Molecular motions of water: The effect of charged and hydrophobic solutes
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Citation for published version (APA):
3 Experimental Techniques

In this chapter we describe the samples on which the measurements in this thesis were performed. Subsequently, we give a general description of the measurement techniques that were used, followed by the experimental realization of these techniques.

3.1 Samples

All samples that are described throughout this thesis have in common that they contain water, for which we used purified (Millipore) water. The substances that we solvated in water for the different measurements were used as purchased. For the measurements in Chapter 5, neat water (4% D$_2$O in H$_2$O) was examined. In Chapters 6 and 7, we used solutions containing the salts NaCl, KCl, CsCl, LiCl, NaClO$_4$, NaI, Cs$_2$SO$_4$, Mg(ClO$_4$)$_2$, LiI, MgCl$_2$, Na$_2$SO$_4$ and MgSO$_4$; and the acids HCl, HClO$_4$ and HI (all from Sigma Aldrich). In Chapter 8, we studied the photoacid 8-hydroxy-1,3,6-pyrenetrisulfonic acid (HPTS) inside a water nanopool, i.e. a reverse micelle formed by either the ionic surfactant sodium diocetyl sulfosuccinate (AOT) in isooctane apolar solvent or the non-ionic surfactant polyoxyethylene(4)lauryl ether (BRIJ-30) in cyclohexane apolar solvent (all chemicals purchased from Sigma Aldrich). The chemical structures of these molecules are shown in Fig. 3.1A-C. In Chapter 9 we describe measurements on mixtures of water with the amphiphilic molecule 1,1,3,3-Tetramethylurea (TMU, >99% purity, purchased from Sigma Aldrich), shown in Fig. 3.1D. Finally, in Chapter 10 we examine stacked lipid bilayers with different hydration levels, consisting of the lipid 1,2-Dioleoyl-sn-Glycero-3-Phosphocholine (DOPC, purchased from Avanti Polar Liquids), shown in Fig. 3.1E.

The different aqueous solutions were contained between windows or in a cuvette of a material that is transparent to light of the wavelength used in the specific measurement: Infrasil Quartz in the case of THz measurements and CaF$_2$ in the case of mid-infrared and visible measurements. To make sure that enough light was transmitted to be detected, an optical path length between 25 and 250 $\mu$m was used. In some cases, the sample cells were equipped with a Peltier element to be able to vary the temperature.
3.2 Measurement techniques

The measurements that are described in this thesis were recorded using the experimental techniques described in the following.

3.2.1 Terahertz transmission spectroscopy

In the terahertz time-domain transmission setup, an optical terahertz pulse (duration $\sim$3 ps) is created and detected with high temporal resolution (<150 fs), as explained in Sections 2.2.3 and 2.2.4. If the terahertz pulse propagates through a medium, it can experience refraction and absorption, the former leading to a delay of the pulse and the latter to a decrease in amplitude of the pulse, with respect to a pulse propagating through air, see Fig. 3.2. Therefore, the comparison of the transmission of THz pulses through air and through a sample enables the determination of the complex refractive index of the sample $\hat{n} = n - i\kappa$, where $n$ is the refractive index and $\kappa$ the extinction coefficient. The
THz pulse that is measured in the time domain contains frequency components in the region 0.2-1.6 THz. Hence, taking the Fourier transform makes it possible to determine the refractive index of the sample as a function of frequency $\nu = \omega / 2\pi$ in this range. In the case of polar liquids, it is most convenient to describe the material properties in terms of the complex dielectric function $\hat{\epsilon} = \epsilon' - i \epsilon'' = \hat{n}^2$. For polar liquids, $\hat{\epsilon}$ shows a marked frequency dependence, which is caused by dielectric relaxation phenomena, i.e. processes related to reorientations of dipoles, as described in Section 2.2. Since water molecules have a permanent dipole moment, this technique is highly suitable for our studies to learn about the reorientation processes in aqueous solutions. This technique was used for the measurements in Chapters 6, 7, 9 and 10.

