Structure and dynamics of complex hydrogen-bonded systems
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CHAPTER 2

Experimental methods

2.1 Introduction

To study the molecular dynamics in liquids and molecular devices one needs a tool which allows to influence and monitor the relaxation processes and structural changes at the relevant time scales. Femtosecond lasers based on Ti:Sapphire technology are generally used to perform these experiments because of the high peak power and stability of the laser light which enables the saturation of vibrational transitions and at the same time provides fast monitoring of structural and dynamical changes.

Femtosecond lasers typically generate a train of pulses at 800 nm with a repetition rate on the order of a kHz. To study the vibrations of a molecule, a laser source in the mid-IR spectral range is needed. Therefore we need to convert 800 nm laser pulses down to wavelengths ranges from 3 to 7 µm. Using the high peak powers we employ a non-linear optical generation scheme based on an optical parametric amplification (OPA) which allows us to down-convert the 800 nm laser pulses to signal and idler with wavelengths of approximately 1 and 2 µm, respectively. Various non-linear crystals and generation schemes can subsequently be used to mix signal, idler and/or 800 nm laser beams to obtain the desired mid-IR laser pulses.

2.2 Light generation

2.2.1 Frequency mixing processes

Wavelength conversion in time-resolved experiments like the ones described in this thesis is generally achieved using frequency-mixing in non-linear optical crystals. Any frequency-mixing process can be described using non-linear response theory in which the induced polarization is usually expressed as a power series in the
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The terms in the equation represent the linear, second order and third order processes, assuming \( \chi^{(i)} \) is constant. The first process describes the absorption and refraction of light, the second is responsible for various non-linear effects on surfaces, e.g., second-harmonic generation (SHG) and sum-frequency generation (SFG), while the third is essential for the four-wave mixing response. To describe the generation of light in non-linear optical crystals, the second term \( P^{(2)}(t) = \chi^{(2)}E^2(t) \) needs to be considered. Assuming the electric field of the light source to be given by

\[
E(t) = E_1 e^{i\omega_1 t} + E_2 e^{i\omega_2 t} + c.c.,
\]

the second-order polarization is, assuming a frequency independent \( \chi^{(2)} \), given by

\[
P^{(2)}(t) = \chi^{(2)}(E_1^2(t)e^{-2i\omega_1 t} + E_2^2(t)e^{-2i\omega_2 t} + 2E_1(t)E_2(t)e^{-i(\omega_1 + \omega_2)t} + 2E_1(t)E_2^*(t)e^{-i(\omega_1 - \omega_2)t} + c.c.)
\]

This expression has frequency components different from \( \omega_1 \) and \( \omega_2 \) that are associated with SHG, SFG and difference frequency generation (DFG).

\[
\begin{align*}
\text{SHG} & \Rightarrow 2\omega_1 \quad \text{and} \quad 2\omega_2 \\
\text{SFG} & \Rightarrow \omega_1 + \omega_2 \\
\text{DFG} & \Rightarrow \omega_1 - \omega_2.
\end{align*}
\]

The last term in Eq. 2.3 describes the process of optical rectification which leads to generation of a constant electric polarization and a subsequent DC voltage in the medium.

The efficient generation of these new frequencies also depends on the spatial variation of the interacting fields. Thus, the light that is generated in different parts of the non-linear crystal can interact destructively, thus decreasing the intensity of the generated light. To ensure that the interference is constructive, the wave vectors of the fields (see Fig. 2.1) must obey the so-called phase-matching condition.

\[
\Delta \vec{k} = \vec{k}_1 + \vec{k}_2 - \vec{k}_3 = 0
\]
Since efficient amplification of radiation can occur only when the wave vectors of the non-linear polarization and the generated light match, the phase-matching condition can for difference-frequency processes be written as

\[ k_3 = k_1 - k_2 \]  

(2.6)

which since \( k = \omega/c \) can also be written as

\[ n_3 \omega_3 = n_1 \omega_1 - n_2 \omega_2. \]  

(2.7)

The interacting fields are customary called from the most to the least intense pump (\( \omega_p \)), signal (\( \omega_s \)) and idler (\( \omega_i \)), which allows us to rewrite Eq. 2.7 as

\[ n_p \omega_p = n_s \omega_s + n_i \omega_i \]  

(2.8)

It can be shown that since \( \omega_p = \omega_s + \omega_i \), for materials with “normal” dispersion (the refractive index (n) increases with rising frequency) it is not possible to fulfill the phase-matching condition.

