DEVELOPMENT OF A PASSIVELY STABLE AND DISPERSION COMPENSATED TRANSIENT GRATING APPARATUS TO MEASURE ULTRAFAST DYNAMICS

by

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ABSTRACT

Understanding carrier dynamics in materials like semiconductors is essential to effectively predict and model the performance of the semiconductor in semiconductor circuits, coherence experiments, and photovoltaic devices. Femtosecond laser pulse experiments have sufficient temporal resolution to accurately measure ultrafast carrier dynamics through a number of transient pump-probe experiments. To measure carrier dynamics in semiconductor samples of particular interest to the field of photovoltaic technology, as well as any sample for which transient measurements are desired, a novel four-wave mixing (FWM) transient grating (TG) apparatus was developed that is passively stable and dispersion compensated with respect to a reference pulse. The TG signal can be used to characterize the input pulse through TG FROG analysis, or through SHG FROG signals generated by the novel apparatus with a slight modification. A CdTe/CdS heterojunction sample was studied using the TG setup by measuring the signal intensity, spectrum, and phase imparted to the signal by the excited lattice in the sample. The phase is extractable using interference between the signal and a reference that passes through an unexcited location of the sample. From three separate measurements of the CdTe/CdS sample, the transient dynamics indicate a short exciton lifetime on the order of several to tens of picoseconds. A high temporal resolution scan reveals a delay of 50 fs between the 3-pulse overlap and the beginning of the lasting response of the sample. Longer temporal range scans and fitting to exponential decay curves indicate fast and slow decay constants, $\tau_1 \approx 7 - 9 \text{ ps}$ and $\tau_2 \approx 25 - 50 \text{ ps}$ respectively. Spectrally, the ultrafast dynamics are non-uniform, which can be attributed to chirped pulses interacting via the instantaneous response of the sample. A TG FROG trace produced in ZnSe affirms the non-uniform spectral structure at early probe delays. The sta-
bility found in the phase measurement demonstrates the utility of the apparatus as a phase-sensitive measurement tool, which can be useful for extracting the change in the complex index of refraction due to excitation.
TABLE OF CONTENTS

ABSTRACT ................................................................. iii
LIST OF FIGURES AND TABLES ........................................ vii
LIST OF ABBREVIATIONS .............................................. xi
ACKNOWLEDGMENTS ................................................... xii
DEDICATION ............................................................... xiii
CHAPTER 1 INTRODUCTION .............................................. 1
  1.1 Introduction to Photovoltaic Devices ............................. 1
  1.2 Measurement of Ultrafast Dynamics ............................... 4
    1.2.1 Transient Absorption ........................................ 4
    1.2.2 Transient Grating ........................................... 5
    1.2.3 Transient Experiments Performed ............................ 9
CHAPTER 2 EXPERIMENT DESIGN ....................................... 15
  2.1 Optical Layout .................................................... 17
  2.2 Measurable Quantities and Methods .............................. 20
  2.3 Data Acquisition ................................................ 22
CHAPTER 3 SIMULATIONS ............................................... 25
  3.1 Fresnel Propagation Simulation .................................. 25
  3.2 Zemax Simulation ................................................ 35
CHAPTER 4 EXPERIMENT RESULTS AND DISCUSSION ................... 43
  4.1 Second Harmonic Generation FROG Measurement ............... 43
LIST OF FIGURES AND TABLES

Figure 1.1 Carrier dynamics in a semiconductor absorber after optical excitation. .................................................. 2

Figure 1.2 The production, diffusion, and dissociation of an exciton at a donor/acceptor interface in an OPV type device. ................. 3

Figure 1.3 The BOXCARS configuration to generate a TG signal. ............... 6

Figure 1.4 An energy diagram of a third order nonlinear process, the interaction of photons 1, 2, and 3 to generate photon 4. ............... 8

Figure 1.5 A diagram indicating the wave vector requirement for the generated beam ($k_4$) for phase matching in the BOXCARS arrangement. .................................................. 8

Figure 1.6 The Ammend-Blank FWM optical arrangement for measurement of transient signals. .......................... 13

Figure 1.7 The 4f imaging system presented by Maznev et al. to optimally overlap the crossed pulses. .......................... 14

Figure 2.1 The TG optical layout used in this thesis to measure ultrafast transient dynamics. .......................... 18

Figure 2.2 A photograph of the physical TG optical setup constructed. .... 19

Figure 3.1 A diagram indicating the procedure to perform a Fresnel propagation simulation through the 4f imaging system .................. 29

Figure 3.2 The transverse beam profile generated from Fresnel propagation through the 4f imaging system. .......................... 30

Figure 3.3 The transverse beam profile generated from Fresnel propagation through the 2f-2f imaging system. .......................... 31

Figure 3.4 The simulated interferograms resulting from interference between the reference and TG signal. .......................... 34

Figure 3.5 Fundamental optical apparatus and beam paths produced by Zemax without windows. .......................... 37
Figure 3.6  Advanced optical apparatus and beam paths produced by Zemax including windows. ........................................ 38

Figure 3.7  Spot diagram for all beams in the sample plane produced by Zemax. 39

Figure 3.8  Comparison between the probe, pumps and reference beam spot diagrams at the sample plane produced by Zemax. ................. 40

Figure 3.9  Ray fan plot for the probe beam at the sample plane. ............. 40

Figure 3.10 Ray fan plot for the reference beam at the sample plane. ......... 41

Figure 3.11 Ray fan plot for the pump beams at the sample plane. ............. 41

Figure 4.1  Single-shot SHG FROG trace measured by the slightly modified apparatus. ......................................................... 44

Figure 4.2  Scanning SHG FROG trace measured by the slightly modified apparatus. ......................................................... 45

Figure 4.3  Spectral panorama of scanning SHG FROG traces measured using varied BBO crystal angles. .......................... 46

Figure 4.4  Measured linear transmission of the CdTe/CdS film on borosilicate. 47

Figure 4.5  Measured linear transmission of the CdS film on borosilicate. .... 48

Figure 4.6  Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 1). ..................... 50

Figure 4.7  Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a long time scale (Day 1). ..................... 50

Figure 4.8  Intensity of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 1). ..................... 51

Figure 4.9  Intensity of the TG signal from the CdTe/CdS sample as a function of delay on a long time scale (Day 1). ..................... 52

Figure 4.10  Fit to the intensity curve for the TG signal from the CdTe/CdS sample as a function of delay (Day 1). ..................... 53

Figure 4.11  Interferograms produced by crossing the reference beam with (top) beam 4 and (bottom) the TG signal from the CdTe/CdS sample (Day 1). ..................... 54
Figure 4.12 Spatial interference fringes of the reference-signal interference from the CdTe/CdS sample at various delays in comparison to the reference-beam 4 interference. ................................. 55

Figure 4.13 Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 2). ......................... 56

Figure 4.14 Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a long time scale (Day 2). ......................... 57

Figure 4.15 TG FROG trace of the pulse in the sample plane using ZnSe (Day 2). .......................................................... 57

Figure 4.16 Intensity of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 2). ......................... 58

Figure 4.17 Intensity of the TG signal from the CdTe/CdS sample as a function of delay on a long time scale (Day 2). ......................... 59

Figure 4.18 Fit to the intensity curve for the TG signal from the CdTe/CdS sample as a function of delay (Day 2). ......................... 60

Figure 4.19 Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 3). ......................... 61

Figure 4.20 Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a long time scale (Day 3). ......................... 62

Figure 4.21 Ultrafast spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a very short (fs) time scale (Day 3). ....... 63

Figure 4.22 Ultrafast intensity of the TG signal from the CdTe/CdS sample as a function of delay on a very short (fs) time scale (Day 3). ....... 63

Figure 4.23 Intensity of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 3). ......................... 64

Figure 4.24 Fit to the intensity curve for the TG signal from the CdTe/CdS sample as a function of delay (Day 3). ......................... 65

Figure 4.25 Transient absorption decay curves typically measured in transient experiments. .................................................. 67

Figure 4.26 Superposition of the fast (red) and ultrafast (blue) TG signal intensity plots for the CdTe/CdS sample (Day 3). ......................... 67
Figure 4.27 Superposition of the slow (black), fast (red), and ultrafast (blue) TG signal intensity plots for the CdTe/CdS sample (Day 3). . . . . 68

Table 2.1 Design features considered for the optical apparatus. . . . . . . . . . 16
LIST OF ABBREVIATIONS

Photovoltaic ....................................................... PV

Highest Occupied Molecular Orbital .......................... HOMO

Lowest Unoccupied Molecular Orbital ......................... LUMO

Transient Absorption ............................................ TA

Transient Grating ................................................... TG

Four-Wave Mixing ................................................ FWM

Crossed-Beam Phase-Matched Coherent Anti-Stokes Raman Scattering BOXCARS

Frequency-Resolved Optical Gating ............................ FROG

Transient Reflection Grating ................................... TRG

Second Harmonic Generation ................................. SHG

Grating-Eliminated No-nonsense Observation of Ultrafast Incident Laser Light E-fields ......................... GRENOUILLE

Cross Polarized Wave ........................................... XPW
I would like to thank the Air Force Office of Scientific Research for funding this project. I owe thanks to my family and friends for continually giving me advice and encouragement, without which I would not have made it this far. I give special thanks to my advisor, Dr. Charles Durfee, for the insight he has given me into the field of optics and for providing me amazing research opportunities. I also greatly appreciate the help and thoughts of my committee members, Dr. Jeff Squier, Dr. Timothy Ohno, and Dr. Mark Lusk. Finally, I would like to thank the Colorado School of Mines where I have had my eyes opened to a world few get to experience.
You have dedicated your lives to us.

Mom and Dad, this one’s for you.
CHAPTER 1
INTRODUCTION

In industry and academia, there is a large interest in transient dynamics of materials on femtosecond time scales. Aside from understanding fundamental physics, transient experiments measuring coherence lifetimes have applications in quantum computing and spintronics [1, 2]. Transient experiments have been performed to ascertain the limits of high speed communications [3]. In particular, measurement of transient dynamics has benefits in the research and manufacture of photovoltaic (PV) devices. For PV devices to be cost-effective, they must be optimized to reach higher energy efficiencies, among other factors. Characterization of the absorbing materials in PV devices is essential for efficiency optimization. In particular, the carrier lifetime and mobility in the absorber are especially useful quantities since they directly contribute to the efficiency of the PV device [4–6]. The development of femtosecond laser technology has led to experimental methods that can extract these essential properties. CdTe and CdS are semiconductors that have been extensively studied in PV research due to their absorption properties and the high PV efficiencies seen thus far [2, 7, 8]. To further understand the potential of CdTe and CdS in PV technologies, as well as measure transient dynamics in other samples of interest, a novel optical apparatus has been designed to measure and characterize ultrafast dynamics in thin film samples.

1.1 Introduction to Photovoltaic Devices

PV devices convert light energy to electrical energy through the absorption of photons. When the absorbing material is optically excited, electron-hole pairs are created. An electron in the conduction band can then interact with holes in the valence band via the Coulomb force [9]. The carriers can travel within the absorber
and either dissociate at an interface between the absorber (donor) and an acceptor material, or recombine. If the carriers dissociate, the electron and hole travel in opposite directions to create electrical current. Recombination of the carriers reduces the efficiency of the PV device. When the electron is excited to the conduction band, it first equilibrates with the other electrons in the conduction band, followed by thermal equilibration with the room-temperature lattice [10–12]. Fast recombination and decoherence may occur during these transitions as well. These processes occur on very short time scales (on the order of femtoseconds) [13, 14]. After equilibration, the excited electrons fill the lowest states in the conduction band and remain for some excited state lifetime (on the order of picoseconds or even nanoseconds [12, 15]), where they can then dissociate from the holes in the valence band or recombine with them. Figure 1.1 shows the excitation of electrons from the valence band to the conduction band and the processes that follow.

