Ultrafast mid-infrared laser spectroscopy : applications and technique developments

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Ultrafast Mid-Infrared Laser Spectroscopy: Applications and Technique Developments

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Abstract

This thesis discusses applications and technique development in ultrafast mid-infrared nonlinear spectroscopies. After a brief introduction in Chapter 1, the vibrational dynamics of a metal carbonyl compound $\text{Os}_3(\text{CO})_{12}$ are investigated with mid-infrared (MIR) pump-probe spectroscopy in Chapter 2. Specifically, the vibrational relaxation dynamics of the four infrared active carbonyl stretching normal modes of $\text{Os}_3(\text{CO})_{12}$ were measured using broad-band frequency resolved MIR pump-probe spectroscopy. The frequency resolved pump-probe traces measured at the fundamental absorptions exhibit marked differences: The two axial modes at frequencies of 2068 cm^{-1} and 2034 cm^{-1} yield similar bi-exponential decay traces, while the two equatorial modes at 2014 cm^{-1} and 2002 cm^{-1} show an extra rising component. The axial-equatorial combination anharmonicity constants are found to be near zero. This results in the appearance of the pump-probe signals of these combination bands at the same frequencies as the fundamental transitions, leading to interference and the resultant anomalous rising features. If unaccounted for, these interferences may lead to erroneous conclusions about the dynamics of these vibrational stretches. To avoid such pitfalls, it is therefore imperative to resolve such ambiguities. No obvious direct vibrational energy transfer between the axial and equatorial CO stretching modes was observed.

Since perturbed free induction decay was observed in the MIR studies on

$\text{Os}_3(\text{CO})_{12}$, this phenomena was studied in further detail for a simpler system, namely $\text{W}(\text{CO})_6$, which is presented in Chapter 3. Perturbation theory in the interaction picture was used to model this coherent signal for the fundamental and overtone transitions, respectively. Broadband MIR pump-probe experiments were carried out to yield transient absorption spectra and kinetic signals at negative time delays. The experimental measurements were compared and fitted with the presented modeling, showing excellent agreement.

In the later part of this thesis, we explore the technical improvements towards pulse-shaping assisted two-dimensional (2D) spectroscopies in a pump-probe geometry with a phase cycling scheme. Chapter 4 outlines the development of pulse shaping technique, which produces shaped pulse trains for 2D spectroscopies in a pump-probe geometry. The generation of amplitude, phase, and polarization controlled pulses in the MIR tunable around $3.5\ \mu\text{m}$ is demonstrated. Two temporally separated sets of individually phase and amplitude shaped pulse profiles in the near-infrared are transferred into the MIR via two independent optical parametric amplification processes in two perpendicularly oriented nonlinear crystals in a common-path geometry. The resulting two shaped MIR light fields of orthogonal polarizations are temporally recombined in a birefringent material.

In Chapter 5, the necessary phase cycling schemes for 2D optical spectroscopy in a pump-probe beam geometry are presented. The theory is derived in the “rotating frame”, which increases the efficiency of the experiment by reducing the number of data points needed to be collected. 2D optical spectra are simulated for the phase cycling pump-probe experiment by solving the Liouville equation that describes the system-field interaction using a non-perturbative method. Pure 2D absorption spectra can be obtained by performing the desired phase cycling steps.

Chapter 1

Introduction

For the past few decades, ultrafast lasers have played a major role in the advancement of chemistry, physics, biophysics, material science etc. [1]. With the invention of the world’s fastest “camera” - the ultrafast laser - scientists are now able to take snapshots of molecules in motion [2]. These snapshots provide information on molecular structures as a function of time, to directly monitor chemical reaction dynamics. These time-resolved experiments have found applications spanning the gas phase [3–6] to the condensed phase [7–9], and from bulk materials [10–14] to nano-materials [15–19]. Recently, ultrafast techniques have been extended from one-dimensional optical spectroscopies to multi-dimensional optical spectroscopies, such as two-dimensional (2D) [20–24], three-dimensional (3D) [25–27] and even four-dimensional (4D) spectroscopy [28, 29]. The traditional pump-probe technique is one of the most extensively developed one-dimensional techniques and has been used extensively to investigate the ultrafast dynamics of chemical reactions, which require pico- to femtosecond time resolution [30–35]. Such experiments are relatively straightforward to perform, but for systems that exhibit congested absorption spectra or have complex structures, pump-probe

spectroscopies have difficulties to reveal the true story of the underlying chemical reaction dynamics. 2D and higher-dimensional spectroscopies are superior in dealing with such complicated absorption spectra due to improved structural sensitivity, by allowing disentanglement of couplings between different vibrational modes. It can be considered to be the optical analog of 2D nuclear magnetic resonance (NMR) [36–38]. As such 2D optical spectroscopies have gained wide popularity in recent years. Most recently there are new approaches to 2D optical spectroscopy, benefiting from the development of pulse shaping techniques and phase cycling theory [39–43].

MIR pump-probe spectroscopy is a common method of choice to study the molecular dynamics as well as chemical reaction dynamics in solution [44–49]. This is because the vibrational absorptions of many important chemical functional groups like -OH [50, 51], -NH₂ [52, 53], -CN [54–56], -CO [34, 35, 57] and so on, fall in the mid-infrared region - the so-called “finger print” region. Such modes can be used as a label of the target molecules during dynamics studies. With the fast development of the ultrafast Ti:Sapphire regenerative amplifier (RGA) laser systems, short pulses tunable around 800 nm with duration down to a few femtoseconds (fs) can be obtained easily. Optical parametric amplifiers (OPAs) and subsequent difference frequency generation (DFG) can then be deployed to convert the 800 nm pulses to the desired mid-infrared (MIR) region [58].

In Chapter 2, the vibrational relaxation dynamics of carbonyl stretching modes in Os₃(CO)₁₂ solution using broad-band pump-probe spectroscopy is investigated. Os₃(CO)₁₂ is a relatively complicated metallic tri-metal carbonyl compound with high symmetry. The twelve carbonyls give four IR active normal stretching modes, ranging from $\sim 2000\text{ cm}^{-1}$ to 2080 cm^{-1} . These four modes belong to two different types, axial and equatorial, respectively, thus it is an in-

interesting system to study the vibrational dynamics of these four different modes. The pump pulses used are broad-band ($\sim 110\text{ cm}^{-1}$), covering the absorptions of the entirety of the carbonyl normal modes.

As will be seen from the vibrational dynamic traces of carbonyls in $\text{Os}_3(\text{CO})_{12}$ in Chapter 2, coherent artifacts are very common during ultrafast dynamics measurements with short pulses. Perturbed free induction decay (PFID) is a type of coherent artifact that occurs at negative time delay between pump and probe pulses [59]. This phenomenon has been widely observed in vibrational spectroscopy from one-dimensional [60–62] to multi-dimensional cases [63,64]. It can interfere with the short term dynamics of interest, and therefore needs to be completely understood or alternatively suppressed by using appropriate filtering techniques [65,66]. The theory about PFID as it occurs in UV pump and IR probe studies have been reported in detail. In this dissertation, Chapter 3 discusses the PFID phenomenon in degenerate MIR pump-probe ultrafast spectroscopy both theoretically and experimentally. To reduce the complexity, instead of $\text{Os}_3(\text{CO})_{12}$, $\text{W}(\text{CO})_6$ is chosen as a simple experimental model to demonstrate the presented theory on PFID.

In a pump-probe experiment the transient absorption spectrum of $\text{Os}_3(\text{CO})_{12}$ is very congested and the dynamics of the various pathways can not be resolved individually, thus the energy relaxation processes in this system is particularly difficult to study. A better approach is coherent 2D-IR vibrational spectroscopy which is fast becoming an essential tool for ultrafast molecular structure and dynamic studies of more complicated systems [20,67–69].

Compared to conventional pump-probe spectroscopy, the experimental setup for coherent 2D-IR spectroscopy is far more complicated. In the widely used boxcar geometry [20,70–73], four beams with individual controllable time delays

arrive at the sample in a non-collinear phase matching condition. The nonlinear four wave mixing signal is generated in a different direction from the incoming beams. One advantage of this boxcar geometry is that the signal obtained is background free. However, the setup is typically very complicated and difficult to carry out. With the advent of pulse shaping techniques [74, 75], a totally collinear pulse train geometry for carrying out 2D optical spectroscopy has been reported [76]. The signal of interest propagates in the same direction as all the other unwanted nonlinear signals. Fortunately, those undesired contributions can be suppressed by using phase cycling methods as explained further below. This, however, necessitates phase stable pulse trains - a condition that is easily met with the use of pulse-shapers. Alternatively, a partial collinear setup has been demonstrated recently and is called 2D-IR spectroscopy in a pump-probe geometry [39, 40, 77, 78]. This design combines the advantages of both non-collinear phase-matched 2D spectroscopy and the totally collinear 2D spectroscopy. The pump pulse trains induce the nonlinear signals in the sample and the signal is heterodyne detected by the probe pulses. Pulse shaping enables the necessary phase stability of the pump pulse trains to be achieved. The signal of interest can be selected by controlling the pump pulse trains created by the pulse shaper. Therefore pulse shaping is a promising approach to 2D-IR spectroscopy.

In principle, laser pulses can be shaped in both the time and the frequency domain, since they form a Fourier transform pair. However, due to the limitations of the instrument response time, ultrafast pulse shaping has not been successfully achieved in the time domain. On the other hand, pulse shaping in the frequency domain using a spatial light modulator (SLM) within a 4-f configuration has been very successful [74, 75, 79]. The most widely used spatial light modulators are acousto-optic modulators (AOM) [80, 81] and liquid crystal

spatial light modulators (LC-SLM) [82–84]. AOMs can be used for phase and amplitude modulations of pulses ranging from the deep-UV to the MIR region with different modulator media. Contrary to that, the LC-SLM cannot reach to the MIR or deep-UV region due to the strong absorptions of the liquid crystal molecules.

In order to study the dynamics with pulse shaper assisted 2D-IR spectroscopy, shaped ultrafast pulse trains in the MIR are needed. None of these SLMs can achieve polarization control directly in the MIR. In fact, MIR shaped pulses with full control over amplitude, phase, and polarization is still a challenging problem. In Chapter 4, we will introduce a new computer programmable pulse shaping technique with full control of the MIR pulses via parametric transfer, called “CAPPUCCINO”. The design was chosen to be based on LC-SLMs due to the fact that high-resolution masks (600 pixels and above) are commercially available. Also the alignment is relatively simple and LC-SLMs are more efficient compared to AOMs.

Once the pulse trains for 2D-IR spectroscopy with a pump-probe geometry are formed, the next consideration is how to isolate the 2D-IR signals of interest. The “pump” pulse trains have the same propagation direction, while they have controllable relative phases. Therefore, the 2D-IR signals can be chosen by providing correct phases to the “pump” pulses, which is known as phase cycling. In Chapter 5, we will present the theory on phase cycling for 2D-IR spectroscopy. This theory is based on the phase cycling technique for completely collinear 2D coherent spectroscopies [85].

The arrangement of this dissertation is as follows:

Chapter 2 presents the vibrational relaxation dynamics of carbonyl stretching modes as studied by MIR pump-probe spectroscopy. The transient absorption

spectra, as well as the pump-probe signals of the fundamental and overtone transitions of the four CO stretching normal modes are compared and discussed.

Chapter 3 presents the theory of PFID as it occurs in degenerate IR pump-probe experiments in the interaction picture. We will also show the experimental PFID signals of the carbonyl stretching mode in $\text{W}(\text{CO})_6$, and compare the experimental results to simulations according to the presented theory. Ultimately, the PFID signals were suppressed from the experimental data using appropriate filtering techniques.

Chapter 4 exhibits the polarization pulse-shaping technique in the MIR via parametric transfer processes from shaped 800 nm and NIR pulses to shaped MIR pulses. We will provide two examples for MIR polarization pulse shaping and characterizations of the shaped pulses.

Chapter 5 applies the concepts of phase cycling and phase cycling scheme selection procedures to a 2D optical spectroscopy experiment, performed with a pump-probe beam geometry. The details of phase cycling theory as applied to a pump-probe geometry case will be outlined, as well as how to obtain a purely absorptive 2D spectrum. Numerical simulations that illustrate the principles are presented. This shows the efficacy of the introduced phase cycling schemes.

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Chapter 2

Ultrafast Vibrational Relaxation Dynamics of the Carbonyl Stretching Modes in $\text{Os}_3(\text{CO})_{12}$

2.1 Introduction

Ultrafast mid-infrared (MIR) spectroscopy has been a staple technique to study vibrational relaxation of molecules in the condensed phase [1, 2]. For the last few decades, transition metal carbonyl complexes have received considerable interest; In this chapter we reveal the potential complications in the assignment of IR signals of these species, and indeed other species with relatively complex vibrational structure. Photoactive transition metal carbonyl compounds play important roles in catalytic applications [3, 4], and have also been used to model systems that undergo carbonyl (CO) photo-addition reactions [5, 6]. Studying the ultrafast vibrational dynamics of metal carbonyl compounds is of great importance to understand photo-induced structural rearrangement processes, the

roles played by the local environment in condensed phase systems, as well as the specific reaction mechanisms of these species. These photochemical mechanisms have been investigated with a variety of ultrafast pump-probe experiments [7–9].

Studies of photo-decomposition and resultant photo-product vibrational relaxation have been reported for monometallic carbonyls $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [10–12], bi-metallic carbonyls like $\text{Mn}_2(\text{CO})_{10}$ [13, 14], and tri-metallic carbonyl clusters such as $\text{Ru}_3(\text{CO})_{12}$ [15], and $\text{Os}_3(\text{CO})_{10}(\text{r-diimine})$ [16]. It was found that following UV-Vis irradiation, a variety of wavelength dependent photo-products can be formed. Therefore, in order to characterize the generated photo-products and their individual vibrational dynamics, the relaxation dynamics of both reactants and products need to be studied.

The vibrational relaxation dynamics of simple metal carbonyl compounds like $\text{Cr}(\text{CO})_6$, $\text{W}(\text{CO})_6$ [17, 18], and $\text{Rh}(\text{CO})_2(\text{acac})$ [19, 20] have also been studied using IR pump-probe experiments and 2D coherent IR spectroscopy. Metal carbonyl clusters with highly complicated vibrational stretching spectra, such as $\text{Co}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ dissolved in CHCl_3 [21], and $\text{W}(\text{CO})_5(\text{X})$ ($\text{X} = \text{CS}, \text{CH}_3\text{CN}, \text{and } \text{CD}_3\text{CN}$) in a variety of alkane solvents [18] have been studied using a tunable sub-picosecond light source. Childs and coworkers measured the transient IR spectra in the vicinity of one of the apical CO stretching mode absorptions of $\text{Rh}_6(\text{CO})_{16}$ in CCl_4 with picosecond time resolved IR saturated spectroscopy [22]. Deconvolution of the observed transient absorption spectra revealed that the contributing fundamental (zero to single quanta transition, $0 \rightarrow 1$), overtone and combination bands (single to double quanta transition, $1 \rightarrow 2$), were significantly spectrally overlapped. However in their analysis, combination bands resulting from the total of the twelve apical COs were not taken into consideration, and it is not clear if these contributed to the observed transient

absorption spectra. In order to correctly analyze time dependent pump-probe traces and consequently acquire accurate dynamical information, it is essential to understand and correctly identify the various combination and overtone transitions, and be able to de-convolve and resolve the various overlapping features contributing to the pump-probe traces.

$\text{Os}_3(\text{CO})_{12}$ is an important multi-metallic carbonyl cluster that has been widely used in the synthesis of organometallic compounds [16, 23, 24], and also as a model to study photo-induced reaction mechanisms [5]. In the spectral region $\sim 2000\text{ cm}^{-1}$, there are four IR active CO fundamental stretching modes [25]. These four stretching modes are equally divided into two independent sets: axial and equatorial modes. As a result the transient absorption spectrum of $\text{Os}_3(\text{CO})_{12}$ is congested, containing the four fundamental ($0 \rightarrow 1$) IR-active transition bands and in principle, sixteen combination/overtone ($1 \rightarrow 2$) bands. In contrast, a system such as $\text{Rh}(\text{CO})_2(\text{acac})$ is much simpler [19, 20], as the transient absorption spectrum contains only two fundamental and six overtone/combination bands. $\text{Os}_3(\text{CO})_{12}$ is therefore a suitably complicated system that provides an excellent model to study and characterize the complications arising from overlapping spectral features.

To the best of our knowledge, this is the first study of the vibrational dynamics of the carbonyl cluster $\text{Os}_3(\text{CO})_{12}$. The frequency resolved ultrafast vibrational population relaxation dynamics of the four CO stretching normal modes of $\text{Os}_3(\text{CO})_{12}$ in CHCl_3 were measured using IR pump-probe spectroscopy. Interestingly, it is observed that the equatorial stretching modes show different vibrational dynamics from the axial stretching modes: a clear rising component for the equatorial modes is seen which is absent in the equivalent axial mode traces. Careful analysis shows that this behavior is due to overlapping of the

various fundamental and combination bands. The resultant interference complicates the interpretation of the observed dynamics and poses a potential pitfall in ultrafast vibrational spectroscopy of such molecules.

This chapter is based on our publication about CO dynamics in $\text{Os}_3(\text{CO})_{12}$ [26], and is arranged as follows: Section 2.2 describes the experimental setup and sample preparation method. Section 2.3 presents the transient absorption spectra of the CO stretching region, as well as the pump-probe signals of the fundamental and overtone transitions of the four CO stretching normal modes. Section 2.4 compares and discusses the vibrational dynamics traces of different CO stretching modes, as well as identifying the origin of the rising component that appears only in the equatorial mode traces. Whilst, Section 2.5 summarizes all the presented findings.

