Simulation of Propagation-Distorted 2DFT Spectra of Dense Rubidium Vapor and Pump-Probe Spectroscopy of Carrier Dynamics in Colloidal Indium Arsenide Quantum Dots

by

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Two-dimensional Fourier-transform (2DFT) spectra of the D\textsubscript{2} line of rubidium vapor in argon buffer gas are simulated using a three-dimensional frequency domain solution of Maxwell’s equations that treats linear propagation distortions exactly. Simulations for the homogeneous optical Bloch model at optical densities of up to 3 are compared to measured rephasing 2DFT spectra. Experimentally observed propagation distortions are qualitatively reproduced in calculated 2DFT spectra, including peak broadening, peak splitting, and peak twisting. Varying beam overlap through the sample is crudely modeled in simulations, demonstrating that reduced beam overlap causes narrowing of the peak shape in the excitation dimension and an overall reduction in signal size. Propagation distortions, including peak splitting depth and peak twist, are found to vary with waiting time and with the excited state lifetime at a fixed total dephasing time, suggesting a coherent mechanism.

A new method for reducing repetitive excitation of the sample by scanning beams with respect to a stationary sample cell using a fast steering mirror is described. This apparatus extends the average time between excitations at any point in the sample to >0.3 s and accommodates a wide variety of sample cell formats, including cryostats, air-tight cuvettes, and flow cells.

Colloidal indium arsenide (InAs) quantum dots (QDs) are interrogated by degenerate pump-probe transient absorption spectroscopy at a photon energy of approximately 1.5 times the band gap using spatially-averaged excitation probabilities lower than in previously reported studies. Signatures of Auger recombination appear with a timescale of 26 ± 5 ps. Carrier cooling and recombination pathways are explored, revealing new dynamics not observed in studies that probe the band edge.
Dedication

For my grandfather, whose great strength has always inspired me to be strong.
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Chapter 1

Introduction

1.1 Two-Dimensional Fourier-transform Spectroscopy

Two-dimensional Fourier-transform (2DFT) spectroscopy is a powerful nonlinear optical technique for studying peak shapes,\(^1\) intra- and inter-molecular coupling,\(^2,3\) excited state relaxation, and coherent dynamics.\(^3\) This technique uses a series of light pulses to excite a material, correlating the initial excitation frequency and the subsequent detection frequency.

An instructive analogy can be made between 2DFT spectroscopy and frequency domain double-resonance spectroscopy.\(^4\) In frequency domain double-resonance, two tunable, narrow-band light sources are incident on the sample, one being the “excitation beam” and the other the “detection beam.” The signal is detected as the change in transmittance of the detection beam at its frequency \(\omega_{\text{det}}\) due to excitation by the excitation beam at its frequency \(\omega_{\text{exc}}\). For two homogeneous two-level systems with different transition frequencies \(\omega_{eg}^a\) and \(\omega_{eg}^b\), positive “diagonal” peaks would be expected at \((\omega_{\text{exc}} = \omega_{eg}^a, \omega_{\text{det}} = \omega_{eg}^a)\) and \((\omega_{\text{exc}} = \omega_{eg}^b, \omega_{\text{det}} = \omega_{eg}^b)\) due to bleaching of the transitions by the excitation beam. If these two-level system are not coupled (e.g. transitions on different molecules), only the diagonal peaks will be present. However, if they are coupled (e.g. transitions from a common ground state on the same molecule), then additional “cross peaks” will appear at \((\omega_{\text{exc}} = \omega_{eg}^b, \omega_{\text{det}} = \omega_{eg}^a)\) and \((\omega_{\text{exc}} = \omega_{eg}^a, \omega_{\text{det}} = \omega_{eg}^b)\). A cross peak at \((\omega_{\text{exc}} = \omega_{eg}^a, \omega_{\text{det}} = \omega_{eg}^b)\) indicates that excitation at \(\omega_{eg}^a\) changes the absorption at \(\omega_{eg}^b\). The simplest mechanism for such a cross peak is reduction in absorption of the detection beam through depletion of a common ground state by the excitation beam. The cross peaks will not appear if the lost ground state absorption
is cancelled by new excited state absorption with exactly the same frequency, strength, lifetime, lineshape, and polarization. A change in any of these for one transition after excitation of another transition is indicative of coupling.

Instead of using monochromatic light and scanning through frequencies one at a time, a 2DFT spectroscopy experiment uses a series of three short pulses to simultaneously excite a range of frequencies in the sample which, in response, radiates a nonlinear signal. The first pulse sets in motion an oscillatory quantum wavepacket that has a dipole moment that oscillates at the resonant transition frequencies of the sample. After a time $\tau$ later, the second pulse excites additional wavepacket motion that either interferes constructively (if in phase) or destructively (if out of phase) with the initially excited oscillating wavepacket. At each point in the sample, this results in populations of excited state and ground state molecules that are modulated as a function of the delay $\tau$. This transfer of population causes transient changes in the absorption spectrum and refractive index of the sample. The third pulse arrives a time $T$ after the second. The third pulse excites molecular wavepackets that are modified by the first two pulses. Their oscillating dipole moments give rise to an oscillating macroscopic electric polarization which naturally radiates the signal field. Interference detection of the signal in a single phase-matched direction (determined by the geometry of the three excitation beams) yields the full electric field (spectrum and phase) of the signal. In practice, this detection usually uses spectral interferometry to measure the field in the frequency domain as a function of $\omega_t$. $\omega_t$ is the Fourier conjugate of $t$, the time since the third pulse. At a single waiting time $T$, spectral interferograms at a series of delays $\tau$ are aggregated to form a two-dimensional data set of field as a function of frequency and delay $\tau$. Taking the complex Fourier transform of the data along the $\tau$ axis yields the complex-valued 2DFT spectrum as a function of $\omega_\tau$, $T$, and $\omega_t$.

The 2DFT spectrum contains information beyond that of the double-resonance 2D spectrum. While the double-resonance spectrum is purely real, the 2DFT spectrum is complex-valued and thus includes both absorptive (real) and dispersive (imaginary) signals. The time domain approach used in 2DFT spectroscopy affords two additional advantages. First, the $T$ dimension includes
population relaxation dynamics with a time resolution that is not limited by the frequency resolution of the other two signal dimensions ($\omega_\tau$ and $\omega_t$). Second, through impulsive, coherent excitation of the sample, coupling to nearby electronic transitions and to vibrations appears as coherent beating of peaks as a function of $T$ in a series of 2DFT spectra.

These simple pictures of 2DFT spectroscopy, although valid for optically thin samples, must be augmented in order to treat realistic experimental conditions including finite optical density, path length, and crossing angles. In optically thick samples, for which the 2DFT signal strength is maximized, 2DFT spectra suffer from absorptive and dispersive distortions due to severe reshaping of the excitation pulses and the signal by the sample; these are known as propagation distortions.

1.2 Illustration of Linear Pulse Propagation Distortions

A simple way to understand distortions of light fields when propagating through an absorptive and/or dispersive medium is through the linear free-induction decay (FID) radiated in response to weak optical excitation. The simplest frequency domain picture of absorption, where photons are instantaneously removed from an incident field as it passes through an absorbing medium, fails to capture the accompanying refractive effects. The complementary time domain picture involving FID captures both linear absorption and refraction in a single perspective and is very instructive in the context of coherent time domain nonlinear spectroscopy.

In this picture, one can imagine a pulse of light propagating through a polarizable medium. In response to the optical electric field, the medium is polarized as electrons are pushed to and fro. If the light is resonant with an electronic transition, these oscillations will build up while the incident field is present and will have a phase shift of $90^\circ$ compared to the driving field, as exemplified by the classical, resonantly-driven harmonic oscillator. For weak fields, the amplitude and phase of the quantum mechanical oscillations generally have the frequency dependence found for a classical driven oscillator. The oscillating polarization within the sample will in turn radiate at all driven frequencies. Resonant or not, the radiated field will have a phase shift of $90^\circ$ compared to the polarization. At resonance, the result is a full $180^\circ$ phase shift with respect to the incident field,
causing destructive interference between the incident and radiated fields; the resulting depletion of the intensity constitutes absorption. Refractive effects arise from the components of the electric polarization that are in phase (far below resonance) or $\pi$ out of phase (far above resonance) with the driving electric field.

Compared to calculations of linear propagation of light in the time domain, which require a convolution of the distorted field at each point in space with the response of the medium to obtain the polarization at that point in space, which radiates to further distort the field, the equivalent frequency domain calculations involve simple multiplication of the electric field by one exponential propagation factor at each frequency to propagate across the entire sample. A time domain calculation in the frequency domain begins by inverse Fourier transformation of the time domain field to obtain

$$\hat{E}(\omega, z) = \int_{-\infty}^{\infty} E(t, z) \exp(i\omega t) \, dt$$

(1.1)

where $\hat{E}(\omega, z)$ is the complex-valued frequency domain electric field. In the frequency domain, plane waves propagating along $z$ are transformed as they propagate according to

$$\hat{E}(\omega, z) = \hat{E}(\omega, z = 0) \exp \left[ i\hat{k}(\omega) z \right]$$

(1.2)

where $\hat{k}(\omega)$ is the complex-valued wavevector. Throughout this chapter, complex-valued quantities are marked with a circumflex (or “hat”). $\hat{k}$ is related to the complex-valued refractive index $\hat{n}$ by

$$\hat{k}(\omega) = \omega\hat{n}(\omega)/c$$

(1.3)

where $c$ is the speed of light in vacuum. This method of light propagation assumes a linear response, in which case each frequency in the time domain field can be propagated independently. After such straightforward linear propagation of the input field at the sample entrance $\hat{E}(\omega, z = 0)$ to the transmitted field at the sample exit $\hat{E}(\omega, z = L)$, the frequency domain transmitted field is Fourier transformed back into the time domain

$$E(t, z = L) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{E}(\omega, z = L) \exp (-i\omega t) \, d\omega.$$

(1.4)
This field emerges from the sample at least $L/c$ later in time and is distorted by both refraction and absorption incorporated through the real and imaginary parts of the complex-valued refractive index.

It is preferable to visualize the field radiated by the sample (the FID) and to do so in a frame of reference that travels with the undistorted excitation pulse. To calculate the FID radiated by a sample, the frequency domain electric field at the sample entrance $\hat{E}(\omega, z = 0)$ is propagated to the sample exit ($z = L$) using eq. 1.2. In addition, a reference field $E_{\text{vac}}$ is propagated through vacuum to the sample exit using $k(\omega) = \omega n_{\text{vac}}/c = \omega/c$. The radiated FID can be calculated from eq. 1.2 using

$$\hat{E}_{\text{FID}}(\omega, z = L) = \hat{E}(\omega, z = L) - \hat{E}_{\text{vac}}(\omega, z = L)$$

(1.5)

where $\hat{E}_{\text{vac}}(\omega, z = L)$ is the electric field transmitted through length $L$ of vacuum, $\hat{E}(\omega, z = L)$ is the transmitted electric field at the sample exit, and $L$ is the optical path length through the sample. $\hat{E}_{\text{vac}}(\omega, z = L)$ is what the transmitted field would be if the medium were replaced with vacuum and serves as a reference field to isolate the effect of the medium on light propagation. Equation 1.5 shows that the transmitted field at the sample exit is the sum of the FID and the field that would be transmitted through vacuum. (For solutes in solutions, the reference field for the FID can be the field that would be transmitted through the neat solvent, but this reference is not guaranteed to generate a causal FID.) Using eq. 1.2, we can rewrite eq. 1.5 (with the phase relative to the vacuum field removed)

$$\hat{E}_{\text{FID}}(\omega, z = L) = \left[ \hat{E}(\omega, z = L) - \hat{E}_{\text{vac}}(\omega, z = L) \right] \exp (-i\omega L/c)$$

(1.6)

I now introduce simple examples to illustrate the linear FID in eq. 1.6. For a Gaussian pulse, the time domain electric field (at a single point in space chosen to be the sample entrance at $z = 0$) can be expressed as

$$E(t) = E_0 e_G(t) \cos (\omega_0 t)$$

(1.7)

with a Gaussian temporal envelope $e_G(t) = \exp \left[ -2\ln(2)(t/\tau_p)^2 \right]$ where $\tau_p$ is the FWHM intensity
pulse duration, \( \omega_0 \) is the central frequency of the pulse, and \( E_0 \) is the pulse’s electric field at \( t = 0 \). Taking the inverse Fourier transform of the time domain electric field in eq. 1.7 yields the frequency domain electric field at the sample entrance,

\[
\hat{E}(\omega, z = 0) = \frac{1}{2} E_0 e_G(\omega - \omega_0) + \frac{1}{2} E_0 e_G(\omega + \omega_0),
\]

(1.8)

where

\[
e_G(\omega) = \frac{\sqrt{2\pi}}{\Delta} \exp \left( -\frac{\omega^2}{2\Delta^2} \right)
\]

(1.9)

is the inverse Fourier transform of \( e_G(t) \) and \( \Delta = 2\sqrt{\ln 2}/\tau_p \) is the spectral bandwidth of the pulse.

In the Lorentz model\(^5\) for the radiation from an exponentially damped oscillating dipole with (undamped) oscillation frequency \( \omega_{jk} \), the complex refractive index is given by

\[
\hat{n}(\omega) = 1 + \frac{N f_{jk} e^2}{2\epsilon_0 m_e} \left[ \frac{1}{\omega_{jk}^2 - \omega^2 - 2\mathrm{i}\Gamma_{jk}\omega} \right]
\]

(1.10)

where \( f_{jk} \) is the transition oscillator strength, \( \Gamma_{jk} \) is the exponential rate of decay for dipole oscillations, \( N \) is the number density of atoms, \( e \) is the electron charge, \( \epsilon_0 \) is the permittivity of vacuum, and \( m_e \) is the electron mass. The time domain envelope of dipole oscillations decays as \( \exp(-t/\tau_{jk}) \) where \( \tau_{jk} = 1/\Gamma_{jk} \) is the polarization relaxation time.

The complex refractive index contains peaks near \( \omega = \omega_{jk} \) and \( \omega = -\omega_{jk} \), which becomes clear once eq. 1.10 is rearranged to

\[
\hat{n}(\omega) = 1 + \frac{N f_{jk} e^2}{2\epsilon_0 m_e} \left[ \frac{1}{2\omega_{eg}} \left( \frac{1}{\omega + \omega_{eg} + \mathrm{i}\Gamma_{jk}} - \frac{1}{\omega - \omega_{eg} + \mathrm{i}\Gamma_{jk}} \right) \right]
\]

(1.11)

where \( \omega_{eg} = \sqrt{\omega_{jk}^2 - \Gamma_{jk}^2} \) is red-shifted from \( \omega_{jk} \) by damping. In terms of the absorptive (imaginary) part of the complex refractive index \( (\kappa) \), eq. 1.11 can be expressed as

\[
\hat{n}(\omega) = 1 + i\kappa(\omega_{eg}) \pi \Gamma_{jk} [\hat{g}(\omega - \omega_{eg}) - \hat{g}(\omega + \omega_{eg})]
\]

(1.12)

where

\[
\kappa(\omega_{eg}) = \frac{N f_{jk} e^2}{4\epsilon_0 m_e \omega_{eg} \Gamma_{jk}}.
\]

(1.13)
\( \hat{g} \) is the complex Lorentzian lineshape function given by

\[
\hat{g}(\omega) = \frac{1}{\pi} \frac{i}{\omega + i\Gamma_{jk}} = \frac{1}{\pi} \frac{\Gamma_{jk} + i\omega}{\Gamma_{jk}^2 + \omega^2}
\]

(1.14)

which obeys the symmetry relation \( \hat{g}(\omega) = \hat{g}^*( -\omega ) \). The complex lineshape function in eq. 1.14 is defined so that its absorptive part is area-normalized, i.e. \( \int_{-\infty}^{\infty} \text{Re} [\hat{g}(\omega)] \, d\omega = 1 \).

Since field oscillations are rapid and obscure phase information, I have chosen to show only the field envelope when illustrating pulse propagation in the time domain. Appendix A shows that for narrow-band pulses (\( \Delta \ll \omega_0 \)) tuned (\( \omega_0 = \omega_{eg} \)) to a narrow resonance (\( \Gamma_{jk} \ll \omega_{eg} \)), the time domain FID is given by

\[
E_{\text{FID}}(t, z = L) = E_0 e_{\text{FID}}(t, z = L) \cos(\omega_{eg}t)
\]

(1.15)

where the FID envelope \( e_{\text{FID}}(t, z = L) \) is the Fourier transform of the demodulated frequency domain FID

\[
e_{\text{FID}}(t, z = L) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{e}_{\text{FID}}(\omega, z = L) \exp[-i\omega t] \, d\omega
\]

(1.16)

with

\[
\hat{e}_{\text{FID}}(\omega, z = L) = e_G(\omega) \exp[-\omega_{eg}\kappa(\omega_{eg})\pi \Gamma_{jk}\hat{g}(\omega)L/c]
\]

(1.17)

This is a remarkably simple result that reveals several complicated aspects of linear pulse propagation.

To connect the amplitude of pulse attenuation and dispersion in eq. 1.2 to experiment, \( \kappa(\omega) \) can be formulated in terms of the sample absorbance \( A(\omega) \) (also known as optical density). The sample transmittance can be written as

\[
T(\omega) = 10^{-A(\omega)} = \exp[-2\omega\kappa(\omega)L/c]
\]

(1.18)

where the factor of 2 in the exponential accounts for the quadratic relationship between intensity and field. Solving for \( \kappa(\omega) \) yields

\[
\kappa(\omega) = \frac{c \ln 10}{2\omega L} A(\omega)
\]

(1.19)
where $L$ is the sample path length. Equation 1.19, evaluated at $\omega = \omega_{eg}$, provides the experimental value of $\omega_{eg} \kappa(\omega_{eg})$ needed in the prior equations. Within the rotating wave approximation, the absolute frequency $\omega_{eg}$ has no influence on the calculation once the optical density is specified.

The examples of pulse propagation illustrated in Figures 1.1–1.5 were calculated using eqs. 1.2–1.19. The time domain plots show the time domain incident field envelope $e_G(t)$, transmitted field envelope, and FID envelope $e_{\text{FID}}(t)$. The frequency domain plots show the electric field peak centered at $\omega = \omega_{eg}$.

For pulses of light long in duration compared to the polarization relaxation time of the medium, as in Figure 1.1, the radiated light from the FID appears nearly coincident with the pulse, rising and decaying in amplitude within the time domain envelope of the pulse. There is only a slight time delay in the peak of the FID envelope compared to the incident field due to the finite time necessary to build up the oscillating polarization in the medium. This delay in the FID envelope causes the later portions of the pulse to be attenuated more heavily than the early portions. An interesting consequence is that for the example in Figure 1.1, the peak of the transmitted light emerges from the sample before the peak of the field transmitted through vacuum. Because the transmitted field is less than the field that would be transmitted through vacuum at every instant in time, this does not violate causality nor does it imply faster-than-light transmission.
Figure 1.1: The electric field envelope in the time domain (top) and the frequency domain (bottom) for a 150 fs intensity FWHM Gaussian pulse propagating through a resonant medium with an exponential polarization relaxation time of 15 fs and a peak optical density of 1. The central frequency of the pulse is equal to the resonant frequency of the sample: $\omega_0 = \omega_{eg}$. The sum of the field transmitted through vacuum and the radiated FID field yields the transmitted field. The “argument” function, signified by $\arg$, returns the phase angle of a complex number. For a complex number $z = re^{i\phi}$, $\arg(z) = \phi$ and $|z| = r$ where $\phi$ and $r$ are real-valued.
In the case of a pulse of light with a short duration compared to the induced polarization decay in the medium, as in Figures 1.2 and 1.3, the radiated FID envelope rises during the incident pulse and trails long afterward. The FID rise takes on an integral-like relationship to the incident pulse, rising fastest near the peak of the incident pulse and reaching its maximum amplitude at the end of the pulse. With the majority of the FID radiation coming after the pulse, the incident field does not seem to be attenuated at all in the time domain picture. However even in this situation, dispersing the pulse in a spectrometer to measure its spectrum will stretch the pulse in time such that the trailing FID destructively interferes with the main pulse in a narrow frequency range. This explains why even ultra-short femtosecond pulses exhibit the narrow absorption lineshapes expected based on the frequency domain view.

In the low optical density limit, the FID radiation decays exponentially on the time scale of the polarization relaxation time $\tau_{jk}$. However by an optical density of 1 (Figure 1.2), the FID begins to show signs of distortion, decaying faster than $\tau_{jk}$. At an optical density of 3 (Figure 1.3), the FID clearly decays much faster than the polarization relaxation time and even crosses through zero near $t = 17$ ps, a sign of ringing.
Figure 1.2: The electric field envelope in the time domain (top) and the frequency domain (bottom) for a 150 fs intensity FWHM Gaussian pulse propagating through a resonant medium with an exponential polarization relaxation time of 15 ps and a peak optical density of 1. The central frequency of the pulse is equal to the resonant frequency of the sample: $\omega_0 = \omega_{eg}$. The sum of the field transmitted through vacuum and the radiated FID field yields the transmitted field. The FID envelope has been multiplied by a factor of 10. The “argument” function, signified by arg, returns the phase angle of a complex number. For a complex number $z = re^{i\phi}$, arg($z$) = $\phi$ and $|z| = r$ where $\phi$ and $r$ are real-valued.
Figure 1.3: The electric field envelope in the time domain (top) and the frequency domain (bottom) for a 150 fs intensity FWHM Gaussian pulse propagating through a resonant medium with an exponential polarization relaxation time of 15 ps and a peak optical density of 3. The central frequency of the pulse is equal to the resonant frequency of the sample: $\omega_0 = \omega_{eg}$. The sum of the field transmitted through vacuum and the radiated FID field yields the transmitted field. The FID envelope has been multiplied by a factor of 10. The “argument” function, signified by arg, returns the phase angle of a complex number. For a complex number $z = re^{i\phi}$, $\text{arg}(z) = \phi$ and $|z| = r$ where $\phi$ and $r$ are real-valued.
In general, absorbance (or optical density) is a logarithmic function of transmittance: \( A = -\log_{10} T \). However at low optical density, the first order term of the Taylor series expansion around \( T = 1 \) suffices, yielding \( A \approx \ln(10)(1 - T) \), which is a reasonable approximation for \( T > 0.9 \). The breakdown of this low optical density approximation is shown in Figures 1.4 and 1.5, where the spectral lineshape imprinted into the pulse through absorption becomes distorted as the sample optical density increase from 1 to 10. At an optical density of 10, the absorbed region is noticeably broader and frequencies near the center of the resonance are almost entirely attenuated, leaving a nearly flat region in the transmitted pulse spectrum. When the transmitted pulse with \( \text{OD}_{\text{max}} = 10 \) is Fourier-transformed into the time domain, the sharply rising edges of the flat region in the pulse spectrum result in ringing of the FID envelope, which crosses through zero several times. This change in sign of the envelope represents a \( \pi \) change in the phase of the cosinusoidal field oscillations. Since at higher optical density the absorbed region of the pulse is broader in frequency, the FID envelope decays more quickly in the time domain with increasing optical density. Positive regions in the FID envelope represent light radiated by oscillating dipoles which were themselves excited by light radiated by dipoles previously excited by the incident electric field. Each successive excitation–radiation cycle adds a 180° phase shift with respect to the incident light. Therefore, after two cycles, the resonantly radiated light has accumulated 360° of phase and interferes constructively with the incident light.
Figure 1.4: The transmitted frequency domain envelope for a 150 fs intensity FWHM Gaussian pulse that has propagated through a resonant medium with an exponential polarization relaxation time of 15 ps at a range of optical densities. The central frequency of the pulse is equal to the resonant frequency of the sample: \( \omega_0 = \omega_{eg} \).
Figure 1.5: The time domain free-induction decay (top) and transmitted frequency domain envelope (bottom) for a 150 fs intensity FWHM Gaussian pulse that has propagated through a resonant medium with an exponential polarization relaxation time of 15 ps at a range of peak optical densities. The central frequency of the pulse is equal to the resonant frequency of the sample: $\omega_0 = \omega_{eg}$. 
In 2DFT spectra, pulse propagation effects are imprinted onto the signal through absorptive and dispersive interactions between the excitation and signal fields and the sample. As shown in Figure 1.6, propagation distortions broaden the experimental 2D peak shape and cause splitting of the peak as optical density increases due to strong attenuation of the signal field near the transition frequency. Propagation distortions are inherently three-dimensional (functions of $\omega_r$, $T$, and $\omega_t$) and exhibit complex features which obscure the underlying microscopic dynamics of the sample. For this reason, it is advantageous to computationally model propagation distortions to aid the interpretation of 2DFT spectra from optically thick samples.

An exact treatment of linear propagation distortions in 2DFT spectra has been derived in the form of a three-dimensional frequency domain solution to Maxwell’s equations.\(^7\) Just as the above calculations of the free-induction decay take advantage of frequency domain multiplication to simplify the time domain convolution in pulse propagation, the 3DFT algorithm of Belabas and Jonas applies propagation distortions to the 3D signal in the frequency domain through simple multiplication by a 3D propagation function. This method treats the full 3D nature of propagation distortions, which is particularly important at high optical density and short waiting times where propagation distortions exhibit coherent effects.
Figure 1.6: Experimental absolute value rephasing 2DFT spectra of Rb vapor in ∼2 atm of argon buffer gas measured\(^6\) at a waiting time of \(T = 200\) fs with a 150 fs pulse duration. The sample optical density is varied between 0.14 and 1.14 based on the temperature of a reservoir of liquid Rb.

1.3 Simulated Absorption Spectrum of Rubidium in Argon

Electronic transitions in atomic vapors have been studied extensively using high-resolution frequency domain spectroscopy. Lineshapes in high-resolution spectra contain information about time domain dynamics and can be a starting point for choosing and evaluating models for peak shapes in 2DFT spectra. Typically, atomic lines contain broadening from multiple sources such as Doppler motion, collisions, and the radiative lifetime. By studying lineshape broadening as a function of various experimental parameters (such as temperature, vapor density, buffer gas pressure, etc.) the effect of broadening processes can be separated and quantified.

For alkali metal vapor with a high pressure of buffer gas, as in ref. 6, non-resonant alkali atom–buffer gas collisions dominate the lineshape. Using the mean time between (\(\bar{\tau}\)) and duration of (\(\tau_c\)) atom–buffer gas collision as parameters, a simple model can be used to describe a collisionally broadened lineshape. When the time interval between collisions is much longer than their duration, collisions can be treated as independent, uncorrelated events. This is known as the “impact approximation.” Under this approximation, the collisional linewidth

\[
2\Gamma_{\text{col}} = N\pi r_{\text{col}}^2 v \approx (\bar{\tau})^{-1}
\]

is proportional to the rate of collisions. In eq. 1.20, \(\Gamma_{\text{col}}\) is the half-width at half-maximum (HWHM) collisional linewidth, \(N\) is the number density of buffer gas molecules, \(r_{\text{col}}\) is the collision radius, and \(v\) is the mean relative speed between metal atoms and buffer gas molecules. The collision radius is derived from the optical collision cross section

\[
\sigma_{\text{col}} = \pi r_{\text{col}}^2
\]

suggesting an alternate form of eq. 1.20:

\[
2\Gamma_{\text{col}} = N\sigma_{\text{col}} v
\]

For an atomic vapor of an alkali metal mixed with a buffer gas [e.g. rubidium (Rb) in argon (Ar)], the contributions to the linewidth of an optical transition can be divided into Lorentzian (homogeneous) components and Gaussian (inhomogeneous) components. Lorentzian sources of broadening include the natural linewidth (\(\Gamma_0\)), the resonant collisional linewidth (\(\Gamma_{\text{self}}\)), and the non-
resonant collisional linewidth ($\Gamma_{\text{col}}$) where $\Gamma$ signifies a half-width at half-maximum (HWHM). Resonant collisional broadening arises from collisions between metal atoms (Rb–Rb) while non-resonant collisional broadening occurs due to collisions between metal atoms and buffer gas molecules (Rb–Ar). The dominant source of Gaussian broadening at low metal vapor and buffer gas density is the Doppler linewidth ($\Gamma_D$). The natural linewidth of an atomic transition is the only source of broadening at low temperature and density where the finite radiative lifetime of a transition’s excited state places a lower bound on the frequency width of the transition through the energy–time uncertainty relation.

The total Lorentzian linewidth (FWHM) is given by

$$2\Gamma_L = 2\Gamma_0 + 2\Gamma_{\text{self}} + 2\Gamma_{\text{col}}$$  \hspace{1cm} (1.22)$$

which is an extension of eq. 1 from ref. 11 to include non-resonant collisional broadening. The total lineshape is given by the convolution of the Lorentzian lineshape with the Gaussian lineshape and is described by the Voigt function which has no analytic form. Likewise, the total linewidth of the Voigt function has no analytic form. However, the total linewidth can be approximated as equal to the Lorentzian linewidth in the limit that the Lorentzian linewidth is much larger than the Gaussian linewidth (i.e. $\Gamma_L \gg \Gamma_G$ where $\Gamma_G \approx \Gamma_D$ is the Gaussian linewidth).

Assuming a Lorentzian lineshape of the form (given by the real component of eq. 1.14)

$$g(\omega) = \frac{1}{\pi} \frac{\Gamma_{jk}}{\omega^2 + \Gamma_{jk}^2}$$  \hspace{1cm} (1.23)$$

where $\Gamma_{jk} = \Gamma_L$, the frequency-dependent absorption cross section can be computed using

$$\sigma(\omega) = \sigma_0 \frac{\omega}{\omega_{eg}} g(\omega - \omega_{eg})$$  \hspace{1cm} (1.24)$$

where $\sigma_0$ is the frequency-integrated absorption cross section,\(^{13}\) which is given by

$$\sigma_0 = \frac{\pi e^2}{2\epsilon_0 m_e c} f_{jk}$$  \hspace{1cm} (1.25)$$
in terms of the absorption oscillator strength $f_{jk}$, the electron charge $e$, the vacuum permittivity $\epsilon_0$, the electron mass $m_e$, and the speed of light $c$. Given the path length ($L$) of the sample cell
and the number density of absorbers \((N)\), the transmittance

\[
T(\omega) = \exp\left[-\sigma(\omega) NL\right]
\]  

(1.26)

and absorbance

\[
A(\omega) = -\log_{10}[T(\omega)]
\]  

(1.27)

can be calculated.

An example of a simulated absorption spectrum for Rb vapor in Ar buffer gas is shown in Figure 1.7. This absorption spectrum was calculated using parameters taken from the literature\(^{10,14–16}\) which are appropriate for the experimental conditions of spectra at \(OD_{\text{max}} = 1.14\) in ref. 6.

This approach to modeling lineshapes, where collisions are approximated as independent, instantaneous events and dynamics are strictly divided into homogeneous Lorentzian components and inhomogeneous Gaussian components, is effective under certain conditions in linear frequency domain spectroscopy. However, such simple models are not always sufficient for modeling peak shapes in 2DFT spectra. The details of fast dynamics and frequency memory are contained in the far wings of frequency domain lineshapes, making them difficult to measure and a challenge to model. The time resolution and additional dimensions in 2DFT spectra affords sensitivity to dynamics which may be absent or unresolved in linear absorption spectroscopy, motivating the use of more complex models in some cases.
Figure 1.7: A linear absorption spectrum of Rb simulated using eqs. 1.22–1.27. Parameters for Rb vapor at 160°C in 2 atm of Ar buffer gas have been used: absorption oscillator strength, $f_{12} = 0.696$; Rb number density, $N = 1.64 \times 10^{20}$ m$^{-3}$; sample cell path length, $L = 500 \, \mu$m; Lorentzian HWHM linewidth, $\Gamma_L \approx \Gamma_{col} = 2\pi c(0.623 \, \text{cm}^{-1})$. 
1.4 Sample Renewal in Pump–Probe Spectroscopy

Time domain laser spectroscopy techniques use sets of pulses with controlled relative delays to interrogate the dynamics of chemical systems. For example, in pump–probe (transient absorption) spectroscopy, two pulses, labeled pump ($pu$) and probe ($pr$), impinge on a sample with a relative delay $T = t_{pr} - t_{pu}$ where $t_{pr}$ ($t_{pu}$) is the time the probe (pump) pulse reaches the sample entrance. The pump–probe transient absorption signal is the change in number of transmitted probe photons due to prior excitation of the sample by the pump. The signal is quantified based on two measurements: the number of transmitted probe photons with ($N_{on}$) and without ($N_{off}$) pump excitation. Subtracting the two yields one signal data point, $\Delta N = N_{on} - N_{off}$. To achieve a sufficient signal-to-noise (SNR) ratio, this is repeated many times and averaged at the same pump–probe delay (this can be done digitally or using a lock-in amplifier). This averaging procedure relies on complete sample relaxation between each pump–probe pulse set such that each $\Delta N$ is an independent measurement. For a sample with slow relaxation dynamics, the rate of data collection may need to be limited (e.g. by reducing the laser repetition rate) to fulfill this requirement.

To achieve both a fast data collection rate and a fully relaxed sample between pulse sets, one can employ a probed-volume sample renewal (PVSR) technique which spreads the laser excitation over a larger area of the sample to maximize the time allowed for individual chromophores to relax before they are re-excited. There are two main ways to accomplish this, either by moving the sample relative to the laser beams or moving the beams relative to the sample. Each approach has inherent advantages and disadvantages. Moving the sample instead of the beam often does not require changes to the optical setup outside of modification of the sample cell and/or its holder. A disadvantage is that moving the sample fast enough to prevent excitation of the same sample volume by consecutive pulse sets is either not feasible (as is often the case for sample stirring and flowing techniques) or induces mechanical vibrations due to moving the entire mass of the sample cell relatively quickly (as in sample spinning and translating techniques). An additional issue is that moving certain types of large or heavy sample cells, such as cryostats, can be quite difficult. These
disadvantages can be addressed by instead fixing the position of the sample cell and scanning the beams over the area of the sample using a fast steering mirror (FSM), as in the method demonstrated here in Chapter 3. Advantages of this method include accommodation of a wide variety of sample cell types, fast scanning, and flexibility in scan pattern. A spiral scan pattern has been developed (see Chapter 3) that minimizes spatial overlap between consecutive pulse sets and maximizes the scan pattern duration. The disadvantage is that this approach requires significant alterations to the optical setup and careful alignment to minimize optical aberrations and signal artifacts.