Figure 1.1: Carrier dynamics in a semiconductor absorber after optical excitation. “(1) Thermal equilibrium before pulse; (2) ‘coherent’ stage straight after pulse; (3) carrier scattering; (4) thermalisation of ‘hot carriers’; (5) carrier cooling; (6) lattice thermalised carriers; (7) recombination of carriers; (8) return to thermal equilibrium.” Figure 6.2 from [12]. Long time scales (> 1 ps) are for Si.
In addition to semiconductor PV devices, organic PV (OPV) cells have become of interest due to their mass-production advantages over semiconductor PV devices. In OPVs, the concept of valence and conduction bands is replaced with HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels. Excitons can be produced between these levels, and dissociation at a donor-acceptor interface can occur. Figure 1.2 depicts the dissociation of an exciton at the donor/acceptor interface for an OPV device.

![Figure 1.2: The production, diffusion, and dissociation of an exciton at a donor/acceptor interface in an OPV type device. LUMO: Lowest Unoccupied Molecular Orbital, HOMO: Highest Occupied Molecular Orbital. Figure 3 from [6].](image)

The timescales of exciton production, diffusion, and dissociation vary among different materials, and although there have been a number of previous studies performed measuring exciton dynamics, there is more that can be understood about these processes. Even in CdTe and CdS bulk heterojunction solar cells, which have been studied extensively for the past few decades and are considered good candidates for large-scale solar cell applications, a full picture of CdTe and CdS transient dynamics has not been developed. Large CdTe and CdS PV modules have reached efficiencies of around 16 %, considerably less than their theoretical efficiencies of 28-30 % [8, 16]. To reach theoretical performance by gaining a better understanding of transient dynam-
ics, comprehensive experiments should be performed. In section 1.2.3, an overview of previously performed experiments is described, and the advantages and possible drawbacks to their arrangements are examined.

1.2 Measurement of Ultrafast Dynamics

Because excited electrons may recombine or lose coherence very quickly before filling the conduction band or LUMO level, measurement schemes must be capable of resolving dynamics on the femtosecond time scale. To measure a short event, an even shorter probe must be used. Femtosecond laser pulses are short enough to measure the femtosecond scale events that occur with exciton production and decay. Thus, optical transient experiments are primarily used for these measurements. Among the primary transient experiments that are used to measure ultrafast dynamics, transient absorption (TA) and transient grating (TG) experiments are particularly useful [13, 17]. The mechanisms behind each of these phenomena will be described below.

1.2.1 Transient Absorption

To measure transient dynamics in a TA experiment, an intense pump pulse (with photon energy above the bandgap of the sample) is focused in the sample, thus exciting the absorber in the excitation region. The valence electrons are excited to an energy state above the conduction band. Through the non-radiative processes described previously, the electrons lose energy to occupy the lowest unoccupied energy state in the conduction band. Once there, they remain in the conduction band for some excited state lifetime (on the order of picoseconds [13]) until they relax to their ground states. During the time that the excited electrons are in the conduction band, a probe pulse with photon energy near the bandgap is incident on the sample. Normally this light would be highly absorbed, however, due to state filling (the filling of the conduction band by electrons from the valence band), the sample absorbs less (sample bleaching), and there will be a higher transmission of the probe [18]. The
delay time between the pump pulse and the probe pulse can be varied, and a time-
resolved measurement of the sample excitation can be obtained, from which excited
state lifetimes and decay constants can be extracted. Further, if a broadband probe is
used, and a spectrometer is used to detect the signal, the spectral transient absorption
signal can be obtained.

Comparison of the transmission of a probe that passes through the sample with
and without the presence of the pump beam provides an indication of the bleaching
of the sample, and therefore, the number of excited electrons. The difference in
transmission is typically on the order of $10^{-5}$, which creates difficulties in measuring
such small changes [17]. As a result, a lock-in or boxcar amplifier is necessary to
isolate signals that only correspond to changes in transmission.

1.2.2 Transient Grating

The TG experiment is similar to the TA experiment in that the sample is excited
by pumping, and a probe with variable delay is passed through the excitation region
and measured. The difference lies in the pumping and detection scheme. Two pump
pulses excite the sample at a crossing angle that creates a spatial interference pat-
tern in the intensity at the sample. The interference pattern maps into a sinusoidal
excitation, which forms a transmission grating in the sample, off of which the probe
can diffract. A detector is positioned to measure the diffracted beam [19]. The ben-
efit of this configuration is background-free detection, resulting in high sensitivity,
and its direction sensitivity [13]. In addition to using transmitted diffracted orders,
the TG experiment can be performed using reflected diffracted signals as seen in the
experiment by Morishita et al. [13] and Katayama et al. [14, 20].

The particular angles between the pump pulses, the probe pulse, and the diffracted
pulse can be controlled experimentally. The BOXCARS (Crossed-Beam Phase-Matched
Coherent Anti-Stokes Raman Scattering) configuration [21] is a useful arrangement
for TG experiments and is shown in Figure 1.3.
BOXCARS, as with any TG, uses four-wave mixing (FWM), a third order nonlinear optical phenomenon in which two pump photons and a probe photon interact to generate a signal photon. The frequency and direction of the signal is determined by the frequencies and angles between the other beams so that energy and momentum is conserved. The BOXCARS arrangement is useful to align optics and predict the location of the diffracted signal. The mechanisms behind nonlinear phenomena, like BOXCARS, is provided below using information from Boyd’s *Nonlinear Optics* [22].

Nonlinear phenomena result from nonlinearities in the potentials that bind electrons to atoms. When low intensity light interacts with the electron, the electron does not experience a large electric field from the light wave. Thus, the electron only moves within the bottom of the potential, where the potential largely resembles that of a harmonic oscillator, which has a linear restoring force. Linear phenomena occur in this regime. However, if high intensity light interacts with the electron, the electron will move further away from its equilibrium position and “feel” the nonlinearities of the potential that are more pronounced at those distances. These nonlinearities result in higher order electric susceptibilities for the material. In linear optics, the complex induced polarization is given by Equation (1.1):

$$\tilde{P}(t) = \epsilon_0 \chi^{(1)} \tilde{E}(t)$$  \hspace{1cm} (1.1)
As the field strength increases, higher order terms become significant, leading to a polarization of the form expressed in Equation (1.2):

\[ \tilde{P}(t) = \varepsilon_0 \left[ \chi^{(1)}(t) \tilde{E}(t) + \chi^{(2)}(t) \tilde{E}^2 + \chi^{(3)}(t) \tilde{E}^3 + \cdots \right] \]  

(1.2)

The nonlinear terms that were added are important when the wave equation in nonlinear media is considered:

\[ \nabla^2 \tilde{E}(t) - \frac{n^2}{c^2} \frac{\partial^2 \tilde{E}}{\partial t^2} = \frac{1}{\varepsilon_0 c^2} \frac{\partial^2 \tilde{P}^{NL}}{\partial t^2} \]  

(1.3)

In this inhomogeneous equation, the nonlinear terms in the polarization (\( \tilde{P}^{NL} \)) act to drive the electric field.

Now consider three beams entering a sample with separate wavelengths and wavevectors \( \{\omega_1, k_1; \omega_2, k_2; \omega_3, k_3\} \), then the total electric field can be written as:

\[ \tilde{E}(t) = E_1 e^{-i(\omega_1 t - \vec{k}_1 \cdot \vec{r})} + E_2 e^{-i(\omega_2 t - \vec{k}_2 \cdot \vec{r})} + E_3 e^{-i(\omega_3 t - \vec{k}_3 \cdot \vec{r})} + c.c \]  

(1.4)

In a centrosymmetric medium, the second order susceptibility \( \chi^{(2)} = 0 \) so that the third order susceptibility \( \chi^{(3)} \) becomes the most significant nonlinear term. The expansion in the polarization includes a term of the form:

\[ \tilde{P}^{(3)}_{FWM}(\omega_1 + \omega_3 - \omega_2, \; \vec{k}_1 + \vec{k}_3 - \vec{k}_2) = 6\varepsilon_0 \chi^{(3)} E_1 E_2^* E_3 \]  

(1.5)

This polarization acts as a driving term for the electric field in Equation (1.3). The solution to the inhomogeneous differential equation is the homogeneous solution plus a particular solution. The particular solution is a distinct field with frequency that must satisfy \( \omega_4 = \omega_1 + \omega_3 - \omega_2 \) for energy conservation. When the wavevector satisfies \( \vec{k}_4 = \vec{k}_1 + \vec{k}_3 - \vec{k}_2 \) the signal field is generated most efficiently. If \( \Delta \vec{k} \equiv \vec{k}_1 + \vec{k}_2 + \vec{k}_3 + \vec{k}_4 = 0 \), the process is phase-matched. Figure 1.4 is an energy diagram indicating how three photons interact to generate the fourth photon. Figure 1.5 depicts the relation between the wave vectors for the BOXCARS arrangement with common wavelengths for all of the beams.
Figure 1.4: An energy diagram of a third order nonlinear process, the interaction of photons 1, 2, and 3 to generate photon 4. Photons 1 and 3 with frequencies $\omega_1$ and $\omega_3$ raise the electron to an elevated virtual energy state $E_V$. Photon 2 with frequency $\omega_2$ stimulates the emission of photon 4 with frequency $\omega_4$ to relax the electron to the ground state $E_O$.

Figure 1.5: A diagram indicating the wave vector requirement for the generated beam ($k_4$) for phase matching in the BOXCARS arrangement. The length of each vector is proportional to its corresponding photon frequency.
The nonlinear optics approach provides a unique perspective on the FWM process when three beams interact simultaneously. However, the TG experiment requires the measurement of the generated signal when one of the three interacting beams enters the sample after the other two. In this situation, the generation of the signal is due to the interaction of the probe pulse with the lasting response of the sample from the pump pulses. The presence of all three pulses at the same time is not necessary if the sample maintains its pumped state while the probe pulse enters the excitation region.

1.2.3 Transient Experiments Performed

Before designing the optical layout of the transient experiment to be performed, it is useful to review examples of previous work to determine the features and drawbacks of other experiments and designs.

In 1997, Sweetser et al. performed a TG experiment in the BOXCARS arrangement using a fused silica sample, which has an instantaneous nonlinear response [19]. Materials that only have instantaneous responses generate a signal only when all three pulses are present. If the probe pulse does not overlap perfectly with the pump pulses, the signal spectrum is generated only by the part of the probe pulse that overlaps with the pumps. As the probe pulse delay is varied, the intensity of the signal will change, peaking when the probe and the pumps are perfectly overlapped. From the signal spectra measured at different delays, the pulse itself can be characterized. This method of characterizing the pulse using a sample’s instantaneous $\chi^{(3)}$ response is called TG FROG (frequency-resolved optical gating). If the sample has a lasting response, then the TG FROG trace will be smeared in the temporal dimension, reducing the effectiveness of measuring the pulse yet revealing information about the sample’s response characteristics.

To measure the excitation dynamics of the material, the lasting response must be measured. Replacing the sample that has an instantaneous response to a sample
with a lasting response will cause the diffracted signal to be present at longer probe delays. The 2000 study by Morishita et al. mentioned above focused on a TG experiment studying Si using reflected diffraction orders. The reflection geometry can give flexibility when designing beam paths. The experiment performed measured the intensity of the signal using photodiodes [13]. The decay curve of the intensity of the signal as a function of probe delay can be fitted using two exponential functions, one with a short decay constant and one with a long decay constant. The short decay constant reveals the time scales of ultrafast dynamics, such as thermal equilibration of the electrons after excitation. The long decay constant corresponds to the lifetime of excitons before recombination. In 2007, Sprinzl et al. performed a similar transient FWM experiment to measure dephasing of carriers and excitons in CdTe and CdS [2].

