SEARCHING FOR SPIN CROSSOVER IN Fe(bpy)$_3$(PF$_6$)$_2$ USING FEMTOSECOND ELECTRON DIFFRACTION AND ULTRAFAST TRANSIENT ABSORPTION

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
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Abstract

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2014

Femtosecond electron diffraction experiments were performed on solid state iron(II) tris(2,2'-bpyridine) bis(hexafluorophosphate). The cation is known to undergo a spin crossover process when solvated in water and irradiated with 400 nm coherent light which results in a transition from a low spin to high spin state within a picosecond which is accompanied by a uniform 0.2 Å Fe-N bond elongation. A femtosecond diffraction experiment was performed on the solid sample and was unable to find evidence of a fast spin crossover transition. Suspecting this may be due to limitations of the apparatus, an ultrafast transient absorption experiment was performed. Emulating the liquid study by Gawelda et al, the pump probe experiment found evidence of spin crossover in the solid state sample. This result awaits verification by an improved transient absorption apparatus and has inspired efforts to perform an improved femtosecond electron diffraction experiment.
## Contents

1 Introduction .............................................. 1  
   1.1 Diffraction ........................................... 1  
       1.1.1 Diffraction and its uses ......................... 1  
       1.1.2 Femtosecond Electron Diffraction ............... 2  
   1.2 Ultrafast Transient Absorption ....................... 3  
   1.3 Transition Metals ................................ 4  
       1.3.1 Spin Crossover in Transition Metal Complexes  4  
       1.3.2 Iron(II) tris(2,2'-bipyridine) bis(hexafluorophosphate) 4

2 Experimental Methods ................................. 8  
   2.1 Materials ........................................... 8  
   2.2 Femtosecond Electron Diffraction .................... 8  
       2.2.1 The Laser ...................................... 8  
       2.2.2 The Electron Gun ................................ 9  
       2.2.3 The Sample Chamber ............................ 10  
       2.2.4 Calibration of spatial overlap and time zero ......... 11  
   2.3 Ultrafast Transient Absorption Apparatus ........... 12

3 Results .................................................. 14  
   3.1 Electron Diffraction .................................. 14  
   3.2 Ultrafast Transient Absorption ....................... 15

4 Discussion .............................................. 21  
   4.1 Dissemination of the Diffraction Experiment ........... 21  
   4.2 Ultrafast Transient Absorption of solid state PolyPy .... 22

5 Conclusion ............................................. 26

Bibliography ............................................. 27
List of Figures

1.1 Structure of the Fe(bpy)$_3$(PF$_6$)$_2$ complex. Hydrogen atoms are not shown. ........................................ 5
1.2 The black line is the linear absorption spectrum of the PolyPy cation. Reprinted with permission from [20]. Copyright 2007. American Chemical Society. .................................................. 6
1.3 Transient absorption spectrum of the aqueous PolyPy cation over 20 ps using a 400 nm excitation. Colour scale uses purple for a strong decrease in differential absorption to red for no change. Reprinted with permission from [20]. Copyright 2007. American Chemical Society. .......................................................... 7
1.4 Cross sections of the pump probe spectrum shown in Figure 1.3. Reprinted with permission from [20]. Copyright 2007. American Chemical Society. ................................................. 7

2.1 A simplified diagram of the femtosecond electron diffraction setup ........................................... 9
2.2 The electron gun. ................................................................................................................................. 10

3.1 Diffraction pattern of PolyPy at -25 degrees rotation. ................................................................. 16
3.2 Diffraction pattern of PolyPy at 4 degrees rotation. ................................................................. 17
3.3 Pump beam profile in the transient absorption measurement. ....................................................... 18
3.4 Linear absorption of the PolyPy crystal. ......................................................................................... 19
3.5 Transient absorption data of PolyPy over 2 ps with 10 fs time steps. ........................................... 19
3.6 Transient absorption data of PolyPy over 20 ps with 50 fs time steps. ....................................... 20
3.7 Transient absorption data of PolyPy taken over 900 ps with 2 ps time steps. ......................... 20

4.1 Time trace of the data of the data from Figure 3.5 along with the spectrum from the substrate. ................................................................. 25
Chapter 1

Introduction

1.1 Diffraction

1.1.1 Diffraction and its uses

The diffraction method is widely used to obtain structural information on materials [1]. It relies heavily on the wavelike properties of particles and their interaction with the material being studied. A typical diffraction experiment fires a beam of particles at the material and has a detector which measures the intensity of particles which deflect away from the main beam. The beam splits in a well defined pattern which is dependent on the sample being studied. The location, intensity and size of these splits, the diffraction pattern, is the data being sought by one performing a diffraction experiment.

One has the choice of several different particles for use in a diffraction study. The most common choices are electrons, neutrons and X-rays [2]. The properties of each allow them to excel in different situations. One of the most important properties to consider in a diffraction experiment is the particle wavelength. The wavelength determines the divergence of the diffracted beams. This can be seen most easily with Bragg’s Law

\[ n\lambda = 2dsin\theta \]

where \( \lambda \) is the wavelength of the diffracting particle, \( d \) is a characteristic distance of the material, \( \theta \) is the angle of the diffracted beam, and \( n \) an integer giving the order of the diffracted beam. For a given material, the angle of the first order diffraction is determined by the wavelength of the diffracting particles. One desires a wavelength which is within a few orders of magnitude of the material’s \( d \) parameter so that the diffraction angle is not so large that it cannot be found or so small the diffracted beams are indistinguishable from the incident beam for a given apparatus size. Of the previously mentioned particles, electrons are the ones used in the diffraction experiments described in this thesis.

A diffraction pattern shows how the electron beam interacts with the sample. A beam with a high number of electrons can provide a more complete diffraction pattern which will contain additional structural information. Powerful beams provide enough information to allow \textit{ab initio} reconstruction of the crystal structure of the sample [1]. Diffraction patterns are not always of a high enough quality to allow of \textit{ab initio} reconstruction but other useful information can be extracted. Chief among those is the detection of changes.

Every material has its own characteristic diffraction pattern. With a diffraction pattern of a high
enough quality, the structure of the material can be extracted. This has a useful corollary: different structures give different diffraction patterns even if they are taken from a material of the same chemical composition. Structural changes of a material manifest themselves within a diffraction pattern through changes of the diffraction spots. A spot in the diffraction pattern can strengthen, weaken, move, change shape or completely disappear and new diffraction spots can arise when a structural change occurs in the material. The phenomena that can be detected in this way are numerous [3]. In this thesis, the movement of atoms upon excitation from the ground state is tracked. This is done using femtosecond electron diffraction.

