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Technical Development of Coherent Two-Dimensional and Three-Dimensional Optical Spectroscopy

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Abstract

The work on this dissertation is focused on the technical development of multidimensional nonlinear optical spectroscopy. Using pulse shaping techniques, two-dimensional (2D) and three-dimensional (3D) optical spectroscopy are performed in the visible spectral region. Technical developments in generating and characterizing polarization-shaped ultraviolet (UV) pulses are explored as well, with the aim of implementing a polarization-based coherent multidimensional optical spectrometer.

Polarization-shaped pulses in the ultraviolet (365 nm) are generated using two independent sum-frequency generation (SFG) processes in two orthogonally orientated β -barium borate crystals. The amplitudes, phases and the delays in the two sets of visible (650 nm) and near infrared (800 nm) pulses that contribute to the two SFG processes are controlled by a liquid crystal spatial light modulator pulse shaper (LC-SLM). The two orthogonally polarized shaped UV pulses are then temporally recombined via a birefringent crystal. The interferometric phase stability is well maintained in this common-path geometry setup.

To characterize the amplitude, phase and polarization of the shaped UV pulses, we present a method referred to as “difference frequency generation cross-correlation tomographic ultrafast retrieval of transverse light E -fields” (DFG-XTURTLE) that combines the technique of tomographic ultrafast retrieval of transverse light E -fields (TURTLE) with the amplitude and phase retrieval algorithm of the cross-correlation frequency-resolved optical gating (XFROG). The handedness of the elliptically shaped pulses can also be retrieved with additional measurements with a quarter-wave retardation plate.

2D optical spectroscopy is performed in a pump-probe geometry via a pulse shaper assisted setup. An acousto-optic programmable dispersive filter (AOPDF) generates the first two interaction pump pulses with controllable delays and relative phases, while a white light continuum provides the third interaction probe pulse. Phase cycling schemes are prerequisite in order to isolate the desired signal. With additional data processing steps, we further retrieve the rephasing and non-rephasing 2D spectra with the same approach.

A full discussion on the phase cycling schemes needed for coherent 3D optical spectroscopy is provided. The experimental demonstration used to measure purely absorptive fifth-order 3D electronic spectrum is based on the same experimental setup used in 2D spectroscopy. In the 3D electronic spectroscopy setup, four pulses are generated using a pulse shaper in 3D spectroscopy, and higher-order phase cycling schemes are needed to remove the unwanted signals. Through data processing, all pathways that contribute to the purely absorptive 3D spectrum are retrieved.

Chapter 1

1 Introduction

Spectroscopic techniques which rely on the application of shaped ultrafast pulse trains have made significant advancement in the analysis of molecular structures and dynamics by providing a multidimensional view [1-3]. Previously, with linear absorption spectroscopy techniques such as UV-Vis and Fourier Transform Infrared (FT-IR) spectroscopy, information about the energy levels and the oscillator strength of the molecule of interest are displayed using a single frequency axis. However, in a complex molecule with various relative close energy levels, the absorption spectrum would be congested, and useful information are usually hidden under broad line shapes which lack distinctive features. The recent advancement of pulse shaping technologies has simplified the technique of performing multidimensional Fourier transform spectroscopy. In general, pulse shapers can control the amplitude of the pulses, the timing of the delays between shaped pulses, and the relative phases of the pulse trains. By varying the parameters systematically, pulse trains can be specifically designed for multidimensional nonlinear optical spectroscopy, similar to the earlier developed two-dimensional nuclear magnetic resonance (2D NMR) experiments [4] known as correlation spectroscopy (COSY) and Nuclear Overhauser effect spectroscopy (NOESY). Coherent 2D spectroscopy is an optical analog of 2D NMR spectroscopy, where the former measures optical transitions while the later measures nuclear spin transitions. While 2D NMR might only probe dynamics on the timescale of milliseconds or longer, 2D optical spectroscopy can push the time resolution limit from picosecond to femtosecond time scale where many

interesting processes occurs [1, 2, 5, 6]. The recent development of ultrafast 3D optical spectroscopy has the potential to provide even more information than its 2D counterpart. The molecular response from nonlinear 2D and the 3D optical spectroscopies, represented as third-order and fifth-order polarization, respectively, are frequency-resolved in more than one dimension, which help to de-congest the spectrum of a complex system and offer more information. Multidimensional optical spectroscopy provides a rich amount of information to understand molecular properties. The analysis of the magnitudes and line shapes of the diagonal and cross peaks in a multidimensional spectrum provide a powerful probe to investigate molecular systems. For instance, one can examine if two peaks observed in a linear absorption spectrum are coupled by the presence of cross peaks in a 2D spectrum, and if the line shapes of the absorption peaks are homogeneously or inhomogeneously broadened [7-9]. In contrast to multidimensional nonlinear optical spectroscopy, transient absorption spectroscopy is another widely used nonlinear experiment that measures coherent higher-order polarization signals. It is commonly applied to study of time-dependent population relaxation processes and chemical dynamics. In principle, the experiment uses two pulses that are separated by a delay τ and both pulses (pump pulse and probe pulse) are crossed in a sample at a small angle. Initially the pump pulse creates a non-equilibrium state, and the change in the sample will be characterized by the change in intensity of the transmitted probe pulse as a function of the delay τ . There is an inherent limitation with transient absorption experiment compared to multidimensional optical spectroscopy. Although transient absorption can select a narrow excitation pump bandwidth, while probing across a broad wavelength, there will be a loss in time resolution according to the time-frequency uncertainty relationship. Similarly, with a broad excitation pump bandwidth, the higher time resolution will be achieved at the expense of lower spectral resolution. The use of multidimensional optical spectroscopy is able to overcome this limitation by providing both high spectral and

temporal resolution. The combination of femtosecond laser with multidimensional Fourier transform technique has expanded our understanding on molecular structures and dynamics on the ultrafast time scale. 2D electronic spectroscopy (2D ES) has revealed energy transfer mechanisms in photosynthetic pigment-protein complexes [10-17] and in the many-body interactions of semiconductors [18-21]. 2D infrared spectroscopy (2D IR) has explored the time-resolved vibrational modes of molecular structures undergoing bond association and dissociation processes [22-25], and also unraveled many-body interactions in direct gap semiconductors by separating the contributing coherent nonlinear optical response [26-28]. Recently, 3D IR has been implemented to characterize bond stretching dynamics by applying three-point frequency fluctuation correlation functions [29]. The development of multidimensional optical spectroscopic techniques promises to uncover more information of molecular properties and provide more valuable insights. With further advancement in pulse shaping technologies, it will undoubtedly stimulate the possibility that the well-developed techniques of multidimensional NMR may be adapted to optical spectroscopy.

1.1 Two-Dimensional Optical Spectroscopy

The advancement of ultrafast laser techniques has allowed the development of multidimensional optical spectroscopy that is analogous to those previously developed in NMR. In multidimensional optical spectroscopy, a sequence of ultrashort pulsed lasers is used to study the system as a function of multiple times, or in their Fourier transform frequency counterparts, so as to reveal the interactions among the molecules in the sample. However, the refined pulse sequence used in NMR is far from being used realized optically as there is much difficulty in phase detection and control in the optical frequency than in radio frequency. Despite the limitation, there is steady advancement

made. Heterodyne method for phase detection, phase cycling and phase matching has been implemented in 2D optical spectroscopy to retrieve the desired signals. Pulse shapers have greatly simplified the measurement using 2D optical spectroscopy and have been demonstrated [31]. 2D optical spectroscopy has been performed at a wide range of spectral domain, from the mid-infrared (MIR) [30-36] down to the visible and ultraviolet (UV) regions [37, 38]. 2D optical spectroscopy is a four-wave-mixing (FWM) technique where a time-ordered three pulses interact with the sample in carefully timed manner to generate a third-order signal in the phase-matched direction. The first pulse interaction with the system creates coherence between the ground and first excited state. After time t_1 , known as the coherence period, the second pulse interaction creates a population on the ground or excited state. After time t_2 or T_w , also known as population time or waiting time, the third pulse interaction creates the second coherence and the signal is emitted after a time t_3 . Similar to NMR, the signal is heterodyne detected to maintain both the amplitude and phase properties. The detected molecular response is a coherent third-order polarization. The signal is doubled Fourier transformed with respect to both t_1 and t_3 to generate a 2D optical spectrum

$$s_{2D}(\omega_\tau, t_2, \omega_l) = iP^{(3)}(\tau, t_2, \omega_l) e^{i\omega_\tau \tau} d\tau \quad (1.1)$$

where $P^{(3)}$ is the third-order polarization signal. The third-order polarization is written as a convolution of the electric field with third-order response function, which is expressed as

$$P^{(3)}(t) = \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_1 R^{(3)}(t_3, t_2, t_1) E_3(t-t_3) E_2(t-t_3-t_2) E_1(t-t_3-t_2-t_1) \quad (1.2)$$

where E_1 , E_2 , E_3 represent the first, second and third laser pulses, t_1 , t_2 , t_3 are the experimental time delays, and $R^{(3)}$ is the third-order response function. The terms $R^{(3)}$ can be represented by double sided Feynman diagrams (DSFDs) which are coherence transfer pathways that gives information on the time progression of the density matrix as it interacts with the electric field. The DSFDs is read from the bottom to top, with the interactions represented by arrows. Arrows pointing inward and outward corresponds to

absorption and emission of a photon, respectively. Figure 1.1 shows three representative diagrams that are processes emitted in the phase matched direction $\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ where $\mathbf{k}$ represents the wave vector of the interactions.

Figure 1.1: Double-sided Feynman diagrams describing ground state bleaching, stimulated emission and excited state absorption.

A 2D spectrum is a contour plot that correlates transitions between two frequency axes at a given population time T_w . The direct visualization of correlation, seen in the off-diagonal region in a 2D spectrum in Fig. 1.2, is a major advantage over linear spectroscopy.

Figure 1.2: A schematic 2D spectrum of two coupled transitions. The peaks on the diagonal axis can be obtained from a linear absorption spectrum. The cross peaks in the off-diagonal axis is due to the coupling between the two transitions.

A cross peak that connects between the excitation and detection frequencies in a 2D spectrum is a direct indication of coupling between two states. The positive peaks are associated with ground state bleaching or stimulated emission, while the negative peaks corresponds to excited state absorption. In general, there are three ways to experimentally set up the spectrometer. The first setup uses a boxcar geometry in which the three pulses are overlapped non-collinearly and the resultant signal is emitted in a phase-matched direction that is background free. Usually an additional beam is needed as a local oscillator to heterodyne-detect the signal [3]. Alternatively, using a fully collinear geometry, the emitted signal is in the same direction as the three excitation pulses, and phase cycling is required to remove any undesired signals that are emitted in the same direction as the desired signal. As excited state population is being measured in the collinear geometry, the signal is emitted as fluorescence which is a required property of the sample [38, 39]. In the third setup using a partially collinear geometry, also known as pump-probe geometry, two collinear pump pulses interact non-collinearly with a third probe pulse. The signal is emitted and heterodyne-detected in the same direction as the probe pulse, which eliminates the need for a separate local oscillator beam that is used in a boxcar geometry [40-42]. However, in using the probe pulse as a local oscillator, the intensity of both components cannot be separately controlled to optimize the signal. The number of phase cycling steps needed to remove the unwanted signals is also significantly reduced in a partially collinear geometry as compared to a collinear one, which means that a lesser number of experiments need to be completed.

1.2 Three-Dimensional Optical Spectroscopy

2D optical spectroscopy has been well established for the past decade, and it has been proven to be a useful tool to investigate chemical and molecular dynamics. 3D fifth-order

optical spectroscopy is an extension of 2D third-order optical spectroscopy, and it provides other observables that elude lower-order spectroscopies such as determining higher vibronic states [43] and providing three-point frequency fluctuation correlation functions to determine the non-Gaussian dynamics in line shape fluctuation [44]. It is possible to obtain third-order 3D optical spectroscopy, where the third axis is generated by Fourier transform over the time t_2 [45, 46]. In this thesis, only fifth-order 3D optical spectroscopy is reported. Fifth-order 3D optical spectroscopy is a six-wave-mixing process (SWM) where five pulses interact with the system to generate a signal which is of coherent fifth-order polarization. It is basically an extension to the previously mention 2D optical spectroscopy by an addition of two pulses to create another coherence period t_5 . In brief, the time t_1 between the first and second pulse interaction is the first coherence period, the time t_3 between the third and fourth pulse interaction is the second coherence period, while the fifth-order signal is emitted at time t_5 , which is the third coherence period, after the fifth pulse interaction. The signal is heterodyne detected and resolved onto three correlated axis. Fourier transforming with respect with these three times t_1 , t_3 and t_5 would generate a 3D optical spectrum. There remains two population times t_2 and t_4 , which is the time between the second and third, and the fourth and fifth pulse interaction, respectively. There is a wealth of information that can be provided with 3D optical spectroscopy. With an additional axis more than a 2D spectrum, absorption signals can be spread out more and there is less congestion in a 3D spectrum. For a 2D spectrum, the cross peaks show couplings only between two absorption peaks. However, for three absorption bands that are coupled, one can only indirectly infer from the integration of cross peaks as a function of population time to determine the nature of the couplings. In 3D optical spectroscopy, the cross peaks present provide direct spectroscopically resolved evidence on the couplings in such multilevel systems. Similar to 2D optical spectroscopy, three general experimental geometries can be implemented to perform 3D optical

spectroscopy, namely the non-collinear [43], collinear and pump-probe geometry [47]. All three setups face the same advantages and disadvantages as compared to their 2D counterparts. Hamm and coworkers [43] first demonstrated a purely absorptive 3D IR spectrum in a non-collinear setup, in which five laser pulses were translated over different mechanical delay stages to generate the fifth-order signal that is heterodyne-detected and frequency-resolved by a spectrometer to give the detection axis. The series of signals are collected by increasing the first and second coherence times in a stepwise manner, and Fourier transforming along these two timings to give the remaining two axes of a 3D spectrum. The timings for the first and second population times are kept fixed for every each 3D spectrum. Engel and coworkers [48] performed 3D electronic spectroscopy using a unique setup known as Gradient Assisted Photon Echo Spectroscopy (GRAPES). However, GRAPES does not allow both population times to be varied, and the 3D spectrum obtained is not purely absorptive. Experimentally in a pump-probe geometry, phase cycling is a requirement to remove unwanted signals and to yield only the desired signals. Unlike in a 2D optical spectroscopy in a pump-probe configuration, the fifth-order signal that is obtained from a 3D optical spectroscopy in a pump-probe configuration is not automatically retrieved as a purely absorptive signal [47]. There are four Feynman pathways that contribute to a purely absorptive 3D spectrum, and the 3D line shape is phase-twisted for each pathway, similar to the rephasing and non-rephasing diagrams in 2D spectroscopy [43]. Summing together the four spectra collected from the four pathways that are chosen by 3D phase cycling schemes yield the purely absorptive 3D spectrum. In some experiments, it is useful to separately obtain specific pathways from various Feynman diagrams, such as to solely investigate coherence transfer [16, 34, 49, 50] and frequency correlations [51]. To obtain such diagrams, causality has to be implemented before phase cycling is performed, and the resultant signals will be well separated in different halves or quadrants in a 2D or 3D spectrum, respectively.

1.3 Phase Cycling for Multidimensional Optical Spectroscopy

In this work 2D and 3D electronic spectroscopy was performed by direct shaping of visible light using a pulse shaper, and by employing phase cycling to remove any unwanted signals in the multidimensional spectrum. Phase cycling is a technique that was initially implemented in nuclear magnetic resonance (NMR) spectroscopy [4], but recently it has been increasingly applied in multidimensional optical spectroscopy. Phase cycling is a method whereby the relative phases of the excitation pulses are systematically varied and the resultant signals collected are proportionally summed to retrieve only the desired signal and to suppress the others. As numerous pathways can be obtained from phase matched signals in multidimensional optical spectroscopy, they will result in multiple unassigned peaks in a multidimensional spectrum. In order to remove the clutter and unambiguously assign the signals by discriminating the pathways, phase cycling is implemented [42, 52, 53]. Phase cycling is necessary only in a collinear or partially collinear geometry, since in a non-collinear geometry the signal is emitted in the phase matched direction that is background free. In a pump-probe geometry, the required number of steps of phase cycling scheme is lesser compared to a collinear setup. Traditionally in a pump-probe geometry, chopping of the pump pulses is applied to remove the background signal. However, this method effectively reduces the frequency at which the signal can be collected by half. Phase cycling provides advantages compared to traditional chopping methods by doubling the rate of data collection, subtracting phase-independent pump-probe signal and enhancing the photon echo signal. It is easy to implement phase cycling with a pulse shaper. With the phase control capabilities of the

pulse shaper, 2D spectroscopy measurements can be performed in the rotating frame which thus lowers the Nyquist limit. In effect, the use of a rotating frame allows collection of fewer data points and reduces experimental collection time [40, 42]. It has been demonstrated that certain schemes are able to fully remove all unwanted signals, while others will result in signals that are aliased and certain conditions are required to unambiguously identify the signals [42, 53]. It is therefore important to determine the phase cycling scheme that requires the least number of steps capable to obtain the desired signals. This will be discussed in detail in the later chapters. As mentioned earlier, the peak shapes and position of the peaks in a multidimensional spectrum can provide much information about the molecular dynamics of a system. Purely absorptive peak shape is desired as it renders the sharpest spectral resolution in presenting well separated peaks. The observed peak shapes collected in a pump-probe geometry pulse shaper assisted 2D spectrometer are purely absorptive and need not be phased, unlike in a boxcar geometry. In addition, through intricate analysis methods, the photon echo signals from different coherence transfer pathways that contributes to the purely absorptive signal can also be retrieved, which will be further elaborated in later chapters.

1.4 Multidimensional Optical Spectroscopy via Pulse Shaping

The advent of pulse shapers has simplified the experimental setup for 2D spectroscopy. The most common commercially available pulse shapers currently employed by a number of research groups mainly include liquid crystal spatial light modulator (LC-SLM), acousto-optic modulator (AOM) [35, 40, 54] and acousto-optic programmable dispersive filter (AOPDF) technology [41, 42]. For both LC-SLM and AOM, the pulses

are spectrally resolved in a 4- f configuration, where the shaping is applied in the Fourier plane. Such a configuration is not necessary for an AOPDF-based setup, where pulses are directly shaped in the crystal. In order to examine different dynamics in a molecular system, a number of pulse parameters can be varied, namely the amplitude, phase, delay and polarization. For general application to multidimensional optical spectroscopy in a pump-probe geometry, it is required to create a multiple pulse train and have control over the phase and delay between the pulse train. This is easily achievable by employing commercially available pulse shaper unit. Although spatial-temporal effects are inherent with the use of a pulse shaper, the effects can be reduced by designing a 4- f line with a spatio-temporal coupling speed as small as possible [55].

1.4.1 Pulse Shaping with Polarization Control

Polarization control adds a degree of selectivity to observe structural dynamics in multidimensional optical spectroscopy, as transition dipoles are directional and the coupling strength of the dipoles provides details on the structural orientation and energy transfer pathways. There have been successful applications of polarization control in 2D spectroscopy to study biological complexes and dyes [41, 56, 57], and also to enhance signal-to-noise ratio [30]. It is always a challenge to implement polarization control in multidimensional optical spectroscopy with a pulse shaper. Polarization control via pulse shaping has been demonstrated by first separating the orthogonal polarizations using a polarizing optic, after which the beams are shaped on separate spatial positions on the SLM then recombined with the same polarizing optic [58]. With this technique, active correction for phase drift between the orthogonal polarized shaped pulses are required to maintain interferometric stability which is critical in multidimensional optical spectroscopy [59]. Complete control over the amplitude, phase, delay and polarization of

the interferometric stable pulse train can be realized with indirect pulse shaping where shaped pulses undergoes parametric transfer into the desired spectral range using two LC-SLMs and two orthogonal nonlinear crystals [60, 61]. In this work, shaped UV pulses with complete control over all pulse parameters are demonstrated [61]. Briefly, the shaped visible pulse train from one SLM is frequency mixed with the shaped NIR (800 nm) pulses from a second SLM via sum-frequency generation (SFG) using two orthogonal nonlinear crystals. One crystal generates a UV polarized electric field that is orthogonal to the other, and the two orthogonally polarized UV light fields are recombined using a birefringent crystal. Long term interferometric stability has been demonstrated for an orthogonally polarized pulse pair, which meant that this pulse shaping technique can potentially be used in 2D spectroscopy with a pump-probe geometry. The ability to characterize polarized shaped pulses is as important as the ability to generate them.

1.4.2 Characterization of Polarization-Shaped Pulses

There are a number of characterization methods that have been developed for pulses with different polarization. A well-established method, denoted as “polarization light interference versus wavelength of only a glint” (POLLIWOG), uses spectral interferometry to characterize orthogonally polarized shaped pulses with a fully characterized reference pulse [62]. Recently, a non-interferometric self-referenced method termed “tomographic ultrafast retrieval of transverse light E -fields” (TURTLE) was developed to characterize arbitrary shaped pulses [63]. This method works on any technique that measures both intensity and phase of a single polarization state, such as frequency-resolved optical gating (FROG) [64]. To characterize the polarization, amplitude and phase of the shaped UV pulses, we developed a new technique, referred to

as “difference frequency generation cross-correlation tomographic ultrafast retrieval of transverse light E -fields” (DFG-XTURTLE). This method is a combination of the cross-correlation frequency-resolved optical grating (XFROG) and TURTLE techniques. In DFG-XTURTLE technique, three linear projections at 0° , 45° and 90° of the shaped UV pulse are frequency mixed with the characterized 800 nm pulse and the resultant DFG signal in the visible is examined with the standard XFROG algorithm. The algorithm first determines the phase relationship of the UV pulses for both the 0° , 90° projections before reconstructing the projection at 45° . In order to establish the interpulse phase, an additional linear spectrum needs to be obtained. The handedness of the shaped pulses can also be retrieved with additional measurements that are described in the later chapters.

1.5 Scope of Work

This thesis will be arranged in the following manner. Chapter 2 will discuss the development of a technique to generate amplitude, phase and polarization controlled ultrafast laser pulses in the UV by nonlinear methods. Chapter 3 describes a method of characterizing polarization shaped pulses in the UV that combines the well-established techniques, difference frequency generation cross-correlation FROG (DFG-XFROG) and TURTLE. Chapter 4 describes various phase cycling schemes that are demonstrated experimentally in 2D optical spectroscopy in a pulse shaper assisted pump-probe geometry and also discusses the theoretical explanations for all schemes so as to provide a better understanding. Chapter 5 reports the theoretical and experimental investigation of various phase cycling schemes for 3D optical spectroscopy in a pulse shaper assisted pump-probe geometry to obtain a purely absorptive 3D spectrum with controllable population delays. Both 2D and 3D multidimensional optical spectroscopic studies were carried out on chlorophyll a in methanol.

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Chapter 2

2 Ultraviolet Polarization Pulse Shaping Using Sum-Frequency Generation

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The generation of shaped ultrafast laser pulse trains with ever increasing complexity has proven to be useful for a variety of experiments. Physiochemical and biophysical researches have benefited from the capabilities of complete control of femtosecond laser pulses. As the transition dipoles are directional, polarization control adds an important degree of freedom to molecular research. For instance, such pulses have been successfully employed in quantum control experiments to actively manipulate the population of specific modes or the outcome of chemical reactions [1-3]. In multidimensional optical spectroscopy, where pulse shapers provide the necessary phase-locked pulse trains for studying systems like atoms, dyes, or complex biological molecules [4-7], polarization control enables the suppression of undesired peaks [8] as well as the enhancement of the signal-to-noise ratio [9]. The ultraviolet (UV) spectral region is interesting for molecular research since it encompasses the electronic excitation bands of organo-chemical and biological molecules [7].

There are two general approaches to the commonly used amplitude and phase pulse shaping techniques. The first is referred to as direct pulse shaping, where direct

modulation is performed on the pulse at the desired frequency. Acousto-optic modulators (AOMs), liquid-crystal spatial light modulators (LC-SLMs), and acousto-optic programmable dispersive filters (AOPDFs) are used for computer-controlled pulse shaping [10]. These are typically available for direct pulse shaping in the visible and near-infrared (NIR). In the UV, pulse shaping with a noncommercial LC-SLM has been extended down to 260nm [11], with an AOM in principal down to 180nm [12] and a recent commercially available version of an AOPDF, which operates down to 200 nm [13]. There are many other direct pulse shaping techniques in the UV, but they are limited in their pulse shaping capabilities, where for instance, the well-established micromirror technique can only modulate the phase [14].

The second method is indirect pulse shaping, where a nonlinear process transfer a directly shaped pulse in an easily accessible frequency range into the desired frequency range [15, 16]. The sum-frequency generation (SFG) [17, 18] or the second harmonic generation [19, 20] is commonly used to access the UV region. This allows one to use commonly available pulse shapers while overcoming limitations of direct pulse shaping such as the absorption of UV light by typical liquid-crystal materials in commercial LC-SLMs.

However, additional technical challenges are introduced with the shaping of the polarization state. An arbitrary polarization-shaped pulse $E(t)$ can be thought of as a linear combination of two orthogonally polarized light fields expressed as:

$$E(t) = \hat{x}E_x(t) + \hat{y}E_y(t)e^{-i\varphi}. \quad (2.1)$$

Combination of two individual sets of orthogonally oriented linear pulse shapes $E_x(t)$ and $E_y(t)$ therefore yields polarization-shaped pulses. The phase φ between $E_x(t)$ and $E_y(t)$ dictates the ellipticity of the created pulses. Various intricate polarization-shaping schemes in the NIR based on 4- f configuration pulse shapers have been developed, which rely on pulse shaping using different spatial parts of the spatial light modulator (SLM) to

shape different pulse components while still maintaining a near common-path geometry [21-23]. To the best of our knowledge, non 4- f configuration pulse shapers such as AOPDFs have not in principle been demonstrated to be capable of polarization shaping in a common-path geometry. To ensure interferometric stability, especially at UV wavelengths, a true common-path geometry between $E_x(t)$ and $E_y(t)$ is desired. Polarization pulse shaping in the UV has, to the best of our knowledge, previously only been demonstrated by Brixner and coworkers at 400 nm [19].

Here we report an indirect pulse shaping method for complete control over amplitude, phase, and polarization tunable at UV frequencies in a true common-path geometry. A new method for polarization shaping in the mid-infrared (MIR) termed Complete Amplitude, Phase, and Polarization Ultrashort pulse Computer Control in the IR via Nonlinear Optics (CAPPUCCINO) [24] was recently reported. In CAPPUCCINO, two sets of temporally separated shaped pulse trains in the NIR are transferred into the MIR via two orthogonal difference frequency generation (DFG) processes using two perpendicularly oriented nonlinear crystals to create the shaped $E_x(t)$ and $E_y(t)$ in quasi common-path geometry. The resulting shaped MIR pulse trains with orthogonal polarization are temporally recombined using a birefringent material to give the polarization-shaped pulse $E(t)$ [Eq. (1)]. In the present work, the DFG processes are substituted with SFG processes to generate UV shaped pulses instead. We have also modified the original CAPPUCCINO configuration to achieve a true common-path geometry. The aim of this work is to develop a technique to create shaped UV pulse trains with complete control over its amplitude, phase, polarization and delay so that it can potentially be implemented in coherent 2D optical spectroscopy.

2.1 Experimental

2.1.1 Optical Setup

A commercially available Ti:sapphire regenerative amplified laser system (Coherent, Legend) provides laser pulses centered at 800 nm and of ~ 150 fs duration, operating at a repetition rate of 1 kHz with an average energy of 1 mJ per pulse. A scheme of the setup is depicted in Fig. 2.1(a).

Figure 2.1: (a) Schematic experimental setup of the UV polarization pulse shaper. OPA: optical parametric amplifier, SLM1: visible spatial light modulator, SLM2, near-infrared (800 nm) spatial light modulator, DG, degrouping crystal (calcite), 1 and 2, orthogonally oriented BBO crystals; RG, regrouping crystal (LiIO₃). (b) Illustration of the polarization sensitive sum-frequency generations.