2.2 Ultrafast Mid-Infrared Pump-Probe Experiment

2.2.1 Ultrafast Laser System

The laser system used in these ultrafast IR pump-probe experiments consists of a Ti:Sapphire regenerative amplifier (Legend, Coherent, 1 kHz, 800 nm, 100 fs) with a Q-switched pump laser (Evolution, Coherent, 1 kHz, 527 nm,), the seed is provided by an oscillator (Vitesse, Coherent, 80 MHz, 800 nm, 100 fs). A dual path optical parametric amplifier (OPA)(Opera, Coherent) and a difference frequency generation (DFG) stage (DFG, Coherent) are used to obtain MIR pulses. The OPA converts the 800 nm pulse to two near IR beams through a 4 mm thick $\beta\text{-BaB}_2\text{O}_4$ crystal (BBO, type II). These two near IR pulses are mixed in a 2 mm

thick AgGaS₂ crystal (AGS, type II). Via the DFG, tunable ultrafast MIR (2.5 to 10 μm) pulses at a repetition rate of 1 kHz are generated by tuning the BBO and AGS crystal angles to achieve phase matching.

2.2.2 Pump-Probe Spectrometer

The MIR pump-probe schematic setup is shown in Figure 2.1. Since the MIR is not visible to the naked eyes, a He-Ne laser (633 nm) is coupled into the MIR beam paths via the Germanium window, to be used to achieve the alignment of the MIR. The generated MIR pulse energy after the DFG was measured to be $\sim 4 \mu\text{J}$. It was split into three channels: pump, probe, and reference pulses. Firstly, it was separated into two beams using a CaF₂ wedge window, the transmitted beam was used as the pump, whilst the reflected beam was divided into both probe and a reference by a 50 : 50 BaF₂ beam splitter. The fluence of the pump pulse is estimated to be $\sim 12 \text{ mJ}\cdot\text{cm}^{-2}$, and the energy ratio between the pump and probe was higher than 18 : 1. The pump pulse was optically chopped at 500 Hz. The pump and probe pulses were focused and overlapped after an off-axis parabolic mirror with a focal length of 160 mm.

The beam diameter of the MIR at the focal point D_F of the first parabolic mirror, defined as the diameter where the intensity is $1/e^2$ of the intensity of a Gaussian beam, can be estimated according to the formula $D_F = 4F\lambda/(\pi D_i)$, where F is the focal length of the first parabolic mirror (160 mm), D_i is the beam diameter at the first parabolic mirror ($\sim 1 \text{ cm}$), and λ is the center wavelength the MIR pulses ($\sim 2030 \text{ cm}^{-1}$). For the MIR spectrally centered at 2030 cm^{-1} , the beam diameter at the focal point is estimated to be $\sim 100 \mu\text{m}$. The intensity I of the pump pulses is estimated using $I = E/(\Delta t A)$, with E the pump pulse energy, Δt the full width half maximum pulse duration (FWHM), and A the

Figure 2.1: Schematic setup of MIR pump-probe experiment. SM1: Spherical mirror, $f = 100$ mm, SM2: Spherical mirror, $f = 150$ mm, Ir1: Iris, Ir2: Iris, Wd: CaF₂ wedge window, BS: CaF₂ beam splitter, 50 : 50, L1: $f = 150$ mm, L2: $f = 75$ mm, L3: $f = 75$ mm, L4: $f = 75$ mm, Chp: Optical chopper, Pol1: BaF₂ wire grid polarizer, (54.7°), Pol2: BaF₂ wire grid polarizer, (144.7°), PM1: Parabolic Mirror, $f = 160$ mm, PM2: Parabolic Mirror, $f = 160$ mm.)

area of the pump beam. The pump energy at the focal point is estimated to be 30% of the DFG output ($4\text{ }\mu\text{J}$), and the pulse duration is about 160 fs (taken from Section 2.2.3). Therefore the pump fluence at the focal point is $\sim 16\text{ mJ}\cdot\text{cm}^{-2}$.

At the focal point, the spatial overlap of the pump and probe pulses was achieved by aligning the two beams through a pin hole ($50\text{ }\mu\text{m}$ in diameter) simultaneously. The temporal overlap between the pump and probe was determined from the transient absorption signal of nonlinear optical materials with strong transient absorption properties (i.e. InAs), where the time zero position between pump and probe is where the transient absorption signal is maximum. The $\text{Os}_3(\text{CO})_{12}$ sample was placed at the focal point, to ensure that the pump and probe were overlapped both spatially and temporally. After the sample, the pump and probe beams were re-collimated by a second off-axis parabolic mirror, and the probe beam was frequency resolved in a monochromator (Dongwoo Opttron Co. DM320i, $f = 320\text{ mm}$, two 150 lines/mm gratings blazed at $4.0\text{ }\mu\text{m}$ and $6.0\text{ }\mu\text{m}$), and detected by a liquid N_2 cooled InSb detector (Infrared Associates. Inc.). The resolution of the monochromator for MIR at $5\text{ }\mu\text{m}$ was $\sim 2\text{ cm}^{-1}$ when the slit width was 0.2 mm . To measure the population-only dynamics, the polarization of the probe pulse was set to the magic angle of 54.7° with respect to the pump pulse, by the placement of a pair of wire-grid BaF_2 polarizers before and after the sample [27].

The MIR reference beam was detected by another InSb detector and sent to a integration boxcar. The pump-probe signal intensity was normalized to the reference pulse in the boxcar, this eliminates the fluctuations in the signal that were due to the laser instability. This was subsequently amplified in a lock-in amplifier, and the data acquired with a National Instruments BNC-2100, a purpose built Labview program was used to collect the data. The length of the

pump-probe delay time was limited to ~ 300 ps due to the limited travel distance of ~ 4.5 cm.

2.2.3 Characterization of Mid-Infrared Pulses

Figure 2.2: *The spectrum of the MIR laser pulses used as pump and probe.*

Figure 2.2 shows the the spectrum of the MIR pulses. The center frequency of the spectrum was tuned to $\sim 2030 \text{ cm}^{-1}$, with a spectral full width at half maximum (FWHM) of $\sim 120 \text{ cm}^{-1}$. The IR pulse duration was characterized by second harmonic generation (SHG) cross-correlation of the pump and probe pulses in a LiIO_3 crystal (0.4 mm, type I). The measurement and the Gaussian fit are shown in Figure 2.3. The FWHM of the cross-correlation was ~ 220 fs, this corresponds to a pulse duration of ~ 160 fs (assuming Gaussian temporal profiles).

Figure 2.3: *Cross-correlation between MIR pump and probe pulses. The polarization of probe pulse is at magic angle.*

2.2.4 Sample Preparation

$\text{Os}_3(\text{CO})_{12}$ powder (Oxkem Limited, U.K.) was dissolved in HPLC grade CHCl_3 (Sigma-Aldrich). The solubility of $\text{Os}_3(\text{CO})_{12}$ in CHCl_3 is low and the saturated solution with a concentration of $\sim 0.9 \text{ mM}$ was used. All the chemicals were used without any further purification. The sample was contained in a transmission cell comprising of two 2 mm thick CaF_2 windows with a sample thickness of $200 \mu\text{m}$ thickness. The solution provided an optical density of ~ 0.7 at the strongest CO stretching absorption centered at $\sim 2068 \text{ cm}^{-1}$.

2.3 Results

2.3.1 Structure and FTIR spectrum of $\text{Os}_3(\text{CO})_{12}$

As shown in Figure 2.4, the molecular structure of $\text{Os}_3(\text{CO})_{12}$ belongs to the D_{3h} point group [28]. The twelve CO groups are classified as axial (in red) and equatorial (in blue) [25]. The FTIR spectrum of $\text{Os}_3(\text{CO})_{12}$ in CHCl_3 was measured and is presented in Figure 2.5. There are four absorption bands from CO stretching modes observed around the 2000 cm^{-1} region, labeled as *a*, *b*, *c*, and *d*, respectively. These four bands are divided into two groups: the two stronger absorption bands, *a* at 2069 cm^{-1} and *b* at 2035 cm^{-1} are the axial normal modes whose components are exclusively from the local modes of the axial CO stretches; the two weaker bands *c* at 2015 cm^{-1} and *d* at 2000 cm^{-1} are the equatorial normal modes whose components are exclusively from the equatorial CO stretching local modes [25, 29]. The positions and relative intensities are in good agreement with previous literature values [25]. For clarity, the remainder of this chapter shall

Figure 2.4: *Structure of $\text{Os}_3(\text{CO})_{12}$. The axial carbonyls are in red and equatorial carbonyls are in blue.*

maintain this labeling system. The transition dipole moment of these bands were estimated by integrating the band areas, to give the values ~ 0.9 D, ~ 0.8 D, ~ 0.5 D, and ~ 0.4 D. The values for modes *a* and *b* are comparable to those in $\text{W}(\text{CO})_6$, ~ 1 D [30].

Figure 2.5: Ground state linear absorption spectrum of $\text{Os}_3(\text{CO})_{12}$ solution in CHCl_3 , with concentration of ~ 0.9 mM. The four fundamental transition bands are labeled as *a*, *b*, *c* and *d*, with frequencies peaked at 2069 cm^{-1} , 2035 cm^{-1} , 2015 cm^{-1} , 2000 cm^{-1} , respectively.

2.3.2 Transient Absorption Spectra

Transient absorption spectra were taken in the frequency range from 1975 to 2100 cm^{-1} at various time delays. As shown in Figure 2.6, there is no obvious time-dependent change of shape and position to the peaks. The four positive bands labeled as *a*, *b*, *c*, and *d*, are nominally assigned to the four fundamental transitions ($0 \rightarrow 1$) of the CO stretches consistent with the FTIR spectrum

(Figure 2.5). The intensities of bands c and d are much weaker than those of bands a and b . The four negative bands labeled as e , f , g and h centered at 2058 cm^{-1} , 2022 cm^{-1} , 2008 cm^{-1} and 1994 cm^{-1} , respectively, are assigned as the overtone transitions ($1 \rightarrow 2$), with overtone anharmonic shifts of $\Delta_{aa} \approx -10\text{ cm}^{-1}$, $\Delta_{bb} \approx -12\text{ cm}^{-1}$, $\Delta_{cc} \approx -6\text{ cm}^{-1}$ and $\Delta_{dd} \approx -8\text{ cm}^{-1}$, respectively. Shoulders i and j are nominally assigned as the combination bands between the two axial modes a and b . Positions and relative intensities of these combination bands will be presented in detail in the Section 2.4.

Figure 2.6: Transient absorption spectra at time delays 0 ps, 10 ps and 80 ps, respectively. Bands a , b , c , and d are the four fundamental transitions centered at 2068 cm^{-1} , 2034 cm^{-1} , 2014 cm^{-1} , and 2002 cm^{-1} , respectively. Bands e , f , g , and h are the individual overtone transitions centered at 2058 cm^{-1} , 2022 cm^{-1} , 2008 cm^{-1} and 1994 cm^{-1} , respectively. The two shoulders i and j contribute from axial-axial combination bands between modes a and b .

2.3.3 Pump-Probe Dynamic Traces

The entirety of the CO fundamental stretching normal modes were simultaneously excited by the broad-band pump. The frequency resolved kinetic measurements are presented in Figure 2.7. Traces A, B, C and D were measured at the fundamental absorption frequency of each mode, as were the individual overtone transitions E, F, G and H. The intensity of trace A was normalized to one at time zero, while the intensities of the remaining traces were scaled according to the transient absorption spectrum probed at a time delay of 200 ps. All traces were fitted with exponential functions convolved with Gaussian functions, representing the instrument response of ~ 160 fs. The negative features before time zero in traces C, D, E and F are due to perturbed free induction decay (PFID) [31]. Details about PFID signals will be discussed from both a theoretical and experimental stance in Chapter 3. A strong positive spike near zero time delay is observed in each trace, this is a well known artifact in one color pump-probe experiments resulting from coherent coupling between the pump and probe pulses [18, 30, 32]. These described coherent features are independent of the dynamics of the CO stretching vibrations, and as such will not be discussed in this chapter.

As can be seen, traces A and B have qualitatively similar dynamics to one another. Both can be fitted well with bi-exponential decays, consisting of a fast decaying component τ of $\sim 1\text{--}3$ ps, and a slow decaying component T_1 of $\sim 500\text{--}600$ ps. The kinetic traces C and D have qualitatively similar features but are markedly different from traces A and B. Instead of a fast decay as in traces A and B, there is an apparent rising component contributing to the traces C and D; also the relative amplitude of the slow decaying component T_1 is greatly reduced compared to those of traces A and B. Adequate fitting of traces C and D required three components, a fast rising component τ of $\sim 2\text{--}15$ ps, an inter-

Figure 2.7: Frequency resolved pump-probe traces and their numerical fits. The intensity of each trace was normalized to that of the trace at 2068 cm^{-1} at 200 ps . Traces A to D were probed at the fundamental transitions at 2068 cm^{-1} , 2034 cm^{-1} , 2014 cm^{-1} , and 2002 cm^{-1} , respectively. Traces E to H were probed at the overtone transitions at 2058 cm^{-1} , 2022 cm^{-1} , 2007 cm^{-1} and 1994 cm^{-1} , respectively. To enable easy comparison among all these traces, the absorption axis on the traces A to D was inverted relative to the traces E to H. All the traces were fitted (solid line in red) with exponential functions convolved with a Gaussian function representing the instrument response ($\sim 160\text{ fs}$), and the fitting results are summarized in Table 2.1.

mediate timescale rising component τ' of $\sim 50\text{--}150\text{ ps}$, as well as a slow decaying $T_1 \sim 400\text{--}750\text{ ps}$. The slow decaying component T_1 in C and D is less obvious compared to those of traces A and B, because of the dominance of the intermediate timescale rising τ' within the scan length ($\sim 300\text{ ps}$) of these measurements. The numerical fits of all the time constants and amplitudes factors are presented in Table 2.1. The listed fast time constants were obtained from shorter scan length experiments of greater temporal accuracy which are not presented. The slow decay T_1 values obtained may be not reliable, due to the limitation of the

travel length. By simply observing traces C and D, one may come to an erroneous conclusion that the observed rising components are indicative of excited state population transfer into the equatorial modes, arising from intra-molecular vibrational energy relaxation from axial modes. In the proceeding sections we will discuss in detail why this is not the case.

Since the pump-probe traces probed at the overtone transition frequencies also indicate the population relaxation dynamics of the first excited vibrational state [33, 34], the trace resolved at the overtone frequency is expected to be qualitatively similar to the trace resolved at fundamental frequency. Traces E, F, G and H are the pump-probe signals probed at the four overtone bands identified as *e*, *f*, *g* and *h* in Figure 2.6. To enable easy comparison between all traces the absorption axis on Figure 2.7(b) is inverted relative to Figure 2.7(a). The overtone traces were fitted with the same procedure as described above. Similar to the fundamental traces, the four overtones traces are separated into two groups, traces E and F (referring to the axial CO stretches) and traces G and H (referring to the equatorial CO stretches). The overtone traces E and F display a “plateau”, and are well fitted by a function consisting of a short exponential decay time constant τ of $\sim 1\text{--}3$ ps, a slow exponential decay time constant T_1 of $\sim 600\text{--}800$ ps, and a small contribution of an intermediate timescale exponential rising time constant τ' of $\sim 10\text{--}40$ ps. The overtone traces G and H are fitted with two decaying components, a fast exponential decay time constant τ of $\sim 5\text{--}30$ ps, and a slow exponential decay time constant T_1 of $\sim 400\text{--}600$ ps.

Interestingly, the traces G and H are distinctly different from traces C and D. This is initially surprising since as mentioned earlier the dynamics of the overtone traces are expected to resemble that of the fundamental traces. However, in traces G and H, there is no rising component as observed in traces C and D.

	A	B	C	D	E	F	G	H
τ	1 (1-3)	2 (1-3)	6 (2-10) 123	8 (2-15) 57	2 (1-3) 26	1 (1-3) 19	28 (10-30)	9 (5-20)
τ'	-	-	(50-150) 450	(50-150) 600	(10-40) 736	(10-40) 689	-	-
T_1	553 (500-600)	514 (500-600)	(400-700)	(450-750)	(650-800)	(600-800)	(400-600)	(400-600)
A_τ	0.245	0.175	-0.037	-0.011	0.159	0.220	0.033	0.014
$A_{\tau'}$	-	-	-0.134	-0.054	-0.033	-0.017	-	-
A_{T_1}	0.886	0.411	0.225	0.067	0.438	0.199	0.056	0.030

Table 2.1: Time constants (in ps) for the pump-probe traces in Figure 2.7 summarized from the dynamics fittings. A to D were measured at the fundamental frequencies, and E to H were at the overtone frequencies. τ is the short term time constant, τ' is the intermediate decaying constant, and T_1 is the slow decaying constant. Within the parentheses are the estimated error limits. A_τ , $A_{\tau'}$ and A_{T_1} are the amplitudes of the three time constants, respectively.

This suggests that the rising components observed in the equatorial fundamental traces C and D do not represent the intra-molecular population transfer. In order to understand the rising components observed in traces C and D, we have to be more careful with the combination bands assignment.

2.4 Discussion

2.4.1 Anharmonicity of the Combination Bands

As mentioned earlier, the four CO normal stretches of $\text{Os}_3(\text{CO})_{12}$ are divided into axial and equatorial modes, therefore there are two types of combination bands according to the coupling difference. The first type is the homo-combination band between axial and axial modes (axial-axial combination band), or between equatorial and equatorial modes (equatorial-equatorial combination band). The second type is the hetero-combination band between axial and equatorial modes (axial-equatorial combination band).

In Figure 2.6, the shoulders i and j are the homo-combination bands between the two axial modes a and b , with the fitted anharmonicity constant $\Delta_{ab} = -14.8 \pm 0.6 \text{ cm}^{-1}$. The homo-combination bands between the two weaker equatorial normal modes c and d are expected to be relatively weak and as a result their peak positions are not able to be resolved (hence exclusion from the fitting procedure described below).

