Love and fear of water: Water dynamics around charged and apolar solutes

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## Experiment

### 3.1 Mid-Infrared Pump Probe

In this section we describe the femtosecond infrared pump-probe (fs-IR) setups that were used to obtain many results described in this thesis. As elaborated on in chapter 4 the concept of the technique is to excite a vibrational mode with an intense laser pulse, the pump, after which the induced absorption changes are monitored by a weaker probe pulse as a function of the delay time between the two pulses. From the analysis of the absorption changes information is obtained on the vibrational lifetime of the excitation, energy transfer and molecular re-orientation.

#### 3.1.1 One Color Pump-Probe Setup

In a one color pump-probe experiment the pulses have the same spectral shapes. The laser system used in these experiments is a regenerative Ti:Sapphire laser (Hurricane, Spectra-Physics) that generates 800 nm pulses with a duration of 110 fs and energy of 0.9 mJ at a repetition rate of 1 kHz. Using a beamsplitter, the output is split into two portions of 70% and 30% of the total energy. The first part is used to pump a white-light seeded commercial Optical Parametric Amplifier (OPA, Spectra-Physics) based on a $\beta$-bariumborate (BBO) crystal. The angle of the BBO crystal is tuned to generate light at $\sim 1.3 \mu$m (signal) and $\sim 2 \mu$m (idler). The idler is frequency doubled in a second BBO crystal to a wavelength of $\sim 1 \mu$m. This 1 $\mu$m pulse is used as a seed in a parametric amplification process (difference frequency mixing, DFG) in a potassium niobate crystal (KNB) crystal that is pumped with the remaining 30% portion of the 800 nm beam. In the DFG process, mid-IR pulses are generated with a full-width-half-maximum (FWHM) of 100 cm$^{-1}$ that are s-polarized. The central wavelength can be tuned between 2300 cm$^{-1}$ and 2700 cm$^{-1}$ by varying the angles of the crystals. The pulses have a duration of 150 femtoseconds an energy of 5-9 $\mu$J depending on the frequency.

The $\sim 2500$ cm$^{-1}$ pulses are sent onto a wedged CaF$_2$ plate. The transmitted part ($\sim 90 \%$) serves as the pump pulse. The reflection from the front side is sent into a variable delay stage with a time-resolution of 6.6 fs. This fraction
Experiment 3.1

Figure 3.1. Detection scheme of the one-color pump-probe setup. After the long wave pass filter to remove any residual signal and idler (LWP), the polarization of the mid-IR light from the Spectra-Physics OPA is first cleaned-up by a polarizer (P1). The CaF$_2$ wedge (W1) splits the beam in a pump (transmitted), probe (front reflection) and reference pulse (back reflection). The polarization of the pump light is rotated by 45° using a tilting half-wave plate (Λ), after which every second pump pulse is blocked by a chopper. The polarization of the reference pulse is cleaned-up by polarizer P2. All pulses are focussed on the sample S by the 45° parabolic mirror PM1. After this point two detection schemes were used. (1) The polarization components of the probe light parallel and perpendicular to the pump polarization are selected by rotating polarizer P3, after which the probe and reference beams are recollimated on PM2 and guided into the detector. (2) An alternative detection method collects the reflection of a polarizer P3, which is now placed after the recollimating parabolic mirror PM2. The polarization of the reflected beam is cleaned-up by polarizer P4, after which all beams are guided into the detector. The reference beam has in this case been omitted for clarity.

forms the probe. With the delay stage we vary the time delay $t$ between pump and probe. The reflection from the back side of the wedged CaF$_2$ plate serves as a reference pulse. The pump is transmitted through a λ/2 plate to rotate its polarization at 45 degrees with respect to that of the probe. The pump, probe and reference are all focussed in the sample using a gold-coated parabolic mirror, but only the pump and the probe are in spatial overlap. After the sample, a mechanically rotated polarizer selects either the polarization component of the probe pulse parallel or perpendicular to the pump polarization. After recollimation of the beams with a second parabolic mirror, the probe and the reference are dispersed with an Oriel monochromator and detected on two separate lines of an Infrared Associates 3×32 mercury-cadmium-telluride (MCT) detector array. The measurement of the reference thus allows for a frequency-resolved correction for shot-to-shot fluctuations of the probe-pulse energy.

The MCT detector has a third array that allows for a different detection scheme that is used in some of the experiments. This detection scheme is identical to that described above till after the sample. Instead of first selecting the parallel or perpendicular component with the rotating polarizer, the probe
and reference are first recollimated with the parabolic mirror. Subsequently, the probe and reference are transmitted through a static polarizer that is positioned such that the vector normal to its surface is under a small angle with the direction of incident probe beam. The polarizer is aligned such that the transmitted probe light is the polarization component that, at the sample position, is perpendicular to the pump polarization. The reflected light thus yields the parallel component. A small fraction of the perpendicular component is reflected as well and an additional polarizer is placed to clean up the polarization of the reflected beam. Both polarization components are detected simultaneously on different array lines of the MCT detector, thereby reducing the measurement time by half. In addition, synchronous measurement of both polarization components improves the signal-to-noise ratio.

