Ultrafast vibrational dynamics of water

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Citation for published version (APA):

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Wave coupling in a nonlinear medium, described in the previous chapter, can not only be used for nonlinear spectroscopy studies, but also for the generation of light pulses in the infrared. Here, we show how the incident and generated E-fields are intertwined and under what conditions energy transfer among waves is efficient. The second part of this chapter gives a description of the experimental setup used for the pump-probe experiments.
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3.1 Nonlinear optical interactions in crystals

There are no laser sources that directly emit intense and ultrashort (fs) laser pulses at wavelengths in the mid-infrared region. The experimentalist is, therefore, forced to search for other methods to generate light with wavelengths around 3 μm. The general way is to make use of the nonlinear polarization that is generated in certain materials under the influence of intense light, as shown in the previous chapter. In particular, three wave mixing processes, in which two incoming fields generate a nonlinear polarization $P^{(2)}$, that acts as a source for a new, third E-field, are used to generate infrared pulses. The second order nonlinear polarization generated by the fields $E_i$ and $E_j$ is given by:

$$P^{(2)}(k, \omega) = \epsilon_0 \chi^{(2)}(\omega = \omega_i + \omega_j, k = k_i + k_j) : E(k_i, \omega_i)E(k_j, \omega_j)$$  \hspace{1cm} (3.1)$$

where $\chi^{(2)}$ is the frequency and wavevector dependent second-order susceptibility. We describe the E-fields by:

$$E_i(z, t) = \mathcal{E}_i(z, t)e^{ik_i z - i\omega_i t}$$  \hspace{1cm} (3.2)

for $i = 1, 2, 3$. $\mathcal{E}_i$ represents the pulse envelope function. As shown in the previous chapter, the newly generated E-field obeys the wave equation (2.18):

$$\left(\frac{\partial}{\partial z} + \frac{1}{v_g} \frac{\partial}{\partial t}\right)\mathcal{E}(z, t)e^{ik z - i\omega t} = \frac{1}{2i\epsilon_0 k c^2} \frac{\partial^2 P^{(2)}}{\partial t^2}$$  \hspace{1cm} (3.3)

If we make use of the slowly varying amplitude approximation (see section 2.3) for the term on the right-hand side, and fill in Eq. 3.1 and 3.2, we get the following coupled wave equations:

$$\left(\frac{\partial}{\partial z} + \frac{1}{v_g} \frac{\partial}{\partial t}\right)\mathcal{E}_1 e^{ik z - i\omega t} = \frac{\chi^{(2)}(\omega_1 = \omega_3 - \omega_2)}{2n_1 c} e^{i\Delta k z} (i\omega_1 \mathcal{E}_2^* \mathcal{E}_3 - 2\frac{\partial}{\partial t}(\mathcal{E}_2^* \mathcal{E}_3))$$  \hspace{1cm} (3.4)

$$\left(\frac{\partial}{\partial z} + \frac{1}{v_g} \frac{\partial}{\partial t}\right)\mathcal{E}_2 e^{ik z - i\omega t} = \frac{\chi^{(2)}(\omega_2 = \omega_3 - \omega_1)}{2n_1 c} e^{i\Delta k z} (i\omega_3 \mathcal{E}_1^* \mathcal{E}_3 - 2\frac{\partial}{\partial t}(\mathcal{E}_1^* \mathcal{E}_3))$$  \hspace{1cm} (3.5)

$$\left(\frac{\partial}{\partial z} + \frac{1}{v_g} \frac{\partial}{\partial t}\right)\mathcal{E}_3 e^{ik z - i\omega t} = \frac{\chi^{(2)}(\omega_3 = \omega_1 + \omega_2)}{2n_1 c} e^{-i\Delta k z} (i\omega_3 \mathcal{E}_1 \mathcal{E}_2 - 2\frac{\partial}{\partial t}(\mathcal{E}_1 \mathcal{E}_2))$$  \hspace{1cm} (3.6)

$\Delta k = k_3 - k_2 - k_1$, the wave vector mismatch. In these equations, two fields generate a nonlinear polarization that is a source for the third field.
The processes involved in a three wave mixing process are depicted in Figure 3.1. If the incoming fields are identical, i.e. $\omega_1 = \omega_2$, the generated $\omega_3 = 2\omega_1$ wave is the second harmonic of the input beam. More general is the sum frequency generation (SFG) process where two different photons add up to a new field at $\omega_3 = \omega_1 + \omega_2$. Alternatively, two incoming fields $\omega_3$ and $\omega_2$ can generate a field at $\omega_1$ (difference frequency generation, DFG) following the energy conservation condition $\omega_3 = \omega_1 + \omega_2$. Because the DFG process leads to an increase in the number of photons with frequency $\omega_1$, it is also known under the name optical parametrical amplification (OPA).

