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Multidimensional Spectroscopy of Semiconductor Quantum Dots

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Multi-Dimensional Spectroscopy of Semiconductor Quantum Dots

by

Jason Bylsma

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science
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Credo ut intelligam. - Saint Augustine
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Abstract

The coherent properties of semiconductor nanostructures are inherently difficult to measure and one-dimensional spectroscopies are often unable to separate inhomogeneous and homogeneous linewidths. We have refined and improved a method of performing multidimensional Fourier transform spectroscopy based on four-wave mixing (FWM) experiments in the box geometry. We have modified our system with broadband beamsplitters in all interferometer arms, high-resolution translation stages and the ability to work in reflection geometry. By improving the phase-stability of our setup and scanning pulse delays with sub-optical cycle precision, we are able to reproduce 2DFT spectra of GaAs multiple quantum wells. With the FWM signal reflected from the sample surface instead of transmitted through, we show that very low pulse powers can be used to generate coherent 2D signals from colloidal PbS quantum dots. Dephasing times are particularly difficult to measure in small colloidal quantum dots due to environmental broadening effects from the colloidal growth. We show that low-temperature pure excitonic dephasing can be measured via time-integrated measurements as well as from the cross-diagonal linewidths of 2DFT spectra. Ultrafast sub-picosecond dephasing times are measured at 5 K in 3 nm PbS quantum dots, while excitation-density-dependence is investigated in these dots. By retrieving the global phase with an all-optical method, we are able to retrieve the real-part 2D spectra of PbS quantum dots.
Chapter 1

Coherent Optical Properties of Semiconductors

A semiconductor can loosely be defined as any material with an energy gap between filled valence band and empty conduction band on the order of 0-3 eV. Direct gap semiconductors have a conduction band minimum (CBM) directly above the valence band maximum (VBM) in the Brillouin zone. An incident radiation field of sufficient energy will excite an electron from the valence band to the conduction band, leaving a hole in the valence band. The utility of optical spectra is therefore evident in that information on electronic and vibrational structure can be obtained directly. The optical spectra of semiconductors at low temperature is dominated by bound electron-hole pairs known as excitons. Optical spectra such as transmission, reflection, luminescence and complex dielectric function in the visible and near-infrared regions provide detailed information on the electronic and optical properties useful in many devices. Laser diodes, photodiodes, solar cells, photonics and other fields all rely on optical spectra to characterize and investigate interesting properties of semiconductor materials.

The coherent regime is defined as the time period during and immediately following excitation by an ultrashort laser pulse. During the coherent period the photoexcitations retain a definite phase relationship with one another and with the excitation pulse. This process of photoexcitation leads to the creation of a macroscopic polariza-
tion in the sample. This macroscopic polarization is essentially an ensemble average of individual photoexcited dipole moments and determines the linear and nonlinear response of the system. We investigate these linear and nonlinear responses in binary semiconductor quantum dots to obtain information about the coherent regime in dimensionally-constrained semiconductors.

This introductory chapter will be laid out as follows: first, we discuss the concept of excitons in semiconductors, including their creation, absorption spectra and oscillator strength. Next, we review important properties of semiconductor quantum dots and confinement effects, looking at PbS quantum dots in particular. Finally, the coherent optical spectroscopy of semiconductors is reviewed in Section 1.3, including relaxation processes that occur in semiconductors after excitation and spectroscopic techniques used to investigate bulk and nanostructure semiconductors. The coherent optical properties of semiconductors are dominated by many-body interactions including excitation-induced dephasing (EID), excitation-induced shift (EIS) and biexciton interactions, but these will not be discussed in this thesis.

1.1 Excitons in semiconductors

After excitation by an incident pulse of sufficient energy ($\hbar \omega > E_g$), where $E_g$ is the bandgap of the semiconductor, an excited electron-hole pair bound by Coulombic forces is created known as an “exciton”. In typical semiconductors, this Coulomb interaction is screened by the valence electrons due to the large dielectric constant [1]. Therefore, the excitons are weakly bound in semiconductor systems and are referred to as Wannier excitons. Wannier excitons have large radii, for example in bulk PbS the excitonic Bohr radius $a_B=18\text{nm}$, equal to about 30 lattice constants.

Wannier excitons are often treated within the effective mass approximation, as opposed to tightly-bound Frenkel excitons which exist in insulators and organic crys-
tals like anthracene, in which electron and hole move with the effective masses of conduction and valence bands, respectively. Within this approximation, the exciton center-of-mass acts as a free particle of total mass $M = m_e + m_h$ and reduced mass $\mu = m_e m_h / (m_e + m_h)$ (with $m_e$ and $m_h$ as the electron and hole effective masses). The motion of electron and hole about this free particle center-of-mass can be considered analogous to the relative motion of electron and proton inside a hydrogen atom, including bound states and continuum states. From the known properties of the hydrogen atom, the binding energy of an exciton with principal quantum number $n$ can be expressed as

$$\bar{E}(n) = -\frac{E_R}{n^2}, \quad (1.1)$$

where $E_R$ is the binding energy of the ground state, known as the exciton Rydberg, related to the reduced mass and Bohr radius [2] by

$$E_R = \frac{\hbar^2}{2\mu a_B^2} \quad (1.2)$$

Therefore, combining the exciton kinetic and internal energies as well as the bandgap, we arrive at the total energy of an exciton in the $n$th excited state with center-of-mass momentum $K$:

$$E_{\text{total},n} = E_g - \frac{E_R}{n^2} + \frac{\hbar^2 K^2}{2M} \quad (1.3)$$

This energy spectrum is schematically illustrated in Fig. 1.1 in the pair picture representation. The pair picture is used to show that electron and hole are created simultaneously upon photon absorption in the conduction and valence bands, respectively. This two-particle process shown in Fig. 1.1a displays excitons ($n=1$, $n=2$, etc.) and electron-hole pairs as excited states along $E(n, k)$. In the continuum states, excitons are assumed to ionize into free electron-hole pairs where their wavefunctions must still be modified by some Coulomb attraction. There remains a residual Coulomb force in addition to the force binding the exciton. This residual Coulomb force induces a
nonlinear response and includes exciton-exciton interactions. Electron-hole pairs are created along the line $E = \hbar ck/n$ where, including exciton-photon effects, the pair picture is converted to the polariton picture. This joint dispersion lifts the degeneracy created when the photon dispersion intersects the dispersion of the $1s$ exciton at $k_0$.

For the 3D bulk semiconductor, the exciton oscillator strength for the $n$th excited state ($n = 1, 2, 3, ...$) is [2]:

$$f_n \propto 1/n^3$$  \hspace{1cm} (1.4)

The exciton absorption spectrum in Fig. 1.1b illustrates this relation as the absorption peaks near bandgap are sharp, decreasing in intensity, and exhibit decreased spacing at higher absorption energies. Experimentally, only the first few peaks are observable due to broadening mechanisms such as phonon scattering. It is also interesting that these exciton absorption peaks corresponding to the $1s$, $2s$, $...$ bound states appear
below the semiconductor bandgap $E_g$ followed by absorption by the continuum. It should be noted that excitons in semiconductors can be distinguished as dark or bright excitons according to whether the exciton is in a spin singlet or spin triplet state. Normally, the excited electron and the hole will have opposite spins so that the total spin $S$ of the electron-hole pair remains zero; this corresponds to a spin singlet state. Alternatively, if the spin is flipped i.e. by interaction with the magnetic component of the incident radiation field, the total spin $S = 1$ and a spin triplet state is the result. In PbS, the triplet state is found below the singlet state in energy, with a splitting due to exchange interaction. The terms bright and dark come from the fact that the spin triplet excitons have small oscillator strengths and are “spin-flip forbidden.”

1.2 Semiconductor quantum dots

The concept of quantum confinement due to size changes in binary nanocrystal structure was introduced and confirmed experimentally in the early 1980s [4, 5]. Over the past 30 years, the natural progression has been to decrease the dimensions to quasi-zero-dimensional structures using a variety of techniques including growth in glasses, solutions, polymers, annealing, organometallic chemistry, and sol-gel techniques. In this thesis, we have obtained samples prepared using “soft” colloidal chemistry synthesis techniques like those introduced by Murray, et al. [6]. These colloidal quantum dots (CQDs) are comprised of an inorganic core capped by organic ligands for chemical and electronic passivation of surface dangling bonds, which prevents agglomeration of the nanoparticles and uncontrolled growth. Also, CQDs have the advantage of being freestanding as opposed to epitaxial quantum dots, which are bound to the substrate, and can therefore easily be dispersed in polar or nonpolar solvents. Another advantage of using CQDs is their size monodispersity which can have $\sigma \leq 5\%$, with particle sizes ranging from $\sim 100$ to $\sim 10,000$ atoms.
When the dimensionality of a semiconductor is reduced below the exciton Bohr radius, $a_B$ of the corresponding bulk semiconductor, the carriers are confined to the boundaries of the material. In the regime of this quantum-size effect, the bulk energy bands become quantized, leading to atomic-like optical behavior in quantum dots, as illustrated in Fig. 1.2.

![Figure 1.2](image)

Figure 1.2: (a) Absorption of a photon in a bulk semiconductor illustrating promotion of an electron from valence to conduction band (b) Illustration of discrete energy levels in a quantum dot and absorption of photon, promoting an electron from an otherwise full valence band to a discrete level of an empty conduction band.

The result of quantum confinement in linear spectroscopy is to produce a set of discrete lines in the interband absorption spectrum, as opposed to continuous bands in the bulk. Experimentally, these lines are broadened due to inhomogeneities in the sample size, shape and structure. As in the past, we consider the quantum dot to have an atomic structure like it’s bulk parent if it contains $\sim 10^3$ atoms and below this size, the atoms begin to cluster, more akin to a molecule. Many IV-VI semiconductors fall into the strong confinement regime where the nanocrystal radius is much smaller
than Bohr radii of the electron, hole and exciton.

\[ a_B = \epsilon \frac{m}{m^*} a_0 \]  

(1.5)

The particle-in-a-sphere model considers an arbitrary particle of mass \( m_0 \) inside a spherical potential well of radius \( a \),

\[ V(r) = \begin{cases} 
0 & r < a \\
\infty & r > a 
\end{cases} \]

After solving the Schrödinger equation in three-dimensions, the energy of the particle is given by

\[ E_{n,l} = \frac{\hbar^2 \alpha_{n,l}^2}{2m_0a^2} \]  

(1.6)

where \( \alpha_{n,l} \) is the \( n \)th zero of \( l \)th order spherical Bessel function \( j_l \). These quantized energies are identical to the free particle kinetic energy term in Eq. 1.2 except that the wave vector \( k_{n,l} = \frac{\alpha_{n,l}}{a} \) is quantized by the spherical boundary condition. The size-dependence of the optical properties of quantum dots is also evident in that \( E \propto \frac{1}{a^2} \). Application of the effective mass approximation, where bands are assumed to be parabolic near extrema in the band diagram, and assuming that effective mass still has meaning for a quantum dot, allows us to solve for the energies given in Eq. 1.5 as the energies of our quantum dot [7], with the modification that \( m_0 \) be replaced by effective mass of conduction or valence band, \( m_{e,v}^{c,v} \). In the strong confinement regime, electron and hole can be treated separately, as each can be described as a particle in a sphere. Therefore the Coulomb attraction term can be added as a first-order correction to the energy.