3.1.2 Two Color Pump-Probe Setup

In a two color pump-probe experiment the pulses are generated in two separate infrared generation stages, thereby enabling for different pulse spectra of both pulses. The infrared pulses used for this experiment were generated using the output of a regenerative Ti:Sapphire laser (Coherent), providing pulses at 800 nm with a duration of 35 fs and a pulse energy of 3.5 mJ at a repetition rate of 1 kHz. The output of the laser is split in three portions of interest: (1) 850 µJ to pump a homebuilt optical parametric amplifier (OPA) to generate the probe light, (2) 850 µJ to pump a TOPAS (LightConversion) and (3) 1.3 mJ to pump a difference frequency mixing stage after the TOPAS to generate mid-IR pulses that are used as pump (Fig. 3.2).

The pump pulses are generated by pumping a TOPAS (LightConversion) based on super-fluorescence. The TOPAS down-converts the pulses in a BBO crystal to signal (p-polarized) and idler (s-polarized) pulses in the range of ∼1600 nm till ∼2400 nm with a total energy of 280 µJ. In most experiments the idler pulses are doubled in a 1 mm BBO crystal to create ∼1 µm pulses, which are finally difference frequency mixed with the 1.3 mJ portion of 800 nm light out of the Ti-Sapphire laser. This last conversion step yields light pulses with a central frequency tunable between 2900 cm⁻¹ and 3600 cm⁻¹ (using KTP as DFG crystal) or between 2300 cm⁻¹ and 2800 cm⁻¹ (using LiNbO₃ as DFG crystal). The spectral bandwidth is 150 cm⁻¹ and pulse energy 50 µJ. The cross-correlate between the pump and probe pulses as obtained in a thin germanium window is 150 fs, mainly determined by the pump pulse duration.

To generate the narrow band pump light the idler out of the TOPAS was upconverted to 1000 nm using a relatively long BBO crystal of 4 mm. The acceptance bandwidth of the crystal is thereby used to make the pulse spectrally more narrow. In a third step the doubled idler was difference frequency mixed in a Lithium Niobate (LN) crystal with 1 mJ pulses of 800 nm to generate mid-infrared pulses. The LN crystal we used had a thickness of 10 mm to narrow the spectral bandwidth even further. The light pulses that we eventually obtained had a pulse energy of 16 µJ and a spectral bandwidth of 50 cm⁻¹ full width half maximum (FWHM).
Figure 3.2. Overview of the two-color setup. With beamsplitters BS1 and BS2, the output of the Ti:Sapphire laser is split into three portions. The beam size of one portion is decreased by the mirror telescope CM1-CM2 and used as a pump in a LightConversion TOPAS to generate signal and idler pulses. The signal pulses are removed by a dichroic mirror (DM1), after which the idler is frequency-doubled in a BBO crystal (C1). The beam size of the doubled idler is blown up by a factor of two in telescope L. The doubled idler and another portion of the 800 nm light are spatially overlapped in a second crystal (C2), the nature of which depends on the desired frequency (see text). Temporal overlap is tuned with delay stage D. Dichroic mirror DM3 removes any residual 800 nm and doubled idler.

The homebuild OPA (Fig. 3.3) is built according to the geometry developed by the group of Peter Hamm. The OPA is white-light seeded and generates a signal and idler pulse in a parametric amplification process in a BBO crystal (2 mm), very much like the commercial OPA discussed in the previous subsection. The signal and idler are difference frequency mixed in a silver-gallium-disulfide crystal (1.2 mm), yielding mid-IR pulses of which the wavelength can be tuned between 8 µm and 2.5 µm. At 4 µm wavelength, the pulse energy is 5 µJ, the FWHM of the pulse spectra is 300 cm⁻¹. The generated pulses are s-polarized.

The detection scheme is shown in Fig. 3.4 and is very similar to what was described for the one color setup. Instead of CaF₂ we used a ZnSe wedge to split off larger portions of the output of the homebuild OPA as the probe and reference light. The light transmitted through the wedge is dumped on a beamblock. Close to the sample the polarizations of both the probe and the reference are cleaned using two polarizers. In this setup the third array of the MCT detector is used to detect (a small fraction of) the pump light. During actual measurements this beam path is blocked by a mechanical switch to avoid pump scatter on the probe and reference arrays.

