Molecular motions of water: The effect of charged and hydrophobic solutes
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Summary

Aqueous systems and spectroscopy

Water plays an important role in our everyday lives, which we experience for instance when we drink, cook, clean, wash, etc. Its importance is also evident on a microscopic level: almost all biological processes occur in aqueous environments. Therefore investigating the interactions between different solutes and the water solvent is highly relevant.

In this thesis, we have studied (i) neat water, and aqueous systems containing three different solutes: (ii) ions, (iii) protons and (iv) amphiphiles. We study the reorientation dynamics of the water molecules in these systems. To this end we have used terahertz time-domain spectroscopy and femtosecond infrared pump-probe spectroscopy. Both measurement techniques are very well suited for studying the ultrafast dynamics in aqueous systems and they are sensitive to the same water reorientation process. Since they probe water reorientation in a different way, these techniques have complimentary advantages.

In terahertz (THz) time-domain spectroscopy, a THz pulse with a duration of $\sim 3$ ps is created and focused into the sample under investigation. In aqueous systems, the main process that is active at low THz frequencies ($< 1$ THz) is dielectric relaxation. This is the effect that water molecules are unable to keep up reorienting with an oscillating electric field, when the driving frequency becomes too high. For bulk water, this results in an absorption peak at 20 GHz, corresponding to a reorientation time scale of 8 ps. Terahertz dielectric relaxation measurements were used to determine the fraction of water molecules that are affected by the presence of a solute and as a result no longer participate in the reorientation process, thus leading to a smaller relaxation strength of the 20 GHz peak. This technique also provides information on the fraction of water molecules that is affected by the movement of charged solutes.

In the femtosecond infrared (fs-IR) pump-probe measurements, we used a linearly polarized infrared pump pulse with a duration of $\sim 150$ fs to resonantly excite the OD-stretch vibration of a subset of HDO molecules in H$_2$O. With a probe pulse that followed after a variable delay, we monitored these vibrationally excited molecules. This was done for pump and probe pulse mutually parallel and perpendicular. Since the pump pulse excites an anisotropic distribution, the probe signal with parallel polarization is larger than for perpendicular polarization. However, after reorientation of the water molecules, the distribution of excited molecules is isotropic and the parallel and
perpendicular signals are equal. Hence, by examining the difference between the two signals as a function of pump-probe delay, we obtained the reorientation dynamics of the water molecules.

**(i) Neat water: the effect of temperature**

We have studied the temperature dependence of the molecular reorientation of HDO molecules in H₂O with fs-IR spectroscopy. This resulted in the second order microscopic reorientation time, which changes from $4.8 \pm 0.3$ ps at $1 \degree C$ to $0.97 \pm 0.05$ ps at $70 \degree C$. These measurements were compared with literature results of THz time-domain spectroscopy, where the first order macroscopic reorientation time is obtained. From this comparison, we extracted the ratio between the macroscopic first order reorientation time and the second order microscopic reorientation time. It turned out that this ratio does not depend on temperature, confirming that the same reorientation process is probed, using the two different techniques.

**(ii) Ions: semi-rigid hydration and cooperativity**

We have studied the effect of ions on the dynamics of water molecules using fs-IR and THz spectroscopy. These techniques are sensitive to the dynamics of different vectors of the water molecule: the dipole vector (THz) and the transition dipole moment (fs-IR). The measurement of these two different molecular vectors revealed that ions with a weakly hydrated counterion are surrounded by a semi-rigid hydration shell. Cations are surrounded by a semi-rigid hydration shell, where water molecules move in a propeller-like fashion with the two hydrogen atoms acting as the rotor blades. In the case of anions, one hydrogen atom points towards the ion and the other hydrogen atom forms the blade of the propeller. Surprisingly, if strongly hydrated cations and anions are combined (as in a MgSO₄ solution), the effect of the ions on water is strongly interdependent and non-additive, and extends well beyond the first solvation shell of water molecules directly surrounding the ion.

**(iii) Protons: mobility and the role of water reorientation**

The high mobility of protons in water is usually attributed to the Grotthuss mechanism, where the interconversion of covalent bonds and hydrogen bonds leads to highly efficient charge transport with limited mass transport. So far, this process was mainly investigated theoretically. We have used THz dielectric relaxation measurements to study the properties of the proton in water. These measurements showed that a small fraction of water molecules no longer participates in the reorientation process, corresponding to $\sim 4$ water molecules per proton, i.e. the Eigen complex [H₉O₄]⁺. We furthermore found that the equivalent of $\sim 15$ water molecules was affected by the moving proton charge. This means that the proton mobility involves a large number of reorienting water molecules.
To assess the connection between proton transfer and the ability of the surrounding water molecules to reorient, we studied proton transfer in water nanopools, in which water reorientation is known to be slower. In this pump-probe experiment, we used a visible pump pulse to electronically excite a photoacid, which is a molecule that becomes highly acidic upon electronic excitation. With the probe pulse (either in the infrared or in the visible regime) that followed after a variable delay, we monitored the dynamics of different modes (either electronic or vibrational) that correspond to the photoacid with or without the proton. This allowed us to follow the dynamics of proton transfer. This experiment was performed for solvated photoacids in reverse micelles with diameters between \( \sim 1.6 \) and \( \sim 5.5 \) nm. The measurements showed that the proton transfer slows down upon decreasing the diameter of the micelle. This result confirms that water reorientation forms the limiting factor for proton mobility.

(iv) Amphiphiles: effects of hydration level and temperature

In biology, the interaction between hydrophobic groups and water plays a crucial role, for instance for the functioning of proteins. We have studied the reorientation dynamics of water molecules around tetramethylurea (TMU), a molecule with four hydrophobic (methyl) groups. This was done for different hydration levels, i.e. TMU concentrations. We performed dielectric relaxation spectroscopy in the GHz\(^b\) and THz range and compared the results with existing fs-IR measurements of aqueous TMU solutions. We found the reorientation dynamics of water molecules in the hydration shell of TMU to be between 3 and 10 times slower than the dynamics of bulk water, depending on the concentration of TMU in water. The data were in good agreement with previous fs-IR measurements, and indicated that the effect of hydrophobic groups on water is strong but relatively short-ranged. We also found that with increasing temperature, the fraction of water contained in the hydrophobic hydration shell decreases, which implies that the overall effect of hydrophobic groups on water becomes smaller.

Finally, we have examined the dynamics of water reorientation in hydrated model membranes, consisting of stacked layers of DOPC lipid bilayers\(^c\). By controlling the number of water molecules per lipid molecule in the system, we studied the interplay between the model membrane and water molecules and its effect on the water dynamics. For decreasing hydration levels, we observed that the collective bulk-like dynamics becomes less pronounced, and that there is an increase of both very slowly reorienting and very rapidly reorienting water molecules. Temperature-dependent measurements revealed the interconversion between these three types of water.

\(^{b}\)The GHz measurements were conducted in the group of prof. R. Buchner at the University of Regensburg (Germany) using electronically created and detected guided waves.

\(^{c}\)DOPC = 1,2-Dioleoyl-sn-Glycero-3-Phosphocholine