1.5 Carrier Dynamics in Colloidal Indium Arsenide Quantum Dots

Semiconductor quantum dots (QDs) are nanometer-scale particles that have the same crystalline structure as the bulk material but are smaller in size than the bulk exciton Bohr radius. Due to their small size, the electronic states of QDs experience quantum confinement, analogous to a quantum particle in a box. The resulting QD electronic structure shares similarities with both molecules and bulk semiconductors. The absorption spectra of QDs contain excitonic peaks reminiscent of molecular electronic transitions atop broad absorption bands akin to bulk semiconductors. Since the lowest energy excitonic transitions in QDs are significantly influenced by quantum confinement, they are very sensitive to the particle size. This quality enables tunability of the band gap energy ($E_g$) through control of QD size, a desirable trait for applications such as solar energy harvesting, fluorescent labelling, and illumination. Due to their unique adjustable electronic properties, QDs have been described as “artificial atoms.” As neither the molecular nor bulk theory alone is sufficient to characterize their electronic properties, QDs are a challenging area of research.

When a semiconductor QD is electronically excited by a photon with energy equal to or greater than the band gap energy, an electron from the valence band (HOMO) is promoted to the conduction band (LUMO), forming an electron–hole pair (or exciton) due to the spatial confinement of the charge carriers imposed by the boundary of the QD. In the early 1980s, a simple model for the excitonic states of quantum dots was developed that treats confined carriers as particles in
a spherical potential well. As in other systems with a centrosymmetric potential (e.g. the hydrogen atom), the electronic wavefunctions in the model are products of a unit-cell electronic wavefunction (that is the same as in bulk) with spherical harmonics and radial functions that specify the overall envelope (and replace the crystal momentum factor in the bulk wavefunction). As in the bulk where the selection rule is that crystal momentum does not change, the selection rules for the strongest optical transitions require the same envelope for electron and hole. In particular, both electron and hole have equal angular momentum, so the lowest energy excitonic transition is to the $1S_e1S_h$ state where both electron and hole have “s-like” spherical harmonic character. This transition is responsible for the lowest energy peak in the absorption spectrum. If excited by a photon with energy greater than the band gap, the excess energy is used to excite carriers with kinetic energy, which subsequently “cool” by transferring energy into lattice vibrations (phonons). In indium arsenide (InAs) and cadmium selenide (CdSe) QDs, it typically takes less than 1 ps for the electron and hole to cool from the second lowest energy excitonic state ($1P_e1P_h$) to the band edge. An experimental study of the cooling pathway for InAs QDs excited just above the $1P_e1P_h$ exciton state is presented in Chapter 4. Once cooled to the band edge, phonon-assisted cooling is no longer effective since the band gap energy ($\sim 1$ eV) is typically much greater than the energy of phonon transitions ($< 0.025$ eV). Therefore, relaxation from the band edge to the ground state through carrier recombination is much slower, occurring on the timescale of 100’s of picoseconds to microseconds and is highly dependent on the semiconductor material and QD surface properties.

When a single QD is excited more than once, resulting in multiple electron–hole pairs, additional cooling and recombination pathways become available. In Auger recombination (AR), one electron–hole pair recombines by transferring its electronic energy to the kinetic energy of either the electron or hole of another pair. This process is typically orders of magnitude faster than single exciton recombination and is a signature of multiply excited dots. Measuring the relative magnitude of AR signatures compared to signatures of single exciton recombination is a common method for quantifying processes which produce multiple excitations in individual dots, such as Multiple Exciton Generation (MEG), also known as Carrier Multiplication (CM). Both MEG and CM refer
to the process whereby excitation of a QD by a single photon with energy greater than twice the band gap results in multiple electron–hole pairs. MEG is under intense study for its potential to increase the efficiency of photovoltaic devices. However, detailed experiments are needed to better understand and quantify the QD relaxation pathways that are coupled to MEG (such as AR) since these auxiliary processes are the basis for observing MEG. This was the motivation for the study of carrier cooling dynamics presented here in Chapter 4.
Chapter 2

Pulse propagation effects in optical 2D Fourier-transform spectroscopy: Theory

A solution to Maxwell’s equations in the three-dimensional frequency domain is used to calculate rephasing two-dimensional Fourier transform (2DFT) spectra of the D₂ line of atomic rubidium vapor in argon buffer gas. Experimental distortions from the spatial propagation of pulses through the sample, including features which have not been previously studied, are simulated in 2DFT spectra calculated for the homogeneous Bloch lineshape model. Spectral features that appear at optical densities of up to 3 are investigated. As optical density increases, absorptive and dispersive distortions start with peak shape broadening, progress to peak splitting, and ultimately result in twisting of the split peaks. In contrast to the low optical density limit, where the 2D peak shape for the Bloch model depends only on the total dephasing time, these distortions of the 2D peak shape at finite optical density vary with the waiting time and the excited state lifetime. Experiment-specific conditions are explored, demonstrating the effects of varying beam overlap within the sample and of pseudo–time domain filtering. For beam overlap starting at the sample entrance, decreasing the length of beam overlap reduces the linewidth along the $\omega_r$ axis but also reduces signal intensity. A pseudo–time domain filter, where signal prior to the center of the last excitation pulse is excluded from the FID-referenced 2D signal, reduces propagation distortions along the $\omega_t$ axis. It is demonstrated that 2DFT rephasing spectra cannot take advantage of an excitation–detection transformation that can eliminate propagation distortions in 2DFT relaxation spectra. Finally, the high optical density experimental 2DFT spectrum of rubidium vapor in argon buffer gas [J. Phys. Chem. A 2013, 117, 6279–6287] is quantitatively compared, both in linewidth
and in depth of peak splitting, to a simulation with optical density higher than that reported.

2.1 Introduction

Optical two-dimensional Fourier-transform (2DFT) spectroscopy\textsuperscript{4,22–26} is a powerful technique for studying electronic coupling across a wide range of systems, from atomic vapors to biological pigment complexes. The extra dimension in 2DFT spectroscopy separates homogeneous from inhomogeneous lineshape broadening and highlights coupling between electronic transitions. However, in order to take advantage of this additional information, one must avoid or account for distortions of the signal caused by the absorptive and dispersive nature of the sample. Avoidance relegates experimental work to sample optical densities (OD) less than 0.1 where such distortions are negligible, allowing 2DFT spectra to be modeled by ignoring spatial pulse propagation effects. For linear optics, this corresponds to a restriction that the exponential in Beer’s law can be described by the first order Taylor series term. In contrast, nonlinear optical signals are typically maximized at optical densities near 0.7,\textsuperscript{27} where propagation effects are significant and must be accounted for.\textsuperscript{2,7,28–35}

Ideally, 2DFT spectroscopy is a measurement of the microscopic nonlinear response of a material.\textsuperscript{4,23,24} From this standpoint, propagation effects are ‘distortions’ of the radiated signal field that change the relationship between the true microscopic nonlinear response and the measured signal field. 2DFT spectra generated by four-wave mixing processes depend on three time intervals, resulting in propagation distortions that are inherently three-dimensional in time or, equivalently, three-dimensional in frequency. Thus, propagation distortions must generally be modeled three-dimensionally, either in the 3D time domain or in the 3D frequency domain.\textsuperscript{7,32}

One can make an analogy between the exponential attenuation of light implied by the 1D frequency domain Beer-Lambert law and the 3D frequency domain propagation distortions discussed here. In a typical absorption measurement, information regarding the microscopic absorption strength (e.g. the molar extinction coefficient, $\epsilon$) of a chromophore at a given wavelength is desired. However, the direct experimental observable is transmission, $T = I/I_0$, which yields a
lineshape that is distorted compared to the microscopic lineshape due to the continual attenuation of the beam as it traverses the sample. This can be corrected by using the Beer-Lambert law,\(^3^6\)

\[ A = -\log_{10}\left[\frac{I}{I_0}\right] = \epsilon CL, \]

which properly accounts for the exponential attenuation of light by connecting the macroscopic measurement of the intensity of transmitted light to absorbance, which is directly proportional to the extinction coefficient (\(\epsilon\)), the number density or concentration (\(C\)) of chromophores, and the path length (\(L\)).

For sufficiently weak excitation fields, propagation distortions in nonlinear optics result from linear reshaping of the excitation pulses and emitted signal field as they propagate through an optically thick medium.\(^7^,2^4^,3^2^,3^4\) At optical densities greater than 0.5, these linear propagation distortions are prominent in 2DFT spectra and can even dominate the overall appearance of the lineshape. While it can be advantageous to increase the signal strength by increasing the optical density of the sample, this strategy also strengthens propagation distortions. By including propagation distortions in modeling 2DFT spectra, even highly distorted experimental spectra could be modeled to extract the fundamental dynamics. This ability would enable the interpretation of 2DFT spectra measured at the optical density where signal is strongest, expanding the range of samples available to 2DFT spectroscopy.

Numerical solutions of the electromagnetic wave equation in one spatial dimension have been used to model spatial propagation, both for intense single pulses\(^3^7^,3^8\) and for nonlinear signals generated by multiple collinear pulses.\(^2^7^,2^9^–3^1^,3^9\) Olson et al.\(^2^7\) used such calculations to distinguish optical density effects from chromophore interaction effects. Propagation of individual pulses has also been studied using nonlinear finite difference time domain (NL-FDTD) approaches to the solution of Maxwell’s equations in three spatial dimensions,\(^4^0^,4^1\) which treat the boundary conditions as well as intense pulse interactions such as self-focusing. The generality of NL-FDTD methods comes at the computational cost of propagating pulses as an explicit function of both the propagation and transverse dimensions, requiring a 3D spatial grid with sub-wavelength steps (\(\lambda/100\) to \(\lambda/10\)) in addition to a time grid.\(^4^0\) Pseudospectral time domain methods can increase the maximum allowable spatial step size to as large as \(\lambda/2\),\(^4^2\) reducing the number of spatial grid points necessary
for a given propagation length.

The 3DFT method\textsuperscript{7} used here to generate and spatially propagate the third-order nonlinear signal is based on an exact, three-dimensional solution of Maxwell’s equations and is valid for non-collinear pulses in the weak field limit. This algorithm calculates the complex-valued 3D frequency domain spectrum, $\hat{S}_{3D}$, from which 2DFT spectra at a range of waiting times can be extracted. It successfully reproduces optical density effects on the integrated two-pulse photon echo signal decay rate\textsuperscript{32} and beam geometry distortions of relative cross-peak amplitudes in 2DFT infrared spectra.\textsuperscript{2} 2DFT spectra calculated using the 3DFT method at waiting times long compared to dipole dephasing dynamics connect to expressions for absolute pump–probe signal size\textsuperscript{34,35} and to experimentally-tested expressions for product 2D peak shapes.\textsuperscript{24}

The 3DFT algorithm uses the nonlinear impulse response\textsuperscript{43,44} (the time-dependent nonlinear polarization excited by three weak, delta-function pulses) as an essential input for the calculation of the signal field radiated by a macroscopic sample. For complicated systems, quantum mechanical time-domain propagation of a model system or ensemble of model systems is needed to calculate this response.\textsuperscript{3,45–47} Several approaches to efficiently calculate the response for a single time delay triple have been developed\textsuperscript{48,49} and could be incorporated into the algorithm used here. An advantage of the 3DFT algorithm is that the third-order nonlinear response is only calculated once for each point on a 3D grid\textsuperscript{32} and does not need to be evaluated at delay-dependent time intervals as in convolution algorithms used to incorporate pulse duration effects.\textsuperscript{50–52} While calculating the third-order nonlinear polarization in the time domain usually involves a 3D convolution of the third-order nonlinear susceptibility with the three excitation pulses [requiring $O(N^2)$ operations where $N$ is the total number of points in the 3D grid], this can be accomplished in the frequency domain by simple multiplication following a 3D fast Fourier transform (FFT) of the third-order nonlinear susceptibility [$O(N \log_2 N)$].\textsuperscript{53} Alternative methods\textsuperscript{54–56} that include interaction with the pulse fields in repetitive (e.g. phase cycled) calculations of the quantum dynamics have also been used to calculate the nonlinear polarization for finite pulses and generate a computational savings over time domain convolution. These methods optimize the calculation of the polarization
for a single time delay triple at one point inside the sample. In contrast, the 3DFT approach is optimized for simultaneous calculation of the entire 3D spectrum, which includes the complete set of 2D spectra (multiplex advantage). Further, propagation distortions can be applied to the 3D signal by a single multiplication in the 3D frequency domain, as opposed to the stepwise pulse propagation and recalculation of the nonlinear polarization for the distorted pulses at each depth within the sample used in the time domain methods.\textsuperscript{27,29,30,40–42} Altogether, this results in reduced computation time. The disadvantage is that 3D FFT algorithms typically require more random access memory (RAM) than a 3D convolution, but 3D FFT grids of $1024^3$ points that can match available experimental resolution are now possible on personal computers. For grids of even larger size which do not fit in RAM, slower methods allow the 3D Fourier transform to be evaluated in sections.\textsuperscript{53}

There are four essential assumptions implicit in the 3D Fourier transform (3DFT) theory and calculations presented here. First, the signal is assumed to be generated by the perturbative third-order nonlinear response of the sample. Second, it is assumed that the excitation pulses and the radiated signal field all propagate through the sample according to linear optics. [This can be checked for the excitation pulses by measuring their free-induction decay\textsuperscript{7,24} (FID) which, unlike absorption measurements, is sensitive to both absorptive and refractive nonlinearity.] Third, the theory assumes that the spectrum and phase of the excitation pulses are uniform across the transverse spatial profile of the pulse (e.g. the beam profile cannot have spatial chirp). Fourth, it is assumed that the excitation beams ($a$, $b$, and $c$) have complete transverse spatial overlap throughout the cell, from the entrance window to the exit window. An approximate treatment of the distortions caused by beams that have no transverse overlap in some portion of the cell is presented below.

In rubidium (Rb) atoms, the $D_2$ ($^5\!S_{1/2} \rightarrow ^5\!P_{3/2}$) electronic transition is isolated from other transitions, suggesting treatment as an effective two-level system. Rubidium vapor is an interesting system for studying the validity of a theoretical model for propagation distortions since its optical density can be easily varied over an order of magnitude at constant path length by adjusting the
temperature of a rubidium reservoir.\textsuperscript{6} The price to be paid is that the linewidth, which is dominated by non-resonant pressure broadening from the argon (Ar) buffer gas, increases with temperature due to the increase in buffer gas pressure from heating the gas at constant volume. However, this effect is expected to be modest over the temperature range (363–433 K) modeled here: the predicted linewidth at 433 K is approximately 9\% greater than that at 363 K.\textsuperscript{57} For low partial vapor pressures (∼1 mTorr) of alkali metal in noble gases at total pressures of ∼1500 Torr, the line broadening in absorption is almost Lorentzian, dominated by pressure broadening from collisions with the noble gas buffer. For the potassium D\textsubscript{1} and D\textsubscript{2} lines, four-wave mixing studies at buffer gas pressures of ∼1500 Torr with ∼200 fs pulses suggest that the homogeneous optical Bloch model (uncorrelated collisions) underlying a Lorentzian lineshape accounts for the nonlinear response with an 8 ps dephasing timescale.\textsuperscript{58}

The homogeneous optical Bloch model includes two phenomenological dipole dephasing processes, each characterized by a single time constant: the population lifetime, $T_1$, and the pure dephasing time, $T_2^*$. Assuming that only the excited state population is affected by the population lifetime $T_1$, the resulting microscopic dipole decay rate is $\Gamma = 1/T_2^* + 1/(2T_1)$.\textsuperscript{59} The macroscopic polarization can also decay through inhomogeneous processes, but this is not included here because the Doppler width is negligible compared to the homogeneous width. Since propagation distortions alter the macroscopic polarization and, consequently, the radiated signal field, the 2DFT spectrum of an optically thick sample will not reflect the chromophore’s true microscopic dynamics. Therefore, caution must be exercised when interpreting the Bloch model rates since the 2DFT spectrum of an optically dense sample can be much wider than that of a thin sample,\textsuperscript{33} suggesting values of $T_2^*$ and $T_1$ which are shorter than the true microscopic values. An expression describing this effect for the homogeneous Bloch model in the impulsive limit is given by eq. 3 of ref. 32. If the line broadening is dominated by isolated binary collisions with a buffer gas, as in ref. 6, the Bloch model is expected to be appropriate for Rb vapor. In contrast, correlated collisions typically necessitate models that include frequency memory.\textsuperscript{44}

This paper follows a paper detailing experimental work by Li et al.\textsuperscript{6} on propagation distor-
tions in 2DFT spectra of rubidium vapor. We present a theoretical and computational treatment of novel distortions observed in the experimental 2DFT spectra. However, quantitative modeling of the experimental lineshapes was not attempted for two reasons. First, the asymmetry between $\omega_\tau$ and $\omega_t$ linewidths in the low-OD experimental spectra is not recovered by the Bloch model or the Kubo stochastic model\textsuperscript{(32)} (in the slow-, intermediate-, and fast-modulation limits). Second, the linewidth and peak OD of experimental linear absorption spectra are inconsistent with predicted linear absorption spectra at each experimental Rb reservoir temperature under the assumption that the Rb vapor density is given by the vapor pressure of Rb at the experimentally measured reservoir temperature. In addition, the linewidth and peak OD implied by the experimental 2DFT spectra do not agree with either the experimental or the predicted linear absorption spectra. In the face of these disagreements, the linewidth was set constant for all simulated 2DFT spectra in order to focus on qualitative OD-dependent features present in the experimental 2DFT spectra. The above disagreements will be addressed further in the Discussion section.

2.2 Theory

2.2.1 Propagation Distortions

A complete mathematical framework for describing propagation and detection distortions on 2DFT spectra in the 3D frequency domain has been developed.\textsuperscript{(2,7,33)} This discussion highlights the essentials necessary to understand the distortions that are the focus of this work. First, in order to discuss the propagation of pulses in a sample, we will define the time domain optical electric field of the excitation pulses,

$$E(r, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{E}(r, \omega) \exp(-i\omega t) \, d\omega$$

where $r$ is spatial position, $t$ is time, and $\omega$ is the angular frequency. $\hat{E}(r, \omega)$ is the frequency domain complex-valued electric field,

$$\hat{E}(r, \omega) = \frac{1}{(2\pi)^3} \iiint \hat{E}(\hat{k}(\omega), \omega) \exp \left[ i\hat{k}(\omega) \cdot r \right] \, d^3\hat{k}$$
where \( \hat{E}(\hat{k}(\omega), \omega) \) is a “wave” which, when integrated over \( \hat{k} \), is equal to the frequency domain complex-valued electric field at the center of the sample entrance plane (\( r = 0 \)) with its spatial variation factored out into \( \exp[i\hat{k}(\omega) \cdot r] \). \( \hat{k}(\omega) \) is the complex-valued wave vector, which incorporates attenuation of the electric field when propagating through absorbing media. Representing the pulses as waves is convenient in that it mathematically separates propagation effects from the input pulse fields, allowing the propagation effects to be collected and dealt with separately. Throughout this paper, vectors and matrices are in bold face type while complex-valued quantities are marked with a circumflex (or “hat”). For normal incidence, the wave vector is \( \hat{k}(\omega) = e_z \hat{n}(\omega) \omega/c \) where \( e_z \) is the unit vector normal to the window–sample interface and \( c \) is the speed of light in vacuum. \( \hat{n}(\omega) = n(\omega) + i\kappa(\omega) = \sqrt{\hat{\epsilon}(\omega)/\epsilon_0} \) is the complex-valued refractive index, \( \hat{\epsilon}(\omega) \) is the complex-valued permittivity (dielectric constant), and \( \epsilon_0 \) is the permittivity of vacuum (MKS units). Attenuation of the field is contained in the imaginary part of the wave vector, \( \text{Im}[||\hat{k}(\omega)||] = \kappa(\omega) \omega/c \), which is related to the napierian (i.e. base e) field attenuation coefficient, \( \alpha(\omega) = \kappa(\omega) \omega/c = A(\omega) \ln(10)/2L \), where \( A(\omega) \) is the decadic absorbance (optical density) and \( L \) is the sample length normal to the window–sample interfaces. \( \alpha \) and \( A \) are linked by \( T = I/I_0 = e^{-2\alpha L} = 10^{-A} \) where \( T \) is the transmittance of the sample. The usage of \( \alpha \) here for the field attenuation coefficient is not to be confused with the intensity attenuation coefficient (napierian absorption coefficient), which is also denoted by \( \alpha \) in some cases.

For a weak absorber (i.e. \( \kappa^2 \ll n^2 \)), the wave vector can be expressed in a more general form that is valid for oblique incidence as well as normal incidence:

\[
\hat{k}(\omega) \approx (\omega/c) \left[ n(\omega) \mathbf{u} + i\kappa(\omega) e_z/(\mathbf{u} \cdot e_z) \right]
\]

(2.3)

where \( \mathbf{u} \) is the unit vector along the direction of propagation (which can be calculated using the ordinary real-valued Snell’s Law [see eq.s A6 and A7 of ref. 7]). The real and imaginary parts of a complex wave vector are normal to planes of constant phase and amplitude respectively and, therefore, point in different directions (see Figure 18-6 of ref. 61) except for normally incident light (i.e. \( \mathbf{u} = e_z \)). The factor of \( 1/(\mathbf{u} \cdot e_z) \) modifies \( \kappa \) to account for the additional path length when beams
are not at normal incidence to the window–sample interface. This is necessary because \( \text{Im}[\hat{k}(\omega)] \) is parallel to the window–sample interface normal, not the propagation vector. Propagation from the sample cell entrance at \( \mathbf{r} \) to the sample cell exit at \( \mathbf{r} + \mathbf{u} \ell \) multiplies the wave by \( \exp[i\omega(n+i\kappa)\ell/c] \), where \( \ell = L/(\mathbf{u} \cdot \mathbf{e}_z) \) is the path length through the sample for a beam propagating along \( \mathbf{u} \).

Given the following three additional assumptions, the propagation matrix for the 3D frequency domain signal field\(^7\) can be simplified to a scalar:\(^{33}\) (1) well-collimated beams, (2) transverse electric (TE) polarized beams, and (3) an isotropic nonlinear susceptibility. We further assume that the sample and windows have the same linear optical properties so that no linear reflections are generated by the window–sample interfaces (see Appendix C of ref. 7). 3D inverse Fourier transformation of the time domain third-order nonlinear response (eq. B3 of ref. 7) yields the 3D frequency domain nonlinear susceptibility, \( \hat{\chi}^{(3)} \), which is multiplied by the three excitation waves \( (a, b, \text{ and } c) \) to form the nonlinear polarization wave inside the sample, \( \hat{\mathcal{P}}^{(3)} \). Further multiplication by the propagation function, \( \Pi^{(3)}_{\text{exit}} \), gives the radiated signal wave referenced to the sample exit, \( \hat{\mathcal{E}}_t \); multiplication by the directional filter function, \( \Phi^{(3)} \), isolates the particular phase-matched signal field that is selected for interference detection with respect to the detection wave, \( \hat{\mathcal{E}}_d \). The detection wave may represent an actual reference pulse propagating through the sample in the direction of the signal, but may also represent an artificial wave that incorporates both the actual reference (which may be routed around the sample) and measured differences between the actual reference and a chosen ideal reference (for example, the reference-tracer phase difference of refs. 62, 22, and 24 or the amplitude distortion from propagating through an absorptive sample treated in ref. 33).

The result is the transmitted 3D frequency domain signal,

\[
\hat{S}_{3D} \approx \hat{\mathcal{E}}_t \hat{\mathcal{E}}_d^* \Phi^{(3)}
\]

\[
\approx \frac{i\omega_t}{2\epsilon_0 c} \left[ \Pi^{(3)}_{\text{exit}} \hat{\mathcal{P}}^{(3)} \right] \hat{\mathcal{E}}_d^* \Phi^{(3)}
\]

\[
\approx \frac{i\omega_t}{2\epsilon_0 c} \left[ \Pi^{(3)}_{\text{exit}} \left( \hat{\chi}^{(3)} \hat{\mathcal{E}}_a \hat{\mathcal{E}}_b \hat{\mathcal{E}}_c \right) \right] \hat{\mathcal{E}}_d^* \Phi^{(3)}
\]

where \( \hat{\mathcal{E}}_{a,b,c,d} \) represent the excitation \( (a, b, c) \) and detection \( (d) \) pulse waves and \( \omega_t = \omega_c + \omega_b - \omega_a \) is the frequency of the transmitted signal wave. The mathematical form of the directional filter is
given by eq. 56 of ref. 7. For this experiment, $\Phi^{(3)}$ is over 50 times wider than the experimental 2DFT spectrum and has no significant effect beyond selecting only two conjugate octants of the 3D frequency domain signal, which physically reflects detection of signal from only one phase-matched direction. Within the rotating-wave approximation, the directional filter is implemented here by calculating the nonlinear response using only diagrams that give a phase-matched signal for the detected beam. Given the three assumptions listed above, the propagation function takes the form (eq. 9 of ref. 33)

$$
\Pi^{(3)}_{\text{exit}}(\hat{k}_a^0, \hat{k}_b^0, \hat{k}_c^0, L) = \frac{\omega_t}{(\hat{k}_s^0 \cdot \mathbf{e}_z)c} \frac{\exp[i(\Delta \hat{k}^0 \cdot \mathbf{e}_z)L] - 1}{i(\Delta \hat{k}^0 \cdot \mathbf{e}_z)} \frac{\exp[i(\hat{k}_s^0 \cdot \mathbf{e}_z)L]}{2.5}
$$

where $\hat{k}_{a,b,c,s}^0$ are the complex-valued, frequency dependent central wave vectors of the excitation pulses ($a$, $b$, $c$) and the signal ($s$) inside the sample, $\omega_t$ is the frequency of the transmitted signal wave, and $\Delta \hat{k}^0 = \hat{k}_p^0 - \hat{k}_s^0$ is the complex-valued 3D phase mismatch between the nonlinear polarization and signal waves, with central wave vectors $\hat{k}_p^0$ and $\hat{k}_s^0$ respectively. A superscript “0” indicates use of the central wave vector approximation where the propagation function for the true wave vector distribution of all beams, which includes the angular spread of wave vectors needed for the focused beam diameter, is evaluated at each beam’s central wave vector. This approximation requires well collimated beams and is implicit in the use of a directional filter. In the limit of $(\Delta \hat{k}^0 \cdot \mathbf{e}_z)L \ll 1$ and small beam crossing angles, the propagation function approaches the normal incidence result, $\Pi^{(3)}_{\text{exit}} \approx [L/\hat{n}(\omega_t)] \exp[i(\hat{k}_s^0 \cdot \mathbf{e}_z)L]$. The proportionality to $L$ physically represents perfectly phase-matched growth of signal over the length of the sample and the exponential represents linear propagation. For a sample much thinner than a wavelength of light, the normal-incidence propagation function further simplifies to $\Pi^{(3)}_{\text{exit}} \approx L/\hat{n}(\omega_t)$.

In the rectangular BOXCARS geometry, three parallel excitation beams are arranged such that each intersects the corner of a rectangle. The beams are focused into the sample, producing a signal beam which intersects the fourth corner of the rectangle (see Figure 1 of ref. 33). The signal
obeys the phase-matching condition

\[ \hat{k}_x^0(\omega_t) \cdot \mathbf{e}_{x,y} = \left[ \hat{k}_a^0(-\omega_a) + \hat{k}_b^0(\omega_b) + \hat{k}_c^0(\omega_c) \right] \cdot \mathbf{e}_{x,y} \]  

(2.6)

with

\[ \hat{k}_i^0(\omega) \cdot \hat{k}_i^0(\omega) = (\omega^2/c^2) n^2(\omega) \]  

(2.7)

for all four beams (\( \gamma = a, b, c, s \)).

The 3D nonlinear susceptibility, \( \hat{\chi}^{(3)} \), is multiplied by the propagation function (eq. 2.5), the excitation pulse waves \( \hat{E}_{a,b,c}(\omega_{a,b,c}) \), the detection pulse wave \( \hat{E}_{d}^*(\hat{k}_d, \omega_t) \), and the directional filter to produce the distorted 3D frequency domain signal,

\[ \hat{S}_{3D}(\omega_a, -\omega_b, -\omega_c) \approx \Pi^{(3)}_{\text{exit}}(\hat{k}_a^0, \hat{k}_b^0, \hat{k}_c^0, L) \]  

\[ \cdot \frac{\omega_t}{2\varepsilon_0 c} \chi^{(3)}(-\omega_a, \omega_b, \omega_c) \]  

\[ \cdot \hat{E}_a(-\omega_a) \hat{E}_b(\omega_b) \hat{E}_c(\omega_c) \]  

\[ \cdot \hat{E}_d^*(\hat{k}_d, \omega_t) \Phi^{(3)}(\omega_a, -\omega_b, -\omega_c) \]  

(2.8)

The distorted 3D frequency domain signal is triple Fourier transformed into the 3D time domain. Given that \( t_a \leq 0, t_b \leq 0, \) and \( t_c = 0 \) are the experimentally controlled arrival times of pulses \( a, b, \) and \( c, \) respectively, we define the time intervals \( T \equiv \min(|t_a|, |t_b|) \) and \( \tau \equiv t_b - t_a. \) The time domain 2D signal, \( S_{2D}(t, \tau; T) \), at fixed waiting time \( T \) is extracted from the 3D time domain signal according to

\[ S_{2D}(t, \tau; T) = S_{3D}(t + \tau + T, t + T, t) \theta(\tau) \]  

(2.9)

\[ + S_{3D}(t + T, t - \tau + T, t) \theta(-\tau) \]

The time domain 2D signal from eq. 2.9 is inverse Fourier transformed (along \( \tau \) and \( t \)) back to the frequency domain to produce the complex-valued 2DFT spectrum,

\[ \hat{S}_{2D}(\omega_t, \omega_{\tau}; T) = \frac{1}{\omega_t e^{(\omega_t)}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} S_{2D}(t, \tau; T) \]  

\[ \cdot \exp(i\omega_{\tau}) \exp(i\omega_t) \, d\tau dt \]  

(2.10)
where $e(\omega t)$ is the detection pulse field envelope, which represents the frequency envelope of the detection field, and $\omega_t$ and $\omega_\tau$ are conjugate to $t$ and $\tau$, respectively. Division by $\omega_t$ removes the radiative distortion that is introduced by the factor of $\omega_t$ on the second line of eq. 2.8. The form of the detection envelope in eq. 2.10 depends on the detection geometry utilized and will be specified for each representation discussed below.

To calculate the complex-valued rephasing 2D spectrum, only the positive-$\tau$ part of the time domain 2D signal is inverse Fourier transformed:

$$R\hat{S}_{2D}(\omega_t, \omega_\tau; T) = \frac{1}{\omega_t} e^{i\omega_t} \int_{-\infty}^{\infty} S_{2D}(t, \tau; T) \theta(\tau) \cdot \exp(i\omega_\tau \tau) \exp(i\omega_t t) \, \text{d} \tau \text{d} t \tag{2.11}$$

Multiplication by the Heaviside unit step function (see p. 61 of ref. 63), $\theta(\tau)$, in eq. 2.11 selects the positive-$\tau$ rephasing pulse ordering, where pulse $a$ comes before pulse $b$, by multiplying $S_{2D}(t, \tau < 0, T)$ by 0 and $S_{2D}(t, \tau = 0, T)$ by $1/2$; this is equivalent to neglecting the second term in eq. 2.9. In this paper, all rephasing spectra will be indicated by “$R$”. Most of the 2DFT spectra depicted here are calculated according to eq. 2.11 to allow for direct comparison to the experimental work by Li et al.\textsuperscript{6}

Since it is instructive to compare distorted and undistorted 2DFT spectra, we define the ideal (undistorted) 2DFT spectrum, $\hat{S}_{2D}^{\text{ideal}}$, which is calculated using eq. 2.10 where the propagation function is taken to be

$$\Pi_{\text{exit}}^{\text{ideal}}(L) = \frac{\omega_t L}{(k_0^s \cdot e_z) c} = \frac{L}{(u_s \cdot e_z)} \tag{2.12}$$

where $k_0^s$ is the real-valued signal wave vector in vacuum and $u_s$ is the unit propagation vector of the signal beam. This “ideal” propagation function is valid for samples with no absorptive or refractive effects (i.e. $\hat{n} = 1$) and neglects the effect of phase mismatch, which even in vacuum only vanishes for collinear beams or zero sample length.\textsuperscript{33} Vacuum phase mismatch is negligible in the experiment of Li et al.,\textsuperscript{6} making eq. 2.12 a good approximation for this work. Since all of the representations of the 2DFT spectrum discussed in the next section are equivalent in the limit
of optically thin samples, the ideal 2DFT spectrum requires no indication of representation and is directly comparable to distorted spectra in any representation.