In some experiments we directly used either the signal or the idler pulses directly out of the TOPAS or homebuilt OPA as the pump or probe (chapter 5). A neutral density filter was used to attenuate the pulse energy in case this was
Figure 3.3. The homebuilt OPA, used in the two-color pump-probe setup, is pumped with 800 nm pulses of 850 µJ. First, a few percent of the 800 nm light is reflected from the front side of a CaF$_2$ wedge (W). A combination of a half-lambda plate (Λ) and a polarizer-cube (P) is used to obtain $p$-polarized light of tunable intensity, which is focussed by lens L1 on a sapphire plate (C1) to generate white light. The white light is refocussed (L2) on a BBO crystal (C2). A second fraction (~10%) of the 800 nm light is split off by a beamsplitter (BS) and focussed by lens L3 on the BBO crystal to spatially overlap with the white light. Temporal overlap is tuned by delay D1. The generated signal pulses are isolated by dichroic mirror DM3 and recollimated by a concave mirror on delay D2. D2 is tuned such that the pulses are in temporal overlap with the remaining part of the 800 nm light in the BBO crystal C2 for a second amplification step. The residual 800 nm light after amplification is removed by dichroic mirror DM1 after which the signal and idler enter the DFG stage. A combination of a dichroic mirror (DM4) and a delay stage (D3) to adjust the path length of the idler pulses is used to have the signal and idler overlapped both in space an time on a silver gallium disulfide crystal (C3) to generate the mid-IR pulses.

needed. Since the energy of photons of the signal is larger than the bandgap in germanium, we used silicium to determine the cross correlate between the pulses. We found in this case the cross correlate between the two signal pulses to be 100 fs.

### 3.2 Formalism of Polarization Resolved Experiments

All infrared experiments in this thesis are polarization resolved. The characterization of the polarization of a light pulse in the experiment is less trivial than measuring the power, but extremely important. A small irregularity may lead to artefacts that are difficult to correct for. In this section we set up a machin-
Figure 3.4. Detection scheme of the two-color pump-probe setup. The light from the (homebuilt) OPA is used for the probe and the reference pulses. The beamsize is first increased by a factor of 2.5 by the telescope CM1 and CM2. The long wave pass filter LWP filters out the signal and idler light and transmits the mid-IR. The LWP is also used to overlap a green laser pointer with the mid-IR for alignment. W1 is a ZnSe wedge that reflects 10% of the light into the delay stage to use as the probe. From the transmitted light a second portion of 10% is reflected by a similar wedge (W2) to use as the reference. The polarization of both beams is cleaned up by polarizers P1 and P2. The pump light is generated in the DFG stage (see text). A dielectric-coated wedge (W3) removes the remaining signal and idler from the beam and reflects a laser pointer with the mid-IR for alignment. Every second pump pulse is blocked by a chopper, and the polarization is tuned by a tilting half-wave plate (Λ, see text). Pump, probe and reference are focussed on the sample S by a parabolic mirror PM1. After the sample, different polarization components of the probe are selected by a mechanically rotated polarizer P3. The beams are recollimated by parabolic mirror PM2, after which the light is steered into the spectrograph. Finally, the light is detected with a liquid nitrogen cooled three line MCT array detector.

To carefully determine the effects of different optics on the light polarization and eventually our observables. To do this we use the Jones formalism of polarization [16]. In this formalism the polarization of light is represented as a vector that spans both the phase and field amplitude in a plane orthogonal with respect to the direction of light propagation. Convenient for most purposes is the frame in which the first element represents the component in the horizontal plane in the lab frame and the second element represents the component in the vertical plane. A light wave with frequency $\omega$ and wavenumber $k$ traveling in the $z$-direction can thus be written as,

$$\vec{E}(\vec{x}, t) = \left( \begin{array}{c} E_{0,x} e^{i\phi_x} \\ E_{0,y} e^{i\phi_y} \end{array} \right) e^{i(kz-\omega t)}$$  \hspace{1cm} (3.1)$$

where the $x$-axis is the horizontal axis and the $y$-axis is the vertical axis perpendicular to the light beam. $E_{0,i}$ and $\phi_i$ denote the $i$-component of the field.
amplitude and relative phase, respectively. The vector of Eq. (3.1) is called the Jones vector and can be regarded as the polarization state of the light. In Dirac notation such a state is written as,

\[
\left( \begin{array}{c}
E_{0,x} e^{i\phi_x} \\
E_{0,y} e^{i\phi_y}
\end{array} \right) = |\Phi\rangle
\] (3.2)

The vector space that the polarization state belongs to has two normalized eigenvectors. A logical choice is the \( p \)-polarization direction and the \( s \)-polarization direction,

\[
|P\rangle = \left( \begin{array}{c} 1 \\ 0 \end{array} \right), \quad |S\rangle = \left( \begin{array}{c} 0 \\ 1 \end{array} \right)
\] (3.3)