1.1.2 Femtosecond Electron Diffraction

Femtosecond electron diffraction differentiates itself from typical electron diffraction experiments through the use of temporally short electron pulses which are less than a picosecond in duration. These short pulses enable the collection of diffraction images with fine time resolution. This is because when individual electrons pass through a sample they will deflect based on the positions of atoms within a material at their time they pass through. That is to say, a infinitely short electron beam would yield a diffraction pattern providing the instantaneous structure of the material. Any real electron beam will provide a diffraction pattern that can be thought of as an average of the material’s structure over the pulse duration. Femtosecond electron diffraction experiments have beam durations that are on the same order as nuclear motion.

Commercial diffraction instruments which yield data from which ab initio reconstruction can be performed have electron beams of long duration. They produce electron beams which form a single continuous wave. These beams with very long durations allow for a large number of particles to be generated and for ambient molecular motions to be averaged out so that the extracted atomic positions are their time averaged positions. When mapping the trajectories of atoms over the duration of a chemical reaction, one does not desire averages. An electron beam which is as short as possible and contains as many electrons as is feasible is desired though these are often conflicting parameters.

Electrons repel one another. The repulsion becomes stronger the closer they are to each other [4]. This leads to difficulties when trying to create dense beams but they are predictable and manageable. Studies show that the length and diameter of the electron beam will slowly grow after being generated but spatial correlations remain [5]. That means electrons near the centre of the beam will remain near the centre of the beam and electrons at the front of the beam will remain there during the expansion. The expansion results in an electron beam which is perfectly usable in femtosecond electron diffraction experiments and the expansion effect can be reduced by minimizing the distance between the electron source and the sample being studied, among other things [6]. Additionally, conservation of spatial correlation can be exploited in femtosecond electron diffraction apparatus.

Electrons can be manipulated by electric fields. A streak camera is a device which uses an electric field to deflect an electron beam. As time passes, the field increases in strength which has the effect of deflecting the beginning of the electron beam at a different angle than the tail. If a streak camera is placed behind the sample within a diffraction apparatus, it will change the diffraction pattern by turning the diffraction peaks into streaks. The streak carries the same spatial correlation as the electron beam and can be used to monitor changes in the sample during the duration of the electron pulse. That is, it allows for the potential of obtaining time resolution smaller than the electron beam duration. A potential pitfall of this approach is the streaked diffraction peaks may overlap with other peaks. When
the streaked diffraction pattern is compared to the unstreaked pattern it becomes clear when this is an issue.

1.2 Ultrafast Transient Absorption

Femtosecond electron diffraction can provide structural information for a dynamic process. Another technique which can be used to obtain time resolved data is ultrafast transient absorption spectroscopy. Much like femtosecond electron diffraction, transient-absorption utilizes a pump probe technique. A laser is used to excite the target and another is used to measure the absorption of the target at a tunable time. This technique can be used to measure the time evolution of the excited state population of a sample. When implemented using a femtosecond laser, it has the ability to monitor systems on the same time scale as nuclear motion [7].

The second laser pulse measures the differential absorption of the sample. This is done by repeating the experiment multiple times. The second laser is a broadband white light pulse which passes through the sample and subsequently hits a spectrometer which measures the wavelength distribution of the beam. This gives the baseline absorption of the sample. Another white light pulse is sent through the sample, but this one is proceeded by a pump pulse which may cause a change in the sample. If the probe pulse causes a significant change in the sample, the white light spectrum will be different. The difference in absorption between the pump on and off trials gives the differential absorption spectrum.

There are a few different processes that can result in a change in absorption of the sample. The sole contributor to the pump off absorption signal is the absorption of the ground state. After the pump pulse excites a large number of molecules, there are fewer molecules left in the ground state. This leads to a negative differential absorption signal corresponding with the absorption of the ground state. This is often referred to as the ground state bleach. There is also a signal associated with stimulated emission. The pump pulse drives the system to an excited state. So long the molecules remain in an excited state, they are susceptible to stimulated emission. The white light pulse can cause excited state molecules to drop to a lower energy level while emitting a photon resonant with the transition. This increases the number of photons in the outgoing light pulse which will increase the signal detected by the resonant wavelengths. There is also excited state absorption. When the excited state is populated it will absorb light to become further excited resulting in a change in the differential absorption spectrum.

This technique allows the electronic evolution of the sample to be tracked after the excitation by monitoring the absorption of the sample over time [8].

The "ultrafast" in ultrafast transient absorption describes the time resolution these measurements can achieve which is a product of the short laser pulse duration. A short pulse duration ensures the laser and sample interaction time is kept short. As is true with femtosecond electron diffraction, short pulses in ultrafast transient absorption experiments minimizes the detector integration time and allows short snapshots of the system to be studied rather than a long time average. The femtosecond lasers used for the pump and probe pulses have a duration of approximately 50 femtoseconds which is shorter than the electron pulses found in a typical femtosecond electron diffraction experiment.

Together with femtosecond electron diffraction, ultrafast transient absorption provides a wealth of information regarding the dynamics of photoexcited systems.
1.3 Transition Metals

1.3.1 Spin Crossover in Transition Metal Complexes

Spin crossover is a phenomenon which occurs in many transition metal complexes [9]. It involves a reversible electronic transition from a low to high spin state [10]. This transition needs to be induced in a straightforward manner such as a change in temperature or through photoexcitation. These compounds have found themselves the subject of extensive research by many research groups due to their potential applications in areas such as spintronics [11]. That is because a single spin crossover complex has the potential to act as a bit in a classical computer which could enable high density information storage in components such as hard drives. Information which could lead to the discovery or design of a completely stable spin crossover compound which only changes state when it is probed is the reason of such interest. Additionally, spin crossover complexes are found in nature. The active site of heme proteins is an iron atom which undergoes spin crossover when the protein is bound by an oxygen molecule, as is the case with hemoglobin [12]. Further understanding of spin crossover will aid in the understanding of these important processes.

The spin crossover phenomena can be aptly described by ligand field theory [13]. It originates from the splitting of the d orbitals of a transition metal complex. The d orbital of an atom is quintuply degenerate. For an octahedral complex, the s and p orbitals of the ligands mix with the d orbitals in such a way that the quintuple degeneracy is broken and split into doubly and triply degenerate states. These two states are typically the HOMO and LUMO of the complex. The low spin state is the ground state of the molecule and the high spin state is an excited state where the spins of the unpaired electrons in the HOMO and LUMO are aligned.

To detect whether a material is predominantly in the low or high spin state researchers have devised several methods. Materials for which a phase change can be induced by varying the temperature or pressure of the material provide the simplest method. For these compounds, the magnetization of the material can be measured using a magnetometer or similar device [14]. Spin crossover compounds which do not undergo an easily induced phase change must utilize other methods. A paper published by McCusker et al in 2006 [15] found that the ultrafast excitation of a Fe$^{2+}$ spin crossover compound was accompanied by a uniform Fe-ligand bond length increase of approximately 0.2 Å. This bond elongation has been found to be a common feature in iron spin crossover compounds [16]. If one was to perform a femtosecond electron diffraction experiment on such a compound, one would expect a significant change in the diffraction pattern following photoexcitation to the high spin state.