3.2.2 Infrared pump-infrared probe spectroscopy

Infrared pump-infrared probe spectroscopy is used to probe directly the reorientation of water molecules in time. In this one-color pump-probe technique, the pump and probe pulses have the same wavelength. Here we use infrared pulses that are resonant with the OD-stretch mode of partially diluted water (4% D$_2$O in H$_2$O) to avoid resonant (Förster) energy transfer between excited stretch vibrations (for details, see Chapter 4). The pump pulse excites the OD-stretch mode and the probe pulse examines the pump-induced changes in absorption $\Delta\alpha$, which is the difference in absorption by a sample that was excited by the pump light and the absorption by an unexcited sample. As discussed in Section 2.2.3, $\Delta\alpha$ contains three contributions: induced absorption of the $1 \to 2$ transition, a reduced absorption of the $0 \to 1$ transition (bleach) and...
stimulated emission of the 1→0 transition (see Fig. 3.3). The pump-induced change in absorption does not live indefinitely, but is limited by the vibrational lifetime of the OD-stretch vibration. This results in the decay of $\Delta \alpha$ as a function of time $t$. The decay of $\Delta \alpha(t)$, however, also depends on the polarization of the pump pulse with respect to the probe pulse. The pump pulse will preferentially excite water molecules with their OD-stretch transition dipole moment along the direction of the polarization of the pump pulse, resulting in an anisotropic initial distribution of excited molecules. These excited water molecules randomize their orientation as a function of time, leading eventually to an isotropic distribution. By probing $\Delta \alpha(t)$ for pump and probe pulses with parallel polarizations $\Delta \alpha_\parallel$ and with perpendicular polarizations $\Delta \alpha_\perp$, we can construct the anisotropy $R(t)$, whose decay reflects the reorientation of water molecules, as shown in Chapter 2. Details on constructing $R(t)$ are given in Section 2.3.3. Polarization-resolved infrared pump-infrared probe spectroscopy was conducted for the measurements in Chapters 5, 6 and 7.

Figure 3.3. The left figure is a schematic representation of a typical pump-probe spectrum before pump excitation at time zero ($t_0$) and after $t_0$ for the water OD-stretch region. In the right figure, the potential energy for the OD bond distance of a water molecules is shown with the ground state and the two first excited states. Also a hydrogen-bonded neighboring water molecule is shown. Before $t_0$ all water molecules have their OD-stretch mode in the vibrational ground state $|0\rangle$. After $t_0$, some water molecules have their OD-stretch mode promoted to the first excited state $|1\rangle$. As a result, the probe pulse measures induced absorption from the first to the second excited state, leading to a positive $\Delta \alpha$. Molecules in the first excited state can also decay to the ground state by stimulated photon emission, leading to a negative $\Delta \alpha$. Additionally, since there are fewer molecules to excite from $|0\rangle$ to $|1\rangle$ after $t_0$ than before $t_0$, the $0 \rightarrow 1$ absorption is smaller (bleach), also leading to a negative $\Delta \alpha$. If the potential energy for the OD-bond distance would be perfectly harmonic, the frequencies of the $0 \rightarrow 1$ and the $1 \rightarrow 2$ transition would be the same and $\Delta \alpha(\omega) \equiv 0$. However, the potential energy landscape is anharmonic and can be described by e.g. the Lippincott-Schröder model [7, 94]. Due to this anharmonicity, the induced absorption is spectrally separated from the bleach and the stimulated emission.
3.3 Experimental techniques

3.2.3 Visible pump-infrared probe spectroscopy

In visible pump-infrared probe spectroscopy, the pump pulses have a wavelength in the visible regime, while the probe pulses are in the infrared regime. This typically means that the sample under study undergoes an electronic transition upon interaction with the pump pulse and the effect of this on vibrational modes is studied. In our studies, we use this technique to study, as a function of pump-probe delay time, the release of a proton from a molecule. To study these dynamics, we take the photoacid HPTS, which upon electronic excitation with 400 nm light becomes very acidic, resulting in the release of a proton. The dynamics of this process can then be followed in time through the vibrational modes of the HPTS molecule, some of which are associated with the molecule in the acidic form (with the proton still attached) and with the molecule in the basic form (with the proton fully donated to the water solvent). There are also vibrational modes associated with the proton itself that can be monitored as a function of time. This technique is employed in Chapter 8.