Since in our experiment nearly all reflections and refractions are in the horizontal plane, however, this choice coincides with the horizontal and vertical states. The polarization state of a \( p \)-polarized light wave can thus be written as,

\[
|\Phi\rangle = E_{0,x} |H\rangle
\] (3.4)

Here the convention is used that the arbitrary phase \( \phi_x \) of an initial state is set to zero. The intensity follows from taking the inner product between the bra and the ket, which for a general polarization state \( |\Phi\rangle \) yields,

\[
I(\omega) = \frac{1}{2} c \varepsilon_0 \langle \Phi | \Phi \rangle = \frac{1}{2} c \varepsilon_0 (E_{0,x}^2 + E_{0,y}^2)
\] (3.5)

Every optical element that interacts with this light can now be represented by a matrix operator, which will be denoted by a boldface capital. Optical elements may introduce mixing of polarization components, phase shifts and absorptions. In the remainder of this section it is assumed that all optical elements are perfect, in the sense that they do not lead to additional losses. An example of an optical element is the polarizer \( PP \), which may be positioned to transmit light in the \( p \)-polarization or \( s \)-polarization direction and is represented by,

\[
PP_p = \left( \begin{array}{cc} 1 & 0 \\ 0 & 0 \end{array} \right), \quad PP_s = \left( \begin{array}{cc} 0 & 0 \\ 0 & 1 \end{array} \right)
\] (3.6)

Polarizers are found in the detection scheme of the two-color setup in positions P1, P2 and P3 (Fig. 3.4). It is trivial to show that \( PP_s \) acting on the state denoted in Eq. (3.4) yields zero, while \( PP_p \) fully preserves the state. For the less trivial case of a polarizer under an angle \( \phi \) with the horizontal plane of the experiment, it is most convenient to rotate the coordinate frame of the polarization state such that the trivial operators \( PP \) from Eq. (3.6) can be used. Let \( |\Phi_f\rangle \) be the final state, then this operation can be written as,

\[
|\Phi_f\rangle = R(-\phi) PP_p R(\phi) |\Phi\rangle
\] (3.7)
where $R(\phi)$ is the matrix of rotation under an angle $\phi$ in a cartesian coordinate system,
\[
R(\phi) = \begin{pmatrix}
\cos(\phi) & \sin(\phi) \\
-\sin(\phi) & \cos(\phi)
\end{pmatrix}
\] (3.8)

The last operator $R(-\phi)$ in Eq. (3.7) is needed to rotate the state back to the labframe. Thanks to the off-diagonal elements in the operator sequence in Eq. (3.7), a mixing will occur between the components of the initial polarization state. This is of course well known: a light wave transmitted through a polarizer that is under $\phi = 45^\circ$ with the initial polarization of the light will obtain a polarization component in the perpendicular direction of initial polarization. Polarizer P3 in Fig. 3.4 rotates mechanically under an angle of $\phi = \pm45^\circ$ to select different polarization components of the transmitted probe light.

Another optical element of interest is the phase retarder ($\Lambda$ in Fig. 3.4). This element consists of a birefringent material that introduces different phase delays in different polarization directions. The Jones-operator $\Lambda$ belonging to this element is given by,
\[
\Lambda = \begin{pmatrix}
e^{i\phi_x} & 0 \\
0 & e^{i\phi_y}
\end{pmatrix}
\] (3.9)

If $\Lambda$ acts on a real Jones vector, polarization dependent phase-shifts are introduced. For $\phi_x \neq \phi_y + n\pi$ (n=1,2,3...), this corresponds to an elliptical polarization of the light. In our setup we use a special case of the phase retarder, the half-wave plate. This element introduces a phase difference $\phi_x - \phi_y = \pm\pi$. Since the initial phase $\phi_x$ is arbitrary, we can choose it such that $\Lambda$ becomes a real valued matrix that only flips the sign of $E_{0,y}$. This does not change a polarization state that was initially $p$-polarized. However, the half-wave plate can be rotated around the axis along the light beam. This action is achieved in the Jones formalism by a rotation of the polarization state equivalent to Eq. (3.7). The half-wave plate thus rotates the polarization of the light while preserving its complex phases: A linearly polarized light wave remains linearly polarized after transmission.

The half-wave plate used in our experiments has an extra degree of freedom: Tilting the optical axis of the birefringent material. This has the advantage that the phase velocities (and hence the phase delays) can be tuned according to the wavelength of the light. Without this degree of freedom the half-wave plate would be specified only for one fixed wavelength. There is another advantage, though. By tilting the half-wave plate, the phase delays can be tuned such that $\phi_x - \phi_y$ is no longer equal to $\pm\pi$ with as a result an elipticity of the polarization after transmission. As we will demonstrate below this is important for polarization resolved experiments.