To measure these, the intensity of the transient signal was measured while varying input laser fluence.

The Morishita and Sprinzl experiments focused on signal intensities only, but more information about the transient dynamics of the samples can be obtained if the intensity of the signal is spectrally resolved. For instance, a 1998 study by Klimov and McBranch describes a phase-sensitive detection scheme for a TA experiment using a white-light continuum to probe ZnS [17]. The acquisition of spectral information revealed important transient features, and the experiment had high sensitivity compared to other TA methods. Despite the spectral information gained, the TA method is inherently less sensitive than TG methods, which are background-free. Spectral measurements can be performed in TG experiments simply by detecting the TG signal using a spectrometer. Katayama et al. perform a transient reflection grating (TRG) experiment on silicon that is spectrally resolved, revealing a large spectral dependence in the TRG signal [20]. A spectrally and temporally resolved signal will indicate which wavelengths of the probe diffract by the grating as a function of delay. From this information, the state-filling dynamics of particular electronic orbitals is
revealed [18].

To obtain more information from the experiment, the phase of the signal can be taken into account. However, the signal phase is highly sensitive to the phases of the pump and probe pulses, and phase stabilization must be incorporated into the design to extract meaningful phase information. The design of the Sweetser experiment included separate delay arms for each of the three input pulses [19]. Although this configuration, as well as the one presented by Gallagher *et al.* in 1998 [23] and another by Selig *et al.* in 2008 [24], adds more control over the relative delays of the pulses, the phase stability of the system is lost. Independent pulse control allows measurement of coherence lifetimes, an important characteristic for determining coupling between atoms or molecules, and thus a sample’s ability to transport excitons. However, the interaction of the separate pulses with separate optics creates relative phase shifts between the pulses. Thus, phase information cannot be obtained with this kind of arrangement unless active stability is utilized. Active stability is complicated and expensive, but increases the amount of information retrievable from the experiment, as demonstrated at JILA using the JILA-MONSTR [25]. If phase stability can be achieved, the phase of the signal can be measured by interfering the signal with a reference pulse. Heterodyne detection is a phase-sensitive measurement, but does not provide spectral information. Spectral interferometry is a more revealing phase-sensitive measurement. From the interference pattern seen at the spectrometer, the spectral phase imparted to the signal by the excitation can be extracted, as well as information about the complex index of refraction change by the excitation alone. More detail will be provided in sections 2.2 and 3.1.

From the experiments mentioned above, it is clear that there are a number of measurable quantities from transient experiments. The specific experiment design, however, can vary while performing the same measurement. The differences in design can significantly change the quality of the measurement or the complexity or cost of
the experiment. For instance, the dispersion of optical elements can affect the pulses before the sample, thus changing the dynamics in the sample and the signal measured. Li et al. presented a dispersion-free FWM design in the BOXCARS arrangement to measure TG FROG traces (frequency-resolved optical gating) in 1999 [26]. The absence of dispersive optics in the design is an advantage to measure a FROG trace for the original pulse, but the beams involved in the FWM process are generated from a single beam through the use of a spatial mask, as seen in Figure 1.3, which lowers the intensity of each of the pulses. Alternatively, if dispersion can be compensated for by using identical optics for each pulse, a dispersion-free design may not be necessary. Geometries of the TG experiment can also vary. In 2005, Hseigh and Psaltis performed a TG experiment using CaF$_2$ in which the pump and probe pulses were coplanar [27]. The coplanar geometry can provide an alternative optical arrangement for the beam paths, but phase stability is difficult to achieve in the coplanar design presented since the separate beams interact with separate optics. Similarly, the Morishita geometry was coplanar and provided control over the crossing angle of the pump pulses [13]. Pelant et al. also had control over the crossing angle in their TG experiment [28]. Varying the crossing angle of the pumps changes the TG line density, which can change the lifetime of the TG as a result of exciton transport. Measurement of the signal at various crossing angles can isolate the exciton diffusion contribution of the TG decay from the exciton recombination contribution. However, the dynamic geometry increases the difficulty in aligning the pulses to be overlapped in the sample. Finally, TG can be performed in either a transmission or reflection geometry. TRG, as performed by Katayama et al. is useful to measure surfaces dynamics of samples [14, 20]. The type of sample to be measured determines which type of TG to perform.

In a 2009 study by Ammend and Blank, a FWM signal was produced in a passively stable, dispersion-compensated interferometer setup using a reference pulse that passes through an unexcited portion of the sample [29]. The fundamental op-
tical layout has many advantages, and has the potential to extract many important quantities from the sample with high sensitivity. Due to its potential, the Ammend-Blank design greatly contributed to the optical design arranged during the experiment design phase of research. Figure 1.6 shows the optical layout of the Ammend-Blank experiment.

Figure 1.6: The Ammend-Blank FWM optical arrangement for measurement of transient signals. Figure 1 from [29].

Despite the benefits of the Ammend-Blank design, the detectors used in the experiment were not spectrometers, so no spectral information was obtained. Additionally, the optical arrangement used in the Ammend-Blank experiment did not allow for optimal overlap of the pulses inside the sample as described by Maznev et al. [30] and also in the article by Hseih and Psaltis [27]. Maznev et al. present a 4f imaging system that aligns the pulse fronts of the crossed pulses to optimize their overlap [30]. The 4f system is shown in Figure 1.7.
Figure 1.7: The 4f imaging system presented by Maznev et al. to optimally overlap the crossed pulses. “(a) Crossed femtosecond beams overlap only over a small region in space.” (b) 4f system using a diffraction grating optimally overlaps pulses. Figure 1 from [30].
CHAPTER 2
EXPERIMENT DESIGN

In designing the optical apparatus presented in this thesis, the previously published work was analyzed for particular strengths. A number of characteristics are advantageous in producing an optimal design. Certainly the design should provide as much information as possible while remaining simple to operate and cost-effective. However, it can be difficult to incorporate many of the beneficial features in a design all at once. For instance, to measure coherence times of an excited sample in a TG experiment, the delay between the individual pump beams must be variable. Adding control over this delay requires using separate optics for the individual beams, which eliminates the possibility of using passive phase stabilization. Active phase stabilization can be used, but its incorporation into the apparatus greatly increases the project cost and complexity. Taking these competing factors into account, the optical design presented in this thesis overcomes many such obstacles and retains a large amount of versatility. The design presented here is based on the Ammend-Blank design with improved pulse overlap in the sample and an improved detection scheme. All of the benefits of the Ammend-Blank design, like passive stability, dispersion compensation, high sensitivity resulting from background-free detection, ease of alignment due to the BOXCARS configuration, and incorporation of a reference pulse, are retained in the modified apparatus. In addition to these advantages, full spectral information is obtained through the use of a spectrometer to detect the signal. Pulse overlap in the sample is improved by incorporating a 4f imaging system. Table 2.1 indicates the design features considered for the experiment and the reasons behind each design decision.
Table 2.1: Design features considered for the optical apparatus.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Decision</th>
<th>Reason</th>
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</thead>
<tbody>
<tr>
<td>Experiment Type</td>
<td>BOXCARS TG</td>
<td>Background-free detection, high sensitivity, signal alignment possible before experiment</td>
</tr>
<tr>
<td>Pump Wavelength</td>
<td>780 nm</td>
<td>Photon energies above bandgap to fill conduction band, no need for ultra broadband pumps</td>
</tr>
<tr>
<td>Probe Wavelength</td>
<td>780 nm</td>
<td>780 nm pulses available from Ti:Sapphire oscillator, pulse bandwidth $\sim 30$ nm</td>
</tr>
<tr>
<td>Pulse Overlap Scheme</td>
<td>4f imaging system$^1$</td>
<td>Results in pulse fronts oriented vertically for optimal overlap in sample; horizontal crossing allows for single-shot FROG</td>
</tr>
<tr>
<td>Dispersion</td>
<td>Dispersion compensation</td>
<td>Dispersive elements useful for splitting beams and offsetting reference, compensate for dispersion in signal to maintain spectral phase stability</td>
</tr>
<tr>
<td>Phase Stability</td>
<td>Passive</td>
<td>Active stabilization is expensive, complicated, and easily avoided by using common optics</td>
</tr>
<tr>
<td>Reference</td>
<td>Through Unexcited Region</td>
<td>Reference useful to obtain relative phase information resulting from excitation only</td>
</tr>
<tr>
<td>Detection</td>
<td>Spectrometer$^1$</td>
<td>Spectral information can be obtained across pulse bandwidth, spectral interference gives spectral phase information</td>
</tr>
<tr>
<td>Delay Control</td>
<td>Probe Only</td>
<td>Can measure dynamics after excitation, but not coherence times; Delay control between pumps eliminates inherent passive phase stability</td>
</tr>
<tr>
<td>Pump Crossing Angle</td>
<td>Fixed</td>
<td>Reduces alignment complexity; Cannot measure exciton diffusion rates</td>
</tr>
</tbody>
</table>

$^1$ Indicates a modification made to the Ammend-Blank design
The choice to use the spectrometer over the photodiodes used by Ammend and Blank is simply to add the ability to measure spectral intensities and relative spectral phase changes due to the excitation. The 4f imaging system (Figure 1.7) improves on the single lens imaging system used in the Ammend-Blank design by creating better pulse overlap by aligning the pulse fronts of the pump beams. The lack of control over relative pump pulse delays prevents the apparatus from measuring coherence times or performing 2D Fourier spectroscopy. However, the apparatus is inherently more phase-stable. Besides using active stabilization, the phase between the pump pulses can be kept stable by using a split mirror with a piezo. The relative pump delays can be controlled while still forcing the different pulses to interact with the same optical bodies. Although this method is not incorporated into the apparatus design, it can be added with little change to the alignment of the system.

2.1 Optical Layout

As mentioned previously, the Ammend-Blank experiment had a large influence on the optical design chosen for this experiment. The fundamental beam paths are left nearly unchanged for this experiment. The only modifications to the beam paths result from the addition of the 4f imaging system and from the change in offset direction for the signal beam after the sample. The reason the reference beam and signal are offset in opposite directions is to create a horizontal crossing angle between the reference pulse and the signal when they recombine after the second diffraction grating. The interference pattern generated can be used to extract the relative spectral phase imparted to the signal. Without the horizontal crossing angle, the spectral phase difference between the signal and reference will still create a spectral interference pattern, but the extraction of the phase through Fourier methods will be more difficult since the three peaks in the Fourier domain may be overlapped. The crossing angle adds interference in the spatial direction, thus offsetting the desired peak from the DC peak in the Fourier domain and improving the sensitivity and accuracy of
the phase extraction method. Section 2.2 provides more detail of this process. To measure the spectrum, an Acton SpectraPro 2300i spectrometer and a thermoelectric cooled Pixis 1024 CCD camera from Princeton Instruments (PI) are used for detection. To accommodate the variable delay of the probe pulse, a PI M510.11 translation stage with a Mercury C863 DC motor controller acts to control large movements of the delay arm. Cascaded on top of the PI M510.11 stage is a ThorLabs T25Z linear translation stage for fine movements. The resulting optical design is presented in Figure 2.1. Figure 2.2 displays a photograph of the physical setup with beam paths drawn.