2.2.2 Representations of the 2DFT Spectrum

2.2.2.1 Experimental Distinctions

In order to address the form of the detection field, the experimental detection geometry must be discussed. In 2DFT spectroscopy, the amplitude and phase of the signal field is retrieved by interference detection with a detection field. Since the 3D signal (eq. 2.4) is dependent on the detection field, it must be well characterized to extract the signal field from the spectral interferograms. The detection field is used to establish both the time axis for the signal field relative to the excitation pulses and the zero of spectral phase. The three representations of 2DFT spectra presented here (attenuated, FID-referenced, and time-referenced) have been discussed in more detail elsewhere.\textsuperscript{2,33}

Experimentally, either the tracer beam ("ref II") or the reference beam ("ref I") can be used for interferometric detection of the signal field. Assumptions regarding the amplitude and phase of the detection field directly influence the amplitude and phase of the 2DFT spectrum extracted from experimental interferograms and can be used to approximately remove certain propagation distortions. The cost of changing representations is that the 2DFT spectrum may no longer be an accurate representation of the signal field that exits the sample. In the BOXCARS geometry, the tracer beam occupies one corner of the rectangle formed on the focusing lens by it and the three excitation beams and copropagates with the signal through the sample and on to the detector. Since the tracer copropagates with the signal, it accrues the same linear absorptive and dispersive distortions as the signal through the sample and common path optics. However, the tracer can influence or be influenced by nonlinear interactions with the excitation pulses. The reference beam bypasses the sample, but later rejoins and copropagates with the signal beam to the detector. In bypassing the sample, the reference beam avoids all sample-induced distortions. However, this also
means that it encounters a different set of optics and travels a different length, taking on phase and attenuation that is not common to the signal. The tracer can be used without the excitation pulses to characterize the time origin and phase of the reference beam relative to the excitation pulses at the sample. For a more detailed description of the experimental geometry, see Figure 2 of ref. 6.

**2.2.2.2 Attenuated**

In the attenuated representation of the 2DFT spectrum, the tracer beam, which propagates along the same path as the signal through the sample, serves directly as the detection field. In this case, assuming a weakly absorbing sample, the complex-valued wave vector of the detection beam is given by

\[
\hat{k}_d^0(\omega_t) = \frac{\omega_t}{c} \left[ n(\omega_t) \mathbf{u}_d + i \left( \mathbf{e}_z \cdot \mathbf{u}_d \right) \right] e^{iL} \tag{2.13}
\]

where \( \mathbf{u}_d \) is the unit propagation vector of the detection beam, which—for the BOXCARS geometry—is collinear with the central wave vector of the tracer beam. In the square BOXCARS geometry, with the detection beam aligned such that \( \mathbf{u}_d = \mathbf{u}_c + \mathbf{u}_b - \mathbf{u}_a \), Maxwell’s equations guarantee that the components of the wave vector parallel to the window–sample interface are the same for \( \hat{k}_s^0 \) and \( \hat{k}_d^0 \) (hence \( \hat{k}_s^0 = \hat{k}_d^0 \) and \( \mathbf{u}_s = \mathbf{u}_d \) when all four frequencies are the same). Thus, all effects for the parallel components of \( \hat{k}_s^0 \) and \( \hat{k}_d^0 \) automatically cancel (recall that the imaginary part of a wave vector attenuates the wave along an axis normal to the window–sample interface).

At the sample exit plane \( (z = L) \), the detection wave has the form

\[
\hat{E}_d(\omega_t) = \hat{E}_d^0(\omega_t) \exp \left\{ i \left[ \hat{k}_d^0(\omega_t) \cdot \mathbf{e}_z \right] L \right\} \tag{2.14}
\]

where \( \hat{E}_d^0(\omega_t) \) is the detection wave at the sample entrance \( (r = 0) \) for zero delay. Since the tracer and signal take the same path through the sample, the tracer beam experiences approximately the same attenuation and dispersion as the signal \( \hat{k}_d^0(\omega_t) \approx \hat{k}_s^0(\omega_t, \omega_b, \omega_c) \). This approximation is valid within a 3D signal frequency-bandwidth window whose width is inversely proportional to the excitation beam crossing angles, is good when the signal beam is well-collimated, and is an equality.
for collinear excitation beam at normal incidence. Replacing $\hat{k}_0^d$ with $\hat{k}_0^s$ yields

$$\hat{E}_d(\omega t) \approx \hat{E}_d^0(\omega t) \exp \left\{ i \left[ \hat{k}_s^0 (-\omega_a, \omega_b, \omega_c) \cdot \mathbf{e}_z \right] L \right\}$$

(2.15)

for the detection wave at the sample exit plane. For small angles of incidence or when $\kappa^2 \ll n^2$, this further simplifies to

$$\hat{E}_d(\omega t) \approx \hat{E}_d^0(\omega t) \exp \left\{ \frac{\omega t}{c} \left[ i (\mathbf{u}_d \cdot \mathbf{e}_z) n(\omega t) - \frac{\kappa(\omega t)}{(\mathbf{u}_d \cdot \mathbf{e}_z)} \right] L \right\}$$

(2.16)

To calculate the attenuated rephasing 2DFT spectrum $[\hat{\mathcal{R}}_S^{\hat{2D}}(\omega_t, \omega_\tau; T)]$ from eq. 2.11, eq. 2.15 is used as the detection wave in eq. 2.8, taking $e(\omega t) = 1$ for the detection pulse field envelope. Using $e(\omega t) = 1$ ignores the effect of the detection field’s spectrum on the amplitude of the signal field recovered from spectral interferograms. As a result, the real part of the attenuated 2DFT spectrum, when integrated over $\omega_\tau$, becomes equal to the spectrally resolved pump-probe signal when directional filtering distortions are negligible.\(^{33}\)

The substitution of $\hat{k}_s^0$ for $\hat{k}_0^d$ in the exponential term of eq. 2.15 is useful in that it results in cancellation of the imaginary part of the final exponential term in the propagation function (eq. 2.5) when both equations are combined to form the 3D signal (eq. 2.4). In contrast, the real parts have the same sign and, consequently, add. Physically, this signifies that while there is cancellation of phase evolution between the signal and tracer (i.e. no relative phase), the attenuation of the signal and detection fields is additive, resulting in stronger absorptive distortions in the 2DFT spectrum.

The spectra measured using the “reference through the sample” in the work by Li et al.\(^{6}\) are fundamentally attenuated rephasing 2D spectra. However, the spectra depicted in Figures 4 and 5 of ref. 6 have been processed with a time domain filter and are no longer in the $\hat{R}\hat{S}_{2D}^-$ representation. The effect of this filter is discussed in the section “Pseudo–Time Domain Filtering” below.

### 2.2.2.3 FID-referenced

While the tracer can be used as the detection field for interferometric detection, attenuation and dispersion of the tracer in an absorptive sample can introduce distortions into the measured
2DFT spectrum. In addition, if the tracer falls within the time window of the sample nonlinear response, it has the potential to interact with the sample in such a way as to alter the radiated signal field or be altered by nonlinear interaction with the sample. To avoid such attenuation and nonlinear interaction, the tracer can be used to characterize the reference and then can be blocked during the experiment, using the reference beam directly for interference detection. In this case, the tracer must be used to characterize the phase accrued by the signal in traversing the sample. Under the same approximations as eq. 2.15, this detection geometry results in the detection wave

\[
\hat{E}_d(\omega_t) \approx \hat{E}^0_d(\omega_t) \exp \left\{ i \Re \left[ k_s^0 (-\omega_a, \omega_b, \omega_c) \cdot e_z \right] L \right\}
\] (2.17)

which can be used in eq. 2.8 to calculate the FID-referenced rephasing 2DFT spectrum, \( R\hat{S}^0_{2D}(\omega_t, \omega_\tau; T) \), from eq. 2.11 given that \( e(\omega_t) = |\hat{E}^0_d(\omega_t)| \). For small angles of incidence or when \( \kappa^2 \ll n^2 \), this further simplifies to

\[
\hat{E}_d(\omega_t) \approx \hat{E}^0_d(\omega_t) \exp \left\{ i \omega_t (u_d \cdot e_z) n(\omega_t) L/c \right\}
\] (2.18)

The FID-referenced representation is essentially the same as the attenuated representation except with the attenuation of the detection field removed. Both \( \hat{S}^-_{2D} \) and \( \hat{S}^0_{2D} \) have the FID phase removed, resulting in a physically meaningful separation of the 2DFT spectrum into absorptive (real) and dispersive (imaginary) parts. However, this comes at the expense of losing a causal time origin such that the 2DFT spectrum of an optically thick sample contains signal that appears to arrive before pulse \( c \).

Fundamentally, the spectra denoted by “reference around the sample” in the work by Li et al., such as those in Figure 3 of ref. 6, are measurements of the FID-referenced rephasing 2D spectrum. However, since only the amplitude (absolute value) of the experimental spectra is shown in ref. 6, the phase evolution contained in the exponential term in eq. 2.17 is hidden.

An approximate form of \( R\hat{S}^0_{2D} \) can be calculated from \( R\hat{S}^-_{2D} \) by using the tracer as the detection wave and later correcting the attenuated 2DFT spectrum for detection wave attenuation.
This procedure results in

\[ R\hat{S}^0_{2D}(\omega_t, \omega_\tau; T) \approx R\hat{S}^-_{2D}(\omega_t, \omega_\tau; T) \]
\[ \cdot \left| \hat{E}^0_d(\omega_t) \right| \exp \left\{ \text{Im} \left[ \hat{k}^0_d(\omega_t) \cdot \mathbf{e}_z \right] L \right\} \]

(2.19)

where

\[ \ell = L / (u_d \cdot \mathbf{e}_z) \]

is the path length through the sample cell for the detection beam and

\[ R\hat{S}^-_{2D}(\omega_t, \omega_\tau; T) \]

is the attenuated rephasing 2D spectrum as described in the previous section. This is an approximation insofar as it substitutes the attenuation of the signal along the complex-valued central wave vector of the detection beam in the sample, \( \hat{k}^0_d(\omega_t) \), for the true signal attenuation, which involves a range of wave vectors and is dependent on the excitation frequencies.

**2.2.2.4 Time-referenced**

Neglecting the effects of signal field propagation, the time-referenced 2D spectrum is a direct reflection of the underlying bulk nonlinear polarization of the sample. This representation is calculated using

\[ \hat{E}^t_d(\omega_t) = \hat{E}^0_d(\omega_t) \exp \left\{ i \left[ \mathbf{k}^0_{sv}(-\omega_a, \omega_b, \omega_c) \cdot \mathbf{e}_z \right] L \right\} \]

(2.20)

as the form of the detection wave where \( \mathbf{k}^0_{sv} \) is the signal central wave vector in vacuum. The time-referenced rephasing 2D spectrum, \( R\hat{S}^t_{2D}(\omega_t, \omega_\tau; T) \), is calculated from eq. 2.11 by using eq. 2.20 as the detection wave in eq. 2.8 given that \( e(\omega_t) = |\hat{E}^0_d(\omega_t)| \).

\( R\hat{S}^t_{2D} \) can be calculated in an approximate way starting from \( R\hat{S}^0_{2D} \):

\[ R\hat{S}^t_{2D}(\omega_t, \omega_\tau; T) \approx R\hat{S}^0_{2D}(\omega_t, \omega_\tau; T) \]
\[ \cdot \exp \left\{ i \text{Re} \left[ \mathbf{k}^0_d(\omega_t) - \mathbf{k}^0_{dv}(\omega_t) \right] \cdot \mathbf{e}_z L \right\} \]

(2.21)

where \( \mathbf{k}^0_{dv} \) is the real-valued central wave vector of the detection beam in vacuum and \( \hat{k}^0_d \) is the complex-valued central wave vector of the detection beam in the sample. The exponential in eq. 2.21 approximates the FID phase due to the sample by using the central wave vector of the detection
beam, which depends on only one frequency, instead of the wave vector of the signal, which depends on all three excitation frequencies. This approximation, just as with eqs. 2.15 and 2.17, is valid for a well-collimated signal beam and becomes exact for collinear excitation beams at normal incidence.

Time-referenced 2DFT spectra have delays from the refractive index of the sample because they are time-referenced to when pulse \( c \) would emerge from the sample if it propagated through vacuum. The time-referenced and FID-referenced representations only differ in the phase of the detection field and, consequently, the phase of the 2DFT spectrum. Therefore, the absolute value 2DFT spectra in these representations are identical: \( |R\hat{S}^L_{2D}| = |R\hat{S}_0^0_{2D}| \). However, the phase differences between time-referenced and FID-referenced 2DFT spectra cause them to be affected differently by time domain filters.

2.2.3 Transformation of 2DFT Spectra

As demonstrated by Yetzbacher et al.,\textsuperscript{33} it is possible to transform calculated and experimental 2DFT spectra in such a way as to approximately remove the distortions caused by attenuation of excitation and signal fields. The result is the excitation–detection transformed 2D spectrum,

\[
\hat{S}^{++}_{2D}(\omega_t, \omega_\tau; T) = \frac{2 \text{Im} \left[ \hat{k}_0^0(\omega_\tau) \cdot e_z \right] L}{1 - \exp \left\{-2 \text{Im} \left[ \hat{k}_0^0(\omega_\tau) \cdot e_z \right] L \right\}} \cdot \exp \left\{ \text{Im} \left[ \hat{k}_d^0(\omega_t) \cdot e_z \right] L \right\} \cdot \hat{S}_0^0(\omega_t, \omega_\tau; T)
\]

\[
\approx \frac{2\omega_\tau \kappa(\omega_\tau) \ell/c}{1 - \exp \left[-2\omega_\tau \kappa(\omega_\tau) \ell/c \right]} \cdot \exp \left[ \omega_t \kappa(\omega_t) \ell/c \right] \cdot \hat{S}_0^0(\omega_t, \omega_\tau; T)
\]

(2.22)

where \( \hat{k}_\tau \) is the wave vector of the initial excitation pulse (\( \hat{k}_a \) or \( \hat{k}_b \)). The second expression in eq. 2.22 arises from approximating \( \hat{k}_0^0(\omega) \approx u \hat{n}(\omega) \omega/c \), which is valid as long as \( \kappa^2 \ll n^2 \) and the angle of incidence is small (i.e. \( u \approx e_z \)). In the rectangular BOXCARS geometry, 2\( \alpha \) and 2\( \beta \) are defined as the external crossing angles (in vacuum or air) between beams \( a \) and \( c \) (as well as \( b \) and
and beams \(a\) and \(b\) (as well as \(c\) and \(d\)) respectively. In this geometry, the path length through the sample is given by \(\ell = L/\gamma\) where \(\gamma = \mathbf{u} \cdot \mathbf{e}_z = (1 - \sin^2 \alpha - \sin^2 \beta)^{1/2}\) and is equal for all beams \((a, b, c, \text{ and } d)\), permitting use of the same \(\ell\) in eq. 2.22 for propagation along both the excitation dimension \((\omega_t)\) and the detection dimension \((\omega_r)\). Equation 2.22 neglects vacuum phase mismatch so that \(\mathbf{u}_s \approx \mathbf{u}_d\). A reformulation of eq. 2.22 in terms of the absorbance of the sample is given by

\[
\hat{S}_{2D}^{++}(\omega_t, \omega_r; T) \approx \frac{A(\omega_r) \ln(10)/\gamma}{1 - 10^{-A(\omega_r)/\gamma}} \cdot 10^{A(\omega_t)/(2\gamma)} \cdot \hat{S}_{2D}^0(\omega_t, \omega_r; T)
\]

where \(A(\omega)\) is the decadic absorbance at normal incidence. In the limit of no coherence (i.e. \(\omega_t = \omega_c\) and \(\omega_a = \omega_b\)), eqs. 2.22 and 2.23 recover the ideal 2DFT spectrum, \(\hat{S}_{2D}^{\text{ideal}}\).

2.2.4 Analytic Bloch Model 2DFT Spectrum

An analytic form is known for the impulsive correlation and relaxation 2DFT peak shapes of the homogeneous optical Bloch model.\(^{64}\)

\[
\hat{S}_{2D}^{\text{ideal}}(\omega_t, \omega_r, T) \propto a(-\omega_r)a(\omega_t) - ia(-\omega_r)d(\omega_t) + \frac{1}{2} \delta(T) [a(-\omega_r)a(\omega_t) + d(-\omega_r)d(\omega_t) - ia(-\omega_r)d(\omega_t) + id(-\omega_r)a(\omega_t)] + a(\omega_r)a(-\omega_t) + ia(\omega_r)d(-\omega_t) + \frac{1}{2} \delta(T) [a(\omega_r)a(-\omega_t) + d(\omega_r)d(-\omega_t) + ia(\omega_r)d(-\omega_t) - id(\omega_r)a(-\omega_t)]
\]

(2.24)

where

\[
a(\omega) = \frac{\Gamma^2}{(\omega_{eg} - \omega)^2 + \Gamma^2}
\]

(2.25)

and

\[
d(\omega) = \frac{(\omega_{eg} - \omega) \Gamma}{(\omega_{eg} - \omega)^2 + \Gamma^2}
\]

(2.26)
are Lorentzian absorptive and dispersive lineshape functions, respectively, with central transition frequency $\omega_{eg}$ and width defined by $\Gamma$, the Bloch microscopic dipole decay rate. $\Gamma$ is equal to the half-width half-maximum (HWHM) of a Lorentzian absorptive lineshape and is the inverse of the dipole decay (or dephasing) time: $\Gamma = 1/T_2$. Equations 2.25 and 2.26 differ from eq. 18 of Gallagher Faeder and Jonas\textsuperscript{64} in that they have been peak normalized through multiplication by $\Gamma$. Here, “impulsive” is used to signify that pulses $a$, $b$, and $c$ have $\delta$-function time domain profiles. Although the analytic 2DFT peak shape in eq. 2.24 is a sum of product lineshapes that have no correlation between the two dimensions $\omega_\tau$ and $\omega_t$, the 2DFT peak shape does exhibit correlation at $T = 0$. This analytic form is useful in that it can be compared to numerical calculations to confirm that they accurately reproduce the spectral lineshape in the Bloch limit, which serves as a basis for understanding more complex coherent phenomena that occur as a function of $T$ with the introduction of propagation distortions.

For the homogeneous optical Bloch model, the absolute value of the impulsive rephasing 2DFT peak shape experimentally measured by Li et al.\textsuperscript{6} is given by

$$
\left| R_{2D}^{\text{ideal}}(\omega_t, \omega_\tau, T) \right| \propto \sqrt{a(\omega_\tau)} a(\omega_t) \propto \left[ \frac{\Gamma^2}{(\omega_{eg} - \omega_\tau)^2 + \Gamma^2} \cdot \frac{\Gamma^2}{(\omega_{eg} - \omega_t)^2 + \Gamma^2} \right]^{1/2}
$$

(2.27)

with FWHM = $2\sqrt{3}\Gamma$ in both the $\omega_t$ and $\omega_\tau$ dimensions (a $\sqrt{3}$ increase in linewidth for both dimensions compared to the real 2DFT relaxation spectrum). As will be shown below, the distortions of 2D peak shapes in absolute value rephasing spectra are more complicated than those for 2D peak shapes in relaxation spectra.
2.2.5 Incoherent 2D Propagation Function

Multiplying the propagation function in eq. 2.5 by the complex conjugate of the propagation factor for the detection field, \( \exp[i \text{Re}(\hat{k}_s^0 \cdot \mathbf{e}_z) L^*] \), as indicated by eqs. 2.4 and 2.17, yields

\[
\Pi_{\text{exit}}^{(3)}(\hat{k}_a^0, \hat{k}_b^0, \hat{k}_c^0, L) \exp \left[ -i \text{Re} \left( \hat{k}_s^0 \cdot \mathbf{e}_z \right) L \right] = \frac{\omega_t}{(\hat{k}_s^0 \cdot \mathbf{e}_z) c} \exp \left[ -2 \omega_t \kappa_z(\omega_t) / c \right] \cdot \exp \left[ -\text{Im} \left( \hat{k}_s^0 \cdot \mathbf{e}_z \right) L \right] - 1
\]

(2.28)

This form of the propagation function is specific to FID-referenced 2DFT spectra. Incorporating eqs 44 and 47 of ref. 7 for \( \hat{k}_s^0 \) and \( \Delta \hat{k}_s^0 \) plus the three assumptions listed below, the 3D propagation function in eq. 2.28 can be simplified to a 2D function of \( \omega_T \) and \( \omega_t \). First, the signal is assumed to be generated in the incoherent limit where \( \omega_a = \omega_b = \omega_T \) and \( \omega_c = \omega_t \). Second, it is assumed that the sample is weakly absorbing \( (\kappa^2 \ll n^2) \) such that the approximate form of the wave vector in eq. 2.3 is valid. Third, \( \hat{n}_{zs} \) and \( \hat{n}_z \) are approximated as equal, which assumes that \( |4(\omega_T/\omega_t)(1 - \omega_T/\omega_t)\sin^2 \beta| \ll 1 \) (i.e. the limit of small fractional bandwidth \( \Delta \omega / \omega \) and small angles of incidence). Under these conditions, eq. 2.28 simplifies to

\[
\Pi_{\text{2D}}(\omega_t, \omega_T, L) = \frac{1}{\hat{n}_{zs}(\omega_t)} \frac{\exp \left[ (-2\omega_T \kappa_z(\omega_T) / c) L \right] - 1}{\exp \left[ -2\omega_T \kappa_z(\omega_T) / c \right]} \cdot \exp \left[ -\text{Im} \left( \omega_t \hat{n}_z(\omega_t) / c \right) L \right]
\]

(2.29)

The factor of \( 1/\hat{n}_{zs}(\omega) \) arises from the boundary conditions for Maxwell’s equations at the sample–window interfaces.\(^7\) Substituting \( \kappa_z(\omega) = \kappa(\omega) \ell / L \) as implied by eqs 41 and 42 of ref. 7, we arrive at the incoherent propagation function appropriate for FID-referenced 2DFT spectra,

\[
\Pi_{\text{2D}}(\omega_t, \omega_T, L) = \frac{L}{\hat{n}_{zs}(\omega_t)} \frac{\exp \left[ -2\omega_T \kappa(\omega_T) \ell / c \right] - 1}{\exp \left[ -2\omega_T \kappa(\omega_T) \ell / c \right]} \cdot \exp \left[ -\omega_T \kappa(\omega_T) \ell / c \right]
\]

(2.30)

All factors besides \( L/\hat{n}_{zs}(\omega) \) represent absorptive propagation distortions and tend to unity as the sample length tends to zero.\(^6\)\(^5\) \( \hat{n}_{zs}(\omega) \) physically represents the effective complex-valued refractive
index for the z-component of propagation of the signal field and is applicable to pulses with arbitrary angles of incidence $\alpha$ and $\beta$ (see eq. 41 of ref. 7). The imaginary component of the complex-valued refractive index can be expressed in the convenient form

$$
\kappa(\omega) = \frac{c}{\omega_{eg}} \alpha_{\text{max}} a(\omega) \tag{2.31}
$$

where $\alpha_{\text{max}} = a(\omega_{eg})$ is the peak attenuation coefficient. $a(\omega)$ is the absorptive lineshape function which, for the homogeneous Bloch model, is given by eq. 2.25. The propagation function in eq. 2.30 is almost the inverse of the excitation–detection transformation in eq. 2.22, but differs by a factor of $L/\hat{n}_{zs}(\omega_t)$ which can contribute a phase shift from the sample–window interfaces when $\kappa$ is not negligible compared to $n$. In the incoherent limit, the FID-referenced 2DFT spectrum becomes

$$
\hat{S}_{2D}^0(\omega_t, \omega_\tau; T) \approx \hat{S}_{2D}^{\text{ideal}}(\omega_t, \omega_\tau, T)
\cdot \frac{\Pi_{2D}^0(\omega_t, \omega_\tau, L)}{\Pi_{\text{exit}}^{\text{ideal}}(L)} \tag{2.32}
$$

where $\Pi_{\text{exit}}^{\text{ideal}}(L) = \ell$ in the rectangular BOXCARS geometry.

To calculate the attenuated 2DFT spectrum starting from eq. 2.24, the factor of $\exp\{-\text{Im}[\hat{k}_0^0(-\omega_a, \omega_b, \omega_c) \cdot \mathbf{e}_z] L\}$ is incorporated into the propagation function, resulting in a form that is specific to the attenuated 2DFT spectrum:

$$
\Pi_{2D}^-(\omega_t, \omega_\tau, L) = \frac{L}{\hat{n}_{zs}(\omega_t)} \frac{\exp[-2\omega_\tau \kappa(\omega_\tau)\ell/c] - 1}{-2\omega_\tau \kappa(\omega_\tau)\ell/c} \tag{2.33}
\cdot \exp[-2\omega_t \kappa(\omega_t)\ell/c]
$$

The modified propagation function in eq. 2.33, when applied to the analytic 2DFT signal calculated using eq. 2.24, yields

$$
\hat{S}_{2D}^-(\omega_t, \omega_\tau; T) \approx \hat{S}_{2D}^{\text{ideal}}(\omega_t, \omega_\tau, T)
\cdot \frac{\Pi_{2D}^-(\omega_t, \omega_\tau, L)}{\Pi_{\text{exit}}^{\text{ideal}}(L)} \tag{2.34}
$$

The analytic expressions in eqs. 2.32 and 2.34 are useful for comparison to numerical calculations of $\hat{S}_{2D}^0$ and $\hat{S}_{2D}^-$ respectively, which should match the analytic results for the limit in which
both \( T \gg T_2 \) and \( 2T_1 \gg T_2 \). While likely more stringent than necessary, these two conditions are sufficient to guarantee that \( \hat{S}_{2D}(\omega_t, \omega_\tau; T) \propto \int_{-\infty}^{\infty} \hat{S}_{2D}(\omega_t, \omega_\tau; T) \, dT \). By the projection–slice theorem,\(^{63,66}\) this proportionality to the waiting-time–averaged 2DFT spectrum guarantees that a 2DFT spectrum has \( \omega_T = |\omega_a - \omega_b| = 0 \), implying \( \omega_a = \omega_b \) and, consequently, \( \omega_c = \omega_t \). In this circumstance, the analytic form of the propagation function in eqs. 2.30 and 2.33 must be valid for any relaxation model. These two conditions imply both that the waiting time must be long enough that all dynamics in \( T \) are finished (\( T \gg T_2 \)) and that the lifetime is sufficiently long that incoherent population relaxation completely dominates the time-averaged 2DFT spectrum (\( 2T_1 \gg T_2 \)).

2.3 Computation

2.3.1 Methods

The program used to calculate 2DFT spectra was written in Fortran 95/2003 and compiled using the Intel Visual Fortran Compiler Professional 11.1.070.\(^{67}\) This program was executed on a computer with a 3.2 GHz Core i7 processor and 24 GB of random access memory (RAM) running 64-bit Windows 7 Professional. The calculations utilized a grid size of 1024\(^3\), where each grid point is a complex, double-precision number, requiring a total of \( \sim 17 \) GB of RAM and \( \sim 8 \) min of execution time. Complex, double-precision Fourier transforms were accomplished using the DFFT3B, DFFT3F, DFFT2B, and DFFT2F subroutines of the International Mathematics and Statistics Library (IMSL) Fortran Numerical Library version 6.0.\(^{68}\)

2.3.2 Approximations

While the effects of finite-bandwidth excitation pulses are easily handled in the 3DFT approach, excitation pulses have been approximated as delta-function pulses. This is a good approximation for this study since the bandwidth of the excitation pulses (\( \Delta \omega_{FWHM}/2\pi c \approx 126 \) cm\(^{-1}\)) is 250 times greater than the linewidth of the D\(_2\) transition (\( \Delta \omega_{FWHM}/2\pi c \approx 0.5 \) cm\(^{-1}\)). The effects of this approximation are even smaller than the effects of neglecting the directional filtering
distortions discussed previously. Over the frequency range shown, the maximum fractional error in the linear susceptibility from the rotating-wave approximation is less than $10^{-4}$, so rotating-wave errors in the 2DFT spectrum are expected to be negligible. The expressions for testing the validity of the 3DFT approach developed by Yetzbacher et al. indicate that the conditions of the experiment by Li et al. satisfy the essential assumptions implicit in the 3DFT theory with one exception: significant error arises from the assumption that excitation beams have complete transverse overlap, as will be discussed below.

2.3.3 Estimation of Convergence

To characterize the error associated with using a discrete and finite-size grid in these calculations, four types of convergence tests were performed. First, the effect of using a grid with a finite time range was explored by comparing two $\tilde{S}_{2D}$ absolute value 2DFT spectra calculated using different grid sizes ($512^3$ vs $1024^3$) with identical time domain sampling intervals. The two compared spectra have the same frequency range because they have the same time step size, but have frequency step sizes differing by a factor of 2 due to their different time ranges. This type of comparison is used to expose problems associated with finite frequency resolution and, equivalently, a finite time range. The percent difference between 2DFT spectra calculated on the two grid sizes is determined by subtracting the absolute value spectra at common $(\omega_r, \omega_t)$ grid points and then dividing by the global maximum of the 2DFT spectrum. For all calculations reported here, the difference between these absolute value spectra at any point is less than 1.5% of the maximum. This error appears as ringing along the 2D diagonal.

Second, the effect of using a grid of discrete time points was tested by comparing two $\tilde{S}_{2D}$ absolute value 2DFT spectra, one on a $1024^3$ grid and the other on a $512^3$ grid with double the time step size. Since both spectra have the same time range, they have an identical frequency step size. However, the spectra have different time step sizes, resulting in different frequency ranges. This comparison is meant to uncover errors related to the finite frequency range and, equivalently, the finite time resolution of the calculation. In order to compare the two spectra, the spectrum
calculated using a 1024$^3$ grid is cropped to the same frequency range as the spectrum calculated on a 512$^3$ grid. For all calculations reported here, the difference between these absolute value spectra at any point is less than 4.5% of the maximum. Consistent with eq. 2.24, this error arises from the imaginary (refractive) peak shape at the edge of the grid as discussed in Comparison to Analytic Theory.

Third, the deviation caused by using a long excited state population lifetime ($T_1 = 30$ ns in most simulations) compared to the time range of the 3DFT grid ($\sim 0.87$ ns in most simulations) has been characterized. To adequately resolve sharp features in the core of the 2D peak shape, which are dominated by fast dephasing dynamics ($\lesssim 20$ ps for the D$_2$ transition of Rb under the conditions of interest here$^6$) and propagation distortions, a grid step size of 850 fs was used in most of the simulations. To quantify the effect of time domain truncation of slow excited state population relation dynamics, a 2DFT spectrum simulated directly at $T_1 = 30$ ns was compared to a 2DFT spectrum that was point-by-point linearly extrapolated, as a function of $1/T_1$, from $T_1 = 120$ ps and $T_1 = 240$ ps to $T_1 = 30$ ns. In both cases, the spectra were absolute value time-referenced rephasing 2DFT spectra ($|\hat{R}^{t_{\text{2D}}}_S|$) with OD$_{\text{max}} = 1.14$; grid time step, 850 fs; grid size, 1024$^3$; dephasing rate, $\Gamma/2\pi c = 0.265$ cm$^{-1}$; center frequency, $\omega_{eg}/2\pi c = 12816.7$ cm$^{-1}$; mixing time, $T = 850$ fs; sample thickness, $L = 500$ µm; and crossing angles, $\alpha = \beta = 4.84^\circ$. The maximum absolute deviation between the 2DFT spectrum extrapolated to $T_1 = 30$ ns from untruncated time domain data and that calculated directly at $T_1 = 30$ ns is less than 0.5% of the maximum.

Fourth, the effect of using a longer waiting time ($T = 850$ fs in most simulations) than that of the experiment ($T = 200$ fs) was determined. Since the nonlinear polarization is calculated on a 3D grid of evenly spaced time/frequency points, choice of waiting times is restricted to integer multiples of the grid time step size. To quantify the difference between simulations at the experimental waiting time versus a longer waiting time, 2DFT spectra simulated at $T = 200$ fs and a grid time step of 200 fs were compared to 2DFT spectra simulated at $T = 850$ fs and a grid time step of 850 fs. In both cases, the spectra were absolute value time-referenced rephasing 2DFT spectra ($|\hat{R}^{t_{\text{2D}}}_S|$) with OD$_{\text{max}} = 1.14$; grid size, 1024$^3$; dephasing rate, $\Gamma/2\pi c = 0.265$ cm$^{-1}$; excited state
lifetime, $T_1 = 30$ ns; center frequency, $\omega_{eg}/2\pi c = 12816.7$ cm$^{-1}$; sample thickness, $L = 500$ µm; and crossing angles, $\alpha = \beta = 4.84^\circ$. The maximum absolute deviation between these 2DFT spectra is less than 3.6%. This difference is largely the result of the two 2DFT spectra having dissimilar frequency ranges and is consequently isolated to the wings of the 2D peak shape. Deviations within the core of the peak are less than 1.5% of the maximum.

### 2.3.4 Comparison to Analytic Theory

The convergence tests above quantify the deficiencies of the second most converged calculation. Comparisons to analytic theory are used to assess the absolute accuracy of the most converged calculations in specific limits. The analytic form of the impulsive Bloch 2DFT spectrum in eq. 2.24 can be used to calculate spectra for comparison to spectra calculated using the 3DFT method with $OD = 0$. This comparison can serve as a test that the 3DFT calculation accurately reproduces the peak shape of the Bloch 2DFT spectrum when propagation distortions are absent.

Analytic 2DFT spectra that include propagation distortions have also been derived above for checking numerical results. The 2D form of the propagation function presented in eq. 2.33 is valid in the limit that $T \gg T_2$ and $2T_1 \gg T_2$. The 2D propagation function (eq. 2.33) can be multiplied by the analytic impulsive Bloch 2DFT spectrum (eq. 2.24) to produce an analytic $\hat{S}_{2D}$ spectrum (eq. 2.34) for comparison to $\hat{S}_{2D}$ spectra calculated numerically using the 3DFT method. The results of this comparison are shown in Figure 2.1 for $OD_{max} = 1$. The primary difference between the analytic $\hat{S}_{2D}$ spectrum in Figure 2.1a and the numerical $\hat{S}_{2D}$ spectrum in Figure 2.1b is that the wings of the lineshape in the $\omega_t$ dimension of the numerical spectrum are lower than those of the analytic spectrum. This effect becomes more pronounced with increasing $|\omega_t - \omega_{eg}|$ and reaches a value of 4.2% at the edge of the plot.