At this point it should be noted that the light pulses used in our experiment have a finite bandwidth and thus consists of a distribution of frequencies. The birefringent material of half-wave plate introduces different phase delays for different frequencies in the pulse spectrum. A rigorous treatment would
therefore utilize a vector of polarization states that allows every frequency component to have its own phase and amplitude components. Let us to this end consider a light pulse in the frequency domain with a certain spectral shape, for which \( E_{0,x}(\omega) \) and \( E_{0,y}(\omega) \) are the spectral envelops of the pulse in the \( x \) and \( y \) polarization directions, respectively,

\[
\vec{E}(\vec{x}, t) = \left( \begin{array}{c} E_{0,x}(\omega) e^{i\phi_x(\omega)} \\ E_{0,y}(\omega) e^{i\phi_y(\omega)} \end{array} \right) e^{i(k(\omega)z-\omega t)} \tag{3.10}
\]

The initial polarization state of such a pulse can thus be written in the previously defined basis as,

\[
|\Phi(\omega)\rangle = E_{0,x}(\omega) |P\rangle + E_{0,y}(\omega) e^{i(\phi_y(\omega)-\phi_x(\omega))} |S\rangle \tag{3.11}
\]

The third optical element we discuss here is the mirror. As we will show below, the reflection by a mirror has a non-trivial effect on the polarization of light in case its initial polarization state is not purely \( |P\rangle \) or \( |S\rangle \). In our experiment we mainly use gold mirrors. Reflection by a metallic surface is expressed in the Fresnel factors \( r_p \) and \( r_s \), which are given in terms of the angle of incidence \( \theta_i \) by [16],

\[
r_p(\nu, \theta_i) = \frac{\sqrt{n^2(\nu) - \sin^2(\theta_i)} - n^2(\nu) \cos(\theta_i)}{\sqrt{n^2(\nu) - \sin^2(\theta_i) + n^2(\nu) \cos(\theta_i)}} \tag{3.12}
\]

\[
r_s(\nu, \theta_i) = \frac{\cos(\theta_i) - \sqrt{n^2(\nu) - \sin^2(\theta_i)}}{\cos(\theta_i) + \sqrt{n^2(\nu) - \sin^2(\theta_i)}} \tag{3.13}
\]

where \( n(\nu) \) is the complex index of refraction. With these Fresnel factors, the Jones operator for reflection \( \mathbf{M} \) is then given by the matrix,

\[
\mathbf{M}(\nu, \theta_i) = \begin{pmatrix} -r_p(\nu, \theta_i) & 0 \\ 0 & r_s(\nu, \theta_i) \end{pmatrix} \tag{3.14}
\]

Using the index of refraction of gold, the reflection under \( \theta_i = 45^\circ \) on a gold mirror of light with a frequency of \( \nu = 2500 \text{ cm}^{-1} \) yields,

\[
\mathbf{M} = \begin{pmatrix} 0.95 + 0.22i & 0 \\ 0 & 0.98 + 0.11i \end{pmatrix} \tag{3.15}
\]

An initial Jones vector with equal phase and amplitude for both polarization directions will acquire a phase difference between the two polarization components after reflection. This is analogue to saying that a light pulse, initially linearly polarized under an angle of \( 45^\circ \) with the horizontal lab frame) acquires an elipticity in its polarization. In our setup this occurs on mirrors \( \text{M1, M2 and PM1} \) after the pump polarization was rotated using the half-wave plate.
For the half-wave plate we found that for certain angles of the optical element we introduce an ellipticity in the transmitted light. In practice this ellipticity is tuned such that it compensates for phase delays acquired by the subsequent reflections. Using Eq. (3.15) it can easily be shown that for 4 µm light the required polarization state immediately after the half-wave plate must be,

$$|\Phi\rangle = E_0 \left( \begin{array}{c} 0.51 \\ 0.49 \cdot e^{0.35i} \end{array} \right)$$

(3.16)
in order to pre-compensate for the subsequent reflections on the gold mirrors. At the sample position S, the pump light will then be linearly polarized again, under 45° with the horizontal plane. Since the refractive index is dependent on the wavelength of the incident light, so is $M$. Different frequency components of a light pulse with a finite bandwidth thus obtain (very small) different polarization ellipticities after reflection.

We will now translate a polarization resolved pump-probe experiment to the formalism described above. To this end we assume a certain response in the sample and investigate how the measured response depends on the (mis)alignment of certain optical components. In absence of a preceding pump pulse, the probe light will be partially absorbed by the sample,

$$S_0(\omega) = e^{-\frac{1}{2} \alpha(\omega)} \left( \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right)$$

(3.17)

where $\alpha(\omega)$ is the absorption in the sample. The factor $\frac{1}{2}$ in the exponent arises from the fact that $S_0$ is an operator acting on the polarization state, which will be squared to obtain the intensity.