Figure 2.1: The TG optical layout used in this thesis to measure ultrafast transient dynamics. The splitting of the input pulse and the probe delay arm are present before the system seen here.
Figure 2.2: A photograph of the physical TG optical setup constructed. Blue beams correspond to pumps. Red beams correspond to probe (thick), signal (thin), and reference (dashed).
Both diffraction gratings used in the design are Edmund Optics transmission grating beam splitters (NT46-069) with 80 grooves/mm made such that the -1, 0, and +1 orders have equal diffraction efficiencies. At 800 nm, the first order diffraction angle is calculated to be $3.669^\circ$ through the use of Bragg’s Law in Equation (2.1), with $n = +1$ and $d = \frac{\text{1 mm}}{80} = 12.5 \mu\text{m}$.

$$n \lambda = 2d \sin(\theta) \rightarrow \theta = \sin^{-1} \left( \frac{800 \text{ nm}}{12.5 \mu\text{m}} \right) = 3.669^\circ$$  \hspace{1cm} (2.1)

To have a symmetric BOXCARS arrangement, the initial separation between the two input beams must result in the same angles through the diffraction grating. This will cause the ±1 orders for both beams to illuminate the corners of a square. Since the focal length of the spherical mirrors is 200 mm, the separation $\Delta x$ between the input beams at the first spherical mirror is calculated in Equation (2.2).

$$\Delta x = 2f \tan(\theta) = 25.65 \text{ mm}$$  \hspace{1cm} (2.2)

### 2.2 Measurable Quantities and Methods

As with the experiment presented by Ammend and Blank, the total signal intensity will be measurable at the spectrometer by summing the number of counts measured by the CCD camera in both the spectral and spatial dimensions. However, integrating in just the spatial domain, while keeping the spectral dimension resolved will provide spectral information about the signal. The temporal resolution of the signal measured by the spectrometer will reveal wavelength-dependent relaxation dynamics. The spectral resolution of the diffracted probe signal may be used to construct the density of state dynamics seen in Figure 1.1. Decay constants for the signal intensity curve can be found by fitting the signal intensity by an exponential function and extracting the $1/e$ time constant. Typically, there is an ultrafast time constant on the order of femtoseconds relating to Auger recombination and carrier-thermalization processes. Additionally, there is a slower decay constant on the order of picoseconds that relates to carrier diffusion and recombination after equilibrium.
with phonons [13].

By using a reference pulse and interfering it with the signal at the entrance slit of the spectrometer, there may be an interference pattern in the spectral domain, and interference in the spatial domain will be present if the pulses are noncollinear. From the interference pattern, the relative spectral phase can be extracted using Fourier methods. Equation (2.3) shows how the interference pattern measured in the spectral domain can be written as a modulated Gaussian.

\[ I(\omega) = I_0 \left( \frac{1}{2} \right) e^{-\left(\omega/\Delta\omega\right)^2 \left[ 1 + \cos(\phi(\omega)) \right]} \]  \hspace{1cm} (2.3)

where \( \Delta\omega \) is the spectral width of the pulse and \( \phi(\omega) \) is the spectral phase imparted to the signal. Taking the Fourier transform of this expression, three Gaussian peaks in the Fourier domain are generated. This is easily seen through the use of the convolution theorem utilized in Equations (2.4) through (2.8).

\[ I(\omega) = I_0 \ast g(\omega) \ast h(\omega) \]  \hspace{1cm} (2.4)

\[ g(\omega) = e^{-\left(\omega/\Delta\omega\right)^2}, \quad h(\omega) = \left( \frac{1}{2} \right) \left[ 1 + \cos(\phi(\omega)) \right] \]  \hspace{1cm} (2.5)

\[ \mathcal{F}\{I(\omega)\} = I_0 \left[ \mathcal{F}\{g(\omega)\} \otimes \mathcal{F}\{h(\omega)\} \right] \]  \hspace{1cm} (2.6)

\[ \mathcal{F}\{g(\omega)\} = \left( \frac{\Delta\omega}{\sqrt{2}} \right) e^{-\Delta\omega^2 t^2/4} \]  \hspace{1cm} (2.7)

\[ \mathcal{F}\{h(\omega)\} = \sqrt{\frac{\pi}{2}} \left[ \delta(t) + \mathcal{F}\{\cos(\phi(\omega))\} \right] \]  \hspace{1cm} (2.8)

where \( t \) is the Fourier transformed variable conjugate to \( \omega \). If \( \phi(\omega) \) is linear in \( \omega \), \( \phi(\omega) = k\omega \), then the Fourier transform of the cosine term in Equation (2.8) becomes two delta functions centered at \( t = \pm k \) with a factor of 1/2 applied to each. Equations (2.6), (2.7), and (2.8) would then indicate that the Fourier transform of the measured intensity is a Gaussian curve convolved with three delta functions. The result is three Gaussian curves, one centered at \( t = 0 \), and two smaller ones (by a factor of two) centered at \( t = \pm k \). The side peaks contain the spectral phase infor-
mation, and the center peak contains the DC information. For a more complicated \( \phi(\omega) \), there will still be three peaks, but the full spectral phase including the higher order terms in the polynomial expansion for \( \phi(\omega) \) will also be contained in the side peaks. If the fringe spacing in the spectral domain is small enough, then the side peaks will be sufficiently separated from the center peak to isolate and center one of them to result in the expression in Equation (2.9). Then an inverse Fourier transform gives the result in Equation (2.10).

\[
\tilde{I}_{\text{sidepeak}}(t) = \left( \sqrt{\frac{\pi \Delta \omega}{4}} \right) e^{-\Delta \omega^2 t^2/4} \otimes \mathcal{F}\{e^{-i\phi(\omega)}\} \tag{2.9}
\]

\[
\mathcal{F}^{-1}\{\tilde{I}_{\text{sidepeak}}(t)\} = I_{\text{sidepeak}}(\omega) = \left( \frac{1}{4} \right) e^{-\langle \omega/\Delta \omega \rangle^2} e^{-i\phi(\omega)} \tag{2.10}
\]

This complex expression contains the spectral phase \( \phi(\omega) \), a quantity that can be extracted by taking the argument of \( I_{\text{sidepeak}}(\omega) \) and unwrapping the result (since the argument function output is a quantity that is wrapped around \( 2\pi \)). If we can track this spectral phase in time, then more information about the sample can be obtained. Any constant shift in the spectral phase would indicate a change in the type of transient grating established in the sample. If the grating is purely refractive, the spectral phase imparted to the signal would be a constant \( \pi/2 \) radians offset from what the spectral phase would be if the grating was purely absorptive (see section 3.1 for the derivation of this quantity). The transient grating may change its refractive/absorptive properties during the dynamics after excitation, and measurement of the spectral phase in time can show such property changes. However, all measurements must be phase stable for reliable spectral phase measurement.

2.3 Data Acquisition

To obtain a time resolved spectrum, the signal received at the spectrometer must be measured as a function of delay. A program written in C++ was developed using imported library functions for the spectrometer and for the PI translation stage used
in the delay arm. After user-defined parameters for the spectrometer and translation stage are entered, a stepping procedure moves the delay arm (in steps as small as 10 µm) while the spectrometer records an image at each step. This step size results in temporal steps of ~ 66 fs for the delay variable. Since the translation stage has a travel length of 200 mm, the range of delays that can be measured spans 1333 ps. The delay arm is positioned such that there is 10 mm of travel before the pump and probe pulses overlap in the sample, indicating time zero for the delay variable. Thus, the probe can arrive ~ 66 ps before the pumps and up to 1264 ps after the pumps excite the sample. To measure ultrafast dynamics, the ThorLabs stage can be used to move in steps as small as 1 µm, corresponding to a delay resolution of ~ 6 fs. The ThorLabs stage has an inch of travel, which is more than is needed to measure ultrafast phenomena on a femtosecond time scale.

The output from the data acquisition program is a series of text files, each containing data from a single image from the spectrometer and labeled according to the image number. Another text file contains the encoder positions measured at each step. The files are formatted for import into Mathematica, where the series of files can be combined to obtain a time-resolved plot of the TG signal. Alternatively, in the interferogram arrangement, the interference pattern can be analyzed to extract the TG signal spectrum and spectral phase with respect to the reference pulse.
To complement the empirical results from the experiment, two main simulations were performed to analyze the optical layout and the expected results from the primary experiment. First, the propagation of the beam through the optical system was simulated through Fresnel propagation in Mathematica. This type of simulation is particularly useful to determine the spectral phase, and consequently the group delay, imparted to the beam by the optics and sample. Second, Zemax was used to model the system and all of the beams to determine how the tilted spherical mirrors and off-axis propagation imparts aberrations to the beams.

### 3.1 Fresnel Propagation Simulation

To obtain a detailed picture of how the laser pulses evolve throughout the experiment, Fresnel calculations must be performed. Fresnel propagation concerns the development of light through space and after interactions with optics by applying phases to the expression of the electric field. These phases can be considered operators as in the quantum mechanical treatment of the problem. However, there is a particular space in which each operator can be considered a simple phase, so Fourier transforms are used. Fresnel propagation is the essence of Fourier optics.

To start, the types of operators that will be useful to this experiment, as well as the spaces they can be applied as a phase, must be understood. There are only three operators that are necessary for a basic understanding of the optical system: propagation in the forward (z) direction, interaction with a thin lens, and interaction with a diffraction grating.

To propagate a pulse forward in space is equivalent to propagating it forward in time, so the operator to perform this shift is essentially the time development
operator. Moving forward in time results in a time shift $\Delta t$ in time-space. Using the shift theorem, the time shift can be written as a phase in the space that is conjugate to time-space, frequency ($\omega$) space. A positive shift $\Delta t$ corresponds to a phase in $\omega$-space written as:

$$U_{\text{prop}}(\omega, \Delta t) = e^{i\omega \Delta t} \quad (3.1)$$

The time shift $\Delta t$ is just the time it takes for the field to propagate forward in space a distance $\Delta z$. Using the speed of light $c$ and the index of refraction $n$, the shift becomes: $\Delta t = n\Delta z/c$. Thus, the propagation phase becomes:

$$U_{\text{prop}}(\omega, \Delta z) = e^{i\frac{\omega}{c}n\Delta z} \quad (3.2)$$

Since the only propagations for the TG experiment will be in air, the index of refraction can be set to $n = 1$. Additionally, the $\frac{\omega}{c}$ factor has units of inverse length, so it can be considered a wavenumber, written as $k$. This concept is especially important when the effects of the diffraction gratings and lenses come into play. These optics will change the direction of propagation, so only a component of the propagation in time will be in the z-direction. There will also be a component of propagation in the transverse (x) direction, and this propagation will be unknown. Therefore, a relation between the $k_z$ and the $k_x$ wavenumbers must be established to follow the evolution of the field along the transverse direction. If the propagation direction is at an angle $\theta$ from the z-axis, then the wavenumbers will be:

$$k_x = k \sin(\theta) = \frac{\omega}{c} \sin(\theta) \quad \ldots \quad k_z = k \cos(\theta) = \frac{\omega}{c} \cos(\theta) \quad (3.3)$$

which gives the relation:

$$k_z = \sqrt{k^2 - k_x^2} = k \sqrt{1 - \frac{k_x^2}{k^2}} \quad (3.4)$$
If $\theta$ is small, then $k_x^2 << k^2$, which allows the square root term to be approximated through binomial expansion. The result is:

$$k_z \approx k \left(1 - \frac{k_x^2}{2k^2}\right) \quad (3.5)$$

With this relation, the propagation operator becomes:

$$U_{\text{prop}}(\omega, \Delta z) = \exp \left[i \left(\omega c - \frac{ck_x^2}{2\omega}\right) \Delta z\right] \quad (3.6)$$

The propagation operator in Equation (3.6) will not only propagate forward in time and $z$, but also in $x$. Since the phase is dependent on $k_x$, and not simply $x$, the phase must be applied jointly in the $\omega$ and $k_x$ spaces.

