Development of a Non-collinearly phase matched Optical Parametric Amplifier and application in Pump-Probe Spectroscopy

by

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Declaration

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Abstract

The presented thesis will discuss pump-probe spectroscopy as a technique to conduct highly time-resolved spectroscopic measurements. Operating principles, theory and technical requirements will be broadly outlined. Specific attention will be given to the role of the Non-collinearly phase matched Optical Parametric Amplifier (NOPA), its construction and development will be presented in conjunction with the theory of parametric interactions and other nonlinear optical effects to give a comprehensive perspective on its possible applications. Characterization of the NOPA is briefly covered. Finally, as a demonstration of the applicability of a NOPA as a pump source in pump-probe spectroscopy, the thesis will present transient absorption measurements taken with the constructed NOPA.
Opsomming

Hierdie Tesis sal Opwek-Afvra spektroskopie, 'n tegniek om hoogs tyd-opgeloste spektroskopiese metings te neem, bespreek. Die beginsels waarop die tegniek rus, teoretiese agtergrond en tegnieke vereistes sal kortlik saamgevat word. Aandag sal spesifiek aan die rol wat die Optiese Parametriese Versterker deur Onsamelynige fase aanpassing (OPVO) in die bogenaamde tegniek speel, gegee word. Die ontwikkeling en vervaardiging van bogenoemde OPVO sal saam met die teorie van parametriese wisselwerking en ander relevante nie-linere optiese verskynsels uitgele word. Om 'n omvattende perspektief van die moontlike toepassings van die OPVO te gee. Karakterisering van die OPVO sal ook kortlik gedek word. Ten slute, om die toepaslikheid van die OPVO as opwek-bron in Opwek-Afvra Spektroskopie te demonstreer: sal tyd-opgeloste absorbsie spektroskopie metings wat met die gebruik van die OPVO geneem is, voorgedra word.
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Chapter 1 - Introduction

Radiative molecular processes such as fluorescence and phosphorescence can occur on nano- to micro-second timescales. In this domain, electronic circuits can still achieve sufficiently fast detection times to temporally resolve the lifetimes of such fluorescent and phosphorescent states.

When we peer into the realm of faster processes such as absorption by intermediate states, molecules undergoing charge transfer and even vibrational motion, which occur on femto- to pico-second timescales, the resolving power achieved by electronic devices becomes insufficent. The electronic circuits that compose these detection devices cannot be built small enough to allow the electrons an adequately fast detection- and recovery time [18].

Optical techniques, specifically compressed laser pulses in the sub-picosecond range, offer us the desired resolution to study such ultrafast processes. Herein lies the basis of pump-probe spectroscopy.

Pump-probe spectroscopy is an optical technique whereby a femtosecond laser pulse is directed at a molecular sample to enact a photo-induced change in the sample (typically an electronic excitation) due to its exposure to resonant light pulses. A second probe pulse is directed at the sample a user-defined time later and changes in the sample are monitored by this pulse. By taking measurements at different times after excitation, a picture of molecular changes as a function of time in the sample emerges. Numerous processes can be detected by the probe pulse, the most prominent being absorption but also including ionization, fluorescence (by observing stimulated emission) and in the case of a two-dimensional spectroscopy setup even diffraction due to gratings caused by transient changes in the refractive index of the sample. These measurements give the user insight into the time evolution of the population of the measured states.

Typically the pump and probe pulses are generated from a common seed pulse and split into a pump and probe beam path. The temporal coherence between the pump and probe pulses is then determined by the difference in optical path length from the point where the beam is split to the point where the pump and probe pulses are focused onto the sample. One of these beams incorporates a mirror pair mounted on a mechanical linear translation stage which, when adjusted, alters the delay time between pump and probe pulse. In so doing, a succession of measurements at later times after excitation can be taken and a time-dependent absorption trace can be recorded. This technique has the advantage that an unlimited amount of samples can be averaged over at each data point provided the shot-to-shot stability of the pump and probe pulses remains within bounds for the duration of the measurement. Indeed, the central idea behind pump-probe spectroscopy is to escape the restrictions imposed by electronic detection systems on measurements done in real time.
and instead to conduct time-resolved measurements by changing the detection time after the sample has been optically addressed by manipulating the aforementioned mechanical delay line.

The temporal resolution is determined by the cross-correlation of the pump and probe pulse with both pulses typically in the sub-picosecond range [18]. Modern mechanical- and piezoelectric translation stages can move accurately and consistently in increments of fractions of micrometers. Taking into consideration the speed of light in air, elementary calculations show that this correlates to temporal delay increments in the order of femtoseconds and therefore do not limit our resolution.

1.1 The Pump-Probe Setup at the LRI

Although multiple configurations of the instruments at our disposal are possible and have to be implemented in a manner determined by the sample and parameter under investigation. I will give a brief overview of the pump-probe setup as it is used at the Laser Research Institute (LRI) at Stellenbosch University. A photograph of the setup can be seen in Figure 1.1. A detailed description of the optical elements used in the setup will follow in Chapters 3 and 4.

The setup is powered by a Clark MXR CPA-series (Chirped Parametric Amplifier) which produces 800 µJ pulses at a 1 kHz repetition rate with 15 fs pulse duration around a fundamental frequency of 775 nm. The CPA output is then split into several beams: two beams of 300 µJ pulses are used to pump each of the two Non-collinear phase matched Optical Parametric Amplifiers (NOPA) our tunable femtosecond pump pulse sources. A schematic represen-
tation of the setup can be seen in Figure 1.9. A beam of around 10 μJ pulses is used for white light generation. The white light is used as probe pulse to monitor very broad spectral intervals in the visible and near infrared spectral range. The remaining pulse energy from the CPA output is directed towards an electron diffraction experiment which can run concurrently to the transient absorption measurements.

Based on optical parametric amplification, the NOPA produces pump pulses between 450-720 nm with energies of around 10 μJ. A compression stage consisting of two fused silica Brewster prisms compresses these pulses to below 30 fs, depending on the bandwidth of the NOPA spectrum.

The pump pulses are then directed towards our mechanical linear translation stage. The pump beam is chosen to incorporate the delay stage since minuscule irregularities in the alignment of the beam onto the delay stage can cause the beam to walk as the delay stage moves. Although the delay stage is only 10 cm long, small angular deviations in alignment are amplified by the mirror so that the beam has to travel before striking the sample. We would like to keep the probe beam as stable as possible since it is coupled into the detection system via an optical fibre. The beamwalk effect is additionally offset by focusing the probe beam to a smaller beam diameter (~100 μm) than the pump beam (~200 μm) within the sample volume. We can then safely assume that the probe pulse is probing a sample volume wherein a maximum cross section of molecules have been excited.

Additionally, the beamwalk is monitored and corrected for by a combination of a CCD camera and a piezoelectric mirror mount. The camera is positioned behind the sample and software that was developed in-house, determines the beam’s centre of mass at a pixel coordinate. When this value changes due to the delay stage moving, a signal is sent to the calibrated piezoelectric mirror mount positioned before the sample, to correct the beam before the next measurement is taken.

The pump beam is also directed through an optical chopper, a wagon wheel that blocks and releases the beam at a fixed frequency. This is done to enable the referencing technique. Assuming our sample decays back to its ground state in less than 1 μs (the time between consecutive pulses), the measurement is divided into pumped (chopper open) and unpumped (chopper closed) intervals. The unpumped interval serves as our reference sample, so that a comparison can be made between pumped and unpumped spectra and changes in absorption can easily be detected and quantified. The optical chopper operates at 500 Hz, half the CPA repetition rate, so that every second pump pulse is blocked. The fast chopping frequency reduces the sensitivity to long term fluctuations of CPA output energy.

The probe beam will typically involve supercontinuum generation in an appropriate medium. The broad spectrum generated can monitor absorption changes in a broad spectral range, affording us the opportunity to monitor several molecular states simultaneously. Provided they absorb within the spectral range of the supercontinuum or emit within the detection window of the detection system. Different non-linear media generate different supercontinua when exposed to high intensity light. It is therefore important to select the non-linear media appropriately in order to ensure that the supercontinuum spectrum covers the range of interest.

When ultrafast dynamics in the sub-100 fs range need to be resolved, it may
Figure 1.2: Schematic diagram of Ultrafast Transient Absorption Spectroscopy Setup
be necessary to use the coherent compressible pulses from a NOPA as probe pulse. This, however, is done at the expense of the broadband capability of white light probe pulses.

Two grating spectrometers coupled to one dimensional line scan cameras complete the detection system. Both spectrometers are capable of a 1 kHz repetition rate meaning every pulse generated by the CPA can be measured individually and averaging is totally determined by the wishes of the user and not limited by the equipment. The probe beam is coupled into one of them after passing through the sample volume. A reflection from a neutral density filter used to control the pump energy is coupled into the other. Since the neutral density filter is placed behind the optical chopper, the second spectrometer can detect whether the sample is being pumped or not. It then signals the measuring software and effectively divides the spectra continually read out by the first spectrometer into probe (pumped) and reference (unpumped) intervals. The ratio of these two spectra is calculated where deviations from unity at certain wavelengths indicate that absorption (state is populated), bleaching (state is depopulated), or stimulated emission from a populated state is occurring.
Chapter 2 - Theory

2.1 Linear optics: Propagation of Laser Pulses

A brief discussion of optical phenomena encountered and employed in pump-probe spectroscopy follows to provide a theoretical foundation for discussions in later chapters. A similar but more thorough discussion can be found in Femtosecond Laser Pulses: Principles and Experiments by Claude Rullière [10].

2.1.1 Propagation of Laser Pulses

The propagation of an electromagnetic wave in matter, assuming the magnetic field fluctuates with a negligibly small amplitude in relation to the electric field amplitude, is given by the following simplification of an equation included in Maxwell’s set of equations

\[ \nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = 0, \]

(2.1)

where \( \frac{1}{c} = \mu_0 \varepsilon_0 \), \( \varepsilon_0 \) and \( \mu_0 \) are respectively the electric and magnetic permittivity of the medium in which the electromagnetic wave is propagating and \( c \) is the velocity of light. The simplest solution to the equation 2.1 is given by a plane wave of the form

\[ E_\lambda = \Re\{E_0 e^{i\omega(t-\frac{\lambda}{c})}\}, \]

(2.2)

where the electric field oscillates along the y axis and the wave propagates along the x axis. The electric field amplitude of this plane wave is periodic in time with angular frequency \( \omega \) and in space with a wavelength given by \( \lambda = \frac{2\pi c}{\omega} \).