An intense pump pulse excites modes in the sample that lead to absorption changes $\Delta \alpha(\omega, t)$ that depend on the polarization direction and the waiting time after the excitation. Following the notation of chapter 4, we can write the absorption of the probe light after excitation by a pump pulse that is $s$-polarized as follows,

$$S(\omega, t) = e^{-\frac{1}{2} \alpha(\omega)} \left( \begin{array}{cc} e^{-\frac{1}{2} \Delta \alpha_{\perp}(\omega, t)} & 0 \\ 0 & e^{-\frac{1}{2} \Delta \alpha_{||}(\omega, t)} \end{array} \right)$$

(3.18)

where the anisotropy $R(\omega, t)$ leads to different absorption changes in the directions orthogonal and parallel to the pump polarization according to,

$$\Delta \alpha_{||}(\omega, t) = (1 + 2R(\omega, t)) \Delta \alpha(\omega, t)$$

(3.19)

$$\Delta \alpha_{\perp}(\omega, t) = (1 - R(\omega, t)) \Delta \alpha(\omega, t)$$

(3.20)

A nonzero anisotropy thus rotates the polarization state of the transmitted probe.

The equation for $S(\omega, t)$ above assumes that the angle between the propagation vector of the pump pulse and the $z$-axis equals zero degrees. In reality, this is experimentally not possible and the angle is rather on the order of $\delta = 10^\circ$ (see Fig. 3.5). To take this angle into account, we have to perform an additional
3.2 Experiment

rotation of the probe frame in the \( y-z \) plane. So far, we did not consider the \( z \)-coordinate, as this is the propagation direction of the probe light. However, the inclination of the pump beam results in a mixing of the response in the \( z \) and \( y \) direction according to,

\[
S(\omega, t) = e^{-\frac{1}{2}\alpha(\omega)} \begin{pmatrix}
    e^{-\frac{1}{2}\Delta \alpha_\perp(\omega, t)} & 0 \\
    0 & e^{-\frac{1}{2}\left(\cos^2(\delta)\Delta \alpha_\parallel(\omega, t) + \sin^2(\delta)\Delta \alpha_\perp(\omega, t)\right)}
\end{pmatrix}
\]  

(3.21)

This expression follows from the fact that the absorption changes in the two directions orthogonal to the pump polarization are identical. In our experiment, the pump is typically not \( s \)-polarized but rather has its polarization at an angle of 45° with the vertical plane. In analogy to the treatment of the polarizer operator (Eq. (3.7)), this is achieved by sandwiching \( S(\omega, t) \) between rotation operators.

The pump-probe experiment now yields an incoming \( p \)-polarized probe pulse \(|\Phi_p(\omega)\rangle\) that either is, or is not, preceded by a pump pulse with a polarization under \( \theta_p = 45° \) with the vertical plane. After the sample, a mechanically rotating polarizer \( P \) rotates over an angle \( \phi = \pm 45° \) with respect to the probe polarization to select either the polarization component of the probe light parallel or perpendicular to the initial polarization of the pump (see Fig. 3.5). The final polarization states with preceding pump can thus be written as,

\[
|\Phi_{f\pm}(\omega, t)\rangle = R(\mp \phi)P_p R(\pm \phi)R(-\theta_p)S(\omega, t)R(\theta_p)|\Phi_p(\omega)\rangle
\]

(3.22)

where the upper signs refer to the parallel polarization component and the lower signs to the perpendicular polarization component of the probe. The final polarization states without preceding pump \(|\Phi_{f\pm}^0(\omega)\rangle\) are obtained by replacing \( S(\omega, t) \) by \( S_0(\omega) \). After the rotating polarizer only the intensity of the light is of interest and further optics can thus be ignored. The detected pump-probe signal of Eq. (4.1) is a function of the intensities measured on the detector and can be expressed in terms of the polarization states as,

\[
\Delta \alpha_{\parallel/\perp}(\omega, t) = -\ln \left\langle \frac{|\Phi_{f\pm}(\omega, t)\rangle}{\langle \Phi_{f\pm}^0(\omega) | \Phi_{f\pm}(\omega) \rangle} \right\rangle
\]

(3.23)

