ULTRAFAST SPECTROSCOPY OF SELF TRAPPED EXCITONS IN
QUASI-ONE-DIMENSIONAL MATERIALS

By

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ULTRAFAST SPECTROSCOPY OF SELF TRAPPED EXCITONS IN QUASI-ONE-DIMENSIONAL MATERIALS

Abstract

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This dissertation studies the transition of electronic excitations from a delocalized state to a localized state. Such processes have a dramatic impact on optical and electronic properties and reflect fundamental interactions in the physics of condensed matter systems. An important example is the self-trapping of excitons: an initially extended free exciton interacts with a deformable lattice, resulting in the formation of a localized self-trapped exciton (STE).

Experiments were performed in a series of quasi-one-dimensional materials called mixed-valence metal-halide linear chain (MX) complexes, in which variation of the chemical structure allows systematic control of the strength of the electron-phonon interaction that drives the dynamics. Results are compared in materials with a range of coupling strengths.

The MX materials studied here were \([\text{Pt(en)}_2][\text{Pt(en)}_2\text{Cl}_2]\cdot\text{ClO}_4 \cdot 4\) or PtCl, and \([\text{Pt(en)}_2\text{I}_2][\text{Pt(CN)}_4]\) or PtICN. The following experiments were carried out:

1. Transient optical absorption experiments were carried out on PtCl, a material with a very strong electron-phonon coupling. These studies revealed the presence of a low frequency 68 cm\(^{-1}\) coherent acoustic phonon modulation associated with the formation of the STE. This frequency
is used to estimate the spatial extent of the STE, which is found to be localized to nearly 1 unit cell. The dependence of the STE response on detection wavelength was also studied.

2. Transient optical absorption experiments were carried out on PtICN, a material with an intermediate electron-phonon coupling. These studies revealed the presence of a coherent acoustic phonon modulation at a frequency of 15 cm$^{-1}$. Using this frequency, the STE is estimated to be localized to approximately 3 unit cells. The effects of pumping with excess energy, the pump power dependence, and the STE decay time were also studied.

3. The vibrational properties of the equilibrated STE were determined using 3-pulse pump-pump-probe techniques. Resonant impulsive Raman excitation of the equilibrated STE in both PtCl and PtICN revealed a downward shift in the optical phonon frequency as the lattice distorts to form the final equilibrated STE.
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CHAPTER 1

Introduction

This work is a study of the localization of electronic states through electron-lattice interactions. Localization of electronic states plays a critical role in determining the properties of a wide range of materials: polaron formation has a profound impact on the charge transport properties of electronic materials, and formation of self-trapped excitons (STE), or exciton-polarons, dramatically changes optical properties and energy transport mechanisms. While the equilibrium properties of quasiparticles are well-established in many systems, a full understanding of the dynamics of the process of quasiparticle formation has yet to be achieved. In addition to its fundamental significance, such knowledge promises a means to understand, and thereby exploit, the fast electronic and optical response of materials.

These studies will be carried out in materials in which the strength of the electron-phonon interactions that drive the dynamics can be systematically tuned. Studies of these model systems will be accomplished using femtosecond time-resolved techniques sensitive to the electronic, vibrational, and structural dynamics that will follow the evolution of an initially photoexcited extended electronic state as it interacts with the deformable lattice to form a localized excitation. The materials used to perform these studies are quasi-one-dimensional materials known as MX chains, which were chosen because they have properties that make them ideal for the study of STEs in the following ways:

- The reduced dimensionality leads to strong electron-phonon interactions. This 1-dimensional nature restricts phonon oscillations to occur mainly along the chain axis. Also, MX chains are synthesized such that the interaction between neighboring chains is negligible.
The chemical composition of MX chains may be chosen in a manner that allows for the electron phonon coupling strength to be “tuned.” An overall goal in this work is to establish a relationship between various properties of STEs and the electron phonon coupling strength.

The strongly absorptive, polarization dependent optical transitions that accompany the self trapping process are ideally suited for study using femtosecond pump-probe techniques.

More on the properties of the MX materials are presented in Chapter 2 along with an explanation of the self trapping process.

Chapter 3 outlines the equipment and techniques used to create and characterize femtosecond laser pulses. Chapter 3 also reviews wavepacket theory, which has been used to model the vibrational dynamics. Another goal of these experiments is to help validate theoretical models by comparing our experimental measurements with theoretical predictions.

Presentations of experimental results start in Chapter 4 where the vibrational dynamics are presented in a material with a strong electron phonon coupling. Optical phonons at the expected frequencies were measured as well some new vibrational modes. In particular, an acoustic phonon response was discovered in the vibrational dynamics. These measurements were motivated by previous measurements made by Morrissey and Dexheimer [F. X. Morrissey, S. L. Dexheimer. Coherent acoustic phonon generation in exciton self-trapping. Phys. Rev. B 81, 094302 (2010)] where an acoustic phonon was measured in a material with a weak electron phonon coupling. As a result, we can now compare the acoustic dynamics in materials with weak and strong couplings. A practical result of measuring the acoustic frequency is that it can be used to estimate the size, or spatial extent, of the self trapped exciton. The spatial extent of the STE in the strong coupling limit is estimated to be ~ 1 unit cell, a result that is consistent with theoretical predictions. The spatial extent reported by Morrissey and Dexheimer,
in the weak coupling limit, was estimated to be ~5 unit cells. The comparison reveals that a strong electron phonon coupling can be linked with more localized electronic excitations.

Chapter 5 presents measurements of the optical and acoustic dynamics in another MX complex that is unique and fairly new to the MX world. Again, optical phonon modes at the expected frequencies were measured and again, an acoustic phonon response was discovered, revealing an estimated spatial extent of ~3 unit cells in this material. Various other experiments are also presented in this chapter. Measurements were made where the sample was excited by photons with energy levels well above the bandgap, examining the effect on the dynamics under conditions where large amounts of excess energy are available after excitation. The dependence of the excited state population on excitation intensity was also examined.

The optical and acoustic phonons measured in Chapters 4 and 5 occur while the STE is stabilizing and help carry the system toward this stabilized state. Chapter 6 presents experiments where the dynamics of the stabilized STEs are measured. This is done by using 2 excitation pulses. The first pulse creates the STE and the second pulse uses impulsive stimulated Raman techniques to measure the properties of the stabilized STE. These “2-pump” experiments were conducted on the same MX materials used in Chapters 4 and 5.
CHAPTER 2

ONE DIMENSIONAL MATERIALS AND SELF TRAPPED EXCITONS

2.1 - Properties of MX Materials

This section describes the structural, optical and vibrational properties of the quasi-one-dimensional materials used to conduct the research throughout this dissertation.

2.1.1 - Structural Properties

The research here was done on halide-bridged mixed-valence transition metal linear chain (MX) complexes. MX complexes are quasi one-dimensional chains of alternating transition metal and halide ions where \( M = \text{Pt, Pd or Ni} \) and \( X = \text{Cl, Br or I} \). The metals and halides combine to form a linear chain that alternates between \( M \) and \( X \) ions with the general form:

\[
- - M^{+3-\delta} - - X^- - M^{+3+\delta} - X^- - - M^{+3-\delta} - -
\]

where the superscripts indicate the overall charge of the metal site and the double dashes indicate larger bond lengths. The MX complexes are of interest as a class of materials because the strengths of the electron-phonon and electron-electron interactions can be systematically tuned by varying the chemical composition.

Platinum-halide complexes have been of particular interest for studies of exciton self-trapping. The most extensively characterized complexes are the series \( \text{Pt(en)}_2\text{Pt(en)}_2X_2Y_4 \), where the halide bridging ion \( X = \text{Cl, Br, or I} \), the transverse ligand \( \text{en} = \text{ethylenediamine, C}_2\text{H}_8\text{N}_2 \), and the counterion \( Y = \text{ClO}_4^- \) or \( \text{PF}_6^- \). The structure of the \( \text{Pt(en)}_2\text{Pt(en)}_2\text{Cl}_2(\text{ClO}_4)_4 \) complex (also referred to as PtCl) determined using x-ray crystallography is shown in Figure 2.2 [1]. The important part of the structure is the covalently bonded Pt-Cl linear chain. Ethylenediamine ligands occupy transverse bonding sites on the
platinum ions. The ClO$_4^-$ counterions spatially separate the chains and neutralize the overall charge in the crystal.

The structure of the ground electronic state of the PtX(en) complexes is a Peierls-distorted commensurate charge density wave (CDW). The periodic variation in M to X bond lengths throughout the chain is known as a Peierls distortion, named after Rudolph Peierls who discussed the nature of such lattice distortions in his book *The Quantum Theory of Solids* in 1955 [2]. He showed that an evenly-spaced 1-dimensional lattice is an unstable arrangement and that a linear chain will tend towards a distorted structure with a doubled unit cell. In other words, the chain is more stable (i.e. in an energetically favorable arrangement) with alternating bond lengths between neighboring sites.

The upper half of Figure 2.1 presents a schematic structure along the chain axis that shows the periodic bond length distortion of the metal-halide bonds and the periodic charge disproportionation (fractional mixed-valence character) of the metal ions. In the chain structure, Pt ions with a nominal valence of +3 undergo charge disproportion to give alternating +(3 + $\delta$) and +(3 – $\delta$) charge states, with a corresponding periodic variation of the metal-halide bond lengths. The degree of charge disproportionation (the CDW amplitude) is given by the parameter $\delta$. The limit $\delta = 0$ would correspond to a uniform valence state of Pt$^{+3}$ for all sites, $\delta = 1$ would correspond to maximum charge-transfer, yielding alternating Pt$^{+2}$ and Pt$^{+4}$ sites, and intermediate values represent fractional mixed valency. The expected structure of the STE state that is formed following optical excitation, as discussed in more detail below, is shown schematically in its most highly localized limit in the lower part of Figure 2.1. Both the amplitude of the CDW and Peierls distortion in the ground electronic state and the spatial extent of the relaxed STE state depend on the relative strengths of the electron-phonon interaction, which creates the lattice distortion, and the electronic transfer (hopping), which results in charge delocalization. In the MX complexes, the electron-phonon interaction is primarily due to coupling of the electronic density on
a metal ion to the symmetric stretching motion of the negatively charged halide ions, and an electron-electron interaction dominated by the on-site coulomb repulsion in the case that two electrons occupy the \( d_{z}^{2} \) chain-axis orbital of a metal ion is also present. For the PtX complexes, the electron-phonon coupling dominates, resulting in the CDW ground state. The amplitude of the ground state CDW in the PtX(en) complexes has been estimated by modeling [3] of x-ray photoelectron spectra in comparison to those of the corresponding monovalent monomers [4]. This modeling shows a systematic decrease in the CDW amplitude through the X = Cl, Br, I series, with estimates of \( \delta \sim 0.91 \) for PtCl(en), \( \delta \sim 0.64 \) for PtBr(en), and \( \delta \sim 0.36 \) for PtI(en). The variation in the relative strength of the electron-phonon coupling through the halide series is apparent in the magnitude of the Peierls distortion, which can be characterized by the ratio \( \rho \) of the short Pt\(^{+3+}\)-X bond length to the long Pt\(^{+3-}\)-X bond length.

Structures of the [Pt(en)\(_{2}\)][Pt(en)\(_{2}\)X\(_{2}\)](ClO\(_{4}\))\(_{4}\) determined by x-ray diffraction give values of \( \rho = 0.743, 0.828, \) and 0.890 (bond lengths are 2.319 Å and 3.122 Å; 2.484 Å and 3.001 Å; 2.712 Å and 3.048 Å) for X = Cl, Br, and I, respectively [5]. The lattice distortion and other properties of the materials discussed below are summarized in Table 2.1 at the end of the chapter.
Figure 2.1 – Schematic representation of a platinum based MX chain. (Top) The Peierls distorted or CDW ground state. The Peierls distortion can be seen in the varying lengths of the bonds where the negatively charged halides X are pulled closer to the platinum site with greater positive charge. (Bottom) Schematic structure of the metastable STE. This depicts the highly localized limit where the STE is confined to 1 chain repeat unit. Reprinted with permission from [8] F.X. Morrissey, J.G. Mance, A.D. Van Pelt, and S.L. Dexheimer. *Femtosecond Dynamics of Exciton Localization: Self-Trapping From the Small to the Large Polaron Limit.* J. Phys. Cond. Matt. 25 (2013) 144204.
The experiments presented in this thesis focus on two platinum-halide materials. The first of these, PtCl, has a very strong electron-phonon coupling and therefore provides a useful comparison to previous studies carried out on PtBr (intermediate coupling) and PtI (weaker coupling). The second compound, [Pt(en)$_2$I$_2$][Pt(CN)$_4$], also referred to as PtICN, is relatively new to the MX class of materials. The structure of PtICN has been determined using x-ray crystallography and is shown in Figure 2.3 [6]. This complex is structurally unique in that it has an unusually large Peierls distortion, $\rho = 0.789$, for an iodide-bridged platinum complex. Unlike the Pt(en)$_2$Pt(en)$_2$X$_2$Y$_4$ complexes described above, which have (en) ligands on all of the Pt ions, PtICN has ethylenediamine and cyanide ligands on alternate metal sites. This results in the phase of the charge density wave being pinned by the ligands, with the CN ligands stabilizing the Pt ion of lower charge and the ethylenediamine ligands stabilizing the Pt ion of higher charge. As a result, the ground state of PtICN is nondegenerate, unlike the Pt(en)$_2$Pt(en)$_2$X$_2$Y$_4$ complexes in which the charge density wave has two possible phases. The chain structure in PtICN is slightly kinked, rather than linear. PtICN does not require counterions in the crystal structure because the overall charge of each chain is neutral.
Figure 2.2 - Crystal structure of $[\text{Pt(en)}_2][\text{Pt(en)}_2\text{Cl}_2](\text{ClO}_4)_4$ (en=ethylenediamine) (a) Three repeat units of the $[\text{Pt(en)}_2][\text{Pt(en)}_2\text{Cl}_2]$ chain. (b) Packing arrangement (viewing down the chain axis) of the chains, separated by $\text{ClO}_4^-$ counterions. A short segment of the extended chain structure is shown. For clarity, H atoms are not shown. Adapted with permission from [16] B. I. Swanson, J. A. Brozik et al. Observation of Intrinsically Localized Modes in a Discrete Low-Dimensional Material. Phys. Rev. Lett. 82 3288–91 (1999).
Figure 2.3 – The chain structure of [Pt(en)$_2$I$_2$][Pt(CN)$_4$] (left) shows Pt atoms bound to alternating ethylenediamine and CN- ligands which pins the phase of the CDW in this material. The packing arrangement (chain arrangement as viewed down the axis) is shown in the lower right. PtICN has order in this plane where bonding occurs between the Pt units with (en) ligands and the Pt units with CN-ligands, shown by the dotted lines in the packing arrangement diagram. Reprinted with permission from [6] J. A. Brozik, B. L. Scott, and B. I. Swanson, *Preparation and Spectroscopic Characterization of [Pt(en)$_2$I$_2$][Pt(CN)$_4$]: A New Quasi-One-Dimensional Mixed Valence Chain Material in a Completely Ordered Lattice*. Journal of Physical Chemistry B 103, (48), 10566 (1999). Copyright 1999 American Chemical Society.
Figure 2.4 – Pictures of PtCl (left) and PtICN (right) crystals taken under a microscope. PtCl forms as long needle-like crystals and the IVCT absorbs light that is polarized parallel to the long side. PtICN forms as hexagonal crystals. The IVCT absorption is always parallel to one of the sides. Finding out which side can be done under a microscope with a polarizer.
2.1.2 - Optical and Electronic Properties

The one-dimensional band structure of the PtX complexes results from hybridization of the chain axis orbitals to form two bands, a higher energy, half-filled band of predominantly Pt 5d\(^z_2\) character, and a lower energy, fully-filled band of predominantly halide p\(_z\) character [9]. The Peierls distortion splits the half-filled 5d\(^z_2\) band to form the valence and conduction bands. The optical properties are also highly anisotropic. The dominant feature in the optical absorption spectrum is polarized along the chain axis and consists of a broad, intense optical intervalence charge transfer (IVCT) transition, in which electron density is transferred between nonequivalent metal sites. The optical absorption spectra of the PtX(en) complexes for light polarized along the chain axis, measured by Buschmann et al [10], are shown in Figure 2.5. These absorption spectra were determined by performing a Kubelka-Munk transformation on diffuse reflectance measurements. The asymmetric profile of the absorption band, with a steep edge at low energy and a Lorentzian-like tail extending to higher energy, has been modeled in terms of a one-dimensional charge transfer band with strong excitonic character [11]. The position of the IVCT band correlates directly with the magnitude of the Peierls distortion, with higher transition energies for the more distorted complexes: the absorption peaks fall at 2.7 eV for Pt(en)Cl, 1.9 eV for Pt(en)Br, and 1.4 eV for Pt(en)I at room temperature [3]. These spectra are also consistent with measurements made by Wada et al, [10]. The optical response of PtICN was determined by diffuse reflectance and is shown in Figure 2.6.