2.1.2 The time-bandwidth product

The frequency spectrum of a laser pulse is determined by the Fourier transform of the function describing the time evolution of the pulse. Conversely, an inverse Fourier transform of the function describing the spectral content of a pulse will determine the shortest possible pulse as a function of time. In the very simple case of a monochromatic plane wave,

\[ E_\phi(t) = \Re\{E_0 e^{i\omega_0 t}\}, \]

(2.3)

the electromagnetic field oscillates at a fixed fundamental frequency \( \omega_0 \) and is unlimited in the temporal extent in which the electric field oscillates. As a consequence of this regular and infinite oscillation, the Fourier transform of this
2.1. LINEAR OPTICS: PROPAGATION OF LASER PULSES

Infinite flat wave envelope in time gives rise to a Dirac distribution of the spectral content of the plane wave. The bandwidth of the wave approaches zero as time approaches infinity.

\[
\lim_{t \to \infty} \int_{-\infty}^{t} e^{i(t - \omega_0)t} dt = \delta(\omega_0).
\]  

(2.4)

If, however, equation 2.2 is multiplied with a Gaussian envelope function so that the duration of the wave is limited, a light pulse is created.

\[
E_y(t) = \Re(E_0 e^{(-\Gamma^2 + i\omega_0 t)}).
\]  

(2.5)

The Fourier transform of the resulting time evolution function where \( \Gamma \) is the parameter determining the shape of the Gaussian envelope, a pulse bandwidth given by the equation below is obtained.

\[
E(\omega) = \exp\left[-\frac{(\omega - \omega_0)^2}{4\Gamma}\right].
\]  

(2.6)

The result is a spectral envelope that also has a Gaussian form, although now directly proportional to \( \Gamma \) whereas the time envelope is inversely proportional to \( \Gamma \). This result, generally speaking, means the broader the spectrum of a pulse the shorter the possible duration if some effort is made to transform limit the pulse. This relation is known as the time-bandwidth product, an optical manifestation of the Heisenberg uncertainty principle.

\[
\Delta x \Delta \nu \geq \frac{\hbar}{2}.
\]  

(2.7)

For Gaussian pulses the time-bandwidth product is given by.

\[
\Delta \nu \Delta t = 0.441
\]  

(2.8)

where \( \Delta \nu \) and \( \Delta t \) are full width at half maximum values of the respective frequency and time envelopes.

2.1.3 Chirped pulses

Equation 2.8 however, only describes the situation where the Gaussian pulse is transform limited, meaning it has the shortest possible duration for its spectral bandwidth. In this situation the instantaneous frequency, given by the time derivative of the phase term \( \Phi(t) \), is constant in time and equal to the central frequency \( \omega_0 \). In reality, broadband optical pulses propagating through transparent media (like air and glass) do not obey a linear phase term in time since they undergo group velocity dispersion. If an arbitrary function describing the frequency-dependent propagation factors in the phase term is included and the quadratic term of the Taylor expansion of said arbitrary function is included as a first estimation, the phase term of Equation 2.5 becomes quadratically time dependent.

\[
E_y(t) = \Re(E_0 e^{(-\Gamma^2 + i(\omega_0 t + \alpha t^2))}).
\]  

(2.9)

The time derivative of the phase term is then given by.
\[ \omega(t) - \frac{\partial \Phi}{\partial t} = \omega_0 + 2\alpha t \]  
(2.10)

Now the instantaneous frequency becomes a linear function of time, with the frequencies red-shifted of the fundamental arriving at any point along the propagation direction before the fundamental frequency and frequencies blue-shifted of the fundamental arriving after. These pulses are said to be chirped.

### 2.2 Second Order nonlinear Effects

In order to generate tunable pump pulses we take advantage of the nonlinear optical properties of non-centrosymmetric crystals. These crystals typically have high second order susceptibilities making them effective media for utilizing nonlinear optical effects such as second harmonic generation and parametric interactions. The NOPA utilizes both effects in order to produce a tunable output.

#### 2.2.1 Second Harmonic Generation

In a classical picture, light propagates through a medium by radiation emitted by successive oscillating electric dipoles that are made to oscillate by the light itself. Higher order susceptibilities are not taken into account. When the intensity of incident light on a medium becomes sufficiently high however, a rationalization of the nonlinear effects seen can be made by suggesting that the high intensity causes the electric dipoles to oscillate anharmonically and they radiate light at the fundamental frequency as well as integer multiples of the fundamental [higher harmonics]. For a plane wave the intensity of the second harmonic is

\[ I(2\omega) = \frac{2\pi^3 \omega^2 \chi^{(2)}(\omega) I^2}{n^2 c^3} \sin^2(\Delta k l / 2), \]  
(2.11)

Equation 2.11 governs the yield of second harmonic radiation in a medium of length \( l \) and second order susceptibility \( \chi^{(2)} \), where \( \chi^{(2)}(\omega) \) represents a spatial average over the directionally dependent \( \chi^{(2)} \). The equation also demonstrates the quadratic relationship between the intensity of the second harmonic and that of the incident radiation. The index of refraction of the medium is given by \( n \) and \( r \) is the speed of light. The dephasing of second harmonic radiation generated at different depths along the propagation axis in the medium is accounted for by the quantity \( \Delta k \). The wavelength dependent nature of the refractive indices of materials results in different optical pathlengths for second harmonic radiation generated at different depths within the medium. The different propagation velocities for the photon with the fundamental frequency and the photon created by second harmonic generation itself causes a deterioration in the phase coherence of the second harmonic light with the pump light. If the length of the medium is \( l \) the dephasing is given by \( \Delta k l \) where

\[ \Delta k l = (k_2 - 2k_1) l \]  
(2.12)

where the wave vector of the second harmonic radiation and fundamental is given by \( k_2 \) and \( k_1 \) respectively. This parameter needs to be minimized in order
2.2. SECOND ORDER NONLINEAR EFFECTS

Figure 2.1 Refractive index of birefringent crystals. The refractive index experienced by a pulse is not only wavelength dependent but also is a function of the relative angle between the pulse’s polarization and the optical axis of the birefringent crystal.

to maximize the second harmonic conversion efficiency. Birefringent crystals with polarization dependent refractive indices are typically employed to prevent the fundamental and second harmonic photons from running out of phase.

Since the second harmonic generated in a nonlinear medium is polarized orthogonally to the fundamental, a birefringent crystal can have the same refractive index for the fundamental and the second harmonic. See Figure 2.1. This results in zero dephasing over a large propagation length. By changing the angle of incidence relative to the crystal’s optical axis, the wavelength region for which this condition holds can be manipulated.

### 2.2.2 Parametric Interactions

Parametric interactions is the name given to interactions in a nonlinear medium between two incident photons of different wavelengths. Photons can be split up or combined in energy should they overlap temporally and spatially in a medium with a nonzero $\chi^{(2)}$. One example of these interactions is sum frequency generation where two photons are combined to form a single high energy photon. The processes relevant for the generation of tunable light pulses involves frequency difference generation and parametric amplification. Since all photons annihilated or generated need to adhere to a phase matching condition in these interactions, certain parametric effects can be suppressed or enhanced by adjusting the incidence angle of both the incident photons.
Figure 2.2 demonstrates the process of optical parametric amplification. A high intensity pump pulse $\omega_1$ and a weak seed pulse $\omega_2$ are incident on the nonlinear medium. The pump pulse excites the medium and the seed stimulates the creation of a photon with frequency $\omega_2$ called the signal photon. The remaining energy is emitted as an idler pulse of frequency $\omega_3 = \omega_1 - \omega_2$. In this process the pump photon is annihilated but a photon of frequency $\omega_2$ (signal) and a photon of frequency $\omega_3$ (idler) are created. The weak seed pulse is thus amplified at the expense of the intensity of the transmitted pump pulse. This process, for the different photons involved, occurs when the phase-matching condition is satisfied. Energy and momentum conservation considerations need to be taken into account for parametric amplification to occur and can be expressed using the following equations:

$$\omega_1 = \omega_2 + \omega_3, \quad (2.13)$$

$$k_1 = k_2 + k_3, \quad (2.14)$$

### 2.3 Third Order nonlinear Effects

In order to generate white light with high intensity femtosecond pulses we require centrosymmetric materials with high third-order susceptibilities denoted by $\chi^{(3)}$. This is the third order correction to the non-linear electrical susceptibility. Numerous processes are responsible for white light generation including four wave mixing and Raman scattering but the dominant processes are self focusing and self phase modulation [13].

#### 2.3.1 Self Phase Modulation

Femtosecond pulses in an isotropic medium, especially when focused and in large part due to their short duration, have high enough intensities that a modulation in the refractive index becomes noticeable. These pulses change the dielectric response of the medium, resulting in an intensity dependent refractive index of the form...
2.3. THIRD ORDER NONLINEAR EFFECTS

![New Frequencies generated by self phase modulation](image)

Figure 2.3  New Frequencies generated by self phase modulation [22].

\[ n = n_c + \frac{1}{2}n_2I(t). \]  \hspace{1cm} (2.15)

Self phase modulation is a consequence of the time dependence of the pulse intensity as seen in Equation 2.15 [16]. Since the wave vector of a pulse and implicitly the phase of the pulse, has a refractive index dependence the frequency of the pulse is affected. Due to the time dependence, chirped pulses will experience different refractive indices for different frequency components. This has the effect of modulating the phase of different frequency components differently. Due to the Fourier duality of time and frequency this phase modulation generates new frequencies within the wave packet spectrum; 

\[ \delta \omega(t) = \omega(t) - \omega_t - \frac{\omega_0n_2}{2c} \frac{\delta I(t)}{\delta t}. \]  \hspace{1cm} (2.16)

Equation 2.16 governs to which extent these new frequencies deviate from the fundamental \( \omega_0 \).

Figure 2.3 shows the spectrum of new frequencies generated due to a Gaussian pulse in a nonlinear medium with positive \( n_2 \).
2.3.2 Self Focusing

In the preceding section it has been shown that under high enough intensities the intensity dependent nonlinear index of refraction starts to play a significant role. A Gaussian light pulse also has a radial intensity distribution resulting in different refractive indices in a nonlinear isotropic medium at different radial distances from the intensity peak. A visualization of this situation can be seen in Figure 2.4.

Supposing the Gaussian intensity distributed pulse travels through a medium with a high $\chi^{(3)}$ of uniforming thickness and positive $n_2$. This results in a longer optical pathlength for rays traveling closer to the radial centre. The uniform slab of nonlinear material effectively becomes a lens focusing the Gaussian pulse with a focal power determined by $n_2$ and the intensity. In bulk material this results in the pulse continually being focused tighter as the radial intensity gradient steepens. This dynamical focusing continues until the effect is balanced by ordinary linear diffraction. This balance between self focusing and linear diffraction generates a stable collimated white light continuum in a process known as filamentation.
Chapter 3 - The NOPA

3.1 Introduction

In order to investigate a large variety of molecules and, perhaps, various transitions of the same molecule, pump-probe spectroscopy demands a broadband tunable light source to provide excitation pulses. Ideally, we would like this source to provide pump pulses with the following properties:

- Tunability needs to be continuous throughout the visible spectrum,
- These pulses need to be sufficiently short to temporally resolve the molecular processes under investigation,
- The pulses need to have sufficient energy to excite a maximum cross section of molecules under investigation within the beam diameter to provide the researcher with an adequately large signal.

All these requirements can be met to a satisfactory degree if a Non-Collinearly phase matched Optical Parametric Amplifier (NOPA) is employed [7, 8].

Since the building of the NOPA that forms part of my Master’s thesis is essentially a duplication of an already existing NOPA used in our laboratory, the question may arise of what benefit is the second NOPA (apart from an educational one to the author) to the laboratory?

Firstly, a second NOPA greatly reduces the transition time between measurements on different molecules. A user can prepare the additional NOPA for an experiment while another is being used for measurements on a different molecule. While one NOPA is involved in measurements performed on a molecular sample, the second NOPA can be prepared for the absorption band of the succeeding sample to be investigated. A flip mirror is used to alternate between the optimized pulses coupled into the experiment. Measurements can then be suspended for longer times without having to align the NOPA for measurements conducted in the interim on another sample requiring a different excitation wavelength and realigning the NOPA when measurements on the original sample resume. This ensures improved repeatability and long term stability. The second NOPA has proven to provide us with greater versatility and flexibility in planning measurement timetables for concurrently running projects.