Approximately 30% of the laser output is frequency doubled to 400 nm and used to pump a two-stage white-light seeded beta-barium borate (BBO) ($d = 2$ mm) based optical parametric amplifier (OPA) to yield tunable pulses in the visible (Vis). The OPA delivers pulse energies of ~ 10 μ J at 650 nm. The pulses are steered into a direct pulse shaper

consisting of a zero-dispersion compressor with a commercial LC-SLM placed in the Fourier plane for amplitude and phase control [Jenoptik SLM-640d, labeled SLM1 in Fig. 2.1(a)]. The pulse width of the visible pulses after dispersion compensation in the 4-f configuration is ~ 100 fs. By using an autocorrelator, the time window for pulse modulation, defined as the maximum achievable temporal delay between two pulses without the occurrence of pronounced side pulses, is measured to be around ~ 4 ps. We create two individual sets of pulse shapes in the visible delayed by a fixed time ΔT_{vis} , indicated by red and blue boxes and “1” and “2,” respectively [see Fig. 2.1(b)]. Those two temporally separated sets will evolve into the two orthogonal polarization components $E_x(t)$ and $E_y(t)$ of Eq. (2.1) in the following sum-frequency generation processes. For this reason they typically consist of completely independent amplitude- and phase-controlled pulse shapes as indicated in Fig. 2.1(b). The orientation of this pulse train is set to $\phi_{\text{vis}} = 45^\circ$ with respect to the laser table before undergoing sum-frequency generations. Throughout the paper, we are using the convention that all polarization angles ϕ are given in reference to the laser table plane according to the coordinate system in Fig. 2.1(b).

The main part of the NIR radiation at 800 nm enters a second pulse shaper featuring a second LC-SLM for amplitude and phase control (Jenoptik SLM-320d, labeled SLM2). Shaping of the 800 nm light is done to match the pulse shapes in the visible, thereby optimizing the subsequent sum-frequency generations. Alternatively, the pulses have been temporally stretched over the desired time window as shown previously [16]. However, our approach allows for improved energy utilization. The modulated 800nm pulses are then set to $\phi_{800} = 45^\circ$ and directed into the “degroupping assembly” [labeled DG in Fig. 2.1(a)], consisting of a birefringent material in a doublepass configuration based on a design by Bartels and co-workers [25]. Because of the differing group velocity indices n_g^o and n_g^e for ordinary and extraordinary waves in birefringent materials, pulse separation

into two orthogonal polarization states for an incident beam oriented at $\phi_{800} = 45^\circ$ occurs according to:

$$\Delta T_{800} = \frac{L}{c} [n_g^o - n_g^e(\Theta)] \quad (2.2)$$

The temporal delay ΔT_{800} between the two polarization states is dictated by material choice and angle Θ with respect to the optical axis via n_g^o and $n_g^e(\Theta)$ and the traveled path length L within the material. Crystal tilting allows for fine tuning of the delay. By choosing a double-pass geometry, walk-off between the two components can be minimized [25]. Here we use a calcite window of 3:1 mm thickness at a cut angle of $\theta = 45^\circ$, which allows for tuning of ΔT_{800} in the range from ~ 0.8 to 3 ps considering an external crystal tilt angle of $\pm 10^\circ$. We emphasize here that this degrouping assembly is of a common-path geometry. This is an improvement over the noncommon-path degrouping assembly reported in our recent paper, which is based on polarization beam splitters and a Michelson interferometer [24].

The pulse trains in the visible and the NIR are temporally and spatially overlapped via a dichroic mirror and steered into two perpendicularly oriented BBO crystals in close proximity ($d = 2$ mm, $\theta = 36^\circ$). The following type I sum-frequency generation can be described by $\text{Vis}(650 \text{ nm}, o) + \text{NIR}(800 \text{ nm}, o) \rightarrow \text{UV}(358.6 \text{ nm}, e)$. In this process the amplitude and phase profile of the visible pulses are transferred to the UV. The polarization state of the resulting UV pulses is dictated by the polarization states of the interacting light fields and the orientation of the nonlinear medium. In effect, the nonlinear crystals act as very selective polarizers. We make use of this effect to achieve polarization shaping. Referring to Fig. 2.1(b), crystal 1 therefore interacts exclusively with the part of the 800 nm pulses oriented at $\phi_{800} = 0^\circ$ and the projection of the 650 nm pulses onto the x axis ($\phi_{\text{vis}} = 0^\circ$) to yield linearly polarized pulses $E_y(t)$ oriented at $\phi_{\text{UV}} = 90^\circ$ in the UV, since only here are the required polarization states o , o , and e for a type I

process fulfilled (denoted by boxes in red color and labeled as 1). Apart from dispersion effects, crystal 2 has no effect on the “group 1” pulses. The creation of the UV pulses $E_x(t)$ oriented at $\phi_{UV} = 0^\circ$ follows analogous considerations (labeled with 2 and blue colors). In effect the two individual sets of visible pulses at $\phi_{Vis} = 45^\circ$ are transferred into two orthogonally polarized pulse shapes $E_x(t)$ at $\phi_{UV} = 0^\circ$ and $E_y(t)$ at $\phi_{UV} = 90^\circ$ in the UV.

However, $E_x(t)$ and $E_y(t)$ remain separated by a time delay ΔT_{UV} , which is compensated for in the “regrouping assembly” of our setup (labeled RG in Fig. 2.1). Analogous to the degrouping assembly, we employ a birefringent material (LiIO_3 , $d = 4$ mm, $\theta = 90^\circ$), which accounts for $\Delta T_{UV} = 3.67$ ps at 360 nm. Here we use a single-pass geometry. The crystal is cut perpendicularly to the optical axis to avoid walk-off. This way we can compensate for the earlier introduced time delays ΔT_{Vis} and ΔT_{800} , respectively, and recombine the orthogonally oriented components $E_x(t)$ and $E_y(t)$ to yield polarization-, amplitude-, and phase-controlled pulses $E(t)$ in the UV in a true common-path geometry. Variation of the phase ϕ between $E_x(t)$ and $E_y(t)$ according to Eq. (1) allows any desired polarization state to be achieved, such as elliptical or circular polarization. We are able to achieve near transform-limited pulses in the UV with pulse durations comparable to the input pulses in the visible. The maximum time window available for pulse shaping is ~ 3 ps. Depending on pulse shaping complexity, we measured pulse energies in the range of 25 to 50 nJ.

2.1.2 Dispersion Effects

The dispersion properties of the two birefringent nonlinear orthogonal oriented BBO crystals of nonnegligible thicknesses (here 2 mm each) have the consequence that the time delays ΔT_{Vis} , ΔT_{800} , and ΔT_{UV} differ substantially from each other. This has to be

taken into consideration during the alignment procedures. To ensure that the incoming beams oriented at $\phi_{\text{vis}} = 0^\circ$ and $\phi_{800} = 0^\circ$ are temporally overlapped in crystal 1, and $\phi_{\text{vis}} = 90^\circ$ and $\phi_{800} = 90^\circ$ are temporally overlapped in crystal 2, we need to introduce an additional time delay of 86 fs between ΔT_{vis} and ΔT_{800} as calculated by the Sellmeier equations. This is because $\phi_{\text{vis}} = 90^\circ$ and $\phi_{800} = 90^\circ$ need to pass through crystal 1 prior to their interaction in crystal 2, whereas $\phi_{\text{vis}} = 0^\circ$ and $\phi_{800} = 0^\circ$ are not affected. This additional time delay is easily introduced in the tunable degrouping assembly. Similarly, after $E_y(t)$ is created in crystal 1, it needs to pass through crystal 2 before it can be utilized in a subsequent experiment. In crystal 2, $E_y(t)$ experiences additional dispersion that $E_x(t)$, after it is created in crystal 2, is not subjected to. This accounts for a time delay of 1.08 ps between $E_x(t)$ and $E_y(t)$, determined by the wavelength and the crystal length of 2 mm. It is possible to measure ΔT_{UV} for the regrouping crystal (here $\Delta T_{\text{UV}} \sim 3.67$ ps), program SLM1 to $\Delta T_{\text{vis}} = 3.67$ ps $-$ 1.08 ps = 2.59 ps, and adjust the degrouping assembly for maximum efficiency around $\Delta T_{800} = 3.67$ ps $-$ 1.08 ps $-$ 0.086 ps = 2.50 ps. In practice, however, we ensure that $E_x(t)$ and $E_y(t)$ are temporally overlapped by crosscorrelation frequency resolved optical gating (XFROG) measurements [26] by adjusting ΔT_{vis} and ΔT_{800} accordingly. Once these parameters are fixed, any further pulse shaping is solely computer controlled by the two pulse shapers. A second effect of the dispersion properties of the two birefringent nonlinear orthogonal oriented BBO crystals is that the creation of $E_x(t)$ and $E_y(t)$ is subjected to different group velocity dispersions (GVDs). After $E_y(t)$ is created in crystal 1, it passes crystal 2 before it can be utilized in an experiment. In crystal 2, $E_y(t)$ experiences additional GVD that $E_x(t)$, after it is created in crystal 2, is not subjected to. Similarly, the two incoming fields in crystal 2 that create $E_x(t)$ are subjected to GVD by first passing through crystal 1 that the incoming fields for creation of $E_x(t)$ are not. As a result $E_x(t)$ and $E_y(t)$ may well achieve

different temporal chirps. Fortunately, this is easily taken care of by individual chirp precompensation in SLM1. The results in this paper are all uncompensated for and show that the differences in chirp between $E_x(t)$ and $E_y(t)$ are minor, even for such large crystal thicknesses. We like to point out that we also use a second set of orthogonal oriented BBO crystals with reduced thicknesses ($d = 0.5$ mm, $\theta = 32.6^\circ$) to minimize dispersion effects at the cost of slightly decreased conversion efficiency. The conversion efficiency is measured to be about 60%–70% of that obtained with the 2.0 mm thick crystals.

2.1.3 Characterization

We use difference frequency generation cross-correlation frequency resolved optical gating (DFG-XFROG) [27] to visualize and analyze the created pulse shapes. The XFROG experiment measures the cross-correlation signal created in a nonlinear BBO crystal ($d = 0.5$ mm, $\theta = 29.2^\circ$) between the pulses in the UV under investigation and a well characterized reference pulse (800 nm, <5 μ J) in a collinear geometry. The resulting signal in the visible is frequency resolved and detected in a spectrometer (Horiba Jobin Yvon, microHR and Triax; Princeton Instruments Pixis100B). Briefly, we select projections at $\Phi = 0^\circ$, 45° , and 90° of the polarized electric field via a linear polarizer. A second linear polarizer maps those projections onto the 45° axis, while a half-wave retardation plate rotates to the plane needed for the subsequent nonlinear DFG process. The second polarizer plate is required since the nonlinear frequency conversion in the DFG-XFROG itself is polarization sensitive. This way we are able to collect DFG-XFROG traces for three representative projections of the polarized electric field under investigation. With a modified tomographic ultrafast retrieval of transverse light electromagnetic-fields (TURTLE) algorithm that relies on the three projections plus the

fully characterized reference beam, we are able to fully describe the characteristics and ellipticity of the created vector field [28, 29].

2.2 Results and Discussion

2.2.1 Single Pulse Creation and Control

To demonstrate the pulse shaping capabilities of our approach in the spectral domain, we created a polarization-shaped test pulse centered around 360 nm. The spectra of the temporally delayed precursor components 1 and 2 obtained via direct pulse shaping in the visible are shown in Fig. 2.2(a) together with an unshaped spectrum.

Figure 2.2: (a) Spectrum of an unshaped pulse in the visible and spectra of the two components '1' and '2' of an amplitude modulated pulse to be transferred into the UV via sum-frequency generation, and (b) the corresponding spectra after the transfer with orthogonal polarization states.

While both components are linearly polarized at 45° in the visible, they will be transferred into orthogonal polarizations in the UV as shown in Fig. 2.2(b). The central spectral slice of ~ 1.5 nm bandwidth at 360 nm is linearly polarized at 0° , while the side lobes exhibit linear polarization at 90° . We observe that the transfer results in a slight deterioration of modulation depth. This results mainly from a convolution of the shaped visible pulses as shown in Fig. 2.2(a) with the pulses at 800 nm. However, spectral restriction of the 800 nm pulses enhances the modulation depth, and here we used a bandwidth of 7 nm. This leads to a successful transfer of the visible pulse shape into the UV via sum-frequency generations. Spectral restriction enhances the modulation depth at the expense of conversion efficiency. It is worth noting that pulse train creation as described in the following sections does not require spectral restriction of the 800 nm pulses.

2.2.2 Pulse Train Creation and Control

Our polarization pulse shaping approach is ideally suited and optimized to produce pulse trains suitable for two-dimensional optical spectroscopies in the UV similar to experiments in a “pump–probe” geometry reported by Weinacht and coworkers [7], with the added benefit of polarization control. This necessitates careful calibration of the required two-pulse sequences. Here we show exemplary two-pulse trains at a fixed time delay. DFG-XFROG traces of a two-pulse train of equal amplitude with orthogonal polarization states and delayed by 1.1 ps are depicted in Fig. 2.3(a).

Figure 2.3: DFG-XFROG traces for polarized two-pulse trains in the UV. All subplots appear on the same scale and are normalized to the most intense peak. The intensities ratios are as expected for (a) a two-pulse train with polarizations set orthogonal to each other and a time delay of 1.1 ps, and (b) a two-pulse train with polarizations at $\phi_{UV} = 0^\circ$ and 45° and a time delay of 1.1 ps.

The middle panel shows a projection at $\Phi = 45^\circ$, while the other two panels depict the projections on

the x-axis ($\Phi = 0^\circ$) and y-axis ($\Phi = 90^\circ$), respectively. The XFROG traces appear as expected, and the apparent chirp was not compensated for as explained above. To further demonstrate the polarization-shaping capabilities, we also created a two-pulse train where the first pulse is polarized at 0° and the second pulse at 45° [see Fig. 2.3(b)]. With our detection method we expect the following intensity ratios: 0.5:0.25 for the projection on the x-axis (upper panel), 0.5:1 for the projection at 45° (middle panel) and 0:0.25 for the projection on the y-axis (lower panel). The measured intensity ratios agree well with

those expected from theory demonstrating the polarization and ellipticity control capabilities of this approach.

2.2.3 Interferometric Phase Stability

Interpulse phase stability is important in two-dimensional spectroscopy, especially in the UV where the demands are much higher than in the IR due to the shorter wavelengths. The common-path geometry allows us to achieve interferometric phase stability without any active interpulse phase stabilization. For demonstration, we created a two-pulse train orthogonally polarized at $\phi_{UV} = 0^\circ$ and 90° in the UV delayed by 1.0 ps. Using a linear polarizer, spectra of the orthogonal polarized two-pulse train projected at $\Phi = 0^\circ$, 45° , and 90° were obtained. These spectra are shown in Fig. 2.4(a).

Figure 2.4: (a) Spectra at three different projections resulting from the interference of an orthogonal polarized two-pulse train delayed by 1.0 ps at 365 nm. (b) The spectrum at $\Phi = 45^\circ$ with interpulse phase $\varphi = 0$ and $\varphi = \pi$, demonstrating our phase shaping capabilities.

The spectra at the 0° and 90° projections contain minimal modulation as expected, as only one pulse of the orthogonally polarized two-pulse train passes through. The small modulation at 0° and 90° results from slight misalignments in the sum-frequency generations and from amplified side pulses due to the pixilation of the SLMs. In the spectrum of the 45° projection, the pronounced fringes clearly show the resultant interference between the orthogonal components, corresponding to a 1.0 ps delay. The interpulse delay was reconfirmed with XFROG measurements. Additionally, to demonstrate interpulse phase control, the relative phase of the two orthogonal pulses was varied, as depicted in Fig. 2.4(b), for a phase shift φ of 0 and π . To demonstrate the long-term stability of the interpulse phase, a spectrum was recorded every minute over a duration of 6 h with the linear polarizer set at $\Phi = 45^\circ$. The resultant spectra were fitted with a linear combination of two Gaussian functions to account for the pulse spectrum envelope and a cosine function for the fringes. The phases of the fitted cosine functions were obtained and shown in Fig. 2.5.

Figure 2.5: Interpulse phase measured for a two pulse train of orthogonal polarization delayed by 1.0 ps at 365 nm over the course of 6 hours at a one minute sampling rate.

As can be seen, the phase stability is excellent and clearly remains within $\pm 2\pi/100$ over the course of the measurement.

2.3 Conclusions

We have reported an indirect pulse shaping technique in the UV based on sum-frequency generation with computer programmable control over amplitude, phase, and polarization state. With the OPA and direct shaping wavelength tunability from about 500 to 690 nm, it is therefore possible to generate shaped UV pulses that are tunable from about 305 to 370 nm. This approach relies on commercially available SLMs and features true common-path geometry to ensure excellent phase stability even in the UV. Experimental

results exemplified the pulse shaping capabilities in the UV, and the polarization-controlled pulse trains presented here will be useful for two-dimensional correlation spectroscopies in a pump–probe geometry.

This present work, together with previously published work [24] in our research group that produces MIR polarization-shaped pulses shows the versatility of our pulse shaping setup. In principle, the same setup is readily interchangeable between producing polarization-shaped pulses in the UV to MIR by switching between SFG and DFG nonlinear optical processes, respectively.

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Chapter 3

3 Characterization of Polarization

Shaped Ultraviolet Femtosecond Laser Pulses

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There has been an interest in polarization-shaped pulses at tunable ultraviolet (UV) wavelengths for different research areas [1-3], but there have not been many appropriate characterization methods being developed. The complete vector-field characterization technique termed POLLIWOG (POLarization Light Interference versus Wavelength of Only a Glint) [4] is a well-established technique, where it uses spectral interferometry to characterize orthogonal polarized pulses with a well-characterized reference pulse, and this technique has been successfully demonstrated at 400 nm [2]; however, such methods are rather difficult to implement in the ultraviolet spectral region as the phases between the two orthogonal polarization needs to be stable, and a self-referenced technique for the reference pulse in the ultraviolet is typically not readily available. There are other techniques that do not need a separate reference pulse, such as self-referenced spectral interferometry [5] and phase characterization by sonogram acquisition [6]; however, to the best of our knowledge no polarization characterization measurement has been

demonstrated yet in the ultraviolet. Other methods, such as ellipsometry [7-9] and cross-phase modulation [10], require a number of measurements to be made, and as such are rather labor intensive. A simpler method referred to as “Tomographic Ultrafast Retrieval of Transverse Light *E*-fields” (TURTLE) [11-13] has been developed recently for full vector characterization. This method can be incorporated in any characterization techniques which retrieve the amplitude and phase of a single polarization electric field, and hence it includes techniques which are noninterferometric. TURTLE has been demonstrated for complex pulse sequences characterization in the near-infrared by second-harmonic generation frequency-resolved optical gating (SHG-FROG) [11]. However, this is impractical in the UV region, where the phase matching angle for the second-harmonic generation is hard to achieve and the nonlinear material may not be transparent in the wavelength of the second harmonic signal. For third-order characterization methods such as the frequency-resolved optical gating (FROG) technique [14], the available energy levels in the UV may be too weak than what is required. To overcome these restrictions, cross-correlation FROG (XFROG) measurement can be performed, where the UV pulse is frequency-mixed with a well-characterized reference pulse of another wavelength to generate a third-order signal. Molecular-alignment gated cross-correlation frequency resolved optical gating (M-XFROG) [15] allows amplitude and phase characterization of UV pulses without phase-matching, whereas difference-frequency generation cross-correlation frequency resolved optical gating (DFG-XFROG) relies on a nonlinear frequency conversion process with phase-matching [16]. Here we choose the latter for the following advantages [16]: Firstly, there is no need to have spectral overlap between the test pulse and the reference pulse, which is a requirement for the interferometric methods. As such, reference pulses that are produced from the Ti:Sapphire chirp pulse amplifier are readily available and easily characterized. Secondly, the reference pulses can be chosen to be more intense than the test pulse so that even

weak pulses can be easily characterized, which is a common case for shaped pulses in the UV [1-3]. Thirdly, detection modes in the visible are easier than in the deep ultraviolet. For instance, using the SHG-TURTLE method to characterize UV pulses centered at 360 nm, we will be detecting signals centered at 180 nm, which is in the vacuum UV region. Whereas by using the DFG-XFROG method, the signal generated will be in the visible spectral region, which is much more convenient and favorable. Lastly, as there is no time-direction ambiguity, XFROG spectrograms are more intuitive to interpret and it simplifies the TURTLE algorithm.

In order to obtain a complete vector-field characterization in the ultraviolet spectral region, three different projections of the vector-shaped test field are needed: two orthogonal linear projections at 0° and 90° , together with an additional projection typically at 45° . These three projections are frequency mixed with a fully characterized reference pulse in a nonlinear crystal, and the resultant DFG signal in the visible spectral range is spectrally resolved by the spectrometer as a function of time delay between the reference pulse and test pulse. To retrieve the complete vector field of the UV test pulses, there are two steps of analysis that needs to be performed. In the first step, the standard DFG-XFROG algorithm is used to retrieve the amplitude and phase measurements of the linear projections at 0° and 90° [17, 18]. In the next step, the TURTLE search algorithm uses the amplitude and phase results obtained in the first step to model the measurement at 45° by finding the correct phase relationship between the orthogonal polarizations [11]. We accordingly refer to the method as DFG-XTURTLE. Additional procedures for the determination of the interpulse phase between temporally separated pulses and to distinguish the handedness of circular/elliptical polarized light are discussed.

3.1 Theory

The complex electric field of an arbitrary polarized pulse or pulse train $\vec{E}_{UV}$ travelling along $\hat{z}$ may be written in the time domain as follows:

$$\begin{aligned}\vec{E}_{UV}(t) &= \vec{E}_{UV,x}(t) + \vec{E}_{UV,y}(t) \\ &= \hat{x} \cdot E_{UV,0x}(t) \cdot e^{i\omega_{UV}t} + \hat{y} \cdot E_{UV,0y}(t) \cdot e^{i\omega_{UV}t + \varphi},\end{aligned}\tag{3.1}$$

where $\vec{E}_{UV,x}(t)$ and $\vec{E}_{UV,y}(t)$ represent the two orthogonal electric field vectors. $E_{UV,0x}(t)$ and $E_{UV,0y}(t)$ are the vector field components along $\hat{x}$ and $\hat{y}$, respectively. ω_{UV} is the angular frequency and φ is the relative phase difference between the two orthogonal components. From this description it is apparent that all information about the polarization state at a given time t is contained in the vector field components $E_{UV,0x}(t)$ and $E_{UV,0y}(t)$ and their relative phase difference φ . Any polarization state can be described via orientation angle ψ , defined as the angle between the major axis and the x -axis, and ellipticity ε , defined as the ratio of major to minor axis. For instance, linear polarization states ($\varepsilon = 0$ or ∞) result for cases where both components are in-phase, e.g., $\varphi = 2m\pi$ with $m = 0, \pm 1, \pm 2$ etc. or 180° out-of phase, e.g., $\varphi = m\pi$ for $m = \pm 1, \pm 3$ etc. Circular polarization states ($\varepsilon = 1$) result for $E_{UV,0x} = E_{UV,0y}$ and $\varphi = +\pi/2 + 2m\pi$ with $m = 0, \pm 1, \pm 2$ etc. (left circular polarization) and for $E_{UV,0x} = E_{UV,0y}$ and $\varphi = -\pi/2 + 2m\pi$ with $m = 0, \pm 1, \pm 2$ etc. (right circular polarization), respectively. All other conditions result in elliptical polarization states. For description of polarization states that vary over time it is often easier to show the complete electric field $\vec{E}_{UV}(t)$ directly.

DFG-XTURTLE attempts to reconstruct the complete electric field of a test pulse $\vec{E}_{UV}(t)$. This is achieved in two steps. In the first step three linear projections at angles η of the test vector shaped electric pulse in the UV are consecutively mixed with a fully characterized reference pulse $E_{Ref}(t)$. $E_{Ref}(t)$ can typically be characterized using SHG-FROG [18, 19]. The projections of the test pulse are along the $\hat{x}$ axis ($\eta = 0^\circ$), the $\hat{y}$ axis ($\eta = 90^\circ$) and a third projection which is typically taken at $\eta = 45^\circ$. The electric field of the difference frequency cross-correlation signal created in a non-linear medium can be expressed as [16]:

$$E_{DFG,\eta} \propto E_{UV,\eta}(t)E_{Ref}^*(t-\tau), \quad (3.2)$$

where the difference frequency cross-correlation signals are centered at $\omega_{DFG} = \omega_{UV} - \omega_{Ref}$. The spectrally dispersed cross-correlation signals as a function of time then yield the three individual DFG-XFROG traces according to:

$$I_{DFG-XFROG,\eta}(\omega,t) = \left| \int E_{UV,\eta}(t)E_{Ref}^*(t-\tau)e^{-i\omega_{UV}t} dt \right|^2. \quad (3.3)$$

A standard DFG-XFROG amplitude and phase retrieval algorithm yields $E_{UV,0x}(t)$ for the projection along the $\hat{x}$ axis at $\eta = 0^\circ$ and $E_{UV,0y}(t)$ for the projection along the $\hat{y}$ axis at $\eta = 90^\circ$. Since XFROG measurements show no ambiguity in time-direction, the only remaining unknown in Eq. 3.1 is then the relative phase φ .

With the help of the third projection this unknown relative phase φ is retrieved in the second step. The two retrieved complex electric fields $E_{UV,0x}(t)$ and $E_{UV,0y}(t)$ can be added according to:

$$E_{UV,\eta}(t) = \cos \eta \cdot E_{UV,0x}(t) + \sin \eta \cdot E_{UV,0y}(t) \cdot e^{i\varphi}, \quad (3.4)$$

to yield the electric field projection at an arbitrary projection angle η . For a projection at $\eta = 45^\circ$ this reads as:

$$E_{UV,45^\circ}(t) = \frac{1}{\sqrt{2}} \cdot E_{UV,0x}(t) + r \cdot \frac{1}{\sqrt{2}} \cdot E_{UV,0y}(t) \cdot e^{i\varphi}. \quad (3.5)$$

Here, r is the intensity ratio $r = \sqrt{I_{\text{DFG-XFROG},90^\circ} / I_{\text{DFG-XFROG},0^\circ}}$, as determined by independent power measurements or the integrated intensity of the DFG-XFROG traces. Initially, φ is arbitrarily chosen. A DFG-XFROG trace for the reconstructed test field from Eq. 3.5 is then calculated according to Eq. 3.3 and compared to the measured DFG-XFROG trace at $\eta = 45^\circ$. The error between the calculated DFG-XFROG trace and the measured DFG-XFROG trace is determined pixel by pixel (i denotes the row, j denotes the column) according to:

$$\text{error}(\varepsilon) = \sqrt{\frac{\sum_{i,j=1}^N [I_{45^\circ}^{\text{meas}}(i,j) - I_{45^\circ}^{\text{calc}}(i,j)]^2}{\sum_{i,j=1}^N [I_{45^\circ}^{\text{meas}}(i,j)]^2}} \quad (3.6)$$

Variation of φ allows to find the smallest error with the help of a search algorithm or by sampling the whole available phase space. This way the relative phase φ is determined and the complete vector-field in the ultraviolet can be reconstructed with few restrictions: A characteristic of XFROG measurements is that the interpulse phase of temporally well-separated components, such as in two-pulse trains, necessitates an additional measurement of a spectrum in the UV (see section 3.3.2). Also the handedness of the electric field remains undetermined. An additional measurement however, can resolve the handedness (see section 3.3.3). As usual the absolute phase cannot be retrieved with FROG techniques.

3.2 Experimental

We recently reported a UV pulse shaper which can have control over the amplitude, phase, delay and polarization of shaped pulse trains tunable in ultraviolet wavelengths [3]. Here, we will characterize shaped UV pulses from this pulse shaper, and the experimental setup for the complete vector field characterization is shown in Fig. 3.1.

Figure 3.1: Schematic experimental setup for the characterization of polarized UV pulse shapes. SHG-FROG/GRENOUILLE is used for reference pulse characterization. The UV pulse shaper provides amplitude, phase and polarization shaped test pulses $\vec{E}_{UV}$. Scheme 1 consists of a Glan-Taylor polarizer at different settings to select various projections (Pol 1), a fixed Glan-Taylor polarizer at 45° (Pol 2) and an optional half-wave retardation plate ($\lambda/2$). Scheme 2 consists of a half-wave retardation plate at different settings to select various projections ($\lambda/2$), a beta-barium borate crystal (BBO) and a band-pass filter to select the DFG signal (Filter).