The luminescence spectra of the PtX(en) complexes following optical excitation of the IVCT were also measured by Wada et al [10]. The luminescence originates from self-trapped excitons and is strongly Stokes-shifted, with peak luminescence energies of approximately half of the IVCT gap energy for each of the complexes [3]. The wavelengths at the peak of the spectra are given in Table 2.1 along with other relevant data that will be discussed throughout this work.
Figure 2.6 – Optical absorption spectrum of PtICN determined from the diffuse reflectance response.

2.1.3 - Vibrational Properties

The vibrational properties of the Pt(en)$_2$Pt(en)$_2$X$_2$(ClO$_4$)$_4$ complexes have been characterized by Raman and far-infrared spectroscopies, [12-18] revealing strong vibrational modes along the chain axis. The chain-axis repeat unit contains four atoms (two metal and two halide ions), which results in four vibrational modes involving motions along the chain axis: one Raman active mode ($\nu_1$) and two infrared-active modes ($\nu_2$ and $\nu_3$), shown schematically in Figure 2.7, in addition to an acoustic mode. Because of the symmetries of the chain-axis modes, only the symmetric stretch chain-axis mode ($\nu_1$), which involves motion of the halide ions symmetrically about the intervening metal ion, is coupled to the optical IVCT transition. For the PtCl complex, Raman measurements at 77 K yield a frequency for the $\nu_1$ mode of 313 cm$^{-1}$ (or a vibrational period of ~ 100 fs) [18]. Because the equilibrium metal-halide bond lengths depend on the charge distribution about the metal ions, the coupling of the Raman-active $\nu_1$ (symmetric stretch) mode to the optical IVCT transition is very strong. Resonance Raman spectra of the MX complexes show an intense response from the symmetric stretch mode, including a strong overtone progression [19]. Vibrational modes associated with transverse motions of the chain elements as well as modes associated with the transverse ligands are also present; however, because the IVCT transition is strongly polarized along the chain axis, these modes have much weaker coupling to the optical transition.

The Raman spectrum of PtICN is shown in Figure 2.8. The symmetric stretch mode appears at 138 cm$^{-1}$. In PtICN, the lower symmetry due to the kinked chain structure results in two additional Raman-active modes that appear at 111 cm$^{-1}$ and 49 cm$^{-1}$, corresponding to the motions shown in Figure 2.9.
Figure 2.8 - Resonance Raman spectrum of \([\text{Pt(en)}_2\text{I}_2][\text{Pt(CN)}_4]\) under 800 nm laser excitation at 77 K.


Copyright (1999) American Chemical Society.
Figure 2.9 - Fully symmetric Raman-active in-plane vibrational modes of PtICN. Figure courtesy of J.A. Brozik. The 138 cm\(^{-1}\) mode represents the symmetric displacement of the I\(^-\) ions about the Pt(en)\(_2\) structures. The 110 cm\(^{-1}\) mode is associated with an offset displacement of the I\(^-\) ions about the Pt(CN)\(_4\) structures and the 49 cm\(^{-1}\) mode is associated with rotation of the ligands about their Pt centers.
2.2 - Self Trapping

A self trapped exciton or STE (other names include exciton-polaron or neutral bipolaron) is an electron hole pair that deforms the surrounding lattice and confines itself. The idea of self-trapping was first suggested by Landau who described the process as “the electron digs its own hole and is trapped there” [29]. Theoretical analysis of the dependence of self-trapping on the dimension of the lattice [2] has shown that while two- and three-dimensional systems generally have a potential barrier between the free and self-trapped states (in which case the self-trapping rate is limited by thermal activation or tunneling), the transition from the spatially extended free state to the localized self-trapped state in a one-dimensional lattice is barrierless. This leads to very fast formation times that are expected to occur on the order of a single vibrational period of the lattice [20, 21].

Exciton self-trapping in the MX complexes is triggered by optical excitation of the IVCT band. The final state of the optical transition is a free exciton that is delocalized along the chain axis that rapidly evolves to form the localized STE state. The STE in the PtX materials consists of a localized region in which the CDW is absent or reduced and the Peierls distortion of the metal-halide bond lengths is accordingly relaxed. The structure of the STE is shown schematically in the lower portion of Figure 2.1 in the small polaron limit, in which the exciton is localized in a single repeat unit of the chain. In general, the spatial extent of the STE will depend on the strength of the electron-phonon interaction and the degree of valence delocalization. In a series of papers, Bishop and co-workers carried out calculations using an extended tight-binding Peierls-Hubbard model with Hamiltonian parameters estimated from spectroscopic measurements and quantum chemical calculations to investigate the properties of the electronic excitations of the PtX materials, including polarons and self-trapped excitons [21-24]. Although this method is approximate, this modeling approach has proven useful for identifying trends associated with the structural tunability of the complexes. The calculations predict that the spatial
extent of the localized electronic excitations in the strongly coupled PtCl material are approximately 1-2 Pt$_2$Cl$_2$ repeat units, and predict larger localization lengths for electronic excitations in the less strongly coupled materials. One of the goals of the work presented here is to quantify the extent of localization in the MX materials, i.e. to measure the spatial extent of the excitons in these materials.
<table>
<thead>
<tr>
<th>Property</th>
<th>PtCl</th>
<th>PtBr</th>
<th>PtI</th>
<th>PtICN</th>
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<td>bond length ratio (L1/L2)</td>
<td>0.743</td>
<td>0.828</td>
<td>0.89</td>
<td>0.789</td>
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<td>charge disproportionation</td>
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<td>peak STE luminescence (nm)</td>
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<td>1632</td>
<td>2067</td>
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<td>excited state frequency (cm⁻¹)</td>
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<td>acoustic frequency (cm⁻¹)</td>
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<td>exciton spatial extent (number of unit cells)</td>
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<td>5</td>
<td>3</td>
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</tr>
</tbody>
</table>

Table 2.1 - Key properties of the MX complexes. Boxes left blank are quantities assumed unmeasured.

Peak absorption and luminescence from Wada [10] and Brozik [6], bond length ratios from Huc et al [7] and Brozik [6]. The numbers in the table below the gray bar come from time resolved transient absorption measurements conducted by Morissey [26], Van Pelt [27], and the work presented here. The acoustic frequency and spatial extent in PtCl and PtICN will be presented in Chapters 4 and 5 of this dissertation.
2.3 - References for Chapter 2


CHAPTER 3

EXPERIMENTAL CONSIDERATIONS

3.1 – Basics of Transient Absorption Measurements

Transient absorption experiments measure the change in the absorption of the sample. An experiment consists of 4 basic steps.

1 - A probe pulse is transmitted through the sample and the absorption is measured.

2 - Optical excitation is induced by absorption of a pump pulse.

3 - Absorption of the probe pulse is measured again.

4 - The change in the absorption, caused by excitation with the pump, is calculated.

The pump-probe experiments presented here will be time resolved which means the absorption is measured as a function of time. This is done by exciting the sample with the pump pulse then waiting a short but accurately measured period of time (the delay time) before measuring the absorption of the probe. Many measurements are made, each at a different delay time, and the result is a plot of the change in absorption vs delay time.

The pump/probe delay time is accurately determined through the movement of a computer controlled mechanical stage with retro-reflecting mirrors as shown in Figure 3.1. Since light travels at a rate of 300 nm per femtosecond, a shift of 1500 nm to the delay stage in Figure 3.1 will delay the arrival of the probe pulse by 10 fs – a typical single step in these experiments. The choppers serve 2 purposes:

1 - Choppers turn like a fan, unblocking and blocking the beam at a specific frequency. Lock-in amplification techniques (discussed further in 3.3.1) filter out any signals not modulated at the chopper frequency, drastically decreasing the effects of background noise.
2 - A chopper blocks and unblocks the pump pulse so that the probe absorption can be measured with and without optical excitation (see steps 1 to 3 above).

The REF detector serves as a reference for the intensity of the probe transmitted through the sample when the pump is not present. The REF intensity is set to match the intensity of the transmitted probe (with optics such as OD filters or crossed polarizers) before running the experiment. The change in transmitted probe intensity divided by the incident intensity is the differential transmittance and will be discussed next. Additionally, dividing the change in probe absorption by the intensity of the reference line serves to filter out noise from power fluctuations in the probe. Modifications and additions to this setup were introduced for each of the experiments presented in Chapters 4-6 and appropriately modified diagrams are presented in these chapters as well.
Figure 3.1 – Simple diagram of a pump-probe experiment. A delay stage is used to increase the relative distance travelled by the probe pulse and create a delay between the arrival time of the pump and probe pulses at the sample. The retro-reflecting mirror introduces a delay of $\Delta t = 2d/c$ ($c =$ speed of light, $d =$ distance moved) to the probe. A chopper modulates the pump beam, and a separate chopper modulates a reference line which serves as a reference intensity for the probe.
3.1.1 - Differential Transmittance

As light travels through a material its intensity decreases exponentially with distance and can be characterized by the absorption coefficient $\alpha$

$$I(x) = I_0 e^{-\alpha x}$$  \hspace{1cm} (3.1)

where $I_0$ is the intensity at $x = 0$. We can define $T_0 = I/I_0$ as the transmittance of a sample that has not been altered by a pump (pump off) and $T$ as the transmittance of the sample which has been pumped into an excited state (pump on). We may then express the induced change in the sample in terms of the differential transmittance

$$\text{Differential Transmittance} = \frac{T - T_0}{T} = \frac{\Delta T}{T}$$  \hspace{1cm} (3.2)

When $T > T_0$ the effect is known as induced transmittance and the overall signal is positive. When $T < T_0$ the differential transmittance shows up as a negative signal and this is called induced absorption.

The signal measured by the detector is the intensity and from that the differential transmittance is calculated. If the differential transmittance is small then the approximation can be made that $\Delta T/T \approx \Delta \alpha/\alpha$ so that $\Delta T/T$ is a good approximation of the change in optical absorbance.
3.2 – Pulse Generation

3.2.1 – Laser System

The pulses used in these experiments came from a home-built ~11 fs Ti:Sapphire oscillator that seeds a Coherent/BMI α-1000/US regenerative Ti:Sapphire amplifier. The amplifier operates at a repetition rate of 1 kHz and outputs a ~35 fs pulse with a ~30 nm (FWHM) wide spectrum which is centered at 800 nm.

The Ti:Sapphire oscillator is pumped with a 5 Watt CW Millennia that we operate at around 2.3 Watts. The Millennia lasing medium is Nd:YVO₄ and it is pumped with two fiber coupled AlGaAs laser diodes. The fundamental lasing wavelength is 1064 nm which is intracavity frequency doubled in an LBO crystal to get a 532 nm output.

The oscillator design, based on [1], uses passive Kerr lens mode-locking [2] to produce 11 fs pulses spaced 11.6 ns apart. A pair of dispersive prisms are used for intracavity dispersion compensation. The spectrum is centered at 795 nm with a FWHM of 55 nm.

The oscillator output is sent through a Coherent/BMI α-1000/US regenerative Ti:Sapphire amplifier system. The amplifier system is comprised of 3 main parts: the stretcher, amplifier, and compressor. The stretcher introduces linear dispersion to the pulse, stretching it out in time. This must be done before the pulse can be amplified to avoid phase distortions due to nonlinear interactions in the amplifying medium as well as damage to the amplifier components. The pulse is then amplified in a Ti:Sapphire based regenerative amplifier. The amplifier uses a Pockels cell (which is a fast voltage controlled waveplate), together with polarizers, to let the pulse into the cavity, allow it to make a set number of round trips, then allow the pulse to exit the cavity. Amplification of the pulse occurs in a Ti:Sapphire crystal where the oscillator pulse is overlapped spatially and temporally with the Nd:YLF
pump pulse. Once the amplified pulse exits the cavity a Faraday rotator is used to switch the beam out of the amplifier. The Faraday rotator is used to separate the input beam, coming from the stretcher, from the amplified beam. These two beams travel in different directions but are overlapped spatially. The Faraday rotator is able to separate these beams using the Faraday effect, which will rotate the polarization of beams travelling through in one direction and not the other. After the polarization of the return beam has been rotated it can be separated from the spatially overlapped incoming beam with a Brewster polarizer.

The amplifier is pumped by a Q-switched, flashlamp pumped, 12 Watt Nd:YLF laser that outputs ~ 500 ns pulses. Q-switching is a technique by which high powered optical pulses can be generated. The Q-switch uses an acousto-optic modulator to control the gain in the laser cavity. Lowering the gain in the cavity allows time to build a large population inversion in the lasing medium. When the cavity is switched to high gain the built up population inversion is quickly depleted, resulting in the output of a high energy pulse. The Nd:YLF lasing rod is stored in a housing physically close to two flashlamps that pump the rod. The flashlamps emit bright, noncoherent light in all directions and the housing, surrounded by a diffuse coating, is built with curved walls that reflect and focus the flashlamp light into the lasing rod. There are 2 lasing lines at 1053 nm and 1047 nm that have polarizations orthogonal to one another. A Brewster polarizer is used to select only the 1053 nm line, which is then frequency doubled in an LBO crystal. The 526.5 nm pulse is ejected from the cavity using a 45 degree dichroic mirror that reflects at 1053 nm and transmits at 526.5 nm. The result is an output pulse train centered at 526.5 nm, operating at a rep rate of 1kHz.

After the oscillator pulses have been stretched and amplified they need to be recompressed. This is done in the compressor, which is essentially reverses the effects of the stretcher. The beam is dispersed spectrally and an optical path length is created that depends on wavelength. Changing the
distance between the gratings changes the relative difference in path length of photons at different wavelengths. By viewing the pulse autocorrelation while adjusting the distance between gratings, the optimal distance that gives the shortest pulse can be found.

There are limits to how well the compressor can compensate for all of the dispersion in the pulse. The grating arrangement introduces a wavelength dependent change in path length that compensates for second and third order dispersion. Higher order dispersion cannot be reversed with the compressor. In order to compensate for higher-order dispersion and get a nearly transform limited pulse we have installed a Femtojock P pulse shaper from Biophotonic Solutions. The Femtojock uses a spatial light modulator (SLM) [4] to adjust the dispersion. An SLM is a thin layer of nematic liquid crystal sandwiched between glass plates. The liquid crystal is comprised of rod shaped molecules that are aligned with parallel axes. Application of an electric field causes the molecules to rotate, causing a change in the refractive index of the material in a particular spatial plane. Small electrodes span the length of the SLM, effectively dividing it into pixels that can be controlled individually with an applied voltage. The pulse is spatially and spectrally dispersed onto the SLM with a grating and the phase is adjusted as a function of wavelength. The Femtojock SLM has 128 pixels.