More importantly, the NOPA’s afford the laboratory the opportunity to conduct NOPA-NOPA pump-probe experiments. In the case where a molecule shows very fast transition kinetics for example in the sub-5fs regime where even coherent molecular vibrations can be resolved, the spectral chirp of the supercontinuum generated to probe these processes may lead to insufficient
temporal resolution of these ultrafast dynamics since the white light pulse itself has a duration larger than 150 fs which is the duration of the CPA pulse from which white light is generated. To overcome this limitation a solution could be to monitor the spectral changes with a probe pulse from a second NOPA. The temporal resolution is then determined by the convolution of the temporal profiles of both the pump and probe pulse, or the cross-correlation of the two pulses. This, however, can only be done at the expense of being able to simultaneously probe states in other spectral regions, as the NOPA probe pulse spectrum is much narrower than the white light spectrum. Once a picture is made of the various simultaneous processes with the broadband detection pump-probe setup, however, a detailed and highly time-resolved population or depopulation of a specific molecular state in a specific spectral region, can be measured with a NOPA-NOPA setup [21]. Achieving similar temporal resolution with the conventional supercontinuum is, in principle, possible by using a prism compressor to minimize the chirp of the white light pulse, but achieving this on a day-to-day basis would require considerably more effort.

Finally, a second NOPA in our laboratory would facilitate the operation of a two-dimensional spectroscopy setup that is currently under development. A photograph of the second NOPA that has been developed can be seen in Figure 3.1.
3.2 Principles of Parametric Amplification

The NOPA I have duplicated makes use of parametric amplification in two stages and in both stages uses frequency doubled pump pulses of the CPA [21]. Due to energy conservation the spectral region that can be amplified by parametric amplification is red-shifted of the pump frequency. In order to provide amplified light in the visible region the CPA fundamental at 775 nm is up-converted to its second harmonic at 387 nm. Since both parametric amplification and second harmonic generation are processes that require a medium with a large $\chi^{(2)}$, the nonlinear crystal BBO (β-barium borate) is used. The CPA output is split with a beam splitter: the majority of the intensity is transmitted to a BBO crystal which is orientated to maximize our second harmonic yield.

The reflected light from the beam splitter is focused in a sapphire crystal to generate a supercontinuum. This process is discussed in the theory chapter. The broad spectrum allows for seed pulses for amplification at any wavelength that comprises the supercontinuum. The inherent group velocity dispersion of spectrally broad pulses causes the pulses to be chirped and increases the pulse length of the white light pulse. By adding a mechanical translation stage to the optical path of the pump pulse before parametric amplification in both stages we can delay pump and seed pulses relative to one another and thanks to group velocity dispersion, control which frequencies overlap in time with the pump pulse within the BBO crystal. The pump pulse has a duration of typically 100 fs whereas the chirped seed pulse has a duration of around 2 μs. The spectral components of the supercontinuum that fulfill the phase-matching condition within the volume of the BBO crystal are amplified. The interaction is an example of type I phase matching: the seed and amplified light and idler pulse have the same polarization but are polarized orthogonally to the pump light.

The pump light is directed towards the BBO crystal at an angle to the seed pulse. Hence the noncollinearity in the term 'Noncollinearly phase matched Optical Parametric Amplifier'. This has two basic advantages. Firstly, it eliminates the need to filter the pump wavelength from the amplified light since the beams are already spatially separated. Secondly, the adjustment of this angle in effect the phase-matching angle provides another degree of freedom in adjusting for which spectral region the phase-matching conditions are met [17, 21]. The most fundamental benefit however is that the phase matching curve can be adjusted with the manipulation of this angle to allow broadband amplification due to broadband phase matching. After compression, a broad bandwidth pulse translates to ultrashort pulse duration.

In Figure 3.2 the non-collinear setup is demonstrated. Note that the photon with the same frequency as the seed photon created by annihilation of the pump photon is emitted in the same direction as the seed photon. As a result the idler pulse that is also created by this process is emitted in such a direction as to conserve the momentum of the original pump photon. As is determined by equation 2.14. A photograph of the light generated in the setup can be seen in Figure 3.3.
Figure 3.2 Non-collinear phase matching.

Figure 3.3 Non-collinear phase matching: Note idler pulse reflected from paper, the pump pulse blocked by the mask and the amplified pulse being reflected from the mirror to the next amplification stage. The super-fluorescent ring can also be seen.
3.3. THE SETUP

Figure 3.4: Overview of NOPA components. The light red line indicates the path of the CPA fundamental, the blue line indicates the path of the second harmonic pump beam, while the white line indicates the path of the white light seed pulse for the first amplification stage. The dark red line indicates the idler pulse generated at both amplification stages and the green line indicates the signal pulse that is generated at the first amplification stage and amplified further at the second amplification stage. The crystals and optical components are labelled and referred to in the text.

3.3 The Setup

The sections that follow will refer, via characters enclosed in brackets, to NOPA components depicted in Figure 3.4.

3.3.1 The Input

The outgoing CPA pulses are coupled into the NOPA, and are split by a beam splitter (1) with a broadband anti-reflective coating on the back side. This is done so that ~4% of the CPA pulse intensity is reflected off the front surface (to limit dispersion) and not off the back surface to provide a well-defined single Gaussian pulse. The transmitted pulse undergoes second harmonic generation in a 3.7 mm BBO crystal [A] cut in such a way that the front surface plane makes an angle of 3C degrees with the optical axis of the crystal. It is mounted in a mirror mount so that the inclination angle can be optimized to deliver maximum second harmonic generation (SHG) efficiency which for SHG at 775 nm would be 30.2 degrees. The frequency doubled pulse serves as pump pulse in parametric amplification. The comparatively low-intensity reflected light is used to generate white light. The reflected light is reflected by a broadband plane mirror (2), into the white light generation stage.

3.3.2 The White Light Generation Stage

The white light generation stage is assembled from multiple individual components. The CPA fundamental pulse at 775 nm passes firstly through a variable neutral density filter (3) that can be adjusted by a linear translation stage in order to control the intensity of the pulse by attenuating the beam. Then
through an iris diaphragm \textsuperscript{4} to control the numerical aperture of the incident beam. Both intensity and numerical aperture are important parameters in the generation of supercontinuum \textsuperscript{17, 3}. It is important that these two parameters, intensity and numerical aperture, are controlled so that only a single white light filament is generated. The white light pulses have an energy of around 2 \( \mu \text{J} \). More energy means more filaments each with an additional quanta of energy of around 2 \( \mu \text{J} \). The increased energy due to multifilamentation will, however, cause the coherence of the white light pulse to deteriorate. The intensity of the generated white light is limited by the damage threshold of the medium used for supercontinuum generation. The core components of the white light generation stage are the lens pair that form an optical telescope either side of the 3 mm sapphire crystal \textsuperscript{B}. The focusing lens \textsuperscript{5}, is a BK7 lens with a focal length of 5 cm, it is placed on a mechanical translation stage, that is adjustable in 3 perpendicular directions (henceforth referred to as an XYZ stage), to correct beam alignment caused by refraction and that the focus can be moved relative to the sapphire crystal. The focus can be moved slowly from in front of the crystal towards the front surface, this protects the crystal from being damaged by high-intensity light beyond its damage threshold and allows us to maximize the length of crystal along which supercontinuum can form. Sapphire is the nonlinear medium used for supercontinuum generation since it produces a stable continuum over most of the visible range with relatively gradual spectral structures. The interaction length of the crystal, for supercontinuum to form and broaden in, is limited by the effects of group velocity dispersion and phase mismatch that become more apparent in longer crystals. Longer crystals also affect the mode quality of the output \textsuperscript{16, 3}. A plano-convex fused silica lens \textsuperscript{6} with a focal length of 3 cm refocuses the diverging outgoing white light beam in front of the first amplification stage. It is also positioned on an XYZ stage to maintain alignment and collimation. Finally a band-pass filter \textsuperscript{7} is placed in the beam path to filter the intensity of light around the fundamental and improve the relative intensity distribution over the white light spectrum. A photograph of the white light generation stage can be seen in Figure 3.5.

3.3.3 The First Amplification Stage

The pump light for the first amplification stage is reflected off a 22\% beam splitter \textsuperscript{8}. It reflects 22\% of the intensity at 395 nm. The beam splitter is positioned on a mechanical translation stage to adjust the temporal overlap of the blue pump pulse with the broad group velocity dispersed supercontinuum. The reflected light is then incident on a focusing mirror with focal length of 15 cm with a highly reflective coating for 395 nm \textsuperscript{9}. These two aforementioned retro-reflections effectively filter out the fundamental. The reflected pump beam is then overlapped with the seed light from the white light stage at an angle. Since the seed is amplified, only the angle of incidence of the pump pulse is adjusted. A 1 mm BBO crystal \textsuperscript{10} is inserted at the point of overlap. The amplified light yield has a quadratic relationship with the intensity of pump light. The intensity at the focus will, however, damage the crystal. For this reason the pump light is focused in front of the crystal so that the diameters of the pump and seed pulses match within the crystal. This improves the efficiency of the process without damaging the crystal. The diameters of the beams are kept to a minimum however since the yield of the second order
3.3. THE SETUP

![Image](image_url)

Figure 3.3: The white light generation stage.

The process has a quadratic intensity dependence. The BBO crystal is placed on a mount so that the inclination angle can be adjusted and is placed on a mechanical linear translation stage so that the crystal can be moved relative to the beam loci, adding an extra parameter to optimize amplified output. A photograph of the first amplification stage can be seen in Figure 3.6.

3.3.4 The Second Amplification Stage

The amplified seed pulse is directed via two silver mirrors (10 and 12) onto a 2 mm BBO crystal (C). A fused silica lens (14) is placed in its path to position the focus near the second BBO crystal. The transmitted pump light from the 22\% beam splitter at 395 nm is reflected via two highly reflective mirrors at 387 nm and 45 degree incidence angle (11 and 13), efficiently filtering the fundamental. The pump light is reflected over a combination of a 15 degree steering mirror at 387 nm (16) and a focusing mirror with a focal length of 25 cm (15). The pump light again is directed at an adjustable angle to the BBO crystal which finds itself mounted on a mirror mount and translation stage. Special care must be taken in this stage to ensure that the pre-amplified white light from the first stage is phase-matched with the pump light (and not a different white light region) and indeed amplified further. If different spectral regions are amplified in either stage, the output power would merely be the sum of the two individual powers and not a multiplicative amplification if the same photons are amplified in both stages.
3.3.5 The Output and Compressor

The NOPA output is collimated with a protected silver focusing mirror with focal length of 50 cm. The reflective broadband optics avoid additional dispersion and higher order chirp experienced by pulses traveling through transmitting optics like glass.

The NOPA pulse’s chirp is compensated for by a pair of fused silica Brewster prisms. This is achieved by aligning the pair in such a way so as to compensate for group velocity dispersion experienced by the different frequency components of the broadband NOPA pulse and eliminate chirp. The NOPA pulse enters the first prism at the edge and the frequency-dependent refractive index will disperse the spectral components in different directions. The prism is rotated to the angle of minimum deviation with respect to the angle of incidence. The prisms are also specially cut so that the angle of minimum deviation corresponds to the Brewster angle. Since the pump pulse is polarized orthogonally to the incoming ray and surface normal this ensures that all the light is transmitted.

The second prism is placed an adjustable distance away from the first prism. This prism is also aligned to the angle of minimum deviation relative to the dispersed NOPA pulse. It is positioned in such a way, that the slower short wavelength components of the NOPA pulse strike the tip of the prism and the faster long wavelength components travel through the prism closer to the base. The optical pathlength in the prism is then greater for red components, delaying the red components with respect to the blue components. This configuration, if
3.4. CHARACTERIZATION

Figure 3.7 The folded compressor: the first prism is on the right, the dispersed pulse is then reflected off the mirror on the far left into the second prism. The linear translation stage responsible for changing the delay between pump and probe pulse can be seen in the background.