1.3.2 Iron(II) tris(2,2’-bipyridine) bis(hexafluorophosphate)

In this thesis, solid state iron(II) tris(2,2’-bipyridine) bis(hexafluorophosphate), Fe(bpy)$_3$(PF$_6$)$_2$, is studied using both femtosecond electron diffraction and ultrafast transient absorption spectroscopy. This compound will be referred to as PolyPy for the remainder of this thesis. The structure of PolyPy can be seen in Figure 1.1. This image was produced by using the crystal structure of PolyPy resolved by Dick et al [17]. The cation of PolyPy, [Fe(bpy)$_3$]$^{2+}$, is composed of a iron atom coordinated to the nitrogen atoms of three bidentate bipyridine ligands in an approximately octahedral arrangement. The cation has been studied extensively by other research groups [18] [19].

A study by Dr. Gawelda et al found the PolyPy cation undergoes spin crossover upon photoexcitation...
by 400 nm light [20]. The low spin $^1A_1$ ground state and $^5T_2$ high spin state are analogous to the states described by ligand field theory for an octahedral Fe$^{2+}$ atom where the high spin state involves the excitation of two electrons from the LUMO. The energy difference between these states is large so there are no phase transitions from the low spin to high spin states. It’s important to note that a photoexcitation from a singlet to a quintet state is optically forbidden. This transition proceeds indirectly through a method I shall summarize from the Gawelda study.

An aqueous cation in the ground state absorbs a single photon with a wavelength of 400 nm to transition to a singlet metal to ligand charge transfer state ($^1$MLCT). The singlet MLCT state is part of a band of states in which charge has been transferred from the iron atom out the the bipyridine ligands. From here, the cation begins a non-radiative decay to the high spin state. In less than 20 fs, the $^1$MLCT state decays to a $^3$MLCT state. The transition away from the $^3$MLCT state takes about 120 fs. The complex is found in the high spin state 1 ps following that. The path taken to get to the high spin state from the $^3$MLCT one is unclear but Dr. de Graaf [21] shows in a theoretical investigation that the equilibrium geometry of the MLCT band intersects with the potential energy surface of the $^5T_2$ state and suggests the $^3$MLCT decays directly to the $^5T_2$ state but far from its ideal geometry. The $^5T_2$ state then vibrationally relaxes to its optimal geometry resulting in an overall Fe-N bond elongation of 0.2 Å from the low spin state. The PolyPy cation remains in the high spin state for a 665 ps before returning to the low spin state. The spin crossover phenomenon of the aqueous PolyPy cation is fully reversible and completes a full cycle in less than a nanosecond.

Most of this information was found via a spectroscopic study. Figure 1.2 shows the white light absorption of the aqueous PolyPy cation. The important features here are the peaks located near 523 nm and 370 nm. These absorption peaks are due to the transition from the ground state to MLCT states.
Figure 1.3 shows the transient absorption spectrum of the aqueous PolyPy cation along with two cross-sections. Note that the two peaks from Figure 1.2 decrease sharply after time zero and remain there. This is due to the depletion of the ground state upon photoexcitation. Figure 1.4 shows more cross-sections. The 523 nm crosssection shows the almost instantaneous ground state depletion. The 370 nm and 640 nm traces show something more interesting. The traces don’t just change their baseline but show evidence of a short lived dynamic by the existence of a peak. The existence of this peak provides evidence of a multi-step process and hence, spin-crossover. Note that for PolyPy, the low-spin to high-spin transition is optically forbidden therefore it cannot proceed through a single step.

It has been established that the aqueous PolyPy cation undergoes spin crossover when exposed to 400 nm light. This thesis investigates whether the solid state form of PolyPy undergoes spin crossover as well. If it does, it could shed light on this class of compounds. PolyPy is a relatively simple spin crossover compound [12]. It is an iron atom surrounded by three bipyridine ligands. It can act as a model system to understand the spin crossover process for complicated systems and perhaps aid in the design of stable solid state spin crossover complexes. Furthermore, spatially resolving the spin crossover process of solid state PolyPy will aid efforts to understand the active sites of hemoglobin and other heme proteins whose active sites consist of an iron atom which undergoes spin crossover [12].
Chapter 1. Introduction

Figure 1.3: Transient absorption spectrum of the aqueous PolyPy cation over 20 ps using a 400 nm excitation. Colour scale uses purple for a strong decrease in differential absorption to red for no change. Reprinted with permission from [20]. Copyright 2007. American Chemical Society.

Figure 1.4: Crossections of the pump probe spectrum shown in Figure 1.3. Reprinted with permission from [20]. Copyright 2007. American Chemical Society.
Chapter 2

Experimental Methods

2.1 Materials

The solid iron(II) tris(2,2’-bipyridine) bis(hexafluorophosphate) crystal used in these studies was obtained through a collaboration with Dr. Wojciech Gawelda of the European XFEL in Hamburg Germany. The crystal he supplied was further processed by Dr. Cheng Lu of the University of Toronto Goh group. Cheng used a microtome to cut thin slices off of the crystal for use in experiments. The slices were over 100 µm long and a variety of sample thicknesses were used. The crystals prepared for the electron diffraction experiments were approximately 100 nm thick and were placed on copper transmission electron microscope meshes. Whereas the samples used in the femtosecond transient absorption experiments were approximately 300 nm thick and placed on simple microscope slides.

2.2 Femtosecond Electron Diffraction

2.2.1 The Laser

The enabling component of the femtosecond electron diffraction apparatus is the laser. It excites the sample and triggers the electron gun with a single pulse. Diffraction experiments shown in this thesis use a neodymium-doped yttrium lithium fluoride pumped titanium-sapphire laser. This laser will output a pulse of 800 nm light which has a 50 fs duration, approximately. The pulse is routed through optics and the rest of the setup as shown in Figure 2.1. The laser pulse is split into two parts: one to trigger the electron gun and another to photoexcite the sample.