The Femtojock uses multiphoton intrapulse interference phase scan (MIIPS) techniques to measure the phase of the pulse. To run a MIIPS scan one focuses the pulse in a nonlinear crystal to invoke second harmonic generation. The spectrum of the second harmonic is measured as the SLM adjusts the wavelength dependent phase of the fundamental beam. The frequency doubled spectrum contains all of the information necessary for the computer controlled Femtojock system to determine the phase vs wavelength of the fundamental pulse. The phases are then adjusted with the SLM and the result is a pulse compressed to within 1% of the theoretical Fourier transform limit.
3.2.2 - Continuum Generation

When MX materials are excited the absorption spectrum of the excited state is strongly red shifted. In order to measure the transmittance of the probe in this region it is necessary to increase the bandwidth of the laser pulse. This can be done through continuum generation. The continuum is generated by focusing high intensity ~35 femtosecond pulses in a sapphire plate where self phase modulation causes an intensity dependent shift in the refractive index of the medium.

\[ n = n_0 + n_2 I(t) \] (3.3)

which results in a phase shift

\[ \varphi = n_2 I(t) \omega_0 x / c \] (3.4)

and the instantaneous frequency of the field becomes

\[ \omega(t) = \omega_0 + \frac{d\varphi}{dt} = \frac{n_2 \omega_0 x}{c} \frac{dI}{dt} \] (3.5)

For a pulse with a sech\(^2\) intensity profile of the form

\[ I(t) = I_0 \text{sech}^2(t/\tau_0) \] (3.6)

the instantaneous frequency is

\[ \omega(t) = \omega_0 + \frac{2\omega_0 n_2 I_0 x}{c\tau_0} \text{sech}^2(t/\tau_0) \tanh(t/\tau_0) \] (3.7)

which is shown graphically in Figure 3.2. The result is a red shift on the trailing edge of the pulse and a blue shift on the falling edge. The resulting increase in the bandwidth of the pulse is quite large. In our lab, the input beam is a 35 fs pulse centered at 800 nm with a bandwidth of 30 nm FWHM. After continuum generation the pulse has a useful spectral content ranging from ~400-1000 nm.
Figure 3.2 – Frequency shifting from self phase modulation. The shift in frequency is proportional to the time derivative of the intensity. This results in the leading edge of the pulse being blue shifted and the trailing edge being red shifted.
3.3 - Detection and Data Acquisition

3.3.1 – Lock-in Amplification

A common method used to measure differential transmittance involves the use of a lock-in amplifier and a chopper. The sample is placed at the shared focus of the pump and probe beam. After transmission through the sample the pump is blocked and the intensity of the probe is measured as shown on the left side of Figure 3.3. The chopper periodically blocks and unblocks the pump while the intensity of the probe is measured with a photodiode. While the chopper is blocking the pump, the signal on the photodiode is $T'$ and when the pump is unblocked the photodiode sees $T_0$. This is depicted on the right side of Figure 3.3.
Figure 3.3 – Schematic of signals in a pump probe experiment. The pump and probe are overlapped in the sample, and the pump is chopped, shown on the left. The signal seen by the detector is shown on the right. The square wave is the chopper signal. When it is high, the pump is being blocked and the transmittance is higher. When it is low the pump is unblocked and the transmittance is lower (induced absorbance). The square wave shown in blue has an amplitude of $\Delta T$. 
The job of the lock-in amplifier is to pick out $\Delta T^*$ from any background noise. The lock-in reads the chopper square wave and the modulated probe signals shown in Figure 3.3. The lock-in then creates a sine wave at the frequency of the chopper signal and multiplies it by the probe signal. The result is proportional to $\Delta T^*$ and can be represented as a product of 2 sinusoids of frequency $\omega$

$$V \propto \Delta T \sin(\omega - \varphi_L) \sin(\omega - \varphi_P)$$  \hspace{1cm} (3.8)

$$= \frac{\Delta T}{2} \cos(\varphi_L - \varphi_P) - \frac{\Delta T}{2} \cos(2\omega + \varphi_L + \varphi_P)$$  \hspace{1cm} (3.9)

Where the subscripts $L$ refer to the lock-in, $P$ to the probe, $\omega$ is frequency, $\phi$ is phase and $V$ is the voltage read out from the lock-in. The lock-in then uses a low pass filter to remove the frequency dependent term and the remainder is a DC signal proportional to $\Delta T^*$. The phase of the lock-in can then be adjusted to maximize the signal, effectively matching the lock-in and probe phases and setting the cosine term equal to magnitude 1. The proportionality factor can be established by splitting off a portion of the probe and creating a reference line that serves as the denominator in the differential transmittance equation.

When the lock-in adjusts the phase it is effectively setting the cosine phase in Equation 3.9 equal to 0 or $\pi$. One gives a negative signal, the other positive. These two signals correspond to channels X and Y on the lock-in and this is known as Phase Sensitive Detection (PSD). Figure 3.3 shows an induced absorbance (the “pump off” signal is lower). In an induced transmittance signal, the “pump off” signal would be higher than “pump on” and would end up looking like the induced absorbance except 180 degrees out of phase. Thus, choosing the appropriate lock-in phase of 0 or $\pi$ (or equivalently choosing either channel X or Y) is important because it determines whether the signal will be recorded as an induced transmittance or absorbance.
It is sometimes useful to remove the phase dependence of a signal. If one wishes to simply monitor the intensity of a beam (as opposed to the differential transmittance which is a measurement of the change in intensity) then the phase is irrelevant and only the magnitude of the signal is desired. Such is the case when employing the use of a reference line. The phase dependence can be removed from the signal by recording $R$ instead where

$$R^2 = X^2 + Y^2.$$  \hspace{1cm} (3.10)

Recording $R$ will always give a positive signal.

### 3.3.2 – Fast Readout CCD Detector

In the lock-in measurements described in the previous section, the detector was a photodiode that has a voltage response linearly proportional to the total incident energy. Therefore, the recorded probe response is integrated over all wavelengths incident on the photodiode. Measurements can be made at specific wavelengths by using a bandpass filter, but this results in throwing away information at wavelengths blocked by the filter. The use of a CCD camera, combined with a spectrometer, provides a method by which time resolved pump probe measurements can simultaneously be recorded at a wide range of wavelengths.

The CCD detector used here has a fast readout time, enabling the measurement of the spectrum of each laser pulse, in a 1 kHz pulse train, individually. $\Delta T/T$ can then be calculated with a minimum of 2 pulses, a probe pulse before excitation and a probe pulse after excitation. The CCD array is a 1340 x 680 pixel array with the ability to measure the intensity incident on each pixel individually. It is mounted in the exit plane of a spectrometer that disperses the beam onto the CCD array, effectively assigning each column of pixels to a specific wavelength. The result is the simultaneous measurement of time resolved differential transmittance signals at 1340 different wavelengths.
The camera and choppers are synchronized to the laser by a triggering circuit I designed and built. The circuit is controlled by a PIC16F84A programmable microcontroller. The microcontroller reads the laser pulse train as a TTL logic input and outputs trigger signals to both the camera and choppers telling the camera when to acquire data and when to read out data, and telling the chopper when to block the pump and when to let it pass. Trigger pulses are sent to the camera in bunches with breaks between each bunch that give the computer time to store the data in memory and calculate $\Delta T/T$. The number of pulses per bunch and pause time can be adjusted with DIP switches built into the circuit.

Data is read out to a computer via USB and managed using a Labview program I also wrote, with the help of my colleague Josef Felver. The main purpose of the Labview program is to read the camera data and calculate $\Delta T/T$. It must first determine which probe pulses were passed through the sample in the presence of the pump (“pump on”) and which ones passed through the sample while the pump was being blocked by the chopper (“pump off”). It can then calculate $\Delta T/T$ for each pair of “pump on” and “pump off” pulses, separately for each of the 1340 pixels. The result is a measurement of the spectrum of $\Delta T/T$ for every pulse pair. $\Delta T/T$ is then averaged over many pulses to remove noise from laser intensity fluctuations.

The Labview program also controls the nano-positioning delay stages that determine the delay time between the pump and probe. When time resolved data is desired, $\Delta T/T$ is measured and averaged, the stage is moved, $\Delta T/T$ is measured and averaged again and so on until a plot of $\Delta T/T$ vs delay time is available at all wavelengths within the probe spectrum.
3.4 – Pulse Characterization

3.4.1 - Spatial Characterization of Gaussian Beams

It is often necessary to measure the spot size of a beam. Since lasers often take on a Gaussian intensity profile, the definition of the beam “radius” is generally left to convention. The resulting calculations of the beams cross sectional area and flux obviously depend on the defined radius so it is important to be consistent in such definitions. This section is a brief reference for the conventional terminologies and methods for beam size measurements.

A Gaussian beam has an electric field profile

\[ E = E_0 e^{-r^2/w_0^2} \]  \hspace{1cm} (3.11)

where \( w_0 \) is called the Gaussian beam radius. The resultant intensity is the square of the electric field

\[ I = E_0^2 e^{-2r^2/w_0^2} \]  \hspace{1cm} (3.12)

In terms of other common parameters

\[ I = E_0^2 e^{-2r^2/w_0^2} \]  \hspace{1cm} (3.13)

\[ = E_0^2 e^{-4\ln(2) \cdot r^2/FWHM^2} \]  \hspace{1cm} (3.14)

where \( w_0 \) and the FWHM are related by the factor

\[ w_0 = 0.849 \, FWHM \]  \hspace{1cm} (3.15)

The FWHM (Full Width at Half Max) of the beam is easily measured when looking at a graph so it is useful but \( w_0 \) is both conventional and more mathematically convenient. It is often referred to as the radius of the beam. Figure 3.4 illustrates these points.
A common method for measuring the spot size of a Gaussian beam is to run it through a circular pinhole of known radius and measure the intensity before and after the pinhole. The power transmitted through a pinhole of radius \( \rho \) is obtained by integrating over the intensity profile. This is easily solved analytically to give the beam radius:

\[
w_0 = \sqrt{-\frac{2\rho^2}{\ln (1 - P/P_0)}}
\] (3.16)

where \( P \) is the power measured transmitted through the pinhole, \( P_0 \) is the power measured entering the pinhole, and \( \rho \) is the radius of the pinhole. Figure 3.5 plots the power transmitted through a pinhole as a function of the beam’s relative radius.

Care should be taken to choose a pinhole with an appropriate radius. If the beam radius is much larger or smaller than the pinhole radius then small errors in the measured powers can result in large errors in the calculated spot size. Calculation of the propagation of error between the power \( \phi \equiv P/P_0 \) and the relative radius of the beam \( R \equiv w_0/\rho \) gives

\[
\Delta \phi = \left| \frac{\partial \phi}{\partial R} \right| \Delta R \Rightarrow
\]

\[
\Delta R = (0.25)R^3 e^{2/R^2} \Delta \phi
\] (3.17)

which is plotted in Figure 3.6 assuming a reasonable error of \( \pm 1\% \) in the measurement of \( \phi \). Figure 3.6 shows how important it is to avoid choosing a pinhole that is large compared to the size of the beam. For example, small errors in the measurement of the power are amplified by several orders of magnitude in the calculation of \( R \) when making measurements where \( R < 0.5 \) (where the beam radius is less than half the pinhole radius).
A general guideline might be to choose a pinhole radius that is between 1 and \(\frac{1}{2}\) the expected beam radius (which translates to transmitting 40%-87% of the power) to avoid miscalculating the spot size.

Once the beam radius is accurately determined, the area often needs to be defined in order to calculate the energy density. The conventional cross sectional area for Gaussian beam is an intuitively analogous to that of a circle

\[
A = \pi w_0^2 
\]

Note also that the Rayleigh range

\[
z_R = \frac{\pi w_0^2}{\lambda} 
\]

and spot size at the focus of a lens

\[
w_{focus} = \frac{\lambda f}{\pi w_{lens}} 
\]

are conventionally written in terms of the beam radius.
Figure 3.4 – Relevant Gaussian optics parameters for beam size measurements.
Figure 3.5 – The fraction of intensity transmitted through a pinhole vs relative beam radius. A reference to this graph will help establish a quick calculation of the expected drop in power through a pinhole. A Gaussian beam with radius $w_0$ entering a pinhole with radius $\rho = w_0$ will transmit 86% of its power.
Figure 3.6 – The error in determining the beam radius vs the spot size (spot size normalized by pinhole radius). It is evident that for a beam with radius $\omega_0$ and a pinhole with radius $\rho$; if $\omega_0 \leq 0.75\rho$ the error in determining the spot size grows quickly ($\rho = 0.4w_0 \Rightarrow \Delta R = 430\%$) and thus, measurements made with relatively large pinholes should be avoided. An optimal pinhole radius of $0.87w_0$ ($w_0 = 1.15\rho$) yields an error of 1.7% in $w_0$ for powers read within an accuracy of 1%.
3.4.2 - Temporal Characterization of Femtosecond Pulses

Knowing the temporal length of a femtosecond pulse is often a necessity. However, because the pulses are short compared to the response time of most detectors, many conventional temporal pulse measurement methods will not work. One common technique is to set up an autocorrelation as shown in Figure 3.7 and measure the autocorrelation function in Equation 3.23. However, this requires the use of a frequency doubling crystal and a setup that may be different from the one desired when running the experiment. In the experiments outlined here, crystals were often mounted onto a sapphire plate. By moving off of the crystal and translating the sapphire plate into the focus of the beams, it was easy to record a pump probe signal that is the result of cross phase modulation between the pump and probe. This section discusses a method of extracting the autocorrelation function from the cross phase modulation (XPM) response of the pulse with itself.

The setup is that of a degenerate pump probe measurement performed in a nonlinear medium. At sufficiently high pump intensities the Kerr effect causes a change in the refractive index of the medium that is proportional to the pump intensity.

\[ \Delta n \propto \text{Intensity} \quad (3.22) \]

This causes a phase shift in the probe that changes as the pump and probe are temporally scanned over one another. By measuring the spectrum of the probe as a function of delay one gathers all of the necessary information to retrieve both the autocorrelation function and the wavelength resolved phase of the pulse.

In order to retrieve the autocorrelation function

\[ A(\tau) = \int I(t - \tau)I(t)dt \quad (3.23) \]
one should calculate the change $\Delta G$ in the centroid of the XPM spectra as a function of delay.

$$\Delta G(\tau) = G(\tau) - G_0$$  \hspace{1cm} (3.24)

where $G_0$ is the centroid of the XPM spectrum at a delay of $\tau = 0$ fs [4]:

$$\Delta G(\tau) = \frac{\int uS(u, \tau)du}{\int S(u, \tau)du} - \frac{\int uS(u, 0)du}{\int S(u, 0)du}$$  \hspace{1cm} (3.25)

where $S(v, \tau)$ is the spectrum as a function of delay $\tau$ and frequency $v$. One can also show, as discussed in [4-6], that $\Delta G$ is proportional to the derivative of the autocorrelation function

$$\Delta G(\tau) = \frac{2\pi n_2 z}{E\lambda} \frac{dA(\tau)}{d\tau}$$  \hspace{1cm} (3.26)

where $n_2$ is the material nonlinear index, $z$ is the interaction length, $\lambda$ the wavelength, and $E$ is the total energy of the pulse (which is equivalent to the integral of the spectrum seen in the denominators of Equation 3.25). However, in practice, the shift in the centroid of the spectrum is very small and heavily influenced by noise. When mechanical stages are used to set the delay, it can take around a minute to scan through the pulse overlap region and, with only one reference spectrum per minute at $\tau = 0$, long term noise is problematic.

A solution is to substitute the reference spectrum $G_0 = G(\tau = 0)$ with the measured “pump off” spectrum $G(\tau = \pm \infty)$. The derivative of the autocorrelation (and $\Delta G$ according to Equation 3.26) is zero at the peak $(\tau = 0)$ and well outside of the overlap region $(\tau = \pm \infty)$. And thus, according to Equation 3.24, $G(\tau = \pm \infty) = G(\tau = 0)$.

It is thus more effective (for a setup like the one used here where a chopper is used to switch between “pump on” and “pump off” readings every other pulse) to choose the reference centroid $G_0$ to
be the “pump off” pulse that immediately follows each “pump on” pulse. This removes significant long term noise.

In summary, subtraction of the centroid of the “pump off” XPM spectra from the centroid of the “pump on” XPM spectra results in a function proportional to the derivative of the autocorrelation.

\[
\Delta G(\tau) = \left( \frac{\int u S(u, \tau) du}{\int S(u, \tau) du} \right)_{PUMP\ ON} - \left( \frac{\int u S(u) du}{\int S(u) du} \right)_{PUMP\ OFF} \propto \frac{dA(\tau)}{d\tau}
\] (3.27)

In practice, dispersive nonlinear effects such as self phase modulation can affect the pulse as it travels through the nonlinear medium, causing a loss of symmetry in \(\Delta G\) (which is ideally symmetric with respect to \(\tau=0\)) and distortions to the retrieved autocorrelation. However, these can be corrected and very accurate autocorrelation functions can still be retrieved in the presence of such effects.

The phase of the pulse can also be calculated from the XPM spectra [4,7] using iterative mathematical techniques. However in order to retrieve the phase, these methods require measurement of the spectrum both before and after passing through the nonlinear medium.

3.4.3 - Pump Probe Overlap Effects

The temporal intensity profile and resulting temporal width of femtosecond pulses can be measured using the cross correlation technique. This technique usually involves measuring the sum frequency response of a material as a function of the delay between two pulses. The two pulses are physically crossed in a nonlinear crystal at a shared focus as shown in Figure 3.7 and the delay is incremented while recording the power output of the center beam at each step.