Given that the majority of the spectral amplitude in the wings of a Bloch lineshape is in the imaginary part, which contains information regarding refractive effects that are dominated by short-time dynamics, most of the disagreement between the analytic and numerical spectra in Figure 2.1 is confined to the imaginary part of the spectrum. The real parts of the numerical and
Figure 2.1: Absolute value 2DFT relaxation spectra for Bloch model in the $\hat{S}_{2D}$ representation (a) calculated using the analytic form of the 2DFT spectrum in eq. 2.34 and (b) calculated numerically from eq. 2.8 and eq. 2.15. The scaled difference between spectra in (a) and (b), calculated according to $|\text{(a)} - \text{(b)}| \times 10$, is presented in (c). Peak optical density, $OD_{\text{max}} = 1$; grid time step, 850 fs; grid size, $1024^3$; dephasing rate, $\Gamma/2\pi c = 0.265 \text{ cm}^{-1}$; excite state lifetime, $T_1 = 30 \text{ ns}$; center frequency, $\omega_{eg}/2\pi c = 12816.7 \text{ cm}^{-1}$; waiting time, $T = 100.3 \text{ ps}$; sample thickness, $L = 500 \mu\text{m}$; and crossing angles, $\alpha = \beta = 4.84^\circ$. There are 19 contours, evenly spaced every 5\% from 5\% to 95\%, in (a) and (b) but only 8 contours, spaced every 0.5\%, in (c). The dotted line indicates the diagonal: $\omega_t = -\omega_r$. 
analytic $\hat{S}_{2D}^-$ spectra differ by less than 0.7% for $OD_{\text{max}} = 1$.

The differences in Figure 2.1 are an artifact of the Fourier-transform since they occur near the edges of the 2DFT grid where the signal amplitudes must be equal due to the cyclic nature of the conjugate axis in the FFT algorithm (see Figure 11.4 of ref. 63). Since the FFT of a real-valued time domain signal obeys $\hat{S}(-\omega) = \hat{S}^*(\omega)$, the imaginary part of the frequency domain spectrum has odd symmetry and, therefore, must tend towards zero at the edge of the frequency domain grid. The magnitude of this artifact will be negligible in the limit that the frequency range of the 3DFT grid is much greater than the linewidth of the spectrum.

Motivated by the disagreement between experiment and simulation with regard to the magnitude of absorptive distortions at a given optical density, a comparison between 2D propagation function “spectra” calculated by the 3DFT method and those calculated from a simple analytic expression was undertaken to verify, at least in the incoherent limit, that the 3DFT method correctly accounts for the magnitude of signal attenuation. When $2T_1 \gg T_2$ and $T \gg T_2$, signal generation is restricted to cases where $\omega_a = \omega_b$. In this limit, the ratio $\hat{S}_{2D}^- / \hat{S}_{2D}^{\text{ideal}}$ approaches the incoherent propagation function:

$$
\lim_{\omega_a \to \omega_b} \frac{\hat{S}_{2D}^-(\omega_t, \omega_r; T)}{\hat{S}_{2D}^{\text{ideal}}(\omega_t, \omega_r; T)} = \frac{\Pi_{-2D}^- (\omega_t, \omega_r, L)}{\Pi_{\text{exit}}^{\text{ideal}} (L)} \ell
$$

(2.35)

In the incoherent limit, the ratio of complex valued 2DFT spectra in eq. 2.35 becomes equal to the ratio of absolute value 2DFT spectra if the phase introduced by $\hat{n}_{zs}$ can be neglected over the entire frequency range in eq. 2.33. Figure 2.2a shows the 2D version of the propagation function calculated using the ratio of absolute value numerical 2DFT spectra indicated by the left-hand side of eq. 2.35, where $\hat{S}_{2D}^{\text{ideal}}(\omega_t, \omega_r; T)$ is calculated as $\hat{S}_{2D}^0(\omega_t, \omega_r; T)$ with $OD_{\text{max}} = 0$ (see eq. 2.12). A plot of the ratio of absolute value analytic propagation functions indicated by the right-hand side of eq. 2.35 is almost visually identical to Figure 2.2a. Figure 2.2b depicts the difference (multiplied by a factor of 100) between the numerical 2D propagation function (ratio of absolute value 2DFT spectra indicated by the left-hand side of eq. 2.35) and the analytic 2D propagation function in
Figure 2.2: The 2D propagation function, $|\Pi_{2D}(\omega_t, \omega_\tau, L)/\ell|$, for the $\hat{S}_{2D}$ representation. Panel (a) is calculated with the Bloch model from the ratio of absolute value numerical 2DFT spectra given by eq. 2.35. The absolute value of the difference between the numerical propagation function in (a) and the absolute value of the analytic form given by eq. 2.33 is multiplied by 100 in panel (b). Peak optical density, $OD_{\text{max}} = 1$; grid time step, 850 fs; grid size, $1024^3$; dephasing rate, $\Gamma/2\pi c = 0.265$ cm$^{-1}$; dephasing time, $T_2 (= 1/\Gamma) = 20$ ps; excited state lifetime, $T_1 = 30$ ns; center frequency, $\omega_{eg}/2\pi c = 12816.7$ cm$^{-1}$; waiting time, $T = 100.3$ ps; sample thickness, $L = 500$ µm; and crossing angles, $\alpha = \beta = 4.84^\circ$. There are 100 color levels, meaning that each color represents a 1% range. There are 9 contours in panel (a), evenly spaced every 10% from 10% to 90%. The dotted line indicates the diagonal: $\omega_t = -\omega_\tau$. 

$\frac{\omega_t - \omega_\tau}{2\pi c}$ (cm$^{-1}$)

$\frac{\omega_\tau + \omega_\tau}{2\pi c}$ (cm$^{-1}$)
the incoherent limit, \( \Pi_{2D}/\ell \) (ratio of absolute value 2D propagation functions indicated by the right-hand side of eq. 2.35), where \( \Pi_{2D} \) is calculated using eq. 2.33. Given that \( T_1 = 1500T_2 \), a converged accuracy limit for this comparison is likely set by the use of \( T \approx 5T_2 \) in Figure 2.2a.

For frequencies where the distorted 2DFT signal (\( |\hat{S}_{2D}^-| \)) is above the 5% level, the difference shown in Figure 2.2b never exceeds 0.07%. At the extremes of the diagonal, a ringing artifact of the discrete Fourier-transform is visible with an amplitude of up to \( \sim 0.6\% \). Ringing, which is more pronounced along the diagonal than the antidiagonal in Figure 2.2c, only appears in the numerical 2D propagation function (eq. 2.35) and only at frequencies far from resonance, where the artifact is non-negligible compared to the amplitude of the signal. The difference has a local minimum along each dimension at \( |\omega| = \omega_{eg} \).

Equation 2.35 can simplified for the case \( -\omega_\tau = \omega_\ell = \omega_{eg} \) given that \( \hat{n}_{zs} = \hat{n}_z \) under these conditions. This yields the attenuation at peak center for \( \hat{S}_{2D}^- \) 2DFT spectra in the incoherent limit,

\[
\left| \frac{\Pi_{2D}(\omega_{eg}, \omega_{eg}, L)}{\Pi_{\text{ideal}}(L)} \right| = \frac{\gamma}{|\hat{n}_z(\omega_{eg})|} \frac{1 - 10^{-A(\omega_{eg})/\gamma}}{10^{-A(\omega_{eg})/\gamma}}
\]

(2.36)

where \( A(\omega_{eg}) = \text{OD}_{\text{max}} \) is the decadic absorbance (optical density) of the sample at normal incidence and \( \gamma = (1 - \sin^2 \alpha - \sin^2 \beta)^{1/2} \) accounts for the additional path length at oblique incidence (see eq. 2.23). When at least one of \( -\omega_\tau = \omega_\ell \) (i.e. \( \omega_a = \omega_b = \omega_c \)) or \( \beta = 0 \) is true, using \( \hat{n}_z \) in place of \( \hat{n}_{zs} \) is exact, as is the case in eq. 2.36. The single-point attenuation in eq. 2.36 can be readily calculated by hand to check a more complicated 3DFT code. For an optical density of 1, the ratio \( |\hat{S}_{2D}^-|/|\hat{S}^\text{ideal}_{2D}| = |\Pi_{2D}^-|/|\Pi_{\text{ideal}}| \) at the peak center in Figure 2.2b (0.03828 ± 0.00003) is only 0.11% higher than the attenuation predicted by eq. 2.36 using the same parameters (0.03824), a discrepancy attributable to ringing. Inverting the numerical ratio of \( |\Pi_{2D}^-|/|\Pi_{\text{ideal}}| = 0.03828 \) using eq. 2.36 with \( \hat{n}_z(\omega_{eg}) = 0.9929 + 0.0003i \) and \( \gamma = 0.9929 \) yields \( \text{OD}_{\text{max}} = 0.9997 \pm 0.0003 \) (which agrees within error with \( \text{OD}_{\text{max}} = 1 \)). The attenuation factors appearing in eqs. 2.35 and 2.36 have been experimentally tested to 10% accuracy in frequency integrated pump-probe experiments for peak optical densities of up to 1 (see the absorption coefficient dependent terms in eqs. 24 and 26).
of ref. 34).

The comparison in Figures 2.1 shows that our calculations by the 3DFT method quantitatively reproduces the Bloch lineshape of an undistorted 2DFT spectrum. Likewise, the comparison in Figure 2.2 between the incoherent 2D propagation function calculated by the 3DFT program and that calculated using the analytic expression in eq. 2.33 demonstrates quantitative agreement, matching in signal attenuation over the entire range of relevant frequencies at a peak optical density of 1. This agreement with experimentally tested expressions confirms that the 3DFT program properly accounts for the magnitude of propagation distortions given the sample’s optical density. This rules out many possible errors in the program’s code as causes of disagreement between experiment and simulation. This comparison does not ensure the accuracy of coherent propagation effects at waiting times that are not long compared to the total dephasing time (i.e. \( T \gg T_2 \)).

2.4 Results

Line broadening coefficients reported from frequency domain experiments\textsuperscript{10,11,15,70–72} at Ar buffer gas pressures from 0 atm to 100 atm indicate that at the buffer gas and Rb vapor pressures deduced from the experimental temperatures,\textsuperscript{6} line broadening is dominated by non-resonant, binary Rb–buffer collisions. This, along with the Lorentzian lineshape and simulations of prior time-resolved experiments\textsuperscript{38,58} on alkali metal vapors with Bloch models, motivated use of an optical Bloch model that describes the lineshape of the Rb D\textsubscript{2} transition with a single, homogeneous broadening timescale, \( T_2 \). This timescale enters the Bloch model as the dipole decay rate (or total dephasing rate) \( \Gamma = 1/T_2 \) in the exponential decay of dipole oscillations \( \mu(t) = \mu_0 \sin(\omega_{eg}t) \exp(-\Gamma t) \).

A total dephasing time \( T_2 = 20 \) ps, corresponding to a dipole decay rate of \( \Gamma = 50 \) rad/ns and a Lorentzian absorption lineshape\textsuperscript{72} with FWHM = \( \Gamma/(\pi c) = 0.53 \) cm\textsuperscript{-1}, was used for the calculations presented here. All plots of 2DFT spectra presented here have been peak normalized. This normalization means that comparison of different spectra based on apparent integrated intensity or peak height is not possible since these properties are not indicated by the plots even though the underlying calculations contain such information. When varying the optical density of sim-
Figure 2.3: Absolute value rephasing 2DFT spectra ($R_{2D}t$ representation) for Bloch model with peak optical densities of (a) 0, (b) 0.14, (c) 0.59, and (d) 1.14. Grid time step, 500 fs; grid size, $1024^3$; dephasing rate, $\Gamma/2\pi c = 0.265$ cm$^{-1}$; excited state lifetime, $T_1 = 30$ ns; center frequency, $\omega_{eg}/2\pi c = 12816.7$ cm$^{-1}$; waiting time, $T = 500$ fs; sample thickness, $L = 500$ µm; and crossing angles, $\alpha = \beta = 4.84^\circ$. There are 19 contours, evenly spaced every 5% from 5% to 95%. The dotted line indicates the diagonal: $\omega_t = -\omega_\tau$. The inset in (d) is an expanded view of the peak center.
ulated 2DFT spectra, only the strength of the linear response, the source of certain propagation
distortions, is modified. The nonlinear response is held constant, meaning that changes in optical
density do not affect the strength of signal generation within the sample. Experimentally, this
would require a sample in which the nonlinear response comes from a different chromophore than
the linear response so that they could be varied independently.

The time-referenced 2DFT rephasing spectra in Figure 2.3 illustrate the effects of increasing
OD and can be compared to the experimental spectra in Figure 3 of ref. 6, but have one difference:
$T = 500$ fs in the calculation vs. $T = 200$ fs in the experiment. The undistorted 2DFT spectrum in
Figure 2.3a exhibits a star-shaped 2D Lorentzian lineshape which is symmetric in width between
the $\omega_\tau$ and $\omega_t$ dimensions, both of which directly reflect the underlying dipole decay rate. This
symmetry is a property of rephasing 2DFT spectra and is not observed in 2DFT relaxation spectra,
which included both positive and negative $\tau$ values and are naturally wider in $\omega_t$. While increasing
the optical density in the subsequent spectra of Figure 2.3 causes the lineshape to broaden in both
dimensions, the width in $\omega_t$ increases at a greater rate than that in $\omega_\tau$. The resulting lineshape
asymmetry, barely visible at a peak optical density of 0.14, is pronounced by the time the optical
density reaches 0.59. Although the $\text{OD}_{\text{max}} = 0.14$ spectrum is arguably in agreement with the
undistorted spectrum, by $\text{OD}_{\text{max}} = 0.59$ this is clearly not the case as the lineshape in Figure 2.3c
has been broadened considerably and also shows signs of peak splitting due to an absorptive dis-
tortion at $\omega_t \approx \omega_{eg}$. The $\text{OD}_{\text{max}} = 1.14$ spectrum is broader still and its peak is split in the $\omega_t$
dimension down to the 70% contour. Looking closely at the line center in the inset of Figure 2.3d,
there is a subtle clockwise twisting of the lineshape, whereby the two halves of the split peak have
rotated towards the diagonal and are no longer displaced from each other just along $\omega_t$, but also
slightly along $\omega_\tau$. This may arise from an effect known as “phase-twist”\textsuperscript{2,4} which, for an undistorted
homogeneous optical Bloch lineshape, occurs only at $T = 0$ and is the result of mixing between the
absorptive and dispersive components of the lineshape.\textsuperscript{64}
Figure 2.4: Absolute value rephasing 2DFT spectra ($R\hat{S}_t^{2D}$ representation) for Bloch model with waiting times a) $T = 0.85$ ps, b) $T = 8.5$ ps, and c) $T = 85$ ps. Peak optical density, $OD_{\text{max}} = 1$; grid time step, 850 fs; grid size, $1024^2$; dephasing rate, $\Gamma/2\pi c = 0.265$ cm$^{-1}$; dephasing time, $T_2 (= 1/\Gamma) = 20$ ps; excited state lifetime, $T_1 = 240$ ps; center frequency, $\omega_{eg}/2\pi c = 12816.7$ cm$^{-1}$; sample thickness, $L = 500$ µm; and crossing angles, $\alpha = \beta = 4.84^\circ$. There are 19 contours, evenly spaced every 5% from 5% to 95%. The dotted line indicates the diagonal: $\omega_t = -\omega_r$. Dotted grid lines mark 0.5 cm$^{-1}$ increments.
Figure 2.5: Absolute value rephasing 2DFT spectra ($\hat{R}\hat{S}_{2D}$ representation) for Bloch model with excited state lifetimes a) $T_1 = 30$ ps, b) $T_1 = 60$ ps, and c) $T_1 = 240$ ps, all at waiting time $T = 0.85$ ps. Peak optical density, $OD_{\text{max}} = 1$; grid time step, 850 fs; grid size, $1024^3$; dephasing rate, $\Gamma/2\pi c = 0.265$ cm$^{-1}$; dephasing time, $T_2 (= 1/\Gamma) = 20$ ps; center frequency, $\omega_{eg}/2\pi c = 12816.7$ cm$^{-1}$; sample thickness, $L = 500$ µm; and crossing angles, $\alpha = \beta = 4.84^\circ$. There are 19 contours, evenly spaced every 5% from 5% to 95%. The dotted line indicates the diagonal: $\omega_t = -\omega_r$. Dotted grid lines mark 0.5 cm$^{-1}$ increments.
2.4.1 Lifetime and Waiting Time Dependence of Propagation Distortions

The 2D lineshape of an optically thin sample with Bloch model dynamics has no waiting time \((T)\) dependence outside of pulse overlap due to the lack of frequency memory. However, samples with finite optical density distort their excitation pulses, spreading them out in time in a frequency dependent way, such that time intervals between field–matter interactions within the sample (and even their time-ordering) are not necessarily the same as for the excitation pulses at the sample entrance, introducing distortions of the 2D lineshape that are dependent on both the waiting time \((T)\) and the excited state lifetime \((T_1)\). The effect is most pronounced when \(T\) and \(T_1\) are on the order of \(T_2\) such that a non-negligible component of the linear free-induction decay from pulses \(a\) and \(b\) persists through the waiting period until the arrival of pulse \(c\). This distortion only vanishes at long \(T\) (i.e. \(T \gg T_2\)) in the limit that \(2T_1 \gg T_2\), at which point lifetime dephasing is no longer competitive with pure dephasing.

An unintuitive consequence of this phenomenon is that the signal at off-resonant frequencies can be absolutely larger for a sample with a larger linear attenuation compared to a sample with a smaller linear attenuation but the same nonlinear response. As long as the excited state lifetime and the waiting time are of similar magnitudes, the wings of a distorted 2DFT spectrum can be enhanced compared to an undistorted 2DFT spectrum.

Figure 2.4 illustrates the waiting time \((T)\) dependence of the absolute value rephasing 2DFT spectra for an optically thick sample at a fixed value of \(T_1\). Three distinct effects can be noted. First, the diagonal twisting of the split peak decreases with increasing \(T\). This is expected since phase-twist occurs during pulse overlap (i.e. from \(T = 0\) until \(T \gg T_2\)). Second, the lineshape subtly narrows along the \(\omega_t\) dimension with increasing \(T\), a signature which is most apparent in the lower contours. Third, and perhaps most interesting, the depth of the absorptive distortion at \(\omega_t \approx \omega_{eg}\) decreases as \(T\) increases. Going from \(T = 0.85\) ps to \(T = 85\) ps, the valley at \(\omega_t \approx \omega_{eg}\) becomes shallower by about one 5% contour. This suggests that the severity of absorptive distortions at line center might be reduced by measuring 2DFT spectra at longer \(T\) where the trailing FID from
pulses $a$ and $b$ is no longer present.

The excited state lifetime ($T_1$) dependence of 2DFT spectra at $T \ll T_2$ is presented in Figure 2.5. The same three effects observed in Figure 2.4 are also seen here. However, the scaling of these features with $T_1$ is the inverse of the scaling with $T$; as $T_1$ increases, the $\omega_t$ width increases slightly, peak twisting increases, and the absorptive distortion at $\omega_t \approx \omega_{eg}$ deepens. Enhancement of the peak splitting is more pronounced for variation of $T_1$ in Figure 2.5, where the splitting deepens by 3 contour levels, than for variation of $T$ in Figure 2.4, where the splitting loses 1 contour level of depth.

2.4.2 Varying Beam Overlap Through Sample

The decision to include the effects of varying beam overlap was influenced by two observations in comparing the calculations to the experimental spectra\(^6\) at OD > 0.5. First, the aspect ratio of the 2D lineshape in the experimental spectra, represented by the ratio of widths $\Delta \omega_t/\Delta \omega_r$, was larger than what could be produced in the calculation by varying OD and $\Gamma$. Second, the larger depth of the absorptive distortion along the line $\omega_t \approx \omega_{eg}$ compared to that along the line $\omega_r \approx -\omega_{eg}$ in the experimental spectra was indicative of disproportionate attenuation in the $\omega_t$ dimension compared to the $\omega_r$ dimension. Although Figure 2.2 shows that the propagation function already has such an asymmetry, the experimental spectra\(^6\) have an even larger difference between the two dimensions.

Varying beam overlap will occur to some extent in any 2DFT experiment involving non-collinear excitation beams with a finite focal spot size and sample path length. If the focal points of the excitation beams spatially coincide, then the beams will completely overlap only in the plane parallel to the windows that contains the focal point. Assuming that the beams cross at the center of the sample cell and that the sample cell length is much shorter than the Rayleigh range, the beam overlap for Gaussian beams with waist $w_0$ crossing at angle $2\alpha$ is reduced by a factor of $\exp[-(\tan(\alpha)L/2)^2/w_0^2]$ at the windows. This effect is illustrated in Figure 2.6, where only two beams are shown for simplicity. Since the focal spot in Figure 2.6 is nearer to the entrance of the
Figure 2.6: Depiction of beam overlap varying through the sample. Black vertical lines represent the entrance (left) and exit (right) windows. Laser beams are denoted by red parallelograms and only two beams are shown for simplicity. The experimental beam overlap varies continuously between perfect overlap and no overlap as a function of propagation depth into the sample. To gain insight into the qualitative effects to be expected from varying beam overlap, the sample is crudely divided into a region of perfect overlap (A) followed by a region of no overlap (B). In Region A (between the entrance window and the blue dashed line), where excitation beams are well overlapped, the nonlinear signal is generated and propagated over the length $L_{nl}$. In Region B (between the blue dashed line and the exit window), the nonlinear signal generated in Region A is propagated according to the linear optical properties of the sample over the length $L_{isp}$ without any further nonlinear signal generation.
sample cell, the beams are well overlapped in the front portion of the cell, between the entrance window and the blue dashed line, but are poorly overlapped towards the back of the cell, between the blue dashed line and the exit window.

If the position of the sample cell with respect to the common focal point of the excitation beams is adjusted to maximize the intensity of the radiated signal, the focal point will lie nearer to the entrance window for an optically thick sample due to a trade-off between attenuation of all three excitation beams before signal generation versus attenuation of the one signal beam after signal generation. Therefore, we approximate the effect of varying beam overlap as perfect beam overlap in some front portion of the sample cell and no beam overlap in the remainder as would be expected experimentally when sample cell placement is optimized by maximizing integrated signal intensity. In the crude approximation used here to examine the qualitative effects of varying beam overlap, the fraction of the sample length over which nonlinear signal is generated, given by

$$f_{nl} = \frac{L_{nl}}{L_{nl} + L_{lsp}}$$

(2.37)
can be varied, but the total sample length $L = L_{nl} + L_{lsp}$ is fixed to the thickness of the sample cell.

Since pulse $c$ is linearly propagated before scattering off the grating produced by pulses $a$ and $b$, the generated signal at each depth is imprinted with this distortion of pulse $c$ before linearly propagating through the remainder of the sample cell. The result is that signal generated at any point in the sample appears as if it were generated at the sample entrance and linearly propagated over the total sample length (as implied by the final exponential of eq. 2.5) such that distortions of the 2DFT spectrum along the $\omega_t$ dimension are insensitive to changes in the length and location of the signal generation region. However, the linear propagation of pulses $a$ and $b$ prior to signal generation and, consequently, the propagation distortions along the $\omega_r$ dimension are sensitive to such changes, increasing in magnitude as the signal generation region shrinks and moves towards the sample exit.
2.4.2.1 Implementation in calculation

When implementing this approximate treatment of varying beam overlap, the propagation function $\Pi$ for Region A should use $L_{nl}$ in place of $L$ and be multiplied by

$$\exp \left\{ i \left[ \hat{k}_d^0(\omega_t) \cdot e_z \right] L_{lsp} \right\}$$

(2.38)

to incorporate linear propagation of the signal field in Region B. In eq. 2.38, $\hat{k}_d^0(\omega)$ is the central wave vector of the detection beam in the sample and $L_{lsp}$ is the length of the region in which the signal field is linearly propagated following the nonlinear signal generation region. In addition to the expression in eq. 2.38, an expression is needed that describes the linear propagation of the detection field through region B. This expression is specific to the representation of the spectrum to which it is applied and, therefore, will be defined below for each representation. The linear propagation term in eq. 2.38 and a linear phase evolution term for the detection field are applied to the FID-referenced representation to yield the signal-propagated FID-referenced rephasing 2DFT spectrum:

$$R\hat{S}^{0,\text{VBO}}_{2\text{D}}(\omega_t, \omega_\tau; T) = R\hat{S}^{0}_{2\text{D}}(\omega_t, \omega_\tau; T) \cdot \exp \left\{ i \left[ \hat{k}_d^0(\omega_t) \cdot e_z \right] L_{lsp} \right\} \cdot \exp \left\{ -i \text{Re} \left[ \hat{k}_d^0(\omega_t) \cdot e_z \right] L_{lsp} \right\}$$

(2.39)

For small angles of incidence and $\kappa^2 \ll n^2$, eq. 2.39 can be approximated as

$$R\hat{S}^{0,\text{VBO}}_{2\text{D}}(\omega_t, \omega_\tau; T) \approx R\hat{S}^{0}_{2\text{D}}(\omega_t, \omega_\tau; T) \cdot \exp \left\{ -\omega_t \kappa(\omega_t) \ell_{lsp}/c \right\}$$

(2.40)

where $\ell_{lsp} = L_{lsp}/(u \cdot e_z)$ is the additional path length for linear propagation of the detection pulse with unit propagation vector $u$ through the linear signal propagation length, $L_{lsp}$. The superscript “VBO” stands for varying beam overlap and indicates that the 2DFT spectrum includes the effects of varying beam overlap distortions. Since the signal and detection fields accrue the same amount of
phase when propagating through the linear signal propagation length ($L_{lsp}$), the phase propagation term on line 3 of eq. 2.39 cancels the oppositely-signed phase propagation contained within the complex exponential term on line 2 of eq. 2.39. This leaves only the attenuation of the signal field over the linear signal propagation length, which is represented by the real-valued exponential terms on the last line of eq. 2.39 (and eq. 2.40).

This distortion can also be applied to the time-referenced representation to yield

$$R^t_{2D} \hat{S}^{t, \text{VBO}}_2(\omega_t, \omega_r; T) \approx R^t_{2D} \hat{S}^{t, \text{VBO}}_2(\omega_t, \omega_r; T)$$

$$\cdot \exp \{ i \omega_t [n(\omega_t) - n_v] L_{lsp}/c \}$$

$$\cdot \exp \left[ -\omega_t \kappa(\omega_t) L_{lsp}/c \right]$$

(2.41)

which is valid for small angles of incidence and $\kappa^2 \ll n^2$ where $n$ is the real part of the refractive index of the sample and $n_v = 1$ is the real-valued refractive index of vacuum. Eq 2.41 shows that physically, varying beam overlap introduces two components arising from propagation through Region B: a dispersive component due to the difference in phase accrued by the signal field propagating through $L_{lsp}$ of sample compared to vacuum (line 2) and an absorptive component due to attenuation of the signal field from propagating through $L_{lsp}$ of sample (line 3).

### 2.4.2.2 Resulting calculated spectra

The spectra in Figure 2.7 demonstrate the effect of varying beam overlap where the signal is generated and propagated from the entrance window to a distance $L_{nl}$ into the sample, after which the signal is linearly propagated through the remainder of the sample length ($L_{lsp}$), as shown in Figure 2.6. For constant total sample length $L = L_{nl} + L_{lsp}$, the main result of varying beam overlap is to narrow the peak shape in the $\omega_r$ dimension by eliminating some of the linear propagation distortion of pulses $a$ and $b$. This helps to increase the horizontal-to-vertical aspect ratio of the peak shape in the calculation, bringing it closer to that of the experiment. Twisting of the split peak in Figure 2.7a is greatly diminished as $f_{nl}$ decreases and is no longer visible by $f_{nl} = 0.2$ (Figure 2.7c). Varying beam overlap also deepens the absorptive distortion along the line
Figure 2.7: Absolute value rephasing 2DFT spectra ($\hat{R}^{t_{\text{tVBO}}}_{2D}$ representation) for Bloch model where signal is generated and propagated through the first (a) 100%, (b) 60%, and (c) 20% of the sample cell and linearly propagated through the remainder. Peak optical density, $\text{OD}_{\text{max}} = 1.14$; grid time step, 850 fs; grid size, $1024^3$; dephasing rate, $\Gamma/2\pi c = 0.265$ cm$^{-1}$; excited state lifetime, $T_1 = 240$ ps; center frequency, $\omega_{eg}/2\pi c = 12816.7$ cm$^{-1}$; waiting time, $T = 850$ fs; total sample length, $L = L_{nl} + L_{lsp} = 500$ µm; and crossing angles, $\alpha = \beta = 4.84^\circ$. There are 19 contours, evenly spaced every 5% from 5% to 95%. The dotted line indicates the diagonal: $\omega_t = -\omega_r$. 
\[ \omega_t = \omega_{eg} \] except when \( T \gg T_2 \). Since the signal field is always propagated over the entire sample path length even when signal generation is confined to some front portion of the sample cell, outside of coherent effects which may be present when \( T \) is not very much greater than \( T_2 \), changing \( f_{nl} \) does not alter the shape of the spectrum in the \( \omega_t \) dimension as long as the total sample length is held constant.

### 2.4.3 Excitation-Detection Transformation of Rephasing 2DFT Spectra

When applied to a distorted 2DFT relaxation spectrum (including both positive and negative \( \tau \)), the excitation-detection transformation is capable of recovering the ideal (i.e. undistorted) 2DFT relaxation spectrum even for sample optical densities as high as 1. However, as illustrated in Figure 2.8, applying this transformation to a 2DFT rephasing spectrum does not recover the ideal rephasing spectrum. Given the power and simplicity of the excitation-detection transformation, it is a major disadvantage of 2DFT rephasing spectra that this transformation cannot be utilized to obtain the ideal 2DFT rephasing spectrum. The reason for this failure is that while the full \( \tau \) range 2D signal has some components which are real-valued, even functions of \( \tau \), taking only the rephasing (positive \( \tau \)) part of the spectrum makes half of the real-valued, even components appear to be real-valued, odd functions of \( \tau \). When the signal is subsequently Fourier transformed with respect to \( \tau \), these artificial real-valued, odd components transform into imaginary-valued, odd components. As is apparent in Figures 2.8b and 2.8d, the ideal rephasing spectrum contains signal at values of \( \omega_\tau \) for which there is no signal in the complete 2DFT relaxation spectrum, as illustrated by the lack of signal at the extremes of \( \omega_\tau \) in Figure 2.8d. When the 2DFT spectrum is truncated at \( \tau = 0 \), signal amplitude is transferred from near the line center, which is dominated by real components, to the far wings, which are dominated by imaginary components. Thus the “excitation frequency” in the 2DFT rephasing spectrum does not reflect the physical excitation frequency.

This rearranged signal is not amplified appropriately by the excitation–detection transformation since it appears in the wrong location. The result is that the \( R_{2D}^{++} \) spectrum (Figure 2.8a)
Figure 2.8: Absolute value 2DFT spectra for a Bloch model. (a) is $\hat{R}\hat{S}^{++}_{2D}$ with OD$_{\text{max}} = 1.14$, (b) is $\hat{R}\hat{S}^{t}_{2D}$ with OD$_{\text{max}} = 0$ (representing the ideal rephasing spectrum), and (c) is $\hat{S}^{t}_{2D}$ with OD$_{\text{max}} = 0$ (representing the ideal relaxation spectrum). Note the difference in axis scales when comparing to other figures. Grid time step, 850 fs; grid size, 1024$^3$; dephasing rate, $\Gamma/2\pi c = 0.265$ cm$^{-1}$; excited state lifetime, $T_1 = 30$ ns; center frequency, $\omega_{eg}/2\pi c = 12816.7$ cm$^{-1}$; waiting time, $T = 100.3$ ps; sample thickness, $L = 500$ μm; and crossing angles, $\alpha = \beta = 4.84^\circ$. There are 19 contours, evenly spaced every 5% from 5% to 95%. The dotted line indicates the diagonal: $\omega_t = -\omega_r$. 
neither matches the ideal rephasing spectrum (Figure 2.8b) nor the ideal relaxation spectrum (Figure 2.8c). While all four spectra in Figure 2.8 have similar linewidths in the \( \omega_t \) dimension, when comparing the linewidths in the \( \omega_\tau \) dimension, the \( \hat{R}\hat{S}_{2D}^{++} \) spectrum is narrower than the ideal rephasing spectrum and yet wider than the ideal relaxation spectrum. The overall narrowest lineshape is found in the ideal \( \hat{S}_{2D}^t \) spectrum in Figure 2.8c, which—unlike the ideal rephasing spectrum—is easily recovered using the excitation-detection transformation on \( \hat{S}_{2D}^0 \) with peak optical densities in excess of 1 as long as \( T \gg T_2 \). At \( T = 100.3 \) ps, the \( \hat{S}_{2D}^{++} \) spectrum with OD\(_{\text{max}}\) = 1.14 and the same parameters as in Figure 2.8 has contours which are visually indistinguishable from the ideal \( \hat{S}_{2D}^t \) spectrum, the two differing by no more than 0.08% (relative to the peak of the spectrum) at any point.

At shorter waiting times, the propagation function is no longer well described by a 2-dimensional function. Despite this complication, the excitation–detection transformation still performs well when applied to 2DFT relaxation spectra at short \( T \). For example, at \( T = 850 \) fs, the \( \hat{S}_{2D}^{++} \) spectrum with OD\(_{\text{max}}\) = 1.14 (not shown) and the ideal \( \hat{S}_{2D}^t \) spectrum (which is identical to Figure 2.8c) differ by no more than 13% (relative to the peak of the spectrum), the majority of the disagreement occurring near the line center where \( T \)-dependent peak twist is most pronounced. In contrast, the same comparison done using 2DFT rephasing spectra results in a difference of up to 20% between a \( \hat{R}\hat{S}_{2D}^{++} \) spectrum with OD\(_{\text{max}}\) = 1.14 (not shown) and an “ideal” \( \hat{R}\hat{S}_{2D}^t \) spectrum with OD\(_{\text{max}}\) = 0 (which is identical to Figure 2.8b).