As described in Section 3.1, the TURTLE retrieval algorithm requires three projections of the test pulse at $\eta = 0^\circ$, 45° , and 90° to be collected. We present two schemes in Fig. 3.1 that can be adopted to perform such measurements. Scheme 1 selects the three projections by the rotation of a Glan-Taylor polarizer (Pol 1) at $\phi = 0^\circ$, 45° , and 90° . As the following DFG process is polarization dependent, necessary optics are needed to satisfy the phase

matching conditions [here Type I: Signal (363 nm, e) – Ref (800 nm, o) $\rightarrow$ DFG (665 nm, o)]. Specifically, the selected electric field from Pol 1 projected onto a second polarizer (Pol 2) that is set at $\phi = 45^\circ$ and a half-wave retardation plate ($\lambda/2$) rotates the projection into the plane that is needed for phase-matching in a nonlinear DFG process. For scheme 2, the only optic needed to select the three projections is the half-wave retardation plate ($\lambda/2$), which is orientated at $\phi = 0^\circ$, 22.5° , and 45° , while the phase matching condition for the DFG crystal itself acts as a linear polarizer. Although XFROG traces from scheme 2 appears to be more intuitive and energy efficient, the half-wave retardation plates are strongly wavelength dependent, which necessitates a range of retardation plates for different wavelength tuning. However, scheme 1 works well over a wide wavelength range (note that the half-wave retardation plate is not absolutely necessary), although it is less energy efficient and less intuitive. For example, for a linear polarization test pulse at 45° , the intensity ratio of the DFG signal for three projections $\phi = 0^\circ$, 45° , and 90° in scheme 1 will be 1:4:1, which is less intuitive, while in scheme 2 it will be 1:2:1, which is as expected. For a circular polarized pulse, the DFG signal intensity ratio in scheme 1 will be 1:2:1, while scheme 2 yields a ratio of 1:1:1. To choose either scheme, the DFG-XTURTLE phase retrieval algorithm must take into account the specific optical setup that is used. Here, the data presented were collected only with scheme 2, while we note that previously we chose scheme 1 instead [3]. The DFG signal in the visible is generated in a nonlinear *beta*-barium borate crystal (BBO, $d = 0.5$ mm, $\theta = 29.2^\circ$) between the UV test pulses and a well-characterized reference pulse (800 nm, <5 mJ) in a collinear geometry as a function of time delay, introduced by a mechanical translation stage (Physics Instruments, M415.DG). To characterize the reference pulse, we use SHG-FROG in the GRENOUILLE configuration (Swamp Optics, GRENOUILLE 8-50-USB) [18]. The resultant DFG signal is frequency resolved in a spectrometer (Horiba Jobin Yvon, Triax; Princeton Instruments Pixis 100B) as a function of delay time,

and the measured spectrogram can be expressed as $I_{\text{DFG-XFROG},\eta}(\omega,t)$, as shown in Eq. (3.3). As described in section 3.2, the DFG-XTURTLE algorithm is able to reconstruct the complete vector field, and we present various results in the following section.

3.3 Results and Discussion

3.3.1 Characterization of Orientation (ψ) and Ellipticity (ϵ)

The initial set of experiments were done to demonstrate the ability of the DFG-XTURTLE algorithm to characterize polarization shaped pulses and hence we used half-wave and quarter-wave retardation plates to create simple polarized pulses shapes. The three DFG-XFROG spectrograms of a linear polarized pulse orientated at 45° at projections $\phi = 0^\circ$, 45° , and 90° are shown in Fig. 3.2. The integrated intensity ratio is 1:2.05:0.99, which is in approximate agreement to the expected ratio of 1:2:1 for an ideal linear polarized pulse orientated at 45° . Figure 3.2(b) depicts the intensity and phase of two orthogonal field components $E_{\text{UV},0x}(t)$ and $E_{\text{UV},0y}(t)$ as retrieved by a standard XFROG retrieval algorithm using a commercial FROG retrieval program (Femtosoft Technologies, FROG 3.08a) or a self-written code based on a principal-components generalized-projections (PCGP) algorithm [17]. There is a positive quadratic phase chirp, or a positive linear chirp, for both orthogonal field components, as shown in Fig. 3.2(b). This is due to the presence of a negative linear chirp in the reference pulse. Using the two orthogonal field components together with the well-characterized reference pulse $E_{\text{Ref}}(t)$ and the XFROG trace $I_{\text{DFG-XFROG},45^\circ}(\omega,t)$ as the input for the TURTLE algorithm, we determined the error of the algorithm as a function of the relative phase φ , as presented in Fig. 3.2(c). The minima on the error plot will correspond to the retrieved relative phase between $E_{\text{UV},0x}(t)$ and $E_{\text{UV},0y}(t)$. As shown in Fig. 3.2(c), the value of the relative phase

is close to 0 radians, which is expected for linear polarized pulses. This exemplifies the ability to characterize the complete vector field according to Eq. (3.5), and in Fig. 3.2(d) we present a schematic diagram of the reconstructed field with arbitrarily chosen absolute phase, including its projections on the plane of the cube for clarity.

Linear Polarization

Figure 3.2: Linear polarized light at 45° : (a) DFG-XFROG traces for projections at 0° , 45° and 90° ; (b) Intensity and phase of $E_{UV,0x}(t)$ and $E_{UV,0y}(t)$ as retrieved by an XFROG retrieval algorithm; (c) Error of the XTURTLE phase retrieval algorithm; (d) Reconstructed vector field.

Minor prepulses and postpulses are retrieved by the algorithm. In general, the algorithm characterizes the test pulse presented in Fig. 3.2 to be linearly polarized ($\varepsilon \sim 0$) and oriented at $\psi \sim 45^\circ$.

Figure 3.3 shows the corresponding results for a circular polarized pulse. The integrated intensity ratio of the DFG-XFROG spectrogram of the circular polarized pulse at projections of 0° , 45° and 90° as shown in Fig. 3.3(a) is 1:0.99:0.87, respectively, in close comparison to the expected ratio of 1:1:1 for an ideal circular polarized pulse. The ratio indicates slight deviation from $\varepsilon = 1$. Figure 3.3(b) shows the intensity and phase of the two orthogonal field components $E_{UV,0x}(t)$ and $E_{UV,0y}(t)$. Both components exhibit linear positive chirp due to the presence of negative linear chirp in the reference pulse. In Fig. 3.3(c), two well-defined minima are retrieved with the TURTLE algorithm that represent the relative phase between $E_{UV,0x}$ and $E_{UV,0y}$, which indicates two possible solutions corresponding to left-circular polarization and right-circular polarization, respectively. Accordingly, there exist two possibilities for the phase of $E_{UV,0y}(t)$ with respect to $E_{UV,0x}(t)$ as indicated in Fig. 3.3(b). This shows that although the TURTLE algorithm is able to determine the ellipticity of a vector field, it has ambiguities in determining the handedness of the field. In section 3.3.3, we will demonstrate how to eliminate this ambiguity to resolve the correct handedness.

Circular Polarization

Figure 3.3: Circular polarized light: (a) DFG-XFROG traces for projections at 0° , 45° and 90° ; (b) Amplitude and phase of $E_{UV,0x}(t)$ and $E_{UV,0y}(t)$ as retrieved by an XFROG retrieval algorithm; (c) Error of XTURTLE phase retrieval algorithm; (d) Reconstructed vector field.

Next, more complex polarization shaped pulses were created using our recently established UV pulse shaper [3]. Specifically, the orientation and ellipticity evolved over

the pulse duration. The pulses are shaped starting with a linear polarization oriented at $\sim 0^\circ$, before changing into elliptical, and then ending with a linear polarization orientated at $\sim 90^\circ$. The corresponding XFROG traces are depicted in Fig. 3.4(a), the retrieved intensities and phases of the orthogonal components are shown in Fig. 3.4(b), whereas Fig. 3.4(c) exemplifies the reconstructed vector field.

Changing Polarization

Figure 3.4: Changing polarization: (a) DFG-XFROG traces for projections at 0° , 45° and 90° ; (b) Amplitude and phase of $E_{UV,0x}(t)$ and $E_{UV,0y}(t)$ as retrieved by an XFROG retrieval algorithm; (c) Reconstructed vector field.

The XTURTLE algorithm has no problem in retrieving such pulse shapes, which may be of interest in coherent control experiments.

3.3.2 Characterization of Interpulse Phase

Shaped pulses that are well separated in time are used in many applications. For example, polarization controlled pulse trains with variable time delays are commonly used in two-dimensional optical spectroscopy [20, 21], and it is important to know their relative phases. For XFROG measurements, the relative interpulse phase of a two-pulse train is not retrieved in the XFROG traces for temporally well-separated electric fields unlike with self-referencing techniques. To obtain the interpulse phase relationship in our characterization technique, a spectrum which shows the interference fringes between two pulses that is temporally separated is needed to be analyzed. Here we present the method procedure of characterizing a two-pulse train with orthogonal polarization with an interpulse delay of 1.75 ps. The three DFG-XFROG traces of projections orientated at $\phi = 0^\circ$, 45° , and 90° are shown in Fig 3.5(a), while the retrieved intensities and phases are depicted in Fig. 3.5(b). As the second pulse shows a small amount of ellipticity, there is an ambiguity in handedness assignment as shown in the retrieved phase in Fig. 3.5(b). In Fig. 3.5(c), the spectrum of the projection at $\eta = 45^\circ$ obtained using a linear polarizer is depicted. The spectrum of an orthogonally polarized two-pulse train is needed to determine the interpulse phase. The fringes in the spectrum clearly show interference between the orthogonal components, and it corresponds to a delay of 1.75 ps, in agreement with the XFROG measurements. The contrast ratio of the fringes is limited by the spectrometer resolution. With a central wavelength of 363.1 nm as indicated in Fig. 3.5(c) the interpulse phase was determined to be $\varphi = 0$. The reconstructed electric field is shown in Fig. 3.4(c).

Double Pulse Train

Figure 3.5: Double Pulse Train: (a) DFG-XFROG traces for projections at 0° , 45° and 90° ; (b) Amplitude and phase $E_{UV,0x}(t)$ and $E_{UV,0y}(t)$ as retrieved by an XFROG retrieval algorithm; (c) UV spectrum at a projection of 45° ; (d) Reconstructed vector field.

3.3.3 Characterization of Handedness

In the characterization technique used in previous sections, there is an ambiguity in determining the handedness for circular or elliptical polarized pulses. In principle, there are several ways of determining the correct handedness. One method is to introduce opposing chirps in the orthogonal components so that the XFROG trace will be unique at 45° . This will result in only one distinct minimum in the XTURTLE retrieval algorithm, revealing the correct handedness. This method requires pulse shaping capabilities and is demonstrated by Xu *et al.* [13]. Another method is to use quarter-wave retardation plates to resolve the ambiguity and identify the correct handedness. For example, an additional quarter-wave retardation plate oriented at 45° transforms right circular polarization components into linear polarized light oriented at 0° (p polarization), while left circular polarization components are transformed into linear polarized light oriented at 90° (s polarization). With three XFROG measurements at projections of 0° , 45° and 90° , one can easily determine the handedness of the polarized state. We note that it is not important to set the quarter-wave retardation plate at 45° , as any other angles would work as long as the symmetry is broken in the initial projections. Hence this method is robust, simple and easy to implement in order to determine the handedness of the shaped pulses. We demonstrate the flexibility of this method by orientating the quarter-wave retardation plate at -22.5° .

In our demonstration, right-handed polarization is expected to enhance the XFROG intensity towards the 90° projection, whereas for left-handed polarization intensity enhancement towards the 0° projection is expected. In Fig. 3.6 we show the XFROG measurements for a simple circular polarized pulse orientated at $\phi = 0^\circ$, 45° , and 90° (see section 3.3.1.). Figure 3.6(a) shows the three projections of the XFROG traces without insertion of a quarter-wave retardation plate. As shown earlier in Fig. 3.3(c), there is an

ambiguity in assignment of the correct handedness as the error plot shows two minima. By introducing a quarter-wave retardation plate orientated at -22.5° , the XFROG traces shown in Fig. 3.6(b) reveal that the handedness of an initial shaped pulse has a right circular polarization. In general, this method of determining handedness is also applicable for more complex pulse shapes, such as alternating handedness within a pulse.

Figure 3.6: Determination of handedness: (a) DFG-XFROG traces for projections at 0° , 45° and 90° ; (b) DFG-XFROG traces for projections at 0° , 45° and 90° with an additional quarter-wave retardation plate.

3.4 Conclusion

In conclusion, DFG-XTURTLE enables a full vector-field characterization for ultraviolet pulses, which are not easily accessible with self-referenced techniques. It combines the new technique of TURTLE with the well established XFROG amplitude and phase retrieval algorithm. The ambiguities of interpulse phase and handedness can be easily overcome with additional measurements. Furthermore, characterization of mid-infrared pulses is possible by switching from a DFG to a SFG (sum-frequency generation) nonlinear optical process [22].

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Chapter 4

4 Phase Cycling Schemes for Pump-Probe Beam Geometry Two-Dimensional Electronic Spectroscopy

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In Chapter 2, we described how polarization pulse shaping in the ultraviolet wavelength can be performed, with the aim of implementing polarization control in two-dimensional optical spectroscopy. Prior to performing polarization control, here we will investigate the phase cycling schemes needed to obtain a two-dimensional spectrum in a pump-probe geometry with only a single polarization used for all excitation pulses. Two-dimensional electronic spectroscopy (2DES) has been used to study electronic couplings in chromophores and to observe energy transfers in light-harvesting complexes [1-3]. 2DES is a four-wave-mixing process, where three pulses with controllable interpulse delays interact with the sample, after which an emitted nonlinear optical signal is then detected. Fully non-collinear [4, 5], partially non-collinear [6-8], and collinear beam geometries have been previously adopted elsewhere to perform 2DES [9-11].

In a box-car geometry, three excitation pulses with separate beam paths interact with the sample, and the emitted signal is heterodyne-detected with a local oscillator in a phase-matched background-free detection. 2DES is a phase sensitive technique, as the excitation pulses travel over different beam paths, it is sometimes difficult to maintain a stable phase relationship, especially in the ultraviolet to visible wavelengths, where a difference of approximately 1 fs will change the relative phase by π radians or more. Therefore, care must be taken to phase the signal and to maintain interpulse phase stability [12, 13].

In a collinear phase coherent approach, the pulse phase dependent fourth-order population is measured, as opposed to third-order nonlinear polarization emitted from the non-collinear approach [9, 10]. The signal emitted is not background-free, and requires phase cycling to retrieve the desired signal. As fluorescence detection is used instead of absorption, this method is limited to samples which exhibit fluorescence.

2DES performed in a partially collinear or pump-probe beam geometry is a recent advancement, which promises a more compact and streamlined approach, compared to the conventional box-car beam geometry. This partially collinear geometry can overcome some problems faced by fully non-collinear and collinear approaches. The first two collinear excitation pulses are created by an optical pulse shaper, while the third excitation pulse interacts non-collinearly with the sample. As the emitted signal is in the same direction as the third excitation pulse, the third pulse acts also as a local oscillator that heterodyne-detects the signal. The delay and relative phase between two pulses can be controlled by pulse modulation with the pulse shaper. Data collection is performed in the rotating frame near the resonant frequency. This results in a slower modulating signal, and thus allows data to be sampled at smaller delay time step sizes [7, 14]. In order to optimize data collection for 2D spectroscopy done in a pump-probe geometry, phase

cycling is needed to retrieve the desired signal. The prime objective of this paper is to explain and demonstrate the efficacy of various phase cycling schemes that can be used in such experiments.

Phase cycling is an essential component for partially non-collinear or collinear geometry 2D spectroscopic experiments [9, 14, 15]. In phase cycling, the desired 2D signals can be retrieved by the weighted summation of data collected from using different interpulse phases, ϕ_{21} . Phase cycling can be easily implemented using a pulse shaper to select different pathways by systematically changing the relative interpulse phase, which is cycled over 2π radians in a number of equally spaced steps. In the pump-probe configuration, Myers *et al.* [6] have shown that other than the pure absorptive signal, the rephasing and non-rephasing contributions can also be retrieved. In their approach, the signal was collected in two separate scans with $\phi_{21} = 0$ and $\phi_{21} = \pi/2$, using either chopping or phase difference detection method. In the phase difference method, signals with $\phi_{21} = 0$ and $\phi_{21} = \pi$ are collected. The signals are subtracted from each other to remove the intense background pump-probe signal, while effectively doubling the duty-cycle and hence increasing the signal-to-noise ratio of the experiment. This phase difference detection can be defined as a two-step phase cycling scheme. For the phase difference detection, the Ogilvie group needs to collect signals with interpulse phases of $\phi_{21} = 0, \pi, \pi/2$ and $3\pi/2$. The same signal can be obtained with chopping, but only half as intense compared to the phase difference method. In the context of this chapter, what they have performed is similar to a four-step phase cycling scheme, where four sets of data need to be collected and linearly combined.

Here, we experimentally demonstrate both two- and three-step phase cycling schemes, denoted as 1×2 and 1×3 phase cycling schemes, respectively. We show that the results obtained using a four-step 1×4 phase cycling scheme can be obtained using a three-step

1×3 phase cycling scheme. This reduction in the phase cycling steps improves the potential efficiency of this form of 2D spectroscopy. We implemented phase cycling to isolate the pure absorptive signal with the minimum number of phase cycling steps required for a pump-probe geometry. Rephasing and non-rephasing signals from a 1×2 and 1×3 phase cycling schemes were also retrieved from the pure absorptive 2D spectrum, with further post-data processing that will be described in detail.

Section 4.1 outlines the theory of phase cycling and the explanation of how the various phase cycling schemes can recover the desired 2D spectra. Section 4.2 details the experimental setup used in this study and section 4.4 presents the experimental results and comparison with theory.

4.1 Theory

In a pump-probe beam geometry 2DES experiment (Fig. 4.1), the electric field can be expressed as:

$$\begin{aligned}
E(t) = & A_1(t + T_w + \tau) \exp(-i\omega_L t + i\phi_{21} + i\Delta\omega_{ref} \tau + i\mathbf{k}_{pump} r) \\
& + A_2(t + T_w) \exp(-i\omega_L t + i\mathbf{k}_{pump} r) \\
& + A_3(t) \exp(-i\omega_L t + i\mathbf{k}_{probe} r) + c.c.
\end{aligned} \tag{4.1}$$

where τ and $\phi_{21} = \phi_2 - \phi_1$ is the delay and relative phase between the first two excitation ‘pump’ pulses with pulse envelope A_1 and A_2 , respectively. A_3 is the pulse envelope of the ‘probe’ pulse. ω_L is the pulse center frequency of the laser, while $\Delta\omega_{ref}$ is the difference between the ‘rotating frame’ reference frequency ω_{ref} and ω_L . Usually when rotating frames are evoked, the laser center frequency serves as the reference frequency. In this case, we make a distinction between the laser frequency and the reference frequency.

The third-order nonlinear response function of a four-wave mixing experiment for a two-level system with a energy difference of $\hbar\omega_{10}$ can be expressed as:

$$R_R(\tau, t) = \Theta(\tau)\Theta(t)\exp(i\omega_{10}\tau)\exp(-i\omega_{10}t)F_R(\tau, t) \quad (4.2)$$

$$R_{NR}(\tau, t) = \Theta(\tau)\Theta(t)\exp(-i\omega_{10}\tau)\exp(-i\omega_{10}t)F_{NR}(\tau, t) \quad (4.3)$$

where R_R and R_{NR} are the rephasing and non-rephasing response functions, respectively. Θ is the Heavyside step function, ω_{10} is the resonant frequency of the two-level system, and F is the peak shape function that contains the dephasing, population decay details of the system [16].

Figure 4.1: Schematic diagram of a 2D spectroscopy experiment in a pump-probe beam geometry.

If we assume that the pulses are impulsive Dirac delta functions, the frequency resolved measurement after a spectrometer with a square-law detector can be described as:

$$\begin{aligned}
\tilde{S}(\phi_{21}; \tau, \omega_t) &= \Re e \left[F_R(\tau, \omega_t - \omega_{10}) \exp(i\Delta\omega_{10}\tau) \exp(i\phi_{21}) \right. \\
&\quad \left. + F_{NR}(\tau, \omega_t - \omega_{10}) \exp(-i\Delta\omega_{10}\tau) \exp(-i\phi_{21}) + P \right] \\
&= F_R(\tau, \omega_t - \omega_{10}) \exp(i\Delta\omega_{10}\tau) \exp(i\phi_{21}) \\
&\quad + F_{NR}^*(\tau, \omega_t - \omega_{10}) \exp(i\Delta\omega_{10}\tau) \exp(i\phi_{21}) \\
&\quad + F_R^*(\tau, \omega_t - \omega_{10}) \exp(-i\Delta\omega_{10}\tau) \exp(-i\phi_{21}) \\
&\quad + F_{NR}(\tau, \omega_t - \omega_{10}) \exp(-i\Delta\omega_{10}\tau) \exp(-i\phi_{21}) + P
\end{aligned} \tag{4.4}$$

where $\Delta\omega_{10} = \omega_{10} - \omega_{ref}$ is the resonance frequency detuned from the reference frequency ω_{ref} . $F_R(\tau, \omega_t - \omega_{10})$ and $F_{NR}(\tau, \omega_t - \omega_{10})$ are the Fourier transforms about t of $F_R(\tau, t)$ and $F_{NR}(\tau, t)$ from Eq. (4.2) and Eq. (4.3), respectively. The last term P contains all signals that are not dependent on ϕ_{21} . P usually dominates any set of data taken as they include the pump-probe signals from individual pulses and linear absorption contributions.

The oscillations of the signal over τ , at $\Delta\omega_{10}$ frequency, effectively place the data acquisition in the rotating frame of frequency ω_{ref} . Capturing data in the rotating frame permits under-sampling, which decreases the data acquisition time. By detuning the reference frequency away from the absorption frequency, the period of the signal's oscillation corresponds to the difference between the absorption and reference frequency [7, 9].

Due to the measurement of only the real part of the combined rephasing and non-rephasing signals, we can only obtain pure absorptive peak shapes. Ogilvie and co-worker demonstrated a procedure to separately obtain rephasing and non-rephasing signal [6]. This is done by a data processing procedure that subjects the data of Eq. (4.4) to the causality condition. The resultant processed data give:

$$\tilde{S}'(\phi_{21}; \tau, \omega_t) = \left[F_R(\tau, \omega_t - \omega_{10}) \exp(i\Delta\omega_{10}\tau) \exp(i\phi_{21}) \right. \\
\left. + F_{NR}(\tau, \omega_t - \omega_{10}) \exp(-i\Delta\omega_{10}\tau) \exp(-i\phi_{21}) + P \right] \tag{4.5}$$

Briefly, this data processing is done by first performing inverse Fourier transform about ω_t of Eq. (4.4) to give:

$$\begin{aligned}
\tilde{S}(\phi_{21}; \tau, t) = & \Theta(\tau)\Theta(t)\exp(i\Delta\omega_0\tau)\exp(-i\omega_0t)\exp(i\phi_{21})F_R(\tau, t) \\
& + \Theta(\tau)\Theta(-t)\exp(-i\Delta\omega_0\tau)\exp(-i\omega_0t)\exp(-i\phi_{21})F_R^*(\tau, -t) \\
& + \Theta(\tau)\Theta(t)\exp(-i\Delta\omega_0\tau)\exp(-i\omega_0t)\exp(-i\phi_{21})F_{NR}(\tau, t) \\
& + \Theta(\tau)\Theta(-t)\exp(i\Delta\omega_0\tau)\exp(-i\omega_0t)\exp(i\phi_{21})F_{NR}^*(\tau, -t) \\
& + \tilde{P}
\end{aligned} \tag{4.6}$$

Causality dictates that there be no signal before $t = 0$. We therefore discard the terms that contain $\Theta(-t)$ in Eq. (4.6). Upon Fourier transforming about t , we obtain Eq. (4.5).

We shall henceforth term Eq. (4.4) and Eq. (4.5) as the non-causality imposed and causality imposed signals, respectively. Both Eq. (4.4) and Eq. (4.5) contain numerous terms. Useful 2D spectra signals, such as the pure absorptive, rephasing or non-rephasing signals can only be separated by using phase cycling schemes.

The theory of phase cycling and phase cycling scheme selection has been presented in our previous papers [14, 15]. Briefly, a 2D spectrum measured as a function of interpulse phase ϕ_{21} contains a summation of signals from different processes that are weighted with different interpulse phase terms $\exp(i\beta\phi_{21})$:

$$S(\phi_{21}) = \sum_{\beta} s_{\beta} \exp(i\beta\phi_{21}) \tag{4.7}$$

where β is an integer. For the different terms in Eq. (4.7), β is decided by how the light field interacts with the system and can be determined from the double sided Feynman diagrams that describes different processes [14]. For example, the rephasing and non-rephasing signal terms have $\beta = 1$ and $\beta = -1$, respectively.

Eq. (4.4) and Eq. (4.5) are examples of such series described in Eq. (4.7). In order to obtain a specific term $s(\beta)$ from the summation series in Eq. (4.7), experiments need to be repeated to obtain $S(\phi_{21})$ at different ϕ_{21} . They can then be linearly combined according to the following equation that describes a $1 \times L$ phase cycling scheme:

$$s_{1 \times L}(\beta) = \frac{1}{L} \sum_{l=0}^{L-1} S(l \cdot \Delta\phi_{21}) \exp(-il\beta \cdot \Delta\phi_{21}) \quad (4.8)$$

where $s_{1 \times L}(\beta)$ is the signal obtained from the $1 \times L$ phase cycling scheme. After the summation of the signal, the data is Fourier transformed about τ to yield a 2D spectrum. L is the size of the phase cycling scheme and hence determines the number of experiments that needs to be performed. The aim of the phase cycling scheme selection procedure is to be able to obtain the desired signal with the smallest value of L without aliasing. We shall present below the different kinds of phase cycling schemes and the theoretical outcome.

4.1.1 1×2 Phase Cycling Scheme

For a 1×2 phase cycling scheme, the relative interpulse phase is cycled through $\phi_{21} = 0$ and π radians. In targeting to acquire signal $s(\beta = 1)$ (the term that comes with a $\exp(i\phi_{21})$ term attached), the data are linearly combined, according to Eq. (4.8):

$$s_{1 \times 2}(\beta = 1) \propto S(\phi_{21} = 0) + S(\phi_{21} = \pi) \exp(-i\pi) \quad (4.9)$$

Applying to the case of non-causality imposed signal of Eq. (4.4), all the terms are retained, except for the background P term. The 1×2 phase cycling scheme cannot discriminate between terms weighted with $\exp(i\phi_{21})$ and $\exp(-i\phi_{21})$ due to aliasing [14]. Upon Fourier Transform about τ , the resultant real part of the 2D spectrum consist of two pure absorptive peaks at $(\omega_\tau, \omega_t) = (-\Delta\omega_{10}, \omega_{10})$, and $(\omega_\tau, \omega_t) = (\Delta\omega_{10}, \omega_{10})$, respectively. These two pure absorptive peaks are mirror images of each other about the $\omega_\tau = 0$ axis. This is because the Fourier transform of a real function in the time domain will result in the signal and its aliased part in the positive and negative frequency domain, respectively.

For the case of the causality imposed signal of Eq. (4.5), similarly, only the background P term is discarded. After Fourier transformation about τ , we obtain the rephasing signal in the negative frequency $(\omega_\tau, \omega_t) = (-\Delta\omega_{10}, \omega_{10})$, while the non-rephasing signal appears in the positive frequency $(\omega_\tau, \omega_t) = (\Delta\omega_{10}, \omega_{10})$, as shown in Eq. (4.10):

$$\tilde{s}_{1 \times 2}^C(\beta=1)(\omega_\tau, \omega_t) = \tilde{F}_R(\omega_\tau + \Delta\omega_{10}, \omega_t - \omega_{10}) + \tilde{F}_{NR}(\omega_\tau - \Delta\omega_{10}, \omega_t - \omega_{10}) \quad (4.10).$$

The rephasing and non-rephasing signals are separated on the 2D spectra by $2\Delta\omega_{10}$ in the ω_τ axis. For both the non-causality imposed and the causality imposed 2D spectra, by detuning the reference frequency nearer to the absorption frequency, the two peaks on the opposing side of the ω_τ axis will move closer to $\omega_\tau = 0$. In the event where the reference frequency is set near or equal to the absorption frequency, it might be difficult to discriminate the actual signal from the aliased signal. To avoid such ambiguities, a 1×3 phase cycling scheme is necessary.