The measured intensity in a cross correlation is understood in terms of the polarization response to the applied electric fields inside the medium. To second order, the polarization is

\[
P = \chi^{(2)}|E_1 + E_2|^2 = \chi^{(2)}|E_1|^2 + \chi^{(2)}|E_2|^2 + \chi^{(2)}|E_1 E_2|^2
\] (3.28)
Each of the three terms represents a physically separate pulse exiting the nonlinear crystal as shown in Figure 3.7. Conservation of momentum results in a new pulse which exits the crystal in the direction of the sum of the k vectors of pulses 1 and 2. This is the result of the frequency sum (second harmonic generation for identical pulses) of the two fields. To calculate the total energy as seen by a detector at a given delay, one needs to integrate over the duration of the pulses. To get the intensity profile, the combined field is obtained as a function of the delay $\tau$ between the two pulses

$$ I(\tau) \propto \int_{-\infty}^{\infty} dt \ |E_1(t)E_2(t - \tau)|^2 = \int_{-\infty}^{\infty} dt \ I_1(t)I_2(t - \tau) $$

(3.29)

which is known as the cross correlation function. When the two pulses are identical, this is an autocorrelation. Autocorrelations are often done by splitting a pulse and cross correlating it with itself to obtain the intensity profile. The pulses used here can be approximated to have a sech$^2$ profile. Substitution of a sech$^2$ function into the autocorrelation function results in an intensity autocorrelation profile $I(\tau) = 1.543*I(t)$. The time axis of the measured autocorrelation intensity profile may then be divided by 1.543 to get a good representation of the pulse’s intensity profile.
Figure 3.7 – Schematic of a cross correlation between 2 pulses. The second order process of sum frequency generation results in a pulse with a new k vector which is the sum of the momentum vectors from pulses 1 and 2. Only this pulse is detected.
In an optical pump probe experiment there are similar processes that occur in the pump – probe overlap region. When the pump interacts with the sample there is a change in the absorption

$$\Delta \alpha(t) = \int_{-\infty}^{\infty} dt' A(t' - t) l_{pu}(t')$$  \hspace{1cm} (3.30)

characterized by the sample’s response $A(t' - t)$ to the excitation. The induced change in the intensity of the probe is then $\Delta l_{pr} = \Delta \alpha l l_{pr}$ so using the above equation gives

$$\Delta l_{pr}(\tau) = a l \int_{-\infty}^{\infty} dt' A(t - \tau') \int_{-\infty}^{\infty} dt' l_{pr}(t' - \tau') l_{pu}(t')$$  \hspace{1cm} (3.31)

which is a function of the delay $\tau$ and is just the cross correlation function convolved with the response function [8] which, in the overlap region, for a step function response, looks like the integral of the cross correlation intensity profile.

Analysis of the polarization to third order results in several new responses

$$\Delta l_{pr}(\tau) \propto \gamma(\tau) + \beta_1(\tau) + \beta_2(\tau)$$  \hspace{1cm} (3.32)

$$\gamma(\tau) = \int_{-\infty}^{\infty} dt A(t - t) \int_{-\infty}^{\infty} dt' l_{pr}(t' - t) l_{pu}(t')$$  \hspace{1cm} (3.33 a)

$$\beta_1(\tau) = Re\{ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt dt' E_{pr}^*(t - \tau) E_{pu}(t) E_{pr}(t' - \tau) E_{pu}^*(t') A(t - t') \}$$  \hspace{1cm} (3.34 b)

$$\beta_2(\tau) = Im\{ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt dt' E_{pr}^*(t - \tau) E_{pu}(t) E_{pr}(t' - \tau) E_{pu}^*(t') A_R(t - t') \}$$  \hspace{1cm} (3.35 c)

where the pump and probe fields are noted by the $pu$ and $pr$ subscripts [9]. $A(t)$ is the complex response function which is proportional to the third order susceptibility tensor. $A_R$ is the real part and $A_i$ is the imaginary part.
\( \gamma(\tau) \) (the “non-coherent” response) is the cross correlation convoluted with the response function. It has the same form as the one derived from the second order interaction. It is nonzero as long as the response is nonzero so it contributes a signal outside the overlap region. In fact, outside of the overlap region, this term represents the measured pump-probe signal that is generally the aim of the experiment. If the relaxation processes in the sample are really fast compared to the width of the pulse, the response function may be estimated as a step function, in which case \( \gamma(\tau) \) takes the form of the integral of the intensity cross correlation profile (inside the overlap region).

\( \beta_1(\tau) \) is a coherent response which is symmetric with respect to \( \tau = 0 \) and only contributes in the region where the pump and probe overlap. For the case of a step function response, \( \beta_1(\tau) \) is proportional to the autocorrelation intensity profile.

\[ \beta_2(\tau) = -\beta_2(-\tau) \] is anti-symmetric about \( \tau = 0 \). Furthermore, \( \beta_2(\tau) = 0 \) for transform limited pulses.

In general, one wishes to isolate the response function from the rest of the data. However, the relative contributions of these effects as well as others depend on polarization, material relaxation times, time-bandwidth products of the pulses, relative power and phases of the pump and probe etc. so precise subtraction of the overlap effects from the data is complicated. However, if the two pulses are identical and nearly transform limited, the anti-symmetric coherent contribution may be negligible and the signal prior to \( \tau = 0 \) should be a near mirror image of the coherent response about the \( \tau = 0 \) axis.

Figure 3.8 shows an example of a coherent spike in PtCl.
Figure 3.8 – Example of the coherent spike in the pump probe overlap region. In blue is pump probe data taken on PtCl with a degenerate, 800 nm, nearly transform limited pulse. The dominant response in the overlap region is well represented by the coherent cross correlation effect from $\beta_1(\tau)$. The red is a sech$^2$ function on top of the data (a function that adequately describes the autocorrelation intensity profile of the pulses used) showing how well the overlap region resembles this shape. Other, less prominent coherent effects (or deviations from an ideal sech$^2$ profile) may be responsible for the small deviations from the fit at negative delay. The oscillations at positive delay are a product of the non-coherent response function.
3.5 – Vibrationally Impulsive Excitation

3.5.1 - Wave Packet Dynamics

In order to time resolve the vibrational dynamics, the pulses used must be short compared to the vibrational periods. Impulsive excitation techniques are measurements made under these conditions. When within the impulsive limit, the bandwidth of the pulse covers multiple vibrational levels within one electronic state. Additionally, the observation of the vibrational dynamics is only possible when the electronic excitations are coupled to the vibrational modes.

When the above conditions are met, excitation produces nonstationary vibrational wavepackets that can be generated on the potential energy surface of both the ground state and the excited state [13,14]. This wavepacket motion modulates the transient absorbance, making it possible to time-resolve the vibrational motion in a pump-probe experiment.

A diagram of the excited state dynamics are shown in Figure 3.9. The molecule is initially in the ground vibrational state, on the surface of the ground state potential. The wave packet is then impulsively excited by the pump. It will oscillate on the excited state surface at the frequency characteristic of the potential well until interaction with the probe either drives the packet back to the ground state (stimulated emission, which shows up as an induced transmittance) or up to a higher lying state (absorption, which shows up as an induced absorbance). In either process, information is revealed about the time evolution of the wave packet on the surface of the excited state. The vertical arrows indicate that no motions occur in the nuclei of the system. This is according to the Franck-Condon principle which states that the electronic transitions will occur quickly compared to the vibrational period of the nucleus.
A diagram of the ground state dynamics is shown in Figure 3.10. The ground state wavepackets are generated by the resonantly enhanced stimulated Raman process. A pump pulse brings the system to the excited state where the non-stationary wave packet starts to evolve on the potential energy surface. Then, after evolution but within the duration of the pump pulse, a second interaction occurs and drives the wavepacket back down to the ground state. The wavepacket is now displaced from its original position on the ground state surface, allowing it to oscillate and facilitating measurement of the ground state frequency by absorption of the probe back to the excited state. It is evident that, in the limiting case of a delta function pulse, the ground state Raman interaction becomes impossible since the pump does not have the temporal width to place the wave packet in to the excited state, let it evolve, then drive it back down to the ground state. Also, the temporal width of the pulse must be sufficiently short compared to the time scale of a vibrational period in order to resolve the oscillatory motion of the wave packet. Thus, in the limit of a delta function pulse or a pulse large compared to the vibrational period, the response will show no ground state oscillations.
Figure 3.9 – Wavepacket dynamics for probing the excited state potential. Figure from [17].
Figure 3.10 – Wavepacket dynamics for probing the ground state potential. Figure from [17].
3.6 – References for Chapter 3


CHAPTER 4

OPTICAL AND ACOUSTIC PHONON DYNAMICS IN PTCL

4.1 – Introduction

This chapter presents time resolved transient absorption measurements on PtCl that probe the response of the material, after excitation, as the system evolves to form the equilibrated STE. This work was motivated by previous experiments carried out in PtBr [1] where it was discovered that a coherent acoustic phonon response contributes to formation of the STE. The observation of coherent acoustic phonons in PtBr (a material with an intermediate electron-phonon coupling) motivated measurements in PtCl (a material with a strong electron phonon coupling) so that we may study the acoustic response as a function of coupling strength.

This chapter will start with a review of previous work done in PtBr and PtCl. Next, the research performed here, on PtCl, will be presented. Presentation of this work will be broken up into two parts. In the first part we present the measured frequencies of the optical and acoustic phonons that accompany formation of the STE. In the second part we look at the dependence of the vibrational response on detection wavelength.

4.2 – Review of Previous Work

4.2.1 – Optical and Acoustic Phonon Dynamics in PtBr

The experiments that are reviewed in this section are transient absorption measurements carried out by F. X. Morrissey and S. L. Dexheimer in PtBr [1]. Pump-probe measurements were performed using the techniques outlined in Chapter 3. The differential transmittance was measured using a photodiode and lock-in amplifier and wavelength resolution was achieved with bandpass filters. The experiments were carried out with a 35 fs, 800-nm pump and a near-infrared continuum probe.
using the same setup as the one shown in Figure 5.1. Resolution of the wavepacket dynamics was made possible by using pulses that were short compared to the period of the lattice vibrations in the material.

The ground state optical absorption spectrum of PtBr is shown in Figure 2.5. A pump wavelength of 800 nm was chosen because it lies within the IVCT absorption spectrum. A probe wavelength of 940 nm was chosen because it lies within the red-shifted absorption of the self-trapped exciton. The purpose of the experiment was to measure the excited state dynamics and time resolve the lattice vibrations that carry the system toward the equilibrated STE structure.

Results of the transient absorption measurements made in PtBr at a temperature of ~ 77 K are shown in Figure 4.1 along with a nonlinear least squares fit to a sum of exponentials and exponentially damped cosines.

\[ y(t) = \sum_n A_n e^{-t/\tau_n} \cos (\kappa_n 2\pi ct - \phi_n \pi /180) \]  

(4.1)

The individual components from the nonlinear fit are shown in Figure 4.2. Note that pure exponentials without any oscillations can be represented as zero-frequency components if Equation 4.1 is used or as simple exponentials as shown in the formula in Figure 4.1. The 2 equations are 2 different ways of writing the same equation.
Figure 4.1 – Differential transmittance measured in PtBr (light gray) at ~ 77 K along with a nonlinear fit to exponentials and exponentially damped cosines (thick blue). The IVCT transition was pumped at 800 nm, and the response was probed at 940 nm, within the red-shifted absorption spectrum of the self-trapped exciton. Reprinted with permission from [1] F. X. Morrissey and S. L. Dexheimer. *Coherent acoustic phonon generation in exciton self-trapping*. Phys. Rev. B 81, 094302 (2010). Copyright 2010 by the American Physical Society.
Figure 4.2 – Oscillatory components from the fit in Figure 4.1. The response includes an excited state optical phonon at 109 cm$^{-1}$ and a low frequency acoustic modulation at 11 cm$^{-1}$. The response also includes oscillations at the ground state Raman frequency and its second harmonic at 172 cm$^{-1}$ and 344 cm$^{-1}$ respectively. Reprinted with permission from [1] F. X. Morrissey and S. L. Dexheimer. *Coherent acoustic phonon generation in exciton self-trapping*. Phys. Rev. B 81, 094302 (2010). Copyright 2010 by the American Physical Society.
The formation of the STE is evident by the appearance of its red-shifted optical absorbance with a time constant $\tau_{\text{form}} = 250 \text{ fs}$, and the lifetime of the metastable STE population is given by the time constant $\tau_{\text{decay}} = 12.6 \text{ ps}$. The response is modulated by wavepacket oscillations at frequencies of 11, 109, 172, and 344 cm$^{-1}$. The oscillations at 172 and 344 cm$^{-1}$ reflect wavepacket motion on the ground state potential energy surface, as discussed in Chapter 3 and depicted in Figure 3.10. The 172 cm$^{-1}$ oscillation is the Raman-active symmetric stretch optical phonon mode that involves motion of the halides symmetrically about the Pt ions in directions parallel to the chain axis. The 344 cm$^{-1}$ mode is a second harmonic of the 172 cm$^{-1}$ oscillation. Previous measurements of the Raman spectrum of PtBr [2] show peaks at these frequencies and support assignment of these modes to the ground state vibrations. The line widths of the peaks in the Raman spectrum are also consistent with the damping times measured in the time resolved response.

The oscillation at 109 cm$^{-1}$ was originally identified in measurements on PtBr carried out at room temperature by Dexheimer et al [19]. This wavepacket modulation is assigned to an excited-state optical phonon mode that reflects wavepacket dynamics in the excited state, specifically, motions that carry the system from the initially excited state (which, according to the Franck-Condon principle, has the same atomic positions as the ground state structure) toward the deformed structure of the STE. This motion primarily involves motion of the halide ions relative to the Pt ions and therefore corresponds to an optical phonon mode. This assignment was based on detailed measurements of the dynamics throughout the absorption band of the STE. The 109 cm$^{-1}$ frequency does not appear in the Raman spectrum ground electronic state and has a dephasing time similar to the formation time of the STE.

The measurement carried out by Morrissey and Dexheimer at low temperature shown in Fig. 4.1 revealed an additional component to the vibrational dynamics -- a low frequency oscillation at 11 cm$^{-1}$
that was assigned to coherent acoustic motion associated with self-trapping, the first time this process was experimentally identified.

In principle, both optical and acoustic phonons can be involved in the electron-phonon interactions that drive the self-trapping process. The physics behind self-trapping through acoustic interactions was worked out by Toyozawa [4]. Acoustic phonons with a range of wavelengths can couple to the electronic excitation and create the lattice deformation that stabilizes the self-trapped state. However, the dominant contributions are expected from phonon modes with wavelengths on the order of the spatial extent of the STE. For self-trapping by coupling to acoustic modes, the dispersion of the phonon branch allows the energy associated with stabilization of the exciton to be dissipated in the lattice in the form of propagating acoustic waves [3]. The process of the lattice deforming during self-trapping was modeled by Brown et al [5,6]. Brown calculated the evolution of a system after electronic excitation, assuming a linear electron-phonon coupling to a 1-dimensional lattice with an acoustic dispersion relation. The results, shown in Figure 4.3, depict graphs of the lattice displacements at a series of time delays. As the figure shows, energy is carried away by counter-propagating acoustic pulses that are replicas of the deformation around the STE.

Thus, measurement of the frequency of the acoustic wave provides a means by which the spatial extent of the lattice distortion can be estimated. Morrissey approximates the FWHM of a half cycle of the acoustic cosine wave to represent the size of the lattice distortion. The wavelength of the acoustic wave is determined from the acoustic velocity and the measured 11 cm$^{-1}$ acoustic frequency

$$\lambda = \frac{V_{\text{sound}}}{f}$$

(4.2)

where the appropriate units for the frequency is $f = (11 \text{ cm}^{-1})*(3*10^{10} \text{ cm/s}) = 0.33 \text{ THz}$ and $V_{\text{sound}}$ is velocity of sound in the material which was calculated to be 5 km/s. Equation 4.2 leads to a calculation
of the spatial extent of the STE to be about 5 unit cells of the Pt-Br chain, a result that agrees well with theoretical predictions made by J. T. Gammel et al [7].
Figure 4.3 – Schematic of an acoustic wave involved in formation of the STE in a one dimensional lattice. The traces represent the lattice distortion as a function of site number along the linear chain. (a)

4.2.2 – Self Trapping Dynamics in PtCl

This section will outline previous femtosecond time-resolved studies of excitons in PtCl. Several transient absorption measurements were done prior to the ones that will be presented in the next section, as well as some time resolved luminescence measurements.

In 1997, Kanner et al [8] conducted transient absorption measurements on PtCl with ~250 fs time resolution. In the measurements, a pump pulse centered at a wavelength of 406 nm was used to excite the IVCT transition and the response was probed from 1.4 – 2.4 eV to measure the induced absorbance resulting from the formation of the STE. The time resolved measurements were run from ~0-500 ps. The response showed a large induced absorbance that formed in a time within the time resolution of the measurement and decayed on a timescale of tens of ps.

In 1998 Tomimoto et al [9] reported time resolved luminescence measurements on PtCl using femtosecond fluorescence up-conversion techniques with 180 fs time resolution. The sample was pumped at 388 nm to excite the IVCT and luminescence of the STEs was measured from ~620 – 1300 nm. The authors reported 200 – 400 fs exponential components attributed to fast vibrational relaxation, as well as a long term exponential decay in the luminescent intensity, occurring on a timescale of ~20 ps, associated with depopulation of the STEs. The formation of the STE was assumed to occur within the time resolution of the measurements.