### 2.4.4 Pseudo–Time Domain Filtering

When viewed in the pseudo–time domain (Fourier conjugate domains to \( \omega_t \) and \( \omega_\tau \)), representations other than \( \hat{R}\hat{S}_{2D}^t \) and \( \hat{S}_{2D}^t \) have signal that appears to arrive at the sample exit before pulse \( c \). The source of this apparent “non-causal” signal is that the detection waves used in these other representations are not true time references due to their propagating through the sample and taking on dispersion that is unaccounted for. While the phase accrued by the detection wave from traversing the sample serves to cancel that accrued by the signal, the variable conjugate to \( \omega_t \) has
Figure 2.9: The Bloch model $R\hat{S}_{2D}^0$ 2DFT spectrum Fourier transformed into the pseudo–time domain and integrated over $\tau$ (a), with (dashed red) and without (solid blue) pseudo–time domain filtering. The resulting absolute value rephasing 2DFT spectra, (b) without and (c) with pseudo–time domain filtering. Plots (a) and (c) here are comparable to the experimental plots found in Figures 4a and 4c of ref. 6, respectively. Peak optical density, $OD_{max} = 2.17$; grid time step, 500 fs; grid size, $1024^3$; dephasing rate, $\Gamma/2\pi c = 0.265 \text{ cm}^{-1}$; excited state lifetime, $T_1 = 30 \text{ ns}$; center frequency, $\omega_{eg}/2\pi c = 12816.7 \text{ cm}^{-1}$; waiting time, $T = 500 \text{ fs}$; sample thickness, $L = 500 \mu\text{m}$; and crossing angles, $\alpha = \beta = 4.84^\circ$. There are 19 contours, evenly spaced every 5% from 5% to 95%. The dotted line indicates the diagonal: $\omega_t = -\omega_\tau$. 
been “shuffled” so that it is no longer a true time that can be used to discern the time-ordering of events. While the time ordering of and time delay between pulses are experimentally controllable, the timing of electric field–chromophore interactions are not. Therefore, in the case of an optically thick sample that reshapes the excitation, detection, and signal fields, a given experimental pulse sequence with known pulse timings will have signal contributions from a range of electric field–chromophore interaction intervals and orderings. The larger the temporal smearing of excitation and detection pulses, the larger the range of electric field–chromophore interaction intervals and orderings contributing to the signal. The term “pseudo–time domain” is invoked since this filter is applied along a time dimension that is referenced to an experimental pulse delay which—except for the case of collinear beams, delta-function pulses, and a thin sample—does not specify a unique interaction time and ordering. Therefore, these axes do not necessarily represent true elapsed time and are more properly viewed as the Fourier conjugates of $\omega_t$ and $\omega_\tau$.

An interesting consequence of the loss of apparent causality in $R \hat{S}_{2D}^0$ is that it may also provide a means to reduce absorptive distortions of the signal field, which are not accounted for in $R \hat{S}_{2D}^0$. It was first observed experimentally by Li et al.\textsuperscript{6} that applying a pseudo–time domain filter that truncates the signal before pulse $c$ reduces the appearance of absorptive distortions in the $\omega_t$ dimension. The result of applying such a filter to a calculated $R \hat{S}_{2D}^0$ spectrum is illustrated in Figure 2.9. To produce Figure 2.9c, an $R \hat{S}_{2D}^0$ spectrum (Figure 2.9b) has been Fourier transformed into the pseudo–time domain, multiplied by $\theta(t)$, and then Fourier transformed back into the frequency domain. This procedure is consistent with the processing of experimental data illustrated in Figure 4c of ref. 6. The filter narrows the spectrum in the $\omega_t$ dimension and greatly reduces the absorptive distortion at $\omega_t \approx \omega_{eg}$ without significantly altering other aspects of the lineshape. While the validity of such a filtering procedure is not without question, its reduction of absorptive distortions thought to arise from propagation of the signal is immediately apparent. However, the ideal result would be to measure the full 2DFT relaxation spectrum and perform the excitation–detection transformation since this procedure most accurately recovers the undistorted spectrum, whose linewidth and lineshape are physically reflective of the microscopic dipole dynamics.
2.5 Discussion

Although differences remain, the simulations qualitatively reproduce many different propagation distortions of the experimental 2DFT spectra, including varying beam overlap distortions and peak shape broadening, splitting, and twist. Additionally, the effects of pseudo–time domain filtering, in both $t$ and $\tau$ dimensions, have been modeled and the trade-offs of using these filters have been addressed. In this section, comparisons between simulated and experimental 2DFT spectra will be further developed, highlighting both areas of agreement and disagreement as well as suggesting experimental methods which minimize propagation distortions and facilitate theoretical modeling. Finally, we discuss strategies for decoupling propagation distortions and the nonlinear optical response of samples at high optical density.

2.5.1 Optical Density Effects

Although the range of linewidths observed when varying the optical density from 0.14 to 1.14 in Figure 3 of ref. 6 is larger than the range for simulations in Figure 2.3, both show that increasing the optical density of a sample increases its linewidth in addition to altering its lineshape. Both experimental and simulated 2DFT spectra exhibit the onset of peak splitting at OD$_{\text{max}} = 0.59$, the result of strong attenuation of the signal near the resonant frequency ($\omega_{eg}$). Similar optical density–dependent peak shape broadening was previously reported in simulations of absolute value rephasing 2DFT photon echo spectra at zero waiting time by Keusters and Warren$^{31}$ and in simulations of complex-valued 2DFT relaxation spectra by Yetzbacher et al.$^{33}$ At the highest optical density, subtle twisting of the split peak in Figure 2.3d is mirrored in the experimental 2DFT spectrum. The experimental and simulated OD$_{\text{max}} = 1.14$ 2DFT spectra also share a significant absorptive distortion around $\omega_t = \omega_{eg}$, although the distortion is more pronounced in the experiment, where it cuts all the way down through the 5% contour level (vs. the 70% contour of the simulation). Discrepancies at high optical density will be discussed further below.

Splitting and twisting of the experimental 2D peak shape at high optical density were pre-
dicted by Yetzbacher et al. in a simulation of real (absorptive) 2DFT relaxation spectra, and the observation of these features in absolute value rephasing 2DFT spectra of Rb vapor by Li et al. largely motivated this collaboration. The prior simulation (Figure 5 of ref. 33) demonstrates subtle peak splitting and twist in an $\hat{S}_{2D}$ 2DFT spectrum for a homogeneous Bloch model in the lifetime-dephasing limit at a peak optical density of 0.87. By comparison, the simulations presented in Figure 2.3 are in the pure-dephasing limit of the homogeneous Bloch model where peak splitting and twist are more prominent for the same optical density, an effect discussed further below. At optical densities beyond those explored by Yetzbacher et al., twisting is clearly visible near the center of the peak in Figures 2.3d, 2.5c, and 2.10, which have optical densities ranging from 1 to 3.

Twisting requires a correlation between $\omega_t$ and $\omega_\tau$. Although the effect of phase-twist on the real part of 2DFT spectra is similar in appearance to the peak shape twist observed here, phase-twist is only observed during pulse overlap (i.e. when $T \approx 0$) in ideal 2DFT spectra. However, with the inclusion of propagation distortions, phase-twist could occur for larger waiting times due to the temporal overlap of pulse $c$ with the trailing FID of pulse $a$ or $b$. Since phase-twist does not affect peak shapes in ideal absolute value rephasing 2DFT spectra, for it to be responsible for the peak shape twist observed here would require a complicated interaction between phase-twist and propagation distortions, a conclusion consistent with the appearance of peak twist only at relatively high optical density.

Peak splitting is simpler to understand than peak twisting and is the result of resonant absorption of pulses $a$ and $b$ (for splitting in the $\omega_\tau$ dimension) and pulse $c$ and the signal (for splitting in the $\omega_t$ dimension). Just as with peak shape broadening, this distortion is more severe along the $\omega_t$ dimension than along $\omega_\tau$, even in simulations where excitation beams are perfectly overlapped through the entire sample length. This similarity between peak shape broadening and splitting highlights their common source: preferential attenuation of the signal and excitation fields near $-\omega_\tau = \omega_t = \omega_{eg}$.
2.5.2 Waiting Time and Excited State Lifetime Dependence

If the radiated linear free-induction decay from pulses \( a \) and \( b \) is non-negligible at the end of the waiting period (i.e. \( T \gg T_2 \)), propagation distortions will have 3-dimensional features that are not reducible to lower dimensionality. Figures 2.4 and 2.5, although without analogs in the experimental work, demonstrate this 3-dimensional nature of propagation distortions by varying the waiting time and excited state lifetime, respectively, at a fixed total dephasing time.

In simulations of absolute value rephasing 2DFT correlation spectra for the homogeneous Bloch model, Keusters and Warren\(^{31} \) reported asymmetric peak shape broadening at a peak optical density of 0.32, with more severe broadening in the \( \omega_t \) dimension than in \( \omega_r \). In addition, they found that this asymmetry was larger in the pure-dephasing limit (\( T_2 = T_2^* \)) than in the lifetime-dephasing limit (\( T_2 = 2T_1 \)).

At a higher optical density (OD\(_{\text{max}}\) = 1) than studied by Keusters and Warren,\(^{31} \) our simulations show that—in addition to peak shape broadening—peak shape twist and splitting are also affected by the ratio \( T_1:T_2 \). Figure 2.5 explores intermediate excited state lifetimes compared to the pure- and lifetime-dephasing limits simulated by Keusters and Warren.\(^{31} \) The trend we observe of larger peak shape broadening asymmetry at a longer excited state lifetime is in agreement with what they report.\(^{31} \) Not visible in their work at lower optical density is the trend of peak shape twist and splitting with the ratio \( T_1:T_2 \), both of which are enhanced at longer excited state lifetimes in Figure 2.5. These spectra show that the ratio \( T_1:T_2 \) is important for an optically dense sample since it controls the fraction of signal generated from interactions with the incident fields of pulses \( a \) and \( b \) versus their radiated FID. When the excited state lifetime is not very much longer than the total dephasing time (\( T_1 \gg T_2 \)), signal stimulated from the incident fields of pulses \( a \) and \( b \) experiences more severe excited state population relaxation than the signal stimulated from their linear FID due to the longer “waiting time” between interactions 2 and 3 when interacting with the main part of the pulse rather than its trailing FID.

Figure 2.4 demonstrates that varying the waiting time has similar effects on the 2DFT spec-
trum as varying the excited state lifetime. Shorter waiting times exhibit more severe peak shape twist, broadening, and splitting. These simulated 2DFT spectra illustrate the importance of the ratio $T:T_2$, which determines if and to what extent the linear FID from pulses $a$ and $b$ is able to bridge the waiting period to pulse $c$, mixing in signal from unintended interaction orderings. Given the complexity of propagation distortions in the coherent regime, it is beneficial from the point of view of interpretation and modeling to first characterize the 2DFT spectrum at $T \gg T_2$ before investigating dynamics at shorter waiting times were coherent effects are present. Since simulating a 2DFT spectrum at a long waiting time is typically a 2-dimensional problem, it is more straightforward in this limit to separate microscopic dipole dynamics from propagation distortions and to determine the optical density of the sample from its 2DFT spectrum.

2.5.3 Comparison to Experiment

The absorption lineshape broadening of a gas-phase chromophore can often be factored into homogeneous Lorentzian components—such as non-resonant collisional (or pressure) broadening, resonant self broadening, and lifetime broadening—and inhomogeneous Gaussian components, such as Doppler broadening. Collisional broadening is caused by chromophore–buffer gas collision while self broadening comes about due to chromophore–chromophore collisions. Based on the literature values\cite{10,15,16,73} of these sources of broadening for Rb in Ar buffer gas, collisional broadening dominates, accounting for greater than 98% of the total linewidth under the conditions of the experiment.\cite{6} This prediction is based on using the experimental Rb reservoir temperature to determine the vapor pressure\cite{74} and number density of Rb in the sample cell. To estimate collisional broadening, it is assumed that 2 atm of Ar is loaded into the cell at 298 K and that its pressure increases as the cell is heated at constant volume, as in the experiment.\cite{6} It should be noted that there is approximately $\pm$20\% variation between sources in the reported Rb vapor pressure curve\cite{9,14,74} and collisional broadening coefficient.\cite{9,15,70,75–78} However, it appears that such uncertainty is insufficient to account for the differences between the results of calculations and experimental measurements.

At the lowest Rb reservoir temperature (90°C, $OD_{\text{max}} = 0.14$), the predicted Lorentzian
FWHM linewidth (1.14 cm\(^{-1}\)) is more than three times larger than the linewidth estimated from the experimental absorption spectrum (\(~0.35\) cm\(^{-1}\)). The disagreement persists at the highest Rb reservoir temperature (160°C, \(\text{OD}_{\text{max}} = 1.14\)) where theory predicts a linewidth of 1.25 cm\(^{-1}\) while the experimental absorption spectrum indicates a linewidth of \(~0.51\) cm\(^{-1}\). Owing to the inconsistency between the experimental absorption spectra and these simple theoretic predictions of the lineshape, the dephasing rate used in these simulations was set to \(\Gamma = 50 \text{ rad/}ns = 0.265 \text{ cm}^{-1}\), corresponding to a FWHM of 0.53 cm\(^{-1}\), a compromise between the experimental and predicted linewidth estimates.

In addition, with values for the linewidth, Rb number density, and integrated absorption cross section, the absorption spectrum can be simulated for comparison to experiment. Since this calculation relies on the experimentally reported Rb reservoir temperature to determine the Rb number density in the optical path of the excitation beams, it will fail in the case of an inhomogeneous temperature or Rb vapor distribution throughout the sample cell. While linear absorption measurements are sensitive to the integrated number density of chromophores but not to chromophore density gradients, 2DFT spectra are sensitive to both, and the simulations of 2DFT spectra presented here assume a uniform chromophore distribution in calculating propagation distortions. Using the experimentally measured Rb reservoir temperature to calculate the Rb number density in the beam path, the experimentally measured integrated optical density can be plotted against Rb number density. While the Beer-Lambert law predicts a linear relationship between concentration and optical density, the experimental plot is nonlinear and appears to saturate as Rb number density increases. Despite this, the \(\text{OD}_{\text{max}}\) predicted by this method agrees to within 2% with the experimental value at the highest Rb reservoir temperature. However, this agreement may be coincidental since the predicted \(\text{OD}_{\text{max}}\) falls off approximately exponentially with decreasing temperature, as expected by the nearly exponential dependence of Rb vapor pressure on temperature, while the experimental \(\text{OD}_{\text{max}}\) decreases linearly with decreasing temperature. This difference in scaling results in substantial disagreement in optical density, with predicted values being a factor of 1.4 to 6.2 lower at all except the highest experimental temperature. Furthermore, the extent of
propagation distortions in the experimental 2DFT spectra imply optical densities that are higher than what is measured in the experimental absorption spectra. This difference is evidenced by simulated 2DFT spectra, calculated with optical densities taken from experimental linear absorption spectra, having considerably milder propagation distortions than experimental 2DFT spectra at the same Rb reservoir temperatures. As with the disagreement in linewidth, these inconsistencies cast uncertainty on the reliability of the experimental absorption measurements as a source of $\text{OD}_{\text{max}}$ and $\Gamma$ for 2DFT spectrum simulations and also suggest that the Rb reservoir temperature may not be directly indicative of the Rb vapor density in the path of the excitation beams. These discrepancies may result from differences in beam power or buffer gas pressure between measurements of the linear absorption spectrum and the 2DFT spectrum, which were taken on different days. However, the optical density used in the simulations can easily be varied to best reproduce the propagation distortions present in the experimental 2DFT spectra.

No asymmetry is present in undistorted (OD = 0) rephasing 2DFT spectra calculated using the homogeneous Bloch model, which produces a symmetric star-shaped peak in absolute value. At the lowest experimental optical density ($\text{OD}_{\text{max}} = 0.14$), only minor propagation distortions are expected and simulations do not reproduce the asymmetry in linewidth between the $\omega_\tau$ and $\omega_t$ dimensions observed in the experiment. While absorptive distortions broaden lineshapes more severely along $\omega_t$ than along $\omega_\tau$, the 2:1 aspect ratio of the $\text{OD}_{\text{max}} = 0.14$ experimental 2DFT spectrum is only recovered in simulations at $\text{OD}_{\text{max}} > 1$, by which point peak splitting becomes evident. Both the mean time between Rb–Ar collisions ($\bar{\tau} \approx 10$ ps) and the collision duration ($\tau_c \approx 2$ ps),$^7$ estimated for the experimental conditions,$^6$ are longer than the experimental waiting time ($T = 200$ fs). This might lead one to doubt the applicability of the homogeneous Bloch model in favor of the Kubo stochastic model or inhomogeneous Bloch model for this experiment. However, these models produce either a symmetric star-shaped peak, in the case of the Bloch model in the homogeneous limit and the Kubo stochastic model in the fast-modulation limit, or a diagonally-elongated peak that is roughly elliptical, in the case of the Bloch model in the inhomogeneous limit and the Kubo stochastic model in the slow-modulation limit. Calculations by Keusters and
Warren\textsuperscript{31} for a pure dephasing Bloch model indicate that higher intensity pulses reduce propagation asymmetry at OD\textsubscript{max} = 0.32 in the absolute value rephasing 2DFT spectrum; this suggests that high intensity pulses would not cause asymmetry at low optical density. On the experimental side, scattered light with intensity less than 2\% of the peak shape maximum lies along ω\textsubscript{τ} = −1.004ω\textsubscript{t} and is coincident with the diagonal within the likely uncertainty of this check while potential ghost peaks are below 5\% of the peak amplitude of the 2DFT spectrum. The origin of this asymmetry in the 2D peak shape is not understood, perhaps indicating that the two-level homogeneous Bloch model is not adequate to describe the nonlinear optical response of this system.

Comparing “reference around” experimental 2DFT spectra by Li et al.\textsuperscript{6} to simulated 2DFT \( \hat{R}\hat{S}_{2D}^t \) spectra using the experimentally reported values for OD\textsubscript{max} = (0.14, 0.59, 1.14) and \( f_{nl} = 0.8 \), clear disagreement in the width of the 2DFT lineshape and the depth of the absorptive distortion near \( \omega_t = \omega_{eg} \) is noted. While reducing the fraction of the sample in which the signal field is generated (Figure 2.7) does increase the aspect ratio of the 2D lineshape and slightly deepens the absorptive distortion near \( \omega_t = \omega_{eg} \), it does nothing to increase the linewidth in the \( \omega_{\tau} \) dimension, which is needed to better match the experimental spectra. Outside of the dephasing rate, which is already set to a larger value than observed in the experimental linear absorption spectrum, optical density is the only handle for changing the \( \omega_{\tau} \) width. To recover the \( \omega_{\tau} \) width of the experimental OD = 1.14 “reference around” spectrum (Figure 3 of ref. 6), the OD\textsubscript{max} used in the simulation was increased to \( \sim 3 \), as illustrated in Figure 2.10. Since a \( \sim 25 \) K increase in temperature of the Rb vapor sample cell is sufficient to cause a factor of 3 increase in the number density of Rb, a 3-fold increase in optical density might be within the combined uncertainty of the temperature and linear absorption measurements. Optical pumping and local heating of the sample by the excitation beams might also contribute to the disagreement in lineshape. Given the likely uncertainty in optical density, model values of OD\textsubscript{max} \( \approx 3 \) and \( f_{nl} \approx 0.8 \) may best represent the actual experimental conditions.
Figure 2.10: Absolute value rephasing 2DFT spectra with additional signal propagation ($RS_{\text{2D}}^{t,VBO}$ representation) for Bloch model with (a) OD$_{\text{max}} = 2$, $f_{nl} = 1$; (b) OD$_{\text{max}} = 3$, $f_{nl} = 1$; (c) OD$_{\text{max}} = 3$, $f_{nl} = 0.8$; and (d) OD$_{\text{max}} = 3$, $f_{nl} = 0.6$ where $f_{nl} = L_{nl}/(L_{nl} + L_{lsp})$ is the fraction of the sample length over which nonlinear signal is generated. Grid time step, 500 fs; grid size, $1024^3$; dephasing rate, $\Gamma/2\pi c = 0.265$ cm$^{-1}$; excited state lifetime, $T_1 = 240$ ps; center frequency, $\omega_{eg}/2\pi c = 12816.7$ cm$^{-1}$; waiting time, $T = 500$ fs; sample thickness, $L = L_{nl} + L_{lsp} = 500$ µm; and crossing angles, $\alpha = \beta = 4.84^\circ$. There are 19 contours, evenly spaced every 5% from 5% to 95%. The dotted line indicates the diagonal: $\omega_t = -\omega_\tau$. 
2.5.4 Implications for Experiment

Through characterization of pseudo–time domain filtering, which includes filtering both in $\tau$ (to produce rephasing 2DFT spectra) and in $t$, it appears that these processing techniques provide no clear advantage over application of the excitation–detection transformation to 2DFT relaxation spectra for recovering the ideal lineshape. The $\hat{S}_{2D}^{++}$ spectrum not only matches the ideal 2DFT relaxation spectrum (Figure 2.8c) to a high degree, but it also has a narrower 2D lineshape than the $R\hat{S}_{2D}^{++}$ spectrum (Figure 2.8a). However, any well-characterized pseudo–time domain filter can be applied to simulations using the 3DFT method, as exhibited in Figures 2.8 and 2.9. The effect of a pseudo–time domain filter that removes signal that appears to arrive before pulse $c$ in the $t$ dimension, presented in Figure 2.9, matches some of the experimental signatures of this filter in Figure 4 of ref. 6. In particular, simulations capture both the narrowing of the lineshape in $\omega_t$ and the reduction in the depth of the absorptive distortion near $\omega_t = \omega_{eg}$.

Despite the crude nature of the approximation used, our treatment of varying beam overlap was able to capture the experimental signature of this distortion wherein the aspect ratio of the 2D lineshape is larger than that produced by the propagation function alone. This analysis also illustrates two important points. First, it reinforces the observation that the signal is always effectively propagated over the entire length of the sample cell regardless of where it is generated within the sample cell. As evidence, it can be seen in Figure 2.7 that reducing the length of the region over which signal generation occurs does not alter the lineshape in the $\omega_t$ dimension as long as the total sample length is held constant. Second, it shows the disadvantage of using a sample cell with a path length longer than the overlap length of the incident laser beams since any region where beams are not well overlapped will not contribute significantly to signal generation, but will attenuate and distort the signal.

Simulations of “reference around”-type $R\hat{S}_{2D}^{t}$ 2DFT spectra exhibit a strong dependence on the exact placement of a pseudo–time domain filter around $t = t_c \equiv 0$, which was used in the work by Li et al. to discriminate against scatter from excitation pulses. Moving the filter by 1 ps
into positive $t$ causes the height of the spectrum at $\omega_T = \omega_t = \omega_{tg}$ (relative to the peak of the spectrum) to decrease by a factor of 3, greatly enhancing the depth of the absorptive distortion. This sensitivity indicates that even a small uncertainty in the position of a pseudo–time domain filter around $t = 0$ can significantly alter the 2DFT spectrum.

Using the method put forward by Hybl et al., 24 2DFT spectra at long waiting times ($T \gg T_2$) can be simulated with no adjustable parameters, relying only on independent 1D spectra of the sample and excitation pulses. Such simulations are valuable for comparison to experimental 2DFT spectra in the long $T$ limit. They can also be compared to 2DFT spectra simulated by the 3DFT method in order to test lineshape models and to estimate the magnitude of propagation distortions. Furthermore, experimental 2DFT spectra taken under conditions where the optical density and lineshape model, as well as its parameters, can be predicted from prior literature results provide the opportunity to simulate distorted 2DFT spectra with no adjustable parameters even at short waiting times where coherent effects are present in both the 2D peak shape and the propagation distortions.

Distorted 2DFT spectra at short waiting times often disguise their true peak shape and peak width under coherent effects and absorptive line broadening, making them a poor source of information on which to base simulations. If the Bloch model is truly appropriate (and there are physical grounds to doubt this at waiting times less than the time between collisions or the collision duration), all of the parameters necessary for the 3DFT simulation are available from the experimental geometry and independent spectroscopic measurements. So, for cases where there is no reliable source of lineshape information in the literature, simulations of distorted 2DFT spectra at arbitrary $T$ with no adjustable parameters may still be possible.

Through the challenge of modeling extreme propagation distortions, this study suggests a set of measurements to aid quantitative theoretical modeling. Measurement of the free-induction decay of each of the excitation pulses can check linear propagation of the excitation fields, which is a requirement of the theory underlying these calculations. Linearity of absorption, however, does not guarantee linear propagation. 7,24,69 Well-resolved linear absorption spectra are also critical to
this check. As with free-induction decay measurements, absorption spectra indicate the optical density of the sample and, for the homogeneous Bloch model, determine the lineshape function. The theory requires that excitation beam overlap homogeneously fill the entire sample path length, which can be accomplished by either using shallow beam crossing angles or a sufficiently thin sample cell. For the homogeneous Bloch model, 2DFT relaxation spectrum measured at $T \gg T_2$ and low optical density can independently determine the lineshape parameters since coherent effects are minimized at long $T$, leaving a “product-lineshape” which is simpler to interpret. For a detailed analysis of 2DFT spectra at long waiting times, see the appendix of ref. 24. 2DFT relaxation spectra at $T \gg T_2$ but with higher optical densities, once corrected for propagation distortions using the excitation–detection transformation (exact when $T \gg T_2$), would reveal the dependence of homogeneous Bloch model parameters on chromophore density. Although increasing the optical density in this experiment would also increase the buffer gas pressure, the predicted $\sim 9\%$ increase in linewidth from 363 K to 433 K due to Rb–Ar collisions is small compared to the linebroading caused by propagation distortions over the same range. Alternatively, long-$T$ spectra could serve an independent measurement of the sample optical density if the lineshape model parameters are known from an independent source. These measurements and experimental checks enable unambiguous assignment of a lineshape model, lineshape parameters, and optical density in the incoherent limit and serve as a foundation for modeling the addition of coherent effects at short waiting times.

### 2.6 Conclusions

2DFT spectra of the collision-broadened D$_2$ line of rubidium in argon buffer gas have been simulated using a 3DFT method and compared to experimental 2DFT spectra from Li et al. These simulations illustrate that even for the simplest lineshape models, propagation distortions alter the 2DFT spectrum in complicated and sometimes unexpected ways. The optical Bloch model, separable into independent $\omega_\tau$, $\omega_t$, and $T$ dynamics in the low OD limit, exhibits a complex interplay between all three dimensions in the presence of propagation distortions, hindering analysis of spec-
tral features when using 2-dimensional representations of a truly 3-dimensional object ($\chi^{(3)}$). Such challenges reveal the need for a 3-dimensional approach to computationally model experimental 2DFT spectra and aid in their interpretation.

Prior theory has been extended to describe 2DFT rephasing spectra as well as a new incoherent 2D propagation function and its domain of validity. For the optical Bloch model, it was found—through comparison to simulations by the 3DFT method—that the 2D propagation function is exact in the limit that $T \gg T_2$ and $2T_1 \gg T_2$. In addition, these comparisons demonstrated that even for a lineshape model without frequency memory, propagation distortions caused by an optically dense sample introduce complex spectral dynamics during the waiting time.

As in the experimental 2DFT spectra, an increase in optical density results in asymmetric linebroadening in simulated spectra, with the $\omega_t$ linewidth increasing more than the $\omega_\tau$ linewidth. At optical densities greater than 0.5, peak splitting in the $\omega_t$ dimension, caused by resonant absorption of the signal and pulse $c$ at $\omega_t \approx \omega_{eg}$, is observed in both experimental and simulated 2DFT spectra. The waiting time–dependence and excited state lifetime–dependence of Bloch model 2DFT spectra were explored, showing that these parameters affect the linewidth, depth of peak splitting, and magnitude of peak twist. As $T$ increases, the $\omega_t$ linewidth slightly increases, peak splitting deepens, and peak twist disappears. The opposite trends are observed when increasing the excited state lifetime.

A crude model was used to demonstrate the effect of varying beam overlap within the sample and to aid in modeling experimental spectra where signatures of this distortion appear. For a fixed total sample length with the signal generation region starting at the entrance window–sample interface, decreasing the length of the signal generation region was found to decrease the magnitude of absorptive distortions along the $\omega_\tau$ dimension while leaving the $\omega_t$ dimension largely unchanged. This observation is in agreement with previously developed theory which suggests that in the incoherent limit, where $\omega_t = \omega_c$, the $\omega_t$ dimension always experiences attenuation over the total sample length, regardless of the location and length of the signal generation region, due to the combined propagation of pulse $c$ and the signal over the entire sample. The increase in lineshape
aspect ratio \((\Delta \omega_t/\Delta \omega_r)\) produced by this model is a feature shared with experimental 2DFT spectra, which exhibit a larger aspect ratio than simulations that exclude this effect.

The excitation–detection transformation exactly recovers the ideal 2DFT relaxation spectrum when applied to a \(\hat{S}^0_{2D}\) spectrum at \(T \gg T_2\) and still approximately recovers the ideal spectrum at shorter waiting times. However, there is no value of \(T\) where the ideal 2DFT rephasing spectrum is recovered when the transform is applied to a \(R\hat{S}^0_{2D}\) spectrum. Given the effectiveness of the excitation–detection transformation, the inability of 2DFT rephasing spectra to utilize this transform is a significant disadvantage compared to 2DFT relaxation spectra. When the ideal 2DFT rephasing spectrum is desired, it can be extracted from the excitation–detection transformed 2DFT relaxation spectrum since a relaxation spectrum contains both the rephasing and the nonrephasing spectrum.

Simulated 2DFT spectra which have been modified by a pseudo–time domain filter that eliminates signal prior to \(t = t_c = 0\) show qualitative agreement with comparably filtered experimental spectra, both exhibiting a decrease in linewidth and peak splitting along the \(\omega_t\) dimension. However, spectra processed with this filter are still considerably more distorted than the excitation–detection transformed 2DFT relaxation spectrum, which is the recommended representation for presentation and analysis of 2DFT spectra.

Increases in the optical density of 2DFT spectra were accompanied by asymmetric lineshape broadening, peak twist, and strong absorptive distortions around \(\omega_t = \omega_{eg}\). By comparison to linewidths predicted from the literature, it was shown that propagation distortions are responsible for nearly all of the change in linewidth across the experimental range of optical densities. Calculations of 2DFT spectra at a range of optical density, waiting times, and excited state lifetimes demonstrated that propagation distortions induce spectral dynamics during the waiting time even for the homogeneous Bloch lineshape model, which—in the low optical density limit—only undergoes population relaxation during the waiting time. This was manifested by an increase in linewidth, deeper peak splitting, and increased peak twist as \(T\) increased and \(T_1\) decreased. Simulations of \(R\hat{S}^{t,VBO}_{2D}\) spectra with optical densities of 2–3 and \(f_{nl}\) of 0.6–0.8 resemble high–optical density ex-
perimental “reference around” 2DFT spectra in linewidth and peak splitting depth. Within the likely uncertainty in Rb vapor density and buffer gas pressure, it appears that quantitative modeling of experimental “reference around” 2DFT spectra is possible.
Chapter 3

Sample Renewal by Beam Scanning with Applications to Noncollinear Pump–Probe Spectroscopy at Kilohertz Repetition Rates

An optical beam scanning apparatus that minimizes repetitive sample excitation in laser spectroscopies is described. Scanning crossed laser beams with respect to a stationary sample can accommodate a wide variety of sample cell formats, including those for which it has traditionally been difficult to limit repetitive excitation such as cryostats, films, and air-tight cuvettes. Use of a space-filling scan pattern greatly increases the time before a point in the sample cell is resampled by the laser while ensuring minimal shot-to-shot spatial overlap. Both an all-refractive and an all-reflective version of the apparatus are demonstrated. Characterization shows that the beam scanning apparatus does not measurably alter the pump-probe time delay (less than the 0.4 fs measurement uncertainty for a 75 fs pulse duration), the laser focal spot size (less than the 6% measurement uncertainty for a 44 µm focal spot), or the beam overlap (less than the 15.5% measurement uncertainty for a 44 µm focal spot), leading to pump-probe and autocorrelation transients which are fair reflections of the sample being interrogated.

3.1 Introduction

In time-resolved optical spectroscopies, sequences of pulses, each sequence representing a complete and independent experiment, are repeated in order to record a transient which contains data as a function of the time delay(s) between pulses. In addition, the use of repetitive pulse sequences is typically necessary in order to build up the signal-to-noise ratio (SNR) of data at
each time delay. In such cases, it is imperative to allow sufficient time between pulse sequences to prevent prior pulse sequences from influencing the signal measured by subsequent pulse sequences. In experiments employing continuous light sources, such as frequency-resolved absorbance spectroscopy, this is equivalent to requiring that the photon fluence through the sample be low enough that each photon interacts with the sample independently, unaffected by prior photons. Whether pulsed or continuous light sources are used, repetitive excitation artifacts come about when excited chromophores do not have adequate time to relax to thermal equilibrium with the bath before being probed again. It is well established that such artifacts, which can arise from long-lived intermediates, can influence or even dominate the dynamics observed in a variety of molecular systems.\textsuperscript{80–84} For example, in the accumulated grating photon echo experiment, a photon echo is stimulated from a frequency grating built up by repetitively exciting the sample.\textsuperscript{85,86} In this technique, a bottleneck in the optical pumping cycle causes the accumulation of a steady-state electronic distribution which is not thermalized with its surroundings.\textsuperscript{85,87} More recently, it has been reported in studies of semiconductor quantum dots that signals resulting from the buildup of photo-products can mimic signatures of multiple exciton generation.\textsuperscript{88–93}

In order to increase the duty cycle of data collection without inducing such artifacts, probed-volume sample renewal (PVSR) techniques attempt to ensure that each pulse sequence samples fully equilibrated chromophores that have no memory of prior pulse sequences. In a probed-volume sample renewal technique, the excitation beams interrogate different portions of the sample over time in order to minimize the time-averaged laser flux at any given spot in the sample. These techniques involve either moving the sample with respect to stationary laser beams (sample cell spinning,\textsuperscript{80,94–99} translating,\textsuperscript{84,100–103} flowing,\textsuperscript{81–84,91,100,104,105} and stirring\textsuperscript{88,89}), or moving the laser beams with respect to a stationary sample cell (spinning lens\textsuperscript{106}). We present a sample renewal technique which implements the latter strategy by quickly scanning two crossing laser beams such that each pulse sequence probes a portion of the sample not excited by prior pulses, taking advantage of the area of the sample cell to maximize resampling time. The advantages of this technique include average resampling times in excess of 1 second, low shot-to-shot spatial
overlap, flexibility in sample cell format (rectangular, cylindrical, cryostat, etc.), and interferometric stability. Compared to flowing or stirring, which require only one scatter-free spot on the sample cell, sensitivity to light scattering points over the entire probed area is a disadvantage.