The two-photon emission may even occur when the $\omega_1$ and $\omega_2$ fields are not initially present. In this case, the zero-point fluctuations of the electric field, which arise in the quantum description of light, are responsible for the spontaneous birth of an $\omega_1$, $\omega_2$ couple of photons. The lower of the two frequencies is called the idler, the higher of the two the signal pulse. As soon as some of the photons are generated at the right frequencies, they are amplified by means of OPA. This process is known as parametric superfluorescence [33, 53] and forms the basis of the OPG/OPA stages discussed in the next section.

The generation of electric fields at new frequencies does not only depend on the energy conservation law, but, in order to be efficient, also on the phase matching condition. Only when $\Delta k = 0$, constructive interference of the three waves over a longer propagation length will occur. For perfect phase-matching of collinear beams, the phase-matching condition reads:
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\[ n_1 \omega_1 + n_2 \omega_2 = n_3 \omega_3 \]  

(3.7)

It is clear that this condition together with energy conservation \((\omega_3 = \omega_1 + \omega_2)\) can never be fulfilled in ordinary dispersive materials, for which the refractive index increases with \(\omega\). Birefringent crystals, i.e. crystals for which the refractive index differs for different polarizations of the incoming light can solve this problem. Most crystals used for nonlinear optics are uniaxial crystals having two indices of refraction, \(n_0\), the ordinary refractive index, for polarizations orthogonal to the plane containing the wavevector \(k\) and the optical axis of the crystal, and \(n_e(\theta)\), the extraordinary refractive index, for polarizations parallel to this plane. If the highest frequency wave \(\omega_3\) is polarized in the direction that gives the lower of the two refractive indices, the ordinary dispersion can be compensated and phase-matching is possible.

Uniaxial crystals are divided in positive \((n_e > n_o)\) and negative \((n_e < n_o)\) uniaxial crystals. Furthermore, difference is made between type I, type II and type III phase matching. Type I phase matching stands for the situation where the two lower frequency waves \((\omega_1\) and \(\omega_2)\) have the same polarization, perpendicular to the pump; in type II phase matching the signal polarization is perpendicular to pump and idler and in type III phase matching the idler polarization is perpendicular to pump and signal. The phase-matching condition is fulfilled by changing the orientation of the crystal with respect to the propagation direction of the incident light. It can be shown that light polarized in the plane containing \(k\) and the crystal axis, experiences an extraordinary refractive index \([113]\):

\[ \frac{1}{n_e(\theta)^2} = \frac{\sin^2 \theta}{\tilde{n}_e^2} + \frac{\cos^2 \theta}{\tilde{n}_o^2} \]  

(3.8)

with \(\tilde{n}_e\) the principal value of the extraordinary refractive index. By changing the angle \(\theta\), a value of \(n_e(\theta)\) can be chosen such that the phase-matching condition is fulfilled.

3.2 Setup for femtosecond mid-infrared pump-probe spectroscopy

This section describes the generation of mid-infrared pulses that are resonant with the OH–stretch vibrational modes of hydrogen-bonded liquids and short enough to follow their dynamics \([15]\). Furthermore, a description of the pump-probe setup and the preparation of the samples is given.

3.2.1 Generation of mid-infrared laser pulses

The basis of our setup is formed by a commercial regenerative amplifier system (Quantronix Titan). The RGA is seeded by 800 nm light from a Ti:Sapphire oscilla-
Figure 3.2. The experimental setup used for the generation of femtosecond mid-infrared pulses. For a description of the setup see text. BS70: beam splitter reflection 70%; DM: dichroic mirror; BD: beam dump; R1064: Nd:YAG mirror; LWP: long wave pass filter; BBO and KTP: crystals; black bars without name: dielectric 800 nm mirrors.

The 800 nm pulses are split into a probe and a pump part by means of a beam-splitter directly after the regenerative amplifier. To generate the mid-infrared pump pulses, a commercial 5-pass OPG/OPA stage (TOPAS) is used. This stage is based on a BBO crystal and generates signal and idler pulses that are tunable between 1 and 2.6 μm. This is a type II phase-matching process, implying that the polarization of the signal is perpendicular to that of the idler and the pump. The total energy of the generated pulses is approximately 250 μJ. An 800 nm filter inside the TOPAS blocks the remaining pump light. Typical wavelengths for signal and idler pulses, are 1260 and 2200 nm, respectively.

The idler pulses are separated from the signal pulses by a dichroic mirror and subsequently frequency-doubled in a second BBO-crystal. The resulting 1100 nm light is mixed with a fresh part of the 800 nm beam in a difference frequency generation.
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process in a KTiOPO₄ (KTP) crystal, giving pulses with a central wavelength near 3 μm. The unwanted wavelengths are subsequently filtered out by different filters: an 800 nm mirror reflects the remaining pump light, a Nd:YAG-mirror (1064 nm) reflects the 1100 nm light, and finally a long wave pass filter filters out residual light at all wavelengths shorter than 2500 nm.