The prisms are positioned carefully so that the sum of the beam path difference in air and in the prism is appropriate for the central pump pulse wavelength and its bandwidth can correct for linear group velocity dispersion experienced by the NOPA pulse and shorten the pulse duration to within 20% of the duration of a Fourier-transform limited pulse.

A folded compressor configuration with a mirror placed between the prisms can be used to make the configuration more compact since compressor lengths can reach 1 m in the case of NOPA pulses with a central wavelength of 650 nm and longer, and space on the optical table is limited. The dispersed light from the first prism is reflected off a mirror to the second prism. A mirror on a magnetic base retro-reflects the light from the second prism back along the same path. Both prisms are mounted on magnetic bases and rotational stages to allow for quick and easy adjustments. The pulse duration is measured by dispersion-free autocorrelation until an optimum configuration is achieved [15, 8]. A photograph of the compression stage can be seen in Figure 3.7.

3.4 Characterization

Figure 3.8 shows pump pulse spectra, the spectrum of NOPA-amplified light used as pump pulses in pump-probe measurements, generated around certain central wavelengths spanning more or less the spectral region accessible for parametric amplification with appreciable energy in the constructed NOPA.

Table 3.1 shows typical energies and bandwidths generated at certain central output wavelengths.

Maybe intuitively, the pulse energies decrease with wavelength. Pulse intensity can, however, be compensated for at longer wavelengths with a broad bandwidth that can be compressed into a shorter pulse. The bandwidth that can be generated is largely dependent on the phase matching angle.

As can be seen in Figure 3.9, the gradient of the optimal phase matching curve as a function of wavelength reaches a local maximum at around 500 nm, where a broader spectrum will therefore be available to parametric amplification. Where the gradient is steeper, pulse bandwidth will typically decrease. The phase matching angle is plotted on the vertical axis as a height difference: this ratio of height difference at a fixed length from overlap along the propagation axis is, in practice, an easily verifiable measure of the phase matching angle.
Figure 3.8: Pump pulse spectra generated in the NOPA

<table>
<thead>
<tr>
<th>Central wavelength λ (nm)</th>
<th>Bandwidth Δλ (nm)</th>
<th>Pulse energy (μJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>480</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>500</td>
<td>25</td>
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<td>7</td>
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</tr>
<tr>
<td>580</td>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td>580</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>708</td>
<td>20</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 3.1 Typical bandwidths and energies measured at different pump wavelengths.
3.4. CHARACTERIZATION

Figure 3.9 Optimum height difference of seed and pump pulse at 16 cm from overlap for the visible region.

For each pump pulse an optimum configuration of the compressor can be achieved in terms of the compressor prism separation and the depth of crystal through which the pulse moves. This second parameter is measured as the depth of crystal that the central wavelength moves through the second prism when the pulse is spatially dispersed. The duration of the pulse is limited by the time-bandwidth product as seen in Equation 2.8. Figure 3.10 shows an example of a pulse with a certain bandwidth compressed by a certain compressor configuration.

The compressor prisms responsible for the compression shown in Figure 3.11 were separated by 84 cm and the central wavelength entered the second prism at a depth of 2 mm. The pump pulse had a bandwidth of 35 nm centred around 885 nm. The temporal profile of the compressed pulse with a spectral content that is shown in the top graph is shown in the bottom graph. The red line represents a Gaussian fit to the measured pulse. Table 3.2 shows optimum pulse durations achieved for different wavelengths with certain compressor configurations.
Figure 3.10 Pulse compression.
### 3.4. CHARACTERIZATION

<table>
<thead>
<tr>
<th>$\lambda$(nm)</th>
<th>$\Delta\lambda$(nm)</th>
<th>Prism spacing</th>
<th>Prism depth</th>
<th>Fourier limit</th>
<th>$\Delta\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>483</td>
<td>16</td>
<td>58 cm</td>
<td>4.5 mm</td>
<td>34 fs</td>
<td>60 fs</td>
</tr>
<tr>
<td>536</td>
<td>45</td>
<td>58 cm</td>
<td>4 mm</td>
<td>9 fs</td>
<td>35 fs</td>
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<td>885</td>
<td>35</td>
<td>84 cm</td>
<td>3 mm</td>
<td>20 fs</td>
<td>43 fs</td>
</tr>
</tbody>
</table>

Table 3.2. Pulse duration as function of pump pulse characteristics and compressor settings.
Chapter 4 - The Probe Pulse

4.1 Introduction

In order to monitor absorption changes in a photo-excited sample it is advantageous to observe a broad spectral region. This allows simultaneous measurement of the population and depopulation of various molecular states. Ideally our probe pulse will have the following properties:

- Broad bandwidth
- Uniform intensity distribution over its entire spectrum
- High pulse to pulse stability

The first requirement allows us to monitor several states simultaneously provided these molecular states display resonant absorption within the spectral window of the pulse. A broader spectrum also means that the pulse duration can be compressed to have a shorter duration, improving temporal resolution. A uniform intensity distribution will allow us to quantify and compare absorption cross-sections. Since pump-probe spectroscopy often employs referencing and averaging techniques over long periods, pulse to pulse stability is important. The method of choice for generating probe pulses that meet the above requirements to a satisfactory degree is supercontinuum generation otherwise known as white light generation.

4.2 Principles of Supercontinuum Generation for use as Probe Pulse

The supercontinuum has proven itself as an effective probe pulse due to its broad bandwidth and stability. A seed pulse is focused into an isotropic medium and by numerous nonlinear processes including self focusing and self phase modulation as discussed in a previous chapter, a supercontinuum is generated. If a single white light filament is generated, the energy of the pulse is stabilized and the phase relation with the pump pulse is maintained. Several parameters can be controlled in order to generate a customized supercontinuum to access spectral regions required for individual absorption experiments.

4.3 The Setup

Components depicted in the schematic diagram of Figure 4.1 will be referred to in the following sections in enclosed brackets.
Figure 4.1 Schematic diagram of the probe beam setup. The red line indicates the CPA fundamental beampath, the green line indicates the pump beampath and the blue line indicates the probe beampath. 1 - variable neutral density filter  2 - 75 mm achromatic lens  3 - 3 mm sapphire crystal  4 - iris  5 - off-axis parabolic mirror  6 - filter  7 - 1000 mm lens. The numbered components are also referred to in the text.
4.3.1 The White Light Generation Setup

A small fraction of the CPA light transmitted through a beam splitter is reflected off a set of 4 highly reflective mirrors (enclosed by a dotted line in Figure 4.1) at 775 nm to create a beam path of several metres before white light is generated. This is done to compensate for the distance traveled by the pulse in the pump beam path as the pump pulse is generated in the NOPA. The discrepancy needs to be compensated for to ensure that pump and probe pulses overlap in time at the sample position. Since our mechanical linear translation stage offers a temporal measurement window of around 560 ps which translates to a 20 cm beampath difference due to the beam being retro-reflected by two mirrors on a 4 cm stage, our pump and probe beampaths cannot differ by more than 20 cm if the pump and probe overlap is to occur within our measurement window. One of the aforementioned set of 4 mirrors is placed on a magnetic base. This allows the user to delay the probe pulse relative to the pump pulse and adopt a configuration so that temporal pump-probe overlap occurs in the sample volume when the linear translation stage, that the pump beam traverses, is at a position where it elongates the optical pathlength of the pump pulse as much as possible. During the measurement, the pump pulse delay is adjusted by incremental steps of the linear translation stage and the probe beam path remains fixed. Therefore, as the pump beam path is shortened when the mirrors on the translation stage are moved forward, the pump pulse arrives with a greater time before the probe pulse creating the time window in which absorption measurements are done before and after temporal overlap excitation. The more the position of the mirrors on the linear translation stage elongate the pump beam path when temporal overlap is achieved (by adjusting the magnetic base-mounted mirror in the probe beampath), the greater the time window after excitation that can be scanned over during the measurement. This pathlength needs to be adjusted to a large extent when switching between NOPAs since the beam path from the different NOPAs to the sample volume differs by close to 2 m and to a lesser extent when switching between pump wavelengths from the same NOPA since the compressor length needs to be adjusted for different wavelengths typically in the range of cm.

Relatively low energy pulses are used in the generation of white light probe pulses when compared to the energies used for pump pulse generation by parametric amplification. Although supercontinuum generation is a third order nonlinear effect and parametric amplification is a second order nonlinear effect, meaning that the former requires higher intensity than the latter, the pulses used for supercontinuum generation are focused more tightly than the pulses used in the NOPA. Focusing is tighter to such an extent that this results in higher incident intensities for supercontinuum generation when compared to the intensities of pulses used in parametric amplification. Pulses of about 100 μJ are transmitted by beam splitters to the probe beam path.

A variable neutral density filter ‘1’, is employed to control the energy of the pulses focused into the $\chi^{(3)}$ crystal. Although large intensities are required for the nonlinear effects that cause the generation of white light, it is desirable tc keep to as close to the lowest energy threshold for supercontinuum generation as possible. Excessively high intensities can cause damage $[3]$. The single filament formed in this energy regime is stable and can be focused on the sample. Higher energies can cause multi-filamentation $[14]$, decreasing the stability and even
4.3. THE SETUP

damaging the crystal. The lowest energy threshold is different for different media and the supercontinuum generated can be manipulated slightly by small changes in pulse energy. For this reason it is necessary to be able to control this parameter.

An iris is placed in the beam path (4), which can reduce intensity by blocking the outer radial regions of the beam cross section but its main role is to adjust the numerical aperture of the beam before it is focused into the crystal, an important parameter in the spectral structure of the supercontinuum [3].

A 75 mm focal length achromatic lens (2) focuses the beam into the crystal. The crystal medium is an important parameter in the generation of a suitable supercontinuum. Different materials react differently in different spectral regions and the supercontinua generated display different spectral features. Experience has shown us that a 3 mm long sapphire crystal (3) provides a stable and flat enough spectrum over the visible region when pumped by a seed pulse at 775 nm. The crystal is placed on a linear translation stage to provide another adjustable parameter; the position relative to the focus. The thickness of the crystal is a compromise between the amount of white light generated and the increased group velocity dispersion created by thicker dispersive media. The thicker the crystal the more the pulse is chirped upon exiting the crystal, greater lengths can also lead to decoherence of the pulse.

A filter (6) is placed in the beam path of the white light to block the intensity of light around the fundamental wavelength. An off-axis parabolic mirror (5) is employed to recollimate the single-filament supercontinuum in the pumped sample volume. The parabolic mirror is a focusing optical element and is preferred over a conventional lens since the parabolic mirror notably improves chirped reduction due to its non-dispersive nature. It is also preferred over a spherical mirror since spherical aberation occurs when the incoming beam is slightly off-centre of the spherical mirror. This is not the case with the parabolic mirror. Enhanced aluminium mirrors are used to direct the pulses to the sample. Enhanced aluminium is used since it displays high reflectivity over almost the entire visible spectrum, broader than the supercontinuum. A 1000 mm focal length lens (7) is used to focus the probe beam into the sample volume.

Should measurement in the UV region be required it has been determined that the second harmonic of the OPA can be used as seed pulse for supercontinuum generation. Quartz showed to perform well in this spectral region for this purpose.