The anharmonic shifts of the combination bands have been shown to depend on the geometry of the molecule by Mills and co-workers [35]. By considering the local mode effects of a Morse oscillator, the vibrational anharmonic shifts for molecules with different point group symmetry have been derived and compared

with experimental spectra [36–38]. Based on this method, the anharmonicities of the hetero-combination bands will be discussed in the following.

Symmetry and Anharmonicity

The vibrational energy of a polyatomic molecule can be expressed as [39]

$$E_v/hc = \sum_{k \leq k'} g_{kk'} l_k l_{k'} + \sum_i \omega_i (v_i + d_i/2) + \sum_{i \leq j} x_{ij} (v_i + d_i/2) (v_j + d_j/2) \quad (2.1)$$

where v_i is the number of the quanta in the normal modes, d_i is the degeneracy of vibration mode i , and l_k is the vibrational angular momentum of degenerate mode k . x_{ii} is the overtone anharmonicity constant for mode i and x_{ij} is the combination anharmonicity constant for modes i and j .

Mills and co-workers [35] showed how the anharmonicities of the normal modes are related to those of the identical local modes that make up the normal modes. They presented a method to calculate the relationship between the overtone anharmonicities and the combination anharmonicities of certain molecular geometries. For example, for a XY_2 molecule with C_{2v} symmetry point group, the overtone anharmonicities of the symmetric and antisymmetric stretches (x_{11} and x_{33}) are related to the combination anharmonicity (x_{13}) as $4x_{11} = x_{33} = x_{13}$ [35]. This method has also been applied to analyze the CO stretching modes of $M(CO)_4$ transition metal complex [37].

Adapting the approach of Mills and co-workers, we show that the combination anharmonicity constant between the equatorial and axial CO modes is zero. In Mills' approach, the starting point is to construct a Hamiltonian in the local harmonic oscillator basis with perturbation terms that include converting the

harmonic potential to a Morse potential as well as an interbond potential and kinetic coupling terms:

$$H_0 = \sum_i \left(\frac{1}{2} g_{rr} \hat{p}_i^2 + \frac{1}{2} f_{rr} r_i^2 \right) \quad (2.2a)$$

$$H'_1 = \sum_i \left(\frac{1}{6} g_{rrr} r_i^3 + \frac{1}{24} f_{rrrr} r_i^4 \right) \quad (2.2b)$$

$$H'_2 = \sum_{i < j} \left(\frac{1}{2} g_{rr'} \hat{p}_i \hat{p}_j + \frac{1}{2} f_{rr'} r_i r_j \right) \quad (2.2c)$$

where g_{rr} is the reciprocal effective mass, f_{rr} , f_{rrr} , and f_{rrrr} are the quadratic, cubic, and quartic force constants, respectively. $g_{rr'}$ and $f_{rr'}$ are the coupling terms. r_i and $\hat{p}_i$ are the internal coordinates (in our case here, they are the local CO stretching modes). The symmetry (normal) coordinate, s_i is related to the internal (local) coordinate, r_i by using $\mathbf{s} = \mathbf{U}\mathbf{r}$, where $\mathbf{U}$ is the matrix for the transformation from local to normal coordinates [40].

In the $\text{Os}_3(\text{CO})_{12}$ molecule, there are twelve local CO stretching modes. Under the D_{3h} point group symmetry, the twelve local modes form six axial normal modes, $A'_1 + A''_2 + E' + E''$, and six equatorial normal modes, $A'_1 + A'_2 + 2E'$ [41]. The A'_1 , A'_2 , and A''_2 modes are non-degenerate, while the E' and E'' modes are doubly degenerate. The A'_2 and A'_1 are non-active modes, A''_2 mode is IR active only, A'_1 and E'' are Raman active only, mode E' is both IR and Raman active. The internal coordinates of the twelve COs are labeled in the $\text{Os}_3(\text{CO})_{12}$ molecule in Figure 2.8. The elements of the matrix $\mathbf{U}$ were obtained based on group theory and are listed in Table 2.2.

Each local coordinate, $\mathbf{r}$ can be expressed as a linear combination of normal coordinate, $\mathbf{s}$ by

$$\mathbf{r} = \mathbf{U}^{-1}\mathbf{s} \quad (2.3)$$

U	r_{11}	r_{21}	r_{31}	r_{12}	r_{22}	r_{32}	r_{13}	r_{23}	r_{33}	r_{14}	r_{24}	r_{34}
$s_{eq}^{(A_1')}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	0	0	0	0	0	0
$s_{eq}^{(A_2')}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	0	0	0	0	0	0
$s_{a1,eq}^{(E')}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	0	0	0	0	0	0
$s_{b1,eq}^{(E')}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0
$s_{a2,eq}^{(E')}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	0	0	0	0	0	0
$s_{b2,eq}^{(E')}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$-\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0	0	0
$s_{ax}^{(A_1')}$	0	0	0	0	0	0	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$
$s_{ax}^{(A_2')}$	0	0	0	0	0	0	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$
$s_{a,ax}^{(E')}$	0	0	0	0	0	0	$\frac{1}{\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$
$s_{b,ax}^{(E')}$	0	0	0	0	0	0	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$
$s_{a,ax}^{(E'')}$	0	0	0	0	0	0	$\frac{1}{\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$
$s_{b,ax}^{(E'')}$	0	0	0	0	0	0	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{2}$	$\frac{1}{2}$

Table 2.2: The elements of the matrix **U**, r is the internal coordinate of the CO local stretching modes as labeled in Figure 2.8, s_{eq} and s_{ax} are the symmetry coordinates of the radial and axial CO normal stretching modes, respectively.

Figure 2.8: *The internal coordinate labeling in the $\text{Os}_3(\text{CO})_{12}$ molecule structure.*

where $\mathbf{U}^{-1}$ is the transpose of $\mathbf{U}$. By substituting Equation 2.3 into Equations 2.2, the Hamiltonian is transformed from local coordinates to normal coordinates that describe the normal mode motions. As a result, H_0 from Equation 2.2a contains the terms describing the normal coordinate harmonic oscillators, while H'_1 from Equation 2.2b now consists of a series of cross terms of normal coordinates. Using the basis functions of the normal modes, perturbative expansions are applied to the H'_1 and H''_2 terms. First and second order perturbations were applied to the cubic terms and only first order perturbation was applied to the quartic terms. These perturbation terms resulting from H''_2 contribute to offset frequencies of the normal mode from the local mode oscillator frequencies. The perturbative terms of the cross terms in H_1 are the source of the combination anharmonicities in Equation 2.1. If there exist cross terms of coordinates s_i and s_j in H'_1 , then the combination anharmonic constant x_{ij} will be non-zero. Conversely, if there are no cross terms between coordinates s_i and s_j , then the combination anharmonic constant x_{ij} will be zero.

The set of axial CO stretching modes are independent of the set of equatorial

CO stretching modes since they cannot be interchanged by any symmetry operator [40]. This entails that the 12×12 transformation matrix $\mathbf{U}^{-1}$ is a block diagonalized matrix, with one 6×6 diagonal block pertaining to the transformation only of the axial modes and another 6×6 diagonal block pertaining to only the equatorial modes. Thus, when expressed as normal coordinates, each local mode contains only contribution exclusively from either the axial normal modes or equatorial normal modes

$$r_{i,ax} = \sum_i \mathbf{U}_{ij}^{-1} s_{j,ax} \quad (2.4a)$$

$$r_{i,eq} = \sum_i \mathbf{U}_{ij}^{-1} s_{j,eq} \quad (2.4b)$$

Substituting the expressions for r_i of Equations 2.4 into H'_1 in Equation 2.2b the resulting terms in H'_1 will therefore not contain any cross terms of s_i and s_j between equatorial and axial modes. Therefore this also suggests that the resultant combination anharmonicity x_{ij} in Equation 2.1 between an equatorial normal mode and an axial normal mode is zero.

This treatment is an idealized treatment, as it only considers pure CO stretches. Other factors such as the consideration of coupling with the Os-C stretches and Coriolis effects are not taken into consideration. These factors will likely cause the combination anharmonicity to deviate from zero. However the effect is not expected to be significant. In a recent reported DFT calculation on a trigonal bipyramidal $Fe(CO)_5$ system (D_{3h} symmetry), in which the equatorial CO stretching mode E' and axial CO stretching mode A_2'' are also independent of each other, the combination anharmonicity was calculated to be 0.6 cm^{-1} , well within the spectral linewidths of the fundamental bands [9].

Anharmonicity of the Hetero-Combination Bands

According to the discussions above, the axial CO stretching modes and the equatorial CO stretching modes are independent of each other, resulting in the axial-equatorial combination anharmonicity constants (Δ_{ac} and Δ_{ad}) being very small, zero or near zero. The shifts of the combination bands will be within the bandwidth of the fundamental bands ($\Delta\nu = 5-11 \text{ cm}^{-1}$), therefore the axial-equatorial combination bands will be in close spectral proximity to the fundamental band positions and given the finite absorption spectral bandwidths. These combination bands will effectively be unresolvable from the fundamental absorption bands.

2.4.2 Fit of the Transient Absorption Spectrum

For the four CO normal stretches, there are four $0 \rightarrow 1$ transitions observed, and in principle sixteen $1 \rightarrow 2$ transitions in all. The bands for these $1 \rightarrow 2$ transitions are found to be spectrally overlapped with the four $0 \rightarrow 1$ transition bands, therefore the assignment of the transient absorption spectrum is more complicated than initial inspection suggests. To obtain the real vibrational population dynamics of the four stretching modes, the positions and relative intensities of the bands (especially for the combination bands) need to be clearly identified. The transient absorption spectrum taken at a time delay of 200 ps (Figure 2.9(a), empty circle in black), was fitted with a series of Gaussian functions (Figure 2.9(a), solid line in red). The fit was optimized with the spectral positions of the fundamental and overtone bands being fixed, and the combination band positions allowed to vary via a shared anharmonicity constant. All amplitudes and bandwidths were fitted to give the best result. The resulting FWHMs of the individual bands ranged from 5.4 to 10.6 cm^{-1} . In Figure 2.9(b), a to j (red solid line) represent the

spectral positions of the components fitted in Figure 2.9(a), with all parameters listed in Table 2.3. The assignments of the fundamental and overtone bands are straightforward, and have been discussed in Section 2.3.2, while the assignments for the combination bands are less obvious.

Figure 2.9: (a) Transient absorption spectrum measured at a delay of 200 ps (black empty circle) and the fit (red solid line) using Gaussian functions with FWHMs ranging from 5.4 to 10.6 cm^{-1} . (b) Representation of the positions of all the bands related. Bands a to j (red solid line) represent the fitted components in Figure 2.9(a), with bands a to d being the four fundamental transition bands, e to g being the four overtone transition bands, i and j being the axial-axial combination bands between modes a and b, respectively; k to r (blue dotted line) represent the eight combination band transitions which will be contributing to components a, b, c, and d, but not explicitly accounted for in the fitting procedure, and their shown amplitudes are not to scale. The fitting results are summarized in Table 2.3

Bands k to r (blue dotted line) in Figure 2.9(b) represent the eight axial-equatorial combination transition bands, which are spectrally overlapped with

	a	b	c	d	e	f	j	h	i	j
Δ/cm^{-1}	—	—	—	—	-6.8	-11.0	-5.3	-9.3	-14.8	-14.8
ω/cm^{-1}	2068	2036	2015	2002	2061	2025	2009	1992	2053	2021
$A/\text{Rel.}$	1.00	0.74	0.33	0.11	-0.62	-0.32	-0.16	-0.05	-0.30	-0.22

Table 2.3: *Positions and amplitudes of the transition bands of the transient spectrum at a time delay of 200 ps according to the Gaussian fittings. Δ is the anharmonicity, ω is the frequency, and A is the relative amplitude.*

the individual fundamental transition bands (shown amplitudes are not to scale). As a result, each of these bands a to d observed here is the sum of the fundamental band and two axial-equatorial combination bands. An initial estimate of the relative amplitudes of the fundamental transitions (a to d), overtone transitions (e to h) and axial-axial combination transitions (i and j) can be obtained from this fit (Table 2.3). We can see that the relative amplitudes of the axial-axial combination bands i and j are $\sim 30\%$ of the amplitude of a and b , respectively. The amplitude of the combination bands in the transient absorption spectrum scales to the product of the square of the transition dipole moment magnitudes, i.e., $\sim |\mu_x|^2 |\mu_y|^2$, where the subscript denotes modes x and y (This is only a rough approximation, as the relative orientation of the transition dipole moments is not taken into consideration). The transition dipole moment magnitudes of the two axial modes a and b and the two equatorial modes c and d are approximately $|\mu_a| \approx |\mu_b| \approx 2|\mu_c| \approx 2|\mu_d|$. The consequence is that the axial-equatorial combination bands are expected to have approximately similar amplitudes. The amplitudes of the axial-equatorial combination bands are in turn expected to be smaller than that of the axial-axial combination bands. The axial-equatorial combination bands k to n in Figure 2.9(b) will be small compared to the strong axial bands a and b that they are spectrally overlapped with. In comparison, the equatorial bands c and d are less intense, as such the relative contribution of the

combination bands o to r will be more substantial. Therefore, it is expected that the measured dynamics of the equatorial fundamental bands c and d will have significant contributions from axial-equatorial combination bands o to r . This will be important for the discussion in the following subsection.

2.4.3 Origin of the Rising Component

Based on the foregoing analysis of the combination anharmonic shifts between axial and equatorial modes, spectral overlap with the fundamental bands is unavoidable. Therefore, the pump-probe kinetic traces at the probe frequencies of the individual fundamental transition bands (a to d) contain not just the dynamics of the fundamental band transitions but also contributions from dynamics of various other processes. These processes can be enumerated using double sided Feynman diagrams that track the evolution of the density matrix elements (Liouville space pathways) [33]. The conventional MIR pump-probe is a third order ($\chi^{(3)}$) nonlinear process. The first two interactions with the light field are concurrent, inducing a vibrational excited state population. It is the ensuing dynamics over the duration of population that the pump-probe experiment measures. The third interaction with the light field converts the population to a coherence that corresponds to the frequency of the probe pulses. Figure 2.10 depicts the double sided Feynman diagrams that contribute to the pump-probe signals frequency resolved at the frequencies of the fundamental bands a to d (columns A to D), and overtone bands e to h (columns E to H), respectively. For each fundamental transition frequency, the measured pump-probe signal contains components with opposite signs; the positive component due to the fundamental band transition ($0 \rightarrow 1$) dynamics is shown in row I, and the negative components associated with the two axial-equatorial combination band transition ($1 \rightarrow 2$) dynamics are

shown in row II and III. For an example, the pump-probe signal measured at 2014 cm^{-1} that is nominally associated with the vibrational excited dynamics of band c consists of processes described by the diagrams CI, CII and CIII. Diagram CI represents the vibrational excited dynamics of band c ; diagram CII has its probe frequency resolved at the axial-equatorial combination band transition $a \rightarrow ac$ which is approximately equal to 2014 cm^{-1} (since Δ_{ac} is zero or near zero), as such diagram CII represents the negative-valued vibrational excited state dynamics of band a . Diagram CIII describes a similar process to diagram CII, and has its probe frequency resolved at axial-equatorial combination band transition $b \rightarrow bc$ also at approximately 2014 cm^{-1} . Analogous to diagram CII, this process represents the negative-valued vibrational excited state dynamics of band b . Therefore the pump-probe signal measured for band c at 2014 cm^{-1} comprises the fundamental transition dynamics of band c , and the negative-valued fundamental transition dynamics of bands a and b . A similar analysis applies for the pump-probe trace at 2002 cm^{-1} (diagrams DI, DII and DIII).

From columns A and B in Figure 2.10, the pump-probe traces A and B (Figure 2.7(a)) will also contain contributions from the axial-equatorial combination band transitions. However, these contributions have a small amplitude compared to those of the fundamental bands a and b , therefore no obvious anomalous rising feature was observed for traces A and B in Figure 2.7(a). For columns E to H, there is only one possible $\chi^{(3)}$ Liouville space pathway resolved at each overtone transition frequency. The axial-axial or equatorial-equatorial combination bands are red shifted away from the overtones by a pronounced anharmonicity. Therefore the frequency resolved pump-probe signals measured for the overtone bands ($1 \rightarrow 2$) do not contain contributions from the combination band transition dynamics. Additionally, there are fifth order ($\chi^{(5)}$) nonlinear processes known as up-pumping (inset in Figure 2.10) which will be discussed in the next section.

Figure 2.10: *The double sided Feynman diagrams for the pump-probe trace components resolved at the frequencies of the fundamental transition and overtone transition bands, columns A to D and E to H, respectively. The inset shows the diagrams of the up-pumping processes.*

Further confirmation of the contributions of the axial-equatorial combination band transitions to the pump-probe traces for the fundamental bands of the equatorial modes, were obtained from pump-probe traces measured with pump spectrum centered at 2015 cm^{-1} . It was red shifted by about 15 cm^{-1} from the original pump spectrum. The pump pulse fluence at 2068 cm^{-1} was $\sim 70\%$ that of original pump pulse, $\sim 8.4\text{ mJ}\cdot\text{cm}^{-2}$, while the fluences at 2034 cm^{-1} , 2014 cm^{-1} and 2002 cm^{-1} remained approximately unchanged. The pump-probe traces resolved at 2014 cm^{-1} for band c with the two different pump spectra are shown in Figure 2.11(a) (identical to trace C in Figure 2.7(a)), and Figure 2.11(b), respectively). Although the intermediate time scale rising component is discernable in Figure 2.11(b), it is far less prominent as compared to Figure 2.11(a). This can be explained by the reduction of the contributions to the pump-probe signal,

Figure 2.11: (a) The pump-probe traces for mode *e* resolved at 2014 cm^{-1} , with pump centered at (a) 2030 cm^{-1} (empty circle in black), and (b) 2015 cm^{-1} (empty upright triangle in black), respectively. The global fit is represented with red solid lines.

of diagrams (such as CII and CIII of Figure 2.10) with interactions first with the light fields at the fundamental $0 \rightarrow a$ (2068 cm^{-1}) and $0 \rightarrow b$ (2034 cm^{-1}) transitions. With reduced spectral intensities at 2068 cm^{-1} , the magnitude of the contributions from the negative valued processes CII and CIII, relative to the positive value process CI ($0 \rightarrow c$, 2014 cm^{-1}), will be diminished, resulting in a pump-probe kinetic trace with a less prominent rising feature.