After the split, the laser pulse bound for the sample must first be converted to the appropriate wavelength. Because PolyPy supposedly undergoes spin crossover when excited by 400 nm light, the laser passes through a barium borate (BBO) crystal which halves the wavelength of the light. Once at the desired wavelength, the pulse enters a delay stage which allows the arrival time of the laser to be adjusted. Light moves at a constant speed so one must adjust the distance it will travel in order to adjust the travel duration. The delay stage, as shown in Figure 2.1, works by taking an incoming beam reflecting it back in the direction it came. When the delay stage is moved along that direction, the incoming and outgoing laser path lengths are changed. For example, if the delay stage moves 1.0 mm backwards the path length of the laser increases by 2.0 mm and as a result the laser will be delayed
Chapter 2. Experimental Methods

Figure 2.1: A simplified diagram of the femtosecond electron diffraction setup

by 6.7 ps. After passing through the delay stage, the laser is directed and focused upon the sample. The delay stage is what allows the femtosecond electron diffraction experiment to adjust the time at which it is taking a picture. The electron beam always arrives at the same time but the arrival time of the excitation laser pulse, which triggers motion within the sample, can be adjusted by the delay stage. This allows the snapshot the electron beam captures to be adjusted.

The electron gun will fire when it is triggered by the other portion of the split laser beam. This is done by utilizing the photoelectric effect. When the photocathode of the gun is hit by the laser, electrons are ejected on the other side. The quantity and speed of the electrons released is directly related to the wavelength of the laser. This is because the energy of a photon is inversely proportional to its wavelength. As such, the 800 nm light emitted by the laser is not used to trigger the electron gun. The laser pulse is directed through two BBO crystals. The first to convert the 800 nm light to 400 nm light and another to convert that to 266 nm light. The 266 nm light is focused upon the photocathode of the electron gun creating an electron pulse.

2.2.2 The Electron Gun

The electron gun produces the electron pulse which is used to perform electron diffraction. Electron beams strongly interact with matter and are destroyed if exposed to atmospheric pressure. As such, the inside of the electron gun and the sample chamber are kept near $10^{-8}$ mbar. When hit by the laser, the photocathode will emit a cloud of electrons into the core of the electron gun. The path these electrons take is shown in Figure 2.2. The emitted electrons share a wide spatial and velocity distribution. To produce a beam from the electron cloud the electrons are accelerated through a 95 kV potential between the photocathode from which the electrons are emitted and the anode they are accelerated toward. The anode has a small pinhole in it which makes any electrons not on a trajectory to pass through pinhole
will hit the anode. This circular pinhole is 700 $\mu$m in diameter. The electrons which pass through the anode form a thin electron beam.

![Image](image.png)

**Figure 2.2: The electron gun.**

The electron beam may not be travelling perpendicular to the surface of the anode as it emerges on the other end of the pinhole so a magnetic lens is used to correct its trajectory. Having a proper heading is critical for the next step. As the electron beam flies, coulomb repulsion between the electrons will lengthen and broaden the electron beam. To counteract this, the electrons enter an RF cavity which compresses the electron beam. This reduces the beam duration but results in a broader pulse. The shorter beam is sent past another magnetic lens which directs and focuses the electron beam upon the sample.

### 2.2.3 The Sample Chamber

The electron beam enters the sample chamber and travels toward the sample. The laser cannot travel along the same path otherwise the mirror which directs the laser would block the electron beam. The mirror which directs the laser toward the sample is placed near the electron beam’s path. The laser approaches the sample at an angle of approximately 15°. The Gaussian electron and excitation pulses are focused upon the same spot of the sample. The electron beam has a full width at half maximum size of 330 $\mu$m. The part of the sample through which the electron beam passes is enveloped by the 520 $\mu$m laser pulse. This ensures the diffraction pattern collected is from the area which has been exposed to laser light.

Following sample excitation, the laser continues through the sample holder and eventually hits a beam dump within the chamber. Thus it has served its purpose. The electron beam, on the other hand, is not to be discarded. It diffracts when it hits the sample. It is transmitted through the sample and proceeds towards the back of the chamber. Given time to travel, the diffraction spots separate from the
undiﬀracted beam. In the path of the electron beam sits a CCD camera. The electron beam and its
diffracted pieces hit the ﬂat camera. Each pixel records the number of electrons that hit it. This gives
a two dimensional image of the electron beam which is transferred to a computer for storage.

The solid samples sit upon copper transmission electron microscope meshes which are mounted in a
sample holder. The sample holder has multiple slots in it to insert sample meshes. The slots are large
holes which hold onto the meshes by their edges. This leaves the interior of the mesh suspended in the
hole which allows electron and laser beams pass through the sample unhindered by the holder. There
are many slots in the sample holder. They are all arranged in a grid. The electron beam can reach these
other slots by the use of the translation motor the sample holder is mounted upon. The motors allow
for full motion in the plane orthogonal to the electron beam which allows the any of the sample slots to
be reached by the ﬁxed electron and laser beams. This allows for multiple samples to be placed in the
sample holder at once which is helpful since the vacuum within the sample chamber must be broken in
order to insert new samples.

In addition to the translation motor, the sample holder sits upon a rotation stage. The rotation
motor turns the sample in the plane parallel to the ground. This gives the sample stage has a wide range
of motion which makes it fairly versatile. The rotation stage allows the angle at which the electron
beam strikes the sample to be easily modiﬁed. The diffraction pattern obtained depends strongly on this
incident angle so the ability to modify it allows for a wide range of data to be collected from a single
sample. This allows the experimenter to ﬁnd and choose sample orientations which provide a strong
signal. If the data is of a high enough quality, it also offers the possibility to collect data at several
sample orientations so that ab initio reconstruction of the sample structure can be performed. The
range of orientations which can be achieved in the current apparatus is limited. At angles higher than
±30°, the electron or laser pulses will hit the solid edge of the sample slot obstructing the experiment;
however, this is is not an issue at lower angles of rotation.

2.2.4 Calibration of spatial overlap and time zero

Before femtosecond electron diﬀraction measurements can be performed, the relationship between the
laser and electron pulses need to be characterized. The two pulses need to hit the same part of the sample
and time delay between them needs to be known. Two mini-experiments are performed to determine
these parameters.

The ﬁrst is used to determine whether the pulses pass over the same spot. This is done by sending
them both at a single target. A pinhole is placed in one of the slots in the sample holder. The pinhole
is a piece of metal that ﬁlls the sample slot and allows nothing to pass by it unless it is directed through
a small hole left in it. The circular hole has a diameter of 50 µm and a thickness of approximately a
millimetre. We can calibrate of the overlap of the two beams by making sure both of them pass through
the pinhole.

The electron beam is ﬁrst. The sample holder is translated so that the electron beam is passing
through the pinhole. This is veriﬁed by the CCD camera. When the electron beam is hitting the metal
plate near the pinhole, the CCD shows nothing but noise. When the sample holder is translated so that
the electron beam passes through, the CCD shows the beam with a signal strength dependent on the
degree of overlap. Once it has been veriﬁed that the electron beam passes through the pinhole, the laser
is calibrated.