3.2.4 Visible pump-visible probe spectroscopy

In addition to monitoring vibrational modes after an electronic excitation, we also monitor changes in the electronic modes through visible pump-visible probe spectroscopy. We apply this technique to the photacid molecule HPTS to examine the electronic changes that occur while a proton is being released from the molecule to the solvent. To this end, we use a pump pulse of 400 nm and a so-called white light probe that covers a range of colors in the visible regime. In a variant of this technique, we block the probe pulse and measure the time-integrated fluorescence of the molecule after pump excitation. We use the technique of visible pump-visible probe (and the fluorescence measurement technique) in Chapter 8.

3.2.5 Auxiliary measurements

In addition to the techniques described above, we use two standard optical transmission measurement setups to examine the absorptive properties of our samples: a double beam spectrometer in the mid-infrared range (Perkin-Elmer 881) and a spectrometer in the UV-Visible range (Jasco V530). Finally (see Chapter 9), we measured the dielectric properties of samples between 200 MHz and 50 GHz with guided electromagnetic waves that were electronically created and detected by an Agilent E8364B vector network analyzer. These waves were propagated through an open-ended coaxial cable attached to the sample. From the complex reflection coefficient we obtained the dielectric properties of the sample in this frequency range. These measurements were done in the group of prof. R. Buchner at the University of Regensburg (Germany).
3.3 EXPERIMENTAL REALIZATIONS

This section describes the experimental realizations of the measurement techniques as described above. The following 4 figures provide a schematic overview of the different setups, explained in detail in the captions.

![Diagram of experimental setup]

**Figure 3.4. Terahertz probe setup.** A small fraction of the laser output is split into two branches: one to generate THz pulses and one to detect the THz pulses. In the THz generation branch, the 800 nm light (~70 µJ per pulse) is loosely focused in a ZnTe crystal (⟨110⟩ orientation, 1 mm thick), where THz pulses with a duration of ~3 ps are generated through optical rectification, as described in Section 2.2.3 and Fig. 2.5. After filtering out the remaining 800 nm light, the THz beam is first collimated and then focused by parabolic mirrors. A mechanical device (shaker) is used to position two cuvettes (with an optical path length of 103 ± 0.5 µm) alternatively in the THz focus – one containing the sample and one the reference sample that is used for calibration. This mechanical device has a duty cycle of 4 seconds: it averages the transmission through the sample for one second; then it has one second to move to the position where the reference sample is in the focus; after this, the average transmission through the reference sample is measured during one second; and finally it has one second to move back. The transmitted THz pulses are collimated and focused in a second ZnTe crystal. Here, also the 800 nm pulses from the sampling branch are focused after passing through a delay line. The electric field of the THz pulses induces a birefringence in the ZnTe crystal, which causes the 800 nm sampling pulses to change their polarization from linear to slightly elliptical, as explained in Section 2.2.4. The 800 nm sampling pulses are then sent through a λ/4 plate (to enhance the sensitivity to the THz induced birefringence) and then the s and p polarization components are separated by a polarizing beam splitter. The intensities of these components are subsequently measured by a differential detector with balanced diodes. The 800 nm light from the sampling beam passes through a variable delay line, which is used to record the quasi-instantaneous electric field of the THz pulses as a function of delay time τ. A 500 Hz chopper before THz generation blocks every other laser shot for active background subtraction. With a Boxcar amplifier (Stanford Research Systems SR250) and AD card THz pulses that are transmitted through the sample and through the reference sample, are recorded.
3.3 Experimental techniques