A global fit (red solid lines) was applied to the traces in Figure 2.11. This was only performed beyond 5 ps using bi-exponential decay functions, with constraint of the two decay time constants to fit both traces whilst allowing their relative amplitudes to float. The bi-exponential fitting time constant T_1 of $420 \pm 100\text{ ps}$. The resulting relative amplitudes are summarized in Table 2.4. It is

noticeable that the ratio between the amplitudes of the rising component and the amplitude of the decaying component is reduced for the red-shifted excitation. This is consistent with the hypothesis presented above in which a reduction of the contributions from the axial-equatorial combination band transitions account for the rising component τ' when the pump pulse is red shifted.

	τ'	T_1	$A_{\tau'}$	A_{τ_2}	$-A_{\tau'}/A_{T_1}$
(a)	120(± 40)	420(± 100)	-0.895	1.417	0.632
(b)	120(± 40)	420(± 100)	-0.289	1.138	0.254

Table 2.4: *The time constants (in ps) and relative amplitudes of global fit to the two pump-probe traces in Figure 2.11 that measured at 2014 cm^{-1} , with pump pulses centered at 2030 cm^{-1} and 2015 cm^{-1} for (a) and (b), respectively.*

2.4.4 Excited State Population Relaxation Dynamics

According to the fitting results for the pump-probe traces (Figure 2.7) summarized in Table I, traces A and B for the axial stretching modes *a* and *b*, exhibit similar dynamics, both consisting of a fast decay τ of 1–3 ps and a slow decay T_1 of 500–600 ps. The fast decay component τ is attributed to direct intra-molecular vibrational energy redistribution (IVR) due to the fast homo-mode coupling between the axial modes *a* and *b*. This is similar to the CO stretch in $Rh(CO)_2(acac)$ with a fast decay of 2.2–4 ps in $CHCl_3$ [19]. The slow decaying component T_1 for both modes *a* and *b* is consistent with other metal carbonyl compounds in $CHCl_3$ solutions attributed to multi-quantum intra-molecular vibrational energy transfer to M-C stretches or M-C-O bends at lower frequencies [21]. The T_1 of CO stretches has been shown to have values on the ps to ns scale, depending on both molecular structure and solvent [17, 19, 21]. The overtone dynamics (traces E and F) contains a fast and a slow decay components τ of ~ 1 –3 ps and

T_1 of $\sim 600\text{--}800$ ps, respectively; this is consistent with the observed dynamics of traces A and B, respectively. Additionally, there is a low amplitude rising component that shows up as a “plateau” with an intermediate timescale τ' of $\sim 10\text{--}40$ ps. This rising component is due to the dynamics of up-pumping [42]. The up-pumping process involves a two-photon absorption of the pump pulse to populate the $v = 2$ level. This process can be represented using the double sided Feynman diagrams E_{up} and F_{up} depicted in the inset of Figure 2.10. The signals of the up-pumping processes are resolved at the frequencies of the overtone bands at 2058 cm^{-1} and 2022 cm^{-1} , respectively, and are opposite in sign with the overtone dynamics (Diagrams EI and FI of Figure 2.10). Therefore trace E with its “plateau” in Figure 2.7 results from the sum of the processes of Diagrams EI and E_{up} while the sum of Diagrams FI and F_{up} give rise to the “plateau” in trace F. The τ' of $\sim 10\text{--}40$ ps gives an indication of the population lifetime decay of the $v = 2$ level. This is similar to the observation that the population lifetime of the $v = 2$ level is shorter than that of the $v = 1$ level [42]. The observed up-pumping process is a fifth order nonlinear optical process compared to the third order nonlinear optical process of the conventional pump-probe signal. In this case, the up-pumping signal should scale with the square of the pump pulse intensity while the conventional pump-probe signal will scale linearly with the pump pulse intensity. A pump pulse power dependence study of the frequency resolved pump-probe signal was carried out. In Figure 2.12, we depict pump-probe traces measured at 2022 cm^{-1} with different relative pump pulse power of 1.00, 0.75, 0.50, and 0.25, respectively. From the fit (solid line) for each trace, it can be seen that the up-pumping component becomes weaker with successively lower pump pulse power. Below ~ 0.25 of its original intensity, the “plateau” feature disappears and only a single long decay remains.

Figure 2.12: The pump-probe traces measured at 2022 cm^{-1} with different relative pump power of 1.00, 0.75, 0.50, and 0.25 of its original intensity. The fitting functions used are the convolution of the exponential functions and a Gaussian function representing the instrument response.

We can further quantify the relation between the pump intensity and the “plateau” contribution in trace F according to the fits of the traces in Figure 2.12, and is summarized in Figure 2.13. The contribution of the “plateau” becomes less as the pump intensity goes down, and will disappear when the pump intensity is reduced to 25%. The amplitude of the “plateau” component (A_2) relative to that of the slow decay component (A_3), A_2/A_3 , was plot as a function of the pump pulse intensity. It can be fitted with a quadratic function to show the pump power square dependence of the up-pumping process. It should be mentioned that with pump intensity reduced to 25% of its original intensity, although traces E and F can be obtained without “plateaus”, the signals for the equatorial modes are too weak to be detected.

Figure 2.13: The dependency of the up-pumping component on the relative pump pulse intensity in trace E at 2022 cm^{-1} . The relative amplitudes A_2/A_3 were obtained from the fitting of traces in Figure 2.12.

Traces C and D (overlooking the contributions from the combination mode dynamics) describe the fundamental transitions for the equatorial modes c and d . Unfortunately, any existing real rising component of the process CI and DI that may be indicative of vibrational energy flow into these modes will be difficult to discern from these measurements. However, if we look at the traces G and H in Figure 2.7(b) which should also illustrate features of excited vibrational state dynamics; there is an absence of any rising components, this suggests that there is no apparent direct vibrational energy transfer from the axial to equatorial modes. The T_1 of the equatorial mode c decays on a time-scale of $\sim 420 \pm 100$ ps according to the slow decay constant of trace C in Figure 2.7(a), and agrees well with the slow decay constants fitted to traces G and H in Figure 2.7(b).

For molecules consisting of large metal nuclei and multi-carbonyls like

$\text{Os}_3(\text{CO})_{12}$, the T_1 of individual CO modes depends on three factors: the coupling between these CO stretches, the coupling strength to the adjacent lower frequency M-C stretches or M-C-O bends, and the local symmetries of these CO stretches [21]. The axial modes a and b are measured to have a slower population decay time constant T_1 (550 ± 50 ps) compared to the equatorial modes c and d (420 ± 100 ps). Due to the limited travel length of the translation stage used (~ 300 ps) there is considerable error in fitting of the decay traces and the upper bound values of errors are given here. From these measurements, we can derive certain results here. It is clear that there are close similarities between the T_1 of the homo-modes (axial-axial and equatorial-equatorial). These similarities have been attributed to the strong coupling between the homo-modes and the resultant direct and fast IVR process. In this experiment, we cannot confirm that the decay times of the hetero-modes are different within the error bounds, however the data tentatively suggests that the difference in the decay time is consistent with the absence of direct IVR between the hetero-modes due to minimal coupling between the axial and equatorial carbonyls. The difference in the T_1 timescale for the equatorial and axial modes may be due to the fact that the equatorial modes are closer in frequency to the M-C stretching or M-C-O bending modes, this results in faster population relaxation to these lower frequency acceptors from the equatorial modes than from the axial modes. These energy relaxation pathways may also provide indirect excitation population transfer between the axial and equatorial modes over a longer timescale.

2.5 Conclusions

MIR pump-probe spectroscopy was used to investigate the vibrational dynamics of the CO stretching modes of $\text{Os}_3(\text{CO})_{12}$ in CHCl_3 . There are four IR active fundamental vibrational stretching normal modes, two strong axial modes a (2068 cm^{-1}) and b (2034 cm^{-1}), and two weak equatorial modes c (2014 cm^{-1}) and d (2002 cm^{-1}). Transient absorption spectra at various time delays as well as pump-probe traces were obtained at these fundamental transition frequencies and the overtone transition frequencies for these IR active modes. An anomalous rising feature in the pump-probe traces for the fundamental transitions of the two equatorial modes c and d was observed, this was deduced to be the result of interference due to the observation of the dynamical behavior of the axial-equatorial combination band transitions, which is spectrally overlapped with these fundamental transitions.

The four IR active normal modes belong to two independent sets. This results in there being two distinct kinds of anharmonic combination bands, axial-axial or equatorial-equatorial combinations and axial-equatorial combinations. The former type is spectrally distinct from the fundamental and overtone band positions and can be easily resolved. The latter type is at the same spectral position as the fundamental bands and as such cannot be spectrally resolved. Therefore, the bands assigned to the fundamental transitions on the transient spectra include contributions from axial-equatorial combination bands. For the pump-probe traces, frequency resolved at the two weak equatorial fundamental bands c and d , the contribution from the axial-equatorial combination bands are significant, giving rise to the anomalous rising component observed in these pump-probe experiments. The processes that contribute to this anomalous rise are identified

as being due to interference from the axial-equatorial combination bands (Figure 2.10, CII, CIII and DII, DIII) which are probing the excited state dynamics of the axial modes a and b . It is worthy of note that the pump-probe signals measured for the two axial modes a and b were minimally affected due to the intensities of the axial-equatorial combination transition bands being weak compared to these pure axial modes. The measured excited state lifetime decays are 550 ± 50 ps for the axial modes and 420 ± 100 ps for the equatorial modes. No clear indication of any direct intra-molecular vibrational energy transfer between the axial and equatorial CO stretching modes was observed.

In summary, $\text{Os}_3(\text{CO})_{12}$ has been identified as a system with spectral overlap between combination and fundamental transition bands which provides possibilities of erroneous interpretation and ambiguities when measuring excited state population dynamics. To investigate the energy transfer dynamics among the different CO modes in a molecule with as complicated vibrational structure as $\text{Os}_3(\text{CO})_{12}$, narrow band pump broad-band probe experiments are needed to selectively excite individual CO stretching modes. In principle, 2D IR spectroscopy would be an appropriate technique to address these ambiguities, as the peaks will be resolved along both the pump and the probe frequency axis, and the dynamics for each stretching normal mode can be measured separately. However, this has to be weighed against the fact that a 2D IR experiment is significantly more difficult to implement than a transient absorption experiment. Amplitude, phase, and polarization pulse shaping in the MIR are discussed in Chapter 4, and the complexity of full controlled pulse shaping the MIR for 2D IR experiments will be presented.

This chapter discussed the molecular vibrational dynamics that occurs in the positive delay time between pump and probe pulses. As mentioned previously, at

negative time delays where the probe proceeds the pump the PFID is observed. Although it is much weaker compared to those vibration modes in $\text{Os}_3(\text{CO})_{12}$, it may become apparent if the real molecular dynamics are relatively weak, and will interfere with the observation of extremely fast dynamical processes. As such, in the following chapter a combined theoretical and experimental study of the PFID phenomenon is presented.

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Chapter 3

Perturbed Free Induction Decay in Ultrafast Mid-Infrared Pump-Probe Spectroscopy

3.1 Introduction

Perturbed free induction decay (PFID) is a common coherent artifact in ultrafast time-resolved infrared (IR) spectroscopies [1]. It occurs at negative time delays, when the probe pulse precedes the pump pulse. Furthermore, PFID is only observed if the duration of the probe pulses is shorter than the coherence dephasing time T_2 of the absorption. For homogeneous lineshapes, the dephasing time T_2 can be estimated to be $\approx 2/\Delta\omega$, with $\Delta\omega$ being the spectral full width at half maximum (FWHM). At the center frequency of the absorption band, the PFID signal rises with the time constant T_2 and vanishes when the probe and pump pulses overlap in time. Away from the center frequency, PFID manifests as oscillations in both the time and frequency domain. Vibra-

tional transitions in the IR region are normally narrow band absorptions of a few cm^{-1} , and therefore result in long vibrational dephasing times T_2 of sub-picoseconds (sub-ps) to picoseconds (ps). As a result, PFID signals are in general obvious and can be readily observed in ultrafast IR spectroscopies, such as ultraviolet/visible (UV/Vis)-pump IR-probe and IR-pump IR-probe experiments. Systems that in which PFID has been observed include: The laser dye IR26 [1], GaAs [2, 3], $\text{Mn}_2(\text{CO})_{10}$ [4], proteorhodopsin [5], the light harvesting compound peridinin chlorophyll- α protein (PCP) [6], and carboxyhemoglobin HbCO [7] in UV/Vis-pump IR-probe spectroscopy; $\text{W}(\text{CO})_6$ and related complexes [8], aqueous molecular cyanides [9], Fmoc-nitrophenylalanine Fmoc-Phe(4- NO_2)-OH [10], and $\text{Os}_3(\text{CO})_{12}$ [11] in IR-pump IR-probe experiments. Compared to vibrational transitions, electronic transitions are usually broadband with $\Delta\omega$ spanning from tens to hundreds of cm^{-1} and accordingly the electronic dephasing times T_2 are normally below hundreds of femtoseconds (fs) down to even just a few fs. Hence, PFID signals are less commonly observed in UV/Vis pump-probe measurements, where probe pulses typically are longer than T_2 . However, PFID signals have been reported in a few studies (with time resolutions below 100 fs), for instance in the semiconductor CdSe [2], and spectral hole burning experiments on Nile blue [2, 12].

The theory of PFID signals has been shown in detail for Vis-pump IR-probe spectroscopy by Hamm et al. [1]. The experimental data agreed well with the simulations based upon the theory. PFID signals in Vis-pump IR-probe spectroscopy were also thoroughly discussed by Wynne et al. [13]. Signals spectrally resolved at fundamental and overtone frequencies were derived and compared. These studies provide a clear understanding of the PFID in Vis-pump IR-probe experiments.

Although PFID signals have been observed and mentioned in many degenerate IR pump-probe experiments, so far no detailed theory about the PFID signals observed in such experiments has been given. Here we explore the theory about PFID signals as they occur in degenerate IR pump-probe spectroscopies, using perturbation theory in the interaction picture for an anharmonic vibrational system [14]. Our presented model focuses on PFID signals arising from a fundamental absorption ($0 \rightarrow 1$) and an overtone absorption ($1 \rightarrow 2$). This scenario is commonly encountered in broadband degenerate IR pump-probe spectroscopies. Since PFID may interfere with and obstruct short time scale vibrational molecular dynamics, PFID signals need to be well understood to clearly observe fast dynamical processes. Alternatively, PFID can be suppressed in the measurements by appropriate filtering methods [15, 16], which will be discussed later in Section 3.4.4 of this chapter.

For this study we have chosen mono-metallic carbonyl $\text{W}(\text{CO})_6$ as a model system. The measured linear absorption spectrum in *n*-hexane is shown in Figure 3.1. It has one IR active CO stretching mode (T_{1u}), which is centered at $\sim 1984 \text{ cm}^{-1}$ with a narrow bandwidth of $\sim 3 \text{ cm}^{-1}$ (FWHM). The overtone absorption frequency ($1 \rightarrow 2$) is red-shifted by the anharmonicity constant of $\sim 12 \text{ cm}^{-1}$, it will be represented in the transient absorption spectrum later. Under the homogeneous broadening approximation, the coherence dephasing time T_2 is $\sim 2.0 \text{ ps}$. Extensive time-resolved ultrafast studies have been reported to investigate the vibrational molecular dynamics and energy relaxation processes. PFID signals were observed during these measurements [8, 17–20]. However, only the PFID for $0 \rightarrow 1$ has been typically noted. In the sub-picosecond IR pump-probe studies on $\text{W}(\text{CO})_6$ in various solutions by Banno et al. [8], PFID signals occur and interfere with the vibrational dynamics at positive time delays (less

Figure 3.1: *The linear absorption spectrum of the carbonyl stretching mode from $W(CO)_6$ in *n*-hexane solution.*

than 2 ps) between pump and probe. In our case, broadband Mid-infrared (MIR) pump-probe studies on the CO stretching mode of $W(CO)_6$ were carried out at negative time delays to better understand the PFID and prevent possible misinterpretations. It will be shown that the PFID signals for $0 \rightarrow 1$ and $1 \rightarrow 2$ are markedly different.

This chapter is arranged as follows: Section 3.2 presents the theory of PFID as it occurs in degenerate IR pump-probe experiments. The frequency resolved signals are derived in the interaction picture. Section 3.3 describes the experimental methods, whereas Section 3.4 shows the experimental results and comparisons to simulations according to the presented theory. In this section the suppression of the PFID signals from the experimental data was also performed.

3.2 Theory

For the theoretical description of a degenerate IR pump-probe experiment, the pulses can be considered as delta pulses if their duration is much shorter than the dephasing time of the absorption. The pulse sequence is depicted in Figure 3.2. The electric fields of the pump and probe pulses will then be:

$$E_{pu}(t) = \delta_{pu}(t)e^{-i\omega_L(t+T)} \quad (3.1a)$$

$$E_{pr}(t) = \delta_{pr}(t+T)e^{-i\omega_L(t+T)} \quad (3.1b)$$

where T is the time delay between the probe and pump pulses, and ω_L denotes the laser center frequency.