4.1.2 1×3 Phase Cycling Scheme

For a 1×3 phase cycling scheme, experiments are repeated with the relative interpulse phase cycled through $\phi_{21} = 0, 2\pi/3$ and $4\pi/3$ radians. The phase cycling scheme to acquire signal $s(\beta=1)$ and $s(\beta=-1)$ are respectively:

$$\begin{aligned} s_{1 \times 3}(\beta=1) \propto & S(\phi_{21}=0) \\ & + S(\phi_{21}=2\pi/3)\exp(-i2\pi/3) \\ & + S(\phi_{21}=4\pi/3)\exp(-i4\pi/3) \end{aligned} \quad (4.11a)$$

and

$$\begin{aligned}
s_{1 \times 3}(\beta = -1) \propto & S(\varphi_{21} = 0) \\
& + S(\varphi_{21} = 2\pi/3) \exp(i2\pi/3) \\
& + S(\varphi_{21} = 4\pi/3) \exp(i4\pi/3)
\end{aligned} \tag{4.11b}.$$

For the non-causality imposed signal, to acquire signal $s(\beta = -1)$, the weighted summation of the detected signal of Eq. (4.11a) selects the terms $F_R^*(\tau, \omega_t - \omega_{10}) \exp(-i\Delta\omega_{10}\tau) + F_{NR}(\tau, \omega_t - \omega_{10}) \exp(-i\Delta\omega_{10}\tau)$ from Eq. (4.4). Upon Fourier transform about τ , we have the 2D spectrum for the non-causality imposed signal $\tilde{s}_{1 \times 3}^{NC}(\beta = -1)$ as:

$$\tilde{s}_{1 \times 3}^{NC}(\beta = -1)(\omega_\tau, \omega_t) = \tilde{F}_R^*(\omega_\tau - \Delta\omega_{10}, \omega_t - \omega_{10}) + \tilde{F}_{NR}(\omega_\tau - \Delta\omega_{10}, \omega_t - \omega_{10}) \tag{4.12}.$$

The real part of Eq. (4.12) gives a pure absorptive peak that appears at $(\omega_\tau, \omega_t) = (\Delta\omega_{10}, \omega_{10})$. The extra mirror image peak ambiguity of the 1×2 phase cycling scheme discussed earlier is no longer present.

When the 1×3 phase cycling scheme is applied to the causality imposed signals (Eq. (5)), the rephasing or the non-rephasing signal can be individually obtained. Eq (4.11a) retrieves the rephasing signal $F_R(\tau, \omega_t - \omega_{10}) \exp(i\Delta\omega_{10}\tau)$, while Eq (4.11b) retrieves the non-rephasing signal $F_{NR}(\tau, \omega_t - \omega_{10}) \exp(-i\Delta\omega_{10}\tau)$. After Fourier transform with respect to τ , the rephasing and non-rephasing 2D spectrums are obtained, respectively. The 2D rephasing signal:

$$\tilde{s}_{1 \times 3}^C(\beta = 1)(\omega_\tau, \omega_t) = \tilde{F}_R(\omega_t + \Delta\omega_{10}, \omega_t - \omega_{10}) \tag{4.13a}$$

appears in the negative half of the 2D spectrum centered at $(\omega_\tau, \omega_t) = (-\Delta\omega_{10}, \omega_{10})$, while the non-rephasing signal:

$$\tilde{s}_{1 \times 3}^C(\beta = -1)(\omega_\tau, \omega_t) = \tilde{F}_{NR}(\omega_t - \Delta\omega_{10}, \omega_t - \omega_{10}) \tag{4.13b}$$

appears in the positive half of the spectrum centered at $(\omega_\tau, \omega_l) = (\Delta\omega_{10}, \omega_{10})$. To obtain the pure absorptive signal, the mirror image of the rephasing spectrum can be taken across the $\omega_\tau = 0$ axis to the positive half of the frequency axis. This mirror image rephasing spectrum is then summed with the non-rephasing spectrum of Eq. (4.13b). The real part of this summation will be the pure absorptive peak and is identical to the real part of Eq. (4.12).

4.1.3 1×4 Phase Cycling Scheme

Although a 1×3 phase cycling scheme suffices to obtain all the desired signals without ambiguity, for completeness, we include here the description for a 1×4 phase cycling scheme as well. In a 1×4 phase cycling scheme, the relative interpulse phase is cycled through $\phi_{21} = 0, \pi/2, \pi$ and $3\pi/2$. For the causality imposed case, to recover the rephasing signal, the phase cycling scheme used is:

$$s_{1 \times 4}(\beta = 1) \propto S(\phi_{21} = 0) + S(\phi_{21} = \pi/2)\exp(-i\pi/2) + S(\phi_{21} = \pi)\exp(-i\pi) + S(\phi_{21} = 3\pi/2)\exp(-i3\pi/2) \quad (4.14a)$$

while to recover the non-rephasing signal, the phase cycling scheme is:

$$s_{1 \times 4}(\beta = -1) \propto S(\phi_{21} = 0) + S(\phi_{21} = \pi/2)\exp(i\pi/2) + S(\phi_{21} = \pi)\exp(i\pi) + S(\phi_{21} = 3\pi/2)\exp(i3\pi/2) \quad (4.14b)$$

The acquired signals of Eq. (4.14a) and Eq. (4.14b) are identical to that obtained by the 1×3 phase cycling schemes stated in Eq. (4.11a) and Eq. (4.11b).

4.2 Experimental

Chlorophyll *a* (Chl *a*) was purchased from Sigma Aldrich as dried sample and dissolved in methanol. The absorption spectrum of Chl *a* in methanol is shown in Fig. 4.2. The absorption band of interest is the Q_y transition at 665nm. The sample solution was placed between two calcium fluoride windows separated by a 500 μm teflon spacer and it has an optical density of 0.06 at the Q_y band.

Figure 4.2: Absorption spectrum of chlorophyll *a* in methanol. The Q_y band is centered at 665 nm.

Our experimental setup is described as follows. The schematic diagram of the experimental setup is shown in Fig. 4.3. The regenerative amplifier (Legend Elite, Coherent) produces pulses having a wavelength of 800 nm, a full width at half maximum

(FWHM) of 40 fs, an energy of 4 mJ per pulse and a repetition rate of 1 kHz. A beam splitter diverts 800 mW of the amplified beam to pump a home-built two-stage optical parametric amplification system in the near infrared region, which is subsequently frequency doubled to generate the pump beam. The laser pulse was tuned to a center wavelength of 665 nm to coincide with the Q_y transition of the Chl *a* molecule. A small part of the amplified beam is focused by a 50 mm lens into a 2 mm sapphire window (Newport) to create a whitelight continuum probe beam. The whitelight continuum is partially compressed by a SF10 prism pair (CVI Melles Griot). The pump beam is sent to an acousto-optic programmable dispersive filter pulse shaper (Dazzler, Fastlite) to generate the first and second excitation pulses with variable delay τ and relative phase ϕ_{21} , as well as compression. After pulse shaping, the pulse train has a FWHM of 56 fs (1.2 times transform limited) from an intensity autocorrelation trace. The crossing angle between the pump and probe is $\sim 4^\circ$. The pulse energy of the pump and probe are 500 nJ and 180 nJ, respectively. The pump beam is focused into the sample cell with a 400 mm planar convex lens to a spot size of 100 μm , while the probe beam is focused into the sample cell with a 500 mm planar convex lens to a spot size of 70 μm . The white light probe beam is then collimated with a 200 mm planar convex lens and sent into a spectrometer.

Figure 4.3: Schematic diagram of the experimental setup for a 2D spectrometer in a pulse shaper assisted pump-probe geometry. The pulse shaper (Dazzler, Fastlite) provides the first two excitation pump pulses by shaping the 665 nm light from the OPA, after which is focussed with a lens (L2) into the sample cell with a spot size of 100 μm . The third interaction is from the whitelight continuum probe light, generated by focussing the 800 nm from the chirp pulse amplifier (Legend Elite, Coherent) using the lens (L1) into the sapphire crystal (S1), and collimating it using a second lens (L1). After delaying across the mechanical translation stage (T1), the whitelight is focussed into the sample cell using a concave mirror (CCM1), with a spot size of 70 μm . Part of the whitelight continuum is used as a reference light instead, using a beam splitter (BS1), to eliminate intensity fluctuation in the probe light. The signal generated is then collimated with the probe light with a lens (L3) and heterodyne-detected and frequency-resolved with a spectrometer (Acton SP2300, PIXIS 100B, Princeton Instruments). During data collection, the whitelight is chopped with an optical chopper (C1) at a rate of 500 Hz to remove the scattered pump light from the sample cell.

A spectrometer (Acton SP2300) is used to frequency resolve the probe signal which is detected by a CCD camera (PIXIS 100B) at 1 kHz. The signal detected is normalized to a reference beam that is taken from the compressed whitelight continuum. To remove scattered light from the 2D spectrum, an optical chopper is placed before the sapphire crystal, chopping the 800 nm used in whitelight generation at a rate of 500 Hz.

To perform phase cycling, the pump pulse is modulated by the pulse shaper according to $E(\omega)\{1+\exp[i(\omega\tau-\omega_{ref}\tau+\phi_{21})]\}$ to create the first two excitation pulses, where $E(\omega)$ is the spectral amplitude of the pulse, ω_{ref} is the reference frequency, τ is the interpulse delay, and ϕ_{21} is the relative phase between the first two pulses. The majority of the presented data are collected in a rotating frame with the reference wavelength set at 760 nm. The resultant effective $\Delta\omega$ is 57 THz. The delay τ is increased with a step size of 3 fs for over 180 fs, below the Nyquist limit of 8 fs. The relative phase ϕ_{21} is cycled for every increment of τ . For a 1×2 phase cycling scheme, the relative phase is shifted between 0 and π . For a 1×3 scheme, the relative phase is cycled over 0, $2\pi/3$, and $4\pi/3$. The waiting time T_w for all the experiments was set at 1 ps.

4.2.1 Data Acquisition

The experimental data was collected in the following manner. The pulse shaper and optical chopper are triggered by a 1 kHz repetition source from the laser. The pulse shaper has two trigger outputs, TRG1 and TRG2, and the former is connected to the CCD camera, while the latter is connected to a data acquisition integrator (NI-DAQ). The mask in the pulse shaper changes at a rate of 1 kHz, and for every change in the loaded mask in the pulse shaper, a trigger is generated out from TRG1. As the masks are continuously cycled in a loop and the start of data collection is from random point in the cycle, it is important to know the sequence of the signals being collected. As such, a trigger signal was sent from TRG2 into the integrator at every start of the first mask, and the signals collected were rearranged accordingly to the corresponding mask sequence.

The loading of the masks needed for a 1×3 phase cycling scheme are as follows. The phases of the first pulse were cycled for every increment of delay τ . With a step size of 3 fs over a coherence time period taken for 180 fs, in principle 183 masks are needed to

obtain a 2D spectrum. However, scattered light would also be captured together with the signal which would appear in the 2D spectrum as a thin diagonal peak in the same position as the fundamental 2D peak. It is therefore imperative to subtract scattered light intensity from the collected signal. To overcome this problem, every mask was loaded twice into the Dazzler pulse shaping program, and a spectrum is taken with and without the whitelight continuum at a collection rate of 1 kHz by chopping the probe beam at 500 Hz. By difference between intensity of the data collected with and without the probe beam would result in the uncontaminated signal.

4.3 Results and Discussions

To demonstrate the validity of the phase cycling schemes outlined in section 4.1, we present the experimental 2DES spectra of the Q_y transition of Chl *a* molecule here.

Figure 4.4 depicts the 2DES spectra of different phase cycling schemes on non-causality imposed data to recover 2D spectra pure absorptive peak shapes.

In Fig. 4.4(a), we show a 2D spectrum without any phase cycling. The 2D spectrum is dominated by an intense peak at $\Delta\omega_\tau = 0$, which is predominantly due to the term P from Eq. (4.4) that is independent of the interpulse phase ϕ_{21} .

Figure 4.4: 2D spectra after implementation of various phase cycling schemes. (a) A 2D spectrum without any phase cycling. (b) 1×2 phase-cycled 2D spectrum with reference wavelength at 700 nm. (c) 1×2 phase-cycled 2D spectrum with reference wavelength at 760 nm. (d) 1×3 phase-cycled 2D spectrum with reference frequency at 760 nm.

Figure 4.4(b) depicts the real part of the 2D spectrum from a 1×2 phase cycling scheme obtained using Eq. (4.9). Here, the reference wavelength is set at 700 nm ($\Delta\omega_\tau = 22$ THz). This phase cycling scheme eliminates the ϕ_{21} -independent signal. Due to the aliasing as explained in section 4.2, a pair of identical absorptive peaks are observed on opposite sides of the $\Delta\omega_\tau = 0$ axis.

Figure 4.4(c) depicts another 2D spectrum from a 1×2 phase cycling scheme. This 2D spectrum is similar to that portrayed in Fig. 4.4(b) except that the reference wavelength is set at 760 nm ($\Delta\omega_\tau = 57$ THz). As compared to Fig 4.4(b), the peak shapes are similar, but the aliased peaks are further apart. Figs. 4.4(b) and 4.4(c) demonstrate that the reference frequencies can be adjusted to achieve undersampling in a rotating frame. In situations where the signal and the aliased counterpart overlap with each other, such as in extremely broad or congested spectra, we will need to perform a 1×3 phase cycling scheme instead to avoid any ambiguities.

Figure 4.4(d) depicts a 2D spectrum with a 1×3 phase cycling scheme described by Eq. (4.12). This phase cycling scheme removes the background signal P as well as the aliased signal. The real part of the spectrum yields the desired 2D pure absorptive peak, as depicted in the figure. The peak shape is similar to what is obtained from a 1×2 phase cycling scheme.

In Fig. 4.5, we present 2D spectra with causality imposed with the procedures outlined in section 4.1.

Figure 4.5: (a) 2D spectrum with the rephasing and non-rephasing signals retrieved from the 1×2 phase cycling scheme. The peak at the top is the non-rephasing signal while the peak at the bottom is the rephasing signal. (b) 2D spectrum with the rephasing signal retrieved from a 1×3 phase cycling scheme. (c) 2D spectrum with the non-rephasing signal retrieved from a 1×3 phase cycling scheme. (d) Sum of the non-rephasing and the mirror image of the rephasing 2D spectra retrieved from a 1×3 phase cycling scheme. The intensity of the pure absorptive spectrum presented here is half of the actual intensity. The peak shape is similar to the pure absorptive peak shape of Fig. 4.4(d).

Figure 4.5(a) depicts the real part of the 2D spectrum obtained from the 1×2 phase cycling scheme on a causality imposed signal. The scheme retrieves both the rephasing and non-rephasing signals in the same 2D spectrum. As stated in Eq. (4.10), the rephasing and non-rephasing signal are in the negative half and the positive half of the ω_t frequency axis, respectively. The rephasing signal is more intense and has a smaller linewidth than

the non-rephasing signal, as is consistent with a linear line shape that is inhomogeneously broadened.

In Figs. 4.5(b) and 4.5(c), 2D spectra of rephasing and non-rephasing signals obtained with a 1×3 phase cycling scheme, respectively are presented. Figure 4.5(b) is the real part of the 2D spectrum obtained using Eq. (4.13a) that selects only the rephasing signal. Figure 4.5(c) is the real part of the 2D spectrum obtained using Eq. (4.13b) that selects only the non-rephasing signal. As can be seen by comparing Fig. 4.5(a) with Figs. 4.5(b) and 4.5(c), the retrieved rephasing and non-rephasing signal peak shapes for both the 1×2 and 1×3 phase cycling schemes are similar. The mirror image of Fig. 4.5(b) is obtained about the $\Delta\omega_\tau = 0$ axis. This resultant mirror image is then summed with the non-rephasing signal (Fig. 4.5(b)) to yield the pure absorptive signal. This summation is depicted in Fig. 4.5(d). The resultant peak shape is similar to the peak shape in Fig. 4.5(d), thus agreeing with the methodology of retrieving the rephasing and non-rephasing spectra for a 1×2 and 1×3 phase cycling scheme stated in the previous section.

Ogilvie and co-workers have shown that both the rephasing and non-rephasing signals can be retrieved by collecting two separate sets of 2D spectra with $\phi_{21} = 0$ and $\phi_{21} = \pi/2$ by using either chopping or phase subtraction method [6]. In the phase subtraction method, an additional set of data at $\phi_{21} = \pi$ (and at $\phi_{21} = 3\pi/2$) are also collected and subtracted from the $\phi_{21} = 0$ signal (and from $\phi_{21} = \pi$ signal). This removes the non-interpulse phase dependent P signal. These two sets of phase subtracted signals are then summed to give the rephasing and non-rephasing signals

$$s_R \propto (S(\phi_{21} = 0) - S(\phi_{21} = \pi)) + i(S(\phi_{21} = \pi/2) - S(\phi_{21} = 3\pi/2)) \quad (4.15a)$$

$$s_{NR} \propto (S(\phi_{21} = 0) - S(\phi_{21} = \pi)) - i(S(\phi_{21} = \pi/2) - S(\phi_{21} = 3\pi/2)) \quad (4.15b).$$

Equations (4.15a) and (4.15b) are equivalent to a 1×4 phase cycling scheme described in the last part of the preceding section in Eqs. (4.14a) and (4.14b), respectively. Since a 1×3 phase cycling scheme obtains the same data as a 1×4 phase cycling scheme, it is more efficient to use a 1×3 phase cycling scheme instead. The flowchart in Fig. 4.6 summarizes the procedures that one can take to obtain the rephasing, non-rephasing and pure absorptive spectrum with a 1×3 phase cycling scheme. The blue arrows in Fig. 4.6 indicate the operations needed to be performed on the collected data set to retrieve the rephasing and non-rephasing spectrum. The pure absorptive spectrum can then be achieved by the sum of the rephasing and non-rephasing spectra. The purple arrows describe the operation if only the pure absorptive spectrum is needed. Following the purple arrows, it does not matter if you choose to acquire terms with the $\exp(-i\phi_{21})$ or $\exp(i\phi_{21})$ phase terms, as the same 2D signal will appear either in the positive or negative ω_τ frequency, respectively. Usually, we choose the term with $\exp(-i\phi_{21})$ as that corresponds to obtaining the pure absorptive peak shape in the positive ω_τ frequency half of the 2D spectrum.

Figure 4.6: Summary of the procedures to obtain the rephasing, non-rephasing and pure absorptive spectrum in a 1x3 phase cycling scheme.

4.4 Conclusion

We have presented experimental 1x2 and 1x3 phase cycling schemes on chlorophyll *a* using a pump-probe geometry. The pure absorptive signal is retrieved from both sets of experiment, without any background pump-probe signal. For the 1x3 phase cycling scheme, we are able to remove the aliased signal that is present in the 1x2 phase cycling scheme. We have also presented the theory and experimental approach for retrieving the rephasing and non-rephasing signals in both the 1x2 and 1x3 phase cycling schemes. We have shown that a 1x3 phase cycling scheme obtains the same signals compared to a 1x4 phase cycling scheme. In a partial rotating frame, a 1x2 phase cycling scheme can

retrieve the rephasing and non-rephasing signals in a single 2D spectrum. However, this may lead to peak assignment ambiguities when the spectrum is congested.

Decreasing the number of phase cycling steps reduces the amount of experimental data sets needed for a 2D spectrum. The implementation of the phase cycling schemes presented in this article is simple and it will be beneficial for research groups performing 2D optical spectroscopy. With a good theoretical understanding of the principle of phase cycling, phase cycling schemes in coherent 2D optical spectroscopy can be extended to higher-order nonlinear optical spectroscopy. This involves the consideration of an increase in the number of response functions that can be measured with more optical pulses. In the next chapter, we will derive and experimentally demonstrate the selection procedures of phase cycling schemes for coherent 3D optical spectroscopy in a pump-probe geometry [17].

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Chapter 5

5 Fifth-Order Three-Dimensional

Electronic Spectroscopy Using a Pump-Probe Configuration

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In chapter 4, the phase cycling scheme for two-dimensional (2D) optical spectroscopy [1-6] in a pump-probe geometry has been well-described. It is noted that phase cycling is not only limited to third-order 2D optical spectroscopy, but it can also be applied to higher-order nonlinear optical experiments such as fifth-order three-dimensional (3D) optical spectroscopy [7-9], which has gained interest over the past few years. The extension of the well-established third-order 2D optical spectroscopies to fifth-order 3D optical spectroscopies brings several new observables to the spectroscopist inaccessible in lower-order spectroscopies. This includes the ability to reach higher vibronic states to better characterize the anharmonicity of the investigated systems [7, 10-12]. 3D spectroscopy also allows higher spectral resolution and declutters congested spectra, by introducing a third frequency axis [12]. In 3D electronic spectroscopy, hidden couplings that were previously obscured in a congested 2D electronic spectrum can now be retrieved [8]. 2D

electronic spectroscopy has been applied to studying energy transfers between excitonic states in light-harvesting complexes [13]. These processes are highly complicated and consist of multiple steps. 2D electronic spectroscopy can only directly observe single step energy transfers and indirectly infer multiple step energy transfer [14]. 3D spectroscopy has the potential to provide direct measurements of multiple step energy transfer between these multilevel electronic systems. A recent topic of debate is the validity of commonly made assumptions, such as linear response theory, Gaussian statistics, and Markovian processes. As shown, 3D spectroscopies can help answer these questions by studying the three-point correlation function [15, 16]. Recent work on liquid water unequivocally showed its heterogeneous structural relaxation dynamics [9]. From these examples alone, it is clear that fifth-order 3D spectroscopy will be of benefit for the optical spectroscopist and the extension to higher dimensions is expected to become even more pertinent with further advances in ultrafast laser technologies.

Figure 5.1(a) shows the fundamental idea of fifth-order 3D optical spectroscopy. The three coherence time periods t_1 , t_3 and t_5 are Fourier transformed to measure the instantaneous frequencies ω_1 , ω_3 and ω_5 , respectively, at waiting times t_2 and t_4 . Third-order 3D optical experiments have also been performed recently [17-19] where an extra frequency dimension can be obtained from a conventional third-order 2D optical spectroscopy experiment by Fourier transforming over the waiting time period. Unlike third-order 3D spectroscopy, which arises from three interactions with the light field, fifth-order 3D spectroscopy requires five interactions with the incoming light field. Fifth-order 3D spectroscopy in its conventional phase-matching implementation requires in its most general case six individual pulses (including a local oscillator pulse) [7]. The intricate optical setup hampers the applicability of 3D spectroscopy, even more so than 2D spectroscopy.

Figure 5.1. (a) Schematic setup for fifth-order 3D optical spectroscopy in a pump-probe geometry. The coherence times t_1 and t_3 , the waiting time t_2 as well as the phases ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 are set by a pulse shaping apparatus, while the second waiting time t_4 is introduced by a delay stage. (b) Double-sided Feynman diagrams (DSFD) for fifth-order 3D spectroscopy on a two-level system in a pump-probe geometry contributing to the desired three-dimensional spectrum with populations during the waiting times. The resulting $\mathbf{k}_{\text{signal}}$ vector as well as the acquired phase ϕ_{signal} and phase signatures are denoted. (c) A brief selection of the multitude of DSFDs for undesired processes that can be eliminated by phase cycling. From left to right, these are pump-probe processes where the first pulse interacts twice, the second pulse interacts twice, or both pulses interact twice. Lower-order processes such as those shown on the far right need to be discriminated as well. Their acquired phase and phase signature are denoted where applicable.

A limited form of fifth-order 3D spectroscopy can be performed using only four pulses (including the local oscillator) as shown in Zanni's work in the infrared [12] and Engel's work in the visible [8], where multiple interactions are made by the second and third pulses, to measure the fifth-order signal. This necessarily means that there is no control over the population times t_2 and t_4 , which will always be equal to zero. The other limitations of using two interactions each for pulses one and three in Zanni's work or pulses two and three in Engel's work to achieve five interactions is that purely absorptive

peaks [7, 9] cannot be obtained. With the advent of 2D spectroscopy performed in a pulse shaper assisted pump-probe configuration, the experimental technique is simplified [20-24]. One further major advantage of such a pulse shaper assisted setup is that it allows the immediate extension to three dimensions and higher-orders without the need of altering the optical setup. Recently, our group demonstrated a method to obtain purely absorptive fifth-order 3D electronic spectra based on a pulse shaper assisted pump-probe beam geometry setup [25]. In our 3D spectroscopy performed using a pump-probe configuration, the first four ‘pump’ pulses are provided collinearly by a pulse shaper, followed by subsequent interaction by a non-collinear probe pulse. In principle, the advantages of 2D spectroscopy in a pump-probe geometry apply to 3D spectroscopy as well, such as intrinsic phasing of various contributions to the overall response function and data collection in the rotating frame, which allows under-sampling [22, 23, 26, 27]. However, similar to the two-dimensional case [23, 27-30], to obtain three-dimensional spectra devoid of peak ambiguities and interferences from other spurious signals, phase cycling is essential. With phase cycling, the desired multidimensional signals can be retrieved by the weighted summation of data collected from using different interpulse phases. Phase cycling can be easily implemented using a pulse shaper by systematically changing the relative interpulse phases, which is cycled over 2π radians in a number of equally spaced steps [27, 28]. Chapter 4 and recent works [21-23] have shown that with the proper understanding of phase cycling theory and phase cycling scheme selection, two-dimensional spectra of desired Liouville pathways, such as rephasing and non-rephasing diagrams can be obtained. In this chapter, the concept of phase cycling is extended to apply to the various implementations of 3D optical spectroscopy in the pump-probe beam geometry. The next section describes a general theoretical framework to choose appropriate phase cycling procedures needed to obtain fifth-order 3D spectra. Section 5.2 presents the experimental procedures for phase cycling in 3D spectroscopy,

while in section 5.3 we report our results that are obtained from various phase cycling schemes. Section 5.4 outlines the possibility of cascaded third-order signals in the 3D spectrum from a pump-probe geometry setup. This chapter summarizes with a brief conclusion in section 5.5.

5.1 Theory

In the framework of diagrammatic time dependent perturbation theory, three-dimensional optical spectroscopy is a fifth-order nonlinear optical experiment where the system interacts five times with the incident light fields. Specifically, in the pump-probe beam geometry, the pump pulse light field interacts four times, while the fifth interaction is provided by the probe pulse. Phase matching conditions result in the induced fifth-order sample polarization, creating a signal light field that is emitted collinearly with the probe pulse, so that it is self-heterodyne detected and thus rendering an external local oscillator unnecessary. Since six light fields participate in the light-matter interaction it is also referred to as a six-wave mixing process (SWM).

A general scheme of a pump-probe geometry 3D optical experiment is shown in Fig. 5.1(a). The required phase-locked four pulse pump train can be readily provided by a pulse shaping apparatus [31], with individually controllable coherence times t_1 , and t_3 , and waiting time t_2 . Due to the limited temporal window of pulse shapers, there is a constraint on the achievable waiting time t_2 , but this constraint may not be crucial in many cases. For instance, Hamm showed that, to study the three-point frequency fluctuation correlation functions, waiting times up to 3 ps are sufficient [15]. Such time delays pose no problem to current pulse shaping technology. All four pump pulses are incident along the wave vector $\mathbf{k}_{pump}$ and have the individual phases ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 , respectively. The probe pulse is delayed by a second waiting time t_4 from the last pump

pulse interaction via a translation stage and is incident onto the sample in the $\mathbf{k}_{probe}$ direction. The signal is emitted with the time delay t_5 . Phase matching conditions make sure that the desired signal field is emitted along the direction of the probe pulse $\mathbf{k}_{probe} = \mathbf{k}_{signal}$, so that the probe pulse intrinsically acts as a local oscillator to self-heterodyne the signal field. We do not take into consideration the phase relationship between the pump and probe pulses, as they interact non-collinearly [15]. In section 5.1.1, we will discuss the phase cycling schemes for such four pump pulse experiments.