![Figure 2.1: Unless special measures are taken as explained in the text, the phase-matching condition (\( \Delta k = 0 \)) cannot be fulfilled in materials with normal refractive indices.](image)

In principle, it is possible to achieve the phase-matching condition using materials with an anomalous dispersion. However, the phase-matching condition is typically fulfilled using birefringent materials in which the refractive index depends on the polarization direction, so that the refractive indices for parallel and perpendicular polarizations are independently adjustable. This method is usually called angle-tuning phase-matching. Uniaxial birefringent crystals have two different indices of refraction. These so-called ordinary and extraordinary indices of refraction are usually denoted as \( n_o \) and \( n_e \), respectively, see Fig. 2.2. Equation 2.9 describes the dependence of the effective refractive index (\( n_{\text{eff}} \)) on the incident angle (\( \theta \)).

\[ \frac{1}{n_{\text{eff}}^2(\theta)} = \frac{\cos^2 \theta}{n_o^2} + \frac{\sin^2 \theta}{n_e^2} \]  

(2.9)
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2.2. Process of phase-matching of the waves generated in different parts of the nonlinear crystal.

By changing the incident angle of light at the birefringent crystal, we can tune the effective refractive index experienced by the interacting fields and thus fulfill the phase-matching condition. This so-called angle tuning technique allows us to efficiently generate various frequencies in the mid-IR spectral range.

2.2.2 Optical parametric amplification and mid-IR light generation

As mentioned before, presently there is no femtosecond laser capable of generating light with wavelengths in the mid-IR. The second order polarization can, apart from the processes described in the previous section, also lead to an optical parametric amplification. In this process an intense pump beam propagates through a non-linear crystal together with a seed beam with a lower frequency. Non-linear interaction of the seed and pump beams in the crystal lead to a stronger output of the light at the seed wavelength. In this process, the photons of the pump beam are split into lower-energy signal and idler photons (Fig. 2.3). Simultaneously, the intense pump beam is proportionally depleted. The frequency of the signal and idler generated using the optical parametric amplification process is determined by the phase-matching and the frequency of pump photons.
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2.3 Experimental setups

2.3.1 Femtosecond laser system

We use a commercially available Ti:Sapphire based laser system as a source of femtosecond laser pulses. The oscillator (MaiTai - Spectra Physics) generates 100 fs pulses at 800 nm at an 80 MHz repetition rate. The output of the oscillator is used to seed a regenerative amplifier (Hurricane - Spectra Physics), which is pumped by a 10 W solid state Nd:YLF laser (Evolution - Spectra Physics) with a repetition rate of 1 kHz. The seeded pulses are stretched to a few hundreds of ps on a grating to avoid any damage in the amplifier's cavity. The Evolution output is then coupled into the amplifier cavity by a Pockels cell which picks a pulse from the oscillator pulse-train. After amplification and recompression on the same grating, pulses of 100 fs duration with 1 mJ energy at 800 nm and with a 1 kHz repetition rate are obtained.

However, there is a significant weakness in the design of the Hurricane laser system. The 80 MHz oscillator output and the 1 kHz Evolution pump are not synchronized. Therefore, the electronics in the Pockels cell controller picks the oscillator pulse that happens to be closest to its internal 1 kHz clock. This results in a jitter of 25 ns (± 12.5 ns from the origin) between the Evolution trigger and the actual output of the Hurricane. Although this is not causing any problems or restrictions for the standard pump-probe or 2D-IR experiments, the jitter is greatly decreasing time resolution for the experiments where two independent and synchronized lasers are needed (Chapter 7). As shown in Subsection 2.3.7, we have overcome this problem by using the oscillator pulses as the external trigger for both the Evolution and UV nanosecond laser.
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2.3.2 Optical parametric amplifier and mid-IR light generation