Figure 3.2: Top: The pulse sequence of pump and probe pulses to observe perturbed free induction decay. Bottom: Double sided Feynman diagrams describing the perturbed free induction decay. R_4 and R_6 are the spectrally resolved PFID signals at the fundamental and overtone frequencies, respectively. k_{pr} , k_{pu} , and k_s are the vectors of probe, pump and signal pulses, respectively.

The third order polarization $P^{(3)}(t)$ for the PFID in a pump-probe experiment reads as:

$$P^{(3)}(t) \propto \left(\frac{i}{\hbar}\right)^3 \int_0^\infty \int_0^\infty \int_0^\infty dt_1 dt_2 dt_3 R(t_1, t_2, t_3) \quad (3.2)$$

$$E_{pr}(t - t_3 - t_2 - t_1) E_{pu}^*(t - t_3 - t_2) E_{pu}(t - t_3)$$

with $R(t_1, t_2, t_3)$ being the response function [21]. In the current pump-probe scheme, $t_1 = T$, $t_2 = 0$ and $t_3 = t$. By solving this equation, we know that the PFID signal $E_{PFID} \propto iP^{(3)}(t) \sim R(T, 0, t)$.

The probe pulses arrive at the sample earlier than the pump pulses, denoted by the time delay T . In the interaction picture, the PFID signals are third order, and can be described using double-sided Feynman diagram (DSFDs), as depicted in Figure 3.2. The overall response function consists of contributions from the two different pathways under consideration according to: $R(T, 0, t) = R_4(T, 0, t) + R_6(T, 0, t)$, where R_4 and R_6 are the signals probed at fundamental and overtone frequencies, respectively. The notations of the response functions are taken from the book by Fayer [22]. In the homogenous limit, R_4 and R_6 can be written as:

$$R_4(T, 0, t) = |\mu_{10}|^4 e^{-i\omega_{10}(t+T)} e^{-(t+T)/T_2} \quad (3.3a)$$

$$R_6(T, 0, t) = |\mu_{10}|^2 |\mu_{21}|^2 e^{-i\omega_{21}t} e^{-i\omega_{10}T} e^{-(t+T)/T_2} \quad (3.3b)$$

with μ_{10} and μ_{21} representing the transition dipole moments of the fundamental and overtone transitions ω_{10} and ω_{21} , respectively.

The generated PFID signal is subsequently heterodyne detected with the probe pulse acting as the local oscillator, and frequency resolved using a spectrometer. The intensity of the recorded PFID signal reads as:

$$S_{PFID}(T, \omega) = \text{Re}[E_{pr}^*(\omega) E_{PFID}(\omega)] \quad (3.4)$$

with $E_{pr}^*(\omega)$ being the complex conjugate of $E_{pr}(\omega)$, which is the Fourier transform of $E_{pr}(t)$ from time to frequency domain, and $E_{pr}^*(\omega) = [E_{pr}(\omega)]^* = e^{i\omega T}$. Therefore the PFID signal obtained from the spectrometer becomes

$$S_{PFID}(T, \omega) \propto \text{Re}[e^{i\omega T} \tilde{R}(T, 0, \omega)] \quad (3.5)$$

where $\tilde{R}(T, 0, \omega) = \tilde{R}_4(T, 0, \omega) + \tilde{R}_6(T, 0, \omega)$ are the Fourier transforms of $R(T, 0, t)$, $R_4(T, 0, t)$, and $R_6(T, 0, t)$, respectively.

According to the DSFDs in Figure 3.2, when probing at the fundamental frequency, the frequency resolved PFID signal $S_{PFID}^{(R_4)}$ will be:

$$S_{PFID}^{(R_4)}(T, \omega) \propto e^{-T/T_2} \frac{(1/T_2) \cos[(\omega - \omega_{10})T] - (\omega - \omega_{10}) \sin[(\omega - \omega_{10})T]}{(\omega - \omega_{10})^2 + (1/T_2)^2}. \quad (3.6)$$

Similarly, when probed at the overtone frequency, the frequency resolved PFID signal $S_{PFID}^{(R_6)}$ can be written as

$$S_{PFID}^{(R_6)}(T, \omega) \propto -e^{-T/T_2} \frac{(1/T_2) \cos[(\omega - \omega_{10})T] - (\omega - \omega_{10}) \sin[(\omega - \omega_{10})T]}{(\omega - \omega_{21})^2 + (1/T_2)^2}. \quad (3.7)$$

Summation of Equations 3.6 and 3.7 gives the total PFID signal $S_{PFID}(T, \omega)$:

$$S_{PFID}(T, \omega) \propto e^{-T/T_2} \frac{(1/T_2) \cos [(\omega - \omega_{10})T] - (\omega - \omega_{10}) \sin [(\omega - \omega_{10})T]}{(\omega - \omega_{10})^2 + (1/T_2)^2} \quad (3.8)$$

$$r \cdot \left[-e^{-T/T_2} \frac{(1/T_2) \cos [(\omega - \omega_{10})T] - (\omega - \omega_{10}) \sin [(\omega - \omega_{10})T]}{(\omega - \omega_{21})^2 + (1/T_2)^2} \right]$$

Here r is the intensity ratio of $S_{PFID}^{(R_6)}(T, \omega)$ to $S_{PFID}^{(R_4)}(T, \omega)$.

3.3 Experimental

The broadband MIR pump-probe experimental setup is described in Chapter 2. Briefly, the MIR spectrum is centered at 1985 cm^{-1} , which is at the fundamental absorption frequency of the CO stretching mode of $\text{W}(\text{CO})_6$, and the spectral bandwidth is 110 cm^{-1} (FWHM). The pulse duration is $\sim 200 \text{ fs}$ as retrieved from the cross-correlation signal, being much smaller than the dephasing time T_2 of the CO stretching mode ($\sim 2.0 \text{ ps}$). Therefore the pump and probe pulses can be treated as δ pulses. The energy of the generated MIR pulses was $\sim 3.8 \mu\text{J}$. It was split into pump and probe pulses in a ratio of $\sim 18:1$, and the pump fluence at sample position was adjusted to be $\sim 11 \text{ mJ/cm}^2$. The polarization of the probe relative to pump was set at the magic angle of 54.7° . $\text{W}(\text{CO})_6$ (Sigma-Aldrich) was dissolved in *n*-hexane (Sigma-Aldrich), and the sample concentration was adjusted to $\sim 1 \text{ mM}$. The thickness of the sample solution is $200 \mu\text{m}$.

3.4 Results and Discussion

3.4.1 Transient Absorption Spectra

The transient absorption spectra in Figure 3.3 were obtained at pump and probe time delays from -2.5 ps to -0.1 ps. The negative valued peak at 1984 cm^{-1} corresponds to the fundamental transition ($0 \rightarrow 1$) of the CO stretching mode [19]. The signal intensity increases as a function of vanishing time delay between pump and probe, as indicated by an arrow in the figure. There are no obvious time-dependent changes in spectral position and line-shape. At lower frequencies, we observe a rising positive feature along with oscillations, that appear less prominent with decreasing time delay. According to Equation 3.8, the oscillations only

Figure 3.3: The transient absorption measurements at a series of time delays between probe and pump pulse. The time delays range from -2.5 ps to -0.1 ps (time sequence is labeled with arrows) with intervals of 150 fs. The intensities are normalized to that of the kinetic trace at 1985 cm^{-1} .

occur off-resonance from the fundamental transition and are frequency dependent. The increasing positive feature corresponds to the overtone absorption ($1 \rightarrow 2$) at $\sim 1972 \text{ cm}^{-1}$. The feature intensity increases and its position shifts red as the time delay between pump and probe decreases. At a time delay of -2.5 ps , the oscillations dominate the signal, while at -0.1 ps the oscillation almost vanishes. The oscillations around 1956 cm^{-1} are mainly due to up-pumping absorption [11].

Figure 3.4: *The global fit of the transient absorption spectra in Figure 3.3.*

The transient spectra in Figure 3.3 were fitted globally and the fitting curves are represented in Figure 3.4. The global fit was carried out using Equation 3.8 as a function of delay time T between pump and probe pulses, and as can be seen that the experimental transient spectra can be fitted very well. For all these fits, the de-phasing time was fitted as $T_2 = 1.9 \text{ ps}$, close to the value of $\sim 2.0 \text{ ps}$ as calculated by the bandwidth of the linear spectrum under the homogeneous broadening approximation. The frequencies of the $0 \rightarrow 1$ and $1 \rightarrow 2$ transitions

were fixed at $\omega_{10} = 1984 \text{ cm}^{-1}$ and $\omega_{21} = 1972 \text{ cm}^{-1}$, respectively. Other parameters for each kinetic trace were allowed to float. According to the fit, the intensity ratio r of $S_{PFID}^{(R_6)}(T, \omega)$ to $S_{PFID}^{(R_4)}(T, \omega)$ was obtained to be ~ 1.28 .

3.4.2 Pump-Probe Kinetic Signals

The kinetic measurements probed at different frequencies are depicted in Figure 3.5. Similarly, the global fit (solid lines) was carried out using Equation 3.8 as a function of frequency ω . It can be seen that the experimental kinetic traces are fitted very well. For all fits, the parameters used are consistent with those for the transient absorption fits. The dephasing time acquired from the fits is 1.9 ps, and the frequencies of the $0 \rightarrow 1$ and $1 \rightarrow 2$ transitions were fixed at $\omega_{10} = 1984 \text{ cm}^{-1}$ and $\omega_{21} = 1972 \text{ cm}^{-1}$, respectively. Other parameters for each kinetic trace were allowed to float. The intensity ratio r of $S_{PFID}^{(R_6)}(T, \omega)$ to $S_{PFID}^{(R_4)}(T, \omega)$ was obtained to be 0.93 according to the kinetic trace fits, smaller than the ratio obtained from fits of the transient absorptions in Figure 3.3 which is 1.28. The ratio r is expected to be $\sqrt{2}$ assuming the dipole moments scale as a harmonic oscillator under the same excitation conditions for both transitions [23]. However, the ratio is excitation power dependent. In the current experiment, the excitation spectrum for the transient spectra in Figure 3.3 was red shifted by $\sim 10 \text{ cm}^{-1}$ from that of for the kinetic traces in Figure 3.5. Therefore, the ratio r of the $S_{PFID}^{(R_6)}(T, \omega)$ absorption to the $S_{PFID}^{(R_4)}(T, \omega)$ is bigger when the spectrum of excitation pulses shifts towards the $1 \rightarrow 2$ absorption.

As can be seen from the kinetic traces, the spectrally resolved signals at individual frequencies are vastly different. When spectrally resolved close to the $0 \rightarrow 1$ transition frequency, the signal is dominated by the exponential dephasing process with a time constant $T_2 = 1.9 \text{ ps}$. When spectrally resolved at the 1

Figure 3.5: The frequency resolved kinetics measured at a series of frequencies and their global fits. The global fits (solid lines) were obtained using Equation 3.8.

→ 2 transition frequency, the kinetics will be the convolution of the exponential signal and an oscillation feature with a period of 2.78 ps, which corresponds to a frequency of 12 cm^{-1} (corresponding to the detuning frequency from the fundamental absorption, which equals to the anharmonicity constant). For the signal probed at the fundamental frequency, the detuning frequency is $\omega - \omega_{10} = 0 \text{ cm}^{-1}$, the $S_{PFID}^{(R_4)}(T, \omega)$ term in Equation 3.8 will be an exponential function, while the $S_{PFID}^{(R_6)}(T, \omega)$ term consists of two components, an exponential and an oscillating components, and is much weaker in intensity compared to the $S_{PFID}^{(R_4)}(T, \omega)$. Therefore the exponential signal $S_{PFID}^{(R_4)}(T, \omega)$ plays a major role in the total observed $S_{PFID}(T, \omega)$ signal. For signals probed off-resonance from the funda-

mental frequency, the detuning frequency is non-zero, and both the $S_{PFID}^{(R_4)}(T, \omega)$ and $S_{PFID}^{(R_6)}(T, \omega)$ comprise exponential and oscillatory characteristics, thus in this case the total signal $S_{PFID}(T, \omega)$ shows clear oscillations, and the frequency is equal to the detuning frequency.

3.4.3 Multi-Dimensional Plots of Experiment and Simulation

The experimental results and simulation are compared in Figure 3.6. The simulation was performed using the function in Equation 3.8, with the previous defined fitting parameters. The plots show the evolution of the PFID signals in both time and frequency domain. As can be seen, the simulation matches the experimental data very well.

Figure 3.6: The experimental 3D plot (left) and the simulation (right). The fundamental absorption frequency is at $\omega_{10} = 1984 \text{ cm}^{-1}$, and the overtone absorption frequency is at $\omega_{21} = 1972 \text{ cm}^{-1}$.

3.4.4 Suppression of Coherent Artifacts with 2D Fourier Filtering Methods

As it has been shown in the previous sections, the PFID as it occurs in degenerate IR pump-probe experiments is well understood and can be simulated accurately with the theory presented. As previously stated, PFID can be suppressed if it interferes with the vibrational relaxation dynamics under investigation. This method is based on a 2D Fourier filtering method in shift-space [15,16]. Here, we applied the method and the results are shown in Figure 3.7. As can be seen the oscillatory behavior of the PFID is successfully suppressed, especially at the $1 \rightarrow 2$ transition frequency, and the coherent spike around 0 ps is minimized as well. The long term dynamics at positive times remains unaffected by this filtering procedure.

Figure 3.7: *The experimental data before (left) and after the 2D Fourier filtering procedure (right). Oscillations and coherent spike are successfully suppressed .*

3.5 Conclusions

Based on perturbation theory in the interaction picture, we explored in detail the theory about PFID signals occurring in IR pump-probe experiments. The PFID signals from the fundamental and overtone absorptions were derived and were found to be different. Usually, in IR pump-probe spectroscopy, the pump-probe signals resolved at the overtone and fundamental absorption frequencies show similar dynamics at positive delay time. According to the theory on the PFID, at negative time delays, when probed at the fundamental absorption frequency, the PFID signal rises exponentially with a time constant of the coherence dephasing time T_2 . While probed at the overtone frequency, the PFID signal shows an oscillatory behavior that decays with T_2 , with the oscillation frequency matching the anharmonicity constant.

To test the developed theory, broadband MIR pump-probe experiments were carried out on the simple model molecule $\text{W}(\text{CO})_6$ with only one IR active CO stretching mode at 1984 cm^{-1} , and its overtone at 1972 cm^{-1} . PFID transient absorption signals were measured at various negative time delays, and the oscillations decay with the time scale of $T_2 \sim 2.0\text{ ps}$. Kinetic signals resolved at different frequencies were also presented. The oscillations in the measurements are determined by the detuning frequencies from the fundamental frequency. The experimental signals were fitted with the functions given in the theory section. In the current experiment it can be seen, that the simulations match the experimental measurements. We also demonstrated the suppression of the PFID with appropriate filtering methods. The theory will be helpful to understand the PFID phenomenon in more complicated molecules with multiple IR absorptions, not only in one dimensional but also for multi-dimensional IR spectroscopies.

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Chapter 4

Indirect Mid-Infrared Polarization Pulse Shaping by Parametric Transfer

4.1 Introduction

Shaped ultrafast laser pulses with full control over amplitude, phase, and polarization are of growing importance in biophysical and physicochemical molecular research. Since many vibrational motions of molecules are within the mid-infrared (MIR) spectral region, arbitrary shaped pulses as well as pulse trains in the MIR will be of benefit for various applications including quantum control of molecular dynamics, and multi-dimensional infrared spectroscopy [1, 2]. Moreover, additional polarization control provides a larger degree of freedom in these applications.

In general, there are two approaches to shape the amplitude and phase of ultrafast laser pulses. One is direct pulse shaping, characterized by shaping the

electric field directly at the desired frequency via a spatial light modulator (SLM). Amplitude and phase control techniques are well developed, and the two major types of computer-controlled SLMs are Acousto-Optic Modulators (AOM) [3] and Liquid-Crystal Spatial Light Modulators (LC-SLM). AOMs are available for pulses from the UV (silica AOM) [4] to the MIR region (germanium AOM) [5]. The extension to include polarization shaping has recently been reported, albeit with a non-common beam path geometry [6]. The other prominent commercially available modulator is the LC-SLM. LC-SLMs have very high transmission efficiency from the visible to the near-infrared (NIR), and as such have been used in direct pulse shaping for the visible [7] and NIR spectral region [8]. However, there is still no suitable material for LC-SLMs in the MIR, as the liquid crystal molecules have strong absorptions in these spectral region.

Direct pulse shaping is not achievable at all wavelengths, due to material limitations. This necessitates indirect pulse shaping, where shaping occurs at an accessible wavelength, before the shaped pulses are parametrically transferred to the desired spectral region. Amplitude and phase shaped MIR pulses have been obtained from shaped NIR pulses by parametrically transferring it to the MIR via an optical parametric amplification (OPA) process or other nonlinear optical processes [9–11]. One advantage of this approach is that well established techniques and instruments for visible and NIR pulse shaping can be deployed to create MIR shaped pulses.

Recently polarization pulse shaping has been demonstrated for ultraviolet (UV), visible, and NIR wavelengths [12–15], whilst in the MIR pulse shaping polarization control is still a challenge. Polarization control uses the fact that

polarization shaped pulses $\mathbf{E}(t)$ can be expressed as a linear combination of two orthogonally polarized pulses according to

$$\mathbf{E}(t) = \hat{\mathbf{x}}E_x(t) + \hat{\mathbf{y}}E_y(t) \quad (4.1)$$

Combining two individual sets of orthogonally oriented linear polarized pulse shapes $E_x(t)$ and $E_y(t)$ therefore yields polarization shaped pulses $\mathbf{E}(t)$. The creation of $E_x(t)$ and $E_y(t)$ in the MIR can be realized by relying on two independent OPA processes in two orthogonally oriented nonlinear crystals. Two sets of individually shaped and temporally separated pulses in the NIR are independently parametrically transferred to the MIR by two orthogonal pump fields at 800 nm in two orthogonally aligned nonlinear crystals. Subsequent temporal recombination of these two sets yields arbitrary polarization, amplitude, and phase control in the MIR.