Subsequently, Van Pelt and Dexheimer carried out measurements with higher time resolution that revealed both the formation of the STE in PtCl and its associated vibrational dynamics [10,11]. In these experiments, the IVCT transition was pumped with 25-fs 600-nm pulses and the excited state was probed over a range of wavelengths near 800 nm. These measurements revealed the formation of the STE via the appearance of its red-shifted absorption spectrum with a formation time of ~ 200 fs. The response was modulated by vibrational wavepacket oscillations, including a rapidly damped component.
at a frequency of \(~180\,\text{cm}^{-1}\) assigned to an excited state optical phonon motion that carries the system from the initial structure to the structure of the self-trapped state. Later, an acoustic phonon was discovered in the self-trapping dynamics in PtCl, as reported in the following section of this dissertation. After this, additional nonlinear fitting was performed on Van Pelt’s original measurements, and an acoustic component was also found to be present. These fitting results are presented in Section 4.3.1 below.

4.3 - Acoustic Phonon Dynamics in PtCl

The discovery of an acoustic response in PtBr, a material with an intermediate electron phonon coupling, motivated further investigation into the transient absorption response in PtCl, the MX material with the strongest electron phonon coupling. In this work, femtosecond vibrationally impulsive excitation is used to time-resolve the coupled electronic and lattice dynamics in PtCl and identify contributions from both acoustic phonons and optical phonons.

Measurements will be presented as follows: First, time resolved experiments done at a single detection wavelength will describe the fundamental oscillatory modes present in the response. Next, time and wavelength resolved measurements will be presented that investigate the dependence of these components on detection wavelength.

The optical response determined by Buschmann et al [22] of PtCl is shown in Figure 2.5. A pump wavelength that lies within the absorption spectrum, centered at 400 nm, was created by frequency doubling the fundamental output of the 800 nm Ti:Sa system described in Chapter 2. A portion of the \(~45\,\text{fs}\), 800 nm pulse was split and frequency doubled using a BBO crystal. The 400 nm pulse was then sent through a prism pair to compensate for the dispersion introduced during the frequency doubling process. The prism pair has the added benefit of separating the residual fundamental 800 nm light, removing the need for a dispersive band pass filter. The 800 nm pulse was then used to probe the
sample. The detector used was different for the two experiments that follow. In the first experiment a photodiode and lock-in amplifier was used as a detector and a bandpass filter was used to obtain wavelength resolution. In the second experiment, the CCD detector outlined in Chapter 2 was used to obtain a time resolved pump-probe signal at many detection wavelengths. A schematic of the setup is shown in Figure 4.4.
Figure 4.4 – Simplified schematic of the setup used to carry out pump-probe experiments on PtCl. A beam splitter is used to redirect some of the 800 nm light through a frequency doubling crystal (BBO) then a dispersive prism pair is used for dispersion compensation. The resulting 400 nm pump beam is chopped to allow detection by lock-in amplification. A computer controlled delay stage is used to control the arrival time of the probe pulse.
4.3.1 – Self-trapping Dynamics in PtCl

The results of a PtCl pump-probe experiment are shown in Figure 4.5. The data is shown in black with the nonlinear fit to a sum of exponentially damped cosines overlaid in red (see Equation 4.1). Figure 4.6 shows the individual damped oscillatory components.

Three strongly damped oscillations show up in the nonlinear fit at frequencies of 68 cm$^{-1}$, 176 cm$^{-1}$, and 244 cm$^{-1}$. There are also 2 exponentials that directly reflect the formation and decay of the STE. The formation component shows up as an increase in the induced absorbance (a decrease in $\Delta T/T$) that occurs as a result of the appearance of the red-shifted excited state absorption spectrum of the STE. The induced absorption, which reflects the STE population, grows on a time scale of 230 fs.

The 176 cm$^{-1}$ component is the excited state optical phonon mode that accompanies the formation of the STE. The oscillation has a dephasing time of 150 fs, comparable to the formation time for the STE. Dependence of the phase of this component on detection wavelength will be discussed in the next section.

The response also includes an oscillation at a frequency of 244 cm$^{-1}$ which is not seen in the transient absorption measurements previously reviewed. It is also not seen in the Raman spectrum. Because this component fits at the sum frequency of the other two oscillations, damps on a similar timescale, and does not show up in the Raman spectrum, we suggest the possibility that this is a sum frequency component. The observation of a sum frequency mode infers a possible coupling between the acoustic and optical phonon responses.

Of particular interest is the presence of a low frequency 68 cm$^{-1}$ oscillatory component. As discussed in the review of PtBr, measurement of the frequency of the acoustic component allows an estimate of the spatial extent of the STE. This requires knowledge of the acoustic velocity, which was
determined from the calculated phonon dispersion relations shown in Figure 4.10. The curves were
calculated, with the assistance of M.D. McCluskey, by diagonalization of the coupled one-dimensional
equations of motion for a unit cell consisting of two Pt ions and two halide ions with nearest-neighbor
and next-nearest-neighbor interactions. The force constants used in the calculations were those
reported by Love et al. [20] based on their analysis of far-infrared and Raman measurements carried out
on a series of isotopically substituted PtX(en).ClO₄ materials. The acoustic velocity is determined
from the derivative of the acoustic branch in the low frequency limit, yielding a value of 7.3 km/s. Following
the approach used by Morrissey and Dexheimer for PtBr as described above, the FWHM of a half cycle
of the acoustic wave is given by

$$\lambda = \frac{V_{\text{sound}}}{f} = \frac{7.3 \text{ km/s}}{(68 \text{ cm}^{-1}) \times (3 \times 10^{10} \text{ cm/s})} = 36 \text{ Å}$$

(4.3)

$$\frac{\lambda}{2} = 18 \text{ Å} \quad \text{FWHM} = 12 \text{ Å}$$

(4.4)

The length of the Cl-Pt-Cl—Pt—chain axis repeat unit that represents a single unit cell along the one-
dimensional chain is 10.874 Å [21] and thus we find that our observed 68 cm⁻¹ frequency corresponds to
a spatial extent for the STE of approximately 1 unit cell, corresponding to the small polaron limit and
reflecting the very strong coupling in this material.

An FFT power spectrum is shown in Figure 4.7, and presents further support for the frequencies
determined through nonlinear fitting analysis. A peak, near 68 cm⁻¹, is further evidence of the existence
of a low frequency acoustic component. The excited state component at 176 cm⁻¹ and the component at
244 cm⁻¹ are not resolved as separate peaks because the difference in the frequencies is smaller than
the width of the peaks. The wide peaks are a direct result of spectral broadening that occurs as a result
of the very fast dephasing times of these components.
As discussed in the previous section, observation of the \( \sim 68 \text{ cm}^{-1} \) component in these measurements prompted additional analysis of Van Pelt’s original measurements of exciton self-trapping in PtCl. In this experiment, excitation was near the onset of the IVCT transition at 600 nm using 25 fs pulses. The response measured at 840 nm is shown in Figure 4.8 [12]. Nonlinear fitting of the response yields 3 oscillations and 2 exponentials, shown in Fig. 4.9. The STE induced absorbance forms in 250 fs, and is accompanied by a 178 cm\(^{-1}\) wavepacket oscillation assigned to the excited state optical phonon mode that carries the system to the self-trapped state. The high time resolution of the measurements also allows the observation of wavepacket oscillations at 313 cm\(^{-1}\), the frequency of the Raman-active symmetric stretch mode of the ground electronic state determined in resonance Raman measurements done by Buschmann et al [2]. Also present in this analysis is a low frequency oscillation at 66 cm\(^{-1}\) that appears at the same frequency and phase (within error) as that found in the experiments presented above, providing additional evidence for contribution from acoustic phonons in the self-trapping dynamics in PtCl. We note that the acoustic phonon dynamics in PtCl are observable at room temperature, unlike those in PtBr. This is likely because of the much lower frequency of the acoustic phonons involved in PtBr, which could be more readily obscured by thermally-induced dephasing or thermal disorder at room temperature.
Figure 4.5 – Pump probe data (black) with nonlinear fit overlaid (red). The data were fit to the sum of exponentially damped cosines. The individual components and oscillations are plotted in Figure 4.6.
Figure 4.6 – Individual damped oscillatory components constructed from the nonlinear fit in the previous figure. Components include an acoustic phonon at 68 cm$^{-1}$, an excited state component at 176 cm$^{-1}$ and an oscillation at the sum frequency of 244 cm$^{-1}$.
Figure 4.7 – FFT power spectrum of pump-probe data in PtCl. The sample was pumped at 400 nm and the response was measured at a detection wavelength of 800 nm.
Figure 4.8 – Transient absorption measurement of PtCl. Sample was pumped at 600 nm to excite the IVCT and the wavepacket dynamics were probed at a detection wavelength of 840 nm. Data were analyzed and presented in [12] J.G. Mance, F.X. Morrissey, A.D. Van Pelt, and S.L. Dexheimer. *Ultrafast coupled electronic and lattice dynamics in exciton self-trapping: Correlation of the localization length and acoustic phonon dynamics.* Ultrafast Phenomena XVII, M. Chergui, et al., eds., pp. 326-328. Oxford University Press (2011)
Figure 4.9 – Components that add up to form the nonlinear fit shown in Figure 4.8. A ground state oscillation (black) shows up at 313 cm\(^{-1}\), an optical phonon excited state oscillation (blue) shows up at 178 cm\(^{-1}\), and an acoustic phonon oscillation (red) shows up at 66 cm\(^{-1}\). There are also two zero-frequency components: an induced absorbance with a formation time of 250 fs (purple) and a long term decay with a time constant of ~20 ps (green).
4.3.2 – Dependence of Phonon Dynamics on Detection Wavelength in PtCl

The data shown in Figure 4.5 were taken at a single probe wavelength. The dynamics depend on detection wavelength within the absorption band of the STE and in order to investigate this dependence, measurements need to be made at many wavelengths. This was made possible through use of the CCD detector discussed in Chapter 2. The same setup (Figure 4.4) was used for these experiments as was with the previous, with the exception of the use of a CCD detector instead of a photodiode and lock-in amplifier.

The spectrum of the probe is shown in Figure 4.11. Pump-probe data was recorded throughout the entire bandwidth of the probe pulse. Reliable \( \Delta T/T \) data is obtained from \( \sim 780 - 820 \) nm. Outside of this region, an accurate calculation of \( \Delta T/T \) is difficult because as the intensity in the wings of the probe pulse spectrum becomes small, the denominator approaches zero and the propagated error in calculating \( \Delta T/T \) becomes very large.

Figure 4.12 shows data taken on PtCl with detection wavelengths ranging from 780 - 820 nm. This data has the same oscillatory frequencies as the data presented earlier and shown in Figure 4.5. The large, strongly damped oscillations correspond to excited state wavepacket motion. The amplitude and phase of the oscillations are seen to change with detection wavelength.

Figure 4.13 shows a several “slices” taken out of the 3D graph shown in Figure 4.12. The spectrum of \( \Delta T/T \) at a delay of 4 ps is shown on the left side of Figure 4.13. A delay of 4 ps was chosen to give the system time to settle into the equilibrated STE structure. It is evident that the STE has stabilized by this point because the excited state oscillations and formation exponential have completely dephased. The left side of Figure 4.12 shows how the signal level increases (marked by a decrease in \( \Delta T/T \)) as the probe wavelength increases. This reflects the shape of the absorption spectrum of the STE, which extends beyond the spectrum of the probe pulse used in this experiment. As the detection
wavelength increases and moves further into the absorption spectrum of the STE, the induced absorption and the amplitude of the excited state oscillations become stronger.

In order to examine the wavelength dependence of the oscillatory response, time resolved slices were taken out of the data shown in Figure 4.12 and nonlinear fitting analysis was done. A global fit was done on 5 data sets with wavelengths ranging from 780 to 820 nm. The dephasing, formation and decay times, as well as all of the frequencies were shared (constrained to have the same value). The amplitudes and phases were not shared. The dependence of the phase on detection wavelength is outlined next.

Figure 4.14 shows the wavelength dependence of the phase of the excited state component as determined from global nonlinear fits. It shows a shift in the phase of the oscillations as the detection wavelength increases. This is a direct consequence of the wave packet motion in the excited state. Pump-probe measurements made in PtBr by S.L. Dexheimer and A. D. Van Pelt [12] also report a similar phase shift of the excited state component that changes with detection wavelength, and relate the phase shift to the excited state wave packet evolution. The phase shift is further evidence that these oscillations are associated with the excited state. If these were ground state oscillations, the phase would flip 180 degrees as the detection wavelength moved over the peak of the probe spectrum (800 nm) shown in Figure 4.11. The monotonic phase shift indicates these are not ground state oscillations. It is worth noting that this data was taken with the Femtojock pulse shaper which adjusts the pulse such that the pump-probe overlap is at delay = 0 fs for all detection wavelengths, ensuring that the observed phase change was not result of pulse dispersion in the probe.
Figure 4.11 – Spectrum of probe used to investigate the spectral dependence the dynamics in PtCl.
Figure 4.12 – Pump probe measurement in PtCl, taken with a CCD detector that simultaneously records the time resolved response throughout the full spectral bandwidth of the probe.
Figure 4.13 – “Slices” taken out of the 3D plot shown in Figure 4.12. The spectral response of $\Delta T/T$ (left) is at a pump-probe delay time of 4 ps. The time resolved response (right) is at a probe wavelength of 815 nm.
Figure 4.14 – Phase dependence of the excited state on wavelength. Results were obtained from nonlinear fits to time resolved “slices” of the data shown in Figure 4.12. The phase of the excited state component changes monotonically through the spectral range of the probe.
4.5 - References for Chapter 4


5.1 – Introduction

In this work, femtosecond vibrationally impulsive excitation is used to time-resolve the coupled electronic and lattice dynamics inherent to the self-trapping process in the strongly coupled quasi-one-dimensional material PtICN and identify contributions from both acoustic phonons and optical phonons to the localization process.

The optical absorption spectrum of PtICN, measured by J.A. Brozik [1], is shown in Figure 2.6. The dominant feature is the IVCT transition which is centered at ~475 nm and trails off around 1000 nm. This chapter will be broken up into two sections where different pump wavelengths were used to examine the formation dynamics. In the first section, the formation dynamics will be examined with a pump pulse centered at 800 nm, on the low energy side of the IVCT absorption spectrum. Experiments that measure the lifetime and saturation of the equilibrated STE will also be presented. In the second section, the effect of excess vibrational energy on the STE formation dynamics will be examined by pump-probe measurements with a pump pulse centered at 400 nm, on the high energy side of the IVCT absorption spectrum.

5.2 – Self-Trapping Dynamics Following Excitation at 800 nm

Experiments presented in this section were pumped with a pulse centered at 800 nm to excite the IVCT. The probe pulse came from splitting the 800 nm output of our system and focusing it into a sapphire plate to generate a continuum. A pair of dispersive prisms was then used to compensate the dispersion created during continuum generation and from propagation through subsequent optical components. A reference line (as discussed in Chapter 3) was used to divide out noise due to power
fluctuations in the probe. Wavelength resolution was achieved by placing a bandpass filter in the reference and transmitted probe beams. The delay between the pump and probe was adjusted with a computer controlled delay stage. The setup is shown in Figure 5.1 and continuum generation is discussed in Chapter 3.

Measurements were made at room temperature and at a temperature of ~ 77 K. The low temperatures were achieved through use of a cryostat with a cold finger, in a vacuum chamber, attached to a liquid nitrogen bath. The samples were mounted on a sapphire plate, which was mounted to the cold finger between layers of indium to provide better thermal contact. They were mounted to the plate with a specially designed thermally conductive epoxy made to withstand cracking at low temperatures. Sapphire was chosen as a mounting substrate because of its optical transparency and high thermal conductivity.
Figure 5.1 – Simplified schematic of the setup used to carry out pump-probe experiments on PtICN. A beam splitter is used to redirect some of the 800 nm light and focus it into a sapphire plate to generate a white-light continuum. A dispersive prism pair is used to compensate for the dispersion introduced during continuum generation. IR wavelengths from ~850-1000 nm are transmitted through the prism pair while wavelengths shorter than 850 nm are removed with a beam block placed near the second prism. The pump beam is chopped and $\Delta T/T$ is recorded using the lock-in amplification techniques discussed in Chapter 3. The reference line is chopped by a separate chopper and helps reduce noise from power fluctuations in the continuum. A computer controlled delay stage is used to control the arrival time of the probe pulse.
5.2.1 - Initial Self-Trapping Dynamics

Results of the time resolved differential transmittance measurements of PtICN, pumped at 800 nm and probed at 980 nm, at a temperature of ~ 77 K are shown in Figure 5.2 along with a nonlinear fit to a sum of exponentially damped cosines. The individual fit components and their frequencies are shown in Figure 5.3.