Now that the transverse propagation can be taken into account, the diffraction grating phase can be used to diffract the field, changing the field’s propagation direction in a way that depends on individual frequency components of the field. There will be a shift in the transverse wavenumber $k_x$. Using the shift theorem again, the operator for the diffraction grating will have the form of a phase in transverse position space, or $x$-space. The specific shift phase will depend on the inherent grating line periodicity. The spatial period written in the grating gives the grating its own wavenumber $k_g = \frac{2\pi m}{d}$, where $m$ is the diffractive order and $d$ is the line spacing for the grating. Thus, the phase that represents the field’s interaction with the diffraction grating is written as:

$$U_g(x, m, d) = e^{ik_gx} = e^{i\frac{2\pi m}{d}x} \quad (3.7)$$

This phase appears to be independent of frequency, but to see any shift in propagation direction, propagation forward in $z$ must occur. This involves a Fourier transform to $k_x$ space, where the grating phase applied will convert to a shift in $k_x$ space. Then, the propagation phase, which depends on both frequency and transverse wavenumber, will be applied, resulting in separate propagation directions for each frequency component (spatial chirp).
Finally, the effect of a thin lens on the field must be calculated. A lens is a dispersive optic, so its operator must depend on frequency. Additionally, the spatial height of the field when it interacts with the lens has an effect on the magnitude of the change in direction the field experiences. Like a diffraction grating, this change in direction corresponds to a shift in \( k_x \) space, or a phase in x-space. However, the amount of the \( k_x \) shift is, itself, linearly dependent on \( x \) and \( \omega \). Therefore, the phase will be linear in \( \omega \) but quadratic in \( x \). Equations (3.8) through (3.10) demonstrate this:

\[
U_{\text{lens}}(\omega, x) = e^{ik_{\text{lens}}(\omega, x)x} \tag{3.8}
\]

\[
k_{\text{lens}}(\omega, x) = \frac{-k_x}{2f} = \frac{-\omega}{c} \frac{x}{2f} \tag{3.9}
\]

\[
\rightarrow U_{\text{lens}}(\omega, x, f) = e^{-i\frac{\omega^2 x^2}{2f}} \tag{3.10}
\]

With the three operators defined in Equations (3.6), (3.7), and (3.10), then full Fresnel propagation simulation can be performed. As a first step, the 4f imaging system described by Maznev et al. in [30] will be simulated to determine if the pulse fronts actually are optimally overlapped at the image plane. This test will determine if the addition of the 4f imaging system to the Ammend-Blank setup will be an improvement to their design. A procedure for the operations involved in the Fresnel propagation through the 4f system is described in the diagram shown in Figure 3.1:

Starting with a Gaussian pulse with center wavelength \( \omega_0 \), spot size \( \Delta x \), and transform-limited duration \( \Delta t \), the electric field is:

\[
E_i(\omega, x) = \sqrt{\frac{\Delta t^2}{2}} e^{-\left(\frac{x}{\Delta x}\right)^2 - \left(\frac{\Delta t}{\Delta t}\right)^2 (\omega - \omega_0)^2} \tag{3.11}
\]

Following the procedure described in Figure 3.1 using Mathematica, the electric field at the image plane is calculated to be:

\[
E_f(\omega, x) = \sqrt{\frac{\Delta t^2}{2}} e^{-\left(\frac{x}{\Delta x}\right)^2 - \left(\frac{\Delta t}{\Delta t}\right)^2 (\omega - \omega_0)^2} e^{i\left(-\frac{\pi}{4} - \frac{2\pi mf}{d} + \frac{4f\omega}{\Delta t}\right)} \tag{3.12}
\]
Comparing the expression in Equation (3.12) to the one in Equation (3.11), it is clear that the field simply picked up a phase from the 4f imaging system:

$$\phi_{4f}(\omega, x) = -\frac{\pi}{2} - \frac{2\pi mx}{d} + \frac{4f\omega}{c}$$ (3.13)

The $-\pi/2$ phase originates from the Gouy phase shift since the 4f imaging system contains a focus, as seen in Figure 1.7. The second term is the same grating phase ramp that was applied to the initial pulse with a factor of -1. This phase belongs in the expression because an image of the grating is being produced with a magnification of -1. Finally, the frequency-dependent term in the phase originates from the time it takes for the pulse to pass through the system. The group delay is given by the derivative of the phase with respect to $\omega$, which gives a group delay of $\tau_g = 4f/c$. This is exactly the time it takes light to travel through a distance of 4f. Because the group delay is x-independent, there is no pulse front tilt or curvature added to the pulse by the system. This means that the +1 and -1 diffractive orders will propagate with pulse fronts parallel to each other, overlapping maximally at the image plane.

It is important to note that the phase added to the field by the optical system is independent of the field that enters the system. The fact that the phase acquired was independent of initial beam parameters proves this assertion. Nevertheless, it is instructive to understand the differences that arise with different initial fields.
Figure 1.7 shows a collimated pulse entering the 4f imaging system, creating a focus between the two lenses. This focus generates the Gouy phase and makes it fairly intuitive to geometrically trace the pulse front through the system. However, when the pulse that enters the system is at a focus, the beamlets collimate between the lenses. In this situation, it is unclear whether the Gouy phase shift would be generated and whether the pulse fronts will be x-independent at the image plane based on a geometric approach. The power of the Fresnel propagation simulation overcomes this confusion. The simulation was performed using a focused pulse as the input, and Figure 3.2, a plot demonstrating the transverse profile of the beam as it propagates through the 4f imaging system, was generated. The final phase was found to be identical, as expected.

![Fresnel Propagation through 4f System](image)

**Figure 3.2:** The transverse beam profile generated from Fresnel propagation through the 4f imaging system. The initial pulse is focused at the diffraction grating at z=0. The pulse propagates f=200mm to the first lens, then 2f to the second lens, then f to the image plane. (a) transverse pulse profile at the grating. (b) transverse pulse profile between the lenses.

After analyzing the 4f imaging system, a comparison should be made to the 2f-2f imaging system that is a part of the Ammend-Blank design. Sending the same initial electric field through the new system the transverse profile is generated and plotted
in Figure 3.3.

Figure 3.3: The transverse beam profile generated from Fresnel propagation through the 2f-2f imaging system. The initial pulse is focused at the diffraction grating at \( z=0 \). The pulse propagates 2f=400mm to the first lens, then 2f to the image plane.

At the image plane, the final field has a different phase:

\[
\phi_{2f-2f}(\omega, x) = -\frac{2\pi mx}{d} + \frac{4f\omega}{c} + \frac{\omega x^2}{2cf} \tag{3.14}
\]

The phase acquired from the 2f-2f imaging system does not include the Gouy phase shift since there is no focus between object and image planes. The grating phase is still present, and so is the propagation phase through a distance of 4f. The main difference is the final, x-dependent term. Since the system is rotationally symmetric, the same quadratic phase with respect to the other transverse direction (y) is also present. Thus, the group delay depends quadratically on the transverse radial direction, which is paraxially equivalent to a spherical wavefront. When the +1 and -1 diffractive orders cross at the image plane, different parts of the pulses will overlap at different times, instead of all at once. From these calculations, it is clear that the 4f imaging system provides for better pulse overlap at the image plane than the 2f-2f imaging system.

The calculation performed for the 4f imaging system provides a form for the electric field of the different diffractive orders at the sample plane in the experimental setup shown in Figure 2.1. For the probe pulse that generates the signal pulse, the \( m \) value in Equation (3.12) can be set to -1. The reference pulse would correspond to an \( m \) value of 0, and a signal alignment pulse would correspond to an \( m \) value of +1.
With these fields, the interaction at the sample can be simulated, and the reference and signal can be propagated through the rest of the system to the spectrometer. There, an interferogram can be calculated to determine the spectral phase difference between the reference and the signal pulses. This simulation can vary based on the type of transient grating used to diffract the probe pulse to generate the signal pulse, and the resulting interferogram will thus vary. Should an interferogram be measured experimentally, the nature of the transient grating produced could be extracted.

The transient grating in the sample will be produced by the interference between the crossed pump pulses. The interference pattern will temporarily write a phase grating into the sample by modulating its complex index of refraction. The sample’s index of refraction will take the form:

\[ \tilde{n}(x) = \tilde{n}_0 + \tilde{n}_1 \cos \left( \frac{2\pi x}{d_{TG}} \right) \] (3.15)

where \( \tilde{n}_0 \) is the sample’s mean index of refraction in the excitation region, \( \tilde{n}_1 \) is the magnitude of the modulation of the index of refraction by the excitation, and \( d_{TG} \) is the interference fringe spacing generated by the crossed pulses. Since the pump pulses are simply ±1 orders generated by the diffraction grating, and the grating is imaged at the sample, the interference from their crossing has fringe spacings \( d_{TG} = d/2 \). This condition causes the probe to diffract in the signal direction with a change in transverse wavenumber \( \Delta k_x = 2k_g \). The signal direction after the sample is the same direction as the signal alignment pulse would be if the sample was absent. Therefore, the signal alignment pulse can be used to simulate the signal during experimental alignment when the sample is not present. It also has another benefit that will be described shortly.

In general, the modulation index \( \tilde{n}_1 \) is complex in nature. The real part of its value corresponds to a refractive modulation, changing the optical path length in the excitation regions, which adds phase to fields that propagate through those regions.
The imaginary part of $\tilde{n}_1$ corresponds to an absorptive modulation, causing photons to absorb differently in regions of excitation. If $\tilde{n}_1$ is purely real, a refractive grating, or phase grating, is established in the sample. Conversely, an absorptive grating, or transmission amplitude grating, is produced in the sample when $\tilde{n}_1$ is purely imaginary.

The phase that is added to the field from the transient grating at the sample plane takes the form:

$$U_{TG}(\omega, x) = e^{i \tilde{n}_1 L} e^{i \tilde{n}_0 L} \exp \left[ \frac{i}{c} \tilde{n}_1 L \cos \left( \frac{2\pi x}{d_{TG}} \right) \right]$$

(3.16)

If $\tilde{n}_1 L$ is small, then the second exponential term in Equation (3.16) can be approximated through expansion:

$$U_{TG}(\omega, x) \approx e^{i \tilde{n}_0 L} \left[ 1 + i \frac{\omega}{c} \tilde{n}_1 L \cos \left( \frac{2\pi x}{d_{TG}} \right) \right]$$

(3.17)

From this form of the phase, it is clear how the complex $\tilde{n}_1$ affects the phase added to the signal. If $\tilde{n}_1$ is purely real, then there will be a factor of $i$ present in the diffraction term of $\phi_{TG}$, creating a $\pm \pi/2$ phase shift in the signal pulse. If $\tilde{n}_1$ is purely imaginary, then the $i$ will vanish from the diffraction term and there will not be a $\pm \pi/2$ phase shift added to the signal pulse. If $\tilde{n}_1 L$ is not small enough to justify the first order expansion in Equation (3.17), then higher order terms must be included:

$$U_{TG}(\omega, x) = e^{i \tilde{n}_0 L} \left[ 1 + i \frac{\omega}{c} \tilde{n}_1 L \cos \left( \frac{2\pi x}{d_{TG}} \right) - \frac{\omega^2}{2c^2} \tilde{n}_1^2 L^2 \cos^2 \left( \frac{2\pi x}{d_{TG}} \right) \right. \right. \left. \left. - \frac{i \omega^3}{6c^3} \tilde{n}_1^3 L^3 \cos^3 \left( \frac{2\pi x}{d_{TG}} \right) + \frac{\omega^4}{24c^4} \tilde{n}_1^4 L^4 \cos^4 \left( \frac{2\pi x}{d_{TG}} \right) + \ldots \right]$$

(3.18)

The diffracted signal observed at the spectrometer results from the probe diffracting with a change in wavenumber equal to $2k_g$, which is primarily generated by the first order ($\cos^1$) term. However, the third order ($\cos^3$) term contains a combination of wavenumbers, including the one that can diffract the probe in the signal direction. In fact, all odd order terms contain this wavenumber, unlike the even orders.
Therefore, if higher order contributions are significant, then there will be corrections to the magnitude of the signal that is diffracted from the odd orders only. However, since the odd order corrections all contain a factor of $i$, there will be no corrections to the phase of the signal. It is important to note that the phase shift itself is entirely governed by the ratio of the real and imaginary parts of $\tilde{n}_1$, and not by its magnitude. Since the diffracted signal phase is proportional to $\tilde{n}_1$, which has a $2\pi$ phase range, then the phase of the signal also has a range of $2\pi$.