The same was attempted with a third harmonic seed pulse, but the energy available proved to be too low to make supercontinuum generation viable.

4.3.2 Pumping the sample volume

The pump beam generated by Type I phase matching in the NOPA, is polarized orthogonally to the probe beam. The pump beam is rotated with a $\frac{1}{4}$ plate relative to the probe beam. The relative angle of pump and probe is set to 54.7 degrees, also known as the magic angle. This angle compensates for the artificial decay that would be seen if the pump and probe pulses were polarized in the same plane. The molecules that absorb the excitation pulse would have dipoles aligned with the polarization of the pulse. After excitation these dipoles rotate in solution as before and may not be detected by the probe.
pulse some time later. This causes an artificially strong signal close to overlap when they have not had time to rotate. Conversely, orthogonal polarization of pump and probe pulses show an artificially weak signal. The magic angle has proven the best in averaging over this artificial effect [9].

4.3.3 The Sample Holder

The sample cell can be a flow cell or stationary cuvette. It is placed on an XYZ mount along with a holder containing 50, 100 and 400 μm pin holes. An appropriate pin hole is selected and used to align the foci of pump and probe, in order to overlap spatially. The cell is additionally on its own linear translation mount so that it can be moved relative to the pin hole holder in the direction of the beam propagation.

4.4 Characterization

4.4.1 Chirp

The inherent chirp of the white light pulse could be significantly improved by employing a parabolic mirror instead of a conventional dispersive element like a lens. See Figure 4.2. The figure indicates the time difference in pump-probe overlap for different wavelengths due to chirp, with the overlap at 520 nm taken as time zero for two different collimating optical elements. The distribution of overlap times across the spectrum is narrower for the parabolic mirror.
4.4. CHARACTERIZATION

4.4.2 Supercontinuum: Materials

Several materials were investigated to study their responses to high intensity light. See Figure 4.3. In terms of stability and white light intensity, sapphire was the preferred medium for supercontinuum generation for measurements in the region from 400 nm to where the zero angle highly reflective mirror blocks transmission around the CPA fundamental at around 750 nm. Sapphire was also the thinnest crystal contributing the least to dispersion.

For measurements that required a supercontinuum extending slightly further into the blue wavelengths, calcium fluoride was suitable.

Some experiments required measurements on states that absorbed near the CPA fundamental and even in the region between 800 and 900 nm. Stable white light can be achieved by rotating the zero angle HR mirror to change the wavelength region that is blocked. Various materials were investigated for this purpose, but sapphire again proved to be most stable in the desired region. See Figure 4.4

4.4.3 Numerical aperture and focus position

Spectra were recorded for white light generation in a KDP crystal. The effect of a change in numerical aperture while all other parameters were kept constant was investigated. See Figure 4.5. The iris before the focusing lens was used to control the numerical aperture. The diameter of the iris is related to the numerical aperture in an air medium by the following approximation.
Figure 4.4: White light spectra with filter transmitting in the near infra-red.

\[ NA \approx \frac{1}{2} \frac{d}{f} \]  \hspace{1cm} (4.1)

where \( f \) is the focal length of the lens and \( d \) is the diameter of the iris in the absence the diameter of the collimated beam.

The white light continuum is weighted more to the blue wavelengths for smaller iris diameters and therefore smaller numerical apertures. An optimal numerical aperture is also observed for intermediate numerical aperture values. The white light becomes increasingly unstable for larger iris diameters.

The especially long KDP crystal, around 2 cm, was also moved relative to the focus and the effect of the depth of the focus in the crystal medium on the supercontinuum generated was recorded. See Figure 4.6.

When the focus is before the crystal the intensity is not large enough for white light generation; the fundamental and second harmonic can be seen. The intensity of the pulse as it enters the crystal is not enough for self-focusing, which is a more pronounced effect for steeper intensity gradients. To overcome the divergence of the beam after the focal point. As the focus is moved into the crystal, spectral broadening occurs and the fundamental and second harmonic peaks diminish. As the focus is moved deeper into the crystal, the white light intensity begins to drop off since the remaining crystal length for white light generation after the focus becomes less. The stability of the white light spectrum also deteriorates after an optimum position.
Figure 4.5: Numerical Aperture dependence of white light spectrum generated in KDP.

Figure 4.6: Change in white light spectrum due to shift in focal position.
4.4.4 Relative polarization of pump and probe beams

Figure 4.7 shows a comparison of measurements done with different relative polarizations of the pump and probe pulse. At magic angle the signal is the average between the artificial decay of the parallel polarized pump and probe pulse measurement and the weak orthogonally polarized measurement. Now a maximum cross-section of the initially excited sample set of molecules interact with the probe pulse without displaying an artificial decay due to molecular rotation.

4.4.5 Linearity of detectors

To characterize the system properly, it needed to be verified that the detector response was linear with light intensity. This would mean that if an absorption signal would increase by a factor of 2, the amount of absorbing molecules in the probe volume has doubled too. The detection system includes an Andor SR163 spectrograph and a 1024 pixel photodiode array from Entwicklungsburo Stresing used as fast line scan camera.

First the detector response was tested for a continuous light source. A torch was used and response measured for a relatively low photon flux. The intensity of light coupled into the detector was changed by placing a series of known absorbers between the torch and the detector. The measured absorbance was then plotted against the known absorbance.

As can be seen in Figure 4.8 the response is linear for a continuous light source. The experiment was repeated for a femtosecond pulse. This is done to...
Figure 4.8 Linear response to continuous light source. The detector response to light shone through a series of materials with a known optical density (OD) was converted into a measured optical density via the Beer-Lambert law.

Ensure that the linear response is maintained even when all the photons arrive within femtoseconds.

Figure 4.9 confirms, however, that this linear response is also true for femtosecond pulses, and the detector array is not momentarily saturated due to an arriving photon so that it cannot detect the next photon.
Figure 4.9: Linear response to femtosecond pulse. The detector response to light shone through a series of materials with a known optical density (OD) was converted into a measured optical density via the Beer-Lambert law.
Chapter 5 - Pump-Probe Spectroscopy

5.1 Introduction

As an example of the use of the NOPA time-resolved absorption measurements conducted on zinc phthalocyanine - single wall carbon nanotube (SWNT) complexes will be presented and discussed. A review of literature related to the topic will be given, beginning with the zinc phthalocyanine alone and progressing to the zinc phthalocyanine-SWN1 complexes. The chapter will conclude with some measurements taken on zinc octa-carboxy phthalocyanine molecules and molecules from a dye called D149, both linked with zinc-oxide nano-particles.

5.2 The Sample

Zinc phthalocyanine (ZnPc) is a well-known photosensitizer used in applications such as photodynamic therapy and blood sterilization [12]. It has a high absorption cross-section in the red and near-infrared spectral regions and is an electron-rich macrocycle [5].

Single wall carbon nanotubes have been studied extensively for their excellent electronic properties. SWNTs readily accept electrons and can transport these electrons along their axes with extremely low resistance. This allows for

Figure 5.1: The zinc phthalocyanine - single wall carbon nanotube complex.
the construction of electronic circuits on a much smaller scale than current conventional electronic devices [5].

Linking these two constituents into an electron donor-acceptor pair bares the promise of creating a photovoltaic cell by creating long lived charged separated states. The electron-rich zinc phthalocyanine absorbs in an abundant part of the solar spectrum and transfers an electron upon photo-excitation to the SWNT. An illustration of the chemical structure of the complex can be seen in Figure 5.1.

It is this charge transfer, and specifically the comparison between the decay of the photo-excited zinc phthalocyanine on its own and when paired with SWNT, that we wish to investigate. Electron transfer is known to occur on a sub-ps time scale depending on the size of molecules and distance between donor and acceptor, electron injection from photo-excited singlet states of molecules adsorbed to the surface of thin films or nano-particles are reported to occur on 10 fs timescales [1, 2]. Electron injection from triplet states are reported to occur between 1 - 100 ps timescales [1]. This gives an impression of the time resolution required and the time regime that needs to be investigated.

5.3 Background

The steady state absorption spectrum of zinc phthalocyanine is given in Figure 5.2. The inset shows the chemical structure of the molecule and the dashed line is the measured fluorescence spectrum when the molecule is excited by light with a wavelength of 660 nm.
The spectrum shows broad Q-band ($S_0 \rightarrow S_1$) absorption centred around 672 nm with smaller peaks at 506 and 545 nm due to higher lying vibrational modes of the $S_1$ state. The fluorescence spectrum shows an emission peak at 680 nm corresponding with a Stokes shift of 8 nm. The broad absorption band centred around 345 nm in the stationary absorption spectrum is reported to be that of the B-band ($S_0 \rightarrow S_2$) [19]. An energy level scheme for the zinc phthalocyanine excited into its $S_1$ state is presented in Figure 5.3.

Note that an absorption band from the excited singlet state overlaps spectrally with the absorption band of the triplet state. Time resolved absorption measurements have also been conducted on zinc phthalocyanine [19]. Figure 5.4 demonstrates the change in optical density as a function of time and wavelength as from [19]. A brief explanation of how to interpret these graphs is given in Section 5.4.2 when the measurements taken in our own laboratory are introduced. The measurements show that the absorption bands of the excited singlet state and fluorescence signal due to stimulated emission from the excited singlet state have similar lifetimes. The time scale of the measurement is linear for the first 2 ps and logarithmic from 2 ps to 6 ns. The unit mOD refers to changes in optical density in thousandths of a unit.

The literature reports a singlet state lifetime of 2.8-3.4 ns, depending on the source consulted [11, 19, 5]. This is seen in the shift of the ground state bleaching band (A$'$, centre of mass to shorter wavelengths, on the logarithmic
Figure 5.4: Transient Absorption Spectrum of Zinc Phthalocyanine in DMSO [19]. A indicates the ground state bleaching band, B₁ indicates the singlet excited state absorption band due to the $S_1 \rightarrow S_{n1}$ transition, B₂ indicates the absorption band due to the $S_1 \rightarrow S_{n2}$ transition. C indicates the absorption of the longer living triplet excited state in the later time window.

The time scale from ps to ns, due to the decay of the red-shifted stimulated emission signal in Figure 5.4. It is also seen in the decay of the excited singlet state absorption band at 630 nm (B₁), as well as the narrowing of the broad absorption band around 450-500 nm (B₂). The aforementioned band not only narrows but the absorption peak shifts from 485 nm to 480 nm, indicating that the triplet state (C) is longer living than the singlet state that absorbs broadly centred at 485 nm. The absorption spectrum of the molecule is composed of the absorption of several states simultaneously. Figure 5.5 shows which states are believed to absorb in which region.

The lifetime of the $S_1$ state is measured to be 2.9 ±0.2 ns in the report by Savolainen et al [19], explaining the decay we see in this temporal region of the stimulated emission signal (effectively the fluorescence lifetime) and the excited state absorption bands centred at 630 nm and 485 nm. The triplet state, however, is still absorbing after 7 ns.

Time resolved measurements conducted on zinc phthalocyanine-single wall carbon nanotube electron donor-acceptor pairs reveal slightly different results. Although, to date, I haven’t found literature that has directly observed or quantified the charge transfer process in a similar sample which occurs in the femtosecond regime, there are indicators of charge transfer in the picosecond to nanosecond regime. From all the articles regarding various ZnPc derivatives attached in numerous ways to SWNTs consulted, some common charge transfer related processes are reported. Severe quenching of the singlet state is reported with the lifetime decreased to around 57 ps [4]. The spectral features of the
5.4. MEASUREMENTS

Figure 5.5: Species resolved absorption spectrum of photo-excited zinc phthalocyanine [15]. The solid grey line is the ground state bleach. The solid black line is the triplet excited state absorption. The dashed line indicates the singlet FSA and the dot-dashed line indicates the stimulated emission signal due to fluorescence. The spectra are extracted from the UTA measurement of Figure 5.4 by global fitting of a kinetic model.