As there has been growing interest to use the rephasing and non-rephasing spectra to observe energy transfers within light-harvesting complexes in 2D spectroscopy [14, 32, 33], groups have previously proposed ways to retrieve signals from the rephasing and non-rephasing processes in a pump-probe beam geometry setup [21, 23]. Similarly, we can independently retrieve signals from the four different pathways that contribute to the pure absorptive 3D spectrum in a pump-probe beam geometry setup, which we will discuss in section 5.1.2.

5.1.1 Purely Absorptive 3D Spectra Using Four Pump Pulses in a Pump-Probe Geometry

The pulse train incident on the sample in a 3D pump-probe experiment in a pump-probe geometry can be expressed in the time domain as:

$$\begin{aligned}
E(t) = & E_1(t + t_4 + t_3 + t_2 + t_1) \exp(-i\omega_L t + i\phi_1 + i\Delta\omega_{ref}t_1 + i\mathbf{k}_{pump}r) \\
& + E_2(t + t_4 + t_3 + t_2) \exp(-i\omega_L t + i\phi_2 + i\Delta\omega_{ref}t_2 + i\mathbf{k}_{pump}r) \\
& + E_3(t + t_4 + t_3) \exp(-i\omega_L t + i\phi_3 + i\Delta\omega_{ref}t_3 + i\mathbf{k}_{pump}r) \\
& + E_4(t + t_4) \exp(-i\omega_L t + i\phi_4 + i\mathbf{k}_{pump}r) \\
& + E_5(t) \exp(-i\omega_L t + i\mathbf{k}_{probe}r) + c.c.
\end{aligned} \tag{5.1}$$

where E_1 to E_5 denote the individual pulse envelopes and ω_L is the pulse center frequency, while $\Delta\omega_{ref}$ is the difference between the pulse center frequency ω_L and a

reference frequency ω_{ref} set by the pulse shaper. In a “rotating frame”, $\Delta\omega_{ref} = \omega_L - \omega_{ref} = 0$ [22, 23]. The macroscopic signal field $S(t_1, t_2, t_3, t_4, t_5)$ is a convolution of the fifth-order nonlinear response function $R^{(5)}(t_1, t_2, t_3, t_4, t_5)$, which contains all relevant information about the system under investigation, and the interacting light fields:

$$S(t_1, t_2, t_3, t_4, t_5) = \iiint \int dt_5 dt_4 dt_3 dt_2 dt_1 R^{(5)}(t_1, t_2, t_3, t_4, t_5) E(\mathbf{k}, t - t_5) E(\mathbf{k}, t - t_5 - t_4) \times E(\mathbf{k}, t - t_5 - t_4 - t_3) E(\mathbf{k}, t - t_5 - t_4 - t_3 - t_2) E(\mathbf{k}, t - t_5 - t_4 - t_3 - t_2 - t_1) \quad (5.2)$$

In the semi-impulsive limit, i.e. when the pulses envelopes are considered as δ -functions while still retaining their carrier frequencies, phases and wave vectors, the emitted light field is directly proportional to the response function [6].

The fifth-order nonlinear response function $R^{(5)}(t_1, t_2, t_3, t_4, t_5)$ consists of various coherence transfer pathways which can be illustrated using double sided Feynman diagrams (DSFDs). In this chapter, we restrict the discussion to a two level system, but the extension to multiple level systems is, in principle, straightforward. The DSFDs of various fifth-order nonlinear optical processes in the pump-probe geometry are depicted in Fig. 5.1(b) using the notation by Hamm [15]. We restrict ourselves to diagrams in the observed $\mathbf{k}_{signal} = \mathbf{k}_{probe}$ direction, as well as DSFDs that exhibit only populations during the last waiting times. When using a phase-locked pump pulse train, as delivered by pulse shapers, the emitted signal acquires a phase signature $\phi_{signal} = \alpha\phi_1 + \beta\phi_2 + \gamma\phi_3 + \delta\phi_4$, where α is the number of first pump pulse arrows pointing to the right minus first pump pulse arrows pointing to the left of the DSFDs. Arrows pointing towards the DSFDs represent absorption, while arrows pointing away represent emission. β , γ , and δ can be calculated accordingly for the second, third and fourth pulse interaction. Practically, we denote the phase signatures in terms of relative phases $\phi_{14} = \phi_1 - \phi_4$, $\phi_{24} = \phi_2 - \phi_4$ and $\phi_{34} = \phi_3 - \phi_4$, since only the interpulse phase relationships matter. In this notation the overall acquired phase signature of the signal is $\phi_{signal} = \alpha\phi_{14} + \beta\phi_{24} + \gamma\phi_{34}$. As can be seen δ

is in fact not necessary to denote a particular coherence transfer pathway. This stems from the fact that in a pump-probe geometry the system necessarily needs to end in a population state for the second waiting time t_4 , which constraints the values of α , β , γ , and δ to be:

$$\alpha + \beta + \gamma + \delta = 0 \quad (5.3)$$

If we furthermore restrict the problem to fifth and lower-order processes while ignoring higher-order terms, only up to four interactions from the four pump pulses need to be considered. This results in a second condition:

$$|\alpha| + |\beta| + |\gamma| + |\delta| \leq 4 \quad (5.4)$$

The signals from the four diagrams in Fig. 5.1(b) in the semi-impulsive limit from Eq. (5.2), give:

$$\begin{aligned} R_1^{(5)}(t_1, t_2, t_3, t_4, t_5) &\propto \Theta(t_1)\Theta(t_3)\Theta(t_5)\exp(-i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3)\exp(-i\omega_{10}t_5)F_1(t_1, t_2, t_3, t_4, t_5) \\ R_2^{(5)}(t_1, t_2, t_3, t_4, t_5) &\propto \Theta(t_1)\Theta(t_3)\Theta(t_5)\exp(+i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3)\exp(-i\omega_{10}t_5)F_2(t_1, t_2, t_3, t_4, t_5) \\ R_3^{(5)}(t_1, t_2, t_3, t_4, t_5) &\propto \Theta(t_1)\Theta(t_3)\Theta(t_5)\exp(-i\Delta\omega_{10}t_1)\exp(+i\Delta\omega_{10}t_3)\exp(-i\omega_{10}t_5)F_3(t_1, t_2, t_3, t_4, t_5) \\ R_4^{(5)}(t_1, t_2, t_3, t_4, t_5) &\propto \Theta(t_1)\Theta(t_3)\Theta(t_5)\exp(+i\Delta\omega_{10}t_1)\exp(+i\Delta\omega_{10}t_3)\exp(-i\omega_{10}t_5)F_4(t_1, t_2, t_3, t_4, t_5) \end{aligned} \quad (5.5)$$

where ω_{10} is the resonance frequency of the two-level system, and $\Delta\omega_{10} = \omega_{10} - \omega_{ref}$ is the resonance frequency detuned from the reference frequency ω_{ref} . Over t_1 and t_3 , the data is collected over a rotating frame at ω_{ref} frequency [22, 23]. $\Theta(t)$ is a Heaviside step function. F_1 to F_4 are functions that account for dephasing and population relaxation dynamics [34], and therefore determine the peak shapes. Each coherence transfer pathway contains valuable information, but for purely absorptive spectra which exhibit the highest possible frequency resolution, the overall response function needs to have contributions from all individual response functions $R_1^{(5)}$ to $R_4^{(5)}$ [15]. A characteristic of using a pump-probe geometry is that all coherence transfer pathways $R_1^{(5)}$ to $R_4^{(5)}$ will automatically emit in the same direction $\mathbf{k}_{signal} = \mathbf{k}_{probe}$, which is beneficial for the collection of purely absorptive spectra. However, there is also a multitude of other processes emitted in the

$k_{\text{signal}} = k_{\text{probe}}$ direction, of which a few examples are depicted in Fig. 5.1(c). They consist of coherence transfer pathways of fifth-order processes, where certain light fields interact more than once with the system, as well as other lower-order processes ($|\alpha| + |\beta| + |\gamma| + |\delta| \leq 2$). Although such processes will not be discriminated by the phase matching condition, they are distinguishable from the desired coherence transfer pathways by their phase signature. The sum of the multitude of undesired processes is denoted with P . One purpose of phase cycling is to get rid of such unwanted signal contributions. In summary, for fixed waiting times t_2 and t_4 the following expression results for the overall phase dependent signal:

$$S(t_1, t_3, t_5) \propto R_1^{(5)}(t_1, t_3, t_5) \exp(+i\phi_{14} - i\phi_{24} + i\phi_{34}) + R_2^{(5)}(t_1, t_3, t_5) \exp(-i\phi_{14} + i\phi_{24} + i\phi_{34}) \\ + R_3^{(5)}(t_1, t_3, t_5) \exp(+i\phi_{14} - i\phi_{24} - i\phi_{34}) + R_4^{(5)}(t_1, t_3, t_5) \exp(-i\phi_{14} + i\phi_{24} - i\phi_{34}) + \dots \quad (5.6)$$

Experimentally, the first two coherence times t_1 and t_3 are typically collected in the time domain, while the third coherence time t_5 is acquired in the frequency domain by spectrally resolving the signal in a spectrometer, which mathematically is a Fourier transform about the t_5 axis (FT_5). For brevity, we will henceforth drop the waiting time variables t_2 and t_4 in our equations. Subsequent self-heterodyned detection of the signal field with a square-law detector is mathematically equivalent to selecting the real part of the product of the signal field and the intrinsic local oscillator field. In the semi-impulsive limit the detected frequency resolved signal $\tilde{S}$ can be expressed, using $S(t_1, t_3, t_5)$ of Eq. (5.6), as:

$$\tilde{S}(\phi_{14}, \phi_{24}, \phi_{34}; t_1, t_3, \omega_5) \propto \Re[\text{FT}_5\{S(t_1, t_3, t_5)\}] \\ \equiv \sum_{\alpha, \beta, \gamma} \tilde{S}(\alpha, \beta, \gamma; t_1, t_3, \omega_5) \exp(+i\alpha\phi_{14} + i\beta\phi_{24} + i\gamma\phi_{34}) \quad (5.7)$$

The summation in the last line of Eq. (5.7) groups all terms according to their phase signature α , β , and γ . Amongst all possible terms, those of interest are:

$$\tilde{S}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5) = \Theta(t_1)\Theta(t_3) \exp(-i\Delta\omega_{10}t_1) \exp(-i\Delta\omega_{10}t_3) \\ \times \left[\tilde{F}_1(t_1, t_3, \omega_5 - \omega_{10}) + \tilde{F}_4^*(t_1, t_3, \omega_5 - \omega_{10}) \right] \quad (5.8)$$

$$\begin{aligned} \tilde{s}_{2+3^*}(\alpha = -1, \beta = 1, \gamma = 1; t_1, t_3, \omega_5) &= \Theta(t_1)\Theta(t_3)\exp(+i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3) \\ &\times \left[\tilde{F}_2(t_1, t_3, \omega_5 - \omega_{10}) + \tilde{F}_3^*(t_1, t_3, \omega_5 - \omega_{10}) \right] \end{aligned} \quad (5.9)$$

$$\begin{aligned} \tilde{s}_{3+2^*}(\alpha = 1, \beta = -1, \gamma = -1; t_1, t_3, \omega_5) &= \Theta(t_1)\Theta(t_3)\exp(-i\Delta\omega_{10}t_1)\exp(+i\Delta\omega_{10}t_3) \\ &\times \left[\tilde{F}_3(t_1, t_3, \omega_5 - \omega_{10}) + \tilde{F}_2^*(t_1, t_3, \omega_5 - \omega_{10}) \right] \end{aligned} \quad (5.10)$$

$$\begin{aligned} \tilde{s}_{4+1^*}(\alpha = -1, \beta = 1, \gamma = -1; t_1, t_3, \omega_5) &= \Theta(t_1)\Theta(t_3)\exp(+i\Delta\omega_{10}t_1)\exp(+i\Delta\omega_{10}t_3) \\ &\times \left[\tilde{F}_4(t_1, t_3, \omega_5 - \omega_{10}) + \tilde{F}_1^*(t_1, t_3, \omega_5 - \omega_{10}) \right] \end{aligned} \quad (5.11)$$

where $\tilde{F}_i(t_1, t_3, \omega_5 - \omega_{10}) = \text{FT}_5 \{ F_i(t_1, t_3, t_5) \exp(-i\omega_{10}t_5) \}$. The asterisk denotes the complex conjugate. Either one of the pair of Eqs. (5.8) and (5.9) or Eqs. (5.10) and (5.11) contains all the relevant terms shown in Eq. (5.5) to obtain the pure absorptive peaks in a 3D spectrum. We shall discuss here the choice of an appropriate phase cycling scheme to measure selectively Eqs. (5.8) and (5.9) from the summation series of Eq. (5.7).

Mathematically, to extract a specific signal $\tilde{s}(\alpha, \beta, \gamma; t_1, t_3, \omega_5)$ with phase signature $\exp(+i\alpha\phi_{14} + i\beta\phi_{24} + i\gamma\phi_{34})$ a three-dimensional Fourier transform of $\tilde{S}(\alpha, \beta, \gamma; t_1, t_3, \omega_5)$ over the interpulse phase-space needs to be performed:

$$\begin{aligned} \tilde{s}(\alpha, \beta, \gamma; t_1, t_3, \omega_5) &= \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} d\phi_{14} d\phi_{24} d\phi_{34} \tilde{S}(\alpha, \beta, \gamma; t_1, t_3, \omega_5) \\ &\times \exp(-i\alpha\phi_{14}) \exp(-i\beta\phi_{24}) \exp(-i\gamma\phi_{34}) \end{aligned} \quad (5.12)$$

In our approach, we experimentally sample the phase spaces in discrete steps and Eq. (5.12) can be written as a discrete Fourier transform:

$$\begin{aligned} \tilde{s}^{L \times M \times N \times 1}(\alpha, \beta, \gamma; t_1, t_3, \omega_5) &= \frac{1}{LMN} \sum_{l=0}^{L-1} \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} \tilde{S}(l\Delta\phi_{14}, m\Delta\phi_{24}, n\Delta\phi_{34}; t_1, t_3, \omega_5) \\ &\times \exp(-il\alpha\Delta\phi_{14}) \exp(-im\beta\Delta\phi_{24}) \exp(-in\gamma\Delta\phi_{34}) \\ &\equiv \frac{1}{LMN} \sum_{l=0}^{L-1} \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} \tilde{S}(l\Delta\phi_{14}, m\Delta\phi_{24}, n\Delta\phi_{34}; t_1, t_3, \omega_5) \\ &\times W_L^{l\alpha} W_M^{m\beta} W_N^{n\gamma} \end{aligned} \quad (5.13)$$

where $\phi_{14} = l\Delta\phi_{14}$, $\phi_{24} = m\Delta\phi_{24}$, and $\phi_{34} = n\Delta\phi_{34}$, L is the number of sample points in the ϕ_{14} -phase space, M is the number of sample points in the ϕ_{24} -phase space, and N is the number of sample points in the ϕ_{34} -phase space. $W_L^{l\alpha}$, $W_M^{m\beta}$, and $W_N^{n\gamma}$ are the respective summation weights. Experimentally, this means a series of experiments need to be

conducted with different interpulse phases ϕ_{14} , ϕ_{24} , and ϕ_{34} , and the resultant series of phase dependent signals added according to the weights $w_L^{l\alpha}$, $w_M^{m\beta}$, and $w_N^{n\gamma}$. For a $L \times M \times N \times 1$ phase cycling scheme, it is desirable to keep L , M , and N minimal as this determines the total number of measurements that need to be performed. In principle, it does not matter which one of the four pulses we should reference the pulse phases to. Therefore, the resultant signals from a $L \times M \times N \times 1$ phase cycling experiment and a $1 \times L \times M \times N$ experiment are the same, the latter being if we reference the interpulse phases to the first pulse. In this work, we have referenced it to the last pulse as it is simpler to set up experimentally.

Phase cycling is a technique that is analogous to theoretical methods developed by research groups to extract relevant terms from a nonperturbative calculation of nonlinear optical signals [35-37].

A related technique to phase cycling can be found in phase modulated 2D fluorescence spectroscopy and related experiments [38-40]. In this technique, instead of phase cycling through the laser pulses with discrete phase steps, phases are introduced in a continuous fashion and the desired signal with its corresponding phase modulation signature can be obtained using a lock-in detector.

The general conditions of Eqs. (5.3) and (5.4) allow 55 coherence transfer pathways to evolve without phase cycling. The phase cycling scheme discussed in this chapter is similar in nature to the phase cycling schemes of 2D collinear optical spectroscopy discussed in a previous work [29]. In the 2D collinear optical spectroscopy discussed in Ref. 27, four interactions with the four collinear pulses lead to a population state which is then detected. After the consideration of aliasing, both rephasing and non-rephasing spectra can be obtained using a $1 \times 3 \times 3 \times 3$ phase cycling scheme. In this present work, the first four interactions with the four pump pulses lead to a population which is then probed by the fifth interaction. The conditions denoted in Eqs. (5.3) and (5.4) are therefore the

same as that presented in Ref. 27 with a four-pulse train. Likewise, a full 27 steps of $1 \times 3 \times 3 \times 3$ (or a $3 \times 3 \times 3 \times 1$) phase cycling scheme can be performed and the appropriate linear combination of the signals provided by Eq. (5.13) can then be applied to extract the signals $\tilde{s}_{1+4^*}(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5)$ and $\tilde{s}_{2+3^*}(\alpha=-1, \beta=1, \gamma=1; t_1, t_3, \omega_5)$ (Eqs. (5.8) and (5.9), respectively).

Upon obtaining the signal of Eqs. (5.8) and (5.9) using the $3 \times 3 \times 3 \times 1$ phase cycling scheme where the first three pulses are each cycled over phases ϕ_{14} , ϕ_{24} , and $\phi_{34} = 0, 2\pi/3$, and $4\pi/3$, we explain here how the data can then be processed to obtain pure absorptive peaks. We make the following simplification that $F_1(t_1, t_3, t_5) = F_2(t_1, t_3, t_5) = F_3(t_1, t_3, t_5) = F_4(t_1, t_3, t_5) = F(t_1, t_3, t_5)$ are real functions and that $F(t_1, t_3, t_5) = F(t_1, t_3)F(t_5) = F(t_1)F(t_3)F(t_5)$. These assumptions are only made for brevity to illustrate in a clearer fashion how pure absorptive peak shapes are obtained. More general expressions may be written if required. We can express the Fourier transform of $F(t_j)$ about any coherence time axis t_j , where $j = 1, 3$, or 5 , as $\text{FT}_j \{ \Theta(t_j) F(t_j) \exp(-i\omega_{10}t_j) \} = A(\omega_j - \omega_{10}) + iD(\omega_j - \omega_{10})$, where $A(\omega_j - \omega_{10})$ and $D(\omega_j - \omega_{10})$ are the absorptive and dispersive terms, respectively. Fourier transformations of Eq. (5.8) about t_1 and t_3 and taking the real part of the signal only then results in a 3D spectrum:

$$\begin{aligned}
\tilde{s}_{1+4^*}^{3 \times 3 \times 3 \times 1}(\alpha=1, \beta=-1, \gamma=1; \omega_1, \omega_3, \omega_5) &= \Re \left\{ \text{FT}_{1,3} \left\{ \tilde{s}_{1+4^*}(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5) \right\} \right\} \\
&= \Re \left\{ \text{FT}_{1,3} \left\{ F(t_1)F(t_3) \exp(-i\Delta\omega_{01}t_1 - i\Delta\omega_{01}t_3) A(\omega_5 - \omega_{10}) \right\} \right\} \\
&= \Re \left\{ \left[\begin{aligned} &A(\omega_1 - \Delta\omega_{10}) + iD(\omega_1 - \Delta\omega_{10}) \\ &A(\omega_3 - \Delta\omega_{10}) + iD(\omega_3 - \Delta\omega_{10}) \end{aligned} \right] A(\omega_5 - \omega_{10}) \right\} \\
&= A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
&\quad - D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10})
\end{aligned} \tag{5.14}$$

From this expression, we can see that the spectrum will be centered at $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$. Also, it is apparent that the spectrum still contains dispersive

contributions along ω_1 and ω_3 . Similarly, the 3D spectrum resulting from

$\tilde{s}_{2+3^*}(\alpha = -1, \beta = 1, \gamma = 1; t_1, t_3, \omega_5)$ of Eq. (5.9) becomes:

$$\begin{aligned}
\tilde{s}_{2+3^*}^{3 \times 3 \times 3 \times 1}(\alpha = -1, \beta = 1, \gamma = 1; \omega_1, \omega_3, \omega_5) &= \Re \left\{ \text{FT}_{1,3} \left\{ \tilde{s}_{2+3^*}(\alpha = -1, \beta = 1, \gamma = 1; t_1, t_3, \omega_5) \right\} \right\} \\
&= \Re \left\{ \text{FT}_{1,3} \left\{ F(t_1) F(t_3) \exp(i\Delta\omega_{01}t_1 - i\Delta\omega_{01}t_3) A_5(\omega_5 - \omega_{10}) \right\} \right\} \\
&= \Re \left\{ \left[\begin{array}{c} A(\omega_1 + \Delta\omega_{10}) + iD(\omega_1 + \Delta\omega_{10}) \\ A(\omega_3 - \Delta\omega_{10}) + iD(\omega_3 - \Delta\omega_{10}) \end{array} \right] A(\omega_5 - \omega_{10}) \right\} \\
&= A(\omega_1 + \Delta\omega_{10}) A(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10}) \\
&\quad - D(\omega_1 + \Delta\omega_{10}) D(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10})
\end{aligned} \tag{5.15}$$

We note that the signal now is centered at $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$. The peaks arising from Eqs. (5.14) and (5.15) lie in different quadrants of the $\omega_5 = \omega_{10}$ plane in a 3D Cartesian coordinate system. Upon reflecting Eq. (5.15) about the $\omega_1 = 0$ plane, we obtain the mirrored spectrum:

$$\begin{aligned}
\tilde{s}_{2+3^*}^{3 \times 3 \times 3 \times 1, M(\omega_1)}(\alpha = -1, \beta = 1, \gamma = 1; \omega_1, \omega_3, \omega_5) &= A(\omega_1 - \Delta\omega_{10}) A(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10}) \\
&\quad + D(\omega_1 - \Delta\omega_{10}) D(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10})
\end{aligned} \tag{5.16}$$

Equations (5.14) and (5.16) can then be summed up to cancel out the remaining dispersive features by obeying the assumption made earlier leading to only the purely absorptive spectrum:

$$\begin{aligned}
\tilde{s}_{1+2+3+4}^{3 \times 3 \times 3 \times 1}(\omega_1, \omega_3, \omega_5) &= \tilde{s}_{1+4^*}(\alpha = 1, \beta = -1, \gamma = 1; \omega_1, \omega_3, \omega_5) + \tilde{s}_{2+3^*}^{M(\omega_1)}(\alpha = -1, \beta = 1, \gamma = 1; \omega_1, \omega_3, \omega_5) \\
&= A(\omega_1 - \Delta\omega_{10}) A(\omega_3 - \Delta\omega_{10}) A(\omega_5 - \omega_{10})
\end{aligned} \tag{5.17}$$

We will now discuss the application of a $2 \times 2 \times 2 \times 1$ phase cycling scheme. In a $2 \times 2 \times 2 \times 1$ phase cycling scheme, the first three pulses are each cycled over phases ϕ_{14} , ϕ_{24} , and $\phi_{34} = 0$ and π . A two-step phase cycle cannot discriminate between summation weightings $\exp(i\phi)$ and $\exp(-i\phi)$ due to aliasing [29]. Therefore, by applying a $2 \times 2 \times 2 \times 1$ phase cycling scheme and using Eq. (5.7) to select the signal $\tilde{s}_{1+4^*}(\alpha = 1, \beta = -1, \gamma = 1; t_1, t_3, \omega_5)$ of Eq. (5.8) with phase signature $\exp(+i\phi_{14} - i\phi_{24} + i\phi_{34})$, we will not be able to exclude signals from signals $\tilde{s}_{2+3^*}(\alpha = -1, \beta = 1, \gamma = 1; t_1, t_3, \omega_5)$, $\tilde{s}_{3+2^*}(\alpha = 1, \beta = -1, \gamma = -1; t_1, t_3, \omega_5)$ and

$\tilde{s}_{4+1^*}(\alpha = -1, \beta = 1, \gamma = -1; t_1, t_3, \omega_5)$ of Eqs. (5.9), (5.10) and (5.11), with phase signatures $\exp(-i\phi_{14} + i\phi_{24} + i\phi_{34})$, $\exp(+i\phi_{14} - i\phi_{24} - i\phi_{34})$ and $\exp(-i\phi_{14} + i\phi_{24} - i\phi_{34})$, respectively. Fourier transformations about t_1 and t_3 of this $2 \times 2 \times 2 \times 1$ phase cycled signal that consist of the sum of Eqs. (5.8) to (5.11), followed by taking the real part will give:

$$\begin{aligned}
\tilde{s}^{2 \times 2 \times 2 \times 1}(\omega_1, \omega_3, \omega_5) &= \Re \left\{ \text{FT}_{1,3} \left\{ \begin{aligned} &\tilde{s}_{1+4^*}(\alpha = 1, \beta = -1, \gamma = 1; t_1, t_3, \omega_5) \\ &+ \tilde{s}_{2+3^*}(\alpha = -1, \beta = 1, \gamma = 1; t_1, t_3, \omega_5) \\ &+ \tilde{s}_{3+2^*}(\alpha = 1, \beta = -1, \gamma = -1; t_1, t_3, \omega_5) \\ &+ \tilde{s}_{4+1^*}(\alpha = -1, \beta = 1, \gamma = -1; t_1, t_3, \omega_5) \end{aligned} \right\} \right\} \\
&= \Re \left\{ \text{FT}_{1,3} \left\{ \begin{aligned} &F(t_1)F(t_3)\exp(-i\Delta\omega_{01}t_1 - i\Delta\omega_{01}t_3)A(\omega_5 - \omega_{10}) \\ &+ F(t_1)F(t_3)\exp(+i\Delta\omega_{01}t_1 - i\Delta\omega_{01}t_3)A(\omega_5 - \omega_{10}) \\ &+ F(t_1)F(t_3)\exp(-i\Delta\omega_{01}t_1 + i\Delta\omega_{01}t_3)A(\omega_5 - \omega_{10}) \\ &+ F(t_1)F(t_3)\exp(+i\Delta\omega_{01}t_1 + i\Delta\omega_{01}t_3)A(\omega_5 - \omega_{10}) \end{aligned} \right\} \right\} \\
&= \Re \left\{ \begin{aligned} &\left[A(\omega_1 - \Delta\omega_{10}) + iD(\omega_1 - \Delta\omega_{10}) \right] \\ &\left[A(\omega_3 - \Delta\omega_{10}) + iD(\omega_3 - \Delta\omega_{10}) \right] A(\omega_5 - \omega_{10}) \\ &+ \left[A(\omega_1 + \Delta\omega_{10}) + iD(\omega_1 + \Delta\omega_{10}) \right] \\ &\left[A(\omega_3 - \Delta\omega_{10}) + iD(\omega_3 - \Delta\omega_{10}) \right] A(\omega_5 - \omega_{10}) \\ &+ \left[A(\omega_1 - \Delta\omega_{10}) + iD(\omega_1 - \Delta\omega_{10}) \right] \\ &\left[A(\omega_3 + \Delta\omega_{10}) + iD(\omega_3 + \Delta\omega_{10}) \right] A(\omega_5 - \omega_{10}) \\ &+ \left[A(\omega_1 + \Delta\omega_{10}) + iD(\omega_1 + \Delta\omega_{10}) \right] \\ &\left[A(\omega_3 + \Delta\omega_{10}) + iD(\omega_3 + \Delta\omega_{10}) \right] A(\omega_5 - \omega_{10}) \end{aligned} \right\} \\
&= A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
&\quad - D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
&\quad + A(\omega_1 + \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
&\quad - D(\omega_1 + \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
&\quad + A(\omega_1 - \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
&\quad - D(\omega_1 - \Delta\omega_{10})D(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
&\quad + A(\omega_1 + \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
&\quad - D(\omega_1 + \Delta\omega_{10})D(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10})
\end{aligned} \tag{5.18}$$

This resultant 3D spectrum will have four peaks, each at the four different quadrants of the $\omega_5 = \omega_{10}$ plane, $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$, $(\omega_1, \omega_3, \omega_5) = (-\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$, $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$, and $(\omega_1, \omega_3, \omega_5) = (-\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$, respectively. Upon reflecting Eq. (5.18) about the $\omega_1 = 0$ plane, we have:

$$\begin{aligned}
\tilde{s}^{2 \times 2 \times 2 \times 1, M(\omega_1)}(\omega_1, \omega_3, \omega_5) = & A(\omega_1 + \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
& + D(\omega_1 + \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
& + A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
& + D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
& + A(\omega_1 + \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
& + D(\omega_1 + \Delta\omega_{10})D(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
& + A(\omega_1 - \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
& + D(\omega_1 - \Delta\omega_{10})D(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10})
\end{aligned} \tag{5.19}$$

And adding the spectrum (Eq. (5.18)) to its mirror image (Eq. (5.19)), yields a 3D spectrum that contains peaks that are purely absorptive:

$$\begin{aligned}
\tilde{s}_{1+2+3+4}^{2 \times 2 \times 2 \times 1}(\omega_1, \omega_3, \omega_5) = & A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
& + A(\omega_1 + \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
& + A(\omega_1 - \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\
& + A(\omega_1 + \Delta\omega_{10})A(\omega_3 + \Delta\omega_{10})A(\omega_5 - \omega_{10})
\end{aligned} \tag{5.20}$$

The four purely absorptive peaks of the 3D spectrum are identical and separated by $2\Delta\omega_{10}$. In practice, $\Delta\omega_{10}$ can be experimentally manipulated with the pulse shaper so that the four identical peaks are well separated. It is therefore sufficient to show only one quadrant of the 3D spectrum. We should note here that reflecting Eq. (5.18) about the $\omega_3 = 0$ plane and the subsequent adding of the spectra will give the same outcome. We have recently demonstrated the measurement of this purely absorptive 3D spectrum [25]. For samples with a congested or broad spectrum with a bandwidth on the order of $2\Delta\omega_{10}$, the aliased signals will overlap in a $2 \times 2 \times 2 \times 1$ phase cycling scheme. To overcome this problem of aliasing, we have to either increase $\Delta\omega_{10}$ by changing ω_{ref} to a further displaced frequency, or we can choose a $3 \times 3 \times 3 \times 1$ phase cycling scheme. In a multileveled or coupled system, a $2 \times 2 \times 2 \times 1$ phase cycling scheme is insufficient to remove undesired signals such as two-quantum absorption signals from $\tilde{s}_{2Q1}(\alpha=1, \beta=1, \gamma=-1; \omega_1, \omega_3, \omega_5)$ and $\tilde{s}_{2Q2}(\alpha=-1, \beta=-1, \gamma=1; \omega_1, \omega_3, \omega_5)$, which will appear at $(\omega_1, \omega_3, \omega_5) = (-2\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$ and $(\omega_1, \omega_3, \omega_5) = (2\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$, respectively. This necessitates a $3 \times 3 \times 3 \times 1$ phase cycling scheme to select the desired signal. However, if there are no peaks appearing in a $3 \times 3 \times 3 \times 1$ phase cycling scheme when choosing

$\tilde{s}(\alpha=1, \beta=1, \gamma=-1)$ and $\tilde{s}(\alpha=-1, \beta=-1, \gamma=1)$, we can assume that both the undesired pathways do not contribute significantly to the overall signal, and a $2 \times 2 \times 2 \times 1$ phase cycling scheme can be used.