3.2 Beam Scanning Design

3.2.1 Refractive Optics Implementation

The apparatus in Figure 3.1 is constructed using only commercially available equipment, of which the core is a fast steering mirror (FSM-300, Newport) and its controller/driver (FSM-CD300B, Newport). The FSM has a front-surface gimbaled, 1 in. diameter, enhanced aluminum-coated mirror whose angle is independently controlled about two orthogonal axes by four voice coils, a type of linear actuator. It has a mechanical angular range of 1.5°, a repeatability of ≤ 3 μrad, and a close-loop amplitude bandwidth of ≥800 Hz. Since the FSM is designed for beam stabilization and scanning applications, for which speed and precision are critical, it is well suited to the needs of PVSR. Compared to dual-axis galvanometer–based systems, which use two separate mirrors in a z-fold–like arrangement, a voice coil–actuated FSM translates the reflected beams less while scanning, leading to a simpler optical setup and reducing aberrations in focusing all beams to the same spot. The optical layout of our sample renewal implementation is very similar to typical apparatus for laser scanning microscopy. The FSM receives two parallel beams, vertically offset by 1.2 cm, at 45° to the surface of the mirror. An antireflection-coated (AR) 2 in diameter plano-convex lens (f = 30 cm) is centered in the path of the reflected beams at a distance of its focal length from the FSM. The distance between the FSM and lens is important because it controls the incident angle of the focused beams on the focal plane, in which the sample cell lies. In geometric optics, any ray emanating from the focal point of a lens will propagate parallel to the optical axis once it has passed through the lens. Therefore, when a lens is placed such that its focal point coincides with the center of the FSM, an angle bisector between the focused beams will, neglecting the effects of optical aberrations, fall normal to the focal plane for all deflection angles of the
Figure 3.1: Schematic of the refractive beam scanning apparatus. Beams propagate from right to left, encountering a fast steering mirror (FSM), focusing lens (L1), sample cell, two irises (I1 and I2), collimating lens (L2), and photodiode (PD). The fast steering mirror (FSM) utilizes a 1 in. diameter aluminum-coated mirror. The focusing lens, L1, is a 2 in. diameter antireflection-coated plano-convex lens with a 30 cm focal length, denoted by the distance \( f \) in the schematic. The sample cell is 5 cm by 1 cm with a 1 mm path length. The collimating lens, L2, is a 1 in. diameter antireflection-coated plano-convex lens with a 25 cm focal length. The photodiode, PD, is a biased silicon PIN photodiode detector which has a large active area diameter (4.57 mm). (a) Side view showing beams deviated up (dashed, black), undeviated (shaded, blue), and deviated down (solid, red). (b) Top down view showing beams deviated left (solid, purple) and deviated right (dashed, green).
FSM. This ensures constant optical path length through the sample cell as well as constant reflective losses from the sample cell interfaces. Past the sample cell are two irises that are centered on the probe beam and closed as far as possible without clipping the probe beam at any point in its scan pattern. The irises are used to block the pump beam and light scattered by the sample. They are positioned 20 cm and 32 cm from the sample cell, by which point the pump and probe scan patterns are spatially separated for a scan pattern whose diameter in the focal plane is 3 mm. Beyond the second iris, there is an AR coated 1 in diameter plano-convex lens \( (f = 25 \text{ cm}) \) that is placed 48 cm from the sample cell and approximately 0.5 cm above the optical axis of the focusing lens. This lens serves to loosely focus the probe scan pattern onto a photodiode (ET-2040, EOT; biased silicon PIN photodiode; 4.57 mm active area diameter) placed 25 cm beyond.

The location of the common focus for the two beams in the sample cell is controlled by the deflection angle of the FSM which is, in turn, controlled by two input voltages: one for the x (horizontal) deflection angle and one for the y (vertical) deflection angle. The FSM is capable of producing an arbitrary scan pattern on the sample cell, within its mechanical constraints on maximum deflection angle \( (1.5^\circ, \text{ mechanical}) \) and bandwidth. Specifically, the FSM-300 can utilize its full angular range up to a frequency of 40 Hz, beyond which the maximum deflection angle is inversely proportional to the square of frequency due to thermal loading of its drive coils.\(^{113}\)

For example, when the focal length of L1 is 20 cm and scanning a circular pattern with a 3 mm radius, the maximum scan velocity achievable by the FSM-300 is 1.38 m/s, enabling center-to-center separation of laser focal spots of up to 138 µm (1.38 mm) for a 10 kHz (1 kHz) laser repetition rate. The FSM-300s 1.5° maximum mechanical deflection angle translates into a maximum pattern radius of 10.5 mm for the same 20 cm L1 focal length.

A tradeoff exists between the maximum size of the scan pattern and the focal spot size of the laser at the sample. While a longer focal length for L1 allows for a larger scan pattern, it also increases the diffraction-limited focal spot size of the laser.\(^{114}\) Since both the maximum scan pattern size and the focal spot size increase linearly with the focal length of L1, the maximum resampling time cannot be increased in this way.
3.2.1.1 Optimization

There are five aspects of the implementation and optimization of the beam scanning apparatus that were found to be very important for proper operation. First, the vertically stacked beam geometry is necessary due to the $90^\circ$ horizontal reflection at the FSM. As noted above in Section 3.2.1, the distance between where a beam falls incident upon the FSM and the plane of the focusing lens determines how the beam is imaged onto the focal plane and having this distance be the same for pump and probe beams guarantees that they will come to a common focus in the sample. The assumption that beam overlap is not dependent on the FSM deflection angle is evaluated in Section 3.5.

Second, to ensure that the sample cell is placed in the focal plane, its z-position (z being the beam propagation direction) is adjusted to maximize the pump-probe signal from a laser dye after which the pitch (vertical angle) and yaw (horizontal angle) of the sample cell are adjusted to overlap the pump beam’s sample cell back-reflection with the incident probe beam and, equivalently, overlap the probe back-reflection with the incident pump. This procedure for optimizing the sample cell angle requires that the sample cell path length be short enough that $w \ll L \tan \theta$ where $w$ is the radius of the collimated laser beam, $L$ is the sample cell path length, and $2\theta$ is the pump-probe crossing angle. Given that $w \approx 2 \text{ mm}$ and $L \tan \theta \approx 0.025 \text{ mm}$ in our setup, this requirement is easily satisfied.

Third, in order to reduce the amount of scattered light reaching the detector, the irises following the sample cell are closed as much as possible without clipping the probe beam. This is done by first centering the irises on the probe beam with the FSM in its undeviated position. Then, with the desired scan pattern running, the iris is closed until the point at which clipping of the probe beam pattern is observed on an oscilloscope as a change in the amplitude of the probe pulse’s waveform from the detector. The iris is then opened slightly to a point where any small change in the opening’s diameter does not visibly affect the peak height of the observed waveform (at least to the 0.5% level).
Fourth, with the FSM in its undeviated position, the horizontal and vertical positions of the
collimating lens are set such that the transmitted probe beam is not deviated horizontally and also
travels parallel to the plane of the laser table. The collimating lens is rotated (yaw) until normal
to the probe beam, judged visually based on back-reflections.

Fifth, the photodiode is initially placed at the point where the probe beam is stationary when
viewed on a card with the FSM actively scanning. Its position is then optimized by minimizing
variation in the probe pulse’s waveform, as observed on an oscilloscope, while the desired scan
pattern is active. This involves horizontal, vertical, and z-direction adjustment as well as rotation
(yaw). These fluctuations are a result of the probe beam moving with respect to the active area of
the detector, causing variations both in position on the detector and in the fraction of the probe
beam incident on the active area.

While the collimating lens does not have strict requirements on its z-position, it is expected
that matching this lens to the focusing lens in both focal length and distance from the sample
cell would be ideal in terms of minimizing differences in probe beam position at the detector for
different FSM deviation angles. The z-position and focal length of the collimated lens used in the
above implementation does not match the ideal case due to space constraints.

3.2.1.2 Idealized Implementation

An ideal implementation of a refractive beam scanning apparatus might have a few key
differences in comparison to the actual apparatus used in this study. Based on geometric optics, if
the collimating lens (L2 in Figure 3.1) is matched to the focusing lens (L1 in Figure 3.1) in focal
length $f$ and distance from the sample cell, the position of the probe beam at a distance $f$ from
the collimating lens should be invariant to FSM deflection angle. Since motion of the probe beam
with respect to the photodiode detector is a source of noise, having the probe beam come to a
stationary point at the detector is an important condition. An ideal implementation of a refractive
beam scanning apparatus, depicted in Figure 3.2, illustrates the use of two lenses of matched focal
length, each located one focal length from the sample cell.
Figure 3.2: Schematic of an idealized refractive beam scanning apparatus with beams (a) deviated up, (b) undeviated, and (c) deviated down. Pump (on bottom at FSM) and probe (on top at FSM) beams travel from right to left, encountering (in order) a fast steering mirror, focusing lens, sample cell, iris, collimating lens, iris, and photodiode detector.
3.2.2 Reflective Optics Implementation

An all-reflective-optics version of this beam scanning apparatus was also constructed (Figure 3.3) and has the advantage of eliminating the dispersion and chromatic aberration caused by refractive optics at the cost of added astigmatism. The primary difference is in the use of 2-inch diameter spherical concave mirrors \( f = 20 \text{ cm}, \) Thorlabs CM508-200-P01 instead of lenses. In order to minimize optical aberrations, the FSM and curved mirrors are used at near-normal incidence. In terms of layout and alignment, the same guiding principles that were used with the refractive optics setup were used here. Just as in the refractive implementation, the sample cell is placed perpendicular to the optical axis of the focusing mirror so as to coincide with its focal plane. However, with the near-normal incidence layout, this must be accomplished in a different way, as described below. Likewise, the optical axis of the collimating mirror after the sample lies parallel to that of the focusing mirror. As in the refractive implementation, the first iris after the sample is placed far enough away that it is able to fully block the pump beam and transmit the probe beam over the entire scan pattern.

3.2.2.1 Optimization

For the most part, the optimization techniques used for the refractive implementation were also used in the reflective implementation. However, there are two notable differences that come about due to use of the FSM and spherical mirrors at near-normal incidence. First, in the limit that beams are at normal incidence to all optics, the requirement of using stacked beams for proper beam overlap in the focal plane is relaxed. Second, since the angle bisector of the beams no longer falls normal to the focal plane, the sample cell cannot be aligned by overlapping back-reflections, as in the refractive setup. Instead, an imaging sensor (ZoomCam USB Model 1598 with lens removed; 330K pixel CMOS sensor; 7.4 \( \mu \text{m} \) pixel pitch; 8-bit depth) is placed in the sample cell position and its position and angle (pitch and yaw) adjusted until the image shows identical beam overlap at all FSM deflection angles visible on the sensor, indicating that it is in the focal plane of CM1. An iris
Figure 3.3: Top down view of the all-reflective-optics beam scanning apparatus (not drawn to scale). Beam paths for two different FSM deflection angles are illustrated: left (solid, purple) and right (dashed, green). Only one beam is visible for each FSM deflection angle when viewed from above since the pump and probe beams are vertically offset. Beams start at the bottom-left of the diagram, travelling from left to right, encountering (in order) a fast steering mirror (FSM), spherical concave mirror (CM1), sample cell, iris (I1), spherical concave mirror (CM2), iris (I2), and photodiode (PD). Both concave mirrors are aligned such that they share a common focal plane, in which lies the FSM, the sample cell, and the front face of the detector. The concave mirrors (CM1 and CM2) have a 2 in diameter, 20 cm focal length (denoted by the distance $f$ in the schematic), and are protected silver-coated. The sample cell is 5 cm by 1 cm with a 1 mm path length. The photodiode, PD, is biased silicon PIN photodiode detector which has a large active area diameter (4.57 mm).
(I3 in Figure 3.3) is placed at a distance \( \sim f \) from the imaging sensor and is then aligned to the back-reflection of the probe beam from the imaging sensor. This iris can be used to properly orient a sample cell in the focal plane by aligning the cell’s probe back-reflection through the iris. As with optimizing the sample cell angle in the refractive implementation, this procedure depends on using a sufficiently thin sample cell and small enough crossing angles so that the probe beam’s back-reflection can be approximated as originating from the pump-probe beam crossing point within the sample cell.

The collimating mirror (CM2) is aligned such that it is parallel to the focusing mirror (CM1), and—consequently—parallel to the focal plane, with the beams centered on its surface. The position of the collimating mirror is set using a combination of ruler measurements and visual inspection. The geometry of the reflective setup constrains the collimating mirror to be a distance \( f \) from the focal plane and displaced from the sample cell (along the axis defined by the intersection of the focal plane and plane of the laser table) the same distance as the focusing mirror is displaced from the sample cell. Based on this knowledge of the experimental geometry, measurements of the collimating mirror’s position relative to the focusing mirror, FSM, and sample cell enable its proper placement. The collimating mirror’s height is set such that the beams are visually centered on its surface. The pitch of the collimating mirror is optimized such that the angle bisector between beams propagates parallel to the laser table based on measurements of beam height (to approximately \( \pm 0.5 \text{ mm accuracy} \) at various positions between the collimating mirror and photodiode (ET-2040, EOT). Since the focusing mirror is oriented parallel to rows of bolt holes in the laser table, the yaw of the collimating mirror is adjusted such that CM2 is visually aligned to rows of bolt holes and, therefore, parallel to the focusing mirror. The yaw of the collimating mirror is further optimized so that the distance between where undeviated beams intersect the focal plane before and after reflection from the collimating mirror is the same as that for the focusing mirror. Roughly speaking, this means that the distance between the sample cell and photodiode is the same as the distance between the sample cell and FSM (\( \sim 6.0 \text{ cm in our setup} \)).
3.3 Sources of Noise and Noise Mitigation

A source of noise that is inherent to any PVSR method that probes a large area of a sample cell is light scattering by the sample. The larger the sample cell area utilized, the more difficult it is to avoid scattering points and, in the case of film samples, variations in optical density. This is a significant dilemma since the period between excitations at a given point in the sample is proportional to the total sample cell area utilized. This source of noise can be minimized by ensuring that the sample is as spatially homogeneous as possible. For a solution phase sample, this involves both thoroughly cleaning the interior and exterior of the sample cell as well as removing scattering aggregates from the sample solution by filtering or dilution. In the case of films, cracks and inhomogeneity in sample thickness can be avoided by limiting the scan pattern to a more homogeneous region of the sample.

To improve signal recovery, several layers of electronics and signal processing are used for pump-probe measurements with this apparatus. First, the photodiode output is amplified by a gated integrator (SR250, Stanford Research Systems) in order to discriminate against noise outside of the time window of the laser pulse. The resulting signal is conditioned by a passive high-pass filter with a cutoff frequency of $f_c = 500$ Hz, which is higher than most frequencies in a typical scan pattern and lower than any chopping frequency used so as not to attenuate the signal. This filter improves rejection of periodic noise, an effect which is discussed further below. Finally, a lock-in amplifier (SR830, Stanford Research Systems)—referenced to an optical chopper (3501, New Focus) that modulates the pump beam—is used to extract the pump-induced change in probe transmission. The optical chopper is synchronized (i.e. phase-locked) to a subharmonic of the laser repetition rate and its phase is adjusted such that pulse clipping is minimized. A variety of chopping frequencies were tested, but best suppression of scanning-related noise was achieved with the highest available chopping frequency (2.5 kHz), which corresponds to one-fourth the laser repetition rate. The digitized output of the lock-in amplifier is read by a PC where additional averaging is done to improve the SNR. Since averaging on multiple time scales allows for rejection of noise over a wider
range of frequencies, not only are 3–10 data points averaged at each pump-probe delay, but 2–100 pump-probe transients are also averaged to achieve the desired SNR.

An unintended consequence of the periodic nature of the scan pattern is that scattering noise is also periodic and can therefore appear in a pump-probe transient as a periodic modulation of the signal size, mimicking the appearance of quantum beats. This arises when there is a well-defined relationship between the period of the scan pattern and the period between data samples, which causes noise sources that are periodic in elapsed time (i.e. wall clock time) to map onto pump-probe delay time as a periodic modulation in the transients. By varying the data sampling rate during the collection of a transient, the correlation between data sampling and beam position is disrupted, reducing this artifact and improving the SNR when averaging multiple transients. At each pump-probe delay, several (typically ~5) data samples from the lock-in amplifier are acquired and averaged. The time interval between acquisitions at a given pump-probe delay is determined by a constant “base interval” multiplied by a factor chosen between 1 and 1.5 by a pseudo-random number generator. The goal is a data sampling rate which varies in time such that data sample times and beam positions do not develop a stable, long-term correlation during an experiment.

3.4 Scan Pattern

The control voltages for the FSM are produced by an external computer sound card (Creative Sound Blaster X-Fi Surround 5.1 Pro USB) capable of producing an audio signal with 24-bit precision and 96 kHz bandwidth. The sound card is controlled using a program written in LabVIEW 2010 (National Instruments, ver. 10.0f2) and is a simple and cost effective solution to producing the AC waveform needed to control the FSM. The LabVIEW program produces the desired scan pattern as two waveforms, representing the x- and y-components of the pattern. These two waveforms are combined to form a stereo audio signal which is output from the external sound card, sent through a dual-channel voltage amplifier (homebuilt, see below), and finally passed to the FSM controller (FSM-CD300). Since the maximum output voltage of the external sound card ($V_{\text{out}}^{\text{max}} \approx \pm 3$ V) limits the accessible angular range of the FSM, a homebuilt amplifier is used to amplify the output
Figure 3.4: This diagram illustrates the space-filling spiral pattern, which consists of an outward-traveling spiral (blue) followed by an inward-traveling spiral (red). Dots indicate the location of laser shots on the sample while arrows show the direction of travel between laser shots. The pattern obeys boundary conditions specifying the minimum ($r_{\text{min}}$) and maximum ($r_{\text{max}}$) radius. Each laser shot is separated (tangentially) by a distance $d$ from the prior (and subsequent) laser shot. Likewise, after each $360^{\circ}$ cycle within the pattern, laser shots are displaced (radially) by the distance $d$. 
of the external sound card to fill more of the input voltage range of the FSM \((V_{\text{max}}^{\text{in}} = \pm 10 \text{ V})\). This amplifier has independently adjustable gain for both channels \((0 < G < 10)\) and automatically limits its output voltage to \(\pm 10 \text{ V}\). Any dual-channel or stereo amplifier with a bandwidth matching or exceeding that of the external sound card or FSM is sufficient for this purpose. Current-sourcing requirements are minimal due to the high impedance of the FSM controller inputs.

The three primary goals in formulating a scan pattern were to (1) increase as much as possible the average time before any position in the sample cell is revisited by the laser (resampling time), (2) minimize shot-to-shot spatial overlap of successive sequences of laser pulses, and (3) avoid driving the FSM beyond its mechanical limitations. These requirements eliminate certain approaches, including rastering line-by-line which cannot simultaneously satisfy goals 2 and 3 above under the experimental conditions of interest; the large bandwidth needed to reverse the mirror’s angular motion when moving from one scan line to the next would cause the FSM to exceed the current limit of its voice coils. An effective solution to these goals is a bidirectional space-filling spiral pattern. This pattern closely resembles an Archimedean spiral with laser shots spaced at a constant distance \(d\) along the path of the spiral, starting at some minimum radius and moving outward. Once the defined maximum radius is reached, the radial velocity is reversed (but not the tangential velocity) such that the beams are spiraled back to the minimum radius. This pattern assures that the centers of successive laser shots are separated by a controlled distance, \(d\), and that laser shots from one angular period of the scan pattern to the next are also separated by the same distance \(d\). The result is that, when considering only either the outward- or inward-traveling section of the pattern, the nearest-neighbor distance of each laser shot is \(d\). The space-filling spiral pattern has the advantage of constant shot-to-shot spatial overlap and maximal use of sample cell area, which is important for achieving long resampling times. The minimum radius parameter allows for better control of resampling time and for avoidance of the center part of the pattern where the angular frequency necessary to maintain the center-to-center spacing \(d\) can surpass the bandwidth limitations of the FSM. The disadvantage of the bidirectional scan pattern is that the outward- and inward-traveling sections of the spiral overlap to some extent at various points within each pattern.
This pattern was implemented by setting a constant tangential velocity $v_{\text{tan}} = dk_{\text{laser}}$ where $k_{\text{laser}}$ is the laser repetition rate and setting the radial velocity to $v_{\text{rad}}(t) = df_{\text{tan}}(t)$ where $f_{\text{tan}}(t) = \frac{v_{\text{tan}}}{2\pi r(t)}$ is the tangential cyclic frequency, $v_{\text{tan}}$ is the tangential velocity, and $r(t)$ is the radius of the pattern at time $t$. In polar coordinates, this pattern is described parametrically with respect to time by

$$r_{\min} = r_{\max} - d \text{ floor} \left( \frac{r_{\max} - r'_{\min}}{d} \right)$$  \hspace{1cm} (3.1)$$

$$t_{\max} = \frac{\pi \left( r_{\max}^2 - r_{\min}^2 \right)}{4d^2 k_{\text{laser}}}$$  \hspace{1cm} (3.2)$$

$$r(t) = \begin{cases} \sqrt{r_{\min}^2 + \frac{4d^2 k_{\text{laser}}}{\pi}}, & \text{if } \text{mod}(t, 2t_{\max}) \leq t_{\max} \\ \sqrt{2r_{\max}^2 - \frac{4d^2 k_{\text{laser}}}{\pi} - r_{\min}^2}, & \text{if } \text{mod}(t, 2t_{\max}) > t_{\max} \end{cases}$$  \hspace{1cm} (3.3)$$

$$\phi(t) = \begin{cases} \frac{\pi}{4} (r - r_{\min}), & \text{if } \text{mod}(t, 2t_{\max}) \leq t_{\max} \\ \frac{\pi}{4} (2r_{\max} - r - r_{\min}), & \text{if } \text{mod}(t, 2t_{\max}) > t_{\max} \end{cases}$$  \hspace{1cm} (3.4)$$

where $r(t)$ is the radius at time $t$, $\phi(t)$ is the angle at time $t$, $r'_{\min}$ is a parameter defining the desired minimum spiral radius, $r_{\min}$ is the implemented minimum spiral radius, $r_{\max}$ is the maximum spiral radius, $d$ is the center-to-center distance between laser shots, $t_{\max}$ is the time required to reach the maximum spiral radius, and $k_{\text{laser}}$ is the laser repetition rate. The floor function is defined such that floor($x$) is equal to the greatest integer not greater than $x$ (e.g. floor(8.6) = 8). The modulo operation, which is signified by mod($a, b$) and yields the integer remainder of division of $a/b$, chooses the form for functions $r(t)$ and $\phi(t)$ based on whether the beams are spiraling away from the center, as when mod($t, 2t_{\max}$) $\leq t_{\max}$, or spiraling towards the center, as when mod($t, 2t_{\max}$) $> t_{\max}$. The implemented minimum spiral radius is calculated from $r'_{\min}$ since, for the pattern to maintain its periodicity, $r_{\min}$ cannot take on arbitrary values, but must be constrained to $r_{\max}$ minus an integer multiple of $d$. The total pattern has a period of $2t_{\max}$ and contains $2t_{\max}k_{\text{laser}}$ laser shots, each separated in time by $1/k_{\text{laser}}$. 
Figure 3.5: A HeNe laser is split into two beams which are reflected off of an FSM and made to overlap on a screen. This figure shows the spatial interference between the two beams at multiple locations in a circular scan pattern. The image is constructed from 5 photographs taken at different locations within the scan pattern which have been normalized in brightness and contrast for better comparison and summed to form a single image. The resulting image is converted to grayscale and then inverted to produce a negative image. The interference fringes do not shift when the FSM is set to scan a circular pattern, indicating a high level of stability in the path length difference between the beams.
3.5 Characterization

A preliminary test was performed before construction of the full beam scanning apparatus with the aim of characterizing the stability of an interferometer on the optical table when using an FSM to scan the beams. A HeNe laser was split with a 50/50 beamsplitter and the resulting two beams were directed, propagating parallel to one another, towards the FSM where a $90^\circ$ reflection sent them to a white screen approximately 7.3 m from the FSM. By adjustment of the last mirror preceding the FSM, one beam was steered such that its image on the screen overlapped with that of the other beam. Due to the angle between the two beams, the image exhibited spatial interference fringes which are sensitive to changes in the relative phase between the beams arising from their path length difference. The FSM was made to scan a circular pattern and photographs were taken of the image at different points in the scan (Figure 3.5). Any changes in fringe location within the beam profile would be indicative of a change in the relative path length, which would translate into a change in the time delay between pulses in a time-resolved experiment. The invariance of the spatial interference fringes with FSM deviation angle shows that the FSM does not induce vibration that would prevent use of an interferometer when scanning.

The refractive beam scanning setup was characterized to quantify how laser spot size, pump-probe overlap, pulse duration, and pump-probe delay vary during beam scanning. The laser focal spot was imaged\textsuperscript{115} in the focal plane as a function of FSM deflection angle using an imaging sensor (ZoomCam USB Model 1598 with lens removed). Placement of the imaging sensor in the focal plane was described in Section 3.2.2.1. The resulting images of pump and probe beams were fit with a 2D elliptical Gaussian to extract the spot widths (44 µm FWHM), which varied by less than 4% for either beam over the full $\sim$2 mm square sampled scanning area. Since the measured spot width varies by as much as 6% depending on how well the imaging sensor is placed in the focal plane, 4% should be viewed as an upper bound on the position-dependent spot width variation. The 2D Gaussian fits also indicate the positions of pump and probe focal spots at each FSM deflection angle, enabling changes in relative spot position to be quantified. Relative spot position is defined
as the spatial separation between pump and probe beam centers in the plane of the imaging sensor. For the same range of FSM deflection angles as above, the root-mean-square (RMS) deviation of the relative spot position (as a percentage of the full-width half-maximum of the focal spot) was 8.2% in the horizontal dimension and 14.5% in the vertical dimension, both of which are within the precision of this measurement (∼15.5%), which is limited by the estimated ±2.5° accuracy of placing the imaging sensor in the focal plane. Assuming that a change in relative beam position is the result of a change in the z-position of the pump-probe crossing point relative to the surface of the imaging sensor, a 14.5% change in the relative spot position corresponds to a 163 µm change in the relative z-position for the refractive implementation depicted in Figure 3.1. This is a relatively small distance compared to not only the sample path length (1 mm), but also the crossing length of the beams (2.25 mm) and the Rayleigh range (5.74 mm). In addition, changes in relative beam position in the plane of the imaging sensor can result from optical aberrations in the focusing optics which cause the z-position of the focus to vary with FSM deflection angle.

To quantify the difference in signal between transients under scanning- and stationary-beam conditions, the normalized RMS deviation (NRMSD)

\[
NRMSD = \sqrt{\frac{1}{n_T} \sum_{i=1}^{n_T} [S_{\text{scanning}}(T_i) - S_{\text{stationary}}(T_i)]^2}
\]

max(S_{\text{stationary}}) - min(S_{\text{stationary}})

(3.5)

is used, where \( S(T) \) is the transient signal at pump–probe delay \( T \), and \( i \) indexes over all \( n_T \) pump–probe delays.

An intensity-detected second-order noncollinear autocorrelation was measured both with the FSM held at a constant deflection angle and with the FSM performing the space-filling spiral pattern. The laser system utilized for these tests produces ∼75 fs pulses at 10 kHz with a wavelength of ∼800 nm and autocorrelations were recorded from −400 fs to 400 fs with 5 fs time steps. The maximum possible pattern size with the 5 mm diameter BBO crystal was used and the resulting autocorrelation showed no apparent difference to the stationary-beam autocorrelation. The normalized RMS deviation (eq. 3.5) between scanning- and stationary-beam autocorrelations was
0.34%, which is less than the normalized RMS deviation (0.39%) between two stationary-beam autocorrelations taken under equivalent conditions. Fitting a Gaussian function to the autocorrelations from $T = -100 \text{ fs}$ to $100 \text{ fs}$ gives a difference between the scanning- and stationary-beam autocorrelations of 1.2% in peak height, 0.074 fs in peak position, and $<0.1 \text{ fs}$ in peak width. The same comparison applied to two equivalent stationary-beam autocorrelations yields a difference of 0.4% in peak height, 0.42 fs in peak position, and 0.27 fs in peak width.

Pump-probe transients of the laser dye IR-144 were taken both with the space-filling pattern and with stationary beams. The time step size was 10 fs and comparisons were restricted to pump-probe time delays between $-500 \text{ fs}$ and $+500 \text{ fs}$ where the signal is most sensitive to changes in pulse timing. The resulting transients have a normalized RMS deviation (eq. 3.5) of 0.73%, which is less than the normalized RMS deviation (1.03%) between two stationary-beam transients. In addition to this quantitative agreement, the qualitative shapes of the transients match at both short and long timescales.

It can be seen in Figure 3.4 that the outward-travelling and inward-travelling spirals cross over one another several times within the pattern. This motivated further characterization of the bidirectional space-filling spiral pattern to quantify the effect of this intra-pattern focal spot overlap. First, the spatial and temporal coordinates of each focal spot within a single cycle of the pattern are calculated for a given set of pattern parameters. Assuming a 2D Gaussian spatial profile, $h(x, y)$, for the focal spots, the integrated overlap between every combination of two focal spots in the pattern is calculated:

$$H_{a,b} = \int_{-\infty}^{+\infty} h_a(x, y) \cdot h_b(x, y) dx dy$$  \hspace{1cm} (3.6)

where $a$ and $b$ index over focal spots in the scan pattern, each taking on integer values from 1 to $N$. Each combination of two focal spots, and consequently each integrated overlap value, also has a specific time interval associated with it. This “resampling” time interval, $\tau_{\text{resampling}}^n$, is equal to the time delay between the two laser shots and is some integer multiple, $n$, of the laser repetition period. For a pattern with $N$ focal spots, there are $N$ resampling time intervals, each with an integer index,
Figure 3.6: A simulation of the integrated overlap $H_n$ between laser focal spots at every resampling time index $n$ during one cycle of the bidirectional space-filling spiral pattern. This particular pattern has 5027 points, a period of 0.503 s, and an average resampling time of 0.331 s. Center-to-center spot separation, $d = 50 \, \mu m$; laser repetition rate, $k_{\text{laser}} = 10 \, \text{kHz}$; full-width half-maximum of Gaussian focal spot, $w_{0}^{\text{FWHM}} = 42 \, \mu m$; maximum spiral radius, $r_{\text{max}} = 3 \, \text{mm}$; desired minimum spiral radius, $r'_{\text{min}} = 1 \, \text{mm}$. The inset is a close-up view which shows the first half of resampling times (up to $n = 2513$) since the two halves are mirror images.
\( n = \tau_{\text{resampling}} k_{\text{laser}} \), ranging from 1 to \( N \) in order of increasing duration. The overlap values for focal spot pairs with equal resampling time intervals are then summed, yielding the total overlap at each resampling time interval (or laser shot-to-shot interval) within the pattern:

\[
H_n = \sum_{a=1}^{N} H_{a,a+n}
\]  

The result of this analysis for typical experimental conditions is illustrated in Figure 3.6. The data point at the end of the pattern with a height of 1 is the perfect overlap which occurs between any two laser focal spots separated by one complete cycle of the pattern, and its value serves as a reference level for comparison to the overlap that occurs at shorter intervals within a single cycle of the pattern. The second highest overlap values, compared to the maximum at \( n = N \), occur at \( n = 1 \) and \( n = N - 1 \). These points represent the overlap between adjacent focal spots and have equal values (\( \sim 0.15 \)) due to the periodicity of the pattern. This mirror symmetry extends to all points in the pattern and obeys the relationship \( H_n = H_{N-n} \). Outside of the points at \( n = \{1, N - 1, N\} \), no other resampling time has an overlap of more than 1.8% of the peak. Overall, only 8.3% of resampling times having an overlap of more than 0.1% and fewer than 0.06% of resampling times have an overlap of more than 2%.

Using the overlap versus resampling time data from this analysis, the average resampling time can be calculated, defined as the weighted average of resampling time using overlap at each resampling time as the weighting factor, yielding

\[
\langle \tau_{\text{resampling}} \rangle = \frac{\sum_{n=1}^{N} \tau_{\text{resampling}} n \cdot H_n}{\sum_{n=1}^{N} H_n}
\]  

For the pattern in Figure 3.6, the average resampling time is 0.331 s, which is about 35% lower than the pattern period of 0.503 s. The average resampling time approaches the pattern period as the ratio of spatial width to spot separation goes to zero (\( w_0^{\text{FWHM}} / d \to 0 \)).