The output of the Hurricane laser system is coupled into a commercial optical parametric amplifier (OPA) from Spectra Physics, see Fig. 2.4. Approximately 1% of the beam is split off and focused into a sapphire plate where a broad spectrum of “white light” continuum is generated. The white light or continuum is predominately caused by self-phase modulation. Another 10% is split off by a beam splitter (BS) to pump the optical parametric generation process in a 1 mm thick type II $\beta$-Barium Borate (BBO) crystal. In this case, the seed is the previously generated white-light continuum, which provides photons with all energies down to IR. This is the first amplification pass, which as explained in the previous chapter, generates the signal and idler. Using a dichroic mirror (DM) only the idler is transmitted and used as a seed for the second main parametric amplification stage, where it is overlapped in time and space with the leftover (~90%) of the 800 nm beam. Typically, an energy of approximately 80 $\mu$J of combined signal and idler at 1 kHz repetition rate and with 100 fs pulse duration is generated.

Unfortunately, due to the strong absorption of BBO at mid-IR wavelengths it is not possible to generate light with these wavelengths directly. We have used two different ways to generate mid-IR frequencies. In the first scheme (see Fig. 2.4) we use as a pump beam approximately 20% of the output of the Hurricane laser system that is split off just before the OPA. The idler tuned to approximately 2000 nm is doubled in a second BBO crystal and overlapped in time and space with the pump light in a 1 mm thick Potassium Titanium oxide Phosphate crystal (KTP) with a cut angle of 42°. Type II DFG takes place and the difference frequency (800 nm - 1000 nm) in the mid-IR is generated. The disadvantage of this scheme is that the KTP crystal starts to absorb at about 4000 nm so the generation of light in the mid-IR range is limited. The output energy is typically 10 $\mu$J per pulse and by focusing the 800 nm beam ($f = 25$ cm) we can generally achieve pulses with a duration of 120 fs and a with a full width at half maximum (FWHM) of about 200 cm$^{-1}$.

The second scheme is to mix the signal and idler directly and again make use of DFG to create mid-IR light. In this case we use a silver gallium sulphate crystal (AgGaS$_2$) which allows for the generation of the mid-IR down to 10000 nm. The disadvantage is a lower output energy (about 1 $\mu$J per pulse with a duration of about 150 fs). To optimize temporal and spatial overlap of the signal and idler we separate them using a dichroic mirror. Due to the dispersion in the OPA the signal arrives at a different time than the idler which we compensate for by a manual delay stage. The signal and idler are focused onto the AgGaS$_2$ crystal (2 mm thick) using mirrors with a 50 cm focal length. The generated mid-IR beam is collimated using a similar mirror and coupled into the pump-probe setup.
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2.3.3 One-color mid-IR pump-probe setup

The pump-probe setup is based on a design reported by Hamm et al.,\textsuperscript{45} see Fig. 2.5. Approximately 5% of the mid-infrared light is split off with a wedged BaF\textsubscript{2} window to obtain probe and reference pulses. The angle of reflection should not be larger than 20° due to the angle dependent reflectivity of linearly polarized light which could cause significantly different intensities for the probe and reference beams. The transmitted light is used as the pump pulse which passes through a half-wave plate that allows for various relative polarizations of the pump with respect to the probe. The pump and probe pulses are focused and overlapped in the sample by means of a \( f = 100 \) mm off-axis parabolic mirror (focal diameters of \( \sim 400 \) and \( \sim 250 \) \( \mu \)m for pump and probe, respectively). The transmission of probe and reference is measured by frequency-dispersed detection using a commercially available monochromator (Oriel - Newport) and a \( 2 \times 32 \) HgCdTe (MCT) array.

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**Figure 2.4:** The experimental setup of the Optical Parametric Amplifier (OPA) and mid-IR light generation setups are shown. The solid, dashed and dotted lines represent 800 nm, near-IR (signal and idler) and white light continuum, respectively. The generated mid-IR light is depicted using the gray solid lines.
detector (IR Associates) with \( T(\omega) \) and without \( T_0(\omega) \) pump present. This is achieved by means of a chopper (Arstec) that is set to allow every second pump pulse to come through. In this way the sample experiences pump pulses with a repetition rate of 500 Hz. The response of the MCT detector decays with a time constant of about 1 µs and therefore we use a sample-and-hold amplifier (designed by Hamm Elektronik, GmbH) that gives enough time for the A/D cards (Measurement Computing) to read-out all 64 MCT channels. All components of the pump-probe setup are controlled using a custom-made measurement program.

![Figure 2.5: The experimental pump-probe setup.](image)

Typically, during pump-probe experiments the normalized absorption change is determined as a function of the delay \( \tau \) between the pump and the probe. This delay is induced using a mechanical delay stage (Newport). To increase the signal-to-noise ratio we divide both the probe with and without pump by the intensity of the reference:

\[
\Delta \alpha(\omega, \tau) = \log \left( \frac{I_{\text{pr}}(\omega, \tau)}{I_{\text{ref}}(\omega)} / \frac{I_{\text{pr},0}(\omega)}{I_{\text{ref},0}(\omega)} \right),
\]

(2.10)

The indices pr and ref represent the transmission spectrum of the probe and the reference beams, respectively. A typical measurement with an error bar of 0.01 mOD requires averaging approximately over 4 minutes (120 thousand pump pulses). In
order to determine the rotational-free decay (RF) and anisotropy (A) signals we control the polarization of the pump with respect to the probe pulse using a zero-order half-wave plate. To completely determine both these signals one needs to measure only the absorption change as a function of delay for the parallel ($\Delta \alpha_\parallel$) and perpendicular ($\Delta \alpha_\perp$) respective polarizations of the pump and probe. Using the formulas

$$\Delta \alpha_{RF} = \frac{1}{3}(\Delta \alpha_\parallel + 2\Delta \alpha_\perp)$$

$$A = \frac{\Delta \alpha_\parallel - \Delta \alpha_\perp}{\Delta \alpha_\parallel + 2\Delta \alpha_\perp}$$

it is possible to calculate the rotational-free and anisotropy signals. It is also possible to measure the rotational-free signal directly by setting up the angle between the polarizations of the pump and the probe to the so-called magic angle ($\arctan \sqrt{2} = 54.7^\circ$).

### 2.3.4 2D-mid-IR pump-probe setup

We measure 2D-mid-IR pump-probe spectra using a modified one-color pump-probe setup, which is extended with a tunable Fabry-Perot etalon positioned in the pump beam. It allows us to excite the sample with a spectrally narrow pump while the probe is left with the original broadband spectrum. In this way we can selectively excite an individual vibrational mode, but still have the possibility to detect the sample response at all wavelengths. The Fabry-Perot etalon consists of two mirrors with $\sim 90\%$ reflectivity that are kept in piezoelectric-controlled mounts and positioned parallel with respect to each other. When a light beam passes through the etalon, multiple-beam interference takes place and the etalon acts as narrowband filter with a series of transmission maxima that are uniformly spaced when expressed in wavelength units. The complete spectrum of the transmitted beam ($A_T$) is calculated by summing all transmitted waves and can be expressed using the reflectivity ($R$) and the interference order ($m$) as

$$A_T = (1 - R) \sum_{m=0}^{\infty} R^m e^{im\phi}.$$  \hfill (2.13)

The phase shift $\phi$ that is experienced between the transmitted and the reflected beam after one roundtrip through the cavity with the length $l$ and refractive index ($n$) is equal to:

$$\phi = \frac{4\pi n l}{\lambda}.$$  \hfill (2.14)
This geometrical series in the Eq. 2.13 can be expressed analytically so the sum becomes

\[ A_T = \frac{(1 - R)}{1 - R e^{i\phi}}. \]  

(2.15)

The intensity of the transmitted beams is given by \( A_T A_T^* \), which, using Euler’s formula, gives the transmission function

\[ T_e = A_T A_T^* = \frac{(1 - R)^2}{1 + R^2 - 2R \cos(\phi)}. \]  

(2.16)