The response contains a fast exponential ($\tau = 1020$ fs) that cannot be explained as simply as the analogous components in PtBr and PtCl. This is because, as time progresses, the exponential component contributes to an increase in $\Delta T/T$, indicating a decrease in the induced absorbance. This has the opposite sign of the contribution from the formation of the STE seen in other PtX complexes, for example PtCl, as shown in Figure 4.8. Van Pelt addressed this issue [2] where he proposed the energy level diagram shown in Figure 5.4. After excitation to the final state of the IVCT by the pump, Van Pelt proposes two possible methods of absorption by the probe: (a) absorption to a higher lying state above the final state of the IVCT and (b) absorption to a higher lying state above the STE. Absorption to state (a) is initially stronger than absorption to state (b) but as the system evolves, population of the final state of the IVCT transition is transferred to the STE state decreasing the available population for transitions to (a). The result is that this exponential still provides a measure the formation time of the STE but does so from a different initial state.

It is interesting to note that the measured STE formation time in PtICN is about 2-3 times longer than in the PtX(en) complexes. This may be a consequence of the kinked structure in PtICN which deviates from the purely 1-dimensional arrangement of the other materials. A direct comparison of the properties of PtICN to the systematic trends seen in the PtX(en) complexes as a function of X is not straightforward because of the different chain structure and ligands. This can be seen in Table 2.1 where it is obvious that the properties of PtICN do not fit into the pattern that the PtX(en) complexes have --
the Peierls distortion in PtICN is between that of PtCl and PtBr, and much larger than that of PtI. However, the PtICN complex provides a useful comparison for investigating the effect of coupling strength on the vibrational dynamics. To date, only the iodide-bridged complex of this structure has been synthesized (i.e. there is no PtClCN or PtBrCN).

The fit results in Fig 5.3 also includes an exponential (zero frequency) component with a lifetime long enough to appear constant on this timescale. Pump-probe experiments to measure this component on longer time scales are presented later in this section.

The response also contains ground state oscillations that appear at the same frequencies reported in the Raman spectrum [2]. The oscillation at 137 cm\(^{-1}\) originates from the ground state symmetric stretch chain axis mode. Other Raman active vibrational modes are also apparent at 110 cm\(^{-1}\) and 49 cm\(^{-1}\). These modes are discussed in Chapter 2 and shown schematically in Figure 2.9.

Two oscillatory components that are not seen in Raman spectroscopy show up at frequencies of 97 cm\(^{-1}\) and 183 cm\(^{-1}\). The 97 cm\(^{-1}\) oscillation is the excited state component and has been reported previously, in room temperature measurements, by Van Pelt [2]. This component is assigned to an optical phonon mode, primarily involving motion of the I\(^-\) ions, that carries the system toward the STE structure. The 183 cm\(^{-1}\) component has not been previously reported. Because the frequency is nearly twice the value of the 97 cm\(^{-1}\) component, and because of the very fast 230 fs damping time, we assign it to a second harmonic of the excited state optical phonon mode. The fact that the frequency is slightly lower than twice the fundamental frequency reflects the anharmonicity of the excited state potential.

Remarkably, the response also includes a significant amplitude, strongly damped, low frequency oscillatory component at a frequency of 15 cm\(^{-1}\), in the range characteristic of acoustic phonons. As discussed in Chapter 4, acoustic phonons can contribute to the self trapping process and have now been observed experimentally in 3 MX complexes: PtCl, PtBr, and PtICN. The acoustic frequencies measured
in PtCl and PtBr agree well with theoretical predictions. However, similar theoretical work has not been
done on PtICN. Using an acoustic velocity estimated from the ground state vibrational properties, we
find that our observed 15 cm\textsuperscript{-1} frequency corresponds to a spatial extent for the STE of approximately
three unit cells, reflecting the strong coupling in this novel system.
Figure 5.2 – Measurement of the time resolved differential transmittance of PtICN at a detection wavelength of 980 nm. The red line represents a nonlinear fit to the data in black. Measurements were taken with pulses 35 fs in duration and the pump spectrum is centered at 800 nm.
Figure 5.3 – Individual exponentially damped cosine components that construct the fit shown in the previous figure. The Raman and excited state components are plotted separately for clarity. The plot on the right shows the ground state Raman active vibrational modes. On the left are the components associated with the excited state formation. The purple line is an exponential that represents the formation of the STE which occurs in ~1 ps. The blue line is the excited state optical phonon component and the green is the second harmonic of this component. The red line is a low frequency acoustic phonon mode.
Figure 5.4 – Energy level diagram for PtICN. Figure reprinted with permission from Van Pelt [2].
Pump probe measurements on PtICN were also performed at room temperature. The room temperature response showed the same oscillatory components as the low temperature response, though, as expected, the dephasing time of the ground state Raman components increases significantly as the temperature is lowered.

5.2.2 - Signal Saturation Properties

Further measurements were made to determine the saturation properties of the pump probe signal in PtICN. The sample was pumped at 800 nm to excite the IVCT transition and probed at 940 nm to measure the response of the STE, and $\Delta T/T$ was measured as a function of pump fluence. The response measured at a delay of 3 ps, following equilibration of the STE, is presented in Figure 5.5. The signal level is proportional to the STE population. Initially, the signal shows a linear dependence on pump fluence, as expected. Then, as the power increases, $\Delta T/T$ saturates, indicating the maximum excitation level that can be achieved.

5.2.3 - Measurement of the Lifetime of the STE

$\Delta T/T$ was also measured over a long enough delay range that the time constant of the slowly decaying exponential component could be determined. Care was taken to make sure that the probe beam did not move as the delay stage moved, ensuring consistent spatial overlap of the pump and probe. This was done by placing a pinhole at the co-focused position of the pump and probe, then measuring the transmitted power of the probe as the delay stage was moved through the entire 250 ps delay range. Any movements of the probe would therefore be seen as a drop in the transmitted power through the pinhole. Measurements carried out at room temperature and at $\sim 77$ K are presented in Figure 5.6. In both cases, the long-term decay of the signal fits to a single exponential, with a time constant of 340 ps at room temperature and 260 ps at low temperature, reflecting the lifetime of the STE. The observation of a temperature dependence indicates that the return of the metastable STE to
the ground state structure involves a thermally activated process. The observation of a single exponential lifetime for the decay of the STE population stands in contrast to the behavior of STEs in the PtX(en) complexes, which have been seen to have an additional decay channel in which the STE can decay into soliton pairs, or states that have a "grain boundary" between charge-density wave regions of opposite phase [3]. In PtICN, there is only one possible phase for the charge density wave, so that soliton states cannot occur and the STE must decay directly to the ground state.
Figure 5.5 – Dependence of the pump probe signal in PtICN on pump fluence. Sample was pumped at 800 nm, and probed at 940 nm. \( \Delta T/T \) was measured at a delay of 3 ps, allowing time for the excited state wavepacket oscillations to dephase. Data was taken at room temperature.
Figure 5.6 – Exponential decay of pump probe signal in PtICN due to relaxation of the STE. The IVCT was pumped at 800 nm, and the induced absorbance of the STE was probed at 980 nm. Measurements made at room temp (red) and ~77 K (blue) are shown with a nonlinear fit (black) that is used to determine the relaxation time. The STE decays with a single exponential lifetime, and the lifetime increases when the sample temperature is lowered.
5.3 – Self-Trapping Dynamics Following Excitation at 400 nm

The PtICN pump-probe experiments presented in this section were pumped with a pulse centered at 400 nm to excite the IVCT. The purpose was to investigate the effect of excitation with large excess energy on the self trapping dynamics.

The 400 nm pump pulse was generated by frequency doubling the 800 nm output of the regenerative amplifier in a BBO crystal. A pair of dispersive prisms was then used for dispersion compensation. The delay between the pump and probe is adjusted with a computer controlled delay stage. The setup is the same as the one used for the PtCl measurements presented in Chapter 4 (and shown in Figure 4.4) except that a fast readout CCD detector was used for these experiments instead of a photodiode and lock-in amplifier. The CCD detector (discussed in Chapter 3) allowed measurement of the response at all wavelengths in the probe spectrum. A 3-dimensional plot of the data is shown in Figure 5.7.

A “slice” of the data, at a probe wavelength of 820 nm, is shown in Figure 5.8 with a nonlinear fit overlaid in red. The components from the nonlinear fit are shown in Figure 5.9.

The fast exponential shows up with a time constant of 800 fs. However, the sign of this exponential is different than it was when pumped at 800 nm where the formation component contributed an increase in ΔT/T as time progressed (i.e. the signal decayed and the induced absorbance decreased). This component likely includes effects from vibrational relaxation that occur as a result of the excess pump energy as well as influence due to relaxation of the STE.

The wavepacket response shows up at the same Raman frequencies with a pump wavelength of 400 nm as it does with a pump wavelength of 800 nm (at room temperature). The ground state Raman
The frequencies obtained here are $134 \text{ cm}^{-1}$ for the ground state symmetric stretch mode and $51 \text{ cm}^{-1}$ and $108 \text{ cm}^{-1}$ for the other two Raman active modes.

The wavepacket also shows the same excited state frequency, within error, showing up here at $95 \text{ cm}^{-1}$ along with the second harmonic at $180 \text{ cm}^{-1}$. The appearance of these components with both $800 \text{ nm}$ and $400 \text{ nm}$ pumps indicates the same self trapping mechanism in both situations.

The $15 \text{ cm}^{-1}$ acoustic component is not evident in this data as it was when pumped at $800 \text{ nm}$. It is possible that it may be obscured by fast vibrational relaxation due to the excess energy available after excitation at $400 \text{ nm}$, which is well above the IVCT band gap.

FFTs of data sets for a range of detection wavelengths are shown in Figure 5.10. The frequencies in the FFT are consistent with those obtained through the nonlinear fit shown in Figures 5.2 and 5.3. The peaks at $134 \text{ cm}^{-1}$ and $51 \text{ cm}^{-1}$ are the ground state Raman active frequencies. The ground state component at $108 \text{ cm}^{-1}$ is much smaller in amplitude then the $95 \text{ cm}^{-1}$ excited state component and its FFT peak is obscured by the excited state component as a result. The peak at $180 \text{ cm}^{-1}$ is the second harmonic of the excited state and its broad width is indicative of its very fast dephasing time. FFTs show the same frequencies at all detection wavelengths.
Figure 5.7 – Pump-probe measurement in PtICN, taken with a CCD detector that simultaneously records the time resolved response throughout the full spectral bandwidth of the probe.
Figure 5.8 – Pump-probe signal in PtICN (black) along with a nonlinear fit to sum of exponentially damped cosines (red). Sample was pumped at 400 nm, within the absorption spectrum of the IVCT in PtICN, and the excited state was probed at 820 nm. Data was taken at room temperature. The components from the nonlinear fit are shown in the next figure.
Figure 5.9 – Nonlinear fit components that sum to create the fit shown in the previous figure. The ground state Raman oscillations are shown on the right and the excited state components on the left. The exponential in purple fits with a dephasing time of 790 fs. Another exponential (not shown) represents depopulation of the STE and occurs on a much slower time scale of 73 ± 10 ps. The 95 cm$^{-1}$ and its second harmonic at 180 cm$^{-1}$ are the optical phonon modes that carry the excited state toward the equilibrated STE structure. The ground state Raman components shown on the right show up at the frequencies expected for measurements made at room temperature.
Figure 5.10 – FFTs of PtICN data at a series of detection wavelengths shown in Figure 5.7. The peaks at 134 cm\(^{-1}\) and 51 cm\(^{-1}\) are the ground state Raman active frequencies. The peaks at 95 cm\(^{-1}\) and 180 cm\(^{-1}\) are the excited state optical phonon component and its second harmonic respectively. Features near zero frequency are non-physical and result from baseline and truncation effects. FFTs show the same frequencies at all detection wavelength.
5.4 – References for Chapter 5


Transist absorption measurements show excited-state wavepacket motion associated with exciton self-trapping. However, a key component of the evolution of the coupled electron-lattice system is missing from these measurements. In the impulsive excitation studies presented in Chapters 4 and 5 the excited state wavepacket motion reflects the initial vibrational dynamics of the photoexcited system, and since the oscillations dephase as the STE forms and relaxes, information on the vibrational properties of the exciton is lost as it evolves to its final equilibrated structure. An important issue that remains for a complete understanding of the physics of the localization process is the evolution of the structure and electronic distribution as the lattice distorts to stabilize the electronic excitation and form the final structurally relaxed self-trapped state. Toward this end, the experiments in this chapter use a pump-pump-probe method to probe the vibrational properties of the STE in its final equilibrated structure. In these experiments, an initial pump pulse excites the IVCT transition to generate a population of excitons. After a time delay to allow equilibration, a second pump pulse impulsively excites the STE. The resulting wavepacket motion is detected as a function of time delay between the second pump and the probe pulse. This response includes an oscillatory component at the frequency of the Raman-active mode of the STE, generated by the resonant impulsive stimulated Raman mechanism acting on the excited state. A schematic wavepacket diagram showing the Raman process originating in the excited state is presented in Figure 6.1. This time-domain excited-state Raman measurement allows us to detect vibrational modes in a time and frequency range that can be difficult to access with established time-resolved Raman methods [2]. This technique was originally developed and applied to
investigate the vibrational modes of the equilibrated STE in PtBr [1], and is applied to PtCl and PtICN here.
6.2 - Pump-Pump-Probe Experiments

In the experiments reported here, we use a pump-pump-probe method that provides a
time-domain Raman probe of the vibrational properties of the STE in its equilibrated structure. A
simplified diagram of the experiment is shown in Figure 6.2. Three pulses are co-focused in the sample
with a set delay between pumps 1 and 2. The wavepacket motion resulting from the second pump pulse
is detected as a function of time delay between the second pump and the probe pulse. The response
originating from the excited state is detected by simultaneously chopping both pump beams at different
chopping rates using a dual-frequency chopper wheel and observing the probe intensity at the sum of
the individual modulation frequencies using a lock-in amplifier. This detection scheme allows a clear
measurement of the vibrational response of the equilibrated STE because the measurement will be
sensitive to only the differential changes requiring the presence of both pump pulses, \((i.e., \Delta(\Delta T/T))\) and
is insensitive to the individual pump responses.
Figure 6.2 – Schematic of the pump-pump-probe experiment setup for PtCl. The delay between pumps 1 and 2 are set and the transmitted probe intensity is recorded as a function of probe delay time. Pumps 1 and 2 are chopped at different frequencies using a single chopper equipped with a dual-frequency wheel. The probe signal is measured with a photodiode and lock-in amplifier at the sum frequency.
6.3 - Pump-Pump-Probe Measurements in PtCl

In the experiments reported here, the vibrational properties of the STE are measured in its equilibrated structure in PtCl. An initial pump pulse, centered at 400 nm, is generated by frequency doubling an 800 nm pump pulse. This pulse is used to excite the intervalence charge transfer transition. A delay of 800 fs between the first and second pump pulses ensures that the population of excitons has relaxed to the equilibrated self-trapped structure and that the wavepacket response generated by the initial pump pulse has decayed away. The population of equilibrated STE is then impulsively excited by the second pump pulse, centered at 800 nm, which lies within the red-shifted absorption band of the STE. This pulse is 45 fs in duration, short compared to the chain-axis vibrations in the complex, and therefore impulsively excites the STE. The resulting wavepacket motion is detected by a time-delayed probe pulse, also 45 fs in duration and centered at 800 nm. All beams are polarized parallel to the chain axis, and the probe pulse is wavelength resolved following transmission through the sample to enhance detection of the oscillatory response.

For comparison, the single-pump-probe response is shown in Figure 6.3 shows the dynamics of the initially generated exciton. This time-resolved differential transmittance ($\Delta T/T$) shows the rapid formation of the STE as evidenced by the appearance of its induced absorbance signal accompanied by a rapidly damped wavepacket oscillation at 176 cm$^{-1}$ that reflects the lattice motion as the system evolves from the initial structure toward the structure that stabilizes the STE. The double-modulated pump-pump-probe response ($\Delta(\Delta T/T)$) corresponding to impulsive excitation of the STE is presented in Figure 6.4 along with a nonlinear fit to the sum of exponentials and exponentially damped cosines. The individual oscillatory components from the nonlinear fit are shown in Figure 6.5.
Figure 6.3 – Time resolved differential transmittance following excitation of the IVCT at 400 nm and probed at a detection wavelength of 820 nm. In the 3-pulse experiments that will be presented, a delay for the second pump is chosen (red arrow) such that the wavepacket oscillations of the excited state have completely dephased.
Figure 6.4 - Time-resolved double-modulated differential transmittance of PtCl following double-pulse excitation to impulsively excite the equilibrated STE, at a detection wavelength of 816 nm, on the red side of the probe pulse spectrum. Data is displayed in black. The red line represents a fit to a sum of exponentially damped cosines and a decaying exponential.
Figure 6.5 - Individual damped oscillatory components reconstructed from the fit shown in the previous figure, including a new frequency component at 160 cm$^{-1}$, assigned to the equilibrated STE, and a long-lived oscillation at 311.5 cm$^{-1}$, the frequency of the Raman-active symmetric stretch mode of the ground electronic state.
Analysis of the double-modulated response reveals two frequency components, a long-lived component at the 311.5 cm\(^{-1}\) frequency of the strongly Raman-active ground state symmetric stretch chain axis mode, and a new oscillatory component at 160 cm\(^{-1}\). We assign the new frequency component at 160 cm\(^{-1}\) to the equilibrated STE, in analogy to the response detected in the related material PtBr(en) [1]. We note that this component is detected only in the double-modulated measurement: it is not present in pump-probe measurements carried out with only a single pump pulse at either 400 nm or 800 nm, nor is it present in the ground state Raman spectrum. The appearance of a wavepacket modulation at the ground state symmetric stretch mode in the double-modulated measurement likely results from depopulation of the ground electronic state by the initial 400 nm pump excitation, thereby reducing the amplitude of the ground state impulsive stimulated Raman response excited by the second pump pulse.