The spatial overlap of the laser is adjusted in a similar way. Recall the laser travels at an angle
towards the sample holder. After passing through the sample, it hits a beam dump. The beam dump is actually a piece of paper which scatters the laser beam. A video camera, which is outside of the sample chamber, images the piece of paper through a window and allows the experimenters to see the final state of the laser. It is important to note that the laser can travel straight enough to pass through the pinhole. The trajectory of the laser beam is tuned by adjusting the orientation of the lens which focuses the laser. When the overlap is poor, nothing can be seen on the paper. When it is satisfactory, the camera can see the laser hitting the paper. Fine adjustments can be made using an effect which occurs when using a pinhole: diffraction. When waves travel through a circular aperture they diffract and produce a diffraction pattern with a strong central peak which is surrounded by rings. When the size of the aperture and and the wavelength are near the same order, the rings can be seen. This is the case with the laser and the pinhole. The aperture diffraction is strongest when the strongest part of the laser, the centre, is in the middle of the pinhole so the lens is adjusted until the brightness of the rings is maximized. When this is complete, both the laser and the electron beams pass through the pinhole. The next step is to determine the relative time of their passing.

When a high powered laser hits a metal, ablation occurs. Ablation is a process by which a laser vaporizes ions from a material resulting in the formation of a plasma above the surface of the material. We use the presence of a plasma to determine $t_0$, the time at which the electrons and laser pulses hit the sample at the same time. The sample holder is translated so that a copper mesh is in the electron and laser beam path. We ablate the copper in the mesh in order to measure the time overlap. Filters used to reduce the laser power are removed so that the laser is of a high enough power to trigger ablation. The laser would destroy any sample we wished to study if these filters were not used during normal experiments. The electron beam is defocused so that it will cover the entire copper mesh. When it is like this, the data collected by the CCD camera is akin to a real space picture rather than a diffraction image. We can move the laser delay stage and take pictures of the copper mesh using electrons. When the laser arrives before the electron beam the ablation plasma is present in the image. The plasma interacts strongly with the electrons which is manifests itself in the CCD pictures as a strong distortion over the mesh. A rough estimate of $t_0$ can be obtained by moving the delay stage and finding the position at which this distortion first appears. Once the spatial and temporal overlap of the electron and laser beams have been determined, we are free to move a sample into the path of the beams and commence femtosecond electron diffraction studies.

2.3 Ultrafast Transient Absorption Apparatus

The transient absorption measurements were performed on another apparatus. This apparatus is slated to be used primarily in coherent control experiments by members of the Miller group. The transient absorption measurements of PolyPy can be thought of as a direct collaboration between myself of the electron diffraction and Ryan Field of the coherent control subgroups of the Miller group. His apparatus is fairly new. This is the first major experiment run on it and it is continuously tweaked and refined. As such, I will give only an overview of the machine and how it is used for the transient absorption measurements.

The centrepiece of the transient absorption apparatus is the laser. It is a femtosecond laser manufactured by Coherent. It produces light pulses which are approximately 50 femtoseconds long. The power in each pulse is high so not all of the laser is needed for transient absorption or coherent control
studies. It is split into two parts after emerging from the laser. A tenth of the laser power is kept for the transient absorption experiment and the other nine-tenths are sent away for use by another, unrelated, apparatus.

The tenth of the pulse used in the transient absorption study undergoes a process akin to the laser in the femtosecond electron diffraction apparatus. It is split into two parts: one to be used as a pump and another to be used as a probe. The pump and probe pulses are then modified and brought back together upon the sample to be studied.

The pump pulse is sent into a part not typically found in a transient absorption instrument: a pulse shaper. The pulse shaper takes an input laser pulse and outputs another pulse with a desired frequency distribution. It changes the incident pulse through the use of computer adjustable mirrors and gratings. Coherent control experiments require exotic laser beam profiles to probe chemical bonds. Transient absorption does not test the limits of the pulse shaper. In these experiments, the pulse shaper proves to be a convenient tool which can be used to easily create a short Gaussian beam profile centred near 400 nm and allows the power of the beam to be adjusted effortlessly. Once it has been shaped, the pulse passes through a chopper wheel which will periodically block the pump pulse which allows a variety of measurements to be taken such as pump-probe absorption and just white light absorption. The pump pulse is then sent through the sample and directed into a beam dump.

The probe pulse goes through a fairly similar process. After being split from the pump pulse, it is converted into a broadband white light pulse spanning the range from 350 nm to 625 nm. Additionally, the pulse passes through a delay stage much like the laser in the femtosecond electron diffraction apparatus does. This allows the arrival time of the probe pulse to be adjusted. After the delay stage and broadband conversion, the pulse is directed to the sample via a series of mirrors.

The pump and probe pulses spatially overlap before being focused and passed through the sample. The sample is a thin piece of PolyPy crystal sitting on top of a standard microscope slide. The slide is held vertically by a clamp which sits upon a full range translation stage. The stage has three knobs which allows the sample to be translated in the three primary directions. Two of the knobs translate the stage along the plane of the microscope slide. Because the slide positioned orthogonal to the laser pulses, this adjusts the part of the sample being illuminated. The other knob moves the microscope slide along its normal direction which allows the sample to be moved into and away from the focal point of the pump and probe pulses. The ultrafast transient absorption apparatus is open to the atmosphere and not in a vacuum chamber so alignment is simple and adjustments can be made quickly by hand.

The laser pulses pass through the thin sample and reach a selective mirror. The pump pulse is deflected to the right into a beam dump whereas the probe pulse is sent to the left to the spectrometer which measures the spectrum of the laser. The wavelength distribution it captures is sent to a computer through a data acquisition card and is stored so it can be analysed at a later time.
Chapter 3

Results

3.1 Electron Diffraction

Diffraction patterns were collected using the femtosecond electron diffraction apparatus as described in chapter 2. The experimental conditions will be given. The sample was a slice of PolyPy crystal which was approximately 100 nm thick. It was mounted on a copper mesh. The experiment was repeated at 10 Hz. All diffraction patterns shown in this thesis are the product of multiple experimental trials captured by the CCD camera. All diffraction patterns shown are from the accumulation of 10 trials or a camera exposure time of about a second.

The electron gun was releasing electron pulses of approximately 300,000 electrons each. The stability of the total number of electrons in the electron beam was measured and it was found to have a standard deviation of less than one percent. The beam had a diameter of 330 µm and was found to have a duration of approximately 600 fs.