Zinc phthalocyanine, for example the strong ground state absorption at 672 nm, are reported to red shift by 2 nm upon electron injection into the SWNT [5]. The emergence of an absorption band in the near infrared around 840 nm, depending on the sample, is also reported and is attributed to the one-electron oxidized zinc phthalocyanine radical that is created by charge transfer [5, 11]. The spectral features of the SWNT also undergo changes upon electron injection but these are located in the infrared from 2-3 μm in an area where our detection system has no sensitivity.

5.4 Measurements

5.4.1 Steady State Spectra

Stationary absorption spectra were taken with a Thermo Scientific Evolution 600 UV-VIS Spectrophotometer. Four samples were investigated ZnPc-H being the sample most similar to the zinc phthalocyanine sample investigated in the article by Savolainen et al [19]. ZnPc-COOH is the reference sample since it is this molecule that is covalently linked or adsorbed to the surface of the SWNTs. The reference sample will be investigated to establish reference values for the lifetimes and spectral positions of certain states before the same measurements are done on the linked and adsorbed samples, and any changes are noted. The solvent for all samples was di-methyl formamide. The only solvent tested that the SWNTs were soluble in.
In the stationary spectrum of ZnPc-H (Figure 5.6), we can clearly see the strong absorbance peak of the Q-band at 669 nm as well as the vibrational shoulders of the transition, the larger one being at 604 nm. The absorption of the B-band can also be seen at around 346 nm. The spectrum is in good agreement with the sample albeit slightly different sample of Savolainen et al.

The reference sample ZnPc-COOH displays the same spectral features albeit a little red shifted. See Figure 5.7. The Q-band absorption peak is found at 683 nm and the vibrational shoulder at 615 nm. The B-band is also notably red shifted. This indicates a slight change in the electronic configuration of the new sample. In the samples where ZnPc-COOH is covalently linked to SWNTs, the electronic integrity of the ZnPc-COOH seems to be intact since the related spectral features can still be resolved.

The diminished absorption, a change of 1.3 OD in the adsorbed case (Figure 5.9) and 1.33 OD in the linked case (Figure 5.8), from an initial OD of 1.4 in the reference sample, indicates that the amount of absorbing ZnPc-COOH molecules have decreased, and that the ratio of ZnPc-COOH molecules to SWNTs, which are much larger particles, differs for the adsorbed sample and the covalently linked sample. The number of ZnPc molecules absorbing in the SWNT-adsorbed sample is 7% of the number in the reference sample, compared to 3.5% in the case of the SWNT-linked sample. More ZnPc molecules per SWNT are attached in the adsorbed sample when compared to the linked sample by a factor of 2. The spectral shifts of the absorption maxima indicate that there is some change in the electronic coupling, either with the SWNTs or the linker molecules and that the ZnPc-COOH molecules are not simply swimming in a soup of SWNTs.
Figure 5.7 Stationary absorption spectrum of ZnPc-COOH.

Figure 5.8 Stationary absorption spectrum of SWNTs covalently linked with ZnPc-COOH.
Figure 5.9: Stationary absorption spectrum of ZnPc-COOH adsorbed to the surface of SWNTs

5.4.2 Transient Absorption Spectra

For the transient absorption measurements the samples were pumped at their respective Q-band absorption maxima. Figure 5.1c shows the data obtained from an ultrafast transient absorption measurement conducted on ZnPc-H with the spectrometer calibrated to observe the visible region. The data is displayed as a 3-dimensional plot with the two independent variables time and wavelength plotted on the horizontal and vertical axes respectively. The dependent variable, the ratio between the pumped and unpumped spectra, is plotted according to a colour scheme. The value is determined by its wavelength-time coordinate. Figure 5.1c shows absorption features in agreement with the absorption features observed in the literature within the experimental time window that the measurements were taken in. The increased signal (larger than 1) means that more light is let through when the sample is pumped since spectra are measured in transmission. This indicates that absorbing electrons are no longer present in a certain state in the numbers that there are in the case of the stationary spectrum, meaning a depopulation of the state that caused absorption in the stationary spectrum upon photo-excitation is occurring. Stimulated emission can also cause an increase in transmission, and by implication an increased signal, where the probe pulse induces a deexcitation. An increased signal can be seen in the ground state bleaching of the Q-band upon excitation around 680 nm. Stimulated emission of fluorescence photons causes broadening of this increased signal in the red flank of the band due to the 5 nm Stokes shift. An increased signal can also be observed around the vibrational shoulder of the $S_1 \rightarrow S_1$ transition at about 905 nm. Excited state absorption bands account
for the decreased signal (smaller than 1); electrons are pumped into these excited states causing an increase in absorption due to the increased population of these states at a wavelength corresponding with the energy transition from the ground state to the excited state. Excited state absorption bands from the singlet state account for the absorption maxima at 621 nm $S_1 \rightarrow S_{n1}$ as in Figure 5.3, and 497 nm $S_1 \rightarrow S_{n5}$ as in Figure 5.3, although the triplet excited state absorption accounts for longer lived absorption in the same spectral region as the $S_1 \rightarrow S_{n5}$ absorption band. Analysis of the data and evaluation of the temporal decay of all the states revealed a rapid decay at a certain time for all states. It was established that the decay was artificial and caused by a non-constant pump-probe beam overlap within the sample. This prompted the inclusion of the piezoelectric mirror - CCD camera beam walk correction system into the setup. The beam walk explains the symmetric narrowing of the ground state bleaching signal where a narrowing of the red flank alone was expected due to the quicker decay of the fluorescence signal.

Figure 5.11 shows the decay of the reference sample ZnPc-COOH. The ground state bleaching and its vibrational shoulder at 586 nm and 514 nm respectively as well as the excited state absorption at 536 nm and the broad
overlapped absorption bands of the triplet and singlet state absorption centered around 493 nm all are long lived. This is expected since the reference ZnPc-COOH is only marginally different from the ZnPc investigated in the literature. Although the measurements are only done over a time window of maximally 600 ps, we can safely assume that the states live much longer and can verify that no decays occur on a sub-100 ps scale.

The change in optical density due to the absorption peaks of the ZnPc-COOH in the covalently linked SWNT-ZnPc-COOH sample was too little and the resulting absorption signal by the attached ZnPc-COOH too small to make any reliable measurements. The absorption features of the SWNTs in the stationary spectrum are simply too dominant. An example of the measurements attempted on the sample can be seen in Figure 5.12.

The figure demonstrates a typical problem experienced when measurements were conducted on the samples that include SWNTs. SWNTs are several hundred nanometers in length. As a result, the pump light experiences significant scattering and the pump-probe overlap cannot be resolved. This is because before the onset of pump and probe overlap there is already a discrepancy between the pumped and unpumped spectra since the detector integrates the incoming light over an interval of 1 μs in which both pump and probe pulse arrive despite the fact that the probe pulse arrives before the pump pulse in the case of the pumped spectra. This problem needed to be overcome if meaningful analysis is to be made of the data. The problem was overcome by placing a razor edge in the compressor stage of the NOPA as shown in Figure 5.13.
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Figure 5.12 UTA spectrum of SWNT-ZnPc-COOH, linked.

Figure 5.13 Razor edge blocks red flank of pump spectrum.
Figure 5.14 Unprocessed raw data from UTA scan of SWNT-ZnPc-COOH 'adsorbed' sample

The razor edge would physically block the red flank of the pump spectrum at a position in the compressor where the spectral components are spatially separated. In this way the red flank of the absorption band would not be pumped and the scattered light signature would be greatly reduced. In this way perhaps a good decay time of the fluorescence could be measured since stimulated emission can be detected in the spectral region of the blocked pump spectrum.

The time resolved measurements were then conducted on the adsorbed SWNT samples that have a greater optical density due to the ZnPc-COOH peaks at the pump wavelength, incorporating the razor edge in the setup.

As can be seen in Figure 5.14, the red flank of the ground state bleaching band does not show scattering before time zero. With the resulting data, decay measurements can be made on the lifetimes of the stimulated emission signal with greater accuracy.

Figure 5.15 shows the data from a UTA scan on the adsorbed sample after the software has corrected for chirp and subtracted the background scattering signal from before time zero from the measurements taken at every time step.

The data was analyzed to establish whether the lifetime of the SWNT-ZnPc-COOH singlet excited state was quenched due to the SWNTs when compared to the ZnPc-COOH sample. The broad excited state absorption band around 500 nm, although providing the strongest absorption signal, was a bad candidate for the measurement of the singlet lifetime since the singlet excited state absorption band overlapped spectrally with the triplet excited state absorption and their respective absorption peaks are separated by a mere 5 nm according to the
5.4. MEASUREMENTS

![UTA spectrum of SWNT-ZnPc-COOH, adsorbed](image)

Figure 5.15  UTA spectrum of SWNT-ZnPc-COOH, adsorbed

literature [15]. This shift in absorption peak due to the longer living triplet state could not be detected within the time window of our measurement. At the very least the decay in this spectral region was known to be non-monoexponential. A better candidate for evaluating the singlet lifetime would be the excited state absorption band at 630 nm. This time could be compared to the lifetime of the stimulated emission signal due to fluorescence and if in good agreement would give some confidence to the lifetime established for the singlet state, since our measurement window spans a mere 600 ps and the decay lifetimes for our reference sample are in the order of ns and a mono-exponential decay is assumed.

Figure 5.16 shows the lifetimes determined by a mono-exponential fit on a typical decay trace at a certain wavelength. These decay fittings were done at central wavelengths of transient signals of interest as discussed in the previous paragraph. Table 5.1 summarizes the lifetimes measured.

As can be seen in Table 5.1 there is a good agreement between the lifetime of the singlet FSA at 630 nm and the stimulated emission in the red flank of the GSB. There also seems to be a good correlation between the decay of the ground state bleach evaluated at the central wavelength and the decay of the vibrational shoulder at 614 nm. This should be longer since the ground state is only populated after other competing processes also decay. If the lifetimes for the reference sample and the SWNT-ZnPc-COOH are compared, we do not see a difference and must infer that the singlet state is not quenched due to the attachment to the SWNTs. The bleaching signal due to pumping into a higher
Figure 5.16: Decay fitting of stimulated emission signal of ZnPc-COOH.

<table>
<thead>
<tr>
<th></th>
<th>ZnPc-COOH</th>
<th>ZnPc-COOH-SWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground State Bleaching</td>
<td>2.71 ns±17 ps</td>
<td>2.96 ns±410 ps</td>
</tr>
<tr>
<td>Vibrational mode of GSE</td>
<td>3.28 ns±52 ps</td>
<td>-</td>
</tr>
<tr>
<td>Stimulated Emission</td>
<td>1.47 ns±60 ps</td>
<td>1.46 ns±120 ps</td>
</tr>
<tr>
<td>Excited State Absorption: $S_1 \rightarrow S_{n1}$</td>
<td>1.39 ns±80 ps</td>
<td>1.47 ns±140 ps</td>
</tr>
</tbody>
</table>

Table 5.1: Lifetimes of selected absorption/bleaching signals.

vibrational mode of the $S_1$ state at around 614 nm was simply too faint to do reliable decay fitting on.