The observation of a shift in frequency from the 176 cm\(^{-1}\) wavepacket oscillation associated with the initially generated exciton to the 160 cm\(^{-1}\) frequency of the final equilibrated STE indicates that further structural evolution takes place during the self-trapping process beyond the initial vibrational wavepacket dynamics. It should be noted that a shift to lower frequency indicates that formation of the final equilibrated state does not simply involve vibrational relaxation within an anharmonic potential well. The observed vibrational modes are expected to involve Pt-Cl stretching motions, with frequencies that are strongly dependent on the local charge states of the Pt ions. It is also worth noting that both the 176 cm\(^{-1}\) frequency associated with the initially excited state and the 160 cm\(^{-1}\) frequency associated with the equilibrated STE are significantly lower than the 311.5 cm\(^{-1}\) frequency of the ground state symmetric stretch vibration, which primarily involves motion within a Cl-Pt\(^{4+}\)-Cl unit. The shifts in the excited state frequencies likely reflect, in part, the degree of delocalization of the excited state electronic wavefunction, and hence reduced charge on the Pt\(^{4+}\) ions. In the initially excited state (i.e. the final state of the intervalence charge transfer transition), the electronic wavefunction is expected to be
delocalized over a larger number of unit cells, while the ions, following the Franck-Condon principle, are initially in the positions associated with the Peierls-distorted ground state. The observed frequency shift can be understood in terms of the evolution of the system from a delocalized to a localized electronic state: the lattice distorts to form the stabilized STE structure and the electronic wavefunction becomes more localized, so that the Pt charge approaches a Pt$^{3+}$ state, as shown in the schematic STE structure in Figure 2.1, weakening the Pt-Cl force constant and reducing the local vibrational frequency.

In summary, these experiments report a new component of the structural relaxation associated with exciton self-trapping by observing the change in vibrational frequency upon relaxation to the final equilibrated self-trapped state, using a pump-pump-probe sequence that probes the resonant impulsive stimulated Raman response of the excited state.
6.4 - Pump-Pump-Probe Measurements in PtICN

In the experiments reported here, the vibrational properties of the STE are measured in its equilibrated structure in PtICN. The setup used is shown in Figure 6.6. An initial pump pulse, 45 fs in duration and centered at 800 nm, is used to excite the intervalence charge transfer transition. A second pump pulse, also 45 fs and 800 nm, impulsively excites the STE. A probe pulse, created through continuum generation from a split off portion of the 800 nm pulse, is used to measure the response of the equilibrated STE. The probe is wavelength resolved to enhance the oscillatory response.
Figure 6.6 – Schematic used for 2-pump experiments on PtICN. The delay between pumps 1 and 2 are set and the transmitted probe intensity is recorded as a function of probe delay time. Pumps 1 and 2 are chopped at different frequencies using a single chopper equipped with a dual-frequency wheel. The probe signal is measured with a photodiode and lock-in amplifier at the sum frequency. The probe is comes from a continuum generated by splitting off a portion of the 800 nm beam.
The pump-pump–probe response is shown in Figure 6.7 along with a nonlinear fit to a sum of exponentials and exponentially damped cosines, and the components from this fit are shown in Figure 6.8. In addition to oscillatory components at the ground state Raman frequencies of 132, 108, and 48 cm\(^{-1}\), the response shows an oscillatory component at 95 cm\(^{-1}\) that we assign to the equilibrated STE in PtICN. The 95 cm\(^{-1}\) frequency associated with the equilibrated STE in PtICN shows only a small \(\sim 2\) cm\(^{-1}\) shift downward from the 97 cm\(^{-1}\) frequency of the wavepacket oscillation that accompanies the initial formation of the STE (as seen in the single-pump-probe measurements on PtICN shown in Figure 5.2). The frequency of the 95 cm\(^{-1}\) component in the pump-pump-probe response was only able to be determined within a standard deviation of 1.5 cm\(^{-1}\), in part because PtICN has a strong Raman active component at 108 cm\(^{-1}\) which is close enough to 95 cm\(^{-1}\) that resolving the two components separately and accurately can be difficult, and in part due to the small, but finite variance between data sets. In order to determine this shift with a statistically significant accuracy, seven separate data runs were carried out, each on separate days given the several hours of data acquisition required for each run. In each experimental run, both single-pump-probe measurements and pump-pump-probe measurements were recorded. All runs were carried out under nominally the same conditions. The average frequencies were determined from nonlinear fitting analysis and the standard deviations of the frequencies were calculated, and the average frequency shifts were also determined.
Figure 6.7 - Time-resolved double-modulated differential transmittance of PtICN following double-pulse excitation to impulsively excite the equilibrated STE. Both pumps are ~45 fs FWHM with spectra centered at 800 nm. This data was taken at a probe detection wavelength of 940 nm. Data is in black and the solid red line represents a nonlinear fit to a sum of exponentially damped cosines and a decaying exponential.
Figure 6.8 – Individual damped oscillatory components reconstructed from the fit shown in the previous figure, including the frequency shifted component at 95 cm\(^{-1}\) (red), assigned to the equilibrated STE, and other components (gray) that do not reflect the dynamics of the equilibrated STE.
The resulting frequencies were 95 +/- 1.5 cm\(^{-1}\) for the equilibrated STE (pump-pump-probe) and 97 +/- 1.8 cm\(^{-1}\) for the initially excited state (single-pump-probe). Additionally, the average change in frequency was 2.0 +/- 1.5 cm\(^{-1}\) and in all 7 cases the frequency of the equilibrated STE was lower than that of the initially excited state. Thus, assuming Gaussian variability, the observation of a shift to lower frequency is valid with a 91% probability. Observation of a shift to lower frequency in the pump-pump-probe signal is consistent with evolution to a more localized charge distribution in the final equilibrated STE state, as discussed above for PtCl.

In summary, these experiments report a new component of the structural relaxation associated with exciton self-trapping in PtICN. The observation of a shift in frequency from the 97 cm\(^{-1}\) wavepacket oscillation associated with the initially generated exciton to the 95 cm\(^{-1}\) frequency of the final equilibrated STE indicates that further structural evolution takes place during the self-trapping process, beyond the initial vibrational wavepacket dynamics.
6.5 - References for Chapter 6


APPENDIX

CONSIDERATIONS IN NONLINEAR FITTING METHODS

A.1 - Linear Regression

Nonlinear regression begins with a set of experimentally measured pairs of data \((y_i, x_i)\) related by the equation \(f(x, A_1, A_2, ..., A_N)\) where \(y_i\) is the dependent variable (also called the response), \(x_i\) is the independent variable (also called the explanatory variable or regressor), and \(A_N\) are the unknown parameters. The goal in a least squares fit is to determine the values for the parameters that minimize the residual sum of squares

\[
S = \sum_{i=1}^{M} [f(x_i, A_1, A_2, ..., A_N) - y_i]^2
\]  

(A1)

summed over all \(M\) data points. The minimum can be found by setting the derivatives of \(S\) with respect to the parameters equal to zero and solving the resulting set of \(N\) equations

\[
\frac{\partial S}{\partial A_1} = 0, \quad \frac{\partial S}{\partial A_2} = 0, \quad \ldots, \quad \frac{\partial S}{\partial A_N} = 0
\]  

(A2)

which amounts to solving the “normal equations” for each \(A_i\)

\[
2 \sum_{i=1}^{M} [f_i - y_i] \frac{\partial f_i}{\partial A_i} = 0
\]  

(A3)

If the relationship between \(f(x_i, A_1, A_2, ..., A_N)\) and the parameters \(A_i\) are linear, that is if the functions can be written in the form

\[
f(x_i, A_1, A_2, ..., A_N) = \sum_{i=1}^{N} g_i(x_i) A_i
\]  

(A4)
(or equivalently, $df/\,dA_i$ is not a function of $A_i$) then Equations A3 has a closed form solution. It is a useful first step in non-linear regression theory to first consider the linear case since linear approximations are often made in nonlinear regression analysis.

Throughout regression theory, it is convenient to use matrix notation. Equation A4 can be written in matrix form as

$$Y = XA$$ (A5)

where the $g_i(x_i)$ are represented by the vector $X$. Then the normal equations may be written

$$(XA - Y)x = 0$$ (A6)

which can be solved for $A$ to give

$$\hat{A} = (X^TX)^{-1}X^TY$$ (A7)

where the accent on $\hat{A}$ is a notation used to denote the best fit value for $A$. This is the explicit solution to determining the parameters in a linear fit and can be calculated with some simple matrix multiplication. If the equation is not linear (such as when parameters appear in an exponent or a cosine function for example) then a closed form solution does not exist and iterative non-linear fitting methods are used to find the solutions to Equations A3.

In practice, there will be some error or noise $\varepsilon$ in the measurement of $Y$. Equation A5 may then be written

$$Y = XA + \varepsilon$$ (A8)

If the noise is truly random then the expectation is for the error to deviate from the data with an average value of 0 and some normally distributed standard deviation $\sigma$. In matrix notation
Variance[\epsilon] = E[\epsilon^T \epsilon] = \sigma^2 I \quad (A9)

Where \( I \) is the identity matrix and \( E[\epsilon^T \epsilon] \) denotes the expected value of \( \epsilon^T \epsilon \). Thus

\[ E[\epsilon] = 0 \quad (A10) \]

\[ E[Y] = XA \quad (A11) \]

And the probability distribution for \( Y \) will be

\[
P(Y) = \frac{1}{(2\pi\sigma^2)^N} \exp \left( -\frac{(Y -XA)^T(Y -XA)}{2\sigma^2} \right) \quad (A12)
\]

where \( N \) is the number of data points. Under these conditions the value \( \hat{A} \) that minimizes the residual sum of squares will vary depending on the noise. Thus, even though there is only one solution \( \hat{A} \) that minimizes the residual sum, if the experiment were run repeatedly, the random noise would result in many different solutions with some probability distribution.

According to Equation A6, \( Y \) is linear with \( \hat{A} \), and thus \( \hat{A} \) will also be normally distributed. The variance in \( \hat{A} \) will then be [1]

\[
\text{Variance}[\hat{A}] = \sigma^2 (X^T X)^{-1} \quad (A13)
\]

Or more generally speaking

\[
\text{Variance}[\hat{A}] = \sigma^2 (G^T G)^{-1} \quad (A14)
\]

where \( G \) is the gradient vector with components

\[ G_j = \frac{\partial f}{\partial A_j} \quad (A15) \]
Equation A14 is generally referred to as the “standard error” in both linear and non-linear fitting and is used as a means to determine the accuracy of a fit. Even though Equation A14 applies only to linear equations, it can still be used to calculate the error in nonlinear equations if they can be approximated by a first order Taylor expansion near the solution. Thus the assumptions that go into linear regression also apply to nonlinear regression. Those assumptions are:

1. The fitting function predicts the expected relationship between \( y_i \) and \( x_i \).
2. The noise is independent of \( y_i \) and \( x_i \), and is expected to be normally distributed with zero mean.

A.2 - Methods of Non-Linear Fitting

Many methods for non-linear fitting exist with various benefits and downfalls to each. The methods discussed here are the method of steepest descent, Gauss-Newton, Levenberg-Marquardt, and the simplex method.

Generally speaking, all of these methods involve iteratively changing the parameters \( \mathbf{A}_n \) until the sum of squares is minimized. A single iteration can be described as a small change \( \Delta_n \) in the parameters \( \mathbf{A}_n \) that decreases the sum of squares. In matrix notation this is

\[
\mathbf{A}_{n+1} = \mathbf{A}_n - \Delta_n 
\]  

(A16)

And the problem becomes determining the step \( \Delta_n \) to use that will converge on the parameter values quickly and minimize the sum of squares.

The method of steepest descent iterates the parameters

\[
\mathbf{A}_{n+1} = \mathbf{A}_n - \rho \mathbf{G}_n 
\]  

(A17)

Where \( \mathbf{G}_n \) is the gradient vector of the residual sum of squares with components
and $\rho$ is calculated at each iteration to minimize the sum of squares $S(A)$. The details behind determining the value for $\rho$ that minimize $S$ is called an “exact line search” and is explained in [1] pg. 597.

The method of steepest descent has the downfall that the direction of steepest descent depends on the scaling of the parameters. In other words, if $S(A_n)$ is replaced with $S(kA_n)$, where $k$ is some constant, then the direction of steepest descent will change (this is not the case for other methods). This can cause the algorithm to zig-zag along the residual surface (called hemstitching) and in turn cause the convergence to take longer than necessary. However, the method of steepest descent has the strength that it works well far from the minimum and rarely converges in local minima.

The Gauss-Newton method is an extension of Newton’s method which is a general method of finding the roots of an equation through iteration. For example, a function $f(x)$ may be Taylor expanded to first order about the point $x_0$ to give

$$f(x) = f(x_0) + f'(x_0)(x - x_0)$$

(A19)

One can set $f(x) = 0$ and solve to get

$$x = x_0 - \frac{f(x_0)}{f'(x_0)}$$

(A20)

Which gives the linearly approximated value of $x$ for which $f(x) \approx 0$. If the value obtained here does not result in a value for $f(x)$ that is close enough to 0 then the process can be repeated iteratively until it converges on the correct value of $x$. In the context of nonlinear regression, one wishes to find the places where $S'(A) = 0$ and the analogue of Equation A20 is
Using A21 iteratively will converge at the point \( A \) where \( S'(A) = 0 \). In other words, Equation A21 is an iterative method for finding extrema in the function \( S(A) \). In matrix notation, Equation A21 may be written

\[
A_{n+1} = A_n - \frac{S'(A_n)}{S''(A_n)}
\]  

(A21)

Where \( G_n \) is the gradient matrix defined in Equation A18 and \( H_n \) is the Hessian matrix with components

\[
H_{jk} = \frac{\partial^2 S}{\partial A_j \partial A_k}
\]  

(A23)

This method uses the tangent plane of a spot on the surface of Figure A1 as a pointer for the direction of descent. Essentially, this means the method will start at the point decided by the starting parameters and “slide” down the surface of the bowl shown in Figure A.1 until a minimum is reached. If the starting point is far enough away from the minimum, or near some other local extremum, then the method can either diverge or give a wrong solution. Equation A21 approximates \( S(A) \) as linear near \( A_n \) which amounts to approximating the surface in Figure A.1 as an ellipsoid bowl. It then moves to the minimum of this predicted bowl. If the actual shape of the surface deviates too far from the linearly approximated symmetric bowl shape (more specifically the bowl predicted by the tangent plane of the starting parameters) then problems with convergence can occur. However, the residual squares for most equations are well approximated by an ellipsoid crater near the minimum so the Gauss Newton method works well here.
Figure A.1 – Simple representation of a residual sum surface for a two parameter model. $S$ is the residual sum of squares and $A_1$ and $A_2$ are the parameters to be fit. For any fit $(A_1, A_2)$ there is one point $S$ in the curve. For a linear model this always takes on a symmetric bowl shape with no local minima. Nonlinear equations may have many local minima but a good model will have one absolute minima that can be approximated as linear near the trough. Least squares regression techniques seek to find the minimum at the bottom of the bowl.
The method of steepest descent works well when the starting parameters are far from the solution while the Gauss-Newton method becomes more advantageous near the minimum. The Levenberg-Marquardt method exploits the strengths of these by using the method of steepest descent until little improvement is being made, then switching over to Gauss-Newton. The Levenberg-Marquardt method may be viewed as a combination of the method of steepest descent and Gauss-Newton that exploits the strengths of each. The algorithm basically uses the sum $\Delta_n$ of the steps from the two methods to give

$$A_{n+1} = A_n - (H_n^{-1} + \rho I)G_n$$

(A24)

So a summary of the three methods is

$$A_{n+1} = A_n - \Delta_n$$

(A25)

$$\Delta_n = \rho G_n$$  Steepest Descent

$$\Delta_n = H_n^{-1}G_n$$  Gauss – Newton

$$\Delta_n = (H_n^{-1} + \rho I)G_n$$  Levenberg – Marquardt

The simplex method (for non-linear regression as opposed to the very different linear method) is a useful technique that stands out from the others in that it does not involve calculating derivatives. It begins with $P+1$ sets of starting parameters, where $P$ is the number of parameters. It then orders the sums of squares

$$S_1 \leq S_2 \leq \ldots \leq S_{P+1}$$

(A26)

And rejects the worst set of parameters $A_{P+1}$. A new set of parameters is calculated by redirecting the vector $A_{P+1}$ toward the centroid $C$ of the remaining of vectors
\[ C = \frac{1}{P} \sum_{n=1}^{P} A_n \]  

(A27)

By implementing the equation

\[ A_{new} = C + \eta(C - A_{p+1}) \]  

(A28)

Where \( \eta \) is a constant that is adjusted until

\[ S_{new} \leq S_p \]  

(A29)

A detailed outline with the specific steps involved in adjusting \( \eta \) is given in [1]. To summarize, \( \eta \) is increased if an iteration gives a better fit then the other P sets of parameters, decreased if it gives a fit that is still worse than the other P sets, and accepted if the fit lands in the middle somewhere. Each iteration rotates the vector \( A_{p+1} \) toward the centroid of the other parameter vectors. The algorithm iterates between creating a new set and rejecting the worst set until it converges on a solution. For the 2 parameter example shown in Figure A1 the algorithm would start with 3 points on the bowl that form a triangle. As it iterates, the area of the triangle gets smaller and closer to the center until it eventually converges at one point on the bottom. The simplex method does not require the calculation of derivatives which makes it much quicker than the other methods and allows one to fit discontinuous functions. It is also much less likely to converge in a local minimum than any other method. The drawback is that, since it does not calculate derivatives, it cannot calculate statistical errors in the parameter solutions.