The difference between purely real and purely imaginary $\tilde{n}_1$ is measurable in the interferogram generated between the signal pulse and reference pulse. Using the Fresnel propagation simulation, an interferogram was generated at the spectrometer for the two cases: purely real $\tilde{n}_1$ and purely imaginary $\tilde{n}_1$. Figure 3.4 shows the absolute phase shift of $\pi/2$ between the two cases. For any complex $\tilde{n}_1$, the phase added to the signal will be contained within $\pm \pi$.

![Figure 3.4: The simulated interferograms resulting from interference between the reference and TG signal. A refractive TG signal has an additional $\pi/2$ absolute phase shift with respect to an absorptive TG signal.](image)

To measure this phase shift, the absolute phase must be measurable in the interferogram at the spectrometer. In many spectral interferometry experiments, the position of the interference fringes can shift by changing a delay arm for one of the
beams. In this type of arrangement, the absolute phase cannot easily be extracted. However, since the design used for this experiment is arranged so that the reference pulse and signal pulse are derived from the same pulse and interact with the same optics, the absolute phase can be measured. To calibrate the positions of the interference fringes, a sample with a purely real \( \tilde{n}_1 \) can be inserted, and the position of the resulting interference fringes measured at the spectrometer recorded. Then, a sample with a purely imaginary \( \tilde{n}_1 \) can be used, and from the number of pixels the fringes have shifted, the change in phase per pixel can be calculated. With this calibration, any sample can be measured, and from the interference fringes, the ratio of the real part of \( \tilde{n}_1 \) to the imaginary part of \( \tilde{n}_1 \) can be calculated simply by determining the location of the fringes. Furthermore, this ratio may change over the duration of the excitation and afterward, and these changes can be measured in time. From such methods, new information about ultrafast dynamics in samples that has never been measured before can be determined.

An alternative to using a sample that generates an absorption TG (imaginary \( \tilde{n}_1 \)) to calibrate the fringe positions is to simply use the signal alignment pulse (beam 4 unblocked from SM1 in Figure 2.1) without a sample, or without pump pulses. When interfering this pulse with the reference, the fringe positions in the interferogram will be equivalent to where their positions would be if a sample with a purely imaginary \( \tilde{n}_1 \) was used. The reason for this is because an absorption grating does not impart any additional phase to the signal, so its absolute phase would be equivalent to the signal alignment pulse’s phase.

### 3.2 Zemax Simulation

To better understand the optical design and how the individual pulses propagate through it, the apparatus was simulated using Zemax due to its 3-dimensional ray tracing abilities and the reports it can produce. The main concern with the design is the angle at which the spherical mirrors are pointed compared to the input and output
beam directions. The off-axis, tilted propagation adds aberrations to the beamlets, which can affect how they overlap in the sample. As mentioned before, optimal pulse overlap in the sample is essential to obtain signals of any kind, especially signals that result from instantaneous nonlinear effects. If a TG FROG trace is to be measured, the pulses must overlap well and be focused within the sample.

To produce the most accurate results possible, the placement of the optics in the Zemax simulation were chosen so that the beams crossed at the sample in the vertical plane. The two beams that interact with the first mirror were made to be parallel, separated by the value of $\Delta x$ calculated in Equation (2.2). The first spherical mirror was tilted at an angle of $6^\circ$ with respect to the input beams, which is the angle that was measured in the physical apparatus. The diffraction grating was placed at the beam crossing in the horizontal plane, which corresponds to the position of the horizontal (x) focus, but not the vertical (y) focus due to astigmatism. Each diffracted order, except for the beam that corresponds to the reference pulse, is then propagated through the second and third spherical mirrors to the sample plane, which is designated as the position of the vertical focus. This designation is made because, experimentally, the two input beams can be made nonparallel to cause the horizontal beam crossing in the sample to coincide with the vertical crossing. The reference pulse is offset horizontally by a window just before reaching the sample. After the sample, the signal beam is offset using another window, and then all of the beams propagate through the last two spherical mirrors to the second grating plane. Since the beam overlap in the sample and the offset by the windows will be known by this point, the rest of the propagation to the spectrometer is unnecessary.

From the simulation, a Zemax-generated ray-trace can be viewed. Figure 3.5 shows the basic layout of the configuration without the windows inserted, and Figure 3.6 shows the full layout with the windows and offset beams.
Figure 3.5: Fundamental optical apparatus and beam paths produced by Zemax without windows.
Figure 3.6: Advanced optical apparatus and beam paths produced by Zemax including windows. The beams shown are the pumps (blue), the reference (pink) and the signal (green).
Also retrievable from the Zemax simulation is the spot diagram in the sample plane, in which the effects of the astigmatism are visible. Figure 3.7 shows all of the beam spots in the sample plane, demonstrating that the astigmatism causes the diffracted orders from each initial beam to cross vertically (y), but there is a horizontal (x) offset between the pump beams and the probe and beam 4. As mentioned before, this offset can be compensated for by changing the horizontal pointing of the pump beams. Additionally, the shape of the spots is elliptical, as seen in Figure 3.8, since the horizontal focus does not occur at the sample plane, whereas the vertical focus does.

![Figure 3.7: Spot diagram for all beams in the sample plane produced by Zemax. Red and green spots correspond to probe and beam 4. Blue and yellow spots correspond to pumps. Purple corresponds to reference.](image)

To minimize the spot size in the sample, the spot should be circular, where the horizontal and vertical foci straddle the sample. To make this happen while maintaining beam overlap, the divergence of the input beams can be changed using a down-collimator. The down-collimator consists of a positive and negative lens that changes the spot size, and maintains the initial divergence of the beam that enters it if the lenses are confocal. By changing the positions of the lenses, the divergence of the beams that enter the experiment can be varied to optimize the signal.
Figure 3.8: Comparison between the probe, pumps and reference beam spot diagrams at the sample plane produced by Zemax.

In addition to the spot diagrams and ray tracing layouts that can be generated in Zemax, ray fan plots for each of the beams can also be produced. These plots can be used to visually quantify the aberrations accumulated. Ray fan plots at the sample plane for the probe, reference, and pumps are shown in Figure 3.9, Figure 3.10, and Figure 3.11 respectively. It is clear that the linear slope of the ray fan plots is different for the different transverse directions, indicating the presence of astigmatism that was accumulated by the tilted, off-axis propagation off the spherical mirrors.

Figure 3.9: Ray fan plot for the probe beam at the sample plane. Different linear slopes in the different transverse directions indicates astigmatism.
Figure 3.10: Ray fan plot for the reference beam at the sample plane. Different linear slopes in the different transverse directions indicates astigmatism.

Figure 3.11: Ray fan plot for the pump beams at the sample plane. Different linear slopes in the different transverse directions indicates astigmatism.
CHAPTER 4
EXPERIMENT RESULTS AND DISCUSSION

After basic construction and alignment of the apparatus, the zero time position of the delay arm was calibrated using a second harmonic generation (SHG) FROG experiment. Then the apparatus was positioned in the BOXCARS TG arrangement to perform a TG FROG measurement. Finally, the CdTe/CdS sample was placed in the sample position to generate TG signals to measure the ultrafast transient dynamics of the samples.

4.1 Second Harmonic Generation FROG Measurement

To calibrate the delay arm position, an SHG FROG experiment was performed. The windows were removed, and only the zero orders of each of the input pulses were allowed to propagate through the system. A 1 mm BBO crystal cut for Type I phase-matching at 800 nm was placed in the sample position. The translation stage was set 10 mm from the end of its travel and then manually positioned until the SHG signal near 400 nm was maximized. In this way, the 10 mm position indicates time zero for the delay arm for all future experiments.

While the SHG crystal was in place, the stepping and image capturing program developed in C++ was tested to capture a full scanning SHG FROG trace. During the capture, it became evident that the horizontal crossing of the beams in the sample was then mapped into the spatial dimension at the spectrometer due to the axes-flipping periscope. Therefore, the SHG FROG trace was generated in a single image, with delay on the vertical axis and spectrum on the horizontal axis of the spectrometer image. Therefore, the novel apparatus is capable of measuring single-shot SHG FROG traces. The delay range $\Delta t$ spanned by the single-shot FROG trace is approximated
by Equation (4.1):

\[ \Delta t \approx \frac{\theta d}{c} \]  

(4.1)

where \( \theta \) is half the crossing angle between the pulses, \( d \) is the thickness of the SHG crystal, and \( c \) is the speed of light. From the values used experimentally, \( \Delta t \) is about 53.3 fs for the setup. The single-shot FROG trace measured is shown in Figure 4.1.

![Single Shot FROG](image)

Figure 4.1: Single-shot SHG FROG trace measured by the slightly modified apparatus.

The single-shot FROG trace is “windowed” in the delay dimension by the delay range allowed by the crystal thickness and crossing angle, as well as “windowed” in the spectral dimension by the phase-matching conditions. If larger delays are to be seen in the trace, the delay arm must be moved, transitioning the setup to a scanning SHG FROG apparatus. Since scanning measurements are to be taken during the TG experiments, this is a good test for the process. The delay arm was scanned in steps of 10 \( \mu \text{m} \), and scanning FROG data was recorded. Since the SHG signal is temporally
resolved in the vertical dimension at the spectrometer, only 5 lines were averaged in each image to reduce temporal blur at each step. Figure 4.2 shows the resulting scanning SHG FROG trace. It matches fairly well with the single-shot FROG result from Figure 4.1, considering the fairly large step size and low line average.

![Scanning FROG](image)

**Figure 4.2:** Scanning SHG FROG trace measured by the slightly modified apparatus.

To overcome the “windowing” of the FROG trace in the spectral dimension, the phase-matching conditions would have to be altered. A short test was performed in which scanning FROG traces were recorded at varied angles of the BBO crystal. This would shift the “window” in the spectral domain, allowing a larger range of wavelengths to be recorded. The FROG traces from each crystal angle were then combined in a panoramic way to produce the plot in Figure 4.3.

