# UNDERSTANDING THE INTERPLAY BETWEEN GEOMETRY AND ULTRAFAST DYNAMICS IN LIGAND FIELD EXCITED STATES OF INORGANIC CHROMOPHORES

By

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### ABSTRACT

# UNDERSTANDING THE INTERPLAY BETWEEN GEOMETRY AND ULTRAFAST DYNAMICS IN LIGAND FIELD EXCITED STATES OF INORGANIC CHROMOPHORES

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After photoexcitation, the relaxation dynamics between excited states of a molecule are governed by both the energies and displacement of these states. For transition metal complexes in particular, ligand modification (via electron withdrawing substituents, electron donating substituents, aromatic substituents, etc) to alter the energetics of the excited states has been well studied. Recently, interest in the displacement of these surfaces from the ground state and the geometric ramifications of this displacement have spurred many studies in several research groups. Here, ligand modifications are made to modify molecular distortions (i.e. displacement), rather than the energetics.

The research presented in this thesis focuses on intersystem crossing processes in electronically simple chromium(III) compounds. With only a few excited states accessible after visible excitation, interpretation of the excited state dynamics is significantly simplified. Ligand substitution and its effect on the kinetics of the system have been studied using ultrafast transient absorption spectroscopy with ~50 fs pulses. The first study presented in this work focuses on identifying the molecular vibrations occurring immediately after excitation and how those motions facilitate intersystem crossing. The second study presented here focuses on modulating the energetics, not through ligand substitution, but with high (25 T) magnetic fields. Over the course of pursuing these measurements, various instrumental and software advances were necessary to both collect and analyze the data. These advancements, along with the findings from both studies, are the focus of the discussions herein.

Copyright by EILEEN DIXON FOSZCZ 2015 To all four of my parents: thank you for always encouraging me to dream and to keep reaching for the stars

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# KEY TO ABBREVIATIONS

LF	. ligand field
MLCT	. metal-to-ligand charge transfer
LMCT	. ligand-to-metal charge transfer
СТ	. charge transfer
ES	. excited state
GS	. ground state
VR	vibrational relaxation
VC	. vibrational cooling
IVR	. intramolecular vibrational redistribution
IC	. internal conversion
FL	. fluorescence
ISC	. intersystem crossing
ISC BISC	. intersystem crossing . back intersystem crossing
ISC BISC PH	. intersystem crossing . back intersystem crossing . phosphorescence
ISC BISC PH acac	. intersystem crossing . back intersystem crossing . phosphorescence . 2,4-pentanedione or acetylacetonate
ISC BISC PH acac TMHD	. intersystem crossing . back intersystem crossing . phosphorescence . 2,4-pentanedione or acetylacetonate . 2,2,6,6-tetramethyl-3,5-heptanedione
ISC BISC PH acac TMHD bpy	. intersystem crossing . back intersystem crossing . phosphorescence . 2,4-pentanedione or acetylacetonate . 2,2,6,6-tetramethyl-3,5-heptanedione . 2,2'-bipyridine
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ISC BISC PH acac TMHD bpy phen Tren(py) <sub>3</sub> MeCN DCM	. intersystem crossing . back intersystem crossing . phosphorescence . 2,4-pentanedione or acetylacetonate . 2,2,6,6-tetramethyl-3,5-heptanedione . 2,2'-bipyridine . 1,10-phenanthroline . tris(2-pyridylmethyliminoetyl)amine . acetonitrile . dichloromethane

PF<sub>6</sub>.....hexafluorophosphate

CIO<sub>4</sub>..... perchlorate

- TA..... transient absorption
- LPSVD ..... linear predictive single value decomposition
- M-L..... metal-ligand (bond)
- FWHM ..... full width at half max
- FROG ..... frequency resolved optical gating
- OPA..... optical parametric amplifier
- YAG..... yttrium aluminum garnet
- CaF2..... calcium fluoride
- ND ..... neutral density
- IRF ..... instrument response function
- XC ..... cross correlation
- OKE..... optical Kerr effect
- FROG ..... frequency resolved optical gating
- XFROG ..... cross-correlation FROG
- GVD ..... group velocity dispersion
- GDD ..... group delay dispersion
- SHG ..... second harmonic generation
- PG..... polarization gating
- WLG ..... white light generation
- XPM ..... cross-phase modulation
- SPM ..... self-phase modulation
- FT..... Fourier transform
- FFT..... fast Fourier transform
- TD FFT..... Time-dependent fast Fourier transform

DFT ..... density functional theory

- TD DFT ..... time-dependent density functional theory
- PCM ..... polarizable continuum model
- CPCM..... conductor-like polarizable continuum model
- G03 ..... Gaussian '03
- G09 ..... Gaussian '09
- CAS SCF..... complete active space self-consistent field
- ISRS..... impulsive stimulated Raman scattering
- GSR ..... ground state recovery
- AMU ..... atomic mass unit
- NHMFL ...... National High Magnetic Field Laboratory
- GPIB..... general purpose interface bus

## 1 Introduction

This dissertation the ultrafast dynamics tris(2,4examines of The ultimate goal of this work is to find a pentanediono)chromium(III),  $Cr(acac)_3$ . "handle" in the ligand framework where substitutions will reliably and predictably alter the photophysics of the compound. Thus, an in-depth understanding of the geometry changes occurring in this molecule over the course of the ultrafast dynamics is imperative. The work in this thesis targets two experimental techniques to gain information about the ultrafast dynamics in these molecules: vibrational coherence and perturbation with a strong magnetic field. The molecules studied in this thesis are transition metal compounds based on an octahedrally coordinated Cr(III) metal center. Utilizing visible excitation, these compounds have nominally two excited states to sample prior to returning to the ground state. This greatly reduces the complications associated with interpreting kinetics in these systems compared to other transition metal compounds, examples of which include Ru(II), Fe(II), and Cu(I) compounds (vide infra). While the simple electronic picture of these Cr(III) complexes makes them attractive candidates for study, ideally the concepts established here will be more broadly applicable in the field of transition metal photophysics.

#### 1.1 Photophysical Processes in Transition Metal Compounds

The focus of this dissertation is on photophysical processes, or processes that occur after the absorption of light and do not cause a permanent change in the composition of the molecule. In general, transition metal compounds contain a variety of absorption features arising from the ligand, metal center, or both, namely  $n-\pi^*$ ,  $\pi-\pi^*$ , d-d, and charge transfer, respectively. The d-d and charge transfer absorptions are of

primary interest, as the n- $\pi^*$  and  $\pi$ - $\pi^*$  transitions are only modestly altered from their pure-organic counterparts. Metal centered d-d transitions, also called ligand field (LF) absorptions, have relatively low extinction coefficients due to the symmetry forbidden nature of the transition between metal-based orbitals. As such, most of these transitions have peak intensities at 100 M<sup>-1</sup>cm<sup>-1</sup> or less.<sup>1</sup> Charge transfer transitions, however, involve the transfer of an electron from a metal orbital to a ligand orbital (metal-to-ligand charge transfer, or MLCT) or from a ligand orbital to a metal orbital (ligand-to-metal charge transfer, LMCT). These transitions are no longer between orbitals on the metal center, so it is easier to obey the symmetry restriction for transitions, leading to strong extinction coefficients, ranging from 10<sup>3</sup> to 10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>.<sup>2</sup> Another important aspect of LF and CT absorptions is their presence in the visible part of the spectrum. As such, the majority of visible excitation studies on transition metal compounds utilize these transitions to initiate photophysical processes.

Light absorption occurs when the incident photon has sufficient energy to promote an electron to a higher energy orbital, or excited state (ES). The Born-Oppenheimer approximation allows the movement of the nuclei to accommodate this electronic change to be neglected, since an electron's motion is instantaneous compared to the rate of nuclear movement.<sup>3</sup> This means that the excited state is generated with the same geometry as the ground state (GS) structure. At this point, the excited molecule has a number of possibilities for dissipating this excess energy and returning to the ground state configuration. These processes are shown schematically in Figure 1.1. The potential energy surfaces are labeled S<sub>0</sub>, S<sub>1</sub>, and T<sub>1</sub>, where the S denotes a state with a singlet multiplicity and the T denotes a state with a triplet

multiplicity. The vertical axis represents the energies of these electronic states, while the horizontal axis relates geometric parameters of the states. The process of absorbing a photon of energy hv is represented by a vertical green arrow moving the system into the S<sub>1</sub> excited state. As the energy of this photon is high enough to excite



# Figure 1.1 Possible Photophysical Processes Between Excited and Ground Potential Energy Surfaces

The ground and excited states are represented as potential energy surfaces displaced along some generalized reaction coordinate,  $\Delta Q$ , and with varying energies. Absorption of a photon is shown as the green arrow, while transitions between states of the same multiplicity ( $S_0 \leftarrow S_1$ ) are shown in orange and transitions between different multiplicities ( $T_1 \leftarrow S_1$ ) are shown in red. The blue oscillating arrows represent vibrational relaxation, or movement to lower vibrational levels within an excited state surface. Radiative transitions are represented as solid arrows; nonradiative transitions are represented as dashed arrows.