In reducing dimensionality of a semiconductor from 3D to 2D, the oscillator strength \( f(n_B) \propto (n_B - \frac{1}{2})^{-3} \) and the quantization of electrons and holes must be
considered. In 2D systems, the increase in oscillator strength of the 1S exciton is due to the fact that electron and hole wave functions overlap in the $z$-direction as well as the reduction in the Bohr radius. In the zero-dimensional case, the exciton binding energy diverges and it is not possible to write a relation such as Eq. 1.3. More properties of zero-dimensional structures, specifically for PbS, will be discussed in the next section.

1.2.1 PbS quantum dots

The most extensively studied quantum dot material is CdSe, which can be synthesized with high quality and near monodispersity, and shows a single emitting ground state that is reasonably well-separated from the first excited state. More recently, the lead chalcogenides have stirred interest due to their tunable emission in the VIS-near IR wavelength range, crucial to the fields of communication and biological applications [8]. Also, it was discovered that these materials display what is known as multiple-exciton generation, where multiple electron-hole pairs are created from a single incident photon, an area of research that promises greatly increased solar-cell efficiency. As opposed to III-V semiconductors such as GaAs with large hole masses, quantum dots of IV-VI materials (lead-chalcogenides), such as PbS with an exciton Bohr radius of 18 nm, have nearly equal electron and hole masses and fall into the strong confinement regime. These materials can be synthesized with radius $R/a_B \lesssim 0.04$. PbS crystallizes in the cubic sodium-chloride structure, with every atom at a site of inversion symmetry. Such highly symmetry atomic configurations are useful for looking at intrinsic polarity in strongly size quantized semiconductor systems. This has an impact on the nature of electron-phonon coupling in PbS because the coupling to acoustic phonons arises due to the deformation-potential and piezoelectricity of the material. The centrosymmetric nature of the PbS lattice means that it is not piezoelectric. PbS has a lattice constant of $a = 5.93 \text{Å}$ and the zero
temperature band gap of the bulk is $E_g = 0.41$ eV. The electronic structure of PbS was first calculated by Kang using an envelope function approach, where the wave functions are forced to zero at the boundary of the QD [9]. This envelope function method is able to predict the energy states as well as electron-phonon coupling behavior of PbS QDs down to 3 nm diameter without avoiding the nonparabolicity of the energy bands neglected in parabolic effective-mass models.

All of the lead-salt binary semiconductors (PbS, PbSe, PbTe) crystallize in the rock-salt structure with direct band gaps at four equivalent $L$-points in the Brillouin zone. Therefore, 1S excitons in these systems are 64-fold degenerate (including spin). The valence band-edge Bloch function has $s$-like symmetry and conduction band-edge Bloch function is $p_z$-like, where $z$ denotes the $\langle 111 \rangle$ direction within the cubic lattice. Selection rules and dipole transition strengths are determined by the transition-matrix element:

$$M_{c,v} = |\langle \Psi_c(r) | e \cdot p | \Psi_v(r) \rangle|^2$$

where $e$ is the polarization of incident light and $|\Psi_c(r)\rangle$ and $|\Psi_v(r)\rangle$ are the total wave functions for conduction and valence electrons, respectively. The symmetry of band-edge Bloch functions leads to isotropy in the transition-matrix element, an important consequence for direct interband transitions of lead-salt QDs. Coulomb interaction and exchange interaction lead to the creation of indirect excitons made of electron and hole from different $L$-valleys, transitions which are shifted by one phonon energy from the direct transitions. These interaction mechanisms lift the degeneracy of primary absorption transitions but these many-body perturbations are negligible compared to the confinement energy [9]. Selection rules for direct transitions are

$$\Delta j = 0, \pm 1, \quad \Delta m = 0, \pm 1, \quad \text{and} \quad \pi_c \pi_v = -1,$$

where $j$ and $m$ are angular momentum quantum numbers and parity of conduction
(valence) band is $\pi_c(\pi_v)$. Important implications of Kang’s analysis are that:

1. The wave function envelope contributes to the transition dipole moment as well as the contribution from the dipole moment of the Bloch functions. This leads to irregularities in inter- and intraband transitions, i.e. one- and two-photon spectra.

2. Kang’s analysis includes fine-structure due to Coulomb interaction between electron and hole as well as exchange interaction as perturbations to an isotropic model. The Coulomb interaction does not split the lowest exciton in PbS QDs. The exchange splitting in PbS is only $\sim10$ meV, much smaller than in II-VI compounds due to the inter-unit-cell component which is absent in other compounds.

The 64 possible exciton states in this band are split by intervalley scattering and exchange interaction. The exchange splitting separates three “bright” states and a single “dark” state, each state having a combination of singlet and triplet character due to the large sin-orbit coupling in PbX quantum dots. The “bright” states are optically allowed, whereas the “dark” states are optically forbidden. Bulk material properties of PbX are compared to CdSe, the prototypical colloidal nanocrystal, in Table 1.1.

Table 1.1: Bulk material properties of PbX and CdSe selected from [10]. Note the large exciton Bohr radii of the lead-chalcogenides and small spin-orbit coupling (SOC) of PbS.

<table>
<thead>
<tr>
<th>material</th>
<th>$\epsilon_\infty$</th>
<th>$R_{ex}$ (nm)</th>
<th>$E_g$ (eV)</th>
<th>SOC (Ry)</th>
<th>$m_e$</th>
<th>$m_h$</th>
<th>$m_{eff}$</th>
<th>anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS</td>
<td>17</td>
<td>23</td>
<td>0.40</td>
<td>0.007</td>
<td>0.08</td>
<td></td>
<td>0.075</td>
<td>1.5</td>
</tr>
<tr>
<td>PbSe</td>
<td>23</td>
<td>66</td>
<td>0.28</td>
<td>0.031</td>
<td>0.04</td>
<td></td>
<td>0.034</td>
<td>2.0</td>
</tr>
<tr>
<td>PbTe</td>
<td>33</td>
<td>152</td>
<td>0.30</td>
<td>0.062</td>
<td>0.024</td>
<td></td>
<td>0.022</td>
<td>12</td>
</tr>
<tr>
<td>CdSe</td>
<td>6</td>
<td>5</td>
<td>1.75</td>
<td>0.12</td>
<td></td>
<td></td>
<td>0.80</td>
<td></td>
</tr>
</tbody>
</table>

The vibrational properties of PbS must also be understood in order to get a grip on the effects of electron-phonon coupling in these strongly confined systems. Electron-phonon coupling limits the magnitude of the nonlinear response of a quan-
tum dot and therefore has direct implications for optical switching and nanocrystal lasing. In many treatments of the electronic properties of quantum dots, size quantization of phonons is neglected. However, the application of spherical boundary conditions results in surface and longitudinal eigenmodes that are confined to the boundaries of the dot. There exist both coupled and uncoupled vibrational modes in highly confined QDs, where uncoupled modes are purely transverse and coupled modes have mixed longitudinal and transverse character and only coupled modes are optically active. The dispersive nature of phonons in lead-salt quantum dots makes them ideal systems for studying phonon confinement.

The dominant source of homogenous line broadening in the optical spectra of quantum dots is the coupling of electrons to phonons and therefore knowledge of electron-phonon coupling is of critical importance. It is generally agreeable in calculations that coupling strength is reduced in quantum dots relative to the bulk [11]. The electron-phonon coupling strength, in terms of the Fröhlich interaction with long-wavelength optical phonons, is proportional to the net charge density in the QD. In PbS, however, the electron and hole wave functions are nearly identical and this leads to overall charge neutrality. The Huang-Rhys parameter, $S$, is a measure of electron-phonon coupling, given by:

$$S = \sum_k \frac{1}{(\hbar \omega_p)^2} |V_{lm}(k)|^2,$$

(1.9)

where the sum is over all phonon wave vectors $k$. As the radius of the dot decreases, coupling between conduction and valence band leads to an increase in electron-phonon coupling strength, [12]. Further reduction of the QD size, however, decreases the value of $S$ due to the extreme confinement of the exciton and local charge neutrality. The interaction of electrons with acoustic phonons occurs mainly due to deformation-potential interaction, which corresponds to a deformation of the crystal structure.
This process is nearly elastic, the main effect of which is the relaxation of electron momentum.

1.3 Coherent optical spectroscopy of semiconductors

The power of linear and nonlinear optical techniques to illuminate scattering processes in semiconductors comes from their ability to detect phase changes that occur upon optical excitation of a medium. Knowledge of the coherent regime in semiconductors is crucial to fields such as nonlinear optics and quantum information. Decoherence in semiconductors is a result of phase fluctuations within an ensemble or between single emitters. These phase fluctuations are typically due to phonons deforming the atomic lattice immediately after excitation. In bulk semiconductors and quantum wells, so-called “pure dephasing” due to exciton-phonon and exciton-exciton interactions dominates the decoherence at low temperature. On the other hand, there is decoherence due to energy relaxation where the amplitude of either of two states goes to zero because other states in the system are relaxing. The coherent regime in semiconductors lasts on the scale of several picoseconds, when a definite phase relationship is maintained between excitation pulses and sample. Therefore, to probe the dynamics of the coherent regime in semiconductors, femtosecond laser pulses must be used as the excitation source. Fortunately, in recent years, reliable sources of ultrafast laser pulses with stable repetition rates and output powers have become commercially available.

1.3.1 Relaxation processes

Outside of the picosecond time scale comprising the coherent regime in semiconductors, there are several processes involved in returning the system to thermo-
dynamic equilibrium after excitation by an ultrafast pulse. Such processes include non-thermal relaxation, cooling of hot carriers, and isothermal relaxations [2].

We have already stated that the coherent regime in semiconductors is destroyed within picoseconds. After the dephasing process, the distribution of the excitation cannot be characterized by a temperature. Within this non-thermal regime lies scattering processes due to carrier-carrier and exciton-exciton effects. The first observation of a non-thermal distribution of photoexcited carriers in bulk GaAs was made by Oudar et al. [13] using pump-probe spectroscopy. Intervaly scattering also occurs during the first few picoseconds after excitation if the photoexcitation energy is sufficiently great. This process occurs when the photoexcited electrons have additional kinetic energy and may scatter to nearby conduction band valleys by the emission of a phonon. In PbS, intervaly scattering from equivalent gaps at L-points due to X-point phonons must be considered. Decreasing the dimensionality of a semiconductor also introduces several subbands into the conduction and valence bands, into which electrons and holes may scatter, significantly complicating the interpretation of spectra.

Carrier-phonon interactions contribute some energy to the lattice during thermalization, but much energy is retained within the electronic system such that non-thermal dynamics give information about carrier-carrier interaction. This thermal regime is the period when hot electron-hole distributions cool, slowly approaching the temperature of the lattice $T_L$ in $\sim 100$ ps. Carrier-phonon interactions remain a highly active area of study in condensed matter physics because in both photoexcitation and the application of electric fields, carriers lose energy to the lattice by the emission of phonons. Many processes in the thermal regime also play a part in the non-thermal regime.