We now assume a frequency independent anisotropy of the form \( R(\omega, t) = 0.4e^{-0.4t} \). The probe spectrum is assumed to have properties similar to the specifications of the one color setup described in section 3.1.1 of this chapter. If Eq. (3.23) is evaluated with these input parameters we can obtain the detected anisotropy using Eq. (4.3). Clearly, in case \( \theta_p = 45°, \phi = \pm 45° \) and \( \delta = 0° \) we reobtain the same dynamics \( R(\omega, t) \) as the actual response that was put in. If \( \theta_p, \phi \) and \( \delta \) assume different values, the detected anisotropy will be different. Firstly, we show a number of anisotropy curves for different values of \( \phi \) in Fig. 3.6A. Such a situation occurs when the rotating polarizer is not well aligned. For increasing deviations of \( \phi \) from \( \pm 45° \) (for every lower curve \( \delta \) is \( 2° \) smaller), the anisotropy starts at a lower value. A simple rescaling does not
Figure 3.5. Pump and probe polarization and beam angles at the sample position. The $p$-polarized probe has its electric field oscillations in the horizontal ($x$-$z$) plane in the lab frame and propagates in the $z$-direction. The propagation direction of the pump makes an angel $\delta$ with the propagation direction of the probe in the vertical ($y$-$z$) plane. The polarization direction of the pump makes and angle of $\theta_p = 45^\circ$ with the polarization direction of the probe. After the sample $S$, a mechanically rotating polarizer (P3) selects different polarization components of the probe light by rotating over an angle $\phi = \pm 45^\circ$ with the probe polarization direction.

yield the same result, since the dynamics are also different. A second example is given in Fig. 3.6B. Here we varied the inclination angle $\delta$ between the pump and the probe in steps of $10^\circ$. It should be noted that an inclination of $10^\circ$ does not yet alter the detected anisotropy strongly: the initial anisotropy at $t = 0$ is $< 2\%$ smaller than 0.4. Finally, the detected anisotropy decays calculated for different angles between the pump and probe polarization are shown in Fig. 3.6C (variation of $\theta_p$ in steps of $2^\circ$). These results are quite similar to the first example, although the deviation between the curves resulting from different angles is not persistent for longer delay times.

We also evaluated the detected anisotropy in case the rotating polarizer P3 is not positioned between the sample $S$ and the second parabolic mirror PM2 but rather after PM2 (see Fig. 3.4). Before the polarization components are selected by the polarizer, one more reflection by a parabolic mirror occurs and Eq. (3.22) is thus to be extended with an additional reflection operator $M(\omega, \theta)$. As we have seen, reflections by gold mirrors induce different phase shifts for different polarization directions and we thus may wonder how strongly the repositioning of the rotating polarizer affects the detected anisotropy. We found that indeed a very small decrease of $R(\omega, t)$ is present for increasing frequencies in case the probe pulse contains a spatial chirp. This frequency dependence is less than a percent of the initial amplitude of the anisotropy per $100 \, \text{cm}^{-1}$ and flips sign in case the polarization of the probe is changed from $p$ to $s$.

### 3.3 Dielectric Relaxation Spectroscopy

The purpose of dielectric relaxation spectroscopy (DRS) is to measure (a part of) the complex permittivity spectrum of a sample, mostly in the sub-THz frequency regime. The permittivity of a dielectric medium is a measure of how
3.3 Experiment

Figure 3.6. Calculated anisotropy decays as would be measured for identical sample responses (red lines) but suboptimal setup parameters due to misalignment. (A) The angle of rotation $\phi$ of the rotating polarizer (P3 in Fig. 3.4) is smaller than $\pm 45^\circ$ by steps of $2^\circ$. (B) The inclination angle $\delta$ between the pump and the probe is nonzero, by steps of $10^\circ$. (C) The angle $\theta_p$ between the pump and probe polarization is smaller than $45^\circ$ by steps of $2^\circ$.

...the medium polarizes upon the application of an external field. The permittivity spectrum of a dipolar solution therefore provides information on the reorientation of dipoles in the solution. At lower frequencies, electromagnetic waves are not easily confined anymore in a collimated beam propagation. We use two types of setups: (1) a far field setup that makes use of freely propagating laser pulses in the THz regime and (2) a near-field setup that measures the reflection of electromagnetic waves in the GHz regime in a waveguide.

3.3.1 THz Spectroscopy

In THz dielectric relaxation spectroscopy the permittivity spectrum is probed by characterizing a THz pulse after transmission through the sample. The far-infrared THz pulse is generated by optical rectification in a ZnTe crystal pumped by (a part of) the output of a Ti:Sapphire pulsed laser (800 nm, $\sim 110$ fs, $\sim 75 \mu$J). The resulting pulse typically comprises a single cycle of the electric field and has a duration of $\sim 1$ ps. Fourier transformation of the pulse yields a frequency spectrum between 0.4 and 1.2 THz. The pulse shape cannot be
Experiment 3.4