the v=7 vibrational level, vibrational relaxation (VR) may occur to dissipate enough energy to relax to a Boltzmann distribution in the  $S_1$  state. This VR process is typically thought of a vibrational motion of the molecule transferring energy to the surrounding solvent as heat (vibrational cooling, VC) or transferring vibrational energy to other modes of the molecule (intramolecular vibrational redistribution, IVR). This is seen as the blue wavy arrow pointing to the bottom of each excited state surface. To return to the ground state from  $S_1$ , the system may nonradiatively decay via internal conversion (IC), again transferring this energy as heat to the surrounding solvent, or emit a photon as fluorescence (FL) to radiatively transition between these states.<sup>4,5</sup> Alternately, the  $S_1$ state may transition to the  $T_1$  state through intersystem crossing (ISC), which occurs by flipping the spin of an electron while maintaining the total energy of the system, hence the horizontal arrow. The system may then undergo VR on the  $T_1$  surface before radiatively or nonradiatively returning to the ground state through phosphorescence or ISC, respectively. In this case, ISC is a vertical transition which dissipates energy of the system to the surrounding solvent media. All of these processes are associated with a rate, and the overall photophysics of the system results from the kinetic competition between these rates.

The geometric aspect of these transitions is represented by the reaction coordinate along the x-axis in Figure 1.1. This reaction coordinate could be a number of geometric changes, from a bond length change to a torsional twisting of the ligands in the molecule or even a combination of modes, and is generally represented as  $\Delta Q$  here. This vertical transition upon absorption of light places the system on the S<sub>1</sub> surface at the  $\Delta Q$  position corresponding to the ground state minimum, i.e. the geometry remains unchanged despite the movement of an electron.<sup>3</sup> The Franck–Condon governs the intensity of a transition, and results in the highest probabilities for transitions where the nuclei are stationary.<sup>6</sup> These stationary positions occur at the turning points, or edges, of the potential energy surface. Another important implication of this  $\Delta Q$  coordinate is

that as the excited state relaxes to the geometry associated with the potential minimum, vibrational relaxation can facilitate the necessary reconfiguration. To look at that another way, *identification of the vibrational modes facilitating a structure change or ultrafast relaxation event provides insight into which structural aspects of the molecule might affect the rate of these events and should be chemically manipulated.* 

Identification of these vibrational modes, either as initially excited or populated through IVR, may be accomplished through a number of techniques. Because the excited state vibrations are of interest, time-resolved techniques are needed. At the most basic level, a light source is required to transition the molecule to the excited state, and then any UV-Visible, IR, Raman, etc., spectroscopic technique may be used to get information about these vibrations.<sup>7,8</sup> The approach employed in this dissertation uses visible light in a pump-probe experiment to investigate these vibrations. Utilizing laser pulses shorter than the period of the molecular vibrations of interest, the nuclear motions of excited state relaxation events may be monitored as a function of time.

## 1.2 Transient Absorption Spectroscopy

#### **1.2.1** General Experimental Considerations

Transient absorption spectroscopy (TA) is a pump-probe technique that investigates excited state absorption as a function of time. The pump pulse promotes a small fraction of the sample to an initial excited state, where at some time delay  $\tau$ , the weak probe pulse interacts with the sample, and the transmitted intensity of this probe pulse is recorded as a function of  $\tau$ . In this way, kinetics of the excited state processes (IC, ISC, VR, etc.) may be inferred from the signal. Since the absorption changes are referenced to the ground state absorption of the molecule, the signals are represented as a change in absorbance, or  $\Delta A$ . Since TA promotes only a fraction of the molecules in solution to the excited state, the signals recorded are actually a mix of ground state and excited state absorption signals, as seen in equation 1.1, below:

$$\Delta A = (\varepsilon_{ES} - \varepsilon_{GS})b[c_{GS}]\eta \tag{1.1}$$

where  $\varepsilon$  is the extinction coefficient for the excited state or ground state, b is the path length of the cell,  $c_{GS}$  is the concentration of the ground state, and  $\eta$  represents the percentage of ground state promoted to excited state by the pump pulse.<sup>9</sup> From this equation, it is easy to see that positive signals result when the excited state extinction





The transient absorption laser pulses, left, shows how the pump pulse (orange) intersects with the probe pulse (green) at a small angle inside the sample cell. The delay between the pulses is changed in order to record the transient signal. Example data, right, showing a transient absorption signal (black dots) for  $[Fe(tren(py)_3](PF_6)_2$ . The inset shows the ground state (black) and approximate excited state (blue) absorption spectra, and the excited state spectrum minus the ground state spectrum is shown in the solid red trace. The TA signal match the simulated difference spectrum quite well. The figure on the right is adapted with permission from reference 10. © (2008) American Chemical Society.

coefficient is greater than the ground state extinction coefficient. Negative signals, however, may result from the loss of ground state absorption, or ground state bleach, upon promotion of some molecules to the excited state. This is typically seen in spectral regions where the ground state extinction coefficient is greater than the excited state extinction coefficient. If the sample is emissive and the probe pulse stimulates emission from the excited state to the ground state, this will also produce a negative TA signal.<sup>4,11</sup> A TA signal of is zero is called an isosbestic point, and it only occurs where the ground state absorptions are identical.

These concepts are illustrated in Figure 1.2, where left panel shows the timing delay of the pump and probe pulses incident on the sample cuvette, and the right panel displays example  $\Delta A$  data from an iron(II) complex. The collected TA signal, shown in black dots, contains regions of positive, negative, and zero signal. The inset in Figure 1.2 shows the ground state and approximate excited state absorption spectra for [Fe(tren(py)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, a spin crossover compound.<sup>10</sup> This molecule represents a special instance where the "excited state spectrum" may be collected explicitly using steady state UV-Visible absorption through synthetic modifications to the ligand. By subtracting the ground state absorption spectrum (black) from the excited state absorption spectrum (blue), the transient absorption signal for this compound may be simulated. This simulated spectrum (red) is a close match to the actual transient absorption signal (black dots) in this case since there is no stimulated emission in this compound. The negative signals occur where the ground state absorbs more, the positive signal occurs where the excited state absorbs more, and there are two isosbestic points from the two crossing points in the ground state spectra.

Excited state absorption may be monitored in a narrow spectral region (single wavelength) or over a broad spectral region (full spectra). The differences are illustrated in Figure 1.3, which shows the interaction of the pump and probe pulses with three different states, GS, ES<sub>1</sub>, and ES<sub>2</sub>. The pump pulse, represented by either the solid red or blue arrows from GS to ES<sub>1</sub>, generates a population on the ES<sub>1</sub> surface according to its energy and the Franck–Condon overlap described above. The subsequent absorption of a probe photon, represented by the dashed arrows from ES<sub>1</sub> to ES<sub>2</sub>, occurs following these same rules.



**Figure 1.3 Potential Energy Diagram of a Transient Absorption Experiment** The solid arrows represent the action of the pump pulse to move an electron from the ground state, GS, to the first excited state,  $ES_1$ . The probe pulse (dashed arrows) is a subsequent absorption into a higher lying excited state,  $ES_2$ .

In the experimental scenario of the blue pump pulse, the molecule is initially

excited into a higher lying vibrational level and the opportunity for vibrational cooling on

the ES<sub>1</sub> state exists. Supposing this happens on a timescale that is fast in relation to ground state recovery, this process should reveal itself in the excited state dynamics. At very early times, while the molecule is still in the initially prepared vibrational level, the red probe pulse will have sufficient energy to promote population into the ES<sub>2</sub> state. However, once the ES<sub>1</sub> state has vibrationally relaxed into lower vibrational levels, this red probe pulse no longer has enough energy to generate ES<sub>2</sub> population. This thought experiment is entirely analogous to monitoring the TA signal at a single wavelength. The full spectral data over the same time window would simultaneously reveal the absorption of all of the probe wavelengths depicted in Figure 1.3 at a given time delay. The actual process of collecting this data is described in detail in Chapter 2, however, a brief note will be made here that the detection methods necessarily bias single wavelength experiments for more accurate kinetic information (i.e. time constants for processes), while the full spectra data often proves invaluable for the assignment of those time constants to specific processes.

For the TA experiments described in this thesis, the pump pulse is moved in relation to the probe pulse, and results in three distinct periods in the data: negative time, time zero, and positive time. Time delays where the probe pulse reaches the sample before the pump pulse are referred to as negative time and display a value of zero in TA signals. In this scenario, the detector records only the ground state absorption of the probe wavelength, which is set to zero in TA data. Time zero occurs when the pump and probe pulses reach the sample at exactly the same time. And at positive time, a decreased pump delay causes the pump pulse to always reach the

sample before the probe pulse, leading the probe to monitor absorption signals from the excited state.

### 1.2.2 Conditions for Vibrational Coherence

Since the time duration of a Gaussian pulse and its spectral bandwidth are bound by a Fourier relationship:

$$\Delta v_p \Delta \tau_p \ge 0.441 \tag{1.2}$$

where  $\Delta \tau_p$  is the pulse duration and  $\Delta v_p$  is the bandwidth of the pulse, the shorter the time duration of the pulse, the larger the spectral bandwidth.<sup>12</sup> With short enough pulses, new features arise in the TA data. Once the pump pulse duration is less than the vibrational period for a particular vibrational mode in a molecule, that mode may now be excited; this corresponds to the "impulsive limit" for excitation.<sup>7,13</sup> Another way to think of this is the pump pulse may now have enough bandwidth to simultaneously excite multiple vibrational levels.<sup>14</sup> If these conditions are met, oscillatory features may be seen in the TA data which correspond to the motion of wavepackets on the potential energy surfaces.<sup>15,16</sup> This oscillatory feature results because "at a given time, the energy of the electronic transition is given by the vertical distance between two surfaces taken at the position of the wavepacket."<sup>13</sup> This means that as the wavepacket moves across the potential energy surface, the Franck-Condon factors change to higher or lower lying vibrational states, causing the absorption intensity to fluctuate. This wavepacket motion is illustrated simplistically in Figure 1.4, depicting the same two potential energy surfaces at different points in time. The far left case represents the wavepacket immediately after formation by the large bandwidth pump pulse. The

wavepacket moves across the excited state surface, with levels hitting the "turning point" of the vibrational level at different times (as can be seen in panels 3 and 4).<sup>3</sup> The wavepacket (and thus the observed oscillations) remains intact until vibrational dephasing has destroyed the coherence between the states (panel 5).



# Figure 1.4 Simplistic Depiction of Wavepacket Motion On an Excited State Potential Energy Surface

A view of two potential energy surfaces and the evolution of a wavepacket on the excited state surface with time is shown here from early time (left) to late time (right). The broad bandwidth pump (represented by the colors on the various vibrational levels) creates a coherent superposition in multiple vibrational levels. This wavepacket moves across the surface until reaching the other edge (panel 2). The exaggerated anharmonicity in this potential leads the vibrational levels to have different turning positions (panels 3 and 4) and causes the wavepacket to dephase (panel 5).

While Figure 1.4 addresses the picture of simultaneous excitation of multiple

vibrational levels, the work by Pollard and Mathies in the impulsive limit better explains the oscillatory signals originating from the ground and excited states, and even the solvent used in the experiment. Their models assume the pump-probe experiment consists of three field-matter interactions: two of which come from the pump pulse, and one that comes from the probe pulse.<sup>17</sup> For excited state absorption, seen in Figure 1.5, below, the two pump interactions (blue arrows) each serve to create a wavepacket on the first excited state,  $v_1$ , and these wavepackets move along the  $v_1$  surface from the forces applied by the excited potential energy surface. At some time delay, the probe pulse (green arrow) promotes one of these wavepackets to excited state  $v_2$ , producing an electronic coherence between  $v_1$  and  $v_2$ , where the two wavepackets propagate until they dephase.<sup>17</sup>



### Figure 1.5 Coherence in Excited State Absorption Signals

The pump pulse interacts with the ground state twice (blue arrows) to create two wavepackets on the  $v_1$  excited state surface. The horizontal arrows indicate the propagation of these wavepackets on the potential until the probe pulse (green arrow) moves one of the wavepackets up to excited state  $v_2$ . The wavepackets continue to produce oscillations in the TA signal until they dephase. Figure adapted with permission from reference 17. © AIP Publishing LLC.

The signals resulting from the ground state and solvent result from Raman processes, and are called impulsive stimulated Raman scattering (ISRS). Though the two processes are slightly different, they may generally be represented by Figure 1.6. Here, the first pump interaction creates a wavepacket on excited state  $v_1$ , which propagates on the potential energy surface until the second pump interaction moves this displaced wavepacket back down to the ground state. This pump created wavepacket on the ground state propagates on the ground state surface until the probe pulse excites it back to  $v_1$  (loss of ground state), or creates a second wavepacket on excited state  $v_1$  (resonance Raman).<sup>17</sup> If the pump pulse is nonresonant, as is the case for the visible pumps and solvents used in this thesis, the pump pulse interacts with a virtual level instead of an electronic excited state. The bandwidth of the pulse is sufficient to drive the vibrational mode on the ground state because it contains a pair of frequencies with a difference tuned to the vibrational mode in question.<sup>18</sup>

An important feature of these diagrams is that *displaced* and *moving* wavepackets generate the oscillatory signal observed. If the wavepacket has neither significant displacement from its initial position nor substantial momentum, it will not appear in the signal.<sup>17</sup> For the situation depicted in Figure 1.6, a very short pump pulse will generate a stationary ground state wavepacket and exhibit only signals from the probe-produced excited state wavepacket.

Since a wavepacket can be formed on either the excited or the ground state potential energy surfaces (or both), these oscillations represent the Raman modes of those states.<sup>19</sup> It is also possible to impulsively stimulate Raman modes in pure solvent, which is completely transparent to visible light. An example of this is seen in Figure 1.7



# Figure 1.6 Loss of Ground State Absorption and Raman Contributions to TA Signals

The two pump interactions (blue arrows) serve to create a displaced wavepacket on the ground state surface which propagates until the probe pulse (green arrow) promotes it back to the excited state  $v_1$ . This diagram is explicitly for ground state bleach, but the Raman diagram is only slightly different. In that case, the probe pulse creates a new wavepacket on  $v_1$ , such that wavepackets are moving on both  $v_0$  and  $v_1$  surfaces. Figure adapted with permission from reference 17. © AIP Publishing LLC.

below, where studies by Paul Champion and coworkers show the utility of using 45 fs pulses to resolve the Raman modes of chloroform in a TA experiment.<sup>20</sup> The oscillatory TA data collected in the time-domain is seen in the top panel, while the frequency components of the signal are shown in panel B after processing the data with Linear Predictive Single Value Decomposition (LPSVD) (see Chapter 2 for more details). For comparison, the traditional Raman spectrum of the compound is shown in panel C. The peaks in the power spectrum in panel B are located at 262, 362-368, and 668 cm<sup>-1</sup>, which are a good match for the traditional Raman peaks (panel C) at 262, 361-367, and

669 cm<sup>-1</sup>.<sup>20</sup> While this example demonstrates the efficacy of this method in nonresonant samples, it is equally suited to resonant samples.<sup>15,20,21</sup>



### Figure 1.7 Coherent Oscillations in Chloroform

Panel A shows the TA data for the entire time-domain trace as well as an expansion of the 100 fs-4 ps region of the data. Using a Fourier-transform based data analysis program on the data gives the results in B, which are compared to the traditional Raman spectrum in C. The accuracy of this method is reflected in the agreement between the TA retrieved oscillations and the Raman data. Figure reproduced from reference 20 with permission. © John Wiley & Sons, Inc.

## **1.3 Background on Vibrational Coherence**

## 1.3.1 Early Experiments - Diatomics and Organics

An early pioneer in the area of vibrational coherence was Dr. Ahmed Zewail and

his team of researchers who sought to map out the transition state of reactive molecules

and visualize bond breaking reactions. His efforts in the field were recognized with the Nobel Prize in Chemistry in 1999 for "for showing that it is possible with rapid laser technique to see how atoms in a molecule move during a chemical reaction."<sup>22</sup> Since its application in analyzing di- and tri-atomics<sup>23–25</sup>, this area of study has progressed to systems of large organic molecules where processes such as proton transfer reactions<sup>26</sup> and *cis-trans* isomerizations may be monitored.<sup>27</sup> While these works are important, the types of excited states, the density of excited states, and relaxation cascades are typically quite different for organic molecules than transition metal complexes.<sup>4</sup> However, they do highlight the ability of this technique to probe geometric changes in the molecule on ultrafast timescales.

### 1.3.2 Vibrational Coherence in Transition Metal Compounds

In the last decade, there has been an increased push to apply this methodology to the study of transition metal compounds. These systems allow for the ligand structure to be subtly modified while minimally affecting the electronic structure of the molecule.<sup>28–30</sup> The coherence studies on transition metal compounds include systems like Zn(II) cytochrome c, Pt dimers, Ru(II) terpyridine-type compounds, Pt and Os halides, Cu(I) phenanthrolines, Fe(II) polypyridyls, Cr carbonyls, and Cr(III) acetylacetonate.<sup>29–35,14,36,37</sup> These studies highlight the retention of coherence through excited state surface crossings, geometry distortions, ligand loss, and solvent interactions. The Ru(II) study, in particular, shows that vibrational coherence, due to the ligand distortion in a halogenated terpyridine, survived both ISC and IC from the initially populated <sup>1</sup>MLCT state to a <sup>3</sup>MC (metal centered) state.<sup>30</sup> In [Fe(bpy)<sub>3</sub>]<sup>2+</sup>, excitation into the <sup>1</sup>MLCT results in <250 fs relaxation through a large density of excited states to the
<sup>5</sup>T<sub>2</sub> lowest energy excited state accompanied by a 0.2 Å Fe-N bond length change.<sup>14,10</sup> The vibrational coherence observed by Chergui *et al.* was assigned to a N-Fe-N bending mode on the <sup>5</sup>T<sub>2</sub> state stimulated by this ultrafast Fe-N bond elongation during the excited state relaxation.<sup>14</sup> The studies on Cu(I) phenanthrolines reveal vibrational coherence that is damped out by a particularly large structural change.<sup>29</sup> In the ground state, Cu(I) is d<sup>10</sup>, preferring a tetrahedral-like coordination environment where the two phenanthroline ligands are 90° from each other. However, excitation into the <sup>1</sup>MLCT excited state produces a formally d<sup>9</sup> Cu(II) and a reduced phenanthroline ligand; the preferred structure of this compound is now a flattened, square planar-like geometry, portrayed in Figure 1.8, below.<sup>38,39</sup> Tahara and coworkers have studied three different Cu(I) phenanthroline systems with varying degrees of ground state structural distortion, afforded by substituents in the 2,9 positions on the ligand, and have observed vibrational coherence in the excited state for all three of them. The coherence seems to



## Figure 1.8 Large Geometric Flattening of Cu(I) bis-2,9-dimethyl-1,10phenanthroline Upon Photoexcitation

The ground state structure is seen on the left, where the ligands are perpendicular to each other, whereas the excited state structure, containing a Cu(II) center and a reduced phenanthroline ligand, flattens the two ligands to achieve a geometry closer to square planar. Reprinted with permission from reference 38. Copyright (2007) American Chemical Society.

dephase on the same timescale as the flattening distortion in each of these molecules, and the oscillatory signals are attributed to Cu-N stretching as the excited state is predicted to have shorter Cu-N bond lengths.<sup>35</sup>

While the examples discussed here highlight the use of MLCT excitations, which affect the M-L bond lengths and cause some structural changes, they also convey the high density of excited states and how analysis of vibrational coherence becomes complicated in the presence of so many surface crossings. The work in this dissertation removes some of these problems by focusing on Cr(acac)<sub>3</sub> and a structurally similar derivative, where there are nominally three potential energy surfaces composing the entire photophysical picture; the quartet ground state, a spin-allowed quartet excited state, and one doublet excited state lower in energy than the initial quartet state.<sup>40</sup> Therefore, there is only one surface crossing in any of the excited state dynamics. Also, the excitation for this system is a ligand field transition where an electron is moved from a nonbonding  $t_{2q}$  orbital to an anti-bonding  $e_q^*$  orbital, thus, the geometry of the excited state is expected to undergo a geometric distortion.<sup>5</sup> By studying the vibrational motions of this molecule in the excited state, both before and during the surface crossing event, we hope to identify the vibrational modes and/or geometric distortions responsible for the ultrafast photophysics observed in the system. In this way, synthetic modifications to the ligand set may be able to alter the timescale of these processes and provide a source of kinetic control in this system.

## 1.4 Contents of this Dissertation

All of the work in this dissertation focuses on the use of TA to investigate ISC in  $Cr(acac)_3$  and  $tris(2,2,6,6-tetramethyl-3,5-heptanediono)Chromium(III), Cr(TMHD)_3.$ 

Before any vibrational coherence could be collected in this lab, the instrumentation and data collection protocols had to be developed and refined to give reliable results. **Chapter 2** covers these aspects, detailing the specific laser setups used to collect this data and the various new programs that had to be written and/or used in order to collect and analyze the data. **Chapter 3** delves into the photophysical background of Cr(acac)<sub>3</sub> and Cr(TMHD)<sub>3</sub> and details the results of experiments utilizing <50 fs excitation pulses to produce vibrational coherence in these systems. **Chapter 4** details the results of ultrafast experiments conducted in fields up to 25 Tesla at the National High Magnetic Field Laboratory in collaboration with Dr. Stephen McGill and Dr. Michael Bishop. Here we hope to use the perturbations of a large magnetic field on the excited states to alter the relaxation dynamics in Cr(acac)<sub>3</sub> and Cr(TMHD)<sub>3</sub>. **Chapter 5** gives an outlook on this work and its impact on science both within this research lab and in the broader scientific community.

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## 2 **Experimental Methods**

This chapter will detail the various instruments used to collect the data presented in this thesis. Modifications or alterations to these methodologies will be addressed specifically in cases where they apply. The molecules described in this thesis were previously prepared by Joel Schrauben and were used without further purification.<sup>1</sup>

## 2.1 Steady State Absorption Measurements

All UV-Visible spectra were collected on a Varian Cary 50 UV-Visible Spectrometer. Typically sample solutions were prepared in 1 mm path length cells. The spectra were collected on the 'fast' setting after blanking with air, and then corrected for a baseline offset by subtracting the value at 800 nm where the sample absorbance should be zero. The flow cells would not fit in the cuvette holder intended for 1 cm cells and were manually held in front of the window. Static cells were held upright while they rested inside the cuvette holder. A comparison of spectra collected with the cell at different angles to the incident beam reveals minimal changes in the peak intensities, indicating that holding the cell does not introduce spectral inaccuracies.

## 2.2 Transient Absorption Measurements

Two separate femtosecond laser systems were used to collect the data presented in this thesis. They have been dubbed "Wile E" and "Road Runner" and will be described in detail below.

## 2.2.1 Wile E

This is the older of our two laser systems, producing approximately 120 fs pulses at the sample position. The system layout is depicted in Figure 2.1. The 76 MHz



#### Figure 2.1 Wile E Laser Table Layout

Cartoon depiction of Wile E. The red beam represents the 803nm light from the Mira and Regen. The white beam is the white light continuum generated in the  $CaF_2$  disc. The green beam represents the tunable pump beam, which is double passed over the delay line to give a ~13 ns time window for the experiment.

modelocked Ti:Sapphire oscillator (Coherent: Mira 900 Basic) is pumped by 532nm light from a 5.4 W solid state Nd:YVO<sub>4</sub> diode laser (Coherent: Verdi). The Ti:Sapphire output power is approximately 5 nJ/pulse, and the output spectrum is centered at 803 nm with 13 nm full width at half maximum (FWHM) as characterized by an Ocean Optics spectrometer. The oscillator output is routed into a Ti:Sapphire regenerative amplifier (regen, Positive Light: Spitfire). The regen is pumped at 1 kHz by a 527 nm, 6.8 W Nd:YLF diode laser (Positive Light: Evolution) and has an output of ~750  $\mu$ J/pulse at 800 nm. This beam is then split by a 70:30 beam splitter with the larger portion pumping an optical parametric amplifier (OPA, Quantronix: TOPAS) to create the visible pump beam; the remaining portion is used to create a white light continuum probe beam utilizing a continuously moving 6 mm CaF<sub>2</sub> disc, a stationary sapphire window, or a stationary 4 mm YAG window (see Appendix B for more information on the white light spectra generated by these media). The OPA output is sent through a telescope which expands the beam diameter to approximately twice its original size in order to mitigate divergence over the long beam path. The beam is then double passed using two retroreflectors (CVI Melles Griot) through a 1.2 m delay line (Aerotech: LMAC-095 actuator and a Soloist CP motion controller), which provides experimental delays out to approximately 13 ns. This is a major alteration to the experimental set-up from previous descriptions, and the hardware required extensive modifications to the LabVIEW programs that drive them, as detailed in Appendix C. To offset this 13 ns delay, prior to white light generation the probe beam is routed as 800 nm light on the table for a distance that compensates for the delay line and the path length inside the OPA. It is converted to white light just prior to the sample in order to minimize dispersion and to maintain the integrity of the white light probe. A small pick off (<10% reflectance) in the 800 nm probe just before white light generation produces the reference beam. The pump beam is attenuated to  $\sim$ 3-5 µJ at the sample position using neutral density filters. The polarization of the probe beam is set to magic angle (54.7°) with respect to the pump beam polarization at the sample position.

In single wavelength experiments, the probe wavelength is selected by inserting 10 nm band pass filters in the white light probe beam after the sample. The filtered probe light and the reference beams are detected by matched photodiodes (Thorlabs: PDA36A). The intensity of the reference beam is attenuated with an iris to match the probe intensity at negative time. By balancing the photodiodes at negative time and employing differential lock-in detection, the change in absorbance may be recorded

directly. The lock-in amplifier (Stanford Research Systems: SR810) is synchronized to a chopper (SR540) which modulates the pump beam at 445 Hz. The computer elements include a shielded BNC connector block (National Instruments: BNC-2110), a shielded cable (National Instruments: SHC68-68-EPM), and a data acquisition card (National instruments: NI PCIe-6320) which performs the analog to digital conversion of the signal. The delay line movements and data collection process are coordinated using a custom LabVIEW program written in the McCusker group; further details are given in Appendix C.

The data from Wile E presented in this thesis are the averaged result of at least 6 scans, where each scan corresponds to the average intensity value when the delay line visits each time delay in the forward direction and then the reverse direction (i.e. down and back). Solvent signals were collected at each wavelength of interest to establish time zero and the instrument response function (IRF). Fitting the cross correlation signals with a Gaussian function gives a FWHM of ~130 fs. A home-built data work up program (Appendix C) corrects the raw data to remove the lock-in's signal modification (scaling) and extracts the actual delta A values along with assigning standard deviation values to each data point.

Full spectra on Wile E are collected using Ultrafast Systems (UFS) spectrometers (CAM-VIS-2, grating #4, and CAM-NIR-1). The UFS visible spectrometer collects ~600 nm spectral window with the current grating. Unfortunately, the dynamic range of the complementary metal oxide semiconductor (CMOS) detector necessitates a large amount of ND filtering on the probe beam before coupling to the spectrometer, which is accomplished by focusing the beam into a 200 µm fiber,

matching the spectrometer dispersion. However, even at the tightest focal spot, the fiber typically cannot capture the entire probe beam leading to an inhomogeneity in data between data sets collected on different days. These challenges have led to a strong preference for the SPEX and its diode array (currently on Road Runner; see below for a full description), and therefore full spectral data recorded over the duration of this work were collected on the SPEX, regardless of laser system.

## 2.2.2 Road Runner

Road Runner is our newest femtosecond laser system and produces 35 fs pulses out of the OPA. The laser system is depicted in Figure 2.2 (below), and it is readily apparent from the number of optics on the table that there are many more possible beam paths for these experiments laid out on the table. The use of magnetic faceplate kinematic mirrors (Thorlabs: KS1R) and dovetail optical rails (Thorlabs RLA##00 family, where ## denotes the length of the rail in inches) have helped to make this system highly variable in very little time and with minimal realignment. All of the pump/probe configurations will be detailed below, but much of the data collection process remains the same and will be covered here first.

The oscillator in this system (Coherent: Mantis) is also a modelocked Ti:Sapphire laser. Unlike the Mira, however, the Mantis employs an optically pumped semiconductor pump laser (5 W, 532 nm) contained within the oscillator cavity to increase stability. The Mantis output (power of ~5 nJ/pulse at 80 MHz, with a spectrum centered 800 nm, >70 nm FWHM) is routed to the regenerative amplifier (Coherent: Legend Elite). The Legend also encompasses the pump laser within the regen footprint; however, the pump source is still an Evolution (6 W output, Coherent)

pumping the Ti:Sapphire rod at 527 nm at a 1 kHz rep rate. The Legend's 800 nm, 23 nm FWHM spectral output is 35 fs in pulse duration and typically 1.20 mJ/pulse. The output passes through at 70:30 beam splitter with 70% routed to an OPA (Coherent: OPerA Solo) to generate the visible pump beam and the other 30% is used as the probe



# Figure 2.2 Schematic of Road Runner Demonstrating the Variability in the Experiments Available With This System

The solid red beam is 800 nm light which is always routed on these paths. The dashed red lines denote optional paths for different probes (i.e. white light continuum or single color from the probe OPA). The many optics on the table reflect the flexibility of the system for multiple TA set ups. beam, either to generate a white light continuum via the 800 nm light or pumping the probe OPA (Coherent: OPerA Solo) to generate a single color probe beam. The time delays are accomplished routing the pump beam through a 1.2 ns delay line (Aerotech ATS100-200 actuator, Aerotech BMS60\_UFA motor, Aerotech Unidex 100 controller). Although the probe beam is also routed through a delay line (Aerotech ATS100-200 actuator, Aerotech 50SMB2-HM motor, Aerotech Soloist MP controller), this is used to compensate for pump path length changes in different experimental set ups, not to actively achieve pulse delays in real time during data collection.

For all of the data collection configurations, the angle between the pump and probe beams as they focus into the sample is kept at a small angle (4° or less) to minimize temporal broadening of the cross-correlation function.<sup>2</sup> Single wavelength measurements are achieved by coupling the transmitted probe beam to a monochromator (Jarrell Ash: MonoSpec 18; 1200 groove/mm grating, blaze 500 nm) where the output is directly incident on a photodiode (Thorlabs, PDA55). The reference beam is generated from a pick off (microscope cover slide) in the probe beam path, and this beam is irised in order to achieve balanced detection. The reference and signal photodiodes are analyzed by two lock-in amplifiers (Stanford Research Systems: SR810). The first lock-in records delta A directly by differential detection (A-B, where A is the signal photodiode and B is the reference) and the lock-in is synced to a chopper modulating the pump beam (SR540, 446 Hz). The second lock-in records only the reference photodiode signal  $(I_0)$  and is synced to the 1 kHz frequency of the regen timing box. In this way, drifts in I<sub>0</sub> over time may be corrected in the data during postprocessing. The X and Y signals from the lock-ins (signal in phase and at  $\pi/2$  phase to

the reference signal, respectively) are taken from the back panel via BNC and sent to a data acquisition card in the computer (National Instruments: PCIe-6320) by a BNC terminal box (National Instruments: BNC-2110) coupled to a shielded cable (National Instruments: SHC68-68-EPM) connected to the card. Data acquisition is accomplished using home-built LabVIEW programs which synchronize the stage movements with the outputs from the lock-ins. The data presented in this thesis represent the delta A values after averaging at least six scans. Single wavelength measurements were collected using a LabVIEW data collection program slightly modified from the program on Wile E where "one scan" sends the delay line in the forward direction for the specified number of points and returns to the starting position. This was done to avoid washing out the oscillations in the data through (possible) errors in stage positioning in the reverse direction.

Time-resolved spectral data are recorded by focusing the white light probe beam into a liquid light guide (Edmund Scientific, 4 mm core diameter) coupled to a SPEX 270M spectrometer equipped with an HC233-0900 image sensor (Hamamatsu) employing a diode array detector (C5964 NMOS, 1x512 pixel array). The diffraction grating inside the SPEX has 300 grooves/mm, as blazed at 600 nm (part number 510 19 095), which gives a linear dispersion of 12.4 nm/mm. The resulting spectral range of the diode array detector is approximately 300 nm. The power supply box for the detector, which also provides the appropriate interface for the computer, is connected to the PC card (National Instruments: NI 6052E) via a National Instruments SH68-68-EP cable, both of which were provided by Hamamatsu with the detector. The spectrometer

entrance slits are typically set at 1 mm (~5 nm resolution), but any differences will be explicitly mentioned with the data.

Data are acquired using a home built LabVIEW program. The first step is to collect "dark counts", which are the scattered pump photons that make it into the liquid light guide while the probe beam is completely blocked. This can be done either with the pump delay stage stationary, while sitting at the starting position (at negative pumpprobe delay), or as a function of the delay position if the scatter exhibits a strong stage position dependence. The next step is to collect the background, or ground state absorption spectrum, at negative time. This is done with both the pump and probe beams incident upon the sample as the LabVIEW program subtracts out the dark counts while collecting the background trace. After collection of the background is complete, the delay line moves through the desired time points while the computer subtracts out dark counts and ratios the background and positive time signals to generate delta A directly. Each one of these scans consists of a "down and back" data positions averaged together. Data work up has been described in detail in Allison Brown's thesis<sup>3</sup>, but briefly the raw data file consists of a matrix of pixel vs time intensity values. The pixels must be converted to wavelength using a calibration file, and the absolute times (stage position in time) must be converted to real times (corrected for time zero). Then this data may be plotted in a graphing program. For short time delays where spectral chirp is present in the raw data, spectra of the pure solvent are collected. The wavelength dependence of time zero in this solvent is fit with a double exponential function, which is then used to correct the probe dispersion present in the molecule's full spectra data.

## One Color Measurements



## Figure 2.3 One Color Experiments on Road Runner

Only one OPA is used for this experiment and the resulting beam is split into both the pump and the probe beams. The monochromator ("mono" in the figure) is used to tune the detection wavelength off of the central wavelength of the probe (pump) pulse.

This configuration utilizes only the pump OPA to generate both pump and probe

beams. The OPA output beam is routed to a 90° periscope to flip the polarization to

horizontal before passing through a folded prism compressor. The compressed beam

is picked off and sent toward the pump delay line where it is split by an anti-reflective

(AR) coated 30:70 (R:T) beam splitter (CVI Laser) into the pump and probe beams; this is depicted in Figure 2.3 (above). The pump beam, transmitted through the splitter, bounces off the retroreflector on the delay line and is routed towards the sample after passing through the chopper wheel. The probe beam is reflected off of the splitter and is routed through the probe delay line before a turning mirror sends it towards the sample. Both beam paths pass through an ND filter wheel (Thorlabs NDC-50C-4, 0-4 OD), a laminated thin film polarizer (400-700 nm, Thorlabs), an achromatic half waveplate (400-700 nm, CVI Melles Griot), and a plano-convex lens (Newport, BK7 glass, 400 mm focal length) before striking the sample cuvette. As previously mentioned, the angle of incidence for the pump and probe beams upon the sample is kept to a minimum, typically 4° or less. The thin film polarizers are used to clean up the beams' polarizations, while the waveplates are used to set the probe polarization at magic angle with respect to the pump polarization. This is checked using a cube polarizer in the sample position and monitoring the transmission on a power meter. After this polarization check, the variable ND filter wheels are adjusted to attenuate the pump power to ~5  $\mu$ J/pulse, while the probe power is set to 1/10<sup>th</sup> the pump power, typically 0.5 µJ/pulse. Single wavelength traces are then collected for both the molecule in solution and pure solvent. The pulse duration is characterized using cross correlation (XC) in the pure solvent and methanol (MeOH), and optical Kerr effect (OKE) or frequency resolved optical gating (FROG) in MeOH. Although methanol is known to give a shorter XC signal than commonly used solvents like acetonitrile (MeCN) or dichloromethane (DCM),<sup>4</sup> it is preferred here because it gives much cleaner signals in the OKE and FROG experiments. MeCN and DCM show long tails in OKE and FROG,

making the pulse duration ambiguous. A full description of pulse characterization is given in section 2.2.3, below.



## Two Color Measurements

## Figure 2.4 Two Color Experiments on Road Runner

The pump beam travels the same path as in the one color experiment but now the reflected beam from the beam splitter before the delay line is blocked. The probe beam travels through its own prism compressor to compress the beam before passing its delay line and being routed into the sample.

The term two color is used here to refer to the configuration where both OPAs are in use on the laser table. As you can see in Figure 2.4 above, the remaining 30% of the regen power transmitted through the beamsplitter at the regen output is steered into the probe OPA. The probe OPA output is then used as the probe and reference beams. The pump OPA output follows the exact same beam path as described in the one color experiment; however, the beam reflected off of the beam splitter before the delay line has been blocked. The probe OPA output strikes a mirror placed on a 3" dovetail rail, which accommodates the beam movement between ports as the wavelength is tuned. After this mirror, the beam is routed to a periscope set at 90° to flip the polarization before passing through the probe line's folded prism compressor. The compressed beam is picked off and steered through the probe delay line before rejoining the path used for the probe in the one color experiment. The pickoff in the probe line is still used as the reference beam for balanced detection. The probe polarization is checked using a cube polarizer in the sample position to ensure magic angle detection, and the powers are checked so that the pump is  $\sim 5 \mu J/pulse$  and the probe 0.5  $\mu J/pulse$ . If adjustment is needed, the appropriate ND filter is turned until the power is correct. The pulses are characterized using pure solvent employing XC, OKE, and FROG techniques as discussed for the one color experiments above. As both prism compressors have to be optimized independently, it is rare that two color experiments would occur in isolation of one color experiments. Typically, the set-up starts as one color, where the pump prism compressor spacing is optimized. Once this is set, the probe arm from the beam splitter is blocked, and the probe OPA is employed. For this reason, the above discussion

assumes that the pump polarization has already been cleaned up and set, and that only the probe polarization needs to be checked.

#### White Light Probe Experiments

If a white light continuum probe is desired, the regen beam transmitted through the beam splitter is routed around the table near the regen and Mantis before passing next to the probe OPA and joining the normal probe beam path on the probe delay line. This can be seen in Figure 2.5 below as the many red beams on the table. The routing on the table achieves the necessary delay to compensate for the pump beam passing into and through the OPA, as well as the distance added by the pump prism compressor.

The probe beam still passes through the ND filter wheel, but a different linear polarizer (Thorlabs: LPNIRE100-B) and waveplate are used to set the polarization of the probe beam, since the one and two color experiments use visible (400-700 nm) optics. These 800 nm optics are already set up further down the beam path, so the visible optics are simply removed from their post holders and set aside. The one/two color probe beam lens is on a dovetail rail and the rail carrier screw is loosened so that the post may be removed from the rail and the lens set aside. The probe turning mirror has a magnetic faceplate mount, so the faceplate may simply be disconnected and set aside to allow the beam to pass. After the 800 nm polarization optics, an iris is set to trim the beam down to a 5 mm diameter before the beam is focused with a plano-convex lens into a continuously moving 4 mm CaF<sub>2</sub> window. These parameters are based off of a report for very stable and spectrally flat white light continuum using CaF<sub>2</sub>.<sup>5</sup> Since



Megerle and coworkers have indicated that the white light generation is best when the input polarization matches the polarization axis of the CaF<sub>2</sub> in the mount, the waveplate

## Figure 2.5 White Light Probe Experiments on Road Runner

The regen beam is routed around the table to match the pump beam path length before being steered onto the probe delay line and following the optic path toward the sample. The 800 nm light is converted into a continuum (represented by the white lines) near the sample position and focused into the sample using reflective optics. Here, the transmitted probe may be coupled into the SPEX, shown at the end of the table.

is set for the best white light spectrum and the ND filter is adjusted to ensure a clean,

single filament beam is produced. The generated continuum strikes a parabolic mirror

and a flat mirror in a folded configuration which focuses and routes the probe beam to the sample (see Figure 2.5).

The pump beam follows the same path previously described for the two color experiments, but now the turning mirror on the rail is removed by loosening the rail carrier screw and removing the entire post holder from the rail, while the lens is pushed up the rail toward the white light set-up. With appropriate pump beam steering, this rail should ensure that the pump beam is the same pulse duration as that measured in a one color experiment and that the lens movement has not introduced any new dispersion to the pulse. As with the one and two color set-ups, the pump turning mirror creates an acute angle ( $\sim$ 4°) with the probe beam incident upon the sample. Since the pump and probe beams at the sample position must be checked and the pump polarization should be rotated to achieve magic angle detection.

The monochromator and the signal photodiode are initially moved over to this sample position to verify the pump/probe overlap as well as the pulse duration. Because the temporal response with the white light probe is longer than for two color experiments, this is not the typical set up for collecting single wavelength traces on Road Runner. Instead, the primary use of this set-up is to collect full spectral data, which is done by coupling the probe beam into the liquid light guide and using the SPEX and full spectra LabVIEW programs as discussed above.

## 2.2.3 Pulse Characterization Techniques

Due to the short nature of the pulses in this experiment, the IRF is determined using both the OKE signal produced by neat solvent and a typical XC. After extensive

trial and error with this short pulse system, we have discovered that the OKE signal is diagnostic of the pulse duration at the sample, while the XC signal gives a better depiction of the actual IRF of the system, accounting for optics after the sample as well (filters, etc). We believe this difference results from the origin of the recorded nonlinear signals, as detailed below.

The XC signal is recorded by placing a nonresonant sample, such as the pure solvent for a particular experiment or MeOH, in the sample holder. TA signals at short delays are then recorded as they would be for regular samples. Because the solution is nonresonant, the only signals present in the data result from the direct overlap of the pump and probe pulses in the solvent.

In order to record the OKE signal, a Glan-laser polarizer is placed after the sample, but before the monochromator. This polarizer, hereafter called the analyzing polarizer, is set perpendicular to the probe beam polarization. This is accomplished by monitoring the signal photodiode voltage on the oscilloscope while rotating the analyzing polarizer cube. The cube is set properly when the voltage reading is at a minimum. The reference photodiode is blocked completely and the data set is collected. The OKE experiment has the advantage of being much more sensitive to the simultaneous presence of the pump and probe pulses as it relies on the strong interaction of their electric fields with the solvent molecules to produce a polarization change in the probe photons so that some light is transmitted to the detector. Argawal<sup>6</sup> succinctly describes this process as follows: "the ordinary OKE process can be understood by two sequential processes: the pump pulse induces the anisotropic refractive index change in the medium and then the activated medium can change the

polarization direction of the probe pulse." In this way, the detector only records a signal when both the pump and probe are temporally overlapped in the sample. Conversely, typical cross correlation measurements rely on simple two photon absorption events and are therefore less sensitive to the temporal overlap of the pump and probe.<sup>4,7</sup>

The resulting data from OKE and XC measurements are fit with a Gaussian curve and the FWHM is extracted. The width of the pump and probe pulses may then be calculated through the following equation:

$$\tau_c = \sqrt{(\tau_{pu}^2) + (\tau_{pr}^2)}$$
(2.1)

where  $\tau_{pu}$  is the pump pulse duration,  $\tau_{pr}$  is the probe pulse duration, and  $\tau_c$  is the measured (convolved) pulse response.<sup>2</sup> For both the XC and OKE responses,  $\tau_c$  is the FWHM of the Gaussian fit. Since this is a one color experiment and the pump and the probe should be (approximately) the same pulse duration, this equation simplifies to:

$$\tau_c = \sqrt{2(\tau_{pu}^2)} \tag{2.2}$$

and therefore, a simple rearrangement of the equation yields the pulse duration of the pump (probe) pulse.

$$\tau_{pu} = \sqrt{\frac{1}{2}} * \tau_c \cong 0.707 * \tau_c$$
(2.3)

A more rigorous pulse characterization technique is FROG (Frequency Resolved Optical Gating) developed by Rick Trebino in the early 1990s.<sup>8,9</sup> The "frequency resolved" aspect of FROG is nothing more than collecting the full spectrum of the nonlinear response instead of passing the transmitted probe through a monochromator.<sup>10</sup> An algorithm is then used to extract the pulse shape and phase from

the 2D spectral and temporal data. A typical second harmonic generation (SHG) FROG setup is depicted in Figure 2.6, which highlights the similarities to a traditional autocorrelation experiment. An incoming pulse of an unknown time duration is split into two pulses which are then focused by a lens and overlapped in a nonlinear crystal where the frequencies combine to produce a photon at twice the frequency of the incoming pulses. As the time delay between the pulses is changed, the upconverted light only appears when the two pulses are interacting in the sample, and as such provides a measure of the pulse duration.



## Figure 2.6 Comparison of Traditional Autocorrelation and SHG FROG Techniques

Traditional autocorrelation (top) employing a second harmonic generation crystal (SHG) where the resulting signal is focused into a photodiode for detection. SHG FROG (bottom) simply replaces the photodiode with a spectrometer and appropriate detector (camera, diode array, etc.). Figure reproduced with permission from reference <sup>10</sup>. © John Wiley and Sons

The conversion from a traditional 1D experiment to a (2D) FROG experiment shown in Figure 2.6 applies to all pulse characterization methods: polarization gate (PG), autocorrelation (SHG), third harmonic generation, transient grating, and self diffraction. The only difference between these methods is the nonlinear phenomenon used to generate the signal. The data in this thesis utilizes PG FROG, as it makes use of the OKE setup with only a change in detection method to record both OKE and FROG signals, as seen in Figure 2.7. PG FROG has several other advantages over other methods, such as automatic phase matching between the pulses at the sample, unambiguous pulse and phase retrieval, and the resulting signals are the most intuitive of all the FROG configurations.<sup>8</sup> Also unlike SHG FROG, the experiment is largely invariant to the wavelength of the pulse; the analyzing polarizer in use is a broadband



### Figure 2.7 General PG FROG Configuration

The pulse in question is split by a beam splitter into both the gate and unknown pulse which are then crossed in a nonlinear medium (fused silica, carbon disulfide, methanol, etc) and the resulting signal passes through the analyzing polarizer and into the spectrometer. The unknown pulse polarization is rotated to 45° from the gate pulse polarization with the analyzing polarizer set to 90° from the pulse polarization. Figure reproduced from reference <sup>10</sup> with permission. © John Wiley and Sons

polarizer rated for use across the visible region. SHG throughout the visible would require a thin nonlinear crystal (100-300  $\mu$ m) at different angles depending on the wavelength of the pulse, and a UV detector to record the resulting signal. FROG

experiments characterizing white light continua have shown that crystal angle-dithering is necessary to achieve phase matching over the bandwidth of the pulse, adding another level of complexity to the experiment.<sup>10,11</sup>

The primary advantage of PG FROG is that you can readily see if the pulses are fully compressed or still contain some residual chirp and the kind of residual chirp (i.e. positive or negative) or pulse distortion. This is illustrated in Figure 2.8, below, which shows example data traces for PG and SHG FROG setups under various pulse conditions.<sup>8</sup> In the case of negative or positive chirp, PG FROG gives a distinct



### Figure 2.8 Example FROG Traces for PG and SHG FROG Geometries

The top row shows the spectral characteristics of the pump, with the time dependent intensity (solid) and phase (dashed). The second row shows the frequency dependent intensity (solid) and phase (dashed). The third row, however, depicts the instantaneous frequency (blue) and the group delay vs. frequency (green). The bottom two rows show the FROG trace response for the given geometry and pulse characteristic. Note the symmetry of the FROG response in the SHG geometry for both negative and positive chirp, whereas PG FROG is able to readily distinguish these cases. Figure reproduced with permission from reference <sup>8</sup>; some data from the original figure has been masked for simplicity. © AIP Publishing, LLC

response for each case, whereas SHG FROG gives identical results; this is the result of the unambiguous pulse and phase retrieval mentioned earlier. For SHG FROG, it would be possible to determine the sign of the chirp by adding a piece of glass to the beam path before the beam splitter (introducing positive chirp) and running the FROG trace again<sup>8</sup>, but this doubles the amount of work necessary to get to an answer readily available with PG FROG. Both PG and SHG FROG give clear indications when other issues are present in the pulse, such as self-phase modulation (SPM), or higher orders of phase distortions (cubic and quartic spectral phase). It is also readily apparent if double pulsing is occurring from one of the optics in the beam line, provided the distance between the main and artifact pulses is within the FROG collection window. These latter issues, SPM and higher order distortions, are not apparent in OKE traces, making FROG very beneficial to pulse characterization.

To collect FROG traces in the one-color set up described above, the monochromator is simply removed after collecting the OKE trace and the transmitted probe beam is coupled into the SPEX by the liquid light guide. A modified LabVIEW program, originally written by Dr. Michael Bishop, snaps the background pump photons incident on the detector at negative time and subtracts that from all positive time points, very similar to the dark counts in full spectra (details given in Appendix C: LabVIEW Data Collection and Work Up Programs). The scan is set up so the nonlinear response of MeOH is well surrounded by areas of zero signal: an "island in a sea of zeroes."<sup>9</sup> The program interpolates the pixel data to give a higher wavelength resolution and the resulting data file is written to a worksheet in a format amenable to the FROG analysis MATLAB programs, *vide infra*.

Once the FROG trace has been collected, it may be processed using an iterative Fourier transform (FT) and generalized projections algorithm.<sup>8,9,11,12</sup> The algorithm works to find both the intensity and phase of the pulse by solving for the electric field which best reproduces the collected FROG trace.<sup>12</sup> The resulting electric field must satisfy both data and nonlinear optical constraints; the data constraint pertains to the magnitude of the electric field in relation to the measured FROG trace, while the nonlinear optical constraint derives from the mathematical form of the signal field in the experiment.<sup>8</sup> The algorithm proceeds to minimize the electric field within one of these constraints, FTs the result, minimizes for the other constraint, FTs again, minimizes the electric field for the first constraint and so on until convergence is reached. This point is determined by comparing the resulting FROG trace to the original FROG trace until the error is sufficiently low. The FROG analysis programs used in this thesis were obtained from Professor Trebino's website<sup>13</sup> and used with minor modifications which will be detailed in Appendix F: FROG Algorithm Modifications and Their Employment. Altogether, three separate programs were needed, "binner", "frogger", and "PG XFROG." The FTs performed in the algorithm go faster with NxN data matrices, so "binner" works to zero pad the data to create an NxN matrix. "Frogger" is responsible for loading the now binned trace and running the iterative FT algorithm on the data until a suitably reproduced trace is obtained. "PG\_XFROG" is the program responsible for determining the electric field of an unknown pulse that is different from the gate pulse, vide infra.

In addition to fully characterizing a pulse by gating it with itself, FROG can also be used to determine the pulse characteristics for an unknown pulse of a different

frequency than a known gate pulse. This is called XFROG (cross-correlation FROG), and is employed to characterize the probe pulse in the two-color experiments. Since the pump pulse remains the same after being characterized for the one-color set up, it is now used as the known gate with the new probe beam from the second OPA. The general schematic for PG XFROG is shown in Figure 2.9.



## Figure 2.9 PG XFROG Experimental Configuration

The orange beam represents the fully characterized reference pulse of one wavelength while the red beam represents the unknown pulse of a different wavelength. The optics are exactly the same as in PG FROG, save for the beam splitter, making this extremely easy to employ for the two-color experiments. Figure reprinted with permission from reference <sup>14</sup>. © Optical Society of America

The data collection proceeds utilizing the same LabVIEW program as in PG FROG;

however, electric field is determined using the "PG\_XFROG" MATLAB program in this

case.

## 2.3 Complications with Shorter Pulses

One of the major differences between the set-up on Wile E and those on Road Runner is the prism compressor; but why is it only needed on one system? This section aims to explain the new challenges that arise when the pulse duration gets shorter. Much of the time and effort getting Road Runner to the current configuration stemmed from encountering and working through these challenges and so the big issues will be summarized here.

## 2.3.1 Prism Compression and Group Delay Dispersion

Any laser pulse duration is related to its spectral bandwidth through the uncertainty relationship, which limits the minimum product of these two quantities based on the pulse shape. For Gaussian pulses, this limit is 0.441, and pulses whose duration is equal to the spectral limit are said to be transform limited.<sup>15</sup> Practically, what this means is that shorter pulse durations require more bandwidth than longer pulse durations. Translating this into tangible numbers for Wile E and Road Runner means that Wile E's 120 fs pulses only require 3.31 nm of bandwidth for a 520 nm transform limited pulse, while Road Runner's 35 fs pulses require 11.36 nm of bandwidth at 520 nm to be transform limited. This increased bandwidth will be subject to group velocity dispersion (GVD) when passing through a transmissive optic, which means "the group velocity of light in a transparent medium depends on the optical frequency or wavelength."<sup>16</sup> Each wavelength will experience a slightly different delay passing through the optic, and with large bandwidths, this equates to a large broadening in the pulse duration (proportional to the bandwidth). This relationship between pulse duration and broadening is shown in Figure 2.10. Here, the effect of group delay dispersion (GDD) on an input pulse duration is plotted for four different lengths of BK7 glass. The GDD is simply the GVD multiplied by the length of the material.<sup>15</sup>

BK7 glass is a common material in lenses, which are used in all of the experimental setups described earlier in this chapter. Assuming 10 mm of BK7 glass accounts for all of the transmissive optics in the pulse train, 35 fs pulses broaden out to about 75 fs after passing through these optics. However, if input pulse is 120 fs, the 10 mm of glass adds only a few fs to the total pulse duration. 10 mm of BK7 glass is a

fairly reasonable assumption given the optics in the beam path required for the experiment: a waveplate, thin polarizer, ND filter wheel, lens, and cuvette face. GVD is therefore unavoidable via the current set-up. This is why special optics are needed on Road Runner to recompress the pulses after this detrimental broadening.



**Figure 2.10 Group Delay Dispersion for Various Lengths of BK7 Glass** The curves shown here represent the pulse broadening experienced by a 520 nm pulse as it passes through 1 mm (yellow), 5 mm (green), 10 mm (blue), or 20 mm (purple) of glass. The red curve shows the ideal case, where there is no pulse broadening, i.e. no transmissive elements in the beam path. Figure based off of data in reference <sup>15</sup>.

As mentioned above, GVD results from the wavelength dependence of the refractive index. This has two major effects on a pulse: angular dispersion and temporal dispersion, or chirp.<sup>17</sup> Positive chirp results in the blue wavelengths being slowed down as they travel through a medium, while negative chirp causes the red wavelengths to slow down.<sup>15,9</sup> Most transparent media causes positive chirp throughout the visible region.<sup>16</sup>

Retaining the 35 fs pulse duration at the sample position requires the implementation of negative chirp to reverse the pulse broadening from the optics in the pulse train. This is accomplished by capitalizing on the angular dispersion of a material, which causes blue wavelengths to exit the material at a sharper angle than redder wavelengths.<sup>17</sup> A prism compressor uses this phenomenon to negate the positive chirp induced while traveling to the sample. The prism compressor on Road Runner is in the folded geometry, meaning that the pulse passes through each prism twice. The first prism acts to spread the wavelengths in space, while the inverted second prism cancels out the angular dispersion. A mirror placed after the second prism reflects the beam back through the prisms so the spatial dispersion is undone.<sup>15</sup> Overall, the redder wavelengths are forced to traverse more glass in the second prism than the bluer wavelengths, allowing them to "catch up." This is shown in Figure 2.11, which demonstrates the introduction of negative chirp to a slightly positively chirped pulse. An optimally aligned compressor will introduce enough negative chirp to the pulse that after it passes through the optics on the way to the sample, it is transform limited.<sup>15</sup>

A folded prism compressor, while less complicated than a 4-prism compressor, still has multiple tuning elements. The prisms must be rotated to the minimum angle of deviation each time the wavelength of the input pulse is changed. This ensures that the exit face of prism 1 is parallel to the entrance face of prism 2 and minimizes reflective losses.<sup>18</sup> The distance between the tips of prisms 1 and 2 is the coarse tuning for the geometry-induced negative GVD, while translating the prisms normal to their base into (and out of) the beam fine tunes the positive GVD without changing the beam paths.<sup>15,18</sup> The reflection of the beam at a slight angle after prism 2 does slightly alter the



**Figure 2.11 Illustration of Angular Dispersion in a Prism Compressor** The input pulse entering this 4-prism pulse compressor has a large bandwidth but the pulse is relatively unchirped. The angular dispersion of the prisms creates negative chirp in the output pulse, where the red wavelengths are now lagging behind the blue wavelengths. To create a folded prism compressor, a mirror is inserted at the dotted line and the beam is reflected back through the first two prisms, following the light gray arrows.

dispersion introduced by the prisms, but the advantages of a less complicated and more

compact setup outweigh this disadvantage.<sup>15</sup>

The prisms used on Road Runner are made from LaKL21, which is useful for pulses longer than 25 fs and at wavelengths greater than 380 nm.<sup>15</sup> Its dispersion characteristics also allow the compressor to be more compact than if SF10 prisms were implemented; this is helpful given the space constraints on the optical table. These prisms are intended for use with horizontally polarized light, but the OPA output in the visible region is vertically polarized. In this case, the polarization is flipped by inserting a 90° periscope into the beam path. Unlike using a waveplate to accomplish this task, the periscope does not add chirp to the pulse.

The step-wise procedure for setting up a folded prism compressor is nicely detailed in reference <sup>15</sup>, and will not be repeated here. However, the material dispersion

information in that document led to the creation of a worksheet that will easily calculate the optimal LaKL21 prism spacing for any wavelength if given the right starting information. This worksheet is now used every time the laser is tuned and has been extremely helpful in speeding up the process of compensating for positive chirp. The worksheet calculates the prism spacing based on a few formulas, presented below, and the concept that the GVD intrinsic to the optical beam path for the experiment should be introduced in equal and opposite magnitude by the prism compressor.<sup>15</sup>

$$GDD_{pulse} = \frac{1}{4(ln2)} \sqrt{\left(\frac{c_B \Delta t_{out}}{\Delta v}\right)^2 - \left(\frac{c_B}{\Delta v}\right)^4}$$
(2.4)

$$\Delta v = \frac{c\Delta\lambda}{\lambda^2} \tag{2.5}$$

$$\frac{\lambda^3}{2\pi c^2} \left[ 4l \left\{ \left[ \frac{d^2 n}{d\lambda^2} + \left( 2n - \frac{1}{n^3} \right) \left( \frac{dn}{d\lambda} \right)^2 \right] \sin \beta - 2 \left( \frac{dn}{d\lambda} \right)^2 \cos \beta \right\} + 4 \left( \frac{d^2 n}{d\lambda^2} \right) \left( 2D_{1/e^2} \right) \right]$$
(2.6)

 $GDD_{prism} =$ 

$$\beta \approx -2\frac{dn}{d\lambda}\Delta\lambda \tag{2.7}$$

Here,  $c_B$  is pulse duration limit described earlier, which is dependent on the pulse shape (0.441 for Gaussian pulses),  $\lambda$  is the central wavelength of the pulse,  $\Delta\lambda$  is the spectral FWHM of the pulse in nm, c is the speed of light,  $\Delta t_{out}$  is the output pulse duration, *l* is the prism spacing,  $D_{1/e2}$  is the beam diameter at  $1/e^2$ , and n (along with its first and second derivatives) is intrinsic to the prism material, available in the paper. Equations 2.4 and 2.5 allow the user to quantify the GVD introduced by optics in the system completely in terms of observables. Once the GVD of the system is known for the wavelength of interest, equation 2.6 may be solved to determine the appropriate prism spacing for that wavelength. The worksheet only needs four values from the user to
determine the prism spacing:  $\lambda$ ,  $\Delta\lambda$ ,  $D_{1/e2}$ , and the uncompressed pulse duration ( $\Delta t_{out}$ ). A spectrum of the OPA output provides  $\lambda$  and  $\Delta\lambda$ , while the uncompressed pulse duration may be measured by removing the steering mirrors into and out of the prism compressor, allowing the beam to bypass the compressor altogether and still remain on the original beam path for a one color experiment. The final variable,  $D_{1/e2}$ , is easily measured using the set of irises set up for aligning the beam into the prism compressor. By placing a power meter after iris 2 and measuring the power as the iris diameter is decreased, the user may generate a Gaussian plot of the beam size which is easily fit to give the FWHM of the beam. While this is not the proper measurement of  $D_{1/e2}$ , the beam out of the OPