Water Interacting with interfaces, ions and itself

Piątkowski, Ł.

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3 Experimental methods

In the experiments presented in this thesis we use ultrashort, femtosecond pulses in the mid-infrared spectral region. The complete experimental setup consists of three main blocks (figure 3.1): the laser system that provides high intensity, ultrashort pulses; a frequency conversion part where we generate mid-IR pulses of desired wavelength, energy and bandwidth, and finally the part where the actual experiment takes place. In the following we briefly describe each of these stages.

![Figure 3.1. Three main blocks constituting the experimental setup used for the experiments presented in this thesis.](image)

3.1 Laser system

In the time-resolved, pump-probe experiments presented in this thesis we use ultrashort laser pulses in the mid-infrared frequency region between 2.8 and 7 µm (1450–3500 cm\(^{-1}\)). These pulses are generated by multiple frequency conversion and amplification processes that are pumped with the near-infrared 800 nm pulses derived from a high energy Ti:Sapphire amplifier system (Coherent - “Legend Duo”). The amplifier is seeded by an oscillator (Coherent - “Mantis”) which delivers 800 nm pulses with a bandwidth of ~80 nm at FWHM (corresponding to a pulse duration of ~35 fs), at a repetition rate of 80 MHz. The seed pulses are subsequently stretched and amplified at a repetition rate of 1 kHz. The pulses are first amplified in a regenerative Ti:sapphire amplifier. This amplifier is pumped with the pulses from a diode pumped frequency-doubled 527 nm Nd:YLF laser (high energy “Evolution”). The resulting pulses are amplified further in a single-pass amplification stage in a Ti:sapphire crystal. After compression we obtain 40 fs pulses, centered at 800 nm, with a pulse energy of 7.5 mJ at a repetition rate of 1 kHz.
3.2 Frequency Conversion

The resulting 800 nm beam is split into four branches. Two of these are used to generate mid-infrared pulses, one is used to characterize the pulses in a $\beta$-barium borate crystal (BBO) based autocorrelator, and the last one is used as an upconversion beam in the sum-frequency generation experiments. A schematic representation of the different frequency conversion stages is shown in figure 3.2.

Figure 3.2. Schematic representation of the generation of the pulses used in the experiments. The 800 nm light from the Ti:Sapphire amplifier is split in four parts using beam splitters (BS). We sample a few $\mu$J of the 800 nm beam and send it to an autocorrelator to monitor the pulse duration during the experiments. We use about $\sim$80% to pump a high energy OPA (HE-TOPAS), which generates (DFG-1) high intensity ($\sim$60-120 $\mu$J), broadband ($\sim$400 cm$^{-1}$) mid-infrared pulses (IR 1). The third part ($\sim$12%) is used to pump the home-built OPA which yields (DFG-2) low energy ($\sim$7 $\mu$J), broadband ($\sim$350 cm$^{-1}$) mid-infrared pulses (IR 2). The remaining part of the 800 nm light is used in the SFG experiments as an up-conversion pulses (IR 4). For the 2-dimensional time-resolved SFG experiments we use high intensity, narrowband mid-infrared pulses (IR 3) that are generated via parametric amplification of the frequency doubled idler from the OPA and pumped with the residual 800 nm pulses from the HE-TOPAS.

The mid-infrared pulses are generated in two separate optical parametric amplifiers (OPA). We use about $\sim$6 mJ to pump a high-energy OPA (Light
Conversion - "HE-TOPAS"). A small fraction of the 800 nm light is focused in a sapphire plate to generate a white light continuum that is used as a seed in three subsequent amplification process in BBO crystals. These processes are pumped with the remaining 800 nm light. The produced signal and idler pulses are used in a difference frequency mixing process (DFG) in a silver gallium disulphide (AgGaS\(_2\)) crystal, resulting in 60-120 \(\mu\)J pulses in a frequency range of 1450-3500 cm\(^{-1}\), with a pulse duration of \(~60\) fs, and with a spectral bandwidth of \(~400\) cm\(^{-1}\) (DFG-1).

About 1 mJ of the original 800 nm beam is used to pump the home-built OPA (OPA-1). Similarly to the high energy TOPAS, this OPA uses white light as a seed. This OPA has two BBO based amplification stages. The resulting signal and idler pulses have energies of 60 \(\mu\)J and 110 \(\mu\)J, respectively, and are used either in a DFG process generating mid-infrared pulses (DFG-2), or in other frequency conversion processes.

The 2-dimensional time-resolved SFG experiments require spectrally narrow and intense mid-infrared excitations pulses. We generate these pulses by means of another optical parametric amplification process (OPA-2) seeded with the idler beam from OPA-1 and pumped with the residual 800 nm beam from the HE-TOPAS. We frequency double the idler in a 3 mm BBO crystal. Due to phase-matching limitations, the resulting \(~1000\) nm pulses have a bandwidth of only \(~10\) nm. We then parametrically amplify these pulses with 800 nm light in a 10 mm long lithium niobate (LiNbO\(_3\)) crystal. We thus obtain mid-infrared pulses in the range of 2200-2800 cm\(^{-1}\), with a bandwidth of 70-150 cm\(^{-1}\) (pulse duration of \(~150-200\) fs) and a pulse energy of 20-50 \(\mu\)J.

### 3.3 IR PUMP-PROBE SETUP

The infrared two-color pump-probe setup used in the experiments is shown in figure 3.3. The probe and reference infrared beams are split (\(~4\%\) reflection) from the main beam (IR 1) using wedged barium fluoride windows. The reference beam is used to correct the detected signal for pulse to pulse fluctuations in the infrared intensity. The remaining transmitted beam is used as a pump. We can use the pump beam directly thus performing the experiment in a one-color configuration (the pump and probe beams have the same central frequency and spectral bandwidth). In the two-color experiment we propagate the pump beam through a home-built Fabry-Pérot interferometer thus spectrally shaping the pump beam in terms of its central frequency (within the original bandwidth) and its bandwidth. This spectral filter consists of an air spaced cavity that is created by two closely spaced parallel semi-transparent windows (reflectivity \(R = 90\%\)). The Fabry-Pérot filter transmits only the wavelengths that constructively interfere in the cavity. By changing the distance between the two windows we can tune the wavelength of the transmitted beam and its bandwidth. The spectral bandwidth of the pump pulses used in the experiments is 40 - 50 cm\(^{-1}\). If the experiment requires beams with very different frequencies (separation larger than the bandwidth of IR 1) we use a separately generated IR 2 beam as the pump (dotted red line in figure 3.3). Thereby we can per-
form two-color experiments with the pump and probe pulses covering a broad ~2.8-8 µm spectral range.

The probe beam is sent onto a delay stage (resolution of ~0.66 fs) that allows us to control the time delay between the pump and probe pulses. Both the probe and the reference beams are focused onto the sample with a gold-coated parabolic mirror (~110 mm effective focal length). Every second pulse in the pump beam is blocked by a chopper wheel rotating with a frequency of 500 Hz. The polarization of the pump pulses is adjusted with a λ/2 plate and set to 45° with respect to the original IR1 beam polarization. The pump beam is focused on the sample with the same parabolic mirror and spatially overlapped with the probe beam. After traveling through the sample, both the reference and the probe beam travel through a wire grid polarizer mounted on a motorized rotation stage. By rotating the polarizer between +45° and -45° with respect to the original polarization we select the polarization component that is parallel or perpendicular with respect to pump beam polarization. The beams are recollimated with a second parabolic mirror. The pump beam is blocked, and the probe and reference beams are propagated to the detection part of the setup. The probe and reference beams are dispersed with a spectrograph and detected with a 2x32 pixel mercury-cadmium-telluride (MCT) detector array (InfraRed Associates). Optionally the spectrum of the pump beam or any other infrared beam (2D TR-SFG pump beam) can be analyzed/recorded in the detection
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3.4 Two-color IR-pump SFG-probe setup

The 2D TR-SFG setup, shown in figure 3.4, uses an IR-pump and an SFG-probe scheme. The three beams used in the experiment: IR probe, IR pump and 800 nm (VIS) are sent onto motorized delay stages that ensure the temporal overlap of the probe and VIS pulses and allow the adjustment of the time delay between the excitation pulse and the detection IR-VIS pulse pair. A combination of a $\lambda/2$ plate and wire grid polarizer in the IR beam paths allow us to control the polarization of the pulses and their intensity. Every other pump pulse is blocked with a chopper wheel rotating at a frequency of 500 Hz. We use a Fabry-Pérot interferometer (SLS Optics) that spectrally narrows the VIS pulses to $\sim15$ cm$^{-1}$, a value that determines the spectral resolution of the recorded SFG signal. The instrumental resolution is $\sim0.7$ cm$^{-1}$. The polarization of the VIS beam is controlled with a cube polarizer. The three beams are focused using calcium fluoride (CaF$_2$) lenses and overlapped at the samples interface. Spatial and temporal overlap of the beams is achieved and optimized by measuring the third-order cross correlation signal of the two infrared and visible beams.
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The SFG signal generated at the interface by the infrared detection pulse and the visible pulse is collected with a mirror, collimated with a lens, and directed to the detection stage. The pumped and unpumped SFG signals travel collinearly. We separate the two signals using a mirror mounted on a galvano scanner motor which is synchronized with the chopper wheel. The pumped and unpumped SFG signals are dispersed using a spectrograph and detected with an electron multiplaying CCD (EM-CCD) camera (Newton DU971P-BV, Andor Technology).