The SHG FROG trace contains information about the pulse duration and the spectral phase contained by the pulse. The shape of the FROG trace depends on the various orders of pulse chirp, which stretch the pulse out in time. Comparison of
4.2 TG Measurement of CdTe/CdS

After the apparatus was deemed to be in working order from the previous tests, testing with a semiconductor sample was performed. One sample that was available from collaborator Tim Ohno was a CdTe/CdS heterojunction sample. S.I. Howard SB7 borosilicate glass (3.3 mm thick) was used as the substrate. In a vacuum chamber, CdS was evaporated from a crucible onto the heated substrate until the thickness of...
the CdS film reached ∼150 nm. The sample was then loaded into a CdTe deposition chamber where the substrate was heated to ∼270 °C, but then unintentionally cooled down to ∼130 °C as a result of a tripped breaker. A thin layer of CdTe may have been deposited during this time. Then, the power was restored and temperature was stabilized at 450 °C for the remaining CdTe deposition. Sulfur may have diffused in the CdTe film due to the power cycling of the substrate heater. As a result, there would be a blended junction between the CdTe and CdS, which would insert carrier recombination centers and reduce the electric field between the p- and n-type materials. Thus, the sample’s performance in a PV device was suspected to be poor. To verify this and to test the TG apparatus, this sample was chosen. The pump and probe center wavelength of 780 nm was chosen to be acceptable for the CdTe/CdS sample because of its linear absorption spectra. Absorption in the sample begins near 800 nm, as shown by the decrease in transmission at that wavelength in the transmission spectroscopy measurement performed on the sample and presented in Figure 4.4:

![Figure 4.4: Measured linear transmission of the CdTe/CdS film on borosilicate. Curves shown are the source spectrum (blue) and sample transmission spectrum (red). The inset focuses on the 700-850 nm region.](image)
Other samples were considered to demonstrate the functionality of the apparatus, one of which was pure CdS. For the CdS sample, absorption starts at around 400 nm, as indicated by the transmission spectrum measured and shown in Figure 4.5. Intense 800 nm pumps can be used to excite the sample if two-photon absorption occurs. Otherwise, pumping at 400 nm can be achieved using the output from an optical parametric amplifier, or from a simple frequency doubling crystal, such as the BBO crystal used for the SHG FROG experiment. The change in diffraction angle by the different wavelength after the first diffraction grating does not affect the diffracted angle of the signal by the sample because the TG generated in the sample always results in a change of $2k_g$ for the diffracted beam, regardless of the pump wavelength (see section 3.1). Since more complexity would be added to the experiment if the test was performed using the CdS sample, the CdTe/CdS sample was deemed a better choice.

Figure 4.5: Measured linear transmission of the CdS film on borosilicate. Curves shown are the source spectrum (blue) and sample transmission spectrum (red).
4.2.1 Measurement Day 1

The first day of measurement performed on the CdTe/CdS sample focused on relatively fast dynamics in addition to the slow dynamics. Steps of 10 µm by the PI translation stage gives a temporal resolution of 66 fs for the fast dynamics. For slower dynamics, the step size was multiplied by a factor of ten and the total range of travel after \( \Delta t = 0 \) was 10 mm, resulting in a delay range of 66 ps. The individual pulse energies entering the sample were approximately 2 \( \mu \)J, and the chirp of the pulses was adjusted such that the pulse was about 75 fs in duration before entering the system. Once in the system, the dispersion from two lenses in a down-collimator, a beam splitter, and the first diffraction grating can adjust the chirp and duration of the pulse that interacts with the sample. Assuming normal dispersion, the pulses would be positively chirped, with long wavelengths at the front of the pulse and shorter wavelengths at the back of the pulse.

First, the TG signal alone was measured at the spectrometer. The spectrum of the signal as a function of time was extracted from the series of images. Fast dynamics of this measurement are plotted in Figure 4.6, and the slower dynamics are plotted in Figure 4.7.

It is clear from Figure 4.7 that the transient grating decays almost entirely after 60 ps. The decay time also depends on wavelength, with shorter wavelengths decaying more quickly than longer ones. On shorter time scales, Figure 4.6 reveals interesting spectral dynamics at first excitation. Shorter wavelengths are detected first, followed by the rest of the spectrum. Additionally, there is a single oscillation in the intensity of the spectrum shortly after excitation near \( \Delta t = 0 \). An explanation for the spectral ramp in intensity at first is that the pulses are chirped when they enter the sample. At small, negative \( \Delta t \) values, the probe pulse enters the sample just before the pump pulses. The back of the probe may interact with the front of the pumps, and if the probe was positively chirped, shorter wavelengths in the probe would diffract before
Figure 4.6: Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 1).

Figure 4.7: Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a long time scale (Day 1).
longer wavelengths in the probe. As for the oscillation, the excitation dynamics of the carriers may create some delay before the lasting TG is established. Thus, the instantaneous response of the sample generates the TG signal at first, then there is a drop in signal intensity as the probe falls behind the pumps, and then the lasting response of the sample begins to take effect to diffract the probe. The time delay between instantaneous response and lasting response may reveal some properties about the sample, such as the thermalization time of the excited electrons.

To further analyze the slower dynamics, the signal intensity as a function of probe delay was calculated by integrating the spectrum as a function of delay. The fast and slow intensity dynamics are plotted in Figure 4.8 and Figure 4.9, respectively.

![Fast Dynamics](image)

**Figure 4.8:** Intensity of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 1).

The fast intensity dynamics retain the oscillation seen before in the spectrum. The shape of the decay curve in Figure 4.9 is somewhat unexpected. Typically, there is a purely exponential decay [13, 14]. However, there appears to be a linear decay until $\Delta t \approx 24$ fs. Afterwards, the decay looks exponential. It is possible that the non-uniform spectral decay contributes to the unexpected signal intensity decay. To
make the linear trend more clear, the intensity data is fitted using a combination of two exponential decay terms with different amplitudes and decay constants, which is typically used to separate the fast and slow components of decay [13, 31, 32]. The functional form used for the fit is given by:

\[ A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \]  

(4.2)

Because of the linear beginning to the decay, the fitting procedure resulted in identical decay constants \( \tau_1 = \tau_2 = 14.6897 \) ps. Additionally, the fit does a poor job of following the data, as shown in Figure 4.10.

After measuring the TG signal alone, the reference pulse was allowed to interfere with the signal to produce an interferogram so that the phase could be observed. The crossing angle produced spatial interference fringes in the vertical dimension of the Pixis camera image. To provide a comparison of the positions of the fringes, the same image was taken by interfering beam 4 with the reference. The relative shift of the fringes in the vertical dimension would provide an indication of the absolute phase.
shift due to the change in the complex index of refraction, as described in section 3.1. Figure 4.11 shows the interferograms measured with the reference pulse interfering with beam 4 and the TG signal respectively.

The relative positions of the fringes produced by interfering the reference with the TG signal can vary with delay. By monitoring these shifts, it is possible to monitor the complex dynamics of the index of refraction after excitation. When this was performed, it was clear that the phase was indeed changing as a function of time, since the fringe maxima moved one or two pixels in the vertical direction. These pixel shifts are presented in Figure 4.12. Since the fringes are spaced by approximately 10 pixels, a shift of 2.5 pixels indicates a phase shift of $\pi/2$. This is the phase shift expected from a change in the TG from an absorptive grating to a refractive grating. A larger fringe spacing at the spectrometer would provide more precise phase measurements. This can easily be done by reducing the tilt of the two windows of the apparatus since the reference-signal horizontal offset at the last spherical mirror generates the
Figure 4.11: Interferograms produced by crossing the reference beam with (top) beam 4 and (bottom) the TG signal from the CdTe/CdS sample (Day 1). The relative vertical shift of the fringes indicates an absolute phase difference between beam 4 and the signal. Since the fringes are oriented horizontally, there is no delay between the pulses. Since the fringes are straight, there is no relative spectral phase between the interfering pulses.
vertical crossing angle between the two at the spectrometer.

Figure 4.12: Spatial interference fringes of the reference-signal interference from the CdTe/CdS sample at various delays in comparison to the reference-beam 4 interference. There is a maximum shift of two pixels in the fringe maxima for the reference-signal delay range measured.

From the measurements performed, the TG apparatus was proven to be capable of measuring transient signals in the CdTe/CdS sample. However, the fact that the TG signal intensity did not decay as expected is a concerning observation. To test whether this feature holds in further measurements, as well as to determine the repeatability of measuring TG signals with the apparatus, more measurements with the CdTe/CdS sample were performed.

4.2.2 Measurement Day 2

The second day of measurement tested the repeatability of the TG measurement with the CdTe/CdS sample, taking the variation of the laser output from day to day into account. The positions and angles of the optics were slightly adjusted before measurement to peak the signal generated from the sample. Comparable pulse characteristics as were used on the first day of measurement were used for Day 2, except
for an adjustment to the pulse chirp to attempt to eliminate chirp at the sample. Figure 4.13 and Figure 4.14 show the fast and slow TG spectra measurements taken on Day 2 with the same step sizes and ranges used on Day 1.

![Fast Dynamics](image)

Figure 4.13: Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 2).

Comparing Figure 4.13 with Figure 4.6, it is clear that changing the chirp of the input pulse makes a difference on the spectral ramp seen at early delays. The slope of the ramp changed from previously, indicating the probe pulse was more compressed and less chirped. The instantaneous response of the sample can provide a way to measure pulse characteristics for early delays, before the lasting response dominates. One way to verify this is to measure the pulse using a sample that has little lasting response but a strong instantaneous nonlinearity to perform a TG FROG measurement. ZnSe was placed in the sample position and a TG FROG trace was generated. The TG FROG trace is displayed in Figure 4.15.
Figure 4.14: Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a long time scale (Day 2).

Figure 4.15: TG FROG trace of the pulse in the sample plane using ZnSe (Day 2).
The TG FROG trace is easy to interpret. At early delays, shorter wavelengths are present, and at longer delays, longer wavelengths are present. The linear slope of the trace indicates the linear chirp of the pulse. The curvature at the top and bottom of the trace results from fourth order chirp, which is difficult to remove.

The similarity between the left side of the TG FROG trace and the left side of Figure 4.13 indicate the sample has an instantaneous response that begins to produce the TG FROG trace, but the rest gets suppressed by the lasting response of the CdTe/CdS sample.

In addition to the wavelength ramp appearing again, the small oscillation in intensity near $\Delta t = 0$ also is present. The oscillation is also visible in the intensity plot. Figure 4.16 and Figure 4.17 show the TG signal intensity as a function of time. The decay of the signal in Figure 4.17 is different than what was measured on Day 1, and is more representative of a typical excitation decay curve.

Figure 4.16: Intensity of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 2).
As before, the decay constants of the signal were found through fitting. The fit model in Equation (4.2) is used again. The fit parameters are more promising this time: $A_1 = 0.9621$, $\tau_1 = 9.3076$ ps, $A_2 = 0.0868$, $\tau_2 = 51.4336$ ps. The difference in the decay constants indicates fast and slow processes may be present, but the amplitudes between the two indicates that the fast processes are dominant. As mentioned previously, the CdTe/CdS sample was produced in a non-optimal way, which would explain the fast decay of the excitons. The fit and the data are presented graphically in Figure 4.18, indicating more agreement between the two.

The noticeable differences between the data taken on Day 1 and the data from Day 2 are grounds for taking another measurement. More could be understood about the variation of the decay constants, and another measurement would provide more insight. Additionally, the ultrafast dynamics can be measured on a finer time scale using the ThorLabs stage mounted on top of the PI stage.
Figure 4.18: Fit to the intensity curve for the TG signal from the CdTe/CdS sample as a function of delay (Day 2). Solid black curve: TG signal intensity; Blue dashed curve: exponential fit.

Fit Model: $A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$

Fit Parameters:

$A_1 = 0.9261$  $A_2 = 0.0868$
$\tau_1 = 9.3076 \text{ ps}$  $\tau_2 = 51.4336 \text{ ps}$
4.2.3 Measurement Day 3

On Day 3 of measurement, the laser pulse that entered the system had significantly less bandwidth than on the previous days due to clipping of the spectrum in the pulse compressor. Nevertheless, the ultrafast measurements are still obtainable with such a pulse. The difference that the smaller bandwidth would make is in the spectral domain, where a smaller range of wavelengths would be visible in the signal. The decay of each wavelength, however, should be fairly unaffected by the decreased bandwidth. The validity of this assumption can be confirmed by the spectrally resolved signals measured. Figure 4.19 and Figure 4.20 report the spectral dynamics of the TG signal on short and long time scales.

![Fast Dynamics](image)

Figure 4.19: Spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 3).