The indirect approach has the advantage that it uses well developed commercially available LC-SLMs. Moreover, the arrangement presented here has the potential for a true common-path geometry with improved interferometric stability in the MIR. We build on this indirect method using LC-SLMs, and develop a new technique named the **C**omplete **A**mplitude, **P**hase, and **P**olarization **U**ltrashort pulse **C**omputer **C**ontrol in the **I**nfrared via **N**onlinear **O**ptics (CAPPUCCINO).

In this chapter, based on our previous publications [16,17], polarization pulse shaping in the MIR is presented as follows: Section 4.2 shows the experimental setup of the home-built MIR pulse shaper, as well as the parametric transfer processes from shaped 800 nm and NIR pulses to shaped MIR pulses. Section 4.3 presents two examples of polarization pulse shaping in the MIR. Finally, Section 4.4 summarizes the work we have done on MIR polarization pulse shaping.

4.2 Experimental

4.2.1 Optical Setup

Details about the laser system used here have been described in Chapter 2. The output from a 1 kHz Ti:sapphire regenerative amplifier (RGA) ultrafast laser system is used as the light source (centered at 800 nm, ~ 150 fs pulse duration, 1 W). The experimental schematic setup of our CAPPUCCINO MIR pulse shaper is depicted in Figure 4.1 in detail. In this setup, a home-built OPA generates NIR signals and the 800 nm pulses are phase and amplitude modulated via direct pulse shaping, using commercial liquid crystal modulators ‘SLM1’ and ‘SLM2’ in 4-f configurations, respectively. The shaped NIR and 800 nm pulses are then parametrically transferred to the MIR through two OPA processes using two orthogonal orientated OPA crystals ‘KNB2’ and ‘KNB3’, respectively. The two resulting orthogonal MIR shaped pulses are then combined in a regrouping crystal ‘LIO’ (LIO_3), resulting in amplitude, phase and polarization controlled MIR pulses.

Near-Infrared Optical Parametric Amplifier

The schematic setup of the home-built OPA is shown in Figure 4.1. About 30% of the 800 nm output from the Ti:sapphire RGA was sent to the OPA. It is a two-stage white-light seeded potassium niobate (KNB) based OPA process, generating NIR signal pulses around $1.04 \mu\text{m}$. About 2% of the input 800 nm was used to perform the white light generation in a sapphire window (2 mm). The remainder of the 800 nm input was used as the pump light. The KNB crystal was cut at 41° (1 mm) for the type I OPA process:

Figure 4.1: Schematic setup of the CAPPUCCINO MIR polarization pulse shaper. OPA, optical parametric amplifier; SLM1: NIR spatial light modulator; SLM2: 800 nm spatial light modulator. Parameters of the optics are listed in the upper right corner.

$$\text{pump } (e) + \text{seed } (o) \rightarrow \text{signal } (o) + \text{idler } (o) \quad (4.2)$$

Direct Pulse Shaper with a 4-f Configuration

Figure 4.2 is the schematic configuration of a direct pulse shaper in a 4-f setup. A 4-f setup is a dispersion free device, composed of two diffraction gratings and two lenses, with the distance between each optical component fixed at the focal length of the lenses. The input light arrives at the first grating and is dispersed in different angles. At the Fourier plane after the first lens, each frequency component is focused and spatially isolated. The spatially spread pulses $E_{in}(\omega)$ are modulated by imposing an amplitude and phase mask $M(\omega)$, created by the SLM by applying voltage to individual SLM pixels, to yield:

$$E_{out}(\omega) = M(\omega)E_{in}(\omega) \quad (4.3)$$

The shaped pulses are then refocused and recombined by the second lens and grating, resulting in shaped re-collimated pulses.

Figure 4.2: The schematic configuration of a frequency domain pulse shaper in a 4-f configuration. SLM: Spatial light modulator which introduces the mask $M(\omega)$.

In our experiment, to achieve phase and amplitude modulation, LC-SLMs (‘SLM1’ and ‘SLM2’ in Figure 4.1) were used to perform the direct pulse shaping

for the NIR and 800 nm respectively. In each LC-SLM, there are two liquid crystal modulator (LCM) arrays orientated orthogonally to each other. The liquid crystal molecules are voltage sensitive and will change their alignment when the supplied voltage changes. The LC-SLMs are computer controlled and different masks can be achieved based on the following equation [18]:

$$E_{out} = E_{in} \exp [j(\Delta\phi^{(1)} + \Delta\phi^{(2)})/2] \\ [\mathbf{x} \cos[(\Delta\phi^{(1)} - \Delta\phi^{(2)})/2] + j\mathbf{y} \sin[(\Delta\phi^{(1)} - \Delta\phi^{(2)})/2]] \quad (4.4)$$

where E_{out} , and E_{in} are the amplitudes of the output and input light on the $\mathbf{x}$ polarization, respectively. $\Delta\phi^{(1)}$ and $\Delta\phi^{(2)}$ are the voltage induced birefringences of the two LCM arrays in the SLM, respectively. Different amplitude and phase masks can be obtained by changing $\Delta\phi^{(1)}$ and $\Delta\phi^{(2)}$, which are functions of the applied voltage, respectively.

4.2.2 Shaping of Near-Infrared Pulses

The simplified schematic setup of the pulse shaper is shown in Figure 4.3(a). About 30% of the output from a 1 kHz Ti:sapphire regenerative amplifier (RGA) laser system centered at 800 nm (~ 150 fs pulse duration, 1 W) was used to generate NIR pulses tunable around $1.04 \mu\text{m}$ in a two-stage white-light seeded potassium niobate (KNB) based optical parametric amplifier. The pulses were subsequently amplitude and phase modulated with a commercial LC-SLM (Jenoptik SLM-S640d) direct pulse shaper denoted as ‘SLM1’. Two temporally separated sets of pulse shapes with a fixed time delay ΔT were created, whose orientation was set to $\phi = 45^\circ$ with respect to the plane of the laser table with a half-wave retardation plate (henceforth, the polarization angle quoted will be with reference

Figure 4.3: (a) Simplified schematic setup of the CAPPUCCINO MIR polarization pulse shaper: OPA, optical parametric amplifier; SLM1, NIR Spatial Light Modulator; SLM2, 800 nm Spatial Light Modulator; DG, degrouping assembly; 1 and 2, orthogonally oriented KNB crystals; RG, regrouping assembly. (b) Detailed representation of the polarization sensitive parametric transfer.

to the plane of the laser table). In Figure 4.3(b) the two sets are indicated by ‘red’ and ‘blue’ boxes and ‘1’ and ‘2’, respectively. These two sets will evolve into orthogonal orientation in the subsequent parametric transfer and consist of completely independent amplitude and phase controlled pulse shapes (Figure 4.3(b)).

4.2.3 Shaping of 800 nm Pulses

The remainder of the 800 nm laser pulses ($650 \mu\text{J}$) was shaped in a second LC-SLM (Jenoptik SLM-S320d) direct pulse shaper, denoted as ‘SLM2’, and used as the pump pulses. The pump pulses were shaped to optimize the subsequent parametric transfer. The polarization of the shaped pump pulse was changed to $\phi = 45^\circ$ via a half-wave retardation plate and then split temporally into an x

component at $\phi = 0^\circ$ and a y component at $\phi = 90^\circ$ in the “degroupping” assembly of our setup. The “degroupping” assembly consists of a polarization beam splitter cube for separation into two orthogonally polarized components. The two sets were temporally adjusted with a translation stage and spatially recombined with a second polarization beam splitter yielding two orthogonally polarized components delayed by ΔT (red and blue boxes, also denoted ‘1’ and ‘2’, in Figure 4.3(b)).

4.2.4 Parametric Transfer to the Mid-Infrared

The two sets of shaped NIR pulses oriented at $\phi = 45^\circ$ and the 800 nm pump pulses oriented at $\phi = 0^\circ$ and $\phi = 90^\circ$ were recombined via a dichroic mirror, timed with a translation stage and slightly focused into two perpendicularly oriented KNB crystals (2 mm, $\theta = 41.1^\circ$, $\Phi = 0^\circ$) labeled ‘1’ and ‘2’ in Figure 4.3. In the two OPA processes that follow, two things are of importance. First, the amplitude and phase profile of the NIR pulses are parametrically transferred to the resulting MIR pulses [10, 11]. Second, an OPA process is highly polarization selective. The polarization state of the generated MIR pulses is governed by the polarization of the input fields and the orientation of the nonlinear medium. Here we have a type-I process:

$$\text{pump (800 nm, } e) + \text{seed (1037 nm, } o) \rightarrow \text{signal (1037 nm, } o) + \text{idler (3500 nm, } o) \quad (4.5)$$

For the scenario in Figure 4.3(b) that means that the 800 nm pump pulse oriented at $\phi = 90^\circ$ (denoted with the red box, labeled ‘1’) only transfers that part of the NIR pulse oriented at 45° into the MIR, which is a projection onto the x axis ($\phi = 0^\circ$). The parametric transfer takes place exclusively in crystal ‘1’ since only here does the pump field act as the extraordinary beam (e). No MIR signal

will be created at $\phi = 90^\circ$. In other words the group of pulses in the red box will be parametrically transferred in the red crystal to create the x component, while passing through the blue crystal with no effect. Analogous considerations apply for the creation of the y component (denoted in blue colors, labeled with ‘2’). This results in the transfer of the shapes of two individual sets of NIR pulses at $\phi = 45^\circ$ into two orthogonally polarized MIR pulses temporally separated by ΔT .

4.2.5 Regrouping of Shaped Mid-Infrared Pulses

A birefringent crystal was used to regroup the two temporally separated and orthogonally polarized beams. In such a medium, differing group refractive indices for ordinary and extraordinary beams (o and e) act to temporally collimate the different polarization components. In practice, ΔT was measured for the regrouping crystal before being programmed into the pulse shaper and adjusted on the degrouping assembly. A lithium iodate (LiIO_3) crystal (4 mm, $\theta = 90^\circ$) was used which accounts for a time delay of approximately $\Delta T = 2$ ps at $3.5 \mu\text{m}$. In this way we can compensate for the introduced time delay ΔT and temporally recombine the orthogonally oriented components to yield arbitrary amplitude, phase, and polarization shaped pulses in the MIR. The energy of the created pulses depends on their complexity and was in the range of 10–50 nJ.

4.2.6 Characterization of Shaped Mid-Infrared Pulses

The MIR spectra were measured with a monochromator (Dongwoo Optron, DM320i) with a InSb detector (InfraRed Associates, Inc., IS-1.0). For the detailed characterization of the MIR polarization shaped pulses we employed sum-

frequency generation (SFG) cross-correlation frequency resolved optical gating (X-FROG) [19] with a reference pulse at 800 nm ($< 5 \mu\text{J}$) in a beta-barium borate crystal ($100 \mu\text{m}$, $\theta = 29.2^\circ$). We look at the x and y components individually or a combination of both. In each case the MIR field passed through an additional polarizer set at 45° to ensure simultaneous SFGs for both polarization components in the polarization sensitive X-FROG process. The resulting traces appear in the visible and NIR region were measured with a spectrometer (Horiba Jobin Yvon, microHR).

4.3 Results and Discussion

4.3.1 Creation and Control of Shaped Single Pulses

To demonstrate the capabilities of this pulse shaper, a pulse centered at $3.5 \mu\text{m}$ was created in which the polarization state of the central spectral region (with a bandwidth of $\sim 75 \text{ nm}$) was linearly polarized at 0° , while the remaining spectral wings had linear polarization at 90° . Figure 4.4(a) shows the spectrum of the two temporally separated components (same polarization) of the NIR seed pulses that will be individually parametrically transferred into the MIR via two orthogonally oriented nonlinear crystals. For comparison, the dotted spectrum refers to an unshaped NIR seed pulse. The successful parametric transfer into the MIR with two orthogonally oriented polarization states is demonstrated in Figure 4.4(b). In this case, the pump pulses were shaped to have their spectrum narrowed to 3 nm .

Figure 4.4: (a) Spectrum of an unshaped seed pulse in the NIR, and spectra of the two components 1 and 2 of an amplitude modulated seed pulse to be transferred to the MIR and (b) the corresponding idler pulse in the MIR after parametric transfer with orthogonal polarization states.

4.3.2 Creation and Control of Two-Pulse Trains

X-FROG Characterizations

Subsequently, two-pulse trains with controllable inter-pulse polarization relation were created. We show in Figure 4.5 the X-FROG traces of a two-pulse train of equal amplitude, temporally separated by 840 fs, with the pulses orthogonally polarized with respect to each other. The middle panel shows the combined polarization components at $\phi = 0^\circ$ and 90° , whereas the other two panels show the individual components. A two-pulse train with the first and second pulses (inter-pulse delay = 840 fs) oriented at $\phi = 0^\circ$ and 45° , respectively is also depicted in Figure 4.6, along with the respective X-FROG traces. Figure 4.6(a)

depicts the X-FROG traces. The observed intensities agree well with the expected values for a polarizer setting of 45° .

Figure 4.5: X-FROG traces for a two-pulse train with temporal separation of 840 fs and orthogonal polarization.

The linear chirp observed in the X-FROG traces comes from the dispersion effect of the two orthogonal orientated birefringent crystals ('KNB2' and 'KNB3'). The orthogonal projections $E_x(t)$ and $E_y(t)$ of the MIR pulses suffer from different group velocity dispersions (GVDs). Therefore the $E_y(t)$ component generated in crystal '1' will obtain additional GVD when passing through crystal '2', whilst the $E_x(t)$ component created in crystal '2' will not be subjected to. Similarly, to generate the $E_x(t)$ in crystal '2', the input lights for the $E_x(t)$ have to pass crystal '1' before crystal '2', the inputs gains additional GVD from crystal '1', while the input lights for generation of $E_y(t)$ in crystal '1' do not. The different GVDs result in different temporal chirps for the two components $E_x(t)$ and $E_y(t)$. The different chirps can be eliminated by the spatial light modulators (SLMs) with additional chirp compensations in the masks.

Figure 4.6: (a) X-FROG traces for a two-pulse train with temporal separation of 840 fs and polarizations of 0° and 45° . (b) The corresponding MIR spectra of the individual x and y components.

Mid-Infrared Spectra

Figure 4.6(b) shows the corresponding MIR spectra of the individual x and y components and reveals the expected modulation in the x component for a two-pulse train with a temporal separation of 840 fs. The slight modulation in the y component results from residual side pulses that were amplified in the OPA process and are estimated to be around 10% in field amplitude for the MIR. These side pulses originate mainly from the pixilation of the SLMs. The presented X-FROG measurement does not fully characterize the ellipticity of the shaped pulses, but full characterization may be performed using more intricate methods [6, 14, 20].

4.4 Conclusions

In summary, we developed a new computer programmable pulse shaping technique named CAPPUCCINO, with full control over amplitude, phase and polarization in the MIR via parametric transfer. One advantage of using indirect pulse shaping is that the SLMs for the NIR are well developed and commercially available. In addition, the optical setup developed has the potential for a true common-path geometry. This will improve the interferometric stability. In this setup, we used beam splitters and translation stage based de-grouping assembly, which can not guarantee true interferometric stability. By replacing these with an assembly based on a birefringent medium, real common-path geometry can be achieved [17, 21]. Since it is known that the cut-off wavelength of a standard LC-SLM is ~ 400 nm, direct UV polarization pulse shaping is also a challenge. It is worth noting that this MIR pulse shaping technique CAPPUCCINO can also be applied to UV polarization pulse shaping beyond the high frequency limit, by switching the OPA process to a sum-frequency generation process. This work has been carried out and the interferometric stability has been demonstrated by our group [17].

As has been shown in this chapter, MIR pulse trains with fully controllable amplitude, phase and polarization can be generated with the MIR polarization pulse shaping (CAPPUCCINO) technique. Creation of specific pulse trains is necessary for 2D IR spectroscopy in a pump-probe geometry and with phase cycling, as will be presented in the following chapter.

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Chapter 5

Phase Cycling Schemes for Two-Dimensional Optical Spectroscopy with a Pump-Probe Geometry

5.1 Introduction

Two-dimensional (2D) photon echo optical spectroscopy is fast becoming an essential spectroscopic tool in the study of chemical and biological dynamics [1–5]. In these experiments, three or four ultrashort pulses with controllable inter-pulse delays interact with a sample. The resultant material nonlinear polarization produces a nonlinear optical signal field that is then detected. This inter-pulse delay-dependant signal can be Fourier transformed to give a multidimensional optical spectrum.

The conventional way of performing 2D optical spectroscopy is to use a non-

collinear phase matching approach in which three interacting pulses are introduced onto the sample from different directions. The signal beam then exits the sample in a unique direction, free of interference from other undesired signals. An additional local oscillator pulse is then introduced in the direction of the signal field for heterodyne detection [6].

As has been demonstrated in the previous chapter, fully controlled phase coherent pulse trains can be generated using a mid-infrared (MIR) pulse shaper (CAPPUCCINO) along an interferometrically stable common path [7]. Therefore an alternative approach to do 2D IR spectroscopy is to use collinear phase coherent pulse trains obtained from pulse shapers, which reduces the mechanical complexity of the experiment, especially for analogous experiments at higher dimensions. This approach necessitates the weighted summation of the signals over a series of experiments repeated at different inter-pulse phases, a technique known as phase cycling [8–10]. Recently, a general theory of phase cycling and the selection procedure of the phase cycling schemes for collinear phase coherent multidimensional spectroscopy has been published [11]. However, a totally collinear beam geometry may have certain limitations such as relying primarily on fluorescence for the observable signal. This limitation will pose problems in measuring the 2D spectra of non-fluorescent systems.