Finally, electrons and holes recombine radiatively or non-radiatively and return the semiconductor to thermodynamic equilibrium. The isothermal regime is named
such due to the fact that carriers, phonons and excitons are at equilibrium with each other and remain at the temperature of the lattice. Radiative recombination time in indirect semiconductors can even reach the $\mu$s to ms range. It should be noted that these time scales are wholly dependent on the species under investigation and the nature of confinement. Environmental effects, particularly in colloidal quantum dots, also has an effect on thermal and non-thermal processes in addition to coherence lifetimes.

### 1.3.2 Spectroscopic techniques

Occasionally, simple linear spectroscopic techniques, such as absorption or photoluminescence measurements are sensitive to decoherence in semiconductors. The main difficulty in using linear measurements is that they cannot distinguish between decoherence due to scattering and dephasing due to inhomogeneous broadening. Inhomogenous broadening is a result of oscillators in an ensemble having different local environments. For example, in gases, Doppler broadening is the main contributor to inhomogenous broadening. In solids however, saturation broadening and pressure broadening also contribute. Also, linear techniques are unable to separate inhomogeneous broadening from homogeneous broadening of individual oscillators due to radiative decay.

To circumvent the problem of inhomogenous broadening, nonlinear spectroscopy is employed to overcome such deleterious effects. Nonlinear spectroscopy is based on using sufficiently intense light so that the induced polarization is no longer proportional to the first power of the electric field.

\[
P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + ..., \tag{1.10}
\]

where $P$ is the polarization induced in the sample, $E$ is the incident electric field and $\chi^n$
is the $n^{th}$-order susceptibility tensor. The $\chi^{(1)}$ term is responsible for linear behavior such as absorption and index of refraction, whereas all even powers of susceptibility are absent in materials with inversion symmetry. Signals for $\chi^{(3)}$ were first observed using Ruby lasers by Maker and Terhune [14].

Nonlinear spectroscopy can be performed in either the time domain, where pulse delays are varied to detect changes in induced nonlinear polarization, or frequency domain, where the frequency of incoming pulses is varied. We will focus on transient (time-domain) techniques in this work. In order to observe nonlinear signals at the same frequency of the incident light, three pulses of high-intensity light must be incident on the sample. The main technique to produce such signals is called transient four-wave mixing (TFWM) and in the degenerate case, all three incident pulses have the same frequency. If incident frequency $\omega$ is near a resonance in the sample, the $\chi^{(3)}$ term can be triply-resonant, and therefore very large in degenerate FWM experiments.

In general, for pump fields $E_m(\omega_m) = \varepsilon_m \exp(i k_m \cdot r - i \omega_m t)$ with $m = 1, 2, 3$, the output field $E_s(\omega_s) = \varepsilon_s \exp(i k_s \cdot r - i \omega_s t)$, with $\omega_s = \omega_1 + \omega_2 + \omega_3$, obeys the wave equation [15]:

$$\nabla^2 + \frac{\omega_s^2}{c^2} \varepsilon(\omega_s) E_s = -\frac{4\pi \omega_s^2}{c^2} P^{(3)}(\omega_s)$$  

(1.11)

where $P^{(3)}(\omega_s) = \chi^{(3)}(\omega_s = \omega_1 + \omega_2 + \omega_3) : E(\omega_1)E(\omega_2)E(\omega_3)$.

In the degenerate case, the nonlinear polarization has three components with different wavevectors. In practice, the first pulse arrives at the sample with wavevector $k_1$ and induces a polarization (coherent superposition between ground and excited state) in the sample. After a delay $\tau$, the second pulse with wavevector $k_2$ arrives and converts the superposition to a population grating. This population grating has a spatial period of $k_2 - k_1$ and is formed due to interference of the second pulse’s electric field with the polarization created by the first pulse. Finally, the third pulse with wavevector $k_3$ arrives after a delay $T$ from pulse 2 and scatters off of the density grating in the phase-matched direction $k_s = -k_1 + k_2 + k_3$. One of many possible
geometries for TFWM experiments is the box geometry, where the three excitation pulses come from three corners of a square and the phase-matched signal direction is the fourth corner of the square.

The decay of the TFWM signal as a function of $\tau$ depends upon the decoherence rate in the sample, and also whether the sample is homogenously or inhomogenously broadened [16]. FWM experiments are analyzed in the limits of homogeneous broadening, where levels are broadened with linewidth $\Gamma_h = 2\hbar/T_2$ ($T_2$ being the dephasing time as in NMR), and inhomogeneous broadening, $\Gamma_{in} > \Gamma_h$. Advantages of using three-pulse TFWM include the ability to directly measure dephasing rate $\gamma_{ph}$ by scanning $\tau$ and the grating relaxation rate $\gamma_{gr}$ by scanning $T$ [17]. Also, this three-pulse technique is able to differentiate broadening mechanisms by varying $\tau$ around zero for a fixed $T$ [18]. For inhomogenously broadened two-level systems using a delta-function approximation for incoming pulses and under the Markovian approximation, the time-integrated signal is:

$$I_s(\tau, T) \propto \theta(\tau)\theta(T)e^{-4\gamma_{ph}\tau}e^{-\gamma_{gr}T}$$

(1.12)

where $\theta(x)$ is the Heavyside step-function. The Markovian approximation states that relaxation times are time dependent and given by the instantaneous polarization and distribution functions [2]. Time-integration of the TFWM signal is done through lock-in detection. It is also possible to time-resolve the signal through up-conversion in a nonlinear crystal. Lastly, FWM spectroscopy is sensitive to spatial diffusion by setting $\tau = 0$ and investigating $T$. When the first two pulses are coincident in time, with the third pulse scanned backwards, the measurement is known as transient grating. Transient grating experiments are able to measure the relaxation rate of the spatially-modulated population as well as relaxation times.
Chapter 2

Principles of Optical 2DFT Spectroscopy

The principles of 2DFT spectroscopy can be thought of as an optical analog to the groundbreaking work done in the field of 2D NMR in the 1970s [19]. Recent work in physical chemistry has also hastened the rise of multidimensional spectroscopy [20]. Optical 2DFT spectroscopy is based on three-pulse TFWM experiments with the addition of coherently tracking the phase evolution of the signal with respect to the phase between excitation pulses. By spreading the TFWM signal out along two frequency axes, we are able to unravel congested spectra and isolate transition pathways. The phase preservation allows us to separate real and imaginary part spectra and identify microscopic contributions to electronic properties that would otherwise be unavailable in simple magnitude measurements.

2.1 Development of 2DFT techniques

Within the last 15 years, techniques have been developed to extend well-established experiments in multidimensional NMR into the IR and visible regimes. Many advancements have been made in the field of Fourier-transform nonlinear optics [21, 22], including electronic [23, 24] and vibrational [25, 26, 27] analogs to Correlation Spectroscopy (COSY) and Nuclear Overhauser Effect Spectroscopy (NOESY). COSY mea-
measurements, proposed by Jean Jeener in 1971, were implemented experimentally in 1976 to identify coupled spins using a series of two RF pulses [28]. NOESY, on the other hand, uses the fact that nearby atoms undergo cross-relaxation by a form of spin-lattice interaction known as the Nuclear Overhauser Effect. This cross-relaxation is examined during the mixing time $T$, to determine correlations among spins. Both methods result in two-dimensional spectra with peaks along the diagonal or along the anti-diagonal, depending on the system under investigation. Naturally, 2D NMR evolved into the microwave regime to probe electronic spins instead of nuclear spins, which occur on the microsecond timescale [29, 30]. Furthermore, optically-driven work was done on atomic vapors [31, 32] and vibrational anharmonicities investigated using IR or visible pulses (Raman) [33, 34, 35, 26].

The building blocks for 2DFT spectroscopies lie in the Fourier transformation of one-dimensional techniques. Consider the pulse electric field, $E(r,t)$, which can be directly measured in experiment:

$$E(r,t) = e(t - k \cdot r/\omega)cos[\phi(t - k \cdot r/\omega)],$$

(2.1)

where $e(t)$ is the pulse envelope, $\phi(t)$ is the temporal phase, $r$ is the position, and $k = (n\omega/c)u$ is the pulse wave vector. The expression in Eq. 2.1 is in the time domain and can be easily expressed in the frequency domain via inverse Fourier transformation as:

$$E(r,\omega) = \int_{-\infty}^{+\infty} E(r,t) e^{i\omega t} dt = e(\omega) e^{i[\phi(\omega)+ik \cdot r]}.$$

(2.2)

This expression is advantageous in that symmetry arguments can be used in analyzing refractive and absorptive terms in optical spectra, relative signs of Bohr frequencies can be selected from different time intervals in 2DFT scans [19, 23], and positive and negative Bohr frequencies appear naturally in elementary quantum mechanics.

The frequency power spectrum of the electric field $I(\omega) \propto |E(\omega)|^2$ is real and
independent of the spectral phase. Therefore, by knowing the power spectrum of the incident field, the spectral phase $\phi(\omega)$ determines $E(t)$. This frequency power spectrum of a pair of pulses depends on the relative phase difference between them. Consider a reference pulse and signal pulse with spectral phase difference $\Delta \phi_{sr}(\omega) = \phi_s(\omega) - \phi_r(\omega)$ between them. The frequency power spectrum of the pulse pair is then:

$$I(\omega) \propto |E_s(\omega) + E_r(\omega)|^2$$

$$\propto e_s^2(\omega) + e_r^2(\omega) + 2e_s(\omega)e_r(\omega)\cos[\Delta \phi_{sr}(\omega)].$$

Eq. 2.3 provides an easy way to determine phase difference of a pair of pulses given the individual pulse spectra are known. Joffre et al. refined the methods used to obtain the phase shift and time delay between pulses from a single spectrum using Fourier algorithms [36, 37]. Time domain interferometry and nonlinear techniques are also able to detect phase shifts between pulse pairs but leave a constant in the spectral phase undetermined. In Fourier transform absorption spectroscopy, the sample is inserted either before or after an interferometer that produces a pair of pulses and delay between them. The transmitted absorption spectrum is then determined by switching frequencies on and off as the delay between pulses is varied. Molecularly, the excitation of each molecule is switched on or off with a period related to the molecule’s absorption frequency until the pulse delay is so large that the transmitted spectrum has many oscillations within the molecular linewidth.

2D spectroscopy using femtosecond pulses was first proposed by Tanimura and Mukamel [38], and experiments later followed [39, 40, 41], where Ref. [41] uses a more advanced technique in heterodyne detection also used in this thesis. The majority of studies investigated vibrational properties of liquid $CS_2$, an ideal system in nonresonant Raman studies due to its large polarizability. Of particular interest was the fifth-order response function $R^{(5)}$ in the time domain, similar to third-order processes.
but resulting from a second interaction due to the probing step with two additional light fields. It was clear that 2D-IR spectroscopy possessed the capability to distinguish homogenous and inhomogenous broadening mechanisms. Later, rephasing and nonrephasing 2D scans were performed to produce correlation spectra revealing the inhomogeneity among individual transition energies [42, 27]. Rephasing measurements can be explained in terms of a photon echo, analogous to the famous spin echo, [43], where a system spontaneously emits a pulse of light at time $2\tau$ after excitation by multiple pulses of light [44]. In rephasing measurements, the phase acquired by coherences during the evolution period $e^{i\omega \tau}$ is the conjugate of the phase acquired during emission $e^{i\omega t}$, see Fig 2.1.

Electronic properties were first studied using 2D techniques by Jonas et al. [23, 45, 46, 47] and other groups soon followed, [22, 24, 48, 49]. The addition of a tracer beam allowed determination of signal phase shift relative to excitation beams along with the time of signal emission, [50], so that 2D spectra could be separated into real and imaginary parts. The first of these experiments, the absolute phase of the 2D spectrum was found to obtain a positive real 2D lineshape, similar to adjustments made in standard NMR [23]. Working with the dye IR144 in methanol, it was suggested that 2DFT spectra resolved the homogenous lineshape in the dye molecule’s local environment. The imaginary spectra were broad and absolute value spectra were nearly featureless, indicating the importance of separating real and imaginary part spectra. Studies of IR144 were also the first to probe coherences in 2D spectra.

Heterodyne detection of photon echoes, along with Fourier transform spectral interferometry, [21, 51, 52], allowed the full characterization of the amplitude and phase of a nonlinear polarization using a known reference pulse. Spectral interferometry is based on measuring the frequency-resolved fringe pattern of the collinear interference
between reference and signal beams:

\[ S(\Omega) \propto A_{\text{sig}}^2(\Omega) + A_{\text{ref}}^2(\Omega) + 2A_{\text{sig}}(\Omega)A_{\text{ref}}(\Omega) \]

\[ \times \cos[\Omega \tau + \phi_{\text{ref}}(\Omega) - \phi_{\text{sig}}(\Omega)] \] (2.4)

where \( A(\Omega) \) and \( \phi(\Omega) \) are the spectral amplitude and phase, respectively [51].

Despite the vast similarities between 2D NMR and 2DFT spectroscopy, there are a few striking differences that must be addressed in order to investigate coherent processes in semiconductor nanostructures. Mainly, NMR uses RF pulses that contain millions of cycles while optical pulses can contain only a few cycles of light. During such femtosecond pulses, nuclei are frozen in place and it is more difficult to unravel complex spectra containing a wealth of information on electronic and vibrational interactions. Also, unlike a spin-flip, electronic and vibrational excitations have a strong influence on the sample environment, making it difficult to obtain information from lineshapes and time evolution [20]. In order to perform 2DFT spectroscopy in the visible regime, it is crucial to actively stabilize all excitation pulses. More about the experimental difficulties of active stabilization will be discussed in the next chapter.

### 2.2 Two-dimensional Fourier transform spectroscopy

Based on traditional degenerate three-pulse FWM with the addition of active phase stabilization of all excitation beams with sub-optical-cycle precision, we obtain the signal in the phase-matched direction \( \mathbf{k}_s = -\mathbf{k}_a + \mathbf{k}_b + \mathbf{k}_c \). The signal phase is determined through the addition of heterodyne detection. Fig. 2.1(a) shows the FWM experimental setup in the box geometry, with the three excitation pulses propagating along the corners of a square and focused by a 300 mm focal length lens. The long focal length leads to a greater focal depth in the sample, adding to the ease of detecting
the FWM signal. The FWM electric field is then emitted along the fourth corner of the square and reflected from the sample.

![Figure 2.1](image)

Figure 2.1: (a) Experimental setup for 2DFTS in the box geometry; (b) Pulse ordering along time axis, with evolution, waiting, emission times labeled as $\tau, T, t$, between first and second pulses, second and third pulses, and third pulse to signal, respectively.

Fig. 2.1 shows an early experimental setup where the signal is transmitted through the sample and the original box is reformed by a 200 mm focal length lens. Ultimately, experiments were performed in reflection geometry as we will see in Fig. 3.3 for cleaner signals. The delay times of each pulse are indicated in Fig. 2.1(b), where the evolution time between the first exciting pulse and the second pulse is labeled as $\tau$, the waiting time between pulses 2 and 3 is $T$, and the emission or detection period between pulse 3 and the photon echo signal (for inhomogenously broadened systems) is $t$.

It is standard to present the FWM electric field in two frequency dimensions
after Fourier transform with respect to the evolution time $\tau$, and the emission time $t$. Frequency-domain heterodyne detection takes care of the variable $t$, so that a numerical Fourier transform with respect to $\tau$ yields the 2D spectrum:

$$S(\omega_\tau, T, \omega_t) = \int_{-\infty}^{+\infty} E(\tau, T, \omega_t) e^{i\omega_\tau \tau} d\tau$$ (2.5)

for a fixed $T$. The absorption frequency is $\omega_\tau$ because it corresponds to the absorption process in excitation. In 2D NMR, it is important to equally weight equal and opposite orders of coherence. In 2DFT spectroscopy, this is accomplished by Fourier transforming both positive and negative values for $\tau$ and $t$, which yields real and imaginary spectra corresponding to absorption and refraction changes [23, 46]. An effect known as phase twist may sometimes arise due to the introduction of either amplitude or phase discontinuities which introduce imaginary dispersive lineshapes after inverse Fourier transformation. Fourier transforming a second discontinuity then mixes the lineshape into the real 2D spectrum. Describing 2DFT spectroscopy in this way is analogous to Correlated Spectroscopy (COSY) and Nuclear Overhauser Effect Spectroscopy (NOESY) from NMR. In COSY measurements, the delay $T$ between the last two pulses is set to zero, whereas in NOESY, the delay $T \neq 0$, allowing population dynamics to occur.

By spreading the FWM signal into two dimensions and Fourier transforming two time variables, it is possible to unravel complex spectra and identify couplings between resonances. Peaks in 2D spectra reveal quantum mechanical coherent pathways. Tracking the phase evolution throughout a 2D scan and correlating it in two frequency dimensions is the power behind the technique, as opposed to relying on the Fourier transformation, which simply presents the FWM field in the frequency domain. 2DFT spectroscopy is still considered a time-domain technique, as it relies on the specific time ordering of the excitation pulses. Previous experiments have
gathered the full information on the FWM electric field, including phase, but phase evolution was not tracked explicitly as a function of delay $\tau$ [53, 54]. Similar to 2DFT spectroscopy, coherent excitation spectroscopy (CES) combines features of coherent photon echo spectroscopy, [55, 56] and energy-selective spectroscopy, [57, 58]; for combinations of these methods performed on exciton systems, see Refs.[59, 60]. CES is a variant of photoluminescence excitation (PLE) spectroscopy, as well as partially nondegenerate FWM, where the FWM signal takes the place of the PL signal. In contrast to PLE spectroscopy, only coherently coupled quantum states are detected because all incoherently coupled processes are suppressed in CES.

To show that phase evolution between the first two pulses yields a constant phase in the emitted field, consider the expression:

$$S_I(\tau, t) = \mu^2_{ij} \mu^2_{ik} e^{i(\omega_{ik} t - \omega_{ij} t)} D(\tau, T, t)$$

(2.6)

where it is assumed that the first pulse is the conjugated pulse and $\mu_{ij}$ and $\mu_{ik}$ are the dipole moments of the transition excited by the first pulse $\omega_{ij}$ and the resultant excited transition $\omega_{ik}$. All of the decay dynamics plus any evolution occurring during time $T$ is lumped into the term $D(\tau, T, t)$ [61]. Therefore, by coherently tracking the signal phase with delay $\tau$ with sub-optical-cycle precision, the frequency of the absorbing transition can be simultaneously tracked with the frequency of the emitting transition. Fourier transforming the data in two dimensions will yield peaks along the diagonal for two-level systems, and three-level systems will also show peaks off the diagonal.

It should be noted that Eq. 2.6 represents a “rephasing” scan, where the conjugate pulse is scanned forward from $\tau = 0$ so that, by definition, rephasing scans have $\tau > 0$, as shown in Fig. 2.2a. After the conjugate pulse arrives with wavevector $k_a$, pulse 2 with wavevector $k_b$ creates a coherent superposition between ground and
excited states in the ensemble and the oscillators dephase with different resonant frequencies in time $\tau$ due to inhomogenous broadening. The third pulse then introduces a conjugated phase evolution in time $t$, causing the oscillators to reverse their phases and resulting in a photon echo with delay $\tau$ after the third pulse in inhomogenously broadened systems [44].

The advantage of using three-pulse excitation to generate the FWM signal is that the pulse-ordering can be varied to obtain different coherences in the sample. For example, by scanning pulse $k_b$ towards earlier time, we obtain a “non-rephasing” (or virtual echo) scan. In this case, shown in Fig. 2.2b, there is no phase conjugation and we obtain a free polarization decay instead of a photon echo. By definition, non-rephasing scans have $\tau < 0$, and the emitted signal is $S_{II}(\tau, t) = \mu^2_{ij} \mu^2_{ik} e^{-i(\omega_{ij}\tau + \omega_{ik}\tau)} D(\tau, T, t)$ in the direction $S_{II} = +k_a - k_b + k_c$. Similarly, there are experiments which probe non-radiative two-quantum coherences along the direction $S_{III} = +k_a + k_b - k_c$. In this case, the first two pulses are not phase-conjugated with respect to one another and it is crucial that all excitation pulses be phase locked. The final pulse (the conjugate pulse) examines coherent transitions from the two-quantum to one-quantum states.

$S_{III}(\tau, \omega_T, \omega_i)$ spectra are then plotted along the double diagonal, with the absorption axis at twice the energy of $S_I(-\omega_T, T, \omega_i)$ or $S_{II}(\omega_T, T, \omega_i)$ spectra. Rephasing and non-rephasing pathways have been investigated experimentally, [46, 27, 62, 63, 64]
and through simulations, [65, 66]. The sign of the emission frequency $\omega_t$ is taken to be positive, whereas the absorption frequency $\omega_\tau$ is negative in a rephasing experiment due to the conjugated phase evolutions in the evolution and emission times. The 2D spectra of rephasing pathways appear in the lower-right quadrant of the 2D plane ($\omega_t > 0$ and $\omega_\tau < 0$) and nonrephasing spectra appear in the upper-right quadrant ($\omega_t$ and $\omega_\tau$ have the same sign). Comparison of rephasing and non-rephasing spectra sheds light on the nature of inhomogeneity and contributions from various quantum mechanical pathways [27, 67, 68].

2.3 Advantages of 2DFT spectroscopy

Throughout many of the references in the previous section, 2DFT spectroscopy continues to prove itself invaluable to researchers investigating quantum mechanical resonances, coupling of pathways in Liouville space, Raman coherences and broadening mechanisms. Being a Fourier-transform technique, 2DFT spectroscopy requires incredibly precise time delays as well as active or passive stabilization methods. These advantages will be discussed in the following subsections.

2.3.1 Origins of coherent response

The great power of 2D spectroscopy lies not in the power of the Fourier transform but from tracking the phase of the TFWM signal as a function of the phase delay between excitation pulses. After compiling one full data set, everything from linear spectra such as absorption to real and imaginary 2D spectra can be extracted from the set of spectral interferograms. A visual aid is shown in Fig. 2.3, summarizing the various spectra that can be obtained.
The origins of the coherent response in semiconductors can be found in comparing real vs. imaginary parts of the sample response. Absorptive and dispersive dynamics are revealed in the complex parts of the 2D spectra. The introduction of the third pulse to generate TFWM signals provides access to many different coherences, including two-quantum coherences. Double-sided Feynman diagrams are useful for describing light-matter interactions, where the vertical axis indicates time and optical pulses are incident on each side of the diagram, putting the system in various excited states. Each diagram corresponds to a coherent pathway in Liouville space. 2DFT spectroscopy is able to separate the effects of ground state bleaching (GSB), excited state emission (ESE) and excited state absorption (ESA) in one intuitive 2D map of emission and absorption frequencies [20]. By choosing the appropriate time period correlation, pulse sequencing and spatial arrangement of pulses, any of 16 possible coherent pathways can be isolated. For example, it has been shown that pathways
contributing to the nonradiative Raman coherence between heavy-hole and light-hole excitons in GaAs quantum wells can be isolated by scanning time variables $T$ and $t$ instead of $\tau$ and $t$.

### 2.3.2 Isolate coupling between transitions

A 2D spectrum yields peaks on along the diagonal for two-level systems and additional off-diagonal peaks for three-level systems. From Eq. 2.6, this can be seen by setting $\omega_{ik} = \omega_{ij}$ for two-level systems such as PbS quantum dots. GaAs multiple quantum wells have been intensively studied with 2D techniques. GaAs is a three-level “V” system with a shared ground state and yields a 2D spectrum with two peaks along the diagonal and two peaks along the cross-diagonal for excitation pulses tuned between the heavy-hole and light-hole. Multidimensional spectroscopy can isolate these various resonances and couplings among resonances in a straightforward way. For example, a two two-level system (separate ground states) with transitions of frequency $\omega_1$ and $\omega_2$ would have 2D spectral peaks along the diagonal at $(\omega_1, -\omega_1)$ and $(\omega_2, -\omega_2)$, where the 2D peak is specified as having emission frequency $\omega_t$ and absorption frequency $\omega_\tau$ of $(\omega_t, \omega_\tau)$. For coupled transitions, as in the “V” system of GaAs, the coherences are no longer independent and give additional cross peaks at $(\omega_1, -\omega_2)$ and $(\omega_2, -\omega_1)$ as well as the two resonance peaks on the diagonal. A one-dimensional spectrum such as absorption or photoluminescence will give identical results for each situation.

Furthermore, coupling mechanisms can be extracted directly from 2D spectra. For example, an incoherent population relaxation from a higher excited state to a lower excited state in a two two-level system would show a single cross peak at lower emission frequency $(\omega_1, -\omega_2)$. As we will see in Chapter 4, IV-VI quantum dots are much simpler, two-level systems without cross-peaks in 2D spectra. Early non-Fourier-transform two-dimensional spectroscopy techniques are also able to isolate
resonance couplings, but 2DFT spectroscopy is the only technique able to lay this information out in a simple map for straightforward interpretation. Also, unlike non-Fourier-transform methods, 2DFT spectroscopy is capable of separating exciton-exciton interactions and exciton-continuum excitations.

2.3.3 Simultaneously extract homogenous and inhomogenous linewidths

In addition to the isolation of resonances and quantum-mechanical pathways, 2D spectra have the additional advantage of displaying inhomogenous broadening as elongation along the diagonal and homogenous broadening across the diagonal. Therefore, important information about fluctuations of oscillators in the sample and the contribution of the size distribution of dots to inhomogeneous broadening can be investigated simultaneously, even with a strongly inhomogenous sample. Current chemical synthesis methods for quantum dots are able to produce samples with size distributions of $\sigma \leq 5\%$, though inhomogeneity can still cause problems. Dephasing time is inversely related to inhomogenous linewidth and can also be read in a straightforward way from a 2DFT spectrum. Again, one-dimensional techniques are incapable of making this distinction.

The linewidths both along the diagonal and across the diagonal of a 2DFT spectrum can be obtained through application of the projection-slice theorem [70]. These linewidths are coupled in the 2D spectrum and it can be difficult to get quantitative information about the nature of broadening in the sample. Resonance line shapes in 2DFT spectroscopy were investigated recently by Siemens et al. [71]. It was shown that adding an inhomogeneously broadened component to a model of a purely homoneous broadened system, as the diagonal linewidth broadens, so does the cross-diagonal. The projection-slice theorem in 2DFTs works by integrating the signal at all points perpendicular to a line in order to project the signal onto that
line. A Fourier transform of this projection is then equivalent to a slice in the plane \((\omega_\tau, \omega_t)\) for (absorption, emission). Ref. [71] shows that in the inhomogeneous limit, the lineshapes along the \(\omega_t\) axis are Lorentzian in real-part spectra \(S_{proj} = \frac{1}{\pi \gamma^2 + \omega_t^2}\) with width \(2\gamma\) and square root of a Lorentzian in the amplitude spectrum.

It is also possible to measure homogeneous and inhomogeneous components that each contribute to the diagonal and cross-diagonal lineshapes. This may be due to excitation-induced many-body effects such as Excitation-Induced Dephasing (EID), and Excitation-Induced Shift (EIS); see [72, 67]. In this case, the lineshape may be a convolution of Gaussian and Lorentzian in the form of a Voigt distribution:

\[
S_{proj} = \frac{exp\left(\frac{(\gamma - i\omega_t)^2}{2\sigma^2}\right)Erfc\left(\frac{\gamma - i\omega_t}{\sqrt{2}\sigma}\right)}{\sigma(\gamma - i\omega_t)},
\]

where \(Erfc\) is the complementary error function.

### 2.3.4 Track evolution of nonradiative coherences

Overlapping Raman coherences in the traditional \((\omega_t, \omega_\tau)\) projection can be isolated by correlating delay periods \(t\) and \(T\) instead. These coherences were isolated in GaAs in 2008 [73] and linewidths of these resonances were obtained. Such nonradiative coherences are of interest to the nascent fields of electromagnetically-induced transparency, slow light and lasing without inversion. The Raman coherence in semiconductors is very weak and difficult to detect without very sensitive instrumentation and a very robust experimental setup. This coherence tends to overlap with contributions from inhomogenous broadening, ground state bleaching and polarization interference. This similarity with polarization interference has shown the Raman coherence to be a factor in quantum beating of the TFWM signal in bulk semiconductors. In 2D experiments, contributions only appear at \(\omega_\tau = 0\) for polarization interference and ground-state bleaching. In Ref. [73], it was shown that these Ra-
man coherences could also be isolated by using narrow-bandwidth excitation pulses to excite only the heavy-hole or light-hole exciton for increased resolution in double-quantum coherence measurements. In conclusion, weak non-radiative coherences can become more prominent in 2DFT spectroscopy through proper time-delay correlation and pulse ordering.
Chapter 3

2DFT Spectroscopy with Active Interferometric Stabilization

One of the most experimentally challenging parts of 2DFT spectroscopy in the visible range is phase-stabilization of all excitation pulses and tracking the phase of the FWM signal. In the case of 2D NMR, the long wavelengths used simplify the process somewhat but in the visible range, many environmental factors contribute to mask crucial information in the desired signal. Several techniques have been employed in the past decade to stabilize the phase of excitation pulses, including diffractive optics [74, 66], pulse-shaping [64, 75, 76, 77] and active stabilization using electronic feedback loops [78, 79]. Non-collinear, partially collinear and fully collinear techniques have been used to generate the TFWM signal, the latter relies on phase cycling to extract the signal from excitation pulses [80, 81]. One of the more common setups used today relies on the box geometry for background-free TFWM signals, [24, 82, 64, 83].

3.1 Multidimensional Optical Nonlinear Spectrometer (MONSTR)

Within the past few years, a novel setup was developed to perform 2DFT scans in the visible wavelength range using the box geometry with active stabilization. Shown in Fig. 3.1 is an unfolded beam path diagram of the setup. The Multidimensional
Optical Nonlinear Spectrometer (MONSTR) is a set of nested and folded Michelson interferometers that produces four output pulses in the box geometry that can be phase-delayed with sub-nanometer precision and stabilized using a co-propogating helium-neon (HeNe) CW laser for active phase-locking [83].

Figure 3.1: Optical path diagram of the MONSTR shown unfolded, showing a single pulse train from a Ti:Sapph local oscillator with multiple beamsplitters creating pulses A*, B, C and Ref. Delay stages X, A, B, and C are shown in the path of pulses C, B, A* and Ref, respectively. Pulses then pass through a common dichroic mirror (DCM) and the co-propogating HeNe beam is reflected by the dichroic, resulting in interference patterns which are monitored at separate diagnostic ports for each combination of pulses [83].
The beam paths shown in Fig. 3.1 would normally require many square feet of real estate on an optical table. The MONSTR’s folded interferometer layout houses all optics within two stacked aluminum plates with a footprint of only (77 cm × 38 cm × 23 cm). The aluminum plates themselves have a mass of 19 kg and are milled out via CNC machining to house all optical mounts and translation stages. All translation stages have a position accuracy of ±10 nm. We have replicated much of the original setup from Ref. [83] with significant improvements.

Many improvements were made to the MONSTR over the previous design and modifications were required due to the lack of certain machining capabilities. A local machining company, Vulcan Machining, specializing in aircraft parts, was used for custom CNC machining of bottom and top plates. Commercial 1/2” mirror mounts and piezo mounts were used to speed up production time. Improvements to our design include the use of broadband, wedged beamsplitters and compensation plates to adjust for dispersion, giving us access to wavelengths from 350-1100 nm without having to change any internal components. The 30 arcmin wedged optics prevent back-reflections from degrading interferometer signals and were oriented such that the thick part of the compensation plate is aligned opposite the thin part of the beamsplitter. Custom 1” mirror mounts for the 1 mm-thick beamsplitters and compensation plates were machined to tight specifications. Copper RF-shielding fingers were used to hold the optic to its mount with appropriate pressure. We have also upgraded to using three stages with 60 mm of travel as opposed to the 50 mm stages in the previous design. This will provide us the opportunity to look at materials with even longer coherence/population lifetimes. Fig. 3.2 shows both plates separated, including all beam paths, optical components and translation stages for delaying excitation pulses. To eliminate any electrical noise to the MONSTR from our high-voltage piezo drivers, we have isolated the MONSTR and any high-voltage connections on the table with 1/8” thick elastomer. This elastomer was placed under all three legs on the MONSTR.
as well as pedestals for external piezo mounts. Lastly, the entire table space for 2D experiments is enclosed in a custom built plexiglass box, isolating excitation beams from air currents and environmental fluctuations.

Alignment of the MONSTR begins with the decks separated, aligning each component to achieve two parallel HeNe beams exiting bottom and top decks of the MONSTR, separated by precisely one inch each. A pulse train from a passively mode-locked Ti:Sapphire oscillator producing pulses of $\sim 150$ fs as well as the CW HeNe beam are sent into the MONSTR and these beams are immediately split, yielding beams for top and bottom decks. Next, the bottom deck beam reaches the first retroreflector mirror pair mounted to stage X. This is the longest of the four translation stages, with a total displacement of 200 mm. After passing through a second coated beamsplitter, beam C is reflected and the Ref. is the transmitted beam reaching a piezoelectric actuator (PZT) mounted to another 1/2” mirror for stabilizing the phase of the bottom deck interferometer. Lastly, the reference pulse hits a retroreflector mounted to stage C, one of three translation stages with a range of 30 mm. The split-off beam for the top deck follows a similar path, with a pair of 60 mm stages for pulses A* and B. The top deck houses two PZTs; one for stabilizing the top deck interferometer and the other for stabilizing the interdeck loop.