When the time slices of the 3-dimensional spectra are analyzed, in effect absorption spectra at various times, a spectral shift of the ZnPc-COOH features due to electron loss in the SWNT-ZnPc-COOH cannot be detected.

Furthermore, when the absorption of the one-electron oxidized ZnPc-COOH is measured in the near-infrared, a change in the ratio of pumped to oxidized molecules from the reference sample to the SWNT-ZnPc-COOH cannot be seen. The optical density of the one electron oxidized ZnPc-COOH is not enhanced by the SWNTs, indicating that electron transfer is not enhanced.

The analysis of our sample therefore concluded that charge transfer was not occurring to a greater extent due to the presence of the electron accepting SWNTs. It was suggested to collaborators on the project to synthesize molecules with shorter linker molecules to bring the ZnPc-COOH and the SWNTs closer together. This will hopefully improve charge transfer in the complex.
5.5. ZINC OCTA-CARBOXY PHTHALOCYANINE SAMPLES

Ultrafast transient absorption measurements were performed on zinc octa-carboxy phthalocyanine (ZnOCPc) molecules in solution (reference sample) adsorbed to ZnO nanoparticles. The chemical structure of ZnOCPc is illustrated in Figure 5.18. The solvent used was 0.1 M NaOH in water. Measurements were conducted over hundreds of ps with 1 ps time steps between measurements and over several ps with 20 fs time steps with the aim of identifying whether charge transfer was occurring and quantifying the time scale of the process if it was.

Figure 5.19 shows the stationary spectrum of ZnOCPc, the now familiar zinc phthalocyanine spectral absorption features are immediately recognizable. The absorption peak of the Q-band at 692 nm and the vibrational mode of the Q-band absorbs maximally at 622 nm. These features are notably red shifted by some 10 nm on average to the steady state spectra of previous ZnPc samples.

Even on the transient absorption spectra the absorption changes are similar, see Figure 5.21. Nc fast dynamics in the order of hundreds of fs to ps can be detected and on the scan over 500 ps taken with 1 ps time steps no significant decay of any absorption or bleaching band was seen. Figure 5.21 shows the UTA spectrum of ZnOCPc taken over the first 650 fs after excitation in high resolution steps and pumped at 660 nm with 130 nJ pump energy. The scan results show again some familiar features. The broad absorption band of the singlet and triplet excited state overlap in the spectral range from 450 nm to 550 nm. The sample was pumped with 960 nm NOPA light (in the blue flank
Figure 5.18: An illustration of the zinc octa-carboxy phthalocyanine molecule.

Figure 5.19: Stationary absorption spectrum of ZnOCPc (not adsorbed).
of the Q-band to ensure spectral separation of the stimulated emission signal and scattering of the pump light. See discussion in Section 5.4.2) the ground state bleaching band can be identified at about 570 nm as well as the bleaching of the vibrational mode at around 620 nm. A strong singlet FSA band can be seen centred around 650 nm. The most noticeable difference in the scan on the new sample is the large Stokes shift of the fluorescence signal at 702 nm. A definite gap can be seen between the stimulated emission signal and the ground state bleaching band corresponding to a Stokes shift of some 15 nm.

The ZnOCPc samples were then adsorbed to the surface of ZnO nanoparticles. Much care was taken in the preparation to remove ZnOCPc samples that were not adsorbed. The sample was for example centrifuged to separate the adsorbed molecules from the unadsorbed ones. The result was a sample with a low optical density due to the ZnOCPc absorber but a greater confidence that the electron donor was attached to the acceptor. Figure 5.20 shows the stationary absorption spectrum of the ZnOCPc adsorbed to ZnO nano-particles sample.

The small bump at 690 nm gives an impression of how low the optical density that is available to pump the ZnOCPc molecules into their excited state is. It also indicates the low fraction of molecules that are adsorbed to the surface. Scans on the longer timescale of several 100 ps in 1 ps intervals yielded no results, in fact the pump probe overlap could not be detected. But on a short time scale of several ps taken in 20 fs intervals the artifact due to pump probe overlap could be seen. The sample was, as with the ZnOCPc sample pumped at 660 nm with 13 fJ pulse energy, Figure 5.22 shows these results. An interesting observation was that the artifact seemed to be enhanced at 540
The strength of the absorption seen at 544 nm in the ZnO:ZnOcPc sample was similar (~1%) to that observed in the pure ZnOcPc sample although the latter had a far greater optical density. This already cast some doubt on the idea that we were witnessing charge transfer. The notion was finally dispelled with after reference measurements were conducted on samples containing only ZnOc nano-particles in solution.

The UTA measurements performed on ZnC nano-particles (Figures 5.23 and 5.24) demonstrated the same enhanced absorption of the artifact at 544 nm. When the pump wavelength was moved to 500 nm the enhanced absorption moved to 490 nm. These results indicated that what was observed was not
5.6. D149 samples

Measurements conducted on D149 molecules in pure form and adsorbed to ZnO nano-particles demonstrated the performance and dynamic range of the measurement setup well. The chemical structure of indoline D149 dye can be seen in Figure 5.25. The solvent used was a 1:1 mixture of acetonitrile and tert.-butanol, producing a D149 concentration of 500 µM in the pure sample. A stationary absorption spectrum of the D149 molecule can be seen in Figure 5.26.

The Q band absorption maximum can be seen at 527 nm and the R band maximum at 388 nm. In the UTA scans the sample was pumped at 540 nm in the red flank of the Q band with pulse energies of 100 nJ. Figure 5.27 shows
the UTA measurement conducted on the pure D149 on a 500 ps scale in 1 ps intervals.

In Figure 5.27, ground state bleaching can be seen centred around 522 nm as well as a stimulated emission signal at 573 nm. An excited state absorption band appears at 590 nm.

Figure 5.28 shows the UTA measurement conducted on the D149 dye molecules adsorbed to ZnO nano-particles. The most notable difference is the emergence of an absorption band at 550 nm that becomes apparent after the bleaching band shifts to the blue after 20 ps.

Figure 5.29 compares the GSB signal from both samples over the long time scale. The signal in the pure D149 sample decays to half its value in 150 ps, with the ZnO adsorbed sample taking somewhat longer with 200 ps.

Figure 5.30 shows the comparison of traces taken in the wavelength regime where the ESA band appears in the adsorbed sample but not in the pure sample. Some significant differences appear. In both samples the absorption signal begins after 2 ps after an ultrafast bleaching signal decays. The pure sample reaches an absorption maximum after 50 ps and then begins to decay whereas the adsorbed sample continues to absorb with increasing optical density up to the end of the measurement at 350 ps.

Figure 5.31 shows the traces taken at the central ESA wavelength. The difference in optical density can be attributed to the reduced concentration of D149 molecules in the adsorbed sample, but again the pure sample decays faster. A similar effect can be seen in the decay of the stimulated emission.
5.6. \textbf{D149 SAMPLES}

![Figure 5.24: UTA spectrum of ZnO nano-particles pumped at 600 nm.](image)

![Figure 5.25: An illustration of the D149 dye molecule.](image)
Figure 5.26 Stationary absorption spectrum of D149 dye molecules.

Figure 5.27 UTA spectrum of D149 dye molecules on 35 fs time scale.
signal shown in Figure 5.32.

Figures 5.33 and 5.34 show the UTA measurements conducted on the D149 dye molecules and the dye molecules adsorbed to ZnQ nano-particles respectively, over a time scale of 3 ps in 21 fs time steps.

Both scans show similar results and analysis of traces show only slight differences in the time constants involved on this ultrashort time scale, that only become significant over the longer time scales that have already been investigated.

5.7 Conclusion

Although no direct evidence of charge transfer has been found, the measurements on the ZnOCPc and D149 dye samples have aided in characterizing the setup. The setup is capable of detecting processes on a sub-100fs scale, well below the resolution required to detect the charge transfer processes on a sub-ps scale. The setup also has the sensitivity to detect changes in transmission of 0.5%. This means that when a sample is excited and shows a bleach signal transmission change of 10% which is often the case, only 5% of the excited molecules need to undergo charge transfer in order for the setup to detect it.
Figure 5.29: Decay traces of ground state bleaching signal for the pure D149 sample and the sample adsorbed ZnO nano-particles.

Figure 5.30: Decay traces of signal between GSH and ESA bands for the pure D149 sample and the sample adsorbed ZnO nano-particles.
5.7. CONCLUSION

Figure 5.31: Decay traces of ESA bands for the pure D149 sample and the sample adsorbed to ZnG nano-particles.

Figure 5.32: Decay traces of stimulated emission signal for the pure D149 sample and the sample adsorbed to ZnG nano-particles.
Figure 5.33  UTA spectrum of D14S over a time scale of 3 ps
Figure 5.34: UTA spectrum of D145 dye molecules adsorbed to ZnO nanoparticles over 3 ps.
Chapter 6 - Summary

The content of my MSc project covered the development of a Non-collinearly phase matched Optical Parametric Amplifier (NOPA) up to the specifications of a commercially obtained NOPA that was already in use in the laboratory. The development of the NOPA arose from a need to be able to generate tunable pump pulses over a continuous spectral range in the visible with adjustable bandwidth and sufficient energy and ultrafast temporal duration to conduct transient absorption spectroscopy measurements. The project also included the development of diagnostic tools for characterizing the ultrafast absorption spectroscopy setup (some of which is contained in this document), and the development of the setup itself to a degree of sensitivity and spectral and temporal resolution to conduct ultrafast absorption spectroscopy. The setup currently routinely achieves sub-100 fs resolution and can reliably detect changes in transmission of 0.5%.

Pump-Probe Spectroscopy was conducted on several samples. Zinc phthalocyanines, electron rich macrocycles that absorb strongly in the near-infrared were attached to our collaborators at Rhodes University to nano-particles such as single wall carbon nanotubes (SWNT) and ZnO. The idea was that a photo-induced charge transfer could be stimulated between the zinc phthalocyanines and the nano-particles with the former and latter acting as electron-donor and acceptor respectively. The samples are candidate molecules for application in solar cell technology.

In detecting and quantifying charge transfer with the ultrafast transient absorption spectroscopy setup, some significant obstacles were encountered. The nano-particles caused significant scattering of the probe light and very low concentrations of zinc phthalocyanines were able to attach themselves permanently to the electron accepting nano-particles. After taking steps to conduct measurements despite these obstacles, we discovered that up to the detection limits of the setup no electron transfer was occurring. Detection of this process in the current setup would mean that 5% of the excited molecules needed to undergo charge transfer. We found that this was not the case. The possibility to de measurements on these molecules in thin film form instead of in solution is a future prospect that may be more favourable for charge transfer. In additional measurements on stimulated Raman scattering in solvents and D149 molecules, some interesting and ultrafast processes were detected that served to give us confidence in the detection capabilities of the setup. The latest measurements also provide potential for further studies and promising future collaborations.
Chapter 7 - Appendix

Guide to setting up a Pump-Probe experiment

Introduction

The following chapter will deal with the practical considerations that need to be taken into account when conducting transient absorption spectroscopy scans using pump-probe spectroscopy, specifically when using the NOPA as the pump source.

Preliminary Investigations

Before any adjustments are made on the pump-probe spectroscopy setup, certain information needs to be ascertained about the sample under investigation. In addition, the sample itself needs to be prepared for measurements. Absorption of the sample is measured by monitoring the transmission of light through the sample. For this reason, the sample is mostly measured in solution. Measurements on thin-film substrates with sufficient transmission have also been conducted, but due to a large signal to noise ratio, with limited success.

The choice of solvent is therefore an important decision. The sample needs to be soluble in the chosen solvent and the solvent should not react with or deteriorate the sample.