A two-dimensional ray tracing simulation of pump and probe beam paths in the reflective optics implementation (for \( r_{\text{max}} = 3 \) mm, 2.9° beam crossing angle, and \( f = 20 \) cm) indicates that
when the sample cell is aligned in the plane of maximum pump-probe overlap (for example, by the method described in Section 3.2.2.1 above) to within $\pm \sin^{-1}[L/(2r_{\text{max}})]$ ($= \pm 9.6^\circ$ for $L = 1$ mm and $r_{\text{max}} = 3$ mm), the pump-probe delay varies by less than 0.16 fs over the full range of the scan pattern. This is less than 6% of a period of 800 nm wavelength light (2.67 fs), suggesting that sample renewal by beam scanning might be appropriate even for noncollinear spectroscopic techniques requiring interferometric stability of pulse delays, such as 2DFT spectroscopy. In addition, 0.16 fs is much less than the calculated crossing-angle delay smearing $\delta t = \alpha_0 w_{\text{fwhm}}^0/c = 3.50$ fs where $2\alpha_0 = 2.86^\circ$ is the crossing angle between beams, $w_{\text{fwhm}}^0 = 42 \mu$m is the diameter of the beam focal spot, and $c$ is the speed of light.

### 3.6 Conclusions

A new probed-volume sample renewal technique that uses a computer-controlled fast steering mirror to scan laser beams across a sample cell was designed, constructed, and characterized. Both refractive and reflective optics implementations were explored. The capability of this technique to provide shot-to-shot sample renewal at a laser repetition rate of 10 kHz is demonstrated. Based on the published specifications of the FSM-300, it is expected that shot-to-shot sample renewal at repetition rates of up to 100 kHz are possible with this apparatus depending on the experimental geometry and scan pattern, with even higher repetition rates possible with a faster steering mirror.

As with other sample renewal techniques, beam scanning is sensitive to spatial variations of the sample. Time domain and frequency domain filtering were found to be valuable in mitigating this source of noise. Additionally, signal averaging on multiple time scales and with a varying data sampling rate reduces the magnitude of noise arising from sample inhomogeneity.

A bidirectional space-filling spiral scan pattern was developed which enables long resampling times while minimizing shot-to-shot overlap. The intra-pattern focal spot overlap was characterized computationally to estimate the effective average resampling time which, for the given experimental conditions, is 0.331 s. This is 35% shorter than the nominal pattern period of 0.503 s.

The extent to which beam scanning alters pump-probe focal spots and timing was char-
acterized for the refractive optics implementation. Upper bounds on the variation of focal spot width (4%) and relative pump-probe spot position (15%) were determined by imaging pump and probe beams in the focal plane at a range of FSM deviation angles. Intensity-detected second-order noncollinear autocorrelations under scanning- and stationary-beam conditions are indistinguishable within the 0.39% uncertainty in signal size. Likewise, pump-probe transients of IR-144 are invariant to beam scanning within the 1.03% experimental uncertainty in signal size. Ray tracing simulations of the reflective optics implementation predict that beam scanning can alter the pump-probe delay by up to 0.16 fs.

Sample renewal by beam scanning extends the ability to limit repetitive excitation to sample cells of practically all sizes and shapes, enabling cleaner spectroscopic measurements in samples for which it is either inconvenient or impossible to move the sample relative to the light source, such as cryostats and other bulky or heavy sample cells. It also decouples sample renewal from the sample cell itself such that many different types of sample cells can share the same sample renewal apparatus and, if desired, the same sample renewal parameters. The flexibility in scan pattern compared to other sample renewal methods allows this technique to be adapted to a wide range of needs and opens up the possibility of using the resampling time as an adjustable experimental parameter to measure dynamics, such as those of carrier trapping in semiconductor nanostructures. In addition, this flexibility enables beam scanning to be used in concert with other sample renewal techniques, such as sample flowing or spinning, to further extend the resampling time.
Chapter 4

Carrier Dynamics in Colloidal Indium Arsenide Quantum Dots

4.1 Introduction

Colloidal quantum dots (QDs) have generated significant interest in recent decades. Their uniquely tunable electronic properties make QDs appealing for such applications as solar energy harvesting (in both photovoltaic and photochemical cells), fluorescent tagging of bio-molecules, and illumination (for example light-emitting diodes, laser diodes, and fluorescent phosphors). It has been proposed\textsuperscript{117,118} that the energy efficiency of solar photovoltaics could be improved over existing single-junction solar cell technology by exploiting the phenomenon of carrier multiplication (CM)\textsuperscript{119,120} in arrays of colloidal semiconductor QDs. CM, also known as multiple exciton generation (MEG) in isolated QDs, is a process by which absorption of a single photon with an energy of at least twice the band gap ($\hbar \nu \geq 2E_g$) produces multiple electron–hole pairs (excitons). Initial studies reported that CM is more efficient in QDs than in bulk semiconductors,\textsuperscript{121–124} making QD photovoltaic devices that utilize CM a promising application. These studies critically rely on the quantification of certain carrier relaxation processes to determine the efficiency of CM using pump–probe transient absorption spectroscopy. However, the reproducibility of these results has been problematic.\textsuperscript{88,89,92,125–127} Irreproducibility has been attributed to sample variations\textsuperscript{88,128} (especially differences in QD surface chemistry), unintended (and unaccounted for) multiphoton excitation,\textsuperscript{125} and repetitive excitation.\textsuperscript{88,89,91}

These experimental complications motivated the thorough evaluation of carrier relaxation in InAs QDs under well-controlled conditions using degenerate pump–probe transient absorption
spectroscopy presented here. Central to this goal is characterization of single- and bi-exciton relaxation dynamics as a function of excitation probabilities that extend into the low excitation probability regime (from 125% down to 9%) and with long intervals between excitations (>0.3 s). Excitation probability, which is the probability of excitation by the pump pulse averaged over the pump and probe spatial profiles, determines the proportion of QDs with zero, one, two, etc. excitations contributing to the pump–probe signal and its control is important when attempting to isolate single-, bi-, and multi-exciton dynamics from one another. The interval between excitations, given by the average resampling time \( \langle \tau_{\text{resampling}} \rangle \) (see Chapter 3), quantifies the length of time before a point in the sample excited by the pump is revisited by the pump. The average resampling time is equal to the laser repetition rate when no probed-volume sample renewal method is used (i.e. stationary sample and stationary beams), but has been extended to >0.3 s in this work through use of beam scanning (see Chapter 3).

Indium arsenide (InAs) has a number of bulk properties that make it a good candidate for studying CM. Its low bulk band gap \( (E_g^{\text{bulk}} = 0.36 \text{ eV}) \) enables the synthesis of QDs with a band gap in the near infrared \( (E_g \approx 1 \text{ eV}) \), which is in the range predicted to be optimal for use in solar photovoltaic devices with CM absorbers.\(^{118}\) InAs has a relatively high electron mobility \( (\mu_n = 27000 \text{ cm}^2/\text{Vs at 300 K}) \)\(^{129}\), implying that phonon-mediated electron cooling, which competes with CM, is slow. Due to a large imbalance between electron and hole effective masses \( (m^*_h/m^*_e \approx 16) \) in InAs\(^{129}\), the electron receives the majority of the excess energy imparted by an absorbed photon with energy greater than the band gap, assuming that the combined momentum of the electron and hole is conserved in the light absorption process. With the majority of the excess energy concentrated into one carrier, the threshold for CM could be lower than in materials with equal carrier effective masses.\(^{124}\) However, it has been suggested that the high effective mass for holes in InAs makes the competing Auger cooling of electrons more efficient,\(^{21}\) and it is unclear how these competing effects are manifested in the CM yield.

To predict the average number of excitations per QD for a given pump pulse fluence (photon flux time-integrated over a pulse) without knowledge of the frequency dependence and time depen-
dence of the absorption cross sections for all optically-allowed excited state absorption transitions within the laser bandwidth, assumptions must be made regarding the absorptive properties of the sample. If a chromophore’s probability of absorbing a photon is unaffected by its prior history of excitation such that excitation events are independent and uncorrelated, then the number of photons absorbed by an ensemble of chromophores during a period of time will obey Poisson statistics. For this to be the case, the chromophore’s absorption cross section must not be affected by excitation (i.e. the ground state and all excited states must have the same absorption cross section within the pump pulse bandwidth and excited state stimulated emission must lie outside the laser bandwidth). Although this rarely holds for molecular systems, it is most likely to be approximately true for QDs at low excitation density in the bulk-like portions of their spectrum.\textsuperscript{130}

Assuming Poisson absorption statistics, the average number of photons absorbed per QD from a single pump pulse at each point in the sample is given by $\langle N_{eh} \rangle = \sigma_a \Phi$ where $\sigma_a$ is the absorption cross section of the QD and $\Phi$ is the pulse fluence at that point. To reflect the experimental conditions, the frequency and spatial dependence of $\Phi$ and the frequency dependence of $\sigma_a$ must be included and averaged over, resulting in the spatially-averaged excitation probability.

A common method for studying CM is through observation of its inverse process: Auger recombination (AR). AR is a relaxation pathway whereby an electron–hole pair recombines by transferring its energy into the electron or hole of another exciton. Since this can only occur in QDs which contain multiple electron–hole pairs, it provides a window through which to study processes that produce multiple excitons within a QD. Pump–probe experiments often take advantage of the large difference in timescale between AR (tens of picoseconds) and single exciton recombination (hundreds of picoseconds to microseconds) to quantify the fraction of QDs that initially contained multiple excitons (after pump excitation) by comparing signal amplitude before and after AR. Unfortunately, when cooling processes occur on timescales similar to or slower than AR, this method is not applicable to hot carrier excitation, where Poisson statistics are most likely to hold.

A handful of studies on carrier dynamics in colloidal InAs QDs have been reported. Pijpers et al.\textsuperscript{128} investigated multi-exciton dynamics in InAs/CdSe/ZnSe core/shell/shell QDs (4.4 nm
diameter core) by transient absorption spectroscopy. When pumping slightly to the blue of the
“1P” transition and probing the “1S” transition, a sub-picosecond carrier cooling time and a 30 ps
biexciton decay time were reported. Schaller et al.\textsuperscript{124} performed transient absorption spectroscopy
on InAs “core only” (4.3 nm diameter) and InAs/CdSe core/shell (3.9 nm diameter cores) QDs,
pumping on the red side of the second exciton peak (“1P”) and probing the “1S” transition. They
reported a carrier cooling time of 0.66 ps (∼0.5 ps/eV) for InAs/CdSe QDs, a biexciton lifetime of
8.3 ps for InAs “core only” QDs, and a single exciton lifetime of 192 ps for InAs “core only” QDs.
Based on transient absorption measurements, pumping at 1.55 eV and probing the first exciton
peak, Ben-Lulu et al.\textsuperscript{126} report 53 ps and 28 ps biexciton lifetimes and 3 ns and 5.2 ns single exciton
lifetimes for InAs/CdSe/ZnSe core/shell/shell QDs with first exciton peaks at 0.95 eV (5.9 nm
diameter cores) and 1.1 eV (4.9 nm diameter cores), respectively. Lastly, Pijpers et al.\textsuperscript{21} report
an electron relaxation time of ∼0.8 ps based on the rise of the transient absorption signal when
pumping the “1P” transition and probing the “1S” transition of 4.4 nm diameter InAs QDs with a
band gap of 1.1 eV. From the instrument response–limited rise time of the “1P”-pump–THz-probe
signal, Pijpers et al. give an upper bound of 150 fs (or 1 − 2 eV/ps) for the hole cooling time. For
the same THz measurements, biexciton time constants of 9.5 ps and 24 ps were reported in 4.0 nm
diameter InAs QDs and 4.9 nm diameter InAs/CdSe/ZnSe core/shell/shell QDs, respectively. As
a whole, these studies suggest a ∼0.8 ps time constant for 1P_e → 1S_e electron cooling and a 10 to
30 ps time constant for Auger recombination in ligand-passivated InAs QDs with a band gap of
approximately 1 eV.

4.2 Experimental Section

4.2.1 Sample Preparation and Characterization

In collaboration with Nathan R. Neale at the National Renewable Energy Laboratory, col-
loidal trioctylphosphine-passivated InAs QDs were synthesized by the hot-injection method follow-
ing the work of Cao and Banin\textsuperscript{131} and others.\textsuperscript{132,133} The dried QDs were stored in a glove box to
prevent air exposure. Samples for linear absorption and pump–probe spectroscopy were prepared immediately before experiments in a glove box by dissolving dried QDs in degassed toluene to produce a concentrated stock solution. An aliquot of stock solution was diluted to achieve the desired optical density and transferred to an air-tight sample cell (cuvette), 5 cm by 1 cm in dimension, with a 1 mm path length. The cuvette is sealed from the outside atmosphere by a PTFE high-vacuum valve (Ace Glass). For all pump–probe measurements, the sample optical density at the center of the laser spectrum ($\lambda = 793$ nm) was 0.10 through the 1 mm sample cell path length.

The QD sample was characterized by linear absorption spectroscopy in the visible and near-infrared wavelength ranges. The linear absorption spectrum is shown in Figure 4.1 along with the laser pulse spectrum. The mean QD diameter is 6.2 nm based on comparison of the central wavelength of the first exciton peak to an empirical sizing curve. The measured absorbance was converted to absorption cross section ($\sigma_a$) using the empirical scaling of absorption cross section at the first exciton peak with QD radius reported by Yu et al. The two lowest energy excitonic transitions, $1S_e 1S_h$ at $\lambda = 1199$ nm and $1P_e 1P_h$ at $\lambda \approx 900$ nm, are labeled 1S and 1P, respectively. The laser pulse spectrum, centered at $\lambda = 793$ nm and with a FWHM bandwidth of $\Delta \lambda = 21$ nm, overlaps with the far-blue wing of the 1P transition.
Figure 4.1: Visible–near-infrared absorption spectrum of colloidal InAs quantum dots (blue). The first (1S) and second (1P) exciton peaks are centered at $\lambda = 1199$ nm and $\lambda \approx 900$ nm respectively. The laser spectrum (red; arbitrarily scaled) is centered at $\lambda_{pu,pr} = 793$ nm and has a full-width at half-maximum bandwidth of $\Delta \lambda = 21$ nm. The small region of negative absorbance near $\lambda = 1700$ nm is the result of imperfect background subtraction of solvent (toluene) absorption features.
Transmission electron microscopy (TEM) images (Figure 4.2) demonstrate that the QDs are roughly spherical in appearance. Although they do have some polygonal features, QDs do not appear to be elongated in any dimension. An analysis of 110 QDs using a spherical shape model indicated a mean (median) QD diameter of 6.18 nm (6.21 nm) with a standard deviation of 0.72 nm.
Figure 4.2: Transmission electron micrograph of the colloidal InAs QD sample. Fitting individual QDs to a spherical shape model yields median and mean QD diameters of 6.18 nm and 6.21 nm, respectively, with a standard deviation of 0.72 nm. The image has a magnification factor of 205,000. A 20 nm scale bar is shown beneath.
4.2.2 Pump–Probe Spectroscopy

The output of a Ti:Saph regenerative amplifier (Coherent RegA; $\lambda = 793$ nm, 10 kHz repetition rate, 85 fs pulse duration) is split into pump and probe beams. An optical chopper (3501, New Focus) that is synchronized (i.e. phase-locked) to the 4th subharmonic of the laser repetition rate amplitude modulates the pump beam at 2.5 kHz (two pulses transmitted and two pulses blocked in each cycle) and is phased such that pulse clipping is minimized. Pump and probe beams then enter an interferometer that controls the time delay ($T$) of the probe pulses relative to the pump pulses. From the interferometer, parallel (but non-collinear) beams propagate into a beam scanning apparatus (Chapter 3) that enables resampling times of $\sim$0.33 s for the measurements reported here. The beam scanning apparatus uses a fast steering mirror (FSM) to move the pump–probe focal spot in a repeating spiral pattern with respect to a stationary sample such that the laser photon flux (and consequently the time-averaged excitation) is spread over a $\sim 25$ mm$^2$ area of the sample cell, reducing repetitive excitation. Pump and probe beams are focused to a common point in the sample by a 20 cm focal length spherical curved mirror (CM1), producing a beam focal spot FWHM of 48 $\mu$m. An identical curved mirror (CM2) collimates the probe beam and brings it to a stationary point at the photodiode detector (PD).

The electrical signal from the probe photodiode is filtered and amplified by a gated integrator (SR250, Stanford Research Systems) which time-integrates the single pulse waveform from the photodiode during a short time window (on the order of the response time of the detector) and amplifies the voltage level. The output is then routed to a lock-in amplifier (SR830, Stanford Research Systems) that is referenced to the optical chopper. The lock-in amplifier isolates and amplifies components of its input waveform that oscillate at the same frequency as, and in phase with, the optical chopper. The resulting pump–probe signal is read digitally from the lock-in amplifier by a PC executing a LabVIEW program that controls data collection. Noise mitigation and signal averaging methods are discussed in Chapter 3. The signal is averaged 3–10 times at each time delay in a scan and 3–25 scans are collected and averaged.
Pump–probe transients from $T = -1$ ps to 1 ns were collected with a 1 nJ probe pulse energy ($E_{pr}$) and at pump pulse energies ($E_{pu}$) ranging from 0.45 nJ to 6.23 nJ (see Table 4.1). The focal spot of pump and probe beams at their crossing point in the sample location was characterized using an imaging sensor (ZoomCam USB Model 1598 with lens removed; 330K pixel CMOS sensor; 7.4 µm pixel size; 8-bit depth), yielding an intensity FWHM beam focal spot size of 48 µm. The pump–probe signal was confirmed to be linear with respect to sample optical density (to within 10% relative to the signal maximum) at both short ($T = 0$) and long ($T = 1$ ns) time delays for optical densities of 0.016 and 0.10, although at an optical density of 0.37 this was no longer the case. Scaling of pump–probe signal with probe pulse energy was also tested. At a probe pulse energy of 1 nJ, the signal was found to be $99 \pm 15\%$ of the linear extrapolation from low pulse energy.

The probe-weighted spatially-averaged excitation probability induced by the pump pulse was calculated for each experimental pump pulse energy. For simplicity, pump and probe beams were approximated such that they (a) overlap perfectly through the entire sample cell, (b) have identical circular Gaussian intensity profiles, (c) have identical spectra, (d) are well-collimated over the length of the sample cell (Rayleigh range $z_R = 6.7$ mm), (e) are linearly attenuated by the sample (i.e. absorption obeys the Beer-Lambert law), and (f) have a frequency bandwidth that is small compared to both their central frequency and the bandwidth of overlapping features in the sample absorption spectrum such that the pulse bandwidth can be neglected (variation in optical density within the pulse FWHM bandwidth is less than 5%). Under these approximations, the pump and probe Gaussian beam spatial profiles\textsuperscript{114} are given by

$$h(r, z) = \frac{2}{\pi w^2} \exp\left(-\frac{2r^2}{w^2}\right) \exp(-\alpha z)$$

where $r$ is the radial polar coordinate perpendicular to the axis along which the beam(s) propagates ($z$), $w$ is the beam spot size [$h(r = w, z = 0)/h(r = 0, z = 0) = 1/e^2$], $\alpha = [\text{OD ln}(10)]/L$ is the intensity attenuation coefficient at the center of the pulse spectrum, OD is the sample optical density, and $L$ is the sample path length. The beam spot size is related to the FWHM diameter...
of beam intensity through \( w = \frac{d_{1/2}}{\sqrt{2 \ln 2}} \). The beam spatial profile at the sample cell entrance \((z = 0)\) has unit area: \( \int_0^{\infty} h(r, z = 0) 2\pi r \, dr = 1 \). Multiplying eq. 4.1 by the number of incident pump pulse photons \([N^0_{pu} = \frac{U^0_{pu}}{(h\omega)}]\) where \( U^0_{pu} \) is the incident pump pulse energy yields the pump pulse photon fluence

\[
\Phi_{pu}(r, z) = N^0_{pu} h_{pu}(r, z) = \frac{U^0_{pu}}{h\omega} h_{pu}(r, z) \tag{4.2}
\]

where variables with a subscript “pu” relate to the pump pulse. Subsequent multiplication of the pump pulse photon fluence in eq. 4.2 by the absorption cross section \((\sigma_a)\) of the QD sample at the central frequency of the pump pulse gives the excitation probability as a function of position within the sample

\[
N_{eh}(r, z) = \Phi_{pu}(r, z) \sigma_a. \tag{4.3}
\]

The number of absorbed photons per QD is assumed to obey Poisson statistics although this cannot be rigorously true since it predicts that there would be no pump–probe signal during pulse overlap, in contradiction to experimental observation. On the other hand, there is no measurable deviation (less than 1%) from the linear pump absorption predicted by Poisson statistics although Poisson statistics are not required for linear pump absorption. (For example, a harmonic oscillator has no nonlinear response and the same net linear absorption for all pulse energies, but has different level population statistics. Non-interacting carriers have the evenly spaced energy levels of a harmonic oscillator.) The probability of a QD having \( n \) excitations,

\[
P_n(r, z) = \frac{[N_{eh}(r, z)]^n \exp [-N_{eh}(r, z)]}{n!}, \tag{4.4}
\]

is then calculated using the Poisson distribution with \( N_{eh} \) as the mean. The Poisson probability coefficients for \( n = 0, 1, 2, \ldots \) in eq. 4.4 are spatially averaged over the probe beam spatial profile

\[
\langle P_n \rangle_{r,z} = \frac{\int_0^{\infty} 2\pi r \, dr \int_0^L dz \, P_n(r, z) \, h_{pr}(r, z)}{\int_0^{\infty} 2\pi r \, dr \int_0^L dz \, h_{pr}(r, z)} \tag{4.5}
\]

by numerical integration. The subscript “pr” in eq. 4.5 emphasizes that the spatial average is weighted by the probe spatial profile. Note that even if the underlying probability of excitation at
each point in the sample has a Poisson distribution, the probe-weighted spatially-averaged Poisson coefficients $\langle P_n \rangle_{r,z}$ do not rigorously obey a Poisson distribution; they approach the underlying distribution as $U_{pu}^0$ goes to zero. Finally, the probe-weighted spatially-averaged excitation probability

$$\langle N_{eh} \rangle_{r,z} = \sum_{n=1}^{\infty} n \langle P_n \rangle_{r,z} \quad (4.6)$$

is calculated. The probe-weighted spatially-averaged excitation probability is linearly proportional to the pump pulse energy: $\langle N_{eh} \rangle_{r,z} = (0.201 \, \text{nJ}^{-1}) U_{pu}^0$ for the conditions of these experiments.
Table 4.1: Experimental incident pump pulse energies, $U_{pu}^0$, and probe-weighted spatially-averaged excitation probabilities, $\langle N_{eh} \rangle_{r,z}$ (eq. 4.6). $\langle P_n \rangle_{r,z}$ (eq. 4.5) is the spatially-averaged probability of exciting a QD $n$ times based on Poisson absorption statistics at each point in the sample. $\langle P_n \rangle_{r,z}/(1 - \langle P_0 \rangle_{r,z})$ is the fraction of excited QDs that have $n$ excitons and $n\langle P_n \rangle_{r,z}/\sum_m m\langle P_m \rangle_{r,z}$ is the fraction of signal arising from QDs with $n$ total excitons on the assumption that the signal is linearly proportional to the number of excitons. Absorption cross section, $\sigma_a(\lambda = 793$ nm) = 2.979 $\times$ 10$^{-15}$ cm$^2$; beam spot size, $w = 41$ µm; optical density, OD($\lambda = 793$ nm) = 0.10.

<table>
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<th>$U_{pu}^0$ (nJ)</th>
<th>$N_{eh}(r = 0, z = 0)$</th>
<th>$\langle N_{eh} \rangle_{r,z}$</th>
<th>$\langle P_0 \rangle_{r,z}$</th>
<th>$\langle P_1 \rangle_{r,z}$</th>
<th>$\langle P_2 \rangle_{r,z}$</th>
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<td>0.69</td>
<td>0.24</td>
<td>0.059</td>
<td>0.012</td>
</tr>
<tr>
<td>3.74</td>
<td>1.67</td>
<td>0.75</td>
<td>0.52</td>
<td>0.29</td>
<td>0.13</td>
<td>0.044</td>
</tr>
<tr>
<td>6.23</td>
<td>2.79</td>
<td>1.25</td>
<td>0.37</td>
<td>0.28</td>
<td>0.18</td>
<td>0.097</td>
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<tr>
<th>$U_{pu}^0$ (nJ)</th>
<th>$\langle P_1 \rangle_{r,z}/(1 - \langle P_0 \rangle_{r,z})$</th>
<th>$\langle P_2 \rangle_{r,z}/(1 - \langle P_0 \rangle_{r,z})$</th>
<th>$\langle P_3 \rangle_{r,z}/(1 - \langle P_0 \rangle_{r,z})$</th>
<th>$\sum_n n\langle P_n \rangle_{r,z}$</th>
<th>$\sum_n 2\langle P_n \rangle_{r,z}$</th>
<th>$\sum_n 3\langle P_n \rangle_{r,z}$</th>
</tr>
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<tr>
<td>0.45</td>
<td>94%</td>
<td>5.6%</td>
<td>0.25%</td>
<td>89%</td>
<td>11%</td>
<td>0.7%</td>
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<tr>
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<td>87%</td>
<td>11%</td>
<td>1.1%</td>
<td>77%</td>
<td>20%</td>
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<tr>
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<td>82%</td>
<td>16%</td>
<td>2.3%</td>
<td>68%</td>
<td>26%</td>
<td>5.7%</td>
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<tr>
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<td>29%</td>
<td>15%</td>
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</table>
Linearity of pump pulse transmission was tested by measuring the pump pulse energy before and after transmission through the InAs sample as compared to a solvent (toluene) blank. A saturation fit (see Section 4.3.2) to the transmitted pump pulse energy in Figure 4.3 suggests that nonlinear contributions to pump pulse absorption are below the 0.2% level for probe-weighted spatially-averaged excitation probabilities up to 1.2.
Figure 4.3: Transmitted pump pulse energy, $U_{pu}^{\text{transmitted}}$, as a function of incident pump pulse energy, $U_{pu}^0$, (blue circles) for the InAs QD sample and a saturation model fit (red line) with $x = 0.926$ and $y = 4.85 \cdot 10^{-5}$. In the lower panel, the linear component of the saturation fit has been subtracted from both the saturation fit (red line) and transmitted pump pulse energy (blue circles). Sample path length, $L = 250 \ \mu m$; optical density, $OD(\lambda = 793 \ \text{nm}) = 0.04$; laser repetition rate, $k_{\text{laser}} = 20 \ \text{kHz}$; beam spot size, $w = 127 \ \mu m$. 
The effect of repetitively exciting the sample was evaluated by measuring the pump power dependence of pump–probe signal at $T = 1$ ns with beam scanning pattern durations of $\tau_{\text{pattern}} = 38.6$ ms and $\tau_{\text{pattern}} = 614$ ms, as illustrated in Figure 4.4. No difference is observed between the two tested pattern durations within the signal-to-noise of the measurement. Assuming that upon excitation by the pump pulse, the quantum yield for entering a long-lived state with lifetime $\tau_{\text{LLS}}$ is $\phi_{\text{LLS}}$ and that excitons in long-lived states do not contribute to pump–probe signal, an upper limit for the quantum yield–lifetime product can be estimated. The steady-state buildup of a trap state population evaluated using a two-state model that includes a ground state (GS) and a trap state (TS)

\[ \text{GS} \]
\[ \text{TS} \]

\[ k_f \]
\[ k_r \]

where the rates for entering and leaving the trap are $k_f = \phi_{\text{LLS}} \langle N_{eh} \rangle_{r,z}/\tau_{\text{pattern}}$ and $k_r = 1/\tau_{\text{LLS}}$, respectively. If the ground state and trap state probabilities sum to 1, then the steady-state probability of the trap state is

\[ [\text{TS}] = \frac{k_f}{k_f + k_r} = \frac{\phi_{\text{LLS}} \langle N_{eh} \rangle_{r,z}/\tau_{\text{pattern}}}{k_r + \phi_{\text{LLS}} \langle N_{eh} \rangle_{r,z}/\tau_{\text{pattern}}}. \]  

(4.7)

Solving for $\phi_{\text{LLS}}/k_r$ yields

\[ \frac{\phi_{\text{LLS}}}{k_r} = \phi_{\text{LLS}} \cdot \tau_{\text{LLS}} = \frac{[\text{TS}] \tau_{\text{pattern}}}{1 - [\text{TS}] \langle N_{eh} \rangle_{r,z}}. \]  

(4.8)

At the highest probe-weighted spatially-averaged excitation probability in Figure 4.4 ($\langle N_{eh} \rangle_{r,z} = 2.72$), the combined uncertainty in the data between the two pattern durations ($2.43 \cdot 10^{-5}$) is 11.3% of the signal size ($2.15 \cdot 10^{-4}$). Therefore, if the trap state yields no pump–probe signal, the trap state could account for as much as 11.3% of the QD population at the highest excitation probability. An upper bound on $\phi_{\text{LLS}} \cdot \tau_{\text{LLS}}$ is thus calculated from eq. 4.8 by substituting $\tau_{\text{pattern}} = 38.6$ ms,
\langle N_{eh} \rangle_{r,z} = 2.72, and \lbrack TS \rbrack = 0.113 on the right-hand side to yield \phi_{\text{LLS}} \cdot \tau_{\text{LLS}} \leq 0.00181. This upper bound on \phi_{\text{LLS}} \cdot \tau_{\text{LLS}} indicates that the percentage of QD population in the trap state is less than 0.03\% for \langle N_{eh} \rangle_{r,z} = 9.0\% and \tau_{\text{pattern}} = 614 ms.
Figure 4.4: Pump–probe signal, $\Delta N/N_0$, measured as a function of probe-weighted spatially-averaged excitation probability, $\langle N_{eh} \rangle_{r,z}$, with beam scanning patterns of time duration $\tau_{\text{pattern}} = 38.6$ ms (blue circles) and $\tau_{\text{pattern}} = 614$ ms (red squares). Sample path length, $L = 1$ mm; optical density, $\text{OD}(\lambda = 793 \text{ nm}) = 0.1$; laser repetition rate, $k_{\text{laser}} = 10$ kHz; beam spot size, $w = 64$ µm.
4.3 Results and Discussion

4.3.1 Pump–Probe Transients

Pump–probe transients over the full 1 ns range of time delays are shown in Figure 4.6. Dynamics prior to $T = 20$ ps are highlighted in Figure 4.5. Pump–probe signal is the change in the number of transmitted probe photons ($\Delta N$) caused by prior pump excitation (compared to without pump excitation) divided by the total number of incident probe photons ($N_0$). Pump–probe transients at a range of excitation probabilities were collected in the following order: $\langle N_{eh} \rangle_{r,z} = 75\%$, $125\%$, $30\%$, $20\%$, $9.0\%$, and $40\%$. To correct for small accumulated errors in delay stage position due to occasional mis-steps (a second harmonic autocorrelation recorded immediately after the experiment showed time zero changes by $+20$ fs compared to the time zero immediately before the experiment), the pump–probe delay axes were adjusted such that the rise of the signal coincides between transients. This involved a $+10$ fs shift for transients with $\langle N_{eh} \rangle_{r,z} = 40\%$ and $\langle N_{eh} \rangle_{r,z} = 125\%$ as well as a $+20$ fs shift for the $\langle N_{eh} \rangle_{r,z} = 75\%$ transient. An increase in signal size with increasing excitation probability is visually apparent. When normalized by excitation probability, as in Figures 4.7 and 4.8, the four lowest excitation transients are in good agreement. However, the 75% and 125% excitation probability transients lie slightly below the others starting at time zero (see Figure 4.8), possibly indicating saturation of the pumped transition. This trend persists through $T = 1$ ns.
Figure 4.5: Pump–probe transients from $T = -1$ ps to 20 ps. Signal $(\Delta N/N_0)$ is plotted as the change in number of transmitted probe photons per incident probe photon, multiplied by a factor of $10^3$. 
Figure 4.6: Pump–probe transients over the full 1 ns range of time delays. Signal \( \frac{\Delta N}{N_0} \) is plotted as the change in number of transmitted probe photons per incident probe photon, multiplied by a factor of \( 10^3 \).
Figure 4.7: Pump–probe transients from $T = -1$ ps to 20 ps, normalized by excitation probability. Signal $\left( \Delta N / N_0 \right)$ is plotted as the change in number of transmitted probe photons per incident probe photon, divided by the spatially-averaged excitation probability $\left( \langle N_{eh} \rangle_{r,z} \right)$, and multiplied by a factor of $10^3$. 
Figure 4.8: Pump–probe transients from \( T = -1 \) ps to 2 ps, normalized by excitation probability. Signal \((\Delta N/N_0)\) is plotted as the change in number of transmitted probe photons per incident probe photon, divided by the spatially-averaged excitation probability \((\langle N_{eh}\rangle_{r,z})\), and multiplied by a factor of \(10^3\).
4.3.2 Saturation Model

To model the power dependence of the signal, transients were fit to a two-level system saturation model. This model relates pump pulse energy (or, equivalently, excitation probability) to signal amplitude through

\[
S_{pp}^{sat}(U_{pu}^0; x, y, T) = \frac{x(T)U_{pu}^0}{1 + y(T)U_{pu}^0} \tag{4.9}
\]

where \(S_{pp}^{sat}(U_{pu}^0; x, y, T)\) is the pump–probe signal, \(x(T)\) is the slope of pump–probe signal with pump pulse energy in the low pulse energy limit, \(U_{pu}^0\) is the incident pump pulse energy, and \(y(T) = 1/U_{pu}^{sat}\) is the inverse of the saturation pump pulse energy. When \(U_{pu}^0 = U_{pu}^{sat}\), the signal is half of its linear extrapolation from low energy given by

\[
S_{pp}^{lin}(U_{pu}^0; x, T) = x(T)U_{pu}^0. \tag{4.10}
\]

Equation 4.10 is the first-order term of the Taylor series expansion of eq. 4.9 around \(U_{pu}^0 = 0\). The low-energy linear extrapolation is expected to contain dynamics from QDs that absorb one pump photon (single exciton QDs) since these signal components are linear in pump excitation. Differences between the saturated signal (eq. 4.9) and the linear signal (eq. 4.10) are indicative of signal components that are not linear with pump excitation and can arise from a number of sources, including nonlinear optical saturation of a pumped transition (for saturation at early time delays), Auger recombination (for saturation at late time delays), and repetitive excitation effects.