Results from the Levenberg-Marquardt method were used in all of the nonlinear fits presented in this dissertation. However, the simplex method was often used first because it was less likely to run off into some unwanted region of parameter space and it tended to converge quicker when the starting
parameters were far from the minimum. Convergence was also tested by iterating several times between L-M and simplex to ensure they both gave essentially the same results.

A.3 - Transforming to Linearity

Some nonlinear equations may be transformed or re-parameterized so that they are linear. For example consider a function that fits an exponential decay

$$y = A_1 e^{-A_2 x}$$  \hspace{1cm} (A30)

If there is some noise in the measurement that increases linearly with \( y \) then we can write

$$y = A_1 e^{-A_2 x} + \varepsilon A_1 e^{-A_2 x}$$  \hspace{1cm} (A31)

which can be rewritten

$$y' \approx A_1' + A_2 x + \varepsilon$$  \hspace{1cm} (A32)

where \( A_1' = e^{A_1} \) and \( y' = \ln (y) \) and the approximation is that \(|\varepsilon| \ll 1\). Not only has this achieved the goal in making the equation linear. Now the error is also linear and will contribute evenly to the sum of squares throughout the data, whereas the amplitude of the error term in Equation A31 is higher at lower \( x \) and will cause the fit to weight the errors disproportionately. However, if the noise varies independent of \( y \) then

$$y = A_1 e^{-A_2 x} + \varepsilon$$  \hspace{1cm} (A33)

and

$$y' \approx A_1' + A_2 x - \varepsilon'$$  \hspace{1cm} (A34)
where $\epsilon' = \epsilon A_1 e^{A_2 x}$. The error in the re-parameterized equation now grows with increasing $x$ and errors or noise in data points at greater $x$ will contribute disproportionately to the residual sum of squares.

Thus one can see that the reasons for transforming an equation are not limited to making it linear in its parameters. It can also be used to adjust for non-constant variances in the error. Blindly fitting a re-parameterized equation can result in poor fits if attention is not paid to the behavior of the errors. However, if the nature of the error is understood, the problem can be solved by appropriately weighting the fit.

A.4 - Weighting

Simply minimizing the sum of squares is not always the best approach. If the error does not have a consistent standard deviation that is independent of $x_i$ and $y_i$ then it may be necessary to weight the fit. An error that increases with $y_i$, as in Equation A31, is a good example. As $x_i$ decreases, the average deviation about $y_i$ will be a larger number and contribute more to the residual sum in Equation A1. The result will tend to fit better for small values of $x_i$ at the expense of a poorer fit for large values. Likewise, if a data set does not have a constant point density (i.e. $\Delta x = x_{i+1} - x_i$ changes) then the regions of data with higher point density (lower $\Delta x$) will contribute more to the sum and the fit will favor this region, resulting in a better fit at high point density at the expense of a poorer fit at low point density. This issue may be solved by interpolating additional data points in the low density region, removing data points in the high density region, or weighting the data points by an appropriate factor.

Weighting data is done by altering the magnitude of the sum of squares by some weighting factor $W_i$ so that Equation A1 becomes
\[ S = \sum_{i=1}^{M} W_i [f(x_i, A_1, A_2, ..., A_N) - y_i]^2 \]  \hspace{1cm} (A35)

For example, a data set with an inconsistent point spacing could then be weighted by the point density such that \( W_i = 1/\Delta x_i \).

**A.5 - ANOVA**

Once the parameters have been determined it is usually necessary to calculate how well the fit worked. There are many different calculations used to assess how well a fit worked. For reference to equations that follow:

\[ \bar{y} = \frac{1}{N} \sum_{i=1}^{N} y_i = \text{average value of measured data} \]

\[ f_i = f(x_i, A_1, A_2, ..., A_p) = \text{value of fitting function at point } x_i \text{ or the "predicted" value of } y_i \]

\( N = \text{number of data points} \)

\( P = \text{number of data parameters in the fitting equation} \)

ANOVA (Analysis of Variance) tables are often constructed in regression analysis. It is a set of statistics based on the various sums of squares. The following statistics will be found in an ANOVA table:

\[ SS_{TOTAL} = \sum_{i=1}^{N} [y_i - \bar{y}]^2 \]  \hspace{1cm} (A36)

\[ SS_{REGRESSION} = \sum_{i=1}^{N} [f_i - \bar{y}]^2 \]  \hspace{1cm} (A37)

\[ SS_{ERROR} \text{ or } SS_{RESIDUAL} = \sum_{i=1}^{N} [f_i - y_i]^2 \]  \hspace{1cm} (A38)
where SS stands for “Sum of Squares.” These terms are additive:

\[ SS_{TOTAL} = SS_{REGRESSION} + SS_{RESIDUAL} \]  

This is somewhat if a statement of conservation. The total sum of squares is the sum of the deviations from the average (i.e. the natural shape or form of the fitting function as predicted by the model) plus the deviations from the fitting function (deviations that cannot be explained by the model).

\( SS_{REGRESSION} \) is the contribution to the physical model or fitting function. \( SS_{RESIDUAL} \) is the portion of the data that cannot be explained by the model. This is shown schematically in Figure A2. For a perfect fit, any deviation from a flat line would be purely explained by the model and the residual sum would be zero. For a realistic but good fit, \( SS_{RESIDUAL} \) is represented purely by noise and looks like random, Gaussian fluctuations about the average. In a poor fit, \( SS_{RESIDUAL} \) is large and a plot of \( SS_{RESIDUAL}(x_i) \) will show obvious signs of non-random deviations from zero.
Figure A.2 – Example of a nonlinear fit to an exponential model. The blue arrows indicate the deviations that contribute to the residual sum of squares, which in this case is random Gaussian noise. The red arrows indicate the deviations that contribute to the regression sum of squares which is a result of the model being exponential.
The additive nature of these two terms suggests that a useful way to assess goodness of fit is to look at the ratio of the residual to the total sums of squares. The $R^2$ value or Coefficient of Determination (COD) is the fraction of the fit that contributes to the model.

$$R^2 = \frac{SS_{\text{REGRESSION}}}{SS_{\text{TOTAL}}} = 1 - \frac{SS_{\text{RESIDUAL}}}{SS_{\text{TOTAL}}}$$  (A40)

It is a measure of the goodness of fit. An $R^2$ of 1 indicates a perfect fit. It is useful for comparing various fit results where the same fitting function was used. However, $R^2$ will increase as more parameters are added to the fitting function even if the extra parameters do not strengthen the model. Thus, it is not reasonable to compare values of $R^2$ for different fitting functions. The adjusted $R^2$ uses the degrees of freedom to account for a change in the number of data points or parameters. It can go up or down depending on whether the addition of a new parameter strengthens the fitting function.

$$\text{adjusted } R^2 = 1 - \frac{SS_{\text{RESIDUAL}}/(N - P)}{SS_{\text{TOTAL}}/(N - 1)}$$  (A41)

In the above equation, the contribution from the residual sum of squares (numerator) is increased as $P$ increases, offsetting the increase in $SS_{\text{RESIDUAL}}$ that can occur with the addition of a parameter that does not strengthen the model.

The mean squares are the averages of the square roots of the sums of squares are obtained by dividing each by its corresponding degrees of freedom.

$$\text{Mean Square of Residual Sum of Squares} = \sqrt{\frac{SS_{\text{RESIDUAL}}}{N - P}}$$  (A42)

$$\text{Mean Square of Regression Sum of Squares} = \sqrt{\frac{SS_{\text{REGRESSION}}}{N - 1}}$$  (A43)
Corrected Total Sum of Squares \[ \frac{SS_{TOTAL}}{N - 1} \]  \quad (A44)

Uncorrected Total Sum of Squares \[ \sum_{i=1}^{N} y_i^2 \]  \quad (A45)

The F-value is the ratio of the two mean squares.

\[
F \text{ value} = \frac{\text{Mean Square of Regression Sum of Squares}}{\text{Mean Square of Residual Sum of Squares}} = \sqrt{\frac{SS_{RESIDUAL}/(N - P)}{SS_{TOTAL}/(N - 1)}} \quad (A46)
\]

For random noise, the ratio of the residual and regression mean squares has an F-distribution which allows the \( p \)-value to be calculated. A formula is not very insightful in this case, suffice to say that the \( p \)-value is the probability of obtaining the calculated F-value or greater by random chance (i.e. the probability of obtaining an F-value at least this large for a model that is incorrect). Typically one decides to reject the null hypothesis (the null hypothesis is that the model is incorrect) if \( p > 0.05 \) or \( p > 0.01 \) depending on whether a 5% or 1% confidence interval is adopted. A \( p \)-value of 0.01 means there is a 1% chance that the agreement of the model is wrong and that the apparent agreement is a result of random chance.

**A.6 - Error Analysis**

Estimated errors are calculated for the parameter values obtained from the fit. They can be thought of as standard deviations though they only fit this description exactly in ideal circumstances. Standard errors for parameters are calculated using the covariance matrix. Covariance is the measure of how independent two parameters are. Generally speaking, the covariance between A and B is

\[
COV(A, B) = \frac{1}{M} \sum_{i=1}^{M} (A_i - \bar{A}) (B_i - \bar{B}) \]  \quad (A47)
If A and B are not correlated, the covariance is zero. If an increase in A tends to correspond to an increase in B then \( COV(A, B) > 0 \) and if a decrease in A tends to correspond to a decrease in B then \( COV(A, B) < 0 \) [6]. The covariance matrix is sometimes standardized (normalized by the standard deviations) and expressed in terms of the correlation coefficient

\[
COR(A, B) = \frac{COV(A, B)}{\sigma_A \sigma_B}
\] (A48)

Such that a maximum correlation yields a correlation coefficient of \( \pm 1 \). For the special case where both terms are the same \( COV(A, A) = \sigma_A^2 \) where \( \sigma_A \) is the standard deviation and \( \sigma_A^2 \) is the variance.

A problem arises because explicitly evaluating Equation A47 would require repeating the experiment M times and doing a nonlinear fit to each of the M data sets. Then the average value for each parameter would give the solution and the standard error would be the standard deviation of the M solutions. In order to calculate errors in a single fit, the matrix F is used

\[
F_{ij} = \frac{1}{\sigma_i^2} \frac{\partial f(x_i, A_1, A_2, ..., A_N)}{\partial A_j}
\] (A49)

where \( \sigma_i \) is the standard deviation such that \( \sigma_i^2 = [|y_i - \bar{y}]^2 \), \( i \) is the data point index, and \( j \) is the parameter index. Then the covariance matrix \( C \) is calculated

\[
C = \frac{SS_{RESIDUAL}}{N - P} (F^T F)^{-1}
\] (A50)

and finally, the error in the parameter \( A_j \) is the square root of the appropriate diagonal component of the covariance matrix \( C \).

\[
\Delta A_j = \sqrt{C_{jj}}
\] (A51)
Note that $\Delta A_j$ converges to the standard deviation of the parameter if the fitting equation is linear, the noise is Gaussian, and the parameters are completely independent (no covariance). In other words, for an ideal system, one can state that there is a 68.3% chance that the “true” value is $A_j \pm \Delta A_j$.

The standard errors reported in a nonlinear fit are calculated using a first order Taylor expansion approximation

$$f(A) \approx f(\hat{A}) + J(\hat{A})(A - \hat{A})$$  \hspace{1cm} (A52)

where $\hat{A}$ is the best fit value of $A$ and $J(\hat{A})$ is the Jacobian with components

$$J_{jk} = \frac{\partial f_j}{\partial A_k}$$  \hspace{1cm} (A53)

From Equation A51 it can be shown that the following statement is true: If $f(A)$ has noise with zero average, a normal distribution, and standard deviation $\sigma^2$ then the parameters obtained through reduction of the sum of squares will have a normal distribution with average $\hat{A}$ and standard deviation $\sigma^2(J^TJ)^{-1}$ ([1], pg. 24). Thus, the error in the parameters is calculated assuming convergence to anything other than their true value is the result of a normal noise distribution, and that function can be approximated by a first order Taylor approximation in the vicinity of $\hat{A}$.

The “dependency” of each parameter is also often calculated. This quantifies how a change in one parameter effects the best fit value for the other parameters. The dependency ranges from 0 to 1 with 0 indicating complete independence and 1 indicating redundancy. If a parameter value is changed from the value obtained at the minimum sum of squares, the residual sum of squares will increase. For completely orthogonal parameters the corresponding change in the value of another parameter cannot decrease the sum of squares. For completely redundant parameters, a change one variable can be offset
with a change in the redundant variable and exactly reproduce the solution. The dependency is calculated from the covariance matrix

$$\text{Dependency of Parameter } j = 1 - \frac{1}{C_{jj}(C_{jj})^{-1}}$$  \hspace{1cm} (A54)

For most nonlinear fitting equations, the covariance matrix gives errors that are very close to standard deviations. Alper [3] evaluated the “true” standard deviation of parameters obtained through L-M non-linear fits using Monte Carlo methods and compared these errors to the ones calculated with the covariance matrix. In one model there was general agreement (10% difference) between errors at the 68.3% confidence level but the errors calculated from the covariance matrix were 50% larger at the 90% level. They applied this difference to the noise not being Gaussian in the tails of the distribution. Another model gave covariance errors 2-3 times larger than the “true” errors do to significant covariance between parameters. In all of these examples, the covariance error overestimates the “true” error, though it is noted that this is not always the case.

The statistics that estimate the standard errors in the parameters cannot be unconditionally trusted to represent a 68.3% confidence interval. The main reasons for bad reports of the standard errors are:

- The equation may be a poor model. It must be assumed that the deviation of the data from the fit represents normally distributed noise in order to propagate the error in the measurement to the error in the true parameter. The idea is that if there were no noise, the fitting function would perfectly describe the response.

- Even if the functional form is correct the equation may be overparameterized. There is no hard line, however, if the dependency of any parameters are > 0.999 then that parameter likely needs to be either removed, constrained or re-parameterized.
• Misrepresentation of the errors may be intrinsic to the fitting equation. The methods used in non-linear fitting approximate the equation as locally linear i.e. as well represented by a first order Taylor expansion. If this approximation is poor then the reported errors will likely be poor as well. The best way to check this is to do Monte Carlo simulations with the function in question and compare the standard deviations in the fitted parameters to the standard errors obtained with the covariance matrix.

• The fit may be poor. It is often assumed when deriving error relationships in nonlinear fitting that \( f(A_{fit}) \approx f(A_{true}) \) i.e. that the function evaluated with the parameter values obtained from the fit is a good approximation of the “true” function which perfectly describes the physical nature of the data.

On the other hand, if analysis indicates a good fit and locally linear approximations hold then it is likely that the standard errors given are good approximations to a 68.3% confidence interval.
A.7 - References from Appendix