Substituting \( \phi \) using Eq. 2.14, assuming that at the maximum transmission \( L = m\lambda_0/2 \), refractive index \( n = 1 \) and for \( \lambda = \lambda_0 + \delta \lambda \) we can write \( T_e(\lambda) \) as

\[ T_e(\lambda) = \frac{(1 - R)^2}{1 + R^2 - 2R \cos(2\pi m \left(1 - \frac{\delta \lambda}{\lambda_0}\right))}. \]  

(2.17)

The \( \cos(\delta \lambda/\lambda_0) \) function can be approximated by a Taylor series expansion and

![Image](image_url)

**Figure 2.6:** Calculated time profile of the Fabry-Perot etalon output for 7th interference order.

as a result we can describe the transmission spectrum close to the maximum of transmission by a Lorentzian function

\[ T_e(\lambda) \propto \frac{1}{\Gamma^2 + (\lambda - \lambda_0)^2}. \]  

(2.18)

By applying a Fourier transformation on the total transmission spectrum (see Eq. 2.17) we get an output time profile of the Fabry-Perot etalon (see Fig. 2.6) as an exponential decay function. It is also possible to explain the time dependence of the Fabry-Perot output in more intuitive way taking the output as a sum of individual transmission peaks delayed by \( \tau = 2Lcn \). As the distance between the mirrors...
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2.3.5 Two-color mid-IR pump-probe setup

In order to perform two-color mid-IR pump-probe experiments we have used a commercially available Ti:Sapphire regenerative amplifier system (Titan - Quantronix) which delivers 100 fs pulses centered at 800 nm with three times the intensity of the Hurricane system. The output of the Titan is split into three beams; the first pumps an OPA, the second is used for difference frequency generation of mid-IR using a KTP crystal, and the last is pumping the commercial 5-pass Traveling wave Optical Parametric Amplifier of Super-fluorescence (TOPAS - Light Conversion). The TOPAS is also an OPA but with the difference that the optical parametric amplification is not seeded with white light but uses the process
of super-fluorescence. The output of the TOPAS is overlapped with 800 nm pulses from the Titan, generating using DFG mid-IR light with an energy of \( \sim 10 \mu J \) and pulses with 80 cm\(^{-1}\) FWHM at 3300 cm\(^{-1}\). The outputs of the TOPAS and the OPA are used as pump and probe pulses, respectively, in the pump-probe setup described in the previous chapter.

### 2.3.6 Three-pulse photon-echo setup

The three-pulse photon-echo technique is a method to study ultrafast processes like vibrational relaxation and spectral diffusion. Our three-pulse photon-echo setup (Fig. 2.8) uses the mid-IR light generated by DFG of 800 nm and the doubled idler in a KTP crystal as described in the previous chapter.

![Diagram of the experimental three-pulse photon-echo setup.](image)

**Figure 2.8:** The experimental three-pulse photon-echo setup.

The mid-IR laser pulses are split into three separate beams of equal intensity by means of 66% and 50% beamsplitters, where each of them is delayed in time with respect to the others using two mechanical delay stages. All three pulses are focused and overlapped in the sample, and recollimated using two 100 mm off-axis parabolic mirrors. They interact with the sample in a certain order creating a system response shown in Fig. 2.9. The first two pulses interfering in the sample imprint a spatial grating of the complex refractive index. The third pulse is diffracted by this grating, producing a signal that is generated in the conjugated phase-matched directions \( \vec{k}_s = \vec{k}_3 + \vec{k}_2 - \vec{k}_1 \) and \( \vec{k}_s' = \vec{k}_3 + \vec{k}_1 - \vec{k}_2 \). By changing the delay between
2. Experimental methods

Experimental setups

the first two pulses $t_{12}$ we can probe the dephasing dynamics, while the signal measured when the delay $t_{23}$ is varied reflects mostly the dynamics of population relaxation and reorientation. The generated photon-echo-peak shift (PEPS) signals are detected simultaneously using single pixel MCT detectors. To minimize the scattering effects of any of the original pulses into the $k_s$ and $k'_s$ directions, we chop one beam and detect the zero-background signal at a 500 kHz repetition rate. In addition we use a beam blocker (mask) for all original beams with two holes that are positioned in the directions of the echo signals.