A steady state absorption spectrum taken with an in-house spectrophotometer contains valuable information regarding the sample under investigation. Absorption peaks in the spectrum indicate accessible transitions from the ground state, largely because the spectral region covered by the spectrophotometer corresponds for the most part with the spectrum of wavelengths that the NOPA can produce. Selected excited states can be accessed by pumping selected absorption bands if this information on the sample is known. Typically, the strongest absorption band is a good candidate.

The strength of the absorption determined by measuring the optical density at a band’s central frequency is also an important parameter. The optical density of an absorption band determines how much pump light intensity is required to excite a certain cross-section of sample molecules. The cross-section in turn needs to be determined from statistical considerations.

Before any setting up of the experiment is done, the CPA’s performance needs to be determined. A photo-diode is used to measure the intensity of the output, and an oscilloscope is used to determine the stability of the pulses. If the CPA beam has enough intensity and shot-to-shot stability, the experiment can proceed.
Preparing the pump source

Input Coupling

Since the NOPA is very sensitive to small deviations in alignment at the input, sometimes due to slight misalignment in the CPA itself, the very first step in preparing the experiment will be to check the alignment of the input coupling into the NOPA. The CPA output is coupled in via a series of highly reflective mirrors at 775 nm mounted on rigid aluminium posts. Mirror mounts allow for slight adjustments in the beam path.

Aligning the NOPA

Attention must be given to the alignment and collimation of the seed pulse. A measuring tool is used to monitor the alignment and collimation. The collimation of the beam can be adjusted by moving the collimating lens on the white light stage in either direction along the beam propagation. The stability and intensity of white light must also be optimised by adjustment of the iris and the variable neutral density filter that control numerical aperture and input intensity respectively. If this does not provide a satisfactory white light pulse, adjusting the crystal position relative to the focus of the focusing lens on the white light stage may be required. Re-collimation will, however, also be necessary.

The pump pulse must now be aligned so that the pump and seed pulse overlap spatially within the BBO crystal of the first amplification stage. Additionally, the pump and seed beam should both fall in a vertical plane that is perpendicular to the table. In this way, spatial overlap will not be affected by adjustments in the linear translation stage that mounts the 22% reflecting mirror that effectively controls the time delay between pump and seed pulses.

Then the linear translation stage needs to be adjusted until temporal overlap is achieved and parametric amplification is observed. It is, however, good practice to continuously optimise spatial overlap by adjusting mirror mounts after every adjustment of the linear translation stage.

After making sure that the main pump pulse is being seeded and not a reflection, the appropriate pump wavelength for the experiment is selected by adjustment of the linear translation stage due to the chirped nature of the seed pulse, and adjustment of the angle between pump and seed pulse. An optimum phase matching angle exists for each frequency and is given in figure 3.4. The angle is determined by checking the beam separation in the vertical direction at a position 11 cm from the spatial overlap within the BBO crystal.

The intensity, spectral content and mode quality of the amplified pulse can be optimised by incremental adjustments of almost all the aforementioned parameters. The phase matching angle has a significant effect on the bandwidth of the pulse. The spatial overlap has a strong influence on the intensity of the amplified light. Whereas the temporal overlap determines the central wavelength of the amplified pulse. The position and angular orientation of the BBO crystal has an effect on both intensity and bandwidth. The seed pulse can also be adjusted to an optimised position. These adjustments are for the most part made and the pulse optimised by trial and error. The spectrum of the amplified pulse is continuously monitored by an Ocean Optics USB4000C
UV-VIS Spectrometer that couples in light from the NOPA output via an optic fibre. The intensity is monitored with a Coherent FieldMax II Laser Power Meter.

The second amplification stage is optimised by following the same procedure as with the first amplification stage. Special care needs to be taken to ensure that seed photons are amplified in both stages resulting in a high intensity output. In practice broad band amplification around the central pump wavelength is preferred for the first amplification stage. This makes the finding of spatial and temporal overlap in the second stage easier and the desired spectrum can be obtained by careful adjustment of the second stage alone.

Output and Compressor

The collimation of the NOPA output is then verified by placing a white card in the near and far field and checking for discrepancies in beam diameter. Should adjustments be necessary, the collimating concave mirror on the magnetic base at the output needs to be moved along the direction of beam propagation.

The NOPA output is then reflected via some mirrors onto the first prism of the compressor stage. The magnetic base mounting the prism is placed so that the beam strikes the tip of the prism. In practise, about 10% of the beam is clipped. The rotational stage is then adjusted until the angle of minimum deviation is found.

The compressor is in a folded configuration so the dispersed pump pulse is first reflected off a mirror before striking the second prism. This is done to save space. The mirror is positioned so they entire spatially dispersed pulse is reflected. The angle of reflection is also kept to a minimum to limit further dispersion. The second prism is placed at a distance from the first prism in the region where we expect, based on previous experience, the pulse to be compressed most. The second prism is positioned so that the pump pulse strikes the tip of the prism, and the prism is rotated to its position of minimum deviation.

A mirror then reflects the beam back along the same path along which it made its first pass along the compressor. Optical tissue is used to monitor the alignment of the two beams, since its semi-transparent nature allows both incident and reflected beam to be observed simultaneously. The reflecting mirror at the end of the compressor is adjusted via screws on the mirror mount to a slight angle however, so that the reflected beam is spatially separated at the compressor exit some 10 cm away by a margin large enough so that a D-mirror can reflect the reflected beam without obstructing the incident beam.

The duration of the pulse is then measured with a dispersionless autocorrelator. Then the thickness of glass that the beam travels through is adjusted by moving a linear translation stage that the second prism finds itself mounted on. The translation stage moves in a direction perpendicular to the base of the prism, maintaining the angle of minimum deviation as the prism is moved. After each incremental change is made, another autocorrelation trace is taken and a trend is observed for pulse length as a function of effective prism thickness. If a linear trend is observed or, more generally, a function without local minima, it will be necessary to lengthen the compression length by moving the second prism further away from the first in the case where pulse length de-
creases with increasing prism thickness and vice versa in the case of the pulse length increasing with increasing prism thickness.

Autocorrelation traces are taken at the new prism position for several prism thicknesses. The process is repeated for as many iterations as is necessary until a parabolic trend is observed with a local minima for an intermediate prism thickness. In this position the pulse is maximally compressed. This can be verified by comparing the measured pulse duration to the theoretical transform limited pulse duration for a pulse with equal bandwidth. In practice, most pump pulses are in the 50 nm bandwidth region, and have transform limited theoretical pulse durations of around 15 fs. For these pulses sub 30 fs pulse durations have been achieved. Pump pulses have energies ranging from 50 to 300 nJ.

The beam is then directed via the D-mirror to series of mirrors to the driver-controlled linear translation stage that controls the delay between pump and probe pulses. Two prisms are positioned in such a way that a beam passing through the centre of both will be parallel to the direction of motion of the linear translation stage. The beam alignment is verified in this way. This is done so that the pump-probe overlap does not disappear as the delay between pulses is changed. The beam then passes the optical chopper. The pump beam is then directed to a variable neutral density filter, which is used to regulate pump energy and the desired pump energy is achieved by moving the filter while monitoring the energy with a power meter. A λ/2 wave plate is used to control the polarisation of the pump beam relative to the probe beam. Finally the pump beam is focused by a focusing mirror before striking the sample.

Preparing the probe pulse

Before any final adjustments are made, the pump-probe overlap needs to be found. To understand how this is done, the method in which measurements are done needs to be discussed first.

Both the pump and probe pulses after overlapping in the sample volume are coupled into a spectrometer. The spectrometer that the pump pulse is coupled into determines when the sample is pumped and when it is unpumped by measuring the intensity of incoming light during intervals when the chopper unblocks and blocks the pump beam respectively. The data is read into custom software into a computer. The probe beam is coupled into the other spectrometer which continuously measures the absorption spectrum of the sample and feeds the data to the same computer. The computer then bins the spectra obtained from the probe spectrometer into pumped and unpumped spectra corresponding to measurements taken during pumped and unpumped intervals as determined by the pump spectrometer. The ratio between pumped and unpumped spectra then reveals the change in optical density in certain spectral regions due to the photo-excitation of the sample. The excited spectra are effectively measured in relation to the unpumped reference spectra. The ratio of pumped and unpumped transmitted spectra is measured. This technique rests on the assumption that all decay processes occur on timescales shorter than 1 ms, the time between successive pulses. The data obtained is displayed on a 3-dimensional graph with time, wavelength and change in optical density assigned to each axis. The temporal overlap is detected in this measurement to be within the measurement window by a sudden jump in either direction from
unity caused by photo-induced absorption changes in the pumped transmission spectrum from the reference transmission spectrum.

A mirror mounted on a magnetic base is moved to a position where the optical pathlength of the probe beam path is estimated to be equal to the pump beam path. This is verified by conducting a transient absorption scan. If the overlap is detected, minor changes to the position of the mirror are made until the overlap is as far back on the translation stage as possible, to leave as much a time window for the transient absorption measurement after excitation as possible as the stage is moved forward. The retro reflection from the magnetic base mounted mirror is then carefully aligned through a pair of fixed iris slots to maintain a constant beam alignment in successive measurements into the white light generation assembly.

The second iris also controls the numerical aperture of the seed pulse for white light generation. A variable neutral density filter controls the energy of the seed pulse. The spectrometer into which the probe light is coupled reads the spectra into the computer continuously. The white light generated in the bulk medium in most cases sapphire crystal, is monitored on the computer until a stable and broadband white light spectrum is obtained by adjustments made on the position of the focus relative to the crystal, the seed pulse energy and the numerical aperture of the seed pulse.

Preparing the measurement

The probe beam is then aligned to pass through the sample volume and focused onto the optical fibre that feeds the light into the spectrometer. The position of the fibre is optimised until the maximum amount of light enters the spectrometer. This maximum is obtained by monitoring the spectra read into the computer.

The spatial overlap of pump and probe then needs to be verified and optimised. The sample holder has a pin hole holder attached. A 100 μm pin hole is positioned so that the focused probe beam passes through its centre. Usually a diffraction grating is not observed, indicating that the focus is smaller than the pin hole diameter. The pin hole is then fixed and the probe beam blocked. The pump beam is then adjusted with screws on the mirror mounts so it passes through the centre of the same pin hole, albeit at an angle. A clear diffraction pattern is observed. This indicates besides the fact that the pump beam has a narrower spectrum, that the focus is in the order of the pin hole size. This confirms that the entire sample volume that is probed is excited and the beams overlap spatially. The sample is then moved into the position of the pin hole.

The remaining preparations are done on custom designed software. Several parameters in the measurement programme need to be set. The threshold value for the pump spectrometer needs to be set. This is the intensity value that will, when exceeded, register a pumped interval. In the case where the threshold intensity is not exceeded an unpumped interval is registered. Calibration programmes for the probe spectrometer are run and the calibration verified with a Mercury-Argon lamp. A programme is then run where the delay stage is moved to a short time after excitation and a transient absorption spectrum is read out online. Fine adjustments are made to the sample position and the pump beam alignment to maximise the absorption signal. The
pump-probe overlap is maintained with the help of a programme that monitors the pump beamwalk and, with a piezo-electric mirror, corrects for deviations as the delay stage moves between measurements. This programme needs to be run and pixel coordinates for the pump beam on the camera monitoring the pump beam saved. The programme also calibrates the movements of the piezo-electric mirror. The measurement, fully automated by our measurement programme, can then be run.
Bibliography