Figure 3.5. Infrared pump-infrared probe setup. Part of the 800 nm light from the laser is used to pump a white-light seeded OPA (Spectra-Physics). The resulting idler pulses, with a wavelength of 2000 nm, are doubled in a BBO crystal and the resulting pulses with a wavelength of 1000 nm are then passed through a KNbO$_3$ (KN) crystal, simultaneously with the remaining 800 nm light from the laser. Through difference-frequency mixing, infrared light with a wavelength of 4 µm (corresponding to a frequency of 2500 cm$^{-1}$ or 75 THz) is created. After passing through a long wave pass filter, the infrared light (∼4 µJ) then passes through a wedged CaF$_2$ window, where the transmitted light (∼95%) is used as the pump; the light reflected at the front is used as the probe; and the light reflected at the back is used as the reference. The pump polarization is then rotated by 45° with respect to the probe and reference using a λ/2 plate and focused in the sample (contained between two CaF$_2$ windows separated by a spacer with a thickness around 25 µm) using a parabolic mirror. The pump beam passes through a 500 Hz chopper in order to increase the sensitivity towards pump-induced changes in the absorption of the sample. The probe light passes through a variable delay line, before being focused on the same spot in the sample as the pump light. With the delay line, the timing can be tuned such that the probe arrives before ($t$ negative) or after the pump pulse ($t$ positive). The reference beam, used to correct for pulse to pulse intensity fluctuations, is focused at a different spot in the sample. After passing through the sample, the pulses pass through a polarizer, which rotates between two positions: selecting the polarization component of the probe that is parallel to the pump polarization or the polarization component of the probe that is perpendicular to the pump polarization. The probe and reference beams are spectrally dispersed through a grating in a spectrograph and detected with a 2×32 pixel liquid-nitrogen cooled HgCdTe (MCT) detector (Infrared Associates). After integration of typically a few hundred laser shots in Boxcar amplifiers, the data contains the pump-induced change in absorption $\Delta \alpha(t, \nu)$ of the sample at each frequency pixel $\nu$ for different time delays $t$ for the two polarizations $\parallel$ and $\perp$. 
Figure 3.6. *Visible pump-infrared probe setup.* About 30% of the output of the laser is used for the visible pump branch, where the 800 nm light is frequency doubled in a BBO crystal ($\theta = 29^\circ$, 2 mm thick) to create 400 nm pump pulses. The polarization is then set at magic angle with respect to the probe light with a $\lambda/2$ plate, ensuring that only isotropic signals are measured. The pump (attenuated to $\sim 1 \mu$J) is then focused in the sample that is mounted in a rotating sample holder to avoid photodegradation. The sample is held between two CaF$_2$ windows separated by a teflon spacer with a thickness of 100-200 µm. The probe pulses are tunable infrared pulses with a wavelength between 8 and 2.7 µm (approximately 1250-3700 cm$^{-1}$ or 40-110 THz). These are created by using the remaining 800 nm light (70% of the laser output) to pump a white-light seeded OPA (Spectra-Physics). The resulting signal (1200-1600 nm) and idler pulses (1600-2400 nm) are separated and then overlapped in time and space in a AgGaS$_2$ (AGS) nonlinear crystal to create infrared light through difference-frequency mixing. The infrared light is subsequently split in two equal parts, that serve as the probe pulse and the reference pulse that is used to compensate for pulse to pulse intensity fluctuations. The probe beam is focused on the same spot in the sample as the pump, whereas the reference beam is focused at a slightly different spot. The relative time delay $t$ between the pump and probe pulses is tuned using a variable delay line. A 500 Hz chopper in the pump branch is used to be sensitive only to pump-induced changes in the absorption of the sample $\Delta \alpha$. The frequency-dependent absorption changes are measured using the same detection scheme as in the infrared pump-infrared probe setup (Fig. 3.5).
3.3 Experimental techniques

![Diagram of experimental setup]

**Figure 3.7.** Visible pump-visible probe setup. The generation of the pump beam in this setup is identical to that in the visible pump-infrared probe setup. To generate visible continuum probe pulses, ~1 µJ of the 800 nm light of the probe branch is focused into a 3 mm thick z-cut sapphire substrate to generate a broadband continuum of wavelengths ranging from over 1000 nm to just below 400 nm. These pulses are focused on the same spot in the sample as the pump pulses. The sample and sample holder are the same as in the visible pump-infrared probe setup. The probe pulses are spectrally dispersed with a grating-based spectrograph (Acton) and detected with a home-built diode array detector. By passing the pump beam through a variable delay line and a 500 Hz chopper, the probe pulses are sensitive to the pump-induced absorption changes ∆α of the sample as a function of pump-probe delay time t for a range of probe frequencies (typically 400-700 nm).