The excitation pulse had a wavelength of 400 nm as described in chapter 2. This pulse was created by the transmission of a 800 nm light pulse through a BBO crystal. The pulse retains its ultrashort temporal length through this transmission. The full width at half maximum size of the laser beam was measured to be 520 µm at the sample holder. Each laser pulse had an energy of 8 µJ. This energy was chosen after much deliberation. In general, the more powerful the pump beam the greater proportion of the sample will be excited. This will produce larger structural changes within the sample and hence result in a stronger change in the diffraction pattern over time. Strong beams provide even illumination of the sample for which the molecules near the back of the sample receive the same photon intensity as those in the front; however, high intensity beams can cause problems. A powerful beam can cause permanent damage to a sample which presents a challenge for an experiment such as this one where many trials are needed in order to collect quality data. Additionally, a higher laser power will increase the probability of multiphoton process, such as multiphoton ionization, which completely change the process being studied. The 8 µJ laser pulse power was chosen after considerable trial and error which will only be summarized here.

This power shows strong changes in the diffraction pattern of the sample, as will be shown later in this chapter, without any significant signs of damage. At higher powers, such as 10 and 12 µJ, the diffraction pattern is noticeably degraded after performing experiments at 10 Hz for minutes whereas at 8 µJ a single slice of sample shows no signs of damage after being studied for weeks. This pulse power is
too low to expect a significant contribution from multiphoton processes. As such, the 8 μJ pulses have a pump power below the threshold where the negative effects of high power take hold. These settings were used in several diffraction experiments.

Each diffraction experiment shown in this thesis utilizes the settings given above. Each was comprised of the same steps. The sample holder is translated so that a piece of PolyPy crystal is in the beam path. An automated scan routine is performed in which the sample holder translates and captures a static diffraction pattern of each part of the crystal. All of these images provide the same diffraction pattern but some are of higher quality than others. Certain pieces of crystal can be damaged, have an uneven thickness, or have a higher incidence of impurities. These factors, among others, will result in lower quality diffraction patterns whereas the diffraction spots may appear to be broader or may stretch out into rings. The spots providing the best static diffraction patterns are chosen and used in further studies.

With a position chosen, a femtosecond electron diffraction experiment is performed. The laser delay stage is moved so that the laser arrives before the electron beam. Diffraction images are taken with the pump laser turned on and off. To take pump off images the laser is blocked using a shutter. The delay stage is moved forward and additional pump on and off images are captured. This is done until the delay stage reaches the last time point desired and the entire process is repeated at least two more times to capture more redundant images which allow for additional data averaging. The same process is performed when collecting diffraction patterns for other crystal orientations. The only major difference is the sample holder remains rotated throughout the process.

After data has been collected, it is subjected to basic processing. In the simplest case, the difference between the pump on and pump off patterns are taken and added up for all of the different times. This results in an image which visualizes the diffraction spots that change throughout the experiment. This reveals subtle changes such as spot broadening or translation as well. When the dynamic spots have been identified, the change they undergo is sought in more detail. This is done by integrating the area under the spot for the pump on and off pulses, taking the difference in integrated spot intensity and then plotting the change in intensity with time. These kinds of plot shows the rate at which these changes occur and reveal the number of discrete steps in which the change occurs.

Figures 3.1 and 3.2 show this kind of data for two different crystal orientations of PolyPy. Unmodified, pump off, diffraction images can be seen in Figures 3.1a and 3.2a. These show how the diffraction spots look. Figures 3.1b and 3.2b show the difference in the diffraction pattern between pump on and pump off experiments while Figures 3.1c and 3.2c show how the numbered diffraction spots in Figures 3.1b and 3.2b change over time.

### 3.2 Ultrafast Transient Absorption

A pump probe transient absorption experiment was performed using solid state PolyPy as the target. The PolyPy crystal used was 300 nm thick and was sitting upon a standard microscope slide. Before the experiment was performed, the beam profile of the pump laser was measured. Figure 3.3 shows this. Figure 3.3a shows the wavelength distribution of the beam along with the relative phase of each component. Figure 3.3b shows the wavelength distribution of the pump pulse with time.

With the wavelength distribution of the pump beam known, transient absorption studies were done. The first experiment to be performed is the measurement of the white light absorption of PolyPy. This is done without a pump pulse. The white light absorption of PolyPy can be seen in Figure 3.4. The
Chapter 3. Results

(a) The diffraction pattern

(b) The total change in diffraction pattern

(c) The change over time

Figure 3.1: Diffraction pattern of PolyPy at -25 degrees rotation.
Chapter 3. Results

(a) The diffraction pattern
(b) The total change in diffraction pattern
(c) The change over time

Figure 3.2: Diffraction pattern of PolyPy at 4 degrees rotation.
(a) The wavelength distribution and relative phases of the pump laser pulse.

Figure 3.3: Pump beam profile in the transient absorption measurement.

white light absorption provides a glimpse of the absorption bands present in the sample. The white light absorption image is not the raw data obtained from the spectrometer but rather it is a relationship between the reading the spectrometer gives after the light passes through the sample and when it passes through only the glass. The exact relationship is a logarithmic ratio between the difference between the sample and glass spectrometer reading over the spectrometer reading when passing only through air. This logarithmic relationship is a by-product of Beer’s Law in which the logarithm of the intensity of transmitted light is proportional to the absorbance, also known as the optical density, of the sample. This calculation is necessary for all of the absorption measurements which are made in this thesis.

In addition to static absorption measurements, time dependent differential absorption measurements are made. This data is collected in much the same way as the data from femtosecond electron diffraction experiments are. The difference is the probe is a beam of white light and the absorbance of the sample is what is measured at each delay stage position. During the collection of this data, the apparatus was running at 83.3 Hz, or one cycle every twelve milliseconds. Each cycle is comprised of six shots with a separation of 1 ms. Each time point is comprised of the average of 64 cycles.

Figures 3.5, 3.6 and 3.7 show pump probe spectra of PolyPy over the time periods of 2 ps, 20 ps and 900 ps respectively.
Figure 3.4: Linear absorption of the PolyPy crystal.

Figure 3.5: Transient absorption data of PolyPy over 2 ps with 10 fs time steps.
Figure 3.6: Transient absorption data of PolyPy over 20 ps with 50 fs time steps.

Figure 3.7: Transient absorption data of PolyPy taken over 900 ps with 2 ps time steps.
Chapter 4

Discussion

4.1 Dissemination of the Diffraction Experiment

Data collected by Dr. Gawelda shows aqueous PolyPy undergoes a fast spin crossover transition upon exposure to a laser pulse of 400 nm light. This change is accompanied by a Fe-N bond elongation of 0.2 Å within a picosecond of illumination. As such, an ultrafast electron diffraction experiment was performed to determine whether this change occurs in the solid state. Figures 3.1 and 3.2 show an important subset of the data collected.

Figure 3.1a shows the diffraction pattern of one crystal plane of PolyPy. Blue is the background while red shows diffraction peaks. The pattern shows expected features such as a large electron beam in the centre of the pattern and a inversion center through it. It shows a well formed diffraction pattern which implies there is nothing obviously wrong with the electron beam or CCD camera. The time dependent diffraction patterns show the type of changes we are investigating.