A partially collinear beam geometry that resembles a pump-probe experiment has recently been introduced that can address the limitations of both the fully collinear and fully non-collinear beam geometry [12–16]. In this geometry, the first two interacting pulses are collinear and form the “pump” part of the experiment, while the third “probe” pulse interacts as well as heterodyne detects the signal. This beam geometry is illustrated in Figure 5.1. This geometry allows 2D spectra with pure absorptive peak-shapes to be obtained automatically. Op-

tical pulse shapers [17–20] can be used to produce the phase locked “pump” pulse trains. The phase locked “pump” pulses shift the experiment into the “rotating frame”, resulting in a slower modulating signal, and hence allows much faster data collection due to taking fewer data points. Zanni et al. have used this feature to efficiently obtain 2D spectra that tracks the formation of hIAPP amyloid [16]. However, to fully obtain the desired 2D spectra without any ambiguities and interference from other spurious signals, it is necessary to apply phase cycling.

Figure 5.1: Schematic of the setup for 2D optical spectroscopy with a pump-probe beam geometry

In this chapter, we apply the concepts of phase cycling and phase cycling scheme selection procedures to a 2D optical spectroscopy experiment performed with a pump-probe beam geometry [21]. We demonstrate that the phase cycling schemes, which are hitherto only applied to collinear pulse beam geometry [11], can also be applied to 2D spectroscopic experiments using a partially collinear beam geometry. In Section 5.2, we outline the phase cycling theory in detail for the 2D IR spectroscopy with a pump-probe geometry case. With the presented theory it is also shown theoretically how to obtain purely absorptive 2D spectra.

In Section 5.3, we present the results from a numerical simulation that illustrates the principles and highlights the efficacy of the phase cycling scheme presented.

5.2 Theory

In the formalism of the perturbative nonlinear polarization theory and diagrammatic perturbation theory, a conventional pump-probe spectroscopic experiment can be viewed as a third order nonlinear optical experiment [22]. In this interpretation, the system interacts twice with the “pump” pulse light field while the “probe” pulse provides the third interaction. The resultant third order nonlinear optical signal emanating in the direction of the “probe” pulse is then detected. This detection can be viewed as a heterodyne detection, with the “probe” pulse functioning as the local oscillator and is equivalent to taking the transient absorption spectrum of the “probe” pulse.

The adaptation of the pump-probe beam geometry to a 2D optical experiment is portrayed in Figure 5.1 and the pulses can be expressed as

$$\begin{aligned}
 E(t) = & A_1(t + T_w + \tau) \exp(-i\omega_L t + i\phi_1 + i\mathbf{k}_{pump} \cdot \mathbf{r}) \\
 & + A_2(t + T_w) \exp(-i\omega_L t + i\phi_2 + i\mathbf{k}_{pump} \cdot \mathbf{r}) \\
 & + A_3(t) \exp(-i\omega_L t + i\mathbf{k}_{probe} \cdot \mathbf{r}) + c.c.
 \end{aligned} \tag{5.1}$$

The “pump” consists of a pair of phase locked pulses with the time delay τ . These “pump” pulses are both incident along the direction of $\mathbf{k}_{pump}$, and have phases ϕ_1 and ϕ_2 , respectively. The “probe” pulse, delayed by a waiting time T_w from the second “pump” pulse, is incident along the direction $\mathbf{k}_{probe}$. The same “probe” pulse then acts as a local oscillator to heterodyne detect the signal emanating

in the $\mathbf{k}_{probe}$ direction. As the “probe” pulse interacts noncollinearly with the “pump” pulses, it is meaningless to consider the phase relationship between the “probe” and the “pump” pulses and is omitted for the expression for the “probe” pulse term in Equation 5.1. We consider here the interaction of the light field shown in Equation 5.1 with a quantum two level system. This can represent an electronic transition or a vibrational transition in a system with an anharmonic potential.

We denote the third order nonlinear system response function as $R^{(3)}(t_1, t_2, t_3)$ and calculate the resultant third order signal field $S(\tau, t)$ by performing the triple integral [22]

$$S(\tau, t) = \int \int \int dt_3 dt_2 dt_1 R^{(3)}(t_1, t_2, t_3) E(\mathbf{k}, t - t_3) \\ \times E(\mathbf{k}, t - t_3 - t_2) E(\mathbf{k}, t - t_3 - t_2 - t_1) \quad (5.2)$$

The third order nonlinear response function $R^{(3)}(t_1, t_2, t_3)$ is a sum of various processes that can be enumerated using double sided Feynman diagrams (DSFDs). In Figure 5.2, we depict the DSFDs of various third order nonlinear optical processes that are possible in the pump-probe beam geometry. The interactions of the system with the light fields are represented by arrows labeling the $\mathbf{k}$ vector and the pulse phase acquired by the system with each interaction.

Since the experiment is set up to measure the heterodyned signal in the probe pulse direction, $\mathbf{k}_{probe}$, we have listed only those third order DSFDs that result in the signal pulse emanating in the $\mathbf{k}_s = \mathbf{k}_{probe}$ direction. This dictates that the signal observed does not have any “pump” pulse wavevector $\mathbf{k}_{pump}$ dependence. This is only possible if the first two pulse interactions impart a wavevector dependence that cancels each other out (i.e. $+\mathbf{k}_{pump} - \mathbf{k}_{pump}$). This condition constrains the

Figure 5.2: DSFDs for a two level system with the partially collinear pump-probe beam geometry. the “pump” pulses are both incident along direction $\mathbf{k}_{pump}$ and have phases ϕ_1 and ϕ_2 , respectively. The “probe” interacts in the direction of $\mathbf{k}_{probe}$, and the signal emits along $\mathbf{k}_s = \mathbf{k}_{probe}$, (a) s_{NR} ($\alpha = 1, \beta = -1$), non-rephasing signal, (b) s_R ($\alpha = -1, \beta = 1$), rephasing signal, (c) s_{P1} ($\alpha = 0, \beta = 0$), signal arising from interacting twice with only the first “pump” pulse and (d) s_{P2} ($\alpha = 0, \beta = 0$), signal arising from interacting twice with only the second “pump” pulse. α and β describe the summed interactions with the first and second pulse, respectively.

diagrams to have only population elements during the T_w period. (For brevity, we have only included diagrams that are at the excited population state during the period. There is another analogous set of diagrams at ground population state during the T_w period).

Out of the diagrams presented in Figure 5.2, s_R is conventionally termed the rephasing or echo process, while s_{NR} is termed the non-rephasing or anti-echo process. s_{P1} depicts the process in which the system interacts twice with only the first “pump” pulse while s_{P2} depicts the process in which the system interacts twice with only the second “pump” pulse. s_{P1} and s_{P2} corresponds to signals

from a regular pump-probe experiment with pump-probe delay of $\tau + T_w$ and T_w , respectively. In this case both these background pump-probe signals s_{P1} and s_{P2} signals are not the desired signals and can be eliminated through phase cycling.

Although only the s_R process is required to obtain an absolute valued photon echo 2D spectrum, contributions from both s_R and s_{NR} are required to obtain a pure absorptive 2D spectrum [23, 24]. In the impulsive regime, when the pulses used are short compared with the dynamics of interest, the signals from the two diagrams s_R and s_{NR} in Figure 5.2 can be solved through Equation 5.2 and expressed as

$$\begin{aligned} s_R(\tau, t) &\propto \exp(-i\phi_1 + i\phi_2) \exp(i\Delta\omega_{10}\tau) \exp(-i\omega_{10}t) F_R(\tau, T_w, t) \\ s_{NR}(\tau, t) &\propto \exp(i\phi_1 - i\phi_2) \exp(-i\Delta\omega_{10}\tau) \exp(-i\omega_{10}t) F_{NR}(\tau, T_w, t) \end{aligned} \quad (5.3)$$

where ω_0 is the resonance frequency of the two level system, and $\Delta\omega_{10} = \omega_{10} - \omega_L$ is the resonance frequency detuned from the laser frequency ω_L . The time evolution over delay τ is in the “rotating frame” of the laser frequency. $F(\tau, T_w, t)$ is the dephasing and population relaxation function that determines the peak-shape. For the ease of later discussion of peakshapes, we will assume that $F_R(\tau, T_w, t) = F_{NR}(\tau, T_w, t) = \exp[-(\Gamma\tau + \Gamma t)]$, and the dynamics can be described in the motionally narrowed limit. The s_{P1} and s_{P2} processes do not depend on the pulse phases and can be expressed as

$$\begin{aligned} s_{P1}(\tau, t) &\propto \exp(-i\omega_{10}t) F_{P1}(\tau, T_w, t) \\ s_{P2}(\tau, t) &\propto \exp(-i\omega_{10}t) F_{P2}(\tau, T_w, t) \end{aligned} \quad (5.4)$$

In this pump-probe geometry, the individual DSFDs in Figure 5.2 cannot be

discriminated directionally. However, the phase relations of the interacting pulses can be manipulated to acquire the desired signal. This can be achieved with the use of phase locked collinear pulses in a phase cycling procedure. In earlier papers, the principles of phase cycling and the phase cycling scheme selection procedure have been developed [8, 11]. With phase cycling, we rely on the different phase dependence to select the desired signal. In these earlier studies, for collinear three or four pulse experiments, phase cycling was applied over all the pulses to obtain the desired nonlinear optical signal. In this case, phase cycling can be applied over the collinear “pump” pulses. Analogous to the $\mathbf{k}$ vectors, the system also acquires the phases of the interacting pulses and gains a phase dependent factor $\exp(i\alpha\phi_1 + i\beta\phi_2)$, 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, β can be calculated in the same way for the second pulse. For instance, the rephasing signal s_R in Figure 5.2(b) results in a phase dependent term, $\exp(-i\phi_1 + i\phi_2)$. $s_i(\alpha, \beta)$ labels each DSFD on Figure 5.2 with its phase dependence. The values α and β are not independent. Since the signal emits in the direction of the probe, $\mathbf{k}_{probe}$, the system must interact once with the probe field. This entails that the time period T_w after the second “pump” pulse must be a population state evolution. In order to be in the population state after interactions of the two “pump” pulses, the number of right-going arrows must be the same as the left-going arrows for the first two pulses. This constrains the values of α and β to be

$$\alpha + \beta = 0 \tag{5.5}$$

Furthermore, if we restrict ourselves to processes of third and lower orders while

ignoring higher order terms, we need consider only up to two interactions from the first two pulses. This results in the condition

$$|\alpha| + |\beta| \leq 2 \quad (5.6)$$

The consideration of such a problem is a special case of the general phase cycling problem for a three or four pulse experiment discussed in Reference [11].

The total signal measured in the $\mathbf{k}_{probe}$ direction is the sum of the processes summarized by the DSFDs in Figure 5.2 and after taking into consideration Equation 5.5, is proportional to

$$S(\phi_{21}; \tau, t) = \sum_{\beta} s(\beta; \tau, t) \exp(i\beta\phi_{21}) \quad (5.7)$$

where $\phi_{21} = \phi_2 - \phi_1$. In the summation of Equation 5.7, $s(\beta = 1; \tau, t) \exp(i\phi_{21})$ and $s(\beta = -1; \tau, t) \exp(-i\phi_{21})$ represent the terms s_R and s_{NR} , respectively, while $s(\beta = 0; \tau, t)$ include both the s_{P1} and s_{P2} terms. This signal $S(\phi_{21}; \tau, t)$ is heterodyne detected using the “probe” pulse as the local oscillator, and spectrally resolved using a spectrometer (equivalent to a Fourier transform about the t -domain). In the impulsive limit, where we assume the local oscillator behaves like a delta-function in time, the measured spectrally resolved signal is $\tilde{S}(\phi_{21}; \tau, \omega_t) = \text{Re}[\sum_{\beta} s(\beta; \tau, \omega_t) \exp(i\beta\phi_{21})]$. This signal, when expressed in detail becomes

$$\begin{aligned} \tilde{S}(\phi_{21}; \tau, \omega_t) = & [A(\omega_t - \omega_{10}) \cos(\Delta\omega_{10}\tau + \phi_{21}) \exp(-\Gamma\tau) \\ & - D(\omega_t - \omega_{10}) \sin(\Delta\omega_{10}\tau + \phi_{21}) \exp(-\Gamma\tau)] \\ & + [A(\omega_t - \omega_{10}) \cos(\Delta\omega_{10}\tau + \phi_{21}) \exp(-\Gamma\tau) \\ & + D(\omega_t - \omega_{10}) \sin(\Delta\omega_{10}\tau + \phi_{21}) \exp(-\Gamma\tau)] \\ & + 2A(\omega_t - \omega_{10}) \end{aligned} \quad (5.8)$$

The terms from the first and second line of Equation 5.8 arise from s_R and s_{NR} , respectively, while the term from the last line in Equation 5.8 arises from s_{P1} and s_{P2} . $A(\omega_t - \omega_{10}) \equiv \Gamma/[(\omega_t - \omega_{10})^2 + \Gamma^2]$ and $D(\omega_t - \omega_{10}) \equiv (\omega_t - \omega_{10})/[(\omega_t - \omega_{10})^2 + \Gamma^2]$ are the absorptive and dispersive Lorentzian line-shape, respectively. Originally from Equation 5.3, the rephasing s_R signal contains only $\exp(i\phi_{21})$ terms while the non-rephasing s_{NR} signal contains only $\exp(-i\phi_{21})$ terms. The heterodyne detection however adds terms with $\exp(-i\phi_{21})$ to s_R and terms with $\exp(i\phi_{21})$ to s_{NR} . The summation in Equation 5.8 can be rewritten as

$$\begin{aligned}\tilde{S}(\phi_{21}; \tau, \omega_t) &= A(\omega_t - \omega_{10}) \exp(-i\Delta\omega_{10}\tau - i\phi_{21} - \Gamma t) + 2A(\omega_t - \omega_{10}) \\ &\quad + A(\omega_t - \omega_{10}) \exp(i\Delta\omega_{10}\tau + i\phi_{21} - \Gamma t) \\ &\equiv \sum_{\beta} s'(\beta; \tau, \omega_t) \exp(i\beta\phi_{21})\end{aligned}\tag{5.9}$$

The problem of extracting the desired term for the 2D spectra, $s'(\beta = 1)$ from the summation in Equation 5.9 can be phrased as a discrete Fourier transform problem [11],

$$\begin{aligned}S'_{1 \times L}(\beta; \tau, \omega_t) &= \frac{1}{L} \sum_{l=0}^{L-1} \tilde{S}(l \cdot \Delta\phi_{21}; \tau, \omega_t) \exp(-il\beta \cdot \Delta\phi_{21}) \\ &\equiv \frac{1}{L} \sum_{l=0}^{L-1} \tilde{S}(l \cdot \Delta\phi_{21}; \tau, \omega_t) W_L^{l\beta}\end{aligned}\tag{5.10}$$

with $\phi_{21} = l \cdot \Delta\phi_{21}$, L is the number of sample points in the ϕ_{21} -space, and $W_L^{l\beta}$ is the summation weight. Experimentally, this amounts to conducting a series of experiments with different interpulse phases ϕ_{21} , and the resultant series of phase dependant signals added according to weight $W_L^{l\beta}$. L determines the number of experiments that needs to be performed, and therefore should be kept

as low as possible. We term this a $1 \times L$ phase-cycling experiment to indicate that the experiment consists of an L -step phase cycling of the second pulse and no phase cycling of the first pulse. The periodic property of discrete Fourier transform, however, introduces aliased signals. The weighted summation of the phase dependent population cannot distinguish between the signals $\exp(i\beta\phi)$ and $\exp[i(\beta + nL)\phi]$, where n is any integer.

We shall now go through and analyze how different values of L will affect the final 2D spectrum of signal $s'(\beta = 1)$.

For $L = 1$, there is effectively no phase cycling, all the terms in Equation 5.9 will show up on the 2D spectrum.

For $L = 2$, the 1×2 step phase cycling scheme cycles the second pulse through $\phi_{21} = 0$, and π . The summation of the two resultant experimental data, as described in Equation 5.10, can be expressed as

$$S'_{1 \times 2}(\beta = 1; \tau, \omega_t) \propto \tilde{S}(\phi_{21} = 0; \tau, \omega_t) + \tilde{S}(\phi_{21} = \pi; \tau, \omega_t)e^{-i\pi} \quad (5.11)$$

This scheme eliminates the background pump-probe signal terms of s_{P1} and s_{P2} and has been experimentally implemented in a recent experiment [16]. However the signal $s'(\beta = 1 - (1 \times 2)) = s'(\beta = -1)$ will also be picked up due to the aliasing. This essentially picks up all the terms due to s_R and s_{NR} as well as extra terms arising from the spectrally resolved heterodyned detection. The resultant signal can be expressed as

$$s'_{1 \times 2}(\beta = 1; \tau, \omega_t) \propto [\exp(i\Delta\omega_{10}\tau) + \exp(-i\Delta\omega_{10}\tau)] \exp(-\Gamma\tau)A(\omega_t - \omega_{10}) \quad (5.12)$$

Upon Fourier transform about the τ -domain, the peaks on the 2D spectra can be described as

$$\begin{aligned} s'_{1 \times 2}(\beta = 1; \omega_\tau, \omega_t) &= [A(\omega_\tau + \Delta\omega_{10}) + iD(\omega_\tau + \Delta\omega_{10}) + A(\omega_\tau - \Delta\omega_{10}) \\ &\quad + iD(\omega_\tau - \Delta\omega_{10})]A(\omega_t - \omega_{10}) \end{aligned} \quad (5.13)$$

which gives two exact copy of peaks that are mirror imaged about the $\omega_\tau = 0$. This will produce ambiguity in the interpretation of the 2D spectrum particularly if the spectrum gets crowded. It is therefore essential to get rid of such redundancy.