![Figure 2.9: Geometry of the beams in the three pulse photon-echo experiments.](image)

2.3.7 Nanosecond UV pump mid-IR probe setup

For the nanosecond UV-pump mid-IR probe experiments we have used a pump-probe setup in which the output of a commercial pulsed Nd:YAG laser system (IB Laser DiNY pQ) was used as a pump beam. The typical output energy of the Nd:YAG laser is $\sim$2 mJ per pulse at 355 nm (tripled 1064 nm fundamental) with a typical pulse duration of 10 ns. To be able to use two independent lasers for time-resolved pump-probe studies one needs to synchronize and control their relative time delay. We have achieved this using the external triggering of both laser systems by means of pulse/delay generators, see Fig. 2.10.

A fast silicon photodiode detects the residual output of the Ti:sapphire oscillator with a repetition rate 80 MHz (1 pulse every 12.5 ns). This signal is amplified and a home-built frequency divider picks up every 80000th pulse which effectively decreases the frequency of the pulse train to 1 kHz (1 pulse every 1 ms). The 1kHz pulses are used to trigger BNC (Berkley Nucleonics Corporation, Model 575) and
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Stanford (Stanford Research Systems, DG 535) pulse generators. The Stanford and BNC pulse generators trigger and Q-switch the Evolution (the pump laser of the Hurricane) and the Nd:YAG nanosecond laser, respectively. The Evolution laser is pumped and Q-switched at a 1 kHz repetition rate, while the pump and Q-switch of the Nd:YAG laser are triggered at 500 Hz and 20 Hz, respectively, to avoid heating effects in the sample cell windows. The chopper and the A/D cards are triggered using the BNC pulse generator at 20 Hz in such a way that they are synchronous and in-phase with the Q-switch of the Nd:YAG laser. It should be mentioned that the build up in the Evolution laser takes a shorter time than in the Nd:YAG laser. Thus we have to use the previous pulse from the kilohertz train that is used as Evolution trigger to trigger the build up process (pump) in the Nd:YAG laser. The synchronization sequence of the Hurricane and Nd:YAG lasers is shown on Fig. 2.11. To be able to control and change the delay between the mid-IR and UV pulses one cannot use a mechanical delay stage because to achieve a delay of 1 µs would require a pathlength of ~300 m. To generate the time delays we use a computer controlled BNC pulse generator which controls and changes the delay of the pump and the Q-switch for the Nd:YAG laser.

The resulting 355 nm pulse train of the Nd:YAG laser is coupled into the pump-probe setup and focused using a CaF₂ lens (f = 20 cm focal length) with the focus at a position ~5 cm behind the sample, which is between the off-axes parabolic mirrors. The probe and reference are then coupled into the monochromator and detected using a 2 × 32 HgCdTe (MCT) array detector. The resulting pump-probe signals are calculated in the same way as described for the one-color pump-probe experiments.

Figure 2.10: Triggering scheme of the Hurricane and Nd:YAG lasers.
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2.3.8 General information about used materials and sample cells.

In the experiments on mixtures of H$_2$O and D$_2$O the sample was kept in a standard IR circular sample cell with 1 mm thick CaF$_2$ windows that were separated by a 50 µm thick Teflon spacer. The temperature is controlled with an accuracy of $\sim 5$ °C using a home-built water-cooled temperature sample cell with Peltier elements to induce or extract heat from the sample.

In the experiments on rotaxanes we have used a sealed rectangular FT-IR sample cell (Apollo-Scientific) with a 1 mm thick spacer. All non-deuterated and deuterated solvents used in this thesis were acquired from Sigma-Aldrich and Euriso-top, respectively. During the UV-IR nanosecond pump-probe experiments we have used a demountable rectangular sample cell with 2 mm thick CaF$_2$ windows and a 1.1 cm thick Teflon spacer. The sample was circulated and bubbled with argon continuously. All FT-IR spectra were measured using a commercially available spectrometer (Vertex 70 Bruker) with a resolution of 1 cm$^{-1}$. To acquire the FT-IR spectra in the spectral region down to 500 cm$^{-1}$ ZnSe windows were used.