![Figure 3.3. Cross correlation trace of pump and probe measured with a LiIO₃-crystal (a), and a typical power spectrum of an infrared pulse (b). The fitted curves are Gaussians with a FWHM of 330 fs and 80 nm, respectively.](image)

The probe pulses are generated in the same way, but with less pump energy. The TOPAS is a three-pass OPG/OPA-stage, giving about 140 μJ of energy for signal plus idler. Due to the use of two different OPG/OPA-stages the wavelengths of the pump and probe pulses can be tuned independently. The pulses can be tuned between 2700-3300 nm (3000-3700 cm⁻¹). Figure 3.3 shows typical pulse characteristics. In the left part, pump and probe pulses were crossed under a small angle in a LiIO₃ to generate the sum-frequency. The intensity of the SFG signal is measured as a function of delay time between pump and probe pulse. Assuming Gaussian time profiles, the duration of the generated infrared pulses is 330/√2=230 fs. The spectral width of the pulses is 80 nm (FWHM), which is sufficiently small in comparison with the absorption bandwidth of the OH-stretch vibration in pure water (400 nm) to enable the probing of different spectral regions. Typical energies are 20 μJ for the pump and ≤ 1 μJ for the probe.

3.2.2 Two color pump-probe setup

Figure 3.4 shows the pump-probe setup. The pump pulse is focussed by a CaF₂ lens on the sample to excite part of the molecules and is blocked afterwards by a beam block. The probe pulses pass a delay-line and are focussed and overlapped with the pump focus in the sample. To assure that the probe pulses monitor a homogeneously
Setup for femtosecond mid-infrared pump-probe spectroscopy

Excited part of the sample, lenses with different focal lengths are used to focus pump and probe. In this way a larger focus for the pump pulse was achieved. The typical sizes of the foci of pump and probe pulses are 200 and 75 μm, respectively. To avoid thermal lensing effects, we collimate and focus the probe beam on a PbSe-detector.

![Diagram of pump-probe setup](image)

**Figure 3.4.** Pump-probe setup, for description see text.

The intensity of the probe beam $I$ is measured with a PbSe-detector as a function of delay between pump and probe pulses. In order to compensate for the pulse to pulse intensity fluctuations in the probe beam, we use a single detector to measure the reference intensity $I_{\text{ref}}$. Using a chopper, both the transmission of the probe beam in the presence of the pump beam ($T$) and in the absence of the pump beam ($T_0$) are measured. The transmission change $\ln(T/T_0)$ is calculated as a function of delay between pump and probe pulse, where $T=I/I_{\text{ref}}$ and $T_0=(I_0/I_{\text{ref}})$.

To cancel the effect of orientational relaxation on the observed dynamics and to probe only the vibrational relaxation, the polarization of the probe pulse is set at the magic angle ($54.7^\circ$) with respect to the polarization of the pump pulse [24] by means of a zero-order $\lambda/2$ plate. If the orientational dynamics is measured, the probe polarization is set at an angle of $45^\circ$ with respect to the pump polarization. In this case, a polarizer is placed after the sample, which enables the measurement of the transmission changes for the probe polarization parallel to the pump polarization $(T/T_0)_{||}$ and perpendicular to the pump polarization $(T/T_0)_{\perp}$. The rotational anisotropy is calculated [24] as follows:

$$R(t) = \frac{\ln(T/T_0)_{||} - \ln(T/T_0)_{\perp}}{\ln(T/T_0)_{||} + 2\ln(T/T_0)_{\perp}}$$

(3.9)

The denominator represents the rotation free signal and is the same as the signal measured with magic angle polarization.

To avoid the accumulation of heat from pump pulses during the experiment, the sample was rotated. In this way, every pump pulse sees a fresh part of the sample.
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We use a nitrogen flow box when pump and probe pulses have frequencies between 3600–3900 cm\(^{-1}\). In this spectral region, rovibrational transitions of gas-phase water molecules present in air lead to the absorption of the ir-light. Without nitrogen flow box, the intensity of the ir-pulses decreases and their power spectrum show dips corresponding to the rovibrational transitions. The nitrogen box provides a water-poor environment.

3.3 Sample preparation

The linear absorption spectra were measured using a Perkin-Elmer spectrometer. The transmittance of the sample was calculated by dividing the intensity of the light with \((I(z))\) and without \((I_0)\) sample. As shown in the previous chapter, the Lambert-Beer law applies for this situation:

\[
T = I(z)/I_0 = e^{-\sigma_0(\omega)\rho_0 z},
\]

where \(\rho_0\) is the density of the absorbers and \(\sigma_0\) the absorption cross section. The samples used in this thesis consist of a thin layer of liquid in between two sapphire or CaF\(_2\) windows. Depending on the density of OH-groups different, spacers are used. For a dilution of pinacol molecules, for example, a spacer of 500 \(\mu\)m was used, whereas for liquid water the number of OH–groups was too high to use the thinnest spacer available (15\(\mu\)m). In that case, we pressed the two windows to a separation of a few \(\mu\)m in order to get a transmission of approximately 10\% at the OH–stretch absorption peak, which is a typical value for most samples used.