Once the alignment is completed for each deck separately, the top plate is carefully lowered with screw jacks onto five heat-treated steel pins, fitting precisely into the metal bushings of the top plate. With the top plate bolted down, a third interferometer is formed. The single DCM mounted to the front of the MONSTR reflects the HeNe and interference fringe patterns are sent to Si photodetectors, one each for bottom, top, and interdeck loops.
Figure 3.2: (a) CAD drawing of MONSTR decks, including beam paths. Incident beam is entering the bottom deck from the right and is sent to the top deck via the periscope between decks. Interferometer error signals emerge as dashed lines from one side of each deck. (BS=beamsplitter, CP=compensation plate, PZT=piezo-electric transducer) (b) 3D computerized model showing top and bottom plates stacked with dichroic mirror (DCM) mounted on the front for reflecting HeNe beams and completing the interferometers.
3.2 Active vs. passive stabilization

Passive methods of achieving phase stabilization include the use of diffractive optics and other pulse-shaping mechanisms. Diffractive optical elements with a square lattice are statically mounted at 45° and a single beam of femtosecond pulses impinges on the element, diffracting into ± first order and resulting in four beams at the corners of a square. Such methods have yielded stability of λ/90 in the short term and λ/40 in the long term [74]. With the addition of spatiotemporal pulse shaping, stability can be improved and published results of λ/67 soon followed, [84]. The spatiotemporal pulse shaper consists of grating, cylindrical lens, and a spatial light modulator (SLM), which forms a sawtooth grating pattern from each beam’s frequency components. The SLM is used for simple shaping tasks such as generating pulse delays; therefore an entire experiment can be executed with the SLM as the only active element. Diffractive-based pulse shaping allows for independent control over individual pulse phase and amplitude profiles as well as eliminating replica pulses that often accompany pulse shaping techniques. The problem with passive techniques is that they rely on movable glass wedges to create delays and therefore suffer from limited delay range. Even with the use of acousto-optic pulse shapers, which generate inherently phase-stable trains of pulses, frequency resolution limits pulse delays to several picoseconds.

Here, we will focus on active stabilization techniques, similar to those employed by Zhang et al. [79]. Due to the long dephasing times in semiconductor nanostructures, optical delay stages common in femtosecond spectroscopy are not accurate enough to maintain phase stability throughout long scans. Position accuracy of Δx ≤ 1nm at λ = 800nm is required to achieve λ/1000 stability. Delay stages have been used in the past to control relative phases between pairs of pulses, solving the phase stability problem but leaving the independent scanning of individual delays unresolved. A HeNe laser operating at 632.8 nm has been used in active phase stabilization by detecting its interference fringes as it co-propogates through the experimental setup.
After splitting the HeNe equally into four beams and reflecting it with the DCM, three sets of interference fringes are created, one tracing the path of pulses C and Ref. another tracing pulses A* and B, and a third set of fringes with contributions from all four paths. The combination of computer-controlled delay stages with sub-nm precision, co-propogation of a HeNe laser for active phase locking, and feedback electronics for piezoelectrically-controlled monitoring of the phase-locked scan result in phase stability of $\lambda/130$ to $\lambda/800$, [83].

### 3.2.1 Phase stabilization procedure

Active phase stabilization relies on electronic feedback loops connected to PZT mirrors to lock on a single HeNe fringe and correct for any fluctuations. The PZTs can be seen colored orange in Fig. 3.2, one for each interferometer. The actuators are secured to 1/2” mirrors with strong adhesive and connected to electronic loop filters outside of the MONSTR. Each servo loop can be locked and unlocked via computer control for spectrum acquisition and stage scanning, respectively. Piezo drivers provide an average of 75 volts and the offsets of the servo loops are centered so that HeNe fringes oscillate around zero when scanning.

Firstly, the exact timing of all pulses must be known precisely. For this, the focus is replicated by placing a 2” window several inches from the main 300 mm focusing lens, as shown in Fig. 3.3. This replica focus is then imaged by a CCD, which yields vertical, horizontal, or diagonal fringes based on the angle of interfering pulses as well as pulse timing. All four pulses combined show a checkerboard pattern, as shown in Fig. 3.4(d).

To find the most precise time-zero values, field correlation graphs are taken by imaging one pair of pulses at a time and scanning one pulse ±30 $\mu$m from the approximate time-zero position. The fringe intensity over this scan range yields a Gaussian curve when integrated across the fringes whose maximum corresponds to a
Figure 3.3: One view of the experiment performed in the reflection geometry, with the FWM signal emerging from the missing fourth corner of the square upon reflection from the sample. Interference fringes from each deck are shown at the CCD camera.

(a) Top Deck  
(b) A*+C  
(c) Bottom Deck  
(d) A*+B+C+Ref

Figure 3.4: Interference patterns captured via CCD from the replica focus created with a 2" window after focusing the box with a 30 cm lens.

more accurate time-zero position. This procedure is repeated in the order Top Deck (scan stage A), Between Deck (scan stage X), Bottom Deck (scan stage C) to obtain time-zero values for all four pulses; note that stage B (pulse A*) is not scanned.

The Reference beam is routed around the sample and can be manually delayed from the signal with a 1/2” translation stage. The Reference is then recombined with
Figure 3.5: Sample field correlation graph for Top Deck pulses A* and B, where only pulse B is scanned ±30 μm from its approximate time zero value, along with the least-square fitting which provides a more accurate time zero.

the signal at an external beamsplitter. As discussed later in the chapter, this forms the basis of what is known as spectral interferometry. A second external, frequency-stabilized HeNe is aligned to precisely trace the path of both signal and reference back to a pair of DCMs outside of the MONSTR, forming an external interferometer. The error signal of this interference is monitored by another high-gain photodetector and stabilized using a fourth “external loop” with a PZT in the Ref. path. Since the external loop is independent of the excitation pulses, it can be locked and unlocked separately. The only downside of having the signal phase-stabilization separate from the HeNe inside the MONSTR is that minute vibrations near the sample environment, possibly due to the cryostat or turbulent air flow from the cryogen, is not accounted
for. Many 2D spectra taken thus far do not indicate these possible phase fluctuations to be a significant issue.

In practice, before any initial locking of servo loops takes place, each interferometer is “dithered” to ensure stable PZT driving. The dithering process consists of driving each piezo with a 10 V sine wave and monitoring the response on a 100M Hz, 4-channel oscilloscope. Once a smooth, symmetric response is obtained with amplitude $\sim 4$ V, the servo loop offset is adjusted so that dithering oscillates symmetrically about 0 V. This procedure is repeated for each loop in the order bottom deck, top deck, interdeck, and external loop. A previous experimental setup that relied on transmitting the signal and all three excitation pulses through the sample, was considerably more challenging to lock the external loop. In the transmission geometry, the third excitation pulse and the Ref. were combined using a custom quarter-silvered window and coupled into a single-mode fiber. A pair of glass prisms were then used to set the correct time delay and maximize the dithering voltage. Besides the difficulty of coupling light into such fibers, using low pulse powers proved to be a significant setback to this design. In reflection geometry, however, the external HeNe is simply aligned with two 1/2” DCMs to yield the cleanest interference fringes and maximize the dithering voltage. In this way, fewer optics need to be adjusted before a scan, which can sometimes compromise the spectral interferograms.

### 3.3 Four-wave mixing generation

Excitation pulses are derived from a passively mode-locked Ti:Sapphire oscillator with a pulse duration of 150 fs and a repetition rate of 76 MHz. The wavelength of all excitation pulses is identical and tunable from 700 nm to 950 nm. Three of the MONSTR’s output pulses propagate with wavevectors $k_a$, $k_b$, and $k_c$ and are focused by a 30 cm lens onto the sample. The fourth pulse (the Reference pulse) is split off and
routed around the sample. Since the experiment is performed in the box geometry, the signal is generated along the phase-matched direction $k_s = -k_a + k_b + k_c$. The sample is mounted in a cold-finger cryostat for low temperature measurements. Upon reflection from the sample, the box is reformed with the signal at the fourth corner of the square.

For time-integrated measurements, a high-frequency optical chopper is inserted into two of the excitation beams and the signal detected at the difference frequency by lock-in detection. Aligning for FWM measurements begins by sending the Reference/Tracer pulse to the sample. The Tracer is reflected from the sample along the fourth corner of the square. By aligning the Tracer with a slow photodetector placed in front of the entrance to the spectrometer, the Tr beam can then be blocked to find the FWM signal due to the three excitation pulses, since it follows the direction of the Tracer. All three excitation pulses must interact in the sample at precise times.
and all delay stages must be set so that this requirement is met.

Since the TFWM signal is dependent upon three incident pulses, a quick check can be done as follows to verify the level of detected signal: by blocking individual pulses, the signal amplitude on the lock-in amplifier should drop significantly unless there is some response from two pulses. The geometry of the setup allows individual delays to be adjusted and respective beams blocked to quickly and qualitatively view system responses such as transient grating signals and TFWM signals. In GaAs, the FWM signal is clear and strong. Peaks in the signal spectrum can be seen at heavy-hole (HH) and light-hole (LH) energies and aligned for the strongest signal. The TI-FWM signal is quite strong at zero-delay. Lock-in detection shows near perfect cancelation of the signal upon blocking one excitation beam, a good indication of strong FWM. In PbS quantum dots however, the signal is much broader spectrally and can closely resemble the laser spectrum. This makes alignment challenging in that it is difficult to differentiate between scattered laser light and FWM signal. Again, checking signal intensity by blocking individual beams reveals the true signal strength.

### 3.4 Fourier transform spectral interferometry

In 2D experiments, the FWM signal is heterodyne detected with the time-delayed Reference pulse for full retrieval of signal phase and amplitude information [52, 51, 50]. As discussed in Chapter 2, Eq. 2.4 shows that full amplitude and phase information can be obtained via spectral interferometry provided the Reference pulse is fully characterized. Spectral interferometry is often more practical than techniques such as time-domain heterodyne detection. The spectral interferogram of signal and Reference is recorded with a 0.75 m imaging spectrometer and thermoelectrically-cooled CCD detector. The CCD has a 2048 × 512 array of 13.5 μm pixels and a dynamic
range of 16 bits. All spectral intensities are set with Neutral Density filters to maximize the dynamic range of the detector. We also have the option of inserting a 50 mm lens in front of the entrance slit of the spectrometer to obtain stronger signal and better resolution. The FWM signal arrives after the time-delayed Reference by about 10 ps, whose delay is adjusted so that a spectral interferogram with dense fringes is resolved. The maximal fringe density is dependent upon the alignment of Reference and signal as well as their degree of collinearity, and by the spectral resolution, which in our case is as small as 0.04 nm.