5.1.2 Separating signals R_1 , R_2 , R_3 and R_4 in phase cycled 3D spectrum

The signals $\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5)$, $\tilde{s}_{2+3}^*(\alpha=-1, \beta=1, \gamma=1; t_1, t_3, \omega_5)$, $\tilde{s}_{3+2}^*(\alpha=1, \beta=-1, \gamma=-1; t_1, t_3, \omega_5)$ and $\tilde{s}_{4+1}^*(\alpha=-1, \beta=1, \gamma=-1; t_1, t_3, \omega_5)$ of Eq. (5.8–5.11) each contains two terms from Eq. (5.5). In order to selectively measure only one single term R_1 , R_2 , R_3 or R_4 from Eq. (5.5), the collected signals of Eq. (5.7) need to be mathematically treated before phase cycling schemes are applied. This procedure is similar to what is done to separate the rephasing and non-rephasing signal from a purely absorptive 2D spectrum by subjecting the data to the causality condition [21, 23]. The signal $\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5)$ shown in Eq. (5.8) is part of the total signal of Eq. (5.7) and contains R_1 and R_4 components. Using $\tilde{s}_{1+4}^*$ as an example, the procedures to impose causality to achieve the resultant signal will be demonstrated. The first step is to inverse Fourier transform about ω_5 , and Eq. (5.8) will become:

$$\begin{aligned} \tilde{s}_{1+4}^C(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, t_5) = & \Theta(t_1)\Theta(t_3)\Theta(t_5)F_1(t_1, t_3, t_5)\exp(-i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3) \\ & + \Theta(t_1)\Theta(t_3)\Theta(-t_5)F_4^*(t_1, t_3, -t_5)\exp(-i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3) \end{aligned} \quad (5.21)$$

By imposing causality, any signal that arrives before $t = 0$ fs is discarded and hence terms containing $\Theta(-t)$ are removed from Eq. (5.21). We note that the R_4 term will be removed from Eq. (5.21). The remaining signal is back Fourier transformed with respect to t_5 to give:

$$\tilde{s}_{1+4}^C(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5) = \Theta(t_1)\Theta(t_3)\exp(-i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3)\tilde{F}_1(t_1, t_3, \omega_5 - \omega_{10}) \quad (5.22)$$

This process of imposing causality is applied on the experimentally collected signal of Eq. (5.7) and the resultant processed signal will be denoted as $\tilde{S}^C(\phi_{14}, \phi_{24}, \phi_{34}; t_1, t_3, \omega_5)$. Analogous to Eq. (5.22), the terms in Eqs. (5.9–5.11) that are also present in Eq. (5.7), upon imposing causality will become:

$$\tilde{s}_2^C(\alpha = -1, \beta = 1, \gamma = 1; t_1, t_3, \omega_5) = \Theta(t_1)\Theta(t_3)\exp(+i\Delta\omega_{10}t_1)\exp(-i\Delta\omega_{10}t_3)\tilde{F}_2(t_1, t_3, \omega_5 - \omega_{10}) \quad (5.23)$$

$$\tilde{s}_3^C(\alpha = 1, \beta = -1, \gamma = -1; t_1, t_3, \omega_5) = \Theta(t_1)\Theta(t_3)\exp(-i\Delta\omega_{10}t_1)\exp(+i\Delta\omega_{10}t_3)\tilde{F}_3(t_1, t_3, \omega_5 - \omega_{10}) \quad (5.24)$$

$$\tilde{s}_4^C(\alpha = -1, \beta = 1, \gamma = -1; t_1, t_3, \omega_5) = \Theta(t_1)\Theta(t_3)\exp(+i\Delta\omega_{10}t_1)\exp(+i\Delta\omega_{10}t_3)\tilde{F}_4(t_1, t_3, \omega_5 - \omega_{10}) \quad (5.25)$$

Now, using the $3 \times 3 \times 3 \times 1$ phase cycling scheme to extract $\tilde{s}_1^C(\alpha = 1, \beta = -1, \gamma = 1; t_1, t_3, \omega_5)$ of Eq. (5.22) from the causality imposed signal $\tilde{S}^C(\phi_{14}, \phi_{24}, \phi_{34}; t_1, t_3, \omega_5)$ followed by Fourier transformation about t_1 and t_3 , will give $\tilde{F}_1(\omega_1 - \Delta\omega_{10}, \omega_3 - \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4)$ which is the 3D Fourier transform of the $R_1^{(5)}$ process as described in Eq. (5.5). Similarly, the $3 \times 3 \times 3 \times 1$ phase cycling scheme can extract $\tilde{s}_2^C(\alpha = -1, \beta = 1, \gamma = 1; \omega_1, \omega_3, \omega_5)$, $\tilde{s}_3^C(\alpha = 1, \beta = -1, \gamma = -1; \omega_1, \omega_3, \omega_5)$ and $\tilde{s}_4^C(\alpha = -1, \beta = 1, \gamma = -1; \omega_1, \omega_3, \omega_5)$ terms of Eqs. (5.23), (5.24) and (5.25), respectively from $\tilde{S}^C(\phi_{14}, \phi_{24}, \phi_{34}; t_1, t_3, \omega_5)$ to give $\tilde{F}_2(\omega_1 + \Delta\omega_{10}, \omega_3 - \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4)$, $\tilde{F}_3(\omega_1 - \Delta\omega_{10}, \omega_3 + \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4)$ and $\tilde{F}_4(\omega_1 + \Delta\omega_{10}, \omega_3 + \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4)$.

When one uses the $2 \times 2 \times 2 \times 1$ phase cycling scheme to attempt to recover $\tilde{s}_1^C(\alpha = 1, \beta = -1, \gamma = 1; t_1, t_3, \omega_5)$, as explained in the previous section, one cannot distinguish between signals with phase terms with phase signatures $\exp(+i\phi_{14} - i\phi_{24} + i\phi_{34})$, $\exp(-i\phi_{14} + i\phi_{24} + i\phi_{34})$, $\exp(+i\phi_{14} - i\phi_{24} - i\phi_{34})$ and $\exp(-i\phi_{14} + i\phi_{24} - i\phi_{34})$. The resultant signal when similarly Fourier transformed about t_1 and t_3 , gives:

$$\begin{aligned} \tilde{S}^{C, 2 \times 2 \times 2 \times 1}(\omega_1, \omega_3, \omega_5) = & \tilde{F}_1(\omega_1 - \Delta\omega_{10}, \omega_3 - \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4) \\ & + \tilde{F}_2(\omega_1 + \Delta\omega_{10}, \omega_3 - \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4) \\ & + \tilde{F}_3(\omega_1 - \Delta\omega_{10}, \omega_3 + \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4) \\ & + \tilde{F}_4(\omega_1 + \Delta\omega_{10}, \omega_3 + \Delta\omega_{10}, \omega_5 - \omega_{10}; t_2, t_4) \end{aligned} \quad (5.26)$$

where the signals for $\tilde{s}_1^{C,2 \times 2 \times 2 \times 1}(\alpha=1, \beta=-1, \gamma=1; \omega_1, \omega_3, \omega_5)$, $\tilde{s}_2^{C,2 \times 2 \times 2 \times 1}(\alpha=-1, \beta=1, \gamma=1; \omega_1, \omega_3, \omega_5)$, $\tilde{s}_3^{C,2 \times 2 \times 2 \times 1}(\alpha=1, \beta=-1, \gamma=-1; \omega_1, \omega_3, \omega_5)$ and $\tilde{s}_4^{C,2 \times 2 \times 2 \times 1}(\alpha=-1, \beta=1, \gamma=-1; \omega_1, \omega_3, \omega_5)$ are all retrieved in a single 3D spectrum. Each of the four processes will be in a different quadrant on the $\omega_5 = \omega_{10}$ plane. The real part of the summation of the four causality imposed signals upon proper mirror imaging will yield a purely absorptive signal.

5.2 Experiment

The experimental setup has been described in detail elsewhere [23, 25]. Briefly, a 1 kHz titanium sapphire regenerative amplifier pumps a home-built optical parametric amplifier (OPA) to generate pulses centered at 665 nm, with a bandwidth of 16 nm, as shown in Fig. 5.2.

Figure 5.2. A linear absorption spectrum of chlorophyll *a* in methanol (black) with the excitation pulse spectrum of the OPA (red) coinciding with the Q_y transition.

The pulses were compressed by an acousto-optic programmable dispersive filter (AOPDF) (Dazzler) to a duration of 50 fs. The 3D experimental setup was based on a pump-probe beam geometry, where the first four pump pulses interacted collinearly, while the last interaction from the probe pulse interacted at a small crossing angle. In the experiment, a four-pulse train (12 nJ per pulse) was created by the AOPDF with variable delays t_1 , t_2 and t_3 between pulses 1 and 2, pulses 2 and 3, and pulses 3 and 4, respectively. A whitelight continuum was created from a sapphire window to form pulse 5. The waiting time t_4 was the delay between pulses 4 and 5, and was set by a mechanical translation stage. We note that, as the whitelight continuum probe is chirped, a different frequency in the whitelight continuum will have a different delay t_4 , which may lead to distortion in the spectra [41]. This problem can be overcome with post-data chirp-correction by characterization of the chirp and adjusting the delay of the corresponding wavelength accordingly [42]. Delays t_1 and t_3 were coherence times, while t_2 and t_4 were population times. The fifth-order signal is emitted in the same direction as pulse 5, and was heterodyne-detected by pulse 5 and frequency-resolved by a spectrometer (PIXIS 100B) to form the emission axis ω_5 . Chlorophyll *a* (Chl *a*) was dissolved in methanol and placed in a 1 mm sapphire cell, and the linear absorption spectrum is shown in Fig. 5.2. An optical density of 0.2 is measured for the sample at 665 nm. It is known that distortions in multidimensional spectrum features can be due to sample thickness and the non-collinear phase matching beam geometry used in most multidimensional spectroscopic setups [43-45]. A pump-probe configuration that is presented in this work, where four out of five interactive pulses are interacting collinearly, will have less spectral distortions compared to a fully non-collinear phase matching beam geometry. In the 3D spectrum reported here, the distortion due to sample thickness is expected to be present and can be reduced by reducing the sample thickness.

To obtain a 3D spectrum, both coherence times t_1 and t_3 were scanned from 0 fs to 140 fs in 10 fs time steps. The population times t_2 and t_4 were kept fixed. The reference wavelength of the pulse shaper was set to 715 nm, such that the Nyquist limit was 15 fs for both the t_1 and t_3 axes, and the difference between the peak absorption of the sample and the reference wavelength was $\Delta\omega_{10} = 31$ THz. To perform phase cycling, for every step taken for the coherence time, the relative phases of the first three pulses, ϕ_1 , ϕ_2 and ϕ_3 were varied with respect to ϕ_4 . For $2 \times 2 \times 2 \times 1$ phase cycling scheme, the phases were cycled between $\phi_j = 0$ and π , while for $3 \times 3 \times 3 \times 1$ phase cycling scheme, the phases were cycled with $\phi_j = 0, 2\pi/3$, and $4\pi/3$, where $j = 1, 2, 3$ for both schemes. Scattered light from the pump beam is removed by subtracting the signal with and without the probe beam using a 500 Hz chopper. To ensure that the pulse train was created accurately, power measurements were made to ensure comparability when phases of the pulses were cycled. A $2 \times 2 \times 2 \times 1$ or $3 \times 3 \times 3 \times 1$ phase cycling scheme is performed on the emitted fifth-order signal by systematic weighted summation as described in Eq. (5.13). The phase cycled data was then zero-padded up to 85 data points and Fourier transformed with respect to t_1 and t_3 to give a 3D spectrum with signals $\tilde{s}_{1+4}^*(\alpha=1, \beta=-1, \gamma=1)$ and $\tilde{s}_{3+2}^*(\alpha=1, \beta=-1, \gamma=-1)$ without any undesired peaks as shown in Eqs. (5.14) and (5.15). The addition of the mirror image of the spectrum to itself yielded the purely absorptive 3D spectrum. To retrieve the signals $\tilde{s}_1(\alpha=1, \beta=-1, \gamma=1)$, $\tilde{s}_2(\alpha=-1, \beta=1, \gamma=1)$, $\tilde{s}_3(\alpha=1, \beta=-1, \gamma=-1)$ and $\tilde{s}_4(\alpha=-1, \beta=1, \gamma=-1)$, we modified the phase cycling data treatment by imposing causality to the collected data as described in Eqs. (5.21) and (5.22) [21, 23].

5.2.1 Results

Without phase cycling, or with insufficient phase cycling, the detected spectrum would be contaminated with spurious peaks due to undesired processes (lower-order signals, pump-probe signals etc.) as denoted by P in Eq. (5.6) and due to aliasing caused by undersampling of the discrete Fourier transform denoted in Eq. (5.13). In the following, we will discuss the 3D spectra that are obtained when we apply a different phase cycling scheme to choose the term $\tilde{s}(\alpha=1, \beta=-1, \gamma=1; t_1, t_3, \omega_5)$ from the signal of Eq. (5.7). In Fig. 5.3, various phase cycling schemes that are insufficient to select the desired signal are presented.

Figure 5.3. Isosurfaces of 3D spectra from insufficient phase cycling steps that results in unwanted signals. (a) Signals from a $1 \times 1 \times 1$ phase cycling scheme. The first-order signal at $(\omega_1, \omega_3, \omega_5) = (0, 0, \omega_{10})$ dominates the spectrum and is ~ 2500 times more intense than the fifth-order signal. (b) A $2 \times 2 \times 1$ phase cycling scheme results in the unwanted third-order signals at $(\omega_1, \omega_3, \omega_5) = (\pm \Delta \omega_{10}, 0, \omega_{10})$, which is ~ 10 times more intense than the fifth-order signal (Fig. 5.4).

In Fig. 5.3(a), the spectrum depicted is measured without any phase cycling, or in the language of phase cycling, a $1 \times 1 \times 1$ phase cycling scheme. The isosurfaces in Fig. 5.3(a) are drawn at an intensity ~ 2500 times of the desired fifth-order signals (signals presented in Fig. 5.4 onwards). It is dominated by a peak from a first-order linear signal

of negative amplitude at position $(\omega_1, \omega_3, \omega_5) = (0, 0, \omega_{10})$. This signal arises from zero interactions with the first four pulses and one interaction from the fifth “probe” pulse. Third-order and fifth-order signals are also present but are less intense than the first-order signal, and hence, they do not show up in the spectrum. The desired fifth-order signals at $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$ remains unobserved under these intense first-order contributions. In Fig. 5.3(b), the $2 \times 2 \times 1 \times 1$ phase cycling scheme removes the first-order signal but is unable to remove the third-order signals at $(\omega_1, \omega_3, \omega_5) = (\pm\Delta\omega_{10}, 0, \omega_{10})$. This arises from the insufficient phase cycling of the third pulse. The signals that have no interaction with the third and fourth pulses are not eliminated. The third-order signals observed at $(\omega_1, \omega_3, \omega_5) = (\pm\Delta\omega_{10}, 0, \omega_{10})$ arises after an interaction each with the first and second pulse followed by an interaction with the fifth “probe” pulse. The isosurfaces in Fig. 5.3(b) are drawn at intensity ~ 10 times that of the isosurfaces in Fig. 5.4(a). Figure 5.4 depicts the isosurfaces of the 3D spectrum obtained from a $2 \times 2 \times 2 \times 1$ phase cycling scheme, shown in Eq. (5.18), at $(t_2, t_4) = (400 \text{ fs}, 300 \text{ fs})$. Using this phase cycling scheme, all the first- and third-order signals are eliminated, and only fifth-order signals remain. In Fig. 5.4(a), the 3D spectrum has four peaks labeled as I, II, III and IV and they are located in the separate quadrants on the plane of $\omega_5 = \omega_{10} = 451 \text{ THz}$ at $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$, $(\omega_1, \omega_3, \omega_5) = (-\Delta\omega_{10}, \Delta\omega_{10}, \omega_{10})$, $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$, and $(\omega_1, \omega_3, \omega_5) = (-\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$, respectively.

Figure 5.4. Isosurfaces of 3D spectra from a $2 \times 2 \times 2 \times 1$ phase cycling scheme with $t_2 = 400$ fs and $t_4 = 300$ fs. Only the peaks from fifth-order processes remain. (a) Peaks I, II, III, and IV represent signals $\tilde{s}_{1+4^*}$, $\tilde{s}_{2+3^*}$, s_{3+2^*} , and s_{4+1^*} , respectively. (b) A magnified view of peak I. The 2D projection at I_{13} is “phase-twisted”, while I_{35} and I_{15} have purely absorptive peak shapes. (c) A magnified spectrum of peak II, with the mirror image taken across $\omega_1 = 0$ to display the signal in a quadrant with an all-positive frequency axis. The

2D projection at Π_{13} is phase-twisted, while Π_{35} and Π_{15} have purely absorptive peak shapes.

As mentioned in the earlier section 5.1.1 with Eq. (5.18), the peaks II, III and IV arise from aliasing. One major concern of aliasing is the possibility of overlapped aliased signals. Here, the reference signal was chosen to ensure that the peaks I, II, III and IV are well separated in the 3D spectrum by $2\Delta\omega_0 = 62$ THz so that there are no ambiguities in peak assignment. An enlarged 3D spectrum of peak I from Fig. 5.4(a) is depicted in Fig. 5.4(b). Figure 5.4(c) depicts an enlarged 3D spectrum of peak II after a mirror image of it is taken about the $\omega_1=0$ axis. We will explain in a later section on why the mirror image is obtained. The 2D projections of these peaks are also presented on the walls of the grid and labeled. To show that the peaks in the 3D spectrum are indeed the fifth-order signals as expected, we provide here the analysis to the positions and features of the observed 3D peaks. As the presentation of 3D peaks is cumbersome in manuscript format, we use 2D projections of the 3D peaks for analysis.

Peak I (Fig. 5.4(a)) and the mirror imaged peak II (Fig. 5.4(b)) can be described in terms of the absorptive and dispersive components extracted from the first term of Eq. (5.18) and the second term of Eq. (5.19), respectively, and they are expressed as:

$$\tilde{s}_I^{2 \times 2 \times 2 \times 1}(\omega_1, \omega_3, \omega_5) \propto A(\omega_1 - \Delta\omega_0)A(\omega_3 - \Delta\omega_0)A(\omega_5 - \omega_{10}) - D(\omega_1 - \Delta\omega_0)D(\omega_3 - \Delta\omega_0)A(\omega_5 - \omega_{10}) \quad (5.27)$$

$$\tilde{s}_{II}^{2 \times 2 \times 2 \times 1, M(\omega_1)}(\omega_1, \omega_3, \omega_5) \propto A(\omega_1 - \Delta\omega_0)A(\omega_3 - \Delta\omega_0)A(\omega_5 - \omega_{10}) + D(\omega_1 - \Delta\omega_0)D(\omega_3 - \Delta\omega_0)A(\omega_5 - \omega_{10}) \quad (5.28)$$

The features of the projections can be simulated by integrating the above functions over the appropriate axis. The 2D projection onto the (ω_1, ω_3) axis that corresponds to the 2D projections I_{13} and II_{13} from Figs. 5.4(b) and 5.4(c), respectively is achieved by integrating Eqs. (5.27) and (5.28), respectively, over ω_5 . Since the absorptive and dispersion components are symmetric and anti-symmetric, respectively, the results are:

$$\tilde{s}_{I_{13}}^{2 \times 2 \times 2 \times 1}(\omega_1, \omega_3) \propto A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10}) - D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10}) \quad (5.29)$$

$$\tilde{s}_{II_{13}}^{2 \times 2 \times 2 \times 1, M(\omega_1)}(\omega_1, \omega_3) \propto A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10}) + D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10}) \quad (5.30)$$

These peaks on the 2D projection will appear with distinctive “phase-twisted” shapes, where the peak broadens outward along the diagonal (or antidiagonal) axis and hence appears twisted [6, 46]. The “phase-twisted” shapes are due to dispersive contributions $D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})$ in Eqs. (5.29) and (5.30). The peaks corresponding to Eqs. (5.29) and (5.30) correspond to the rephasing and non-rephasing peaks, respectively, from 2D spectroscopy [2, 6, 46]. In Figs. 5.5(a) and 5.5(b), the 2D projections I_{13} and II_{13} from Figs. 5.4(b) and 5.4(c) are depicted, respectively. The phase-twisted feature can be seen in the peaks. In the previous section, it is theoretically shown that peak I contains signal from the R_1 and R_4 processes (Eq. (5.8)) while peak II contains signals from the R_2 and R_3 processes (Eq. (5.9)).

Figure 5.5. Comparing the 2D projections of I_{13} and II_{13} from Fig. 5.4 with simulated 2D projections. The phase-twisted feature is evident in both experimental and simulated results. As the simulation did not consider finite bandwidth of the interacting pulses, the resultant line widths in the experimental projections are smaller as compared to the simulated spectra. (a) 2D projection of I_{13} . (b) 2D projection of II_{13} . (c) Simulated 2D projection of I_{13} . (d) Simulated 2D projection of II_{13} .

To show that the experimental 3D spectra is consistent with the derivations, the response functions R_1 , R_2 , R_3 and R_4 [15] were calculated and the corresponding 3D spectra and 2D projections were generated. The two-point frequency fluctuation correlation function of Chl *a* in methanol was obtained from experiment [47]. These simulated 2D projections are presented in Figs. 5.5(c) and (d). The simulation did not take into consideration the finite temporal pulse width of the interacting pulses, and hence, the

simulated 2D projections are broader than the experimental 2D projections which were obtained using a pulse width of ~ 60 fs. However, phase twisted features from both simulation and experiment are clearly consistent.

We now discuss the other 2D projections I_{15} , I_{35} , Π_{15} and Π_{35} . Integrating over ω_3 for Eqs. (5.29) and (5.30), the resultant signals are:

$$\tilde{s}_{I_{15}}^{2 \times 2 \times 2 \times 1}(\omega_1, \omega_5) \propto A(\omega_1 - \Delta\omega_{10})A(\omega_5 - \Delta\omega_{10}) \quad (5.31)$$

$$\tilde{s}_{\Pi_{15}}^{2 \times 2 \times 2 \times 1, M(\omega_1)}(\omega_1, \omega_5) \propto A(\omega_1 - \Delta\omega_{10})A(\omega_5 - \Delta\omega_{10}) \quad (5.32)$$

By integrating over ω_1 for Eqs. (5.29) and (5.30), we have:

$$\tilde{s}_{I_{35}}^{2 \times 2 \times 2 \times 1}(\omega_3, \omega_5) \propto A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \Delta\omega_{10}) \quad (5.33)$$

$$\tilde{s}_{\Pi_{35}}^{2 \times 2 \times 2 \times 1, M(\omega_1)}(\omega_3, \omega_5) \propto A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \Delta\omega_{10}) \quad (5.34)$$

All these 2D projections have purely absorptive peak shapes and should look similar. In Fig. 5.6, the 2D projections I_{15} , I_{35} , Π_{15} and Π_{35} from Figs. 5.4(a) and 5.4(b) are presented.

Figure 5.6. Comparing 2D projections with 2D spectra. All the 2D projections show similar purely absorptive peak shapes as those obtained in 2D spectra. (a) 2D projection of I_{35} . (b) 2D projection of II_{35} . (c) 2D spectrum at $T_w=300$ fs. (d) 2D projection of I_{15} . (e) 2D projection of II_{15} . (f) 2D spectrum at $T_w=700$ fs.

As can be seen, the shapes are absorptive and similar, in contrast to the peak shapes in Figs. 5.5(a) and 5.5(b). In Figs. 5.6(c) and 5.6(f), the experimental purely absorptive 2D spectra of chlorophyll *a* at $T_w = 400$ fs and $T_w = 700$ fs are depicted as an example to show that the I_{15} , I_{35} , II_{15} and II_{35} are indeed purely absorptive line shapes, in contrast to the phase-twisted features of I_{13} and II_{13} of Figs. 5.5(c) and 5.5(d).

As mentioned in section 5.1.1, the 3D spectrum from a $2 \times 2 \times 2 \times 1$ phase cycling scheme can be manipulated to produce a purely absorptive 3D spectrum. This has been demonstrated in our work [25]. In Fig. 5.7(a), the purely absorptive 3D spectrum is obtained by the summation of Fig. 5.4(a) and its mirror image about $\omega_3 = 0$.

Figure 5.7. Purely absorptive peaks obtained from a $2 \times 2 \times 2 \times 1$ phase cycling scheme. (a) Four purely absorptive peaks which are aliased signals of each other. (b) A magnified view of the peak in the $(+\omega_1, +\omega_3, +\omega_5)$ -octant, with the respective 2D projections at the grid plane.