The saturation model (eq. 4.9) was fit to the series of transients independently at each pump–probe time delay \(T\). Examples of saturation fits to the pump–probe signal at \(T = 500\) fs, \(T = 20\) ps, and \(T = 1\) ns are shown in Figure 4.9.

As \(U_{pu}^0\) and \(\langle N_{eh} \rangle_{r,z}\) are linearly related, saturation fits in this study were calculated as a function of \(\langle N_{eh} \rangle_{r,z}\). Reported values of \(x(T)\) and \(y(T)\) are in units of \((\Delta N/N_0)/\langle N_{eh} \rangle_{r,z}\) and \(1/\langle N_{eh} \rangle_{r,z}\), respectively.
Figure 4.9: Pump–probe signal, $\Delta N/N_0$, measured as a function of probe-weighted spatially-averaged excitation probability, $\langle N_{eh}\rangle_{r,z}$ at pump–probe delays of $T = 500$ fs (blue circles), $T = 20$ ps (green squares), and $T = 1$ ns (red triangles) with saturation fits (solid lines) and the corresponding linear reconstructions (dashed lines). Sample path length, $L = 1$ mm; optical density, $OD(\lambda = 793\, \text{nm}) = 0.1$; laser repetition rate, $k_{\text{laser}} = 10$ kHz; beam spot size, $w = 41\, \mu\text{m}$; average resampling time, $\langle \tau_{\text{resampling}} \rangle = 0.33$ s.
The probe-weighted spatially-averaged probability of a QD being excited at least once initially by the pump pulse is given by \(1 - \langle P_0 \rangle_{r,z}\). Since Auger recombination is significantly faster than single exciton recombination,\(^\text{124}\) at pump–probe delays much longer than Auger recombination but much shorter than single exciton recombination, all initially excited QDs have exactly one exciton regardless of the initial number of excitations. In this regime of pump–probe delays, the pump pulse energy dependence of the signal is expected to go as \(1 - \langle P_0 \rangle_{r,z}\). The ability of the saturation model to capture the scaling of \(1 - \langle P_0 \rangle_{r,z}\) is exhibited in Figure 4.10. The saturation fit to \(1 - \langle P_0 \rangle_{r,z}\) at low \(\langle N_{eh} \rangle_{r,z}\) (green dotted line in Figure 4.10) demonstrates the shortcomings of the saturation model in capturing the functional form of \(1 - \langle P_0 \rangle_{r,z}\) as \(\langle N_{eh} \rangle_{r,z}\) increases beyond \(\sim 0.6\).
Figure 4.10: Saturation fit (red line) to $1 - \langle P_0 \rangle_{r,z}$, the probe-weighted spatially-averaged excitation probability of a QD being excited at least once (blue circles), yielding saturation parameters $x = 1.03$ and $y = 0.819$. A saturation fit including only $\langle N_{eh} \rangle_{r,z} \leq 0.25$ (green dotted line) gives $x = 1.00$ and $y = 0.700$ and exposes subtle functional differences between the saturation model and $1 - \langle P_0 \rangle_{r,z}$ that start to become experimentally significant for $\langle N_{eh} \rangle_{r,z} > 0.6$. Sample path length, $L = 1$ mm; optical density, $\text{OD}(\lambda = 793 \text{ nm}) = 0.1$; beam spot size, $w = 41 \mu m$. 
To test the expectation that at pump–probe delays long compared to AR, pump–probe signal as a function of pump pulse energy is proportional to 1 − ⟨P₀⟩ₚₚ, the pump–probe signal at T = 1 ns is compared to 1 − ⟨P₀⟩ₚₚ in Figure 4.11. Although by T = 1 ns, significant single exciton recombination may have taken place, as long as the timescale of AR is much shorter than both T and the timescale of single exciton recombination, the pump–probe signal is expected to be proportional to 1 − ⟨P₀⟩ₚₚ. Figure 4.11 demonstrates the qualitative agreement in pump pulse energy scaling between S_{pp}(T = 1 ns) and a multiplicatively scaled 1 − ⟨P₀⟩ₚₚ (red solid line). In the low excitation probability limit (below the lowest excitation probability used here), ⟨N_{eh}⟩ becomes equal to 1 − ⟨P₀⟩ₚₚ. When 1 − ⟨P₀⟩ₚₚ is multiplied by x(T = 1 ns) such that the linear components of 1 − ⟨P₀⟩ₚₚ and S_{pp}(T = 1 ns) are equal (green dashed line), it is clear that x(T = 1 ns) · (1 − ⟨P₀⟩ₚₚ) falls below S_{pp}(T = 1 ns) for ⟨N_{eh}⟩ₚₚ > 1.
Figure 4.11: Pump–probe signal, $\Delta N/N_0$, measured as a function of probe-weighted spatially-averaged excitation probability, $\langle N_{eh} \rangle_{r,z}$ at a pump–probe delay of $T = 1$ ns (blue circles) compared to the fraction of QDs initially excited by the pump pulse, $1 - \langle P_0 \rangle_{r,z}$, multiplied by an arbitrary constant $a = 7.8 \cdot 10^{-5}$ (solid red line) or by $x(T = 1$ ns $) = 6.8 \cdot 10^{-5}$ (dashed green line) from a saturation fit to the shown pump–probe signal data. Sample path length, $L = 1$ mm; optical density, $OD(\lambda = 793$ nm $) = 0.1$; laser repetition rate, $k_{laser} = 10$ kHz; beam spot size, $w = 41$ $\mu$m; average resampling time, $\langle \tau_{resampling} \rangle = 0.33$ s.
The parameters $x(T)$ and $y(T)$ from a saturation fit to six experimental pump-probe transients with a range of probe-weighted spatially-averaged excitation probabilities are shown in Figures 4.12 and 4.13. $x(T)$ is proportional to the linear signal reconstruction, eq. 4.10, and contains single exciton dynamics. $y(T)$ is proportional to the level of signal saturation at a given pump-probe delay and therefore rises on the timescale of AR and asymptotically approaches a constant value at long pump-probe delays once AR is complete.
Figure 4.12: Saturation model parameter $x$ (black line) as a function of pump–probe delay $T$ and 95% confidence intervals (blue lines). $x$ is the result of independent saturation fits at each $T$ to the set of six transients with probe-weighted spatially-averaged excitation probabilities given in Table 4.1. Sample path length, $L = 1$ mm; optical density, OD($\lambda = 793$ nm) = 0.1; laser repetition rate, $k_{\text{laser}} = 10$ kHz; beam spot size, $w = 41$ μm; average resampling time, $\langle \tau_{\text{resampling}} \rangle = 0.33$ s.
Figure 4.13: Saturation model parameter $y$ (black line) as a function of pump–probe delay $T$ and 95% confidence intervals (blue lines). $y$ is the result of independent saturation fits at each $T$ to the set of six transients with probe-weighted spatially-averaged excitation probabilities given in Table 4.1. Sample path length, $L = 1$ mm; optical density, OD($\lambda = 793$ nm) = 0.1; laser repetition rate, $k_{\text{laser}} = 10$ kHz; beam spot size, $w = 41$ $\mu$m; average resampling time, $\langle \tau_{\text{resampling}} \rangle = 0.33$ s.
Using the fit parameters \( x(T) \) and \( y(T) \) at each time delay \( T \), the linear signal reconstruction (eq. 4.10) can be calculated. This reconstruction agrees well at early pump–probe delays with the \( \langle N_{eh} \rangle_{r,z} = 20\% \) transient, as shown in top panel of Figure 4.14, and the \( \langle N_{eh} \rangle_{r,z} = 9.0\% \) transient. At late pump–probe delays \( (T > 500 \text{ ps}) \), however, the linear reconstruction lies 6\% and 12\% higher than the saturation fit for \( \langle N_{eh} \rangle_{r,z} = 9.0\% \) and \( \langle N_{eh} \rangle_{r,z} = 20\% \), respectively. This comparison suggests that the transients with the lowest probe-weighted spatially-averaged excitation probabilities are dominated by single exciton dynamics but contain small—yet measureable—biexciton contributions. In contrast, the linear reconstruction greatly overestimates the signal size of the \( \langle N_{eh} \rangle_{r,z} = 125\% \) transient, as shown in the bottom panel of Figure 4.14, indicating significant signal saturation at this pump pulse energy.
Figure 4.14: Pump–probe transients (blue circles) with \( \langle N_{eh} \rangle_{r,z} = 20\% \) (top panel) and \( \langle N_{eh} \rangle_{r,z} = 125\% \) (bottom panel) and their respective linear reconstructions (dashed green line) from saturation model fits (solid red line) at each time delay. Sample path length, \( L = 1 \text{ mm} \); optical density, \( \text{OD}(\lambda = 793 \text{ nm}) = 0.1 \); laser repetition rate, \( k_{\text{laser}} = 10 \text{ kHz} \); beam spot size, \( w = 41 \mu\text{m} \); average resampling time, \( \langle \tau_{\text{resampling}} \rangle = 0.33 \text{ s} \).
4.3.3 Reconstructed Single Exciton and Biexciton Signals

To separate single exciton and biexciton signal components in pump–probe transients, a procedure relying on the distinct scaling of multi-excitonic signal components with pump pulse energy was developed. Saturation fits to the pump–probe transients at each pump–probe delay are taken as a complete description of the time and pump pulse energy dependence of the experimental pump–probe signal. The Taylor series expansion of the saturation model is given by

\[
S_{pp}^{\text{sat}}(T) = \sum_{n=1}^{\infty} x(T) \left[ -y(T) \right]^{n-1} U_{pu}^n
\]

\[
= x(T) U_{pu} - x(T) y(T) U_{pu}^2 + \ldots
\]

(4.11)

where \(x(T)\) and \(y(T)\) are saturation model parameters and \(U_{pu}\) is the incident pump pulse energy (the superscript “0” is dropped for clarity).

The probe-weighted spatially-averaged probability of a QD receiving one \(\langle P_1 \rangle_{r,z} \) or two \(\langle P_2 \rangle_{r,z} \) pump-induced excitations can be written as power series

\[
\langle P_1 \rangle_{r,z} = c_1 U_{pu} + c_2 U_{pu}^2 + \ldots
\]

(4.12)

and

\[
\langle P_2 \rangle_{r,z} = -\frac{1}{2} c_2 U_{pu}^2 + \ldots
\]

(4.13)

where \(c_n\) are constants derived from a polynomial fit to numerically calculated values of \(\langle P_1 \rangle_{r,z} \).

Equations 4.12 and 4.13 are constructed such that by eq. 4.6,

\[
\langle N_{eh} \rangle_{r,z} = \langle P_1 \rangle_{r,z} + 2 \langle P_2 \rangle_{r,z} + \ldots
\]

\[
= c_1 U_{pu}.
\]

(4.14)

I define

\[
\langle P_1 \rangle_{r,z}^{\text{linear}} = c_1 U_{pu}
\]

\[
\langle P_2 \rangle_{r,z}^{\text{quad}} = -\frac{1}{2} c_2 U_{pu}^2
\]

(4.15)

such that

\[
\langle P_1 \rangle_{r,z} = \langle P_1 \rangle_{r,z}^{\text{linear}} - 2 \langle P_2 \rangle_{r,z}^{\text{quad}} + \ldots
\]

\[
\langle P_2 \rangle_{r,z} = \langle P_2 \rangle_{r,z}^{\text{quad}} + \ldots
\]

(4.16)
A theoretical form for the pump–probe signal is constructed from eq. 4.16, yielding

\[ S_{pp}^{\text{theory}} = b \left\{ \langle P_1 \rangle_{r,z} E(T) + 2 \langle P_2 \rangle_{r,z} B(T) + \ldots \right\} \]

\[ = b \left\{ \langle P_1 \rangle_{r,z}^{\text{linear}} E(T) + \langle P_2 \rangle_{r,z}^{\text{quad}} [B(T) - 2E(T)] + \ldots \right\} \]  

(4.17)

where \( E(T) \) is the pump–probe signal of one singly excited QD (single exciton) and is peak-normalized, \( B(T) \) is the pump–probe signal of one doubly excited QD (biexciton), and \( b \) is a constant specific to the experimental setup and detection sensitivity. The height of \( B(T) \) is not constrained, thus allowing the common assumption that the initial pump–probe signal is strictly linear with the total number of excitations and is insensitive to their distribution [i.e. \( B(T = 0) = 2E(T = 0) \)] to be tested.

Substituting eq. 4.15 into eq. 4.17 yields

\[ S_{pp}^{\text{theory}} = b \left\{ c_1 U_{pu} - \frac{1}{2} c_2 U_{pu}^2 [B(T) - 2E(T)] + \ldots \right\}. \]  

(4.18)

Equating the terms in eqs. 4.11 and 4.18 that are linear in \( U_{pu} \) and solving for \( E(T) \) gives

\[ E(T) = \frac{1}{b} \left[ \frac{1}{c_1} x(T) \right]. \]  

(4.19)

Doing the same for the quadratic terms and solving for \( B(T) \) gives

\[ B(T) = \frac{2}{b} \left[ \frac{1}{c_1} x(T) + \frac{1}{c_2} y(T) \right]. \]  

(4.20)

Comparing eqs. 4.10 and 4.19, it is noted that \( S_{pp}^{\text{lin}}(T) \) and \( E(T) \) differ only by a constant multiplicative factor and, therefore, have the same pump–probe delay dependence.

\( E(T) \) and \( B(T) \) in Figure 4.15 are calculated according to eqs. 4.19 and 4.20 using coefficients \( c_n \) derived from a smooth 9th-order polynomial fit to \( \langle P_1 \rangle_{r,z} \). For the 9th-order polynomial, the lowest order coefficients are numerically converged, not significantly affected by increases in polynomial order, and obey relationships expected for the polynomial coefficients of \( \langle P_2 \rangle_{r,z} \), etc. Both \( E(T) \) and \( B(T) \) appear to contain many of the same decay timescales in similar proportions, as expected given that initially excited biexcitons also undergo single exciton processes such as cooling and recombination prior to, during, and after AR. At long pump–probe delays (\( T > 300 \text{ ps} \)), \( E(T) \)
and $B(T)$ are equal within their uncertainties, implying that long after AR, all initially excited biexcitons have relaxed to single excitons. In contrast, at short pump–probe delays ($T < 50 \text{ ps}$), $B(T)$ lies above $E(T)$, reflecting the additional signal contributed by a second exciton. Since the amplitude of $B(T)$ is not constrained, its peak height with respect to $E(T)$ is indicative of the relative signal contribution of a biexciton compared to a single exciton. Contrary to the common assumption that a biexciton contributes exactly twice the signal of a single exciton, Figure 4.15 suggests that a biexciton initially yields $\sim 1.8$ times as much signal as a single exciton. The timescale on which $B(T)$ converges to $E(T)$ is indicative of AR and potentially other processes requiring two excitons. Extraction of this timescale is discussed in Section 4.3.5.
Figure 4.15: Reconstructed single exciton, $E(T)$, (blue line) and biexciton, $B(T)$, (green line) signals with 95% confidence intervals (dotted lines). Sample path length, $L = 1$ mm; optical density, $\text{OD}(\lambda = 793 \text{ nm}) = 0.1$; laser repetition rate, $k_{\text{laser}} = 10$ kHz; beam spot size, $w = 41 \, \mu\text{m}$; average resampling time, $\langle \tau_{\text{resampling}} \rangle = 0.33$ s.
4.3.4 Single Exciton Dynamics

The single exciton signal, $E(T)$, is well described by the sum of a 4-exponential decay and an exponentially-damped cosine given by

$$S_{pp}(T) = \sum_{n=1}^{4} A_n \exp \left[ -\frac{T}{\tau_n} \right] + D \cos [2\pi \nu DT] \exp \left[ -\frac{T}{\tau_D} \right]$$  \hspace{1cm} (4.21)

with the parameters listed in Table 4.2. The 4-exponential fit to $E(T)$ is illustrated in Figures 4.16 and 4.17. The fastest time constant in the fit ($\tau = 0.77$ ps) is consistent with prior reports of the $1P \rightarrow 1S$ electron cooling time. Schaller et al.\textsuperscript{124} report a carrier cooling time of 0.66 ps in 3.9 nm diameter InAs/CdSe core/shell QDs based on the rise of “1S” signal when pumping the “1P” state. Similarly, Pijpers et al.\textsuperscript{21} report a 0.8 ps “1P to 1S” electron relaxation time in 4.4 nm diameter InAs QDs. The authors attribute this timescale to electron–hole coupling, proposing that electrons, as a result of their comparatively wide electronic level spacing, primarily cool through an Auger process whereby a hot electron transfers energy to a hole which subsequently cools through phonon emission.\textsuperscript{21}

The longest time constant ($\tau = 1.0$ ns) is attributed to single exciton recombination. Reports of single exciton lifetimes vary widely and are highly dependent on the QD surface chemistry, their level of exposure to oxidation, and the details of their synthesis and handling. Single exciton lifetimes from 192 ps for 4.3 nm diameter InAs “core only” QDs\textsuperscript{124} to 5.2 ns for 4.9 nm diameter InAs/CdSe/ZnSe core/shell/shell QDs\textsuperscript{126} have been reported. The intermediate time constants ($\tau = 5.1$ ps and $\tau = 75$ ps) in the single exciton (low pump pulse energy) signal are not reported in prior studies, which—unlike this work—probe the 1S transition. These time constants may indicate the presence of additional cooling pathways or could be involved in carrier trapping processes.
Table 4.2: 4-exponential with a damped cosine fit (eq. 4.21) to the single exciton signal $E(T)$.
Damped cosine parameters: $D = 0.061 \pm 0.027$, $\nu_D = 6.6 \pm 0.8 \text{ ps}^{-1}$, and $\tau_D = 0.11 \pm 0.09 \text{ ps}$.

<table>
<thead>
<tr>
<th>A</th>
<th>$\tau$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 ± 0.03</td>
<td>0.77 ± 0.08</td>
</tr>
<tr>
<td>0.19 ± 0.03</td>
<td>5.1 ± 1.2</td>
</tr>
<tr>
<td>0.12 ± 0.01</td>
<td>75 ± 15</td>
</tr>
<tr>
<td>0.133 ± 0.005</td>
<td>1061 ± 1</td>
</tr>
</tbody>
</table>

Figure 4.16: Reconstructed single exciton signal, $E(T)$, (blue circles) and a 4-exponential with damped cosine fit (red line). Sample path length, $L = 1 \text{ mm}$; optical density, OD($\lambda = 793 \text{ nm}$) = 0.1; laser repetition rate, $k_{\text{laser}} = 10 \text{ kHz}$; beam spot size, $w = 41 \mu\text{m}$; average resampling time, $\langle r_{\text{resampling}} \rangle = 0.33 \text{ s}$.
Figure 4.17: Reconstructed single exciton signal, $E(T)$, (blue circles) and a 4-exponential with damped cosine fit (red line). Sample path length, $L = 1$ mm; optical density, $\text{OD}(\lambda = 793$ nm) = 0.1; laser repetition rate, $k_{\text{laser}} = 10$ kHz; beam spot size, $w = 41$ µm; average resampling time, $\langle \tau_{\text{resampling}} \rangle = 0.33$ s.
4.3.5 Multi-exciton Dynamics

In bulk-like regions\textsuperscript{130} of a QD’s spectrum, it is a reasonable approximation to treat the pump–probe signal size as directly proportional to the number of electron–hole pairs (excitons) in the sample. In such a case, the signal generated by a QD in a biexciton state is twice that of a QD in a single exciton state. A common method for quantifying the yield of biexcitons generated by the pump pulse is to compare the signal size at pump–probe delays that are short compared to AR, but long compared to carrier cooling, to the signal size at pump–probe delays that are long compared to AR, but short compared to single exciton recombination.\textsuperscript{121} However, this method will not work in our case due to the presence of single exciton relaxation pathways with time constants ($\tau = 5.1$ ps and $\tau = 75$ ps) that are on the order of the expected AR time constant ($\tau_{AR} = 10$ to 30 ps). In addition, this method relies heavily on the assumption that pump–probe signal is strictly linear with the number of excitons which may not be justified when pumping and/or probing an excitonic transition. Instead, an alternative method is proposed.

Given the ability to separate biexciton and single exciton dynamics into $B(T)$ and $E(T)$, the processes unique to biexcitons can be isolated through an algebraic combination of $B(T)$ and $E(T)$. If it is assumed that

$$E(T) = X(T)$$

$$B(T) = XX(T) X(T) + X(T)$$

where $X(T)$ contains the signal for processes involving exactly one exciton and is peak normalized and $XX(T)$ contains the signal for processes involving exactly two excitons, then the dynamics specific to two-exciton processes can be extracted using

$$XX(T) = \frac{B(T)}{E(T)} - 1.$$  \hspace{1cm} (4.23)

Substituting eqs. 4.20 and 4.19 into eq. 4.23 yields

$$XX(T) = 2 \left[ 1 + \frac{c_1}{c_2} y(T) \right] - 1$$

$$= 1 + 2 \frac{c_1}{c_2} y(T).$$  \hspace{1cm} (4.24)
To account for the slight and experimentally insignificant difference in amplitude between $B(T)$ and $E(T)$ at late times, the ratio $B(T = 1 \text{ ns})/E(T = 1 \text{ ns}) = 1.13$ derived from the data in Figure 4.9 is subtracted from $B(T)/E(T)$ instead of 1. The result is illustrated in Figure 4.18 along with a single exponential fit with $\tau = 26 \pm 5 \text{ ps}$. This time constant is consistent with AR and is well within the 8 ps to 53 ps range of reported biexciton lifetimes for InAs QDs.\textsuperscript{21,124,126,128}

The closest comparison in terms of QD core size is a study by Ben-Lulu et al.\textsuperscript{126} who report a 53 ps biexciton lifetime for 5.9 nm diameter InAs/CdSe/ZnSe core/shell/shell QDs. However, their observation of a relatively long biexciton lifetime may be due to the use of core/shell structures as opposed to the as-prepared ligand-capped QDs used in the present study.

The most comparable study of similar sized as-prepared ligand-capped InAs QDs is that of Schaller et al.\textsuperscript{124} wherein a 8.3 ps biexciton lifetime was reported for 4.3 nm diameter InAs “cores”. Given that AR time constants scale with QD volume,\textsuperscript{119,134} a 8.3 ps biexciton lifetime in 4.3 nm QDs would predict a 27 ps biexciton lifetime for the 6.2 nm QDs of the present study. While Schaller et al.\textsuperscript{124} note no difference in pump–probe signal size between transients collected while the sample is “static” compared to when the sample is stirred, insufficient sample renewal can result in repetitive excitation effects such as photocharging which can complicate studies of AR.\textsuperscript{89} Photocharged QDs can undergo trion decay, which is the non-radiative recombination of an exciton through transferring excess energy to a free charge carrier. Since trion decay occurs on timescales similar to AR, it can artificially increase the apparent biexciton yield when inadequate sample renewal leads to photocharging.\textsuperscript{89}
Figure 4.18: The ratio of the reconstructed biexciton and single exciton signals, $B(T)/E(T) − B(T = 1 \text{ ns})/E(T = 1 \text{ ns})$, (blue line) and a single exponential fit (red line). Sample path length, $L = 1 \text{ mm}$; optical density, OD($\lambda = 793 \text{ nm}$) = 0.1; laser repetition rate, $k_{\text{laser}} = 10 \text{ kHz}$; beam spot size, $w = 41 \mu\text{m}$; average resampling time, $\langle r_{\text{resampling}} \rangle = 0.33 \text{ s}$. 
4.4 Conclusions

Carrier relaxation dynamics of 6.2 nm diameter colloidal InAs QDs in the weak excitation regime have been investigated using degenerate pump–probe transient absorption spectroscopy. A beam scanning apparatus was employed to reduce repetitive excitation of the sample, extending the resampling time to >0.3 s. Exposure of the sample to air was minimized during the experiment using a sample cell with a high-vacuum seal.

Electronic relaxation following photoexcitation to the blue side of the 1P_e1P_h state was characterized. A saturation model was fit to transients with excitation probabilities ranging from \( \langle N_{eh} \rangle = 9.0\% \) to 125\%, from which the linear signal was reconstructed. A comparison between the linear reconstruction and a transient with \( \langle N_{eh} \rangle = 20\% \) demonstrates that this measurement is dominated by dynamics of singly excited QDs.

A procedure for isolating biexciton dynamics from single exciton dynamics was developed. This method utilizes the Taylor series expansion of the saturation model along with Poisson-based calculations of the probe-weighted spatially-averaged excitation probability and relies on fewer assumptions than previously reported methods.\(^{121}\) Comparison of reconstructed single exciton, \( E(T) \), and biexciton, \( B(T) \), signals near \( T = 0 \) suggests that a biexciton yields a factor of \( \sim 1.8 \) times the signal of a single exciton, although a factor of 2 is consistent within the 95\% confidence intervals of \( B(T) \). At long pump–probe delays (\( T \geq 300 \) ps), \( B(T) \) and \( E(T) \) converge to the same value within their uncertainties, lending evidence to the expectation that initially excited biexciton recombine through a sub-100 ps process to form single excitons at late times.

The reconstructed single exciton signal was well described by a 4-exponential with a damped cosine fit, yielding time constants of \( 0.77 \pm 0.08 \) ps and \( 1061 \pm 1 \) ps, consistent with electron cooling and single exciton recombination respectively, and two previously unreported time constants of \( 5.1 \pm 1.2 \) ps and \( 75 \pm 15 \) ps that may be the result of carrier cooling or trapping. The reconstructed biexciton signal contains, in addition to the single exciton dynamics, a time constant of \( 26 \pm 5 \) ps that is consistent with Auger recombination, lying between comparable reports of \( 8.3 \) ps\(^{124}\) and
53 ps\textsuperscript{126} for the biexciton lifetime in (4.3 nm diameter and 5.9 nm diameter, respectively) InAs QDs.
Bibliography


Broadening due to Rb–Ar collisions is calculated from eq. 6.1 of ref. 10 using the pressure-broadening coefficient reported by Rotondaro and Perram.  


Equation 2.30 is related to the propagation function for two-beam double-resonance experiments given immediately below eq. 60 of ref. 7 except for two differences. First, $\beta$ is not required to be zero in eq. 2.30. Second, a factor of $\gamma$ arising from $\kappa_z$ in the denominator of eq. 2.29 is present in eq. 2.30 but is missing in eq. 60 of ref. 7.  

[67] Brand names are given as technical information only and does not imply endorsement by NIST or that the product is the best for the purpose.


[79] The mean time between Rb–Ar collisions is calculated using \( \bar{\tau} \approx (N\pi b_0^2v)^{-1} \) given just above eq. 1a by Berman and Lamb\(^{12} \) where \( N \) is the number density of perturber (Ar) atoms, \( b_0 \) is the impact parameter, and \( v \) is the mean relative speed between chromophore (Rb) and perturber (Ar) atoms. Using that \( \sigma_R \approx \pi b_0^2 \), the mean time between collisions can be expressed as \( \bar{\tau} \approx (N\sigma_Rv)^{-1} \) where \( \sigma_R \) is the optical cross section for (Rb–Ar) collisional broadening. In Table 6.2, Lewis\(^{10} \) lists three experimental measurements of \( \sigma_R \) for the Rb D\(_2\) line and the mean of these three values \( (330 \times 10^{-16} \text{ cm}^2) \) was used here for \( \sigma_R \). The collision duration was calculated using \( \tau_c = b_0/v \) given just above eq. 1a by Berman and Lamb.\(^{12} \)


[84] Oberl, J.; Abraham, E.; Ivanov, A.; Jonusauskas, G.; Rullire, C. Picosecond CARS and Transient Absorption Studies of 1,4-Diphenylbutadiene and trans-Stilbene: A Study of Pho-


To avoid saturating the imaging sensor, the laser beams are attenuated using reflective neutral density filters (Inconel metallic coating on glass, Newport) until the beams are just visible in the sensor image such that the pixel value at the center of the beam is less than $\sim 60$ (where the maximum pixel value is 255). An absorptive neutral density filter is placed over the aperture of the imaging sensor (i.e. where the lens was removed) to prevent stray light from reaching the sensor. A grayscale video of the beam(s) containing 74 frames is acquired and the frames are summed to produce a single grayscale image. A background image is acquired in the absence of the beam(s) using the same procedure. The background image is subtracted from the beam image to remove sensor noise such that the image background is flat.


Appendix A

Pulse Envelope Propagation

This appendix starts with eq. 1.6 for the FID in a frame that travels with the undistorted excitation pulse and derives eqs. 1.15–1.17 for the FID envelope under the rotating wave approximation (RWA) and further simplifying assumptions.

\[
\hat{E}_{\text{FID}}(\omega, z) = \hat{E}(\omega, z = 0) \exp \left[ i\omega (\hat{n} - 1) \frac{z}{c} \right] \quad (A.1)
\]

Substituting eqs. 1.19 and 1.12 into eq. A.1 yields

\[
\hat{E}_{\text{FID}}(\omega, z) = \frac{1}{2} \left[ e_G(\omega - \omega_0) + e_G(\omega + \omega_0) \right] \exp \left[ -\omega \kappa(\omega_{eg}) \pi \Gamma_{jk} \{ \hat{g}(\omega - \omega_{eg}) - \hat{g}(\omega + \omega_{eg}) \} \frac{z}{c} \right]. \quad (A.2)
\]

If the pulse spectra and the complex lineshape both have widths narrow compared to the resonance frequency \( \omega_{eg} \), we can make the rotating wave approximation\(^{60} \) to obtain

\[
\hat{E}^{\text{RWA}}_{\text{FID}}(\omega, z) = \frac{1}{2} E_0 e_G(\omega - \omega_0) \exp \left[ -\omega \kappa(\omega_{eg}) \pi \Gamma_{jk} \hat{g}(\omega - \omega_{eg}) \frac{z}{c} \right] + \frac{1}{2} E_0 e_G(\omega + \omega_0) \exp \left[ +\omega \kappa(\omega_{eg}) \pi \Gamma_{jk} \hat{g}(\omega + \omega_{eg}) \frac{z}{c} \right]. \quad (A.3)
\]

We now assume that the resonance is narrow compared to the resonant frequency (\( \Gamma_{jk} \ll \omega_{eg} \)) so that

\[
\omega \hat{g}(\omega - \omega_{eg}) \simeq \omega_{eg} \hat{g}(\omega - \omega_{eg}) \quad (A.4a)
\]

for the resonance at \( \omega = \omega_{eg} \) and

\[
\omega \hat{g}(\omega + \omega_{eg}) \simeq -\omega_{eg} \hat{g}(\omega + \omega_{eg}) \quad (A.4b)
\]
for the resonance at $\omega = -\omega_{eg}$. Further, we specialize to laser pulses tuned to resonance so that $\omega_0 = \omega_{eg}$. This gives

$$
\hat{E}_{\text{FID}}(\omega, z) \simeq \frac{1}{2} E_0 e_G(\omega - \omega_{eg}) \exp \left[ -\omega_{eg} \kappa(\omega_{eg}) \pi \Gamma_{jk} \hat{g}(\omega - \omega_{eg}) \frac{z}{c} \right] + \frac{1}{2} E_0 e_G(\omega + \omega_{eg}) \exp \left[ -\omega_{eg} \kappa(\omega_{eg}) \pi \Gamma_{jk} \hat{g}(\omega + \omega_{eg}) \frac{z}{c} \right].
$$

(A.5)

where $-\omega$ and $+\omega$ in the exponentials of eq. A.3 have been replaced by $+\omega_{eg}$ and $-\omega_{eg}$ respectively.

Defining the demodulated frequency domain FID

$$
\hat{e}_{\text{FID}}(\omega, z) = e_G(\omega) \exp \left[ -\omega_{eg} \kappa(\omega_{eg}) \pi \Gamma_{jk} \hat{g}(\omega) \frac{z}{c} \right]
$$

yields an expression for the FID field

$$
\hat{E}_{\text{FID}}(\omega, z) \simeq \frac{E_0}{2} \left[ \hat{e}_{\text{FID}}(\omega - \omega_{eg}, z) + \hat{e}_{\text{FID}}(\omega + \omega_{eg}, z) \right]
$$

(A.6)

in terms of FID envelopes. We can Fourier transform the frequency domain FID to obtain the time domain FID under the rotating wave approximation

$$
E_{\text{FID}}(t, z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{E}_{\text{FID}}(\omega, z) \exp \left[ -i\omega t \right] d\omega\quad \text{(A.8)}
$$

$$
E_{\text{FID}}(t, z) \simeq \frac{E_0}{2} \left[ \hat{e}_{\text{FID}}(t, z) \exp \left[ i\omega_{eg} t \right] + \hat{e}_{\text{FID}}(t, z) \exp \left[ -i\omega_{eg} t \right] \right]
$$

(A.9)

where the time domain envelope of the FID,

$$
\hat{e}_{\text{FID}}(t, z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{e}_{\text{FID}}(\omega, z) \exp \left[ -i\omega t \right] d\omega,
$$

(A.10)

is the Fourier transform of the demodulated frequency domain FID. The time domain envelope is real-valued because

$$
\hat{e}_{\text{FID}}(-\omega, z) = e_G(-\omega) \exp \left[ -\omega_{eg} \kappa(\omega_{eg}) \pi \Gamma_{jk} \hat{g}(-\omega) \frac{z}{c} \right]
$$

$= e_G(\omega) \exp \left[ -\omega_{eg} \kappa(\omega_{eg}) \pi \Gamma_{jk} \hat{g}^*(\omega) \frac{z}{c} \right]
$$

(A.11)

$= \left[ \hat{e}_{\text{FID}}(\omega, z) \right]^*$. 