The intensity of the spectral interferogram is related to Reference and signal by

$$|E(\omega_t) + E_0(\omega_t)|^2 = |E(\omega_t)|^2 + |E_0(\omega_t)|^2 + 2 \Re\{E(\omega_t)E_0^*(\omega_t)e^{i\omega_t\tau_0}\}.$$  \hspace{1cm} (3.1)

where $E(\omega_t)$ and $E_0(\omega_t)$ are the electric fields of signal and reference, respectively, and $\tau_0$ is the delay between the two. The power spectra of FWM and reference are the first two terms in Eq. 3.1, with an oscillatory term as the net interferometric term,

$$S(\omega_t) = 2 \Re\{E(\omega_t)E_0^*(\omega_t)e^{i\omega_t\tau_0}\}.$$  

Fig. 3.7 shows the spectra of FWM, REF and the spectral interferogram for GaAs multiple quantum wells that must be recorded just before beginning a 2D scan. The FWM signal is clearly discernible from the laser spectrum, producing a spectral interferogram with large fringes at HH and LH energies.
Figure 3.7: Typical spectra of (a) FWM, (b) REF and (c) SI for GaAs multiple quantum wells at 4.3 K. The spectral interferogram shows an inset of the fringe density at the HH wavelength.
3.5 Generating 2DFT spectra

Spectral interferograms are acquired at each delay $\tau$ over the duration of a 2D scan. A complete LabVIEW program was written to simplify and automate data collection during long scans. The algorithm for a basic 2D scan loop is illustrated in Fig. 3.8. A spectral interferogram of FWM signal and Reference is read from the spectrometer’s CCD detector with the electronic loop filters locked, next the appropriate loop filters are unlocked and the scanned stage is moved a distance equal to $N \times \lambda/4$, where $N$ is the undersampling ratio and $\lambda$ is the wavelength of the phase-stabilization laser (HeNe - 632.8 nm for all data in this thesis). Finally, the loops are locked for the next signal acquisition and this process is repeated until the end of the scan.

Figure 3.8: LabVIEW algorithm ensuring identical step size for 2D scans. For each step size, $\lambda$ is the wavelength of the laser used for phase-stabilizing the MONSTR (for HeNe, $\lambda = 632.8$ nm).
A typical step size is one half of a HeNe wavelength, corresponding to a 2× undersampling ratio, or 1.06 fs of time delay. Due to the long decoherence times in semiconductor nanostructures, a 2D scan without phase cycling can take up to ∼2 hours until completion and run through over 3500 steps, depending on the undersampling ratio and total scan length. The time required for long scans can be reduced by increasing the step size and therefore increasing the ratio of undersampling. For example, at 16× undersampling, 3553 steps of 8.44 fs each corresponds to a total scan of 29.98 ps with a spectral limit of 59.26 THz (Nyquist frequency) and an absorption frequency resolution \( \omega_{\tau} \) of 0.03 THz after Fourier transform.

It was observed that many 2D spectra show signs of phase ripple or skipping of HeNe fringes during the scan, so a few simple tests were performed to test accuracy of the stage motion as well as locking of the interference loops. One LabVIEW program was written to simply lock and unlock the loop filters many times to verify that the PZTs were unlocking at the same position within the MONSTR. By checking the offset on the oscilloscope during locking and unlocking, it became clear that the PZTs were not the cause of the inconsistent spectra. A second program was written to test translation stage motion. By scanning one fringe at a time and monitoring the offset on the scope, it was clear that the stages had lower position accuracy than expected. Some steps showed errors as great as 1/8 HeNe fringe. By reading the offset voltage after each HeNe fringe is scanned and calculating the resulting distance \( \delta \) to bring the offset back to zero, any number of fringes could be scanned during each step of a 2D scan without ever skipping a fringe.

\[
\delta = \arcsin \left( \frac{\epsilon}{2} \right) \frac{\lambda}{2\pi} \times \frac{1}{4},
\]

where \( \epsilon \) is the offset error voltage read from the Top Deck loop filter after each move. The value of \( \delta \) can be positive or negative, based on the gain sign chosen on the Top
Deck loop filter as well as the sign of the offset voltage after stepping.

The as-retrieved spectra ultimately form a 2D map of complex FWM electric field as a function of emission frequency, $\omega_t$ and delay $\tau$. By Fourier transforming with respect to $\tau$, we can plot the 2D spectrum as a function of emission frequency, $\omega_t$ and absorption frequency, $\omega_\tau$. Data analysis is performed in Matlab by loading all spectra into a matrix and performing all analysis including FFT operations, retrieval of FWM decay, phase information, projecting FWM intensity onto the absorption frequency axis and ultimately retrieving the 2D amplitude spectra as well as contour plots of real and imaginary parts of the complex 2D spectrum.

Figure 3.9: Front Panel view of the Maser Control Panel program used for automated data collection of 2DFT scans, including controls for spectrometer acquisition, loop filter locking/unlocking and translation stage motion.

All 2D scans can be run from a single master control panel, shown in Fig. 3.9. This program is capable of controlling all translation stages, detectors, feedback loops and spectrometer parameters within a single environment. The master control panel
can run rephasing, nonrephasing, two-quantum, and transient grating scans as well as perform simple linear spectroscopies. All translation stage move commands are performed within the while loop that corrects for offsets of each HeNe fringe and can scan any undersampling ratio of $2^n$ fringes per step without ever skipping a fringe.

3.5.1 All-optical retrieval of global phase

Ref. [85] explains in detail the methods for extracting the global phase in 2D spectra through an “all-optical” method. This allows separation of simple magnitude spectra into real and imaginary parts. In GaAs quantum wells, the real part of the collinearly polarized rephasing spectrum shows a dispersive (derivative of a peak) lineshape, owing to the many-body effects at play. Information on dispersive or absorptive lineshapes is just one of the benefits of separating complex spectra into real and imaginary parts. The method used here has significant benefits over comparison with a separate Spectrally-Resolved Transient Absorption (SRTA) measurement in that the “all-optical” retrieval can be used with cross-polarized excitation and low excitation density. SRTA is done with a two-beam pump-probe geometry that must closely mimic the excitation conditions of the 2D measurement, a requirement that can be difficult to fulfill.

The full phase of the third-order polarization is given by

$$\phi_{P(3)} = \phi_{SR} - \phi_{CAM} - \phi_{TR},$$

(3.3)

where $\phi_{SR}$ is the phase extracted from spectral interferogram of signal and REF, $\phi_{CAM}$ is the phase extracted from interference patterns at the replica focus, as in Fig. 3.4(a), and $\phi_{TR}$ is the modeled phase between tracer and REF which is also done through spectral interferometry. By integrating across the interference fringes from the CCD, the relative phase between Top Deck pulses and Bottom Deck pulses can
be easily measured. The global phase constant is applied in processing the 2DFT spectrum for extraction of real and imaginary parts of the complex 2DFT matrix.
Chapter 4

2DFT Spectroscopy of Semiconductor Quantum Dots

To accurately characterize the quality of 2D spectra acquired with this setup, a GaAs multiple-quantum-well (MQW) sample was investigated as a known reference. After making modifications to the LabVIEW code for highly accurate stage motion, data was collected on the MQW sample to reproduce previously published rephasing, non-rephasing and two-quantum 2DFT spectra. These spectra are discussed in section 4.1.

The first quantum dot sample investigated with this setup was a drop cast of 3 nm diameter PbS quantum dots from NREL. The dots are capped with an organic ligand for surface passivation and to prevent agglomeration of individual dots. Once we obtain several milligrams of dry sample, the dots are dispersed in an 8:1 ratio of hexane:octane, drop cast onto a glass substrate, dried and mounted in a continuous-flow cryostat. Though we were confident the sample had a small size distribution and gave very clean absorption spectra, with the 1s exciton absorption peak at 833 nm, the PbS quantum dots proved difficult to find clean FWM signals at either room temperature or low temperature. Samples are stored in solution in a nitrogen environment within a small acrylic glovebox. All drop casts are done within the nitrogen environment and quickly transferred to the cryostat for mounting. It was found that the proper ratio of hexane:octane yields smoother drop casts with greater
homogeneity upon drying. With the drop cast mounted and cryostat aligned, the
alignment into the MONSTR is performed and spatial pulse overlap on the sample
is imaged with a small CMOS camera. Once all excitation pulses are spatially and
temporally overlapped, the sample is cooled and four-wave mixing signal aligned for
lock-in detection.

Before beginning a scan, it must be verified within reason that the signal shown
on either the lock-in amplifier or the spectrometer that there exists some measurable FWM signal. This can be checked by blocking the Reference/Tracer beam and
monitoring the detected signal. By blocking individual excitation pulses, the lock-in
detected signal should drop to the background level since the FWM signal depends
on a three-pulse excitation. The FWM signal spectrum should also drop to the back-
ground level when blocking individual pulses. Spectrally, we can add the spectral
intensity due to each pulse, and the FWM signal spectrum resulting from three pulses
should be greater than the sum of individual pulses. Dephasing rate measurements
are discussed in Section 4.2. The difficulty in finding FWM from such small colloidal
QDs lies in the fact that the signals are weak, dirty, and spectrally look quite similar
to the laser spectrum. Unlike GaAs, which exhibits two distinct peaks for heavy-hole
and light-hole, PbS yields a much more inhomogenously-broadened spectral signature
that is difficult to separate from scattered light.

The quality of the 2D spectra depend on the quality of the heterodyned spectral
interferogram obtained before beginning a scan. This means that after the FWM
signal is maximized, the Reference must be realigned to be perfectly collinear with
the signal. When this criterion is met, large fringes can be observed in the spectrum.
The density of fringes is then set by delaying the Reference pulse so that Reference
arrives about 10 ps before the signal.

Lastly, the peizo in each interferometer must be dithered so that each loop can
be locked and unlocked throughout the scan without any instability. First, all trans-
lation stages are set to their starting positions to give the proper values of delay $\tau$ and $T$. All piezo drivers are set to dither around 75 volts and a sine wave is sent to each piezo so that the detected interference pattern from each deck gives a 4 volt sine wave on the oscilloscope. Each photodetector has adjustable gain settings and fine gain can be set on each electronic loop filter. Then, each deck is set to oscillate around zero to stabilize the locking by adjusting the offset on each loop filter. After removing the dither signal from the piezo driver, the output from each loop filter is fed back to its corresponding piezo driver, completing the feedback loop. The decks are dithered, then manually locked in the order Bottom deck, Top deck, Between deck, and External loop. The external loop is then unlocked in order to record spectra of FWM signal and Reference, separately. Once the External loop is again locked, a spectral interferogram is recorded and the scan is ready to begin.

Analysis of 2DFT spectra of PbS quantum dots will be discussed in this chapter, including dephasing time in section 4.2, measurement of homogenous and inhomogeneous broadening in section 4.3, and excitation-density dependence studies in section 4.4.

### 4.1 Preliminary spectra

To properly characterize the setup for 2DFT spectroscopy, a sample of GaAs MQWs was examined to identify and eliminate possible sources of phase drift and ripples in the 2DFT spectra. GaAs is the prototypical direct-gap semiconductors due to the well-established processes for growing high-quality heterostructures as well as having band gaps at near-infrared wavelengths. It is known that low-temperature absorption spectra exhibit peaks at the heavy-hole (HH) and light-hole (LH) transition energies, with the strengths of the peaks depending on where the excitation pulses are tuned. Fig. 4.1 shows preliminary spectra taken on GaAs MQWs at 4.3K by
the USF-MONSTR. Data was collected in the reflection geometry with all excitation pulses tuned to the HH with collinear polarization, 500 µW per pulse. It can be seen that clear peaks appear at the HH energy $\sim 1.55$ eV, slightly shifted from previously reported measurements possibly due to sample strain [83]. The $S_1(\omega_r, T, \omega_t)$ spectrum shows the absorption axis $\omega_r$ at negative energies due to the conjugation of the phase evolution between evolution and emission. Comparison of rephasing and nonrephasing spectra can reveal contributions of different coherent pathways and inhomogeneities in the system. Tuning excitation pulses between HH and LH shows a stronger LH peak, shifted by about 10 meV from the HH. In bulk GaAs, the valence band is degenerate but quantum confinement lifts this degeneracy.