This summed 3D spectrum contains four purely absorptive peaks described in Eq. (5.20) that are mirror imaged replicas of each other. In Fig. 5.7(b), we present the peak from the $(+\omega_1, +\omega_3, +\omega_5)$ -octant, together with the 2D projections on the grid wall that shows purely absorptive features.

In Fig. 5.8(a), the 3D spectrum obtained from a $3 \times 3 \times 3 \times 1$ phase cycling scheme that chooses the signal $\tilde{s}_{1+4}^{3 \times 3 \times 3 \times 1} (\alpha=1, \beta=-1, \gamma=1)$ is depicted.

Figure 5.8. Isosurfaces of 3D spectra from a $3 \times 3 \times 3 \times 1$ phase cycling scheme. (a) The signal is the same as peak I and represents $\tilde{s}_{1+4}^*$. (b) A close up view of part (a), with the respective 2D projections on the grid plane. (c) The signal is the same as peak II and represents $\tilde{s}_{2+3}^*$. (d) A magnified spectrum of part (c) mirror imaged across $\omega_1 = 0$ into the

positive axis quadrant, and the corresponding 2D projections. (e) A purely absorptive peak obtained from the summation of part (a) and the mirror image of part (b) across $\omega_1 = 0$. (f) A magnified view of part (e). The 2D projections show purely absorptive peak shapes on all three grid planes of the cube.

The peak is centered at $(\omega_1, \omega_3, \omega_5) = (+\Delta\omega_{10}, +\Delta\omega_{10}, \omega_{10})$, as predicted in Eq. (5.14), and is the same as peak I in Fig. 5.4(a). Comparing Fig. 5.8(a) with Fig. 5.4(a), one can also see that the $3 \times 3 \times 3 \times 1$ phase cycling scheme is able to selectively choose the terms $\tilde{s}_{1+4^*}(\alpha=1, \beta=-1, \gamma=1)$ without the signal $\tilde{s}_{2+3^*}(\alpha=-1, \beta=-1, \gamma=1)$, $\tilde{s}_{3+2^*}(\alpha=1, \beta=-1, \gamma=-1)$ or $\tilde{s}_{4+1^*}(\alpha=-1, \beta=1, \gamma=-1)$ that arises from aliasing. Figure 5.8(b) depicts an enlarged spectrum from Fig. 5.8(a), and the 2D projections at the face of the grid cube are comparable to that of Fig. 5.4(b). Using the same $3 \times 3 \times 3 \times 1 = 27$ data set but in a different linear combination, the signal $\tilde{s}_{2+3^*}^{3 \times 3 \times 3 \times 1}(\alpha=1, \beta=-1, \gamma=-1)$ can then be chosen and the 3D spectrum is depicted in Fig. 5.8(c). The peak is located at $(\omega_1, \omega_3, \omega_5) = (\Delta\omega_{10}, -\Delta\omega_{10}, \omega_{10})$ as predicted in Eq. (5.15). In Fig. 5.8(d), the magnified view of Fig. 5.8(c) is presented in the positive frequency octant by taking the mirror image about the $\omega_1 = 0$ axis. The 2D projections can be compared to Fig. 5.4(c) and is shown to be similar. From these examples, the validity of the phase cycling schemes for 3D optical spectroscopy is shown experimentally. Upon summing the signal from Fig. 5.8(a) and the mirror image of Fig. 5.8(c) about the $\omega_1 = 0$ plane, as prescribed by Eq. (5.17), we obtain, in Fig. 5.8(e), a purely absorptive signal that is similar to the peak from the $(+\omega_1, +\omega_3, +\omega_5)$ -octant in Fig. 5.7(a). In Fig. 5.8(f), it is shown that the close up view of Fig. 5.8(e) and 2D projections are similar to those in Fig. 5.7(b).

To retrieve the signals from individual coherence pathways R_1, R_2, R_3 and R_4 in Fig. 5.1, causality is imposed before applying phase cycling scheme as described in section 5.1.2. Figure 5.9 depicts the 3D spectrum that is obtained from a causality imposed $2 \times 2 \times 2 \times 1$ phase cycling scheme, which is described in Eq. (5.26). Figure 5.9(a) contains

the isosurfaces of four peaks I^c , II^c , III^c and IV^c which represent the processes R_1 , R_2 , R_3 and R_4 , respectively.

Figure 5.9. (a) 3D spectra of a causality imposed $2 \times 2 \times 2 \times 1$ phase cycling scheme. All magnified spectra of II^c , III^c , and IV^c are transformed into the positive quadrant. The 2D projections all show phase-twisted features. (b) Close up view of I^c , (c) II^c , (d) III^c and (e) IV^c . (f) By summing up Figs. (b-e), a purely absorptive spectrum is obtained, and the 2D projection is similar to Fig. 5.7(b).

We compare Fig. 5.9(a) with Fig. 4(a). In Fig. 5.4(a), peaks I and IV are similar, as they contain both processes R_1 and R_4 while peaks II and III are similar, as they contain both processes R_2 and R_3 . However in Fig. 5.9(a), the imposing of causalities has separated all the processes and they each occupy a separate quadrant. A close-up view of peaks I^c, II^c, III^c, and IV^c is depicted in Figs. 5.9(b–e), respectively, where mirror images of the figures are taken about $\omega_1 = 0$ and/or $\omega_3 = 0$ planes for when applicable so that the peaks will appear in the positive frequency octant $(+\omega_1, +\omega_3, +\omega_5)$. For consistency, Fig. 5.9(f) shows a purely absorptive peak that is obtained by the sum of Figs. 5.9(b–e). As expected, it can be seen to be similar to Figs. 5.7(b) and 5.8(f).

For a causality imposed $3 \times 3 \times 3 \times 1$ phase cycling scheme, the signals for $\tilde{s}_1^{C, 3 \times 3 \times 3 \times 1}(\alpha = 1, \beta = -1, \gamma = 1)$, $\tilde{s}_2^{C, 3 \times 3 \times 3 \times 1}(\alpha = -1, \beta = 1, \gamma = 1)$, $\tilde{s}_3^{C, 3 \times 3 \times 3 \times 1}(\alpha = 1, \beta = -1, \gamma = -1)$, and $\tilde{s}_4^{C, 3 \times 3 \times 3 \times 1}(\alpha = -1, \beta = 1, \gamma = -1)$ are shown in Figs. 5.10(a–d), respectively, and they are located at the same positions as the retrieved signals from a causality imposed $2 \times 2 \times 2 \times 1$ phase cycling scheme of Fig. 5.9(a).

Figure 5.10. (a–d) Isosurfaces of 3D spectra from a $3 \times 3 \times 3 \times 1$ phase cycling scheme with causality imposed. The positions of the signals are the same as those in the causality imposed $2 \times 2 \times 2 \times 1$ phase cycling scheme. (e–h) Magnified view of the respective peaks and their 2D projections. All the 2D projections have phase-twisted features.

The enlarged 3D spectra and the 2D projections of the respective signals are shown in Figs. 5.10(e–h). It can be observed that the phase-twisted features look comparable to Figs. 5.9(b–e), according to Eqs. (5.22–5.25). By summing $\tilde{s}_1^{C,3 \times 3 \times 3 \times 1}(\alpha = 1, \beta = -1, \gamma = 1)$, $\tilde{s}_2^{C,3 \times 3 \times 3 \times 1}(\alpha = -1, \beta = 1, \gamma = 1)$, $\tilde{s}_3^{C,3 \times 3 \times 3 \times 1}(\alpha = 1, \beta = -1, \gamma = -1)$, and $\tilde{s}_4^{C,3 \times 3 \times 3 \times 1}(\alpha = -1, \beta = 1, \gamma = -1)$, as shown in Eq. (5.17), we will obtain the purely absorptive peak as shown in Fig. 5.8(f).

Figure 5.11 shows the 2D projections of the 3D spectrum for the R_1 process shown in Fig. 5.10(a).

Figure 5.11. 2D projections of Fig. 5.10(e) in a causality imposed $3 \times 3 \times 3 \times 1$ phase cycling scheme are shown. The projection (a) I^c_{13} , (b) I^c_{35} , and (c) I^c_{15} all show “phase-twisted” features that is akin to a non-rephasing peak shape in a 2D spectrum.

Here, the theoretical derivation for R_1 is presented as an example to predict the peak shape of the signal and compare it with the experimental result. With the simplification that was used in section 5.1.1 that $F(t_1, t_3, t_5) = F(t_1, t_3)F(t_5) = F(t_1)F(t_3)F(t_5)$ and that $\text{FT}_j \{ \Theta(t_j)F(t_j) \exp(-i\omega_{10}t_j) \} = A(\omega_j - \omega_{10}) + iD(\omega_j - \omega_{10})$, we obtain from Eq. (5.23), after Fourier transform, the real part of the 3D spectrum that is due to the R_1 process which can be expressed as:

$$\begin{aligned} \tilde{s}_1^{C, 3 \times 3 \times 3 \times 1}(\alpha = 1, \beta = -1, \gamma = 1; \omega_1, \omega_3, \omega_5) &\propto \text{Re} \left\{ \begin{aligned} &\left[A(\omega_1 - \Delta\omega_{10}) + iD(\omega_1 - \Delta\omega_{10}) \right] \\ &\times \left[A(\omega_3 - \Delta\omega_{10}) + iD(\omega_3 - \Delta\omega_{10}) \right] \\ &\times \left[A(\omega_5 - \omega_{10}) + iD(\omega_5 - \omega_{10}) \right] \end{aligned} \right\} \\ &= A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\ &\quad - D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) \\ &\quad - D(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10})D(\omega_5 - \omega_{10}) \\ &\quad - A(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10})D(\omega_5 - \omega_{10}) \end{aligned} \quad (5.35)$$

In order to obtain the 2D projections onto (ω_1, ω_3) , (ω_3, ω_5) and (ω_1, ω_5) planes, Eq. (5.35) is integrated over ω_5 , ω_1 and ω_3 , respectively. The three resultant expressions are:

$$\tilde{s}_{I_{13}}^{C, 3 \times 3 \times 3 \times 1}(\omega_1, \omega_3) = A(\omega_1 - \Delta\omega_{10})A(\omega_3 - \Delta\omega_{10}) - D(\omega_1 - \Delta\omega_{10})D(\omega_3 - \Delta\omega_{10}) \quad (5.36)$$

$$\tilde{s}_{I_{35}}^{C, 3 \times 3 \times 3 \times 1}(\omega_3, \omega_5) = A(\omega_3 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) - D(\omega_3 - \Delta\omega_{10})D(\omega_5 - \omega_{10}) \quad (5.37)$$

$$\tilde{s}_{I_{15}}^{C, 3 \times 3 \times 3 \times 1}(\omega_1, \omega_5) = A(\omega_1 - \Delta\omega_{10})A(\omega_5 - \omega_{10}) - D(\omega_1 - \Delta\omega_{10})D(\omega_5 - \omega_{10}) \quad (5.38)$$

All three expressions are similar with phase-twisted features and it proves that the experimental data obtained for R_1 shown in Fig. 5.10(a) is consistent with the theoretical derivation. By working out the equations it can be shown that all 2D projections for $\tilde{s}_{II}^{C, 3 \times 3 \times 3 \times 1}$, $\tilde{s}_{III}^{C, 3 \times 3 \times 3 \times 1}$, and $\tilde{s}_{IV}^{C, 3 \times 3 \times 3 \times 1}$ are phase-twisted as well, which is in good agreement with Figs. 5.10(e–h), and the case is also true for 3D spectrum from a causality implemented $2 \times 2 \times 2 \times 1$ phase cycling scheme as shown in Figs. 5.9(b–e).

5.3 Cascading Third-Order Contributions to the Fifth-Order Signal

In higher-order nonlinear spectroscopy, there might be undesired third-order cascades that appear in the same phase-matched direction as the desired fifth-order signal, while having the same intensity dependence. This is evident in fifth-order Raman spectroscopy, where the experiments were contaminated with third-order signals [48-50]. It is therefore important to determine the contributions of third-order cascades to the fifth-order signals. Third-order cascades occur when the third-order polarization response created by three pulse interactions is reabsorbed by the sample to produce a second third-order polarization response after interactions with the remaining two pulses. Sequential and parallel cascades are based on two third-order processes occurring on two separate molecules with a phase-matched direction as the emitted fifth-order signal [7, 51]. The contribution of the third-order cascades is dependent on the optical density of the sample and phase-matching geometry. A way to verify the contribution of cascaded third-order signals is by measuring the signal intensity with varying concentration. A fifth-order signal scales linearly with increasing concentration, while third-order cascades scale quadratically with concentration [51]. In this work, five samples with different concentrations (7 μM , 14 μM , 20 μM , 27 μM and 35 μM) are prepared by diluting the sample with the highest concentration using appropriate amount of solvent. The absorbance of every prepared sample is noted using a UV-Vis spectrometer and an effort was made to make sure aggregates were not formed in any samples. The pathlength of the sample cell is kept fixed. In Fig. 5.12, the peak signal intensity of the 3D spectra shows a linear dependence on concentration, demonstrating that the majority of the signal from the experimental conditions presented here is from fifth-order process rather than cascades.

Figure 5.12. The maximum intensity of the measured pure absorptive signal is plotted against the optical density of sample with various concentrations. A best fit line (dashed) is drawn. The heterodyned fifth-order signal should scale linearly with concentration c , while cascaded third-order signals should be linear with c^2 . This shows that cascaded third-order signals do not contribute significantly to the 3D spectra.

Using a simple calculation [9, 10], together with the consideration of sample absorption, the cascading signal contributes $\sim 10\%$ of the total signal at an optical density of 0.2. With optically thinner samples, the percentage contribution of cascades is further reduced.

5.4 Concluding Remarks

We have presented the theoretical framework on how to obtain fifth-order 3D electronic spectroscopy using a pulse shaper assisted pump-probe beam geometry. The use of the

pulse shaper allows phase cycling to be performed that is able to selectively measure fifth order signal. We discuss how purely absorptive 3D spectra as well as 3D spectra of processes from various coherence pathway processes can be obtained using phase cycling and data treatment. In the most general case, this requires a 27-step phase cycling scheme, but an 8-step phase cycling scheme may be adequate for a two-level system if the rotating frame reference frequency is chosen to be sufficiently far away from the resonance frequencies. There is only a small contribution of cascading third-order contribution to the fifth-order signals in this pump-probe geometry setup, as deduced by the linear relationship between the absorption intensity and sample concentration. The current demonstration is performed on a quasi-two-level system. We are currently working on understanding the applications of the phase cycling schemes and its restrictions for multilevel systems. In principle, the phase cycling scheme selection procedure demonstrated here in 3DES as well as in 2DES [23] can be applied to other nonlinear optical processes including extensions to even higher dimensional optical spectroscopy. It is hoped that this work can spur further theoretical and numerical studies of fifth-order 3D spectroscopy and associated fifth-order optical processes [15, 52, 53] to complement the advancement in experimental technique.

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Summary and Future Works

In this thesis, we have explored the development of two-dimensional (2D) and three-dimensional (3D) electronic spectroscopy via a pulse shaper assisted pump-probe geometry setup. In the multidimensional optical spectrometer, an acousto-optic programmable dispersive filter (AOPDF) generates the pump pulse train with controllable delays and relative phases, while a white light continuum provides the last interaction probe pulse. A full analysis on the 2D and 3D phase cycling schemes, together with additional data processing, that allows only the desired coherence pathways to be chosen is presented. As a proof-of-principle experiment, both 2D and 3D optical spectroscopy studies were performed on the Q_y transition of chlorophyll a .

We have also presented, in this thesis, the development of an indirect pulse shaping technique to generate polarization shaped pulses in the ultraviolet (UV) spectral region. This pulse shaping method can generate interferometrically stable pulse trains and have complete control over pulse parameters such as amplitude, phase, delay and polarization, which makes it a potential technique to be incorporated in multidimensional optical spectroscopy.

Finally, a method to characterize the amplitude, phase and polarization of the shaped UV pulses is presented, termed as “difference frequency generation cross-correlation tomographic ultrafast retrieval of transverse light E -fields” (DFG-XTURTLE). It combines the technique of tomographic ultrafast retrieval of transverse light E -fields (TURTLE) with the amplitude and phase retrieval algorithm of the cross-correlation frequency-resolved optical gating (XFROG). The ambiguity of resolving right-handed or left-handed elliptically polarized shaped pulses can be overcome with additional measurements using a quarter-wave retardation plate.

We have contributed a number of new technical developments which have advanced the current situation of 2D optical spectroscopy. A method to produce polarization shaped UV pulses with interferometric stability has been proposed, with the potential to be used in 2D electronic spectroscopy. In addition, our characterization method (DFG-XTURTLE) that is complementary to the polarization pulse shaping technique can provide us with certainty the shape of the pulses that are created in the UV spectral region. This set of polarization pulse shaping technique allows energy transfer to show up as enhanced cross peaks in a 2D spectrum as transition dipoles are directional in nature.

An important contribution to the field of 2D optical spectroscopy performed in a pump-probe geometry has been the implementation of phase cycling schemes. We have developed phase cycling schemes with the ability to remove unwanted transient absorption background signal and also aliased signals so as to remove any ambiguity in peaks assignment. We have also demonstrated the ability to retrieve both the rephasing and non-rephasing spectra by implementing causality.

Finally, we have implemented the technique of performing 3D optical spectroscopy in a pump-probe geometry using a pulse shaper. By performing 3D phase cycling schemes over the first four pulse interactions, a purely absorptive 3D spectrum is obtained with two population times. Any coherence transfer pathways can in principle be selected if sufficient phase cycling steps are performed, but for demonstration in this thesis we only chose to discuss the four coherence transfer pathways that are needed to obtain a purely absorptive 3D spectrum.

For the past decade, 2D optical spectroscopy has been a common tool to investigate transient structural information for vibrational spectroscopy, and energy transfer dynamics for electronic spectroscopy. Direct evidence of coupling, presented as cross peaks in a 2D spectrum, can only be observed for a coupled two-level system. For coupling between multilevel energy states, which happens for most interesting systems,

2D optical spectroscopy can only indirectly infer their dynamics. With the development of 3D optical spectroscopy, this tool can be applied to investigate chemical dynamics of complex molecular systems with multilevel vibrational or electronic states. Direct observation of multistep energy transfers can be seen in a 3D spectrum with the presence of cross peaks. In the future works, we aim to investigate the multi-step energy transfers in photosynthetic pigment-protein complexes with our developed 3D electronic spectroscopic technique. In biological photosynthetic complexes such as light-harvesting complex II (LHCII), the 14 excitonic states are closely spaced in a congested linear or 2D absorptive spectrum. By resolving energy transfers into additional frequency axis as compared to 2D electronic spectroscopy, 3D electronic spectroscopy provides more valuable insights to the complex energy transfer processes in plants. By correlating the evolution of different 3D cross peaks as a function of both population times, energy transfer dynamics in LHCII can be elucidated with minimum ambiguity, and the role of the antennas in plants can be further understood.

With the advancement in the field of multidimensional optical spectroscopy, new experiments that study higher-order signals are constantly being proposed. In combination with theoretical modeling, it is our hope that the dynamics and kinetics of LHCII can be eventually solved to understand the role of the antenna complexes in photosynthetic complexes.

Appendix

MATLAB Files

A.1 sum_data_automated.m

```
%%%This program sums up the collected data set for 2D spectroscopy%%%

clc
clear all

for nf=1:34; %%%number of delays

    tic

    f_date=20130620;
    start_file=20401;
    Tw_all=[0 20 50 80 100 120 150 180 200 250 300 350 400 500 800 1000 1500
    2000 2500 3000 3500 4000 4500 5000 5500 6000 6500 7000 7500 8000 8500
    9000 9500 10000];
    runs_per_delay=100;

    file_start=start_file+runs_per_delay*(nf-1);
    Tw=Tw_all(nf);

    file_end=file_start+runs_per_delay-1;

    all_file=file_start:file_end;
    app_file=all_file;

    all_file_1=(file_start+1):file_end;
    app_file_1=all_file_1;

    for n=app_file;

        loadfile_sig= sprintf('%d.%d.%d.sig.2D.txt',f_date,n,Tw);
        loadfile_ref= sprintf('%d.%d.%d.ref.2D.txt',f_date,n,Tw);

        load(loadfile_sig);
        load(loadfile_ref);

    end

    sigraw_k_file= sprintf('X%d_%d_%d_sig_2D',f_date,file_start,Tw);
    sigraw_k=eval(sigraw_k_file);
    refraw_k_file= sprintf('X%d_%d_%d_ref_2D',f_date,file_start,Tw);
    refraw_k=eval(refraw_k_file);

    for n=app_file_1;

        sigraw_n_file= sprintf('X%d_%d_%d_sig_2D',f_date,n,Tw);
        sigraw_n=eval(sigraw_n_file);
```

```

sigraw_k= sigraw_k+sigraw_n;

refraw_n_file= sprintf('X%d_%d_%d_ref_2D',f_date,n,Tw);
refraw_n=eval(refraw_n_file);
refraw_k= refraw_k+refraw_n;
end

p0_sigraw=sigraw_k;
p0_refraw=refraw_k;

savefile_sig= sprintf('%d.%d.%d.sig.sum.2D.txt',f_date,file_start,Tw);
savefile_ref= sprintf('%d.%d.%d.ref.sum.2D.txt',f_date,file_start,Tw);

save(savefile_sig,'p0_sigraw','-ascii');
save(savefile_ref,'p0_refraw','-ascii');

clear all

toc

end

```

A.2 phasecycling_1x3.m

```

%%%This program performs a 1x3 phase cycling scheme for 2D
spectroscopy%%%

clear all
close all

cplist=zeros(34,2);

for nf=1:34; %%%number of delays

f_date=20130620;
start_file=20401; %%%
Tw_all=[0 20 50 80 100 120 150 180 200 250 300 350 400 500 800 1000 1500
2000 2500 3000 3500 4000 4500 5000 5500 6000 6500 7000 7500 8000 8500
9000 9500 10000];

runs_per_delay=100;

file_0=start_file+runs_per_delay*(nf-1);
Tw=Tw_all(nf);

loadfile_sigsum= sprintf('%d.%d.%d.sig.sum.2D.txt',f_date,file_0,Tw);
load(loadfile_sigsum);
p0_sigraw_file= sprintf('X%d_%d_%d_sig_sum_2D',f_date,file_0,Tw);
p0_sigraw=eval(p0_sigraw_file);

loadfile_refsum= sprintf('%d.%d.%d.ref.sum.2D.txt',f_date,file_0,Tw);
load(loadfile_refsum);
p0_refraw_file= sprintf('X%d_%d_%d_ref_sum_2D',f_date,file_0,Tw);
p0_refraw=eval(p0_refraw_file);

[a,b]=size(p0_sigraw);

```

```

nstep_0=b/2;
for q=1:nstep_0
    q1=2*q;
    q2=2*q-1;
    p0_ref(:,q)=(p0_refraw(:,q1))-(p0_refraw(:,q2));
    p0_sig(:,q)=(p0_sigraw(:,q1))-(p0_sigraw(:,q2));
end
p0=p0_sig./p0_ref;

[g,h]=size(p0);          %%%%set params
probe_gradient=0.20968;
probe_y_offset=619.514;
disp_probe_start=640;
disp_probe_end=690;
ccd_start=round((disp_probe_start-probe_y_offset)/probe_gradient);
ccd_end=round((disp_probe_end-probe_y_offset)/probe_gradient);
ccd_diff=ccd_start-1;

stepsize=7e-15;
cen_wave=715e-9;
cen_freq=3e8/cen_wave;
pad=513;
ccd_strip_wavelength=665;
ccd_strip=(round((ccd_strip_wavelength-probe_y_offset)/probe_gradient))-
ccd_diff;
diagcutmax=690;

projw5=[3e8*1e-12/(disp_probe_end*1e-9) 3e8*1e-12/(disp_probe_start*1e-
9)];
projw3=[projw5(1) projw5(2)];
projw1=projw3;

contourlvl=16;
lead=1;
lag=1;

y=linspace(cen_freq-(0.5/(stepsize)),cen_freq+(0.5/(stepsize)),pad);
%%%%calibrate axes
y=y./1e12;

for n=ccd_start:ccd_end;
    u(n-ccd_diff)=(probe_gradient*n+probe_y_offset)*1e-9;
end
x=3e8*1e-12./(u);

nstep=h/3;
for k=1:nstep
    k1=3*k-2;
    k2=3*k-1;
    k3=3*k;
    p0a=-log(p0);

    inv1(:,k)=(ifft(p0a(:,k1)));
    zero1=inv1(1:(g/2),:);
    for1=fft(zero1,g);

    inv2(:,k)=(ifft(p0a(:,k2)));
    zero2=inv2(1:(g/2),:);
    for2=fft(zero2,g);

```

```

    inv3(:,k)=(ifft(p0a(:,k3)));
    zero3=inv3(1:(g/2),:);
    for3=fft(zero3,g);

    sig0(:,k)=p0a(:,k1).*exp(i*0) + p0a(:,k2).*exp(i*2*pi/3) +
    p0a(:,k3).*exp(i*4*pi/3);

end

y_osci=linspace(0,(nstep-1)*stepsize*1e15,nstep);

sig2=sig0;          %%%%%pure absorptive
sig2=sig2(ccd_start:ccd_end,:);

% triwin= 1 - 1/nstep*(0:nstep-1);  %%apodization
% for nn=1:239
%     sig2(nn,:)=sig2(nn,:).*triwin;
% end
% sig2(:,1)=0.5*sig2(:,1);

sig3=fftshift(fft(sig2.',pad),1);
sig3=-sig3/3;

sig1r=for1+ for2.*exp(i*2*pi/3)+ for3.*exp(i*4*pi/3);  %%%%%rephasing
sig4r=sig1r;
sig4r=sig4r(ccd_start:ccd_end,:);

sig5r=fftshift(fft(sig4r.',pad),1);
sig5r=-sig5r/3;
rphase=sig5r;
actrphase=sig5r;

sig1nr=for1+ for2.*exp(-i*2*pi/3)+ for3.*exp(-i*4*pi/3);  %%%%%non-
rephasing
sig4nr=sig1nr;
sig4nr=sig4nr(ccd_start:ccd_end,:);

sig5nr=fftshift(fft(sig4nr.',pad),1);
sig5nr=-sig5nr/3;
nrphase=flipdim(sig5nr,1);
actnrphase=sig5nr;

pureabs=rphase+nrphase;

for k=1:pad          %%%%%moving average

    sigavg=movavg(sig3(k,:),lead,lag,1);
    sig3(k,:)=sigavg;

    sigavg1=movavg(rphase(k,:),lead,lag,1);
    rphase(k,:)=sigavg1;

    sigavg2=movavg(nrphase(k,:),lead,lag,1);
    nrphase(k,:)=sigavg2;

    sigavg3=movavg(pureabs(k,:),lead,lag,1);

```

```

    pureabs(k,:)=sigavg3;

end

realname=['real 3x1 zoom ', num2str(Tw),' fs'];
stripname=['real 3x1 ', num2str(ccd_strip_wavelength),' nm'];

pic=figure;
contourf(x,y,real(sig3),contourlvl);colorbar;title(realname);xlabel('\omega_t (THz)','FontSize',10);ylabel('\omega_\tau (THz)','FontSize',10)
%%real 1x3 zoom
hold on
plot(x,x,'Linewidth',2,'Color','white');
hold off
axis image
axis([projw5(1) projw5(2) projw3(1) projw3(2)])
caxis([-max(max(real(sig3))) max(max(real(sig3)))])
% caxis([-0.019 0.019])

% savepic= sprintf('%d.%d.sum.2D.tiff',f_date,Tw);
% saveas(pic,savepic,'tiff')

%%%%%% Pick out cross peaks

cpy=457;
[donotcare,cpy_indx]=min(abs(cpy-y));

cpx=448;
[donotcare,cpx_indx]=min(abs(cpx-x));

sig4=real(sig3);

cplist(nf,1)=Tw;

for ncpy=-2:2

    for ncpix=-2:2

        cplist(nf,2)= cplist(nf,2)+sig4(cpy_indx+ncpy,cpx_indx+ncpix);

    end
end

cplist(nf,2)=cplist(nf,2)./25;

% clear all
% close all
end

