium chloride results in a large fraction of water molecules with slower dynamics. These four compounds were compared in their ability to denature a model peptide. We found that the methyl substituted compounds likely have a different mechanism of denaturation compared to the unmethylated compounds.