Figure 3.1b shows the diffraction pattern changes fairly substantially after photoexcitation. Several of the diffraction spots become stronger, many don’t change at all and the intensity of the central electron beam becomes weaker with time. These results are all consistent. Most of the diffraction spots in Figure 3.1a do not change at all which is expected when a structural change occurs in a solid. The position and orientation of molecules in the crystal lattice will change but the substituents do not so major details present in the diffraction pattern will remain such as the presence of bipyridine ligands, hexafluorophosphate molecules or iron atoms and the general arrangement of these components. The pattern shows spots which become stronger and a central electron beam whose intensity decreases. This is consistent in that each electron pulse holds approximately the same number of electrons so if a change occurs in the sample which results in a greater number of electrons deflecting away from the central beam the intensity of the central beam will decrease since there are fewer electrons left in it.

Another important detail to note is the hollow green patch in the middle of the central beam. This is due to the CCD becoming saturated when the central electron beam hits it so it gives an intensity value corresponding with the maximum value for the CCD. The CCD remains saturated throughout the process so the pixels near the center of the beam read a constant, high, value so when the difference is taken these pixels show no change in diffraction since they remained saturated. The peaks with the strongest changes were numbered and time traces of those peaks are plotted in Figure 3.1c. Only the strongest peaks were plotted because they were the only peaks were the signal was considerably higher.
than the base noise level.

An important detail that is not apparent in this figure is the process which occurs here is completely reversible. Every time the experiment is repeated the data obtained is the same, discounting noise. The sample returns to its pre-excitation state before the experiment is repeated 0.1 seconds later. Additionally, the same sample has been used for weeks and no lasting damage has been observed.

Figure 3.1c shows the intensity of the numbered diffraction peaks from Figure 3.1b as the delay between the laser pump and electron probe pulses increase. It is clear in this Figure that there is a significant change that occurs after the laser passes through the sample. All four spots change by more than 6% over the course of the process. The problem can be seen when looking at the time scale of the observed process.

Spin crossover of the aqueous PolyPy cation takes less than 1 ps. After that transition, it remains in the high spin state for around 700 ps and then returns to the ground state. That means the Fe-N bond length will elongate by 0.2 Å within a picosecond and so we expect a change in the diffraction pattern to occur on the same time scale. Figure 3.1c shows a process for which it takes approximately 120 ps for the diffraction intensity to reach its maximum which is too slow for the process to be spin crossover.

The same process was repeated for several different orientations of PolyPy. Figure 3.2 is similar to 3.1 where 3.2a shows the diffraction pattern, 3.2b shows the difference in diffraction spots and numbers them and 3.2c shows the time evolution of the numbered spots. Figure 3.2 shows a completely different diffraction pattern with different spots changing yet Figure 3.2c shows a process which occurs over a similar timescale of approximately 120 ps. This plot shows the diffraction spots tend to decrease slowly after their maximum value. Because the process is reversible, we know it reaches zero before 0.1 seconds pass.

This long time process occurs but it is highly unlikely to be spin crossover due to the timescale. Many other femtosecond electron diffraction data sets were collected at different timescales and crystal orientations which are not included in this thesis and they all showed the same thing: a slow process which peaks near 120 ps.

There is no evidence the spin crossover process is overlapped with the 120 ps process either. In shorter time scales, all that can be seen is a linear increase from time zero. This continues all the way to the peak at 120 ps. If there was another process occurring, we would expect to see a change in the rate the diffraction pattern changes when it is completed, which we do not. If spin crossover is occurring within the PolyPy crystal, it is masked by the noise level or a limitation of the apparatus. As such, this femtosecond electron diffraction experiment did not provide any evidence the spin crossover phenomenon observed by Gawelda occurs in the solid state but cannot demonstrate its non-existence either. That is why the ultrafast transient absorption experiment was performed. It has the ability to redo the Gawelda experiment in the solid phase. If the observations that suggested the presence of spin crossover in the liquid spectrum can be found in the solid phase, it will suggest spin crossover occurs in the solid state.

4.2 Ultrafast Transient Absorption of solid state PolyPy

The first white light probe experiment performed on solid state PolyPy was the white light absorption experiment. The results of this are shown in Figure 3.4. The results of the analogous liquid experiment are shown by the black dotted line in Figure 1.2. These figures show the absorption bands of the sample without time dependence which gives a basic outline of the identity of the sample. The two plots share
many of the same features which is encouraging. They both share a large feature near 500 nm which is comprised of two peaks which are fairly close together. There is a valley near 420 nm and a smaller peak at a lower wavelength. Additionally, the spectra appear to be approaching zero near 600 nm. There are noticeable differences however. The largest peak appears to have redshifted in the solid state and the peaks are broader in the aqueous phase. This is not surprising since liquid interactions tend to cause spectrum line broadening and small redshifts may be indicative of the different environment. Overall, the absorption spectra of solid and aqueous PolyPy indicate drastic changes have not occurred to the complex but it does not provide insight to the spin crossover transition.

Figure 3.3 shows the shape and composition of the pump laser used in the time dependent study. The lineshapes in Figure 3.3a show the pump laser is approximately Gaussian. The wavelengths component intensity has a approximately Gaussian distribution and the components which make up the majority of the beam have the same phase so the pump laser is essentially Gaussian in the wavelength domain. Figure 3.3b shows the wavelength distribution in time. This image has a major problem. It appears the wavelength distribution remains constant for many femtoseconds before changing again but this has nothing to do with the laser. This is a artifact from a malfunctioning delay stage which is involved in the measurement of the beam shape. It is not the same delay stage used in the experiment. This delay stage has a problem where it does not respond to commands asking for small displacements. It will stays in the same position. That is why the laser in this figure appears to be constant in many sections. The delay stage did not move so the same part of the laser is being observed. Using this data, one can conclude the time profile of the laser is at the worst a poor Gaussian but likely much better. Overall, the pump laser used in the ultrafast transient absorption experiment was well formed.

Ultrafast transient absorption experiments were performed with the pump pulse described. Results of these experiments can be seen in Figures 3.5, 3.6, 3.7 which show timescales of 2 ps, 20 ps, and 900 ps respectively. The short time spectrum would reveal any short time dynamics. The medium time scale is the same scale Gawelda used for the liquid pump probe spectrum shown in Figure 1.3. The longest time scale data was collected to check for long time processes. Before analysing each spectrum individually, the general features shown in each will be discussed.