Again, the chirp of the pulse at the sample plane is evident in the wavelength ramp during the initial dynamics of the signal. The bandwidth is noticeably narrower in these plots when compared to the same plots for Day 1 and Day 2. The small
oscillation in intensity is again observed after the initial build up of signal, which helps to verify the feature as a real signal. At longer delays, the decay of the signal is nearly uniform with respect to wavelength, as in the Day 2 measurements. By using 1 µm steps with the ThorLabs stage, an even shorter delay scale can be explored to resolve the ultrafast dynamics. Figure 4.21 shows the ultrafast results of the fine measurement around the instantaneous response to lasting response transition.

The width of the small oscillation in the delay dimension is widened as a result of the higher resolution measurement. A higher precision measurement of the delay between the two types of responses can therefore be acquired. This measurement is easier to make when considering the intensity only. Figure 4.22 is a plot of the TG signal intensity as a function delay on a femtosecond time scale.

By observing the transition region of Figure 4.22, it is evident that the instantaneous response and the lasting response are both contributing to the generation of
Figure 4.21: Ultrafast spectrum of the TG signal from the CdTe/CdS sample as a function of delay on a very short (fs) time scale (Day 3).

Figure 4.22: Ultrafast intensity of the TG signal from the CdTe/CdS sample as a function of delay on a very short (fs) time scale (Day 3). The dotted green line is a mirror image of the front of the instantaneous response.
the TG signal. The dotted green line in Figure 4.22 is a mirror image of the front of the instantaneous response, providing a scale for the amount of instantaneous response and the amount of lasting response present throughout the transition region. The width of the instantaneous response curve can be approximated using the mirror image curve to be around 150 fs. This is on the same order as the width of the TG FROG trace seen in Figure 4.15, which confirms the probability that the signal measured at early delays is due to instantaneous response. The lasting response begins to take effect approximately 50 fs after the three interacting pulses are overlapped.

Longer time scales reveal exponential decay with decay constants in the same range as the Day 2 values. Figure 4.23 shows the fast intensity dynamics while Figure 4.24 shows the slow intensity dynamics and fit. The fit parameters are: $A_1 = 0.8970$, $\tau_1 = 6.9838$ ps, $A_2 = 0.1750$, $\tau_2 = 24.7740$ ps. Both decay constants decreased from the Day 2 values, but they are in the same range. Variation in the decay constants is not entirely unexpected because their values can depend on the pump pulse intensities [2, 32].

![Fast Dynamics](image)

Figure 4.23: Intensity of the TG signal from the CdTe/CdS sample as a function of delay on a short time scale (Day 3).
Comparison of the decay constants with previous experiments that use CdTe/CdS samples reveal disagreement of results. Ahrenkiel et al. revealed at a conference in 1991 that CdTe/CdS solar cells were measured to have minority carrier lifetimes up to the nanosecond range [15]. James Sites and Jun Pan indicated that CdTe recombination lifetimes spanned 0.2 to 2 ns [33]. An article by Rawalekar et al. concerning ultrafast dynamics in CdTe/CdS quantum dots revealed fast decay constants in the picosecond to tens of picoseconds range, followed by a slow decay on the order of 150 ps [34]. Clearly, previous experiments show that much slower decays than measured here are expected from these types of samples. The comparatively quick decay of the signal to zero that was measured on each of the three days can be attributed to the non-optimal processing of the sample. However, the ultrafast dynamics are still unexplained. The decay constants on the order of picoseconds presented in this thesis would correspond to the slow decay of the carriers based on the total shape of the TG signal decay. The fast decay component that is expected to be in the
femtosecond range is not present in the fit. Additionally, the oscillation seen in the intensity at the transition region between instantaneous response and lasting response (Figure 4.22) is not a typical observation in previous studies. One reason that could explain both the lack of an ultrafast decay constant from fitting as well as the separation of the instantaneous and lasting response signals observed is that the intensity of the instantaneous response signal is abnormally low. If the instantaneous response signal was amplified while the lasting response signal was left unchanged, the total decay curve would match the shape of the curves reported in previous experiments (see Figure 4.25). Additionally, the fitting procedure would result in two decay constants, one of which would be in the picosecond range (the $\tau_1$ values calculated) and one that would correspond to the femtosecond scale decay of the tail of the instantaneous response signal (i.e. the dotted green curve in Figure 4.22). The reason for the instantaneous response signal’s abnormally low amplitude is still uncertain, and may result from the particular sample properties. Nevertheless, the feature actually resolves the transition region between the two types of responses. This resolution makes it possible to isolate the contributions from each in a more precise manner than otherwise possible.

Because the results from Day 2 agree with those from Day 3, the repeatability of the measurement of TG signals is verified. The results from Day 1 are similar, but the differences cannot be entirely ignored. On a particular day of measurement, it is still unclear whether the signals measured in the different delay scales match. Since the ThorLabs stage is used for the ultrafast data, while the PI stage is used for the slower data, there may be disagreements in the reported translational positions. If the differently scaled plots are superimposed and there is agreement, then the two stages can independently be trusted to move to and report precise positions. Figure 4.26 and Figure 4.27 display superimposed images of the TG signal intensity between the different scales, indicating agreement.
Figure 4.25: Transient absorption decay curves typically measured in transient experiments. Curves result from measurement of CdTe/CdSe nanorods during “(a) the first 2 ps and (b) 100 ps following photoexcitation.” CT: carrier transfer. Figure 4 from [35]

Figure 4.26: Superposition of the fast (red) and ultrafast (blue) TG signal intensity plots for the CdTe/CdS sample (Day 3).
Figure 4.27: Superposition of the slow (black), fast (red), and ultrafast (blue) TG signal intensity plots for the CdTe/CdS sample (Day 3).
The measurements performed on the CdTe/CdS sample demonstrated the utility of the TG apparatus designed. Spectrum and phase sensitive measurements over a large range of delays are possible with the existing configuration. Future experiments can be performed with different samples and no change to the optical paths, which would reveal transient dynamics in those samples. These measurements would give more insight into the interesting ultrafast dynamics measured for the CdTe/CdS sample. It may be the nature of the sample that caused the instantaneous response signal to be a smaller magnitude than typically observed. However, it may also be the method of measurement that caused the feature. Testing different samples would help to reveal whether the system causes the feature or not. Additionally, changing the pulses that pump and probe the sample could also reveal changes in the signal. Varying the chirp of the pulse could have an effect on the curves measured. Additionally, cross polarized wave (XPW) generation can be used to shorten the duration of the pulses to approximately 30 fs, which could also change the TG signal curves. Although the phase was not fully analyzed in the experiment performed with the CdTe/CdS sample, it is evident that the apparatus has the ability to provide sensitive measurements of the absolute phase imparted to the TG signal. Understanding the limits of such measurements as well as interesting phase dynamics on all delay scales is left open for future experiments.

The optical design chosen did not allow control over the relative delay between the pump pulses, which prevents measurements of coherence times and 2D Fourier spectroscopy measurements. Adding control over the relative delay creates problems with stability, but passive stability could still be maintained in the apparatus if a
split mirror with a piezo is added. This would cause the pulses to interact with the same optical bodies while adding delay control over one pump pulse.

When considering the spectral phase, it is assumed that the phase is not spatially dependent. This is most likely a valid assumption since the sample should be nearly uniform and because an image of the sample is not produced at the spectrometer. From a simple test performed that added linear phase to the reference pulse, it was found that the fringes measured by the spectrometer had no spatial variation. However, it is possible that an image of the sample could be made at the spectrometer, and a full 2D Fourier analysis could be performed to obtain a spectral and spatial phase map, which would formally determine whether the spectral phase was spatially dependent. However, the offset between the reference and signal causes there to be a horizontal offset at the second grating. To make an image plane would be to capture that horizontal offset also, eliminating the beam crossing, and thus, the interference. The current windows in place would need to be changed, or additional windows would need to be added to allow crossing of the beams at a virtual sample image plane.

Although ultrafast carrier dynamics are of main importance for this experiment, very slow dynamics can also be measured using the current optical design. Small adjustments can be made to extend the delay range if desired. To obtain a larger range of delays, the translation stage for the delay arm can be replaced with a stage that has larger travel. However, the delay arm can simply be modified to accommodate two passes by the probe pulse, thus expanding the temporal range of delays by a factor of two but reducing the delay resolution by the same amount. More passes to the delay arm result in even larger time scales yet less temporal resolution.

If special materials are to be measured that require a large amount of intensity to produce a TG signal (ionization of air for instance), the current optical layout is limited by the damage threshold of the diffraction gratings. There is a focus at the grating since it is positioned at an image plane of the sample, where there needs to
be a focus. To increase the intensity at the sample, the intensity at the grating must also increase. One method of accommodating the increase of intensity is to replace the transmission gratings with reflection gratings, which have a higher damage threshold. The beam paths would change, and the astigmatism may increase due to a need for a larger reflection angle, but the intensity at the sample could increase. Additionally, magnification could be used to decrease the spot size at the sample while keeping the spot size at the grating the same.
To measure ultrafast dynamics, an optical apparatus was designed and constructed based on previous experiments with the addition of several novel design concepts. The optical design uses a BOXCARS arrangement facilitated by a pair of pulses focused through a diffraction grating. All of the pulses are derived from the same input pulse and interact with the same optics with the exception of the delay arm for the probe/reference/beam 4 pulses. As a result, the system is inherently stable. Improving upon the Ammend-Blank arrangement, a 4f imaging system is added to provide for optimal pulse overlap in the sample. The reference pulse passes through a tilted window before the sample to remove it from the excitation region. To enforce dispersion compensation, an identical window offsets the signal pulse in the opposite direction. The relative offset between the reference and the signal cause the two pulses to cross at the spectrometer, another addition to the Ammend-Blank design. The crossing angle allows for phase sensitive measurement of the signal, which can reveal the type of grating, via the complex index of refraction change, established in the sample by the pumps.

Based on the simulation developed in Mathematica, the phases of the pulses at the sample and the spectrometer were calculated, reinforcing the theory behind the 4f system and the extraction of the complex index change based on the absolute phase at the spectrometer. The Zemax simulation provided information about the astigmatism generated due to tilted, off-axis reflection from the five spherical mirrors in the system. From the results, it was clear that beamlet foci at the vertical beam crossing in the sample must be established, and then horizontal crossing can be adjusted for maximal TG signal.
Using the CdTe/CdS sample to test the apparatus, the repeatability of measurements and the ability of the optical system to measure intensity, spectrum, and phase data as a function of probe pulse delay were verified. The resolution of the translation steps results in a probe delay resolution of \( \sim 6 \text{ fs} \), which is sufficient to probe ultrafast dynamics. In the CdTe/CdS, the transition between instantaneous nonlinear response and lasting nonlinear response was resolved, showing \( \sim 50 \text{ fs} \) of delay between pulse overlap and the build up of lasting response, a feature that appears to be unique when compared to the previous experiments that were reviewed. These measurements provide insight to the time scales of ultrafast phenomena like electron thermalization after excitation. The slower dynamics from the CdTe/CdS sample are measured until total signal decay. By fitting the decay curves, slow and fast decay constants were extracted. The fast decay was the more prominent and had a decay constant on the order of several picoseconds (7-9 ps). The slow decay constant was less intense for the CdTe/CdS sample and had a decay constant in the tens of picoseconds (25-50 ps). The ultrafast decay constants on the order of femtoseconds were not present in the fit model because of the abnormally low amplitude of the instantaneous response signal. This feature can be an advantage since the contributions to the TG signal dynamics from instantaneous response and lasting response can be isolated more precisely than otherwise possible. Successful measurement of the TG intensity and spectral decays demonstrates the utility of the novel apparatus and encourages deeper implementation of the process, such as full phase analysis to calculate the complex index of refraction change due to excitation as a function of time. Further, measurement of similar samples produced under different processing conditions would aid the optimization of the manufacturing of PV devices. The industrial and academic applications of the measurement techniques demonstrated reveal the utility of the novel apparatus presented.
REFERENCES CITED