Rephasing and nonrephasing spectra show little phase drift along the absorption energy axis, with very clean peaks along the diagonal at the HH energy. This confirms that our spectrometer calibration is good as well as the phase stability of the system. Two-quantum spectra were also obtained for GaAs and show clean peaks at twice the absorption energy shown in Fig. 4.1. It should be noted that 2D spectra are typically presented as real-part spectra as opposed to amplitude spectra in order to reveal absorptive or dispersive lineshapes. Real and imaginary 2DFT spectra are able to show underlying physical processes in semiconductors. The global phase for MQW measurements is not discussed here and it will be left to take the amplitude spectra qualitatively.
In addition to testing the setup to reproduce previously published 2DFT spectra of GaAs MQWs, we are able to retrieve the FWM decay as well as the ripped FWM phase from the same data set. Fig. 4.2 shows the decay of the retrieved FWM intensity as a function of the delay between pulses A* and B. Quantum beating is observed in the first few picoseconds and the signal dies down to the background level within
about 12 ps.

Figure 4.2: Integrated FWM intensity vs. delay $\tau$ showing beating between LH and HH states for the first 1.5 ps over a total decay time of about 5 ps.

Figure 4.3: (a) Retrieved (Red) FWM intensity and (b) Ripped phase across all signal frequencies, showing a flat phase through the full range of signal frequencies.
Fig. 4.3 shows the retrieved FWM signal with a strong peak at the frequency of the HH, where the excitation pulse was centered. The phase at the HH frequency shows a plateau corresponding to the phase $\phi_{SR}$ between signal and REF. It is this phase along with $\phi_{TR}$ and $\phi_{CAM}$ that is used to calculate the global phase. In order to get a flat phase across the proper frequency range, the proper time delay between signal and REF must be chosen in processing the data.

Moving on to the target of our investigation, absorbance measurements were performed on the drop cast colloidal PbS quantum dots so that all excitation pulses in 2DFT experiments could be tuned to the 1s exciton transition in the material. Absorbance is shown in Fig. 4.4 along with the excitation pulse, showing a laser bandwidth much narrower than the 1s absorbance. Therefore we are only exciting a fraction of the 1s absorbance band. The peak absorbance energy corresponds to a peak wavelength of 833 nm ($d = 3$ nm [8]). It should also be noted that the temperature-dependence of the gap was investigated and showed that there is a small but negligible blue-shift with decreasing temperature, therefore the excitation laser does not need to be tuned for temperature-dependent 2D scans.

Figure 4.4: 1s exciton absorbance in PbS quantum dots with excitation laser spectrum superimposed.
4.2 Dephasing rate measurements

The dephasing rate, inversely proportional to the homogeneous linewidth FWHM \( = 2\hbar/T_2 \), has been measured and calculated in PbS and PbSe quantum dots in the past, with several mechanisms proposed to explain the ultrafast dephasing. Kamisaka et al. calculated room temperature dephasing times of sub-10 fs between several different excited states and in two different sizes of small PbSe clusters [86]. This offers a lower limit on lead-chalcogenide dephasing, as dephasing is known to slow down in larger samples. It was also shown that biexcitonic dephasing occurs at nearly twice the rate of single excitons, similar to what has been observed in quantum wells. Single-dot spectroscopy is capable of isolating intrinsic linewidth separated from ensemble broadening but suffers from high detector noise in the infrared and spectral diffusion limits linewidth resolution. Single-dot studies have found linewidths of 100 ±30 meV at 300 K, suggesting sub-100 fs dephasing in PbS [87]. In contrast, the zero-phonon line (ZPL) width in CdSe and InGaAs epitaxial dots is in the low \( \mu \)eV range at 5 K. All of these studies of homogeneous linewidth and excitonic dephasing in PbS quantum dots therefore suffer from experimental difficulties and few experiments are able to detect and isolate pure dephasing of excitons.

Recently, heterodyne-detected FWM experiments measured temperature and size-dependent sub-ps decays from FWM intensity plots [88]. Similar to the work done here, these measurements used TI-FWM, whose time scale is insensitive to spectral diffusion, but with the addition of heterodyne-detection to magnify the weak FWM signals generated in small PbS dots. Fig. 4.5 shows TI-FWM measurements at 4.5 K at 833 nm excitation for two different values of delay \( T \). With the FWM intensity plotted on a log scale, the exponential fit in each case gives a dephasing time \( \gamma \approx 300 \) fs. Increasing delay \( T \) does not change the observed dephasing, but undesirable coherent interactions at temporal overlap can occur. Although this data is quite noisy, it is similar to what has been observed in similar sizes of PbS QDs.
Figure 4.5: Measured Time-Integrated FWM decay of PbS quantum dots (d = 3 nm) (a) Taken with T=0 fs and (b) T=200 fs. Exponential fits are included to show beating in the FWM signal on top of an exponential decay. The fit corresponds to a dephasing time of about 300 fs in both cases.

Unlike in [88], we observe beating superimposed on the FWM decay with beat period of about 80 fs, corresponding to an energy splitting $\Delta E = 52$ meV. It is known that exchange splitting and intervalley scattering can split the ground state exciton in lead-chalcogenides but it is unclear as to the cause of the beating observed here.

The measured ultrafast dephasing in PbS can be attributed to coupling with acoustic phonons. Overlapping electron and hole wavefunctions due to strong confinement in the lead-chalcogenides have contributions from four $L$ valleys as well as phonons at $X$-points, with large phonon density of states at the $X$-points. With respect to the phonon dispersion curve in PbS, the excitation pulse width is quite
broad spectrally and can excite multiple phonon modes simultaneously. The measured dephasing would have contributions from several acoustic and optical phonon branches.

4.3 Determination of homogenous and inhomogeneous linewidths

Previous linewidth studies of strongly-confined nanocrystals have measured ultrafast dephasing times from the homogeneous linewidth. However, only sensitive four-wave mixing experiments are capable of isolating pure-dephasing from effects such as spectral diffusion and other linewidth broadening mechanisms. Bulk semiconductors as well as two-dimensional epitaxial materials are much easier to work with than colloidal nanocrystals due to the surrounding environment, which can degrade FWM signals in many cases. This is not surprising because of the fact that GaAs is a crystalline sample grown by MBE, while our quantum dots are grown in solution by colloidal chemistry methods and are inherently a more dirty material when looking at sensitive, coherent FWM signals. The measured dephasing of 300 fs from TI-FWM measurements suggests a homogeneous linewidth of $\sim 4$ meV, similar to what we have observed in rephasing scans. Inhomogeneous linewidths are expected to be significantly broader in colloidal samples such as these. The inhomogeneous linewidth along the diagonal of a 2DFT spectrum corresponds to the laser pulse width. Sources of inhomogeneous broadening are large size and shape distribution as well as intrinsic inhomogeneous broadening that couples to the intrinsic homogeneous broadening. Intrinsic inhomogeneous broadening within each dot could result from fluctuations in the atomic structure in these materials. The nature of this coupling was discussed recently and in section 2.3.3 [71].
4.4 Excitation-density dependence

Due to the quality of signals generated in colloidal quantum dot materials, it is sometimes beneficial to use relatively higher pulse powers during alignment. However, higher excitation density can sometimes lead to excitation-induced effects such as sample heating or degradation, higher-order nonlinear effects and additional linewidth broadening. Fig. 4.6 shows rephasing spectra in PbS QDs for excitation pulse powers of 1 mW, 50µW, and 10 µW. It can be seen that for powers as low as 10 µW/pulse, the signal is clearly resolved with little additional phase ripple and no power-dependence of the linewidth at such low excitation power. Real and imaginary-part spectra are also shown with emissive peak and dispersive peak, respectively. Future linewidth analysis must be done to extract the true homogeneous linewidth in PbS quantum dots at low temperature. It is clear from Fig. 4.6 that pulse powers of ∼1 mW are reasonable and do not cause additional excitation-induced effects on the observed linewidth.
Figure 4.6: Rephasing spectra with amplitude (A), real (R) and imaginary (I) parts for (a) 1 mW/pulse (b) 50 µW/pulse (c) 10 µW/pulse.
Chapter 5

Summary and Outlook

In summary, we have replicated and improved upon a previously demonstrated 2DFT spectroscopy setup built around a compact set of nested and folded interferometers that we are calling the USF-MONSTR. Significant improvements have been made to everything from broadband beamsplitters to further stabilizing the HeNe and MONSTR electrically and mechanically to testing, improving and simplifying the scanning procedure and LabVIEW automation. In addition, we have setup a 488 nm single-frequency laser for locking the MONSTR for excitation at visible wavelengths. This is an exciting addition that has not yet been put into practice and is one-of-a-kind in 2DFT spectroscopy. This setup is fully capable of phase-sensitive detection of weak FWM signals of small diameter PbS quantum dots.

Preliminary data collection in the reflection geometry has replicated previously published 2DFT spectra of GaAs quantum wells with minimal phase ripple. In small PbS quantum dots, ultrafast dephasing times of $\sim 300$ fs have been measured by TI-FWM. By explicitly tracking the phase of the signal and all excitation pulses, 2D spectra are produced after Fourier transformation, which are separated into real and imaginary parts after finding the global phase. Amplitude spectra in PbS dots show an inhomogeneously broadened peak along the diagonal with a cross-diagonal linewidth...
of several meV, resulting in much faster dephasing than the µeV linewidths of CdSe or InGaAs quantum dots. Also, real part spectra show a consistently emissive peak while the imaginary spectra are dispersive with as little as 10 µW/pulse excitation power.

Future directions for this work are vast due to the extreme flexibility of the USF-MONSTR. It may be of interest to further study temperature and size-dependence in the linewidth of 3 nm PbS QDs as well as two-quantum signals. The group plans to look at 2D spectra of various sizes of PbS and PbSe quantum dots to investigate confinement effects of electron-phonon coupling and homogeneous/inhomogeneous linewidths in various nanostructured materials. 2DFT spectroscopy in the VIS regime can be done with core-shell CdSe-ZnSe quantum dots with a 488 nm sapphire laser for locking the MONSTR. The versatility of the experimental setup means that by simply exchanging samples mounted in the cryostat, we are able to align the pump beam into the MONSTR and collinearity of signal and REF pulse to run any variety of 2D scans in a 24 hour period.

Furthermore, the observation of “high-temperature” superconductivity was reported several years ago in compounds of iron-pnictide superconductors. The MONSTR is now being used to investigate spin diffusion in electron and hole-doped versions of these materials, specifically $BaFe_{1.84}Co_{0.16}As_2$ and $(BaK)Fe_2As_2$ with transition temperatures $T_c = 30-35$ K. These investigations hope to reveal diffusion lengths by performing transient grating measurements and reveal information about the ferromagnetic/antiferromagnetic properties of these unique superconductor compounds. The group also obtained samples of the more well-understood copper-oxides $YBa_2Cu_3O_7$ (YBCO) and $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ (BSCCO).
Bibliography