One noticeable feature is the curved line near the time of zero. This is most easily seen in the short time plot. This is a common phenomenon in ultrafast pump probe experiments and is due to chirp in the white light laser beam. The effect it has on the spectrum is the time the white light and pump lasers hit the sample concurrently is not the same for each wavelength. They are all offset along this curve. What is also important to note is the signal directly along this time zero curve is not due to PolyPy. This signal is an effect brought about by the glass microscope slide the solid PolyPy sample is sitting upon, not the sample itself. This is known through additional pump probe experiments of only the microscope slide which are not included in this thesis. The substrate provides signal only along the time zero curve. It is likely due to a nonlinear optical process in which the pump and probe lasers interact with the glass slide though not much analysis was done beyond that.

Another feature which appeared in all three spectra is a large peak at 400 nm. This is easily seen in Figure 3.5. This peak is due to pump scatter. The pump laser scatters upon contact with the PolyPy sample which results in a very large peak due to the pump light which scatters off of and makes it to the spectrometer. Evidence for this interpretation, aside from scattering which can be seen by eye after the pump laser passes through the sample, is the spectrometer still detects this signal when the white light beam is blocked but it disappears if the pump laser is not allowed to reach the sample. This
peak and the lower wavelengths were not included in the 20 ps and 900 ps spectra due to the lack of major differences in that region from the short time plot. Additionally, the optical filters used in the experiment were not rated for use on wavelengths less than 400 nm so signals in that region are not trustworthy. With the general features taken care of, it is time to discuss the data from each time scale.

The 20 ps data shown in Figure 3.6 is of the same timescale as the aqueous data shown in Figure 1.3. The solid state spectrum is largely the same as the liquid one on this timescale. There are two major peaks near 520 nm. Like the static absorption spectra showed, there is a red-shift in the larger peak and there is a valley between the two peaks in the solid state. These two signals survive past the 20 ps mark in both the solid and liquid states. These peaks are due to the depletion of the ground state of the sample and so it provides evidence a large population of PolyPy complexes remain in a excited state long after the initial excitation. Except for those two peaks, there are no features of note in the rest of the spectra. The 600 nm region is barren and the 420 nm region is a gulf. Both the solid state and aqueous PolyPy samples provide essentially the same spectrum on this timescale. The liquid spectrum provides evidence for spin crossover on short time scales which will be discussed in due time.

The long time scale spectrum in Figure 3.7 shows many of the same features seen in Figure 3.6. The major difference is over a nanosecond there is a dynamic which causes the two large peaks to have shoulders which oscillate. Their oscillations are anti-correlated to one another and occur with a period near 200 ps. This dynamic is clearly too slow to be directly related to spin crossover, it is likely due to acoustic vibrations within the PolyPy crystal, but it supports what was seen in the diffraction experiment. The diffraction experiment showed long time scale dynamics occurring over a 120 ps time scale and this spectrum shows evidence of long time scale dynamics. The processes seen in each experiment are not necessarily the same process but this data set suggests what the diffraction experiment saw is plausible for the PolyPy crystal and not necessarily a symptom of a problem with the diffraction apparatus. In this case, the lack of fast spin crossover signal in the diffraction experiment is likely due to a lack of sensitivity in the measurement or due to the absence of spin crossover in solid state PolyPy. To ascertain which is more likely, let’s have a look at the short time spectrum.

Figure 3.5 shows the short timescale spectrum of solid PolyPy. An important note to make about this plot is the data was collected on a different spot on the PolyPy sample than the other two were. This spot did not absorb as strongly as the other spot did so that is why the colour scale only goes down to -15 mOD. Most of the features in this plot have been discussed though there is a new feature present immediately after the time zero curve near 620 nm. The signal does not immediately go down to zero. To provide a better view of this, a time trace is taken which is shown in Figure 4.1. The figure shows a dynamic which occurs over 500 fs. We know this is not a single step process due to the inflection point. One process populates a state that increases absorption of the light and another does the opposite. This also occurs on the time scale in which we expect spin crossover phenomenon to occur. Gawelda took a similar time trace which is shown in Figure 1.4. The similar dynamic he observed at 640 nm is one of the identifying characteristics of spin crossover in the aqueous phase. The curve increases at time zero peaks and decreases to a value which is not the same as the background at which it remains constant. We see a similar phenomenon occurring in the solid phase. The large peak in Figure 4.1 clearly not due to the initial substrate signal since the substrate produces 620 nm light, not absorbs, and its signal is not as strong as the one observed. As such, the signal observed is from the PolyPy sample. Spin crossover may indeed occur in solid state PolyPy.

This suggestion calls for additional verification. The data in Figure 3.5 which contains the potential
Figure 4.1: Time trace of the data of the data from Figure 3.5 along with the spectrum from the substrate.

A spin crossover signal was collected during the latest round of spectroscopic experiments. To verify the authenticity of the signal, additional spectra will be collected after several changes are made to the experiment. A previous experiment saw a similar dynamic but the signal remained constant on a value not significantly different from the baseline, which suggests a return to the ground state which is not spin crossover. This offset signal needs to be observed once again. If the signal is found, it will suggest this signal is definitely real and not an accident and additionally a reduction in the noise level of the measurement which will allow reliable analysis of the data. The changes being made are out of the scope of this thesis but a simple change which will be done the substitution of the glass substrate with one that does not react so strongly to the presence of the laser pulses. The presence of spin crossover in solid state PolyPy would also call for changes in the diffraction experiment.

The diffraction experiment saw no evidence for spin crossover but observed a process occur over a longer time frame. The spectroscopic experiments found long time dynamics, which suggest the finding from the diffraction experiment is plausible, but the transient absorption experiments also provide evidence for spin crossover. Short time spin dynamics were not seen in the data collected from the diffraction experiment. Like the spectroscopy experiment, additional electron diffraction experiments are being prepared which are outside of the scope of this thesis.
Femtosecond electron diffraction and ultrafast transient absorption studies were carried out on solid state PolyPy in search of the spin crossover phenomenon in the solid state. The diffraction experiment was largely inconclusive but a sign of spin crossover was found in the transient absorption experiment which is reminiscent of the liquid state experiments performed by Gawelda et al.

This finding has inspired efforts within the Miller group to study spin crossover. The transient absorption experiment is being improved upon to be certain the current finding can be reproduced as well as obtain a spectrum with less noise so that sophisticated data analysis can be performed reliably. Additionally, the discovery of spin crossover in the transient absorption experiment suggests the diffraction experiment was unable to see the structural changes associated with spin crossover. As such, the diffraction apparatus has been modified in the hope a future experiment will be fruitful.

A successful femtosecond diffraction experiment of solid state PolyPy would reveal the motion involved in a spin crossover transition. PolyPy is, structurally, a simple spin crossover compound which could act as a model for the others. Knowing the structural configuration of PolyPy at key transition states could inform the design of spin crossover compounds desired properties. One such compound would be one with a long high spin lifetime that could potentially be used in spintronics. Knowledge of the trajectories the atoms travel could aid the understanding of fundamental biological systems such as hemoglobin.
Bibliography