For $L = 3$, the 1×3 step-phase cycling scheme cycles the second pulse through $\phi_{21} = 0, 2\pi/3$ and $4\pi/3$. The summation of the three resultant experimental data, as described in Equation 5.10, can be expressed as

$$\begin{aligned} s'_{1 \times 3}(\beta = 1; \tau, \omega_t) &\propto \tilde{S}(\phi_{21} = 0; \tau, \omega_t) + \tilde{S}(\phi_{21} = \frac{2\pi}{3}; \tau, \omega_t)e^{-i(2\pi/3)} \\ &\quad + \tilde{S}(\phi_{21} = \frac{4\pi}{3}; \tau, \omega_t)e^{-i(4\pi/3)} \end{aligned} \quad (5.14)$$

This results in only the desired term with $\exp(i\phi_{21})$ is acquired and the signal can be expressed as

$$s'_{1 \times 3}(\beta = 1; \tau, \omega_t) \propto \exp(i\Delta\omega_{10}\tau - \Gamma\tau)A(\omega_t - \omega_{10}) \quad (5.15)$$

This term can then be Fourier transformed in the τ domain to yield

$$s'_{1 \times 3}(\beta = 1; \omega_\tau, \omega_t) \propto [A(\omega_\tau + \Delta\omega_{10}) + iD(\omega_\tau + \Delta\omega_{10})]A(\omega_t - \omega_{10}) \quad (5.16)$$

According to Equation 5.16, if we take only the real valued part of $(s'_{1 \times 3}(\beta = 1; \omega_\tau, \omega_t))$, we obtain the desired pure absorptive 2D spectrum.

For $L = 4$ and above, the recovered 2D spectrum is the same as for the $L = 3$.

One major advantage of using phase locked pulses is the ability to shift the oscillatory signal during the τ period to the “rotating frame” of a reference laser frequency. From Equation 5.3, over the delay τ , the signal is oscillating at $\Delta\omega_{10} = \omega_{10} - \omega_L$. This is to be compared with the oscillating frequency of ω_{10} for the usual non-rotating frame signal. According to the Nyquist theorem, the sampling rate must be at least twice that of the highest frequency to prevent aliasing [25]. If we take the furthest transition frequency from the laser pulse center frequency to be one and a half full width half maximum (FWHM) away (where the spectral intensity is less than 2×10^{-3} times that of the spectral intensity at the center frequency), then by sampling the delay τ -space at intervals about 0.75 times that of the laser FWHM in pulse duration for a Gaussian profiled pulse, it is enough to recover a 2D spectrum with no spurious peaks about the ω_τ -axis.

The implementation of such signal acquisition in the “rotating frame” hinges on the ability to produce high quality pulse trains with stable interpulse phase, and this can be produced easily by pulse shapers [17–20, Chap. 4]. In general, pulse shapers modulate a pulse in the spectral domain by imposing a spectral mask $M(\omega)$ on the input pulse. The output shaped pulse spectrum can be described as $E_{shaped}(\omega) = M(\omega)E(\omega)$ where $E(\omega)$ is the spectral amplitude of the input pulse. In order to produce a pulse pair with a phase difference of ϕ_{21} and delay τ , the required spectral mask can be expressed as

$$M(\omega) = 1 + \exp[i(\omega - \omega_{ref})\tau + i\phi_{21}] \quad (5.17)$$

where the reference frequency ω_{ref} is in general, arbitrary. However ω_{ref} is usually equated to the laser center frequency $\omega_{ref} = \omega_L$, which is the case for this present

study. Upon Fourier transformation, the “pump” pulse pair in Equation 5.1 is obtained. At the other extreme, if the reference frequency is set at zero, $\omega_{ref} = 0$, the mask to produce two phase locked pulse train becomes

$$M(\omega) = 1 + \exp[i\omega\tau + i\phi_{21}] \quad (5.18)$$

In this case, the advantages of the “rotating frame” will be negated as the oscillating term over the delay τ will be at the transition frequency ω_{10} instead of $\Delta\omega_{10} = \omega_{10} - \omega_{ref}$. For such experiments, sampling will have to be carried at time intervals at or below half the inverse of the transition frequency $2\pi/\omega_{10}$ so as to avoid aliasing. Under such condition, for an experiment conducted without any phase cycling, the resultant 2D spectrum will be analogous to Figure 5.3(a) but with peaks widely separated about the ω_τ -axis, and there will be no ambiguities in identifying peaks of $s'(\beta = 1)$ from peaks of $s'(\beta = -1)$. In practice, only the positive ω_τ -positive ω_t quadrant that consists exclusively of $s'(\beta = -1)$ peaks will be presented as data, deeming a 1×2 phase cycling scheme is unnecessary.

Taking both scenarios of Equation 5.17 and Equation 5.18 into account, we consider an example here, for an experiment with pulses of 50 fs FWHM duration centered at 800 nm, interrogating a system with transitions in the 800 nm region. Much experimental effort can be saved in a 1×3 phase cycling scheme experiment cast in the “rotating frame”, as the delay τ can be sampled at intervals of about 35 fs, whereas for a non phase-cycled non rotating-frame experiment, the delay τ needs to be sampled at intervals of 1.3 fs or less.

Experimentally, there are further factors that need to be considered. Due to the fact that noise tends to predominate at the low frequencies, it may be desirable to choose the reference frequency ω_{ref} away from the laser center frequency. In

practice, an optimum ω_{ref} will have to be chosen on one hand to avoid the low frequency noises, and on the other hand to maximize the data collecting efficiency gained from making use of the “rotating frame” [16]. Furthermore, although it introduces aliasing and distortions to signals, it may be possible to carefully implement undersampling for a non phase-cycled non rotating-frame experiment to cut down on the sampling rate.

5.3 Simulation of 2D Spectra

5.3.1 Non-Perturbative Calculation of the Polarization for a Two Level System

In this section, we perform simulations to illustrate the concept and efficacy of phase cycling as applied in acquiring a 2D spectrum in a pump-probe beam geometry.

The most common method to calculate 2D spectra is to solve individual terms of the perturbative series in orders of the interacting optical fields. This method allows one to selectively calculate the 2D spectrum of any particular process. This can be done by identifying the DSFDs of the desired process and translating them into the appropriate equations to solve [1, 2]. Here, we will not be using the perturbative series to calculate the 2D spectra. We will instead be solving the Liouville equation non-perturbatively to ensure that signals of all orders and processes are calculated simultaneously. The Liouville equation is expressed in a series of coupled partial differential equations, and is then solved numerically [26, 27].

The Liouville equation that describes the time evolution of the density matrix $\rho(t)$ can be written as

$$\partial_t \rho(t) = -\frac{i}{\hbar} [H_{mol}(t) - \mu \cdot E(t), \rho(t)] + \Re \rho(t) \quad (5.19)$$

where $H_{mol}(t)$ is the molecular Hamiltonian, and μ is the system transition dipole moment. The system-field interaction is treated semi-classically. $E(t)$ is the electric field as described in Equation 5.1. $\Re$ is the relaxation and dephasing operator.

We consider a two-level system with a ground state ‘0’ and an excited state ‘1’. Invoking the rotating wave approximation (RWA) in the frame of the laser frequency which discards any highly oscillating term, the coupled partial differential equations that describe the elements of the density matrix can be expressed as

$$\begin{aligned} \partial_t \sigma_{10} &= -\Gamma \sigma_{10} - i\Delta\omega \sigma_{10} + i\mu_{10} A(t) [\rho_{00} - \rho_{11}] \\ \partial_t \rho_{11} &= -\gamma \rho_{11} + i\mu_{10} [A(t) \sigma_{01} - A^*(t) \sigma_{10}] \\ \partial_t \rho_{00} &= i\mu_{10} [A^*(t) \sigma_{10} - A(t) \sigma_{01}] \end{aligned} \quad (5.20)$$

where μ_{10} is the transition dipole moment between the ground and excited state. $\Delta\omega = \omega_{10} - \omega_L$ is the resonance frequency detuned from the laser frequency ω_L , $A(t)$ is the pulse envelope function of the incident pulse field as shown in 5.1, σ_{10} is the non-oscillating part of the off-diagonal density matrix element that represents coherence $\rho_{10} = \sigma_{10} \exp(-i\omega_L t)$, and Γ is the total dephasing rate in the form of $\Gamma = 1/2T_1 + 1/T_2^*$, with $T_1 \equiv \gamma^{-1}$ and T_2^* the population decay, and pure coherence dephasing time, respectively. The coupled partial differential equations

can be solved numerically using the fourth order Runge-Kutta method [28] and the function $\sigma_{10}(t)$ can be obtained, from which the material polarization $P(t)$ can be calculated as

$$P(\phi_{21}; \tau, t) \propto \mu_{10} \sigma_{10}(\phi_{21}; \tau, t) \exp(-i\omega_L t) \quad (5.21)$$

We have put in the variables τ and ϕ_{21} to explicitly denote the dependence of the polarization on the interpulse delay and phase, respectively. The spectrally resolved heterodyned signal observed on a spectrometer can then be expressed as

$$I(\phi_{21}; \tau, \omega_t) \propto \text{Im}[A_3^*(\omega_t) P(\phi_{21}; \tau, \omega_t)] \quad (5.22)$$

where $A_3^*(\omega_t)$ is the Fourier transform of the pulse envelope of the “probe” pulse in Equation 5.1 that also serves as the local oscillator for the heterodyne detection, and $P(\omega_t)$ is the Fourier transform of $P(t)$. $I(\phi_{21}; \tau, \omega_t)$ is calculated for different delays of τ . To implement the phase cycling scheme, a series of calculations are performed for different interpulse phases ϕ_{21} according to the phase cycling scheme used and the resultant signals added according to the weights prescribed by Equation 5.10. We have expressed in detail the summation for the 1×2 and 1×3 step-phase cycling schemes in Equations 5.11 and 5.14, respectively. This signal from this weighted summation is then Fourier transformed about the τ -axis to give the 2D spectrum.

5.3.2 Simulated 2D Spectra

We simulate a 2D spectrum of a simple two level system acquired using a pump-probe beam geometry. The three incident pulses have the same central frequency

ω_L at 2025.0 cm^{-1} , with an energy of $0.1 \mu\text{J}$ per pulse. The laser pulses are assumed to have Gaussian envelopes, with the FWHM pulse duration of $\tau_p = 50 \text{ fs}$. The beam is focused to a spot $50 \mu\text{m}$ in diameter. The transition frequency of the two level system ω_{10} is set at 2105.0 cm^{-1} , and the transition dipole moment is $\mu_{10} = 0.2 \text{ debye}$. The population decay is $T_1 = 2.0 \text{ ps}$, and the pure coherence

Figure 5.3: *Simulation of 2D spectra of phase cycling experiments with a pump-probe geometry for a model two-level system to select the $s'(\beta = 1)$ signal. (a), (b) and (c) are real valued 2D spectra with different phase cycling steps: (a) without phase cycling; (b) using a 1×2 -phase cycling scheme, resulting in the desired signal $s'(\beta = 1)$ and an extra $s'(\beta = -1)$ peak due to aliasing; (c) using a 1×3 -phase cycling scheme to obtain a pure absorptive spectrum of only the signal $s'(\beta = 1)$. (d) Imaginary valued 2D spectrum from a 1×3 -phase cycling scheme, resulting in a peak that is dispersive along the ω_τ -axis and absorptive along the ω_t -axis.*

dephasing constant is $T_2^* = 0.6$ ps. The temporal interval between the second and third pulse, the waiting time T_w is set at 0.4 ps.

Figure 5.3(a) depicts the real valued 2D spectrum without phase cycling. Without any phase cycling, the spectrum is dominated by the middle peak at $(\omega_\tau = 0.0 \text{ cm}^{-1}, \omega_t = 2105.0 \text{ cm}^{-1})$ and is mainly attributed to the first order process with a single interaction with the “probe” pulse. Third order processes s_{P1} and s_{P2} also contribute to this peak. These processes which do not depend on the interpulse phase ϕ_{21} and the resulting peaks can be eliminated by taking the difference of spectra collected with and without the set of “pump” pulses, just like a regular pump-probe experiment.

Figure 5.3(b) depicts the real valued 2D spectrum under a 1×2 phase cycling scheme that chooses the $s'(\beta = 1)$ term in Equation 5.9. The middle peak which is due to processes that are independent of ϕ_{21} are absent in the figure. However, as shown in the argument leading to Equation 5.12, this 1×2 phase cycling scheme fails to discriminate the $s'(\beta = 1)$ term from the $s'(\beta = -1)$ term due to aliasing. In Figure 5.3(b), the bottom peak at $(\omega_\tau = -80.0 \text{ cm}^{-1}, \omega_t = 2105.0 \text{ cm}^{-1})$ is due to the $s'(\beta = 1)$ term, while the top peak at $(\omega_\tau = 80.0 \text{ cm}^{-1}, \omega_t = 2105.0 \text{ cm}^{-1})$ represents the $s'(\beta = -1)$ term.

Figure 5.3(c) represents the real valued 2D spectrum under a 1×3 phase cycling scheme. The increment of one step in the phase cycling excludes the $s'(\beta = -1)$ term. The spectrum contains a pure absorptive peak as is predicted by Equation 5.14. Figure 5.3(d) depicts the imaginary valued spectrum counterpart of Figure 5.3(c). This peak appears exactly according to Equation 5.14. The peak can be described by $D(\omega_\tau + \Delta\omega_{10})A(\omega_t - \omega_{10})$, as having a dispersive line-shape about the ω_τ -axis while having an absorptive line-shape about the ω_t -axis.

5.4 Conclusions

In this chapter, we have presented phase cycling schemes for 2D optical spectra using a pump-probe beam geometry. We have shown through theoretical analysis that by using a 1×3 phase cycling scheme over the “pump” pulse train, a purely absorptive 2D spectrum is obtained without interferences from other processes. We also adapted a nonperturbative approach to solving the Liouville equation to simulate the phase cycling acquisition of 2D spectra for a two level system.

There have been theoretical and experimental efforts towards the development of optical spectroscopy of higher dimensions [29,30]. The “pump-probe” approach to 2D spectroscopy can be extended to higher dimensions. For instance, instead of a two pulse “pump” pulse train for a 2D experiment, a three dimensional (3D) experiment can be performed with a four pulse collinear “pump” pulse train. In order to obtain meaningful spectra, phase cycling over these collinear “pump” pulses will be important. The phase cycling scheme selection procedures and analysis presented here will be useful in understanding and choosing the appropriate phase cycling schemes for these multidimensional pump-probe spectroscopic experiments.

With the CAPPUCCINO MIR pulse shaper, and the presented phase cycling techniques, 2D IR experiments can be carried out, which is one of our ongoing projects.

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Summary and Future Work

In this dissertation, the vibrational dynamics of the carbonyl stretching modes of $\text{Os}_3(\text{CO})_{12}$ in CHCl_3 were studied using ultrafast pump-probe spectroscopy. The anomalous rising features in the equatorial mode pump-probe traces are shown to arise from the axial-equatorial combination band transitions, which are spectrally overlapped with the fundamental transitions. No clear indication of any direct intra-molecular vibrational energy transfer between the axial and equatorial CO stretching modes was observed. 2D IR spectroscopy would be an appropriate technique to address these ambiguities, as the peaks will be resolved along both the pump and the probe frequency axis, and the dynamics for each stretching normal mode can be measured separately. Alternatively, to investigate the energy transfer dynamics in a molecule with as complicated vibrational structure as $\text{Os}_3(\text{CO})_{12}$, narrow-band pump broad-band probe experiments are expected to selectively excite the CO stretching modes individually. Narrow-band pump pulses can be obtained by using a Fabry-Perot (FP) etalon interferometer consisting of two highly reflective mirrors. The incident laser beam undergoes several reflections between those two mirrors, resulting in spectrally narrowed and temporally elongated pulses. The bandwidth of the narrowed pump pulses can be tuned by varying the distance between the two mirrors. Currently, work is in progress to build such an etalon to narrow down the bandwidth of the current pump pulses

to obtain pulses of ~ 1 ps time duration. This will be sufficient to excite the individual CO stretching modes in $\text{Os}_3(\text{CO})_{12}$, while maintaining picosecond time resolution.

In the pump-probe kinetic traces of the $\text{Os}_3(\text{CO})_{12}$ experiment, the signal observed at negative time delays between pump and probe pulses is a result of PFID. The theory about PFID for an anharmonic vibrational system in MIR pump-probe experiments was derived in detail based on perturbation theory. Broadband MIR pump-probe experiments were carried out on a simple model system $\text{W}(\text{CO})_6$ with only one IR active CO stretching mode. The measurements fit very well to the simulations according to the presented theory. The PFID signals in the measurements were successfully suppressed by filtering methods. In principle, the theory and methodology can be extended to multiple vibrational absorptions, and PFID in more complicated vibrational systems like $\text{Os}_3(\text{CO})_{12}$ should be able to be studied and suppressed.

Also, a new computer programmable pulse shaping technique named CAPPUCCINO, with full control over amplitude, phase and polarization in the MIR, was developed. With this pulse shaping technique, phase coherent pulse trains will be available for 2D IR spectroscopy. Phase cycling theory for 2D IR spectroscopy with a pump-probe beam geometry was demonstrated, and simulations on a two-level system was presented. Future work will focus on conducting 2D IR experiments on simple molecules to demonstrate the presented phase cycling theory. A full review of the various experimental considerations and its impact on data collecting efficiencies and background noises will be explored. Once this is successfully completed, 2D phase cycling experiments will be completed for more complicated species of interest, such as light harvesting complexes and membrane systems. Moreover, the indirect pulse shaping technique CAPPUCCINO

can also be applied to ultrafast UV region (M. T. Seidel et al., J. Opt. Soc. Am. B, **28** (2011) 1146). Therefore together with the phase cycling theory, 2D optical spectroscopy in the UV within a pump-probe geometry can be constructed to investigate the electronic transition induced dynamics for light harvesting molecules and so on.