42 Experiment 3.4
detected directly. Instead, we make use of the optical Kerr effect in a second ZnTe crystal. The strong electric field of the THz pulse causes a change in refractive index in the crystal, of which the magnitude and sign depends on the field intensity and direction, respectively. An 800 nm laser pulse is spatially overlapped with the THz pulse in the crystal with varying delay time between the pulses. Depending on which part of the single cycle THz pulse is in temporal overlap with the 800 nm pulse, a different change in polarization is induced on the 800 nm pulse by the change in refractive index. After the crystal the polarization components are split using a quarter wave plate and a polarizing beamsplitter. The polarization changes are monitored as a function of pulse delay by a differential detector. Measurements of an empty cuvette and without any cuvette are done to subtract their contribution to the signal. The complex index of refraction $\hat{n}(\nu)$ is obtained from the change in amplitude (due to absorption $\kappa(\nu)$) and delay (due to refraction $n(\nu)$) of the THz pulse upon propagation through the sample [17],

$$\hat{n}(\nu) = n(\nu) - i\kappa(\nu)$$  \hspace{1cm} (3.24)

From the complex index of refraction the permittivity spectrum is obtained by,

$$\hat{\epsilon}(\nu) = \hat{n}^2(\nu)$$  \hspace{1cm} (3.25)

3.3.2 GHz spectroscopy

The permittivity spectrum in the GHz spectral regime is measured using a Vector Network Analyzer (VNA, Rhode & Schwarz GmbH & Co KG, Germany, model ZVA67). The VNA is connected by a phase stable coaxial cable (Rhode-Schwarz, ZV-Z96) to various homebuilt probes to cover different parts of the GHz spectral domain. In the low frequency domain (10 MHz - 2 GHz) we used a probe cell in which the outer coaxial electrode extends several centimeters from the base plane to contain the sample fluid and the coaxial pin sticks 1.8 mm into the sample [18, 19]. For the high frequency domain (0.5 - 67 GHz) we used a probe that exists of a sample container with a coaxial end of which the outer conductor is attached to a circular flange and the inner conductor is capped with a glass bead to prevent sample fluid to enter the coaxial cable [20]. $\hat{\epsilon}(\nu)$ is obtained by measuring phase-resolved the reflections of the oscillatory electromagnetic fields provided by the VNA. In order to calibrate the spectra, known dielectrics were measured like pure water, $N,N$-dimethylacetamide, methanol, ethanol or 2-propanol.

3.4 Samples

In most of the work we used isotopically diluted water as the solvent. Millipore H$_2$O was purified further in a deionizer. D$_2$O (99.99% purity) was purchased from Sigma-Aldrich. Throughout this thesis, the isotope dilution mostly used is 4% D$_2$O in H$_2$O (mol percent). All other solutes used were purchased from Sigma-Aldrich, the details of which are treated in every chapter separately.
3.4 Experiment

Figure 3.7. Schematic picture of the wire flow cell. Water (or another solvent) is pumped by a peristaltic pump into a reservoir in which the content level is kept constant (by means of an overflow) to maintain a constant pressure at the nozzle position. Under the film, the liquid is collected for reuse. Increasing \( H \) will put a larger pressure on the nozzle and increase the flow rate, making the film thicker. The film will become thinner further away from the nozzle (increasing \( h \)).

3.4.1 Wire Flow Cell

A frequently used conventional sample holder consists of two CaF\(_2\) or BaF\(_2\) windows, separated by a thin spacer to create a waterfilm of 10-1000 \( \mu \text{m} \) thickness. Unfortunately, in some experiments the energy of the pump pulses is high enough to create a third order polarization in such windows, emitting radiation known as white-light. This broad band light appears in the measurement results as a very unstable background artefact, obscuring the signal of interest. To solve this problem we made use of a wire flow cell that was constructed similar to the description in reference \[21\]. Water from a reservoir is gently released from a flat nozzle bearing an elongated tungsten wire loop of 125 \( \mu \text{m} \) thickness (Fig. 3.7). The width of the loop is approximately 5 mm. At the bottom of the tungsten wire loop the water is collected in a glass funnel and pumped back into the reservoir using a peristaltic pump. Thanks to the surface tension, the water forms a stable thin film floating in mid air in between the wires. This enables measurements on the sample without any windows. The thickness of the water film depends on the flow rate and distance from the nozzle \( h \). The flow rate is increased by increasing the elevation difference \( H \) between the nozzle and the water level in the reservoir. The film becomes thinner for lower flow rates and at positions further away from the nozzle due to the gravitational pull on the
water. Stable configurations are obtained with film thicknesses of 25-125 µm. A linear spectrum taken from the film close to the nozzle using a fast flow rate resembled closely a linear spectrum from a water-filled conventional sample cell with a 115 µm spacer. For this optical pathlength the absorbance of a pure H$_2$O sample is \( \sim 2 \text{O.D.} \) at the OH-stretch/H$_2$O-bend combination band and \( \sim 0.5 \text{O.D.} \) at the first OH-stretch overtone. The wire flow cell was also tested and found to work with solvents that have a lower viscosity/surface tension than water (e.g. methanol, ethanol and acetone).