```

A.3 sum_data_automated_3D.m

```

%%%This program sums up the collected data set for 3D spectroscopy%%%

clc
clear all
close all

for nf=0:146; %%%number of pump sequence

```



```

tic

f_date=20130529; %%%
file_num=1; %%%
t2=300;
Tw=800;
file_start=1; %%%
runs_per_delay=140; %%%
file_end=file_start+runs_per_delay-1;

all_file=file_start:file_end;
app_file=all_file;

all_file_1=(file_start+1):file_end;
app_file_1=all_file_1;

for n=app_file; %%%number of averages

    loadfile_sig=
sprintf('%d.%d.%d.%d.%d.sig.2D.txt',f_date,file_num,nf,n,t2,Tw);
    loadfile_ref=
sprintf('%d.%d.%d.%d.%d.ref.2D.txt',f_date,file_num,nf,n,t2,Tw);

    load(loadfile_sig);
    load(loadfile_ref);

end

sigraw_k_file=
sprintf('X%d_%d_%d_%d_%d_sig_2D',f_date,file_num,nf,file_start,t2,Tw)
;
sigraw_k=eval(sigraw_k_file);
refraw_k_file=
sprintf('X%d_%d_%d_%d_%d_ref_2D',f_date,file_num,nf,file_start,t2,Tw)
;
refraw_k=eval(refraw_k_file);

for n=app_file_1;

    sigraw_n_file=
sprintf('X%d_%d_%d_%d_%d_sig_2D',f_date,file_num,nf,n,t2,Tw);
    sigraw_n=eval(sigraw_n_file);
    sigraw_k= sigraw_k+sigraw_n;

    refraw_n_file=
sprintf('X%d_%d_%d_%d_%d_ref_2D',f_date,file_num,nf,n,t2,Tw);
    refraw_n=eval(refraw_n_file);
    refraw_k= refraw_k+refraw_n;
end

p0_sigraw=sigraw_k;
p0_refraw=refraw_k;

savefile_sig=
sprintf('%d.%d.%d.%d.%d.sig.sum.2D.txt',f_date,file_num,nf,t2,Tw);
savefile_ref=
sprintf('%d.%d.%d.%d.%d.ref.sum.2D.txt',f_date,file_num,nf,t2,Tw);

```

```

save(savefile_sig, 'p0_sigraw', '-ascii');
save(savefile_ref, 'p0_refraw', '-ascii');

```

```

toc
clear all

```

```

end

```

A.4 pc3D3x1.m

```

%%This program performs a 3x3x3x1 phase cycling scheme for 3D
spectroscopy%%

```

```

clc
clear all
close all

```

```

f_date=20130616; %%%
file_num=1; %%%
t2=300;
Tw=2000;
tot_delay=140e-15;
stepsize=7e-15;
num_of_files=147;
pad1=179;

```

```

disp_probe_start=640;
disp_probe_end=690;

```

```

probe_gradient=0.20968;
probe_y_offset=619.514;
ccd_start=round((disp_probe_start-probe_y_offset)/probe_gradient);
ccd_end=round((disp_probe_end-probe_y_offset)/probe_gradient);

```

```

savefile_sig= sprintf('%d.%d.%d.%d.sum.3D.mat', f_date, file_num, t2, Tw);

```

```

save(savefile_sig, 'pad1');
save(savefile_sig, 'f_date', '-append');
save(savefile_sig, 't2', '-append');
save(savefile_sig, 'Tw', '-append');
save(savefile_sig, 'stepsize', '-append');
save(savefile_sig, 'num_of_files', '-append');
save(savefile_sig, 'disp_probe_start', '-append');
save(savefile_sig, 'disp_probe_end', '-append');
save(savefile_sig, 'probe_y_offset', '-append');
save(savefile_sig, 'probe_gradient', '-append');
save(savefile_sig, 'ccd_start', '-append');
save(savefile_sig, 'ccd_end', '-append');
save(savefile_sig, 'tot_delay', '-append');

```

```

%% Set param

```

```

[aa, bb, cc, dd, phase1, phase2, phase3] = pc3D3x1_param(tot_delay,
stepsize, num_of_files, ccd_start, ccd_end);

```

```

save(savefile_sig, 'aa', '-append');

```

```

save(savefile_sig, 'bb', '-append');
save(savefile_sig, 'cc', '-append');
save(savefile_sig, 'dd', '-append');
save(savefile_sig, 'phase1', '-append');
save(savefile_sig, 'phase2', '-append');
save(savefile_sig, 'phase3', '-append');

%% Chop scattered light

[sigdum] = pc3D3x1_chop(f_date, file_num, t2, Tw, aa, cc, dd, ccd_start,
ccd_end);

save(savefile_sig, 'sigdum', '-append');

%% Phase cycle first set

beta=[1 -1 1];

[sigdum2dfftpad] = pc3D3x1_phasecycle(aa, bb, cc, dd, phase1, phase2,
phase3, beta, sigdum, pad1);

save(savefile_sig, 'sigdum2dfftpad', '-append');

%% Reinitialize param

clc
clear all
close all

f_date=20130616; %%%
file_num=1; %%%
t2=300;
Tw=2000;

savefile_sig= sprintf('%d.%d.%d.%d.sum.3D.mat',f_date,file_num,t2,Tw);
loadfile_sig= sprintf('%d.%d.%d.%d.sum.3D.mat',f_date,file_num,t2,Tw);

%% Phase cycle second set

load(loadfile_sig, 'sigdum');
load(loadfile_sig, 'aa');
load(loadfile_sig, 'bb');
load(loadfile_sig, 'cc');
load(loadfile_sig, 'dd');
load(loadfile_sig, 'phase1');
load(loadfile_sig, 'phase2');
load(loadfile_sig, 'phase3');
load(loadfile_sig, 'pad1');

charlie=[1 -1 -1];

[sigdum2dfftpad1] = pc3D3x1_phasecycle(aa, bb, cc, dd, phase1, phase2,
phase3, charlie, sigdum, pad1);

save(savefile_sig, 'sigdum2dfftpad1', '-append');

%% ReReinitialize param

```

```

clc
clear all
close all

f_date=20130616; %%%
file_num=1; %%%
t2=300;
Tw=2000;

savefile_sig= sprintf('%d.%d.%d.%d.sum.3D.mat',f_date,file_num,t2,Tw);
loadfile_sig= sprintf('%d.%d.%d.%d.sum.3D.mat',f_date,file_num,t2,Tw);

%% Absorptive

load(loadfile_sig,'sigdum2dfftpad');
load(loadfile_sig,'sigdum2dfftpad1');
load(loadfile_sig,'aa');
load(loadfile_sig,'pad1');

[sigdumabspad] = pc3D3x1_absorptive(sigdum2dfftpad, sigdum2dfftpad1, aa,
pad1);

save(savefile_sig,'sigdumabspad','-append');

%% ReReReinitialize param

clc
clear all
close all

f_date=20130531; %%%
file_num=1; %%%
t2=300;
Tw=5000;

savefile_sig= sprintf('%d.%d.%d.%d.sum.3D.mat',f_date,file_num,t2,Tw);
loadfile_sig= sprintf('%d.%d.%d.%d.sum.3D.mat',f_date,file_num,t2,Tw);

%% Plot 3D spectrum

load(loadfile_sig,'sigdumabspad');
load(loadfile_sig,'ccd_start');
load(loadfile_sig,'ccd_end');
load(loadfile_sig,'stepsize');
load(loadfile_sig,'pad1');
load(loadfile_sig,'probe_gradient');
load(loadfile_sig,'probe_y_offset');
load(loadfile_sig,'disp_probe_start');
load(loadfile_sig,'disp_probe_end');

tweak=1.7;

figure
pc3D3x1_display(sigdumabspad, ccd_start, ccd_end, stepsize, pad1,
probe_gradient, probe_y_offset, disp_probe_start, disp_probe_end, tweak)

```

A.5 pc3D3x1_param.m

```

%%This function sets the parameters used in the experiment%%

function [aa, bb, cc, dd, phase1, phase2, phase3] =
pc3D3x1_param(tot_delay, stepsize, num_of_files, ccd_start, ccd_end)

npc1=3;
npc2=3;
npc3=3;

phase1 = linspace(0, (2*pi)-(2*pi/npc1), npc1);
phase2 = linspace(0, (2*pi)-(2*pi/npc2), npc2);
phase3 = linspace(0, (2*pi)-(2*pi/npc3), npc3);

aa=ccd_end-ccd_start+1;
bb=(tot_delay/stepsize)+1;
bb=fix(bb);
cc=(bb*bb)/num_of_files;
cc=fix(cc);
dd=num_of_files;

```

A.6 pc3D3x1_chop.m

```

%%This function performs the removal of scattered light in the data%%

function [sigdum] = pc3D3x1_chop(f_date, file_num, t2, Tw, aa, cc, dd,
ccd_start, ccd_end)

%% minus scatter ligh, normalize signal against reference

npc1=3;
npc2=3;
npc3=3;

sigdum=zeros(aa,cc*npc1*npc2*npc3,dd);

p0_ref=zeros(aa,cc*npc1*npc2*npc3);
p0_sig=zeros(aa,cc*npc1*npc2*npc3);

for np=0:(dd-1)

    tic

    loadfile_sig=
sprintf('%d.%d.%d.%d.%d.sig.sum.2D.txt',f_date,file_num,np,t2,Tw);
    loadfile_ref=
sprintf('%d.%d.%d.%d.%d.ref.sum.2D.txt',f_date,file_num,np,t2,Tw);
    load(loadfile_sig);
    load(loadfile_ref);

    p0_sigraw_file=
sprintf('X%d_%d_%d_%d_sig_sum_2D',f_date,file_num,np,t2,Tw);
    p0_sigraw=eval(p0_sigraw_file);

    p0_refraw_file=
sprintf('X%d_%d_%d_%d_ref_sum_2D',f_date,file_num,np,t2,Tw);
    p0_refraw=eval(p0_refraw_file);

```

```

    for q=1:(cc*npc1*npc2*npc3)
        q1=2*q;
        q2=2*q-1;
        p0_ref(:,q)=(p0_refraw(ccd_start:ccd_end,q1))-
        (p0_refraw(ccd_start:ccd_end,q2));
        p0_sig(:,q)=(p0_sigraw(ccd_start:ccd_end,q1))-
        (p0_sigraw(ccd_start:ccd_end,q2));

    end

    p0a=p0_sig./p0_ref;
    p0=-log(p0a);

    sigdum(:, :, np+1)=p0;

    toc
end

```

A.7 pc3D3x1_phasecycle.m

```

%%This function performs the 3x3x3x1 phase cycling scheme%%

function [sigdum2dfftpad] = pc3D3x1_phasecycle(aa, bb, cc, dd, phase1,
phase2, phase3, beta, sigdum, pad1)

npc1=3;
npc2=3;
npc3=3;

%% 1x3 phase cycle

sigdumpcpc_dim=zeros(aa,cc,dd);
sigdumpc=zeros(aa,cc);

pp11 = exp(-1i * (beta(1)*phase1(1) + beta(2)*phase2(1) +
beta(3)*phase3(1)));
pp12 = exp(-1i * (beta(1)*phase1(2) + beta(2)*phase2(1) +
beta(3)*phase3(1)));
pp13 = exp(-1i * (beta(1)*phase1(3) + beta(2)*phase2(1) +
beta(3)*phase3(1)));
pp21 = exp(-1i * (beta(1)*phase1(1) + beta(2)*phase2(2) +
beta(3)*phase3(1)));
pp22 = exp(-1i * (beta(1)*phase1(2) + beta(2)*phase2(2) +
beta(3)*phase3(1)));
pp23 = exp(-1i * (beta(1)*phase1(3) + beta(2)*phase2(2) +
beta(3)*phase3(1)));
pp31 = exp(-1i * (beta(1)*phase1(1) + beta(2)*phase2(3) +
beta(3)*phase3(1)));
pp32 = exp(-1i * (beta(1)*phase1(2) + beta(2)*phase2(3) +
beta(3)*phase3(1)));
pp33 = exp(-1i * (beta(1)*phase1(3) + beta(2)*phase2(3) +
beta(3)*phase3(1)));

```

```

pp41 = exp(-1i * (beta(1)*phase1(1) + beta(2)*phase2(1) +
beta(3)*phase3(2)));
pp42 = exp(-1i * (beta(1)*phase1(2) + beta(2)*phase2(1) +
beta(3)*phase3(2)));
pp43 = exp(-1i * (beta(1)*phase1(3) + beta(2)*phase2(1) +
beta(3)*phase3(2)));
pp51 = exp(-1i * (beta(1)*phase1(1) + beta(2)*phase2(2) +
beta(3)*phase3(2)));
pp52 = exp(-1i * (beta(1)*phase1(2) + beta(2)*phase2(2) +
beta(3)*phase3(2)));
pp53 = exp(-1i * (beta(1)*phase1(3) + beta(2)*phase2(2) +
beta(3)*phase3(2)));
pp61 = exp(-1i * (beta(1)*phase1(1) + beta(2)*phase2(3) +
beta(3)*phase3(2)));
pp62 = exp(-1i * (beta(1)*phase1(2) + beta(2)*phase2(3) +
beta(3)*phase3(2)));
pp63 = exp(-1i * (beta(1)*phase1(3) + beta(2)*phase2(3) +
beta(3)*phase3(2)));

```

```

pp71 = exp(-1i * (beta(1)*phase1(1) + beta(2)*phase2(1) +
beta(3)*phase3(3)));
pp72 = exp(-1i * (beta(1)*phase1(2) + beta(2)*phase2(1) +
beta(3)*phase3(3)));
pp73 = exp(-1i * (beta(1)*phase1(3) + beta(2)*phase2(1) +
beta(3)*phase3(3)));
pp81 = exp(-1i * (beta(1)*phase1(1) + beta(2)*phase2(2) +
beta(3)*phase3(3)));
pp82 = exp(-1i * (beta(1)*phase1(2) + beta(2)*phase2(2) +
beta(3)*phase3(3)));
pp83 = exp(-1i * (beta(1)*phase1(3) + beta(2)*phase2(2) +
beta(3)*phase3(3)));
pp91 = exp(-1i * (beta(1)*phase1(1) + beta(2)*phase2(3) +
beta(3)*phase3(3)));
pp92 = exp(-1i * (beta(1)*phase1(2) + beta(2)*phase2(3) +
beta(3)*phase3(3)));
pp93 = exp(-1i * (beta(1)*phase1(3) + beta(2)*phase2(3) +
beta(3)*phase3(3)));

```

```

for np=1:dd

```

```

    tic

```

```

        sigdumre = reshape(sigdum(:,:,np), [aa cc*npc1*npc2*npc3]);

```

```

        for k=1:cc

```

```

            sigdumpc(:,k) = (sigdumre(:,npc1*npc2*npc3*k-26) * pp11) +
(sigdumre(:,npc1*npc2*npc3*k-25) * pp12) + (sigdumre(:,npc1*npc2*npc3*k-
24) * pp13) + (sigdumre(:,npc1*npc2*npc3*k-23) * pp21) +
(sigdumre(:,npc1*npc2*npc3*k-22) * pp22) + (sigdumre(:,npc1*npc2*npc3*k-
21) * pp23) + (sigdumre(:,npc1*npc2*npc3*k-20) * pp31) +
(sigdumre(:,npc1*npc2*npc3*k-19) * pp32) + (sigdumre(:,npc1*npc2*npc3*k-
18) * pp33) + (sigdumre(:,npc1*npc2*npc3*k-17) * pp41) +
(sigdumre(:,npc1*npc2*npc3*k-16) * pp42) + (sigdumre(:,npc1*npc2*npc3*k-
15) * pp43) + (sigdumre(:,npc1*npc2*npc3*k-14) * pp51) +
(sigdumre(:,npc1*npc2*npc3*k-13) * pp52) + (sigdumre(:,npc1*npc2*npc3*k-
12) * pp53) + (sigdumre(:,npc1*npc2*npc3*k-11) * pp61) +
(sigdumre(:,npc1*npc2*npc3*k-10) * pp62) + (sigdumre(:,npc1*npc2*npc3*k-

```

```

9) * pp63) + (sigdumre(:,npc1* npc2* npc3* k-8) * pp71) +
(sigdumre(:,npc1* npc2* npc3* k-7) * pp72) + (sigdumre(:,npc1* npc2* npc3* k-
6) * pp73) + (sigdumre(:,npc1* npc2* npc3* k-5) * pp81) +
(sigdumre(:,npc1* npc2* npc3* k-4) * pp82) + (sigdumre(:,npc1* npc2* npc3* k-
3) * pp83) + (sigdumre(:,npc1* npc2* npc3* k-2) * pp91) +
(sigdumre(:,npc1* npc2* npc3* k-1) * pp92) + (sigdumre(:,npc1* npc2* npc3* k)
* pp93);

    end

    sigdumpcpc_dim(:, :, np) = (1/(npc1* npc2* npc3)).*sigdumpc;

    toc

end

%% rearrange and fix correct dimension

sigdumdim = zeros(aa,bb*bb);
sigdumpcpc=zeros(aa,bb,bb);

for nn=1:dd

    for mm=1:cc

        sigdumdim(:, ((nn-1)*cc)+mm)=sigdumpcpc_dim(:, mm, nn);

    end
end

for pp=1:bb

    for qq=1:bb

        sigdumpcpc(:, qq, pp)=sigdumdim(:, (pp-1)*bb+qq);

    end
end

%% 1x2 fftpad

sigdum2dfftpads=zeros(aa,pad1,pad1);
triwin= 1 - 1/bb*(0:bb-1);

for np=1:aa

    tic

    sigdum2d=reshape(sigdumpcpc(np, :, :), [bb bb]);

    %     for npp=1:bb
    %
    %         sigdum2d(:, npp)=sigdum2d(:, npp).*triwin.';
    %     end
    %
    %     for npp=1:bb
    %
    %         sigdum2d(npp, :)=sigdum2d(npp, :).*triwin;

```



```

%      end
%
sigdum2d(1,1)=0.5*sigdum2d(1,1);

sigdum2dffft1=fftshift(fft2(sigdum2d,pad1,pad1));
sigdum2dffftpad(np, :, :)=sigdum2dffft1;

toc
end

```

pc3D3x1_absorptive.m

```

%%This function retrieves a purely absorptive spectrum%%

function [sigdumabspad] = pc3D3x1_absorptive(sigdum2dffftpad,
sigdum2dffftpad1, aa, pad1)

%% Absorptive

sigdumabspad = zeros(aa,pad1,pad1);

for mm = 1:pad1

    sigdumabspad(:, :, mm) = 0.5*(sigdum2dffftpad(:, :, mm) +
sigdum2dffftpad1(:, :, pad1-mm+1));

end

```

A.8 pc3D3x1_display.m

```

%%This function plots the 3D spectrum%%

function pc3D3x1_display(sigdumabspad, ccd_start, ccd_end, stepsize,
pad1, probe_gradient, probe_y_offset, disp_probe_start, disp_probe_end,
tweak)

%% Define axis

cen_wave=715e-9;
cen_freq=3e8/cen_wave;

ccd_diff=ccd_start-1;

freq_tau_pad=1e-12*linspace(cen_freq+(0.5/(stepsize)),cen_freq-
(0.5/(stepsize)),pad1);
for n=ccd_start:ccd_end;
    u(n-ccd_diff)=(probe_gradient*n+probe_y_offset)*1e-9;
end
freq_probe=3e8*1e-12./(u);

[Freq_Xpad, Freq_Ypad, Freq_Zpad]=
meshgrid(freq_tau_pad,freq_probe,freq_tau_pad);

projw5=[3e8*1e-12/(disp_probe_end*1e-9) 3e8*1e-12/(disp_probe_start*1e-
9)];
projw3=[projw5(1) projw5(2)];
projw1=projw3;

```

```

%% Pure Absorptive pad

V = tweak*max(max(max(real(sigdumabspad))));    %%% Maximum Value

f = 1/1;                                         %%% Twiddle Factor

p1=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad),
0.95*V), 'FaceColor', 'red', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p1);
alpha(p1,0.2)

p2=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad),
0.75*V), 'FaceColor', 'red', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p2);
alpha(p2,0.2)

p3=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad),
0.55*V), 'FaceColor', 'red', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p3);
alpha(p3,0.2)

p4=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad),
0.35*V), 'FaceColor', 'red', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p4);
alpha(p4,0.2)

p5=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad),
0.25*V), 'FaceColor', 'red', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p5);
alpha(p5,0.2)

p6=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad),
0.15*V), 'FaceColor', 'red', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p6);
alpha(p6,0.2)

p7=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad),
-0.95*f*V), 'FaceColor', 'blue', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p7);
alpha(p7,0.2)

p8=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad),
-0.75*f*V), 'FaceColor', 'blue', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p8);
alpha(p8,0.2)

p9=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad),
-0.55*f*V), 'FaceColor', 'blue', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p9);
alpha(p9,0.2)

p10=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad,
real(sigdumabspad), -0.35*f*V), 'FaceColor', 'blue', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p10);
alpha(p10,0.2)

p11=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad,
real(sigdumabspad), -0.25*f*V), 'FaceColor', 'blue', 'EdgeColor', 'none');

```

```

isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p11);
alpha(p11,0.2)

p12=patch(isosurface(Freq_Xpad, Freq_Ypad, Freq_Zpad,
real(sigdumabspad), -0.15*f*V), 'FaceColor', 'blue', 'EdgeColor', 'none');
isonormals(Freq_Xpad, Freq_Ypad, Freq_Zpad, real(sigdumabspad), p12);
alpha(p12,0.2)

view(3);
daspect([1 1 1]);

grid on;
box on;
camlight;
camlight(-80,-10);
lighting phong;

% title(['Pure absorptive pad' , num2str(beta)])
ylabel('\omega_5 / THz');
xlabel('\omega_1 / THz');
zlabel('\omega_3 / THz');
axis([projw3(1) projw3(2) projw5(1) projw5(2) projw3(1) projw3(2)])

```

A.9 pc3D3x1_slice.m

```

%%%This function takes a slice of the 3D spectrum at a certain w1
frequency%%%

clc
clear all
close all

f_date=20130531; %%%
file_num=1; %%%
t2=300;
Tw=5000;

% savefile_sig= sprintf('%d.%d.%d.%d.sum.3D.mat',f_date,file_num,t2,Tw);
loadfile_sig= sprintf('%d.%d.%d.%d.sum.3D.mat',f_date,file_num,t2,Tw);

load(loadfile_sig,'pad1');
load(loadfile_sig,'probe_gradient');
load(loadfile_sig,'probe_y_offset');
load(loadfile_sig,'disp_probe_start');
load(loadfile_sig,'disp_probe_end');
load(loadfile_sig,'sigdumabspad');
load(loadfile_sig,'ccd_start');
load(loadfile_sig,'ccd_end');
load(loadfile_sig,'stepsize');

ccd_diff=ccd_start-1;
cen_wave=715e-9;
cen_freq=3e8/cen_wave;
contourlvl=16;
% lead=15;
% lag=20;

freq_tau_pad=1e-12*linspace(cen_freq+(0.5/(stepsize)),cen_freq-
(0.5/(stepsize)),pad1);

```

```

for n=ccd_start:ccd_end;
    u(n-ccd_diff)=(probe_gradient*n+probe_y_offset)*1e-9;
end
freq_probe=3e8*1e-12./(u);

projw5=[3e8*1e-12/(disp_probe_end*1e-9) 3e8*1e-12/(disp_probe_start*1e-9)];
projw3=[projw5(1) projw5(2)];
projw1=projw3;

for n=457:457; %n=441:465;

    slicew1=n;
    [donotcare,slicew1_indx]=min(abs(slicew1-freq_tau_pad));

    slice3d_w1=reshape(sigdumabspad(:,slicew1_indx,:), [ccd_end-ccd_start+1
    pad1]);

    for k=1:pad1 %%%%%moving average

        % sigavg=movavg(slice3d_w1(:,k),lead,lag,1);
        % slice3d_w1(:,k)=sigavg;

        % win=10;
        % mask=ones(1,win)/win;
        % sigavg=filter(mask,1,slice3d_w1(:,k));
        % slice3d_w1(:,k)=sigavg;

        win=80;
        mask=ones(1,win)/win;
        sigavg=conv(slice3d_w1(:,k), mask, 'same');
        slice3d_w1(:,k)=sigavg;

    end

    realname=['real 3x1 zoom ', num2str(n), ' THz', ' t2 = ', num2str(t2),
    ' t4 = ', num2str(Tw) ];

    % pic=figure;
    % contourf(freq_probe, freq_tau_pad,
    real(slice3d_w1).',contourlv1);colorbar;title(realname);xlabel('\omega_5
    (THz)', 'FontSize',10);ylabel('\omega_3 (THz)', 'FontSize',10)
    % hold on;
    % plot(freq_probe,freq_probe,'Linewidth',1.5,'Color','white');
    % hold off;
    % axis image
    % axis([projw5(1) projw5(2) projw3(1) projw3(2)])
    % caxis([-max(max(real(slice3d_w1))) max(max(real(slice3d_w1)))])
    % % figureHandle = gcf;
    % % set(gca,'FontSize',15)
    % % set(findall(gcf,'type','text'),'fontSize',15)
    % % set(gcf, 'Position', get(0, 'ScreenSize'))
    % % caxis([-0.0015 0.0015])

    % pic=figure;
    % colormap((jet(1000)))
    % hold on
    % pcolor(freq_probe, freq_tau_pad, real(slice3d_w1).');shading interp

```

```

% colorbar;colorbar;title(realname);xlabel('\omega_5
(THz)','FontSize',10);ylabel('\omega_3 (THz)','FontSize',10) % this
essentially turns a 3d surface plot into a 2d plot
% axis([projw5(1) projw5(2) projw3(1) projw3(2)])
% caxis([-max(max(real(slice3d_w1))) max(max(real(slice3d_w1))))])
%
% [C,hfigc] = contour(freq_probe, freq_tau_pad, real(slice3d_w1).',[-
0.0001:0.0002:0.007]);
% set(hfigc, 'LineWidth',0.5);
% set(hfigc, 'Color', 'black');
% hold off
%
% hold on
% plot(freq_probe,freq_probe,'Linewidth',1.5,'Color','white');
%
% hold off;
% axis image;
% axis([projw5(1) projw5(2) projw3(1) projw3(2)])

cpy=457;
[donotcare,cpy_indx]=min(abs(cpy-freq_tau_pad));

cpx=457;
[donotcare,cpx_indx]=min(abs(cpx-freq_probe));

diagpeak=real(slice3d_w1(cpx_indx,cpy_indx));
factor_m=1;
normalized_spec=(real(slice3d_w1)./diagpeak).*factor_m;

cpyy=448; %457;448;444
[donotcare,cpyy_indx]=min(abs(cpyy-freq_tau_pad));

cpxx=444;
[donotcare,cpxx_indx]=min(abs(cpxx-freq_probe));

crosspeak=real(normalized_spec(cpxx_indx,cpyy_indx))

figure;
pcolor(freq_probe, freq_tau_pad, real(normalized_spec).');shading
interp; colorbar
% [hC,hC]=contourf(freq_probe, freq_tau_pad,
real(normalized_spec).',contourlvl);colorbar;title(realname);xlabel('\om
ega_5 (THz)','FontSize',10);ylabel('\omega_3 (THz)','FontSize',10)
% set(hC,'LineStyle','none');
hold on;
% [C,hfigc] = contour(freq_probe, freq_tau_pad,
real(normalized_spec).',[1:0.7:4.5]);
% set(hfigc, 'LineWidth',1);
% set(hfigc, 'Color', 'black');
% hold on;
plot(freq_probe,freq_probe,'Linewidth',1.5,'Color','white');
hold off;
axis image
axis([projw5(1) projw5(2) projw3(1) projw3(2)])
caxis([-max(max(real(normalized_spec)))
max(max(real(normalized_spec))))])
[cmap]=buildcmap('mbcgyrw');
colormap(cmap)

% savepic= sprintf('%d.%d.%d.%d.sum.2D.tiff',f_date,n,t2,Tw);

```

```
% saveas(pic,savepic,'tiff')  
  
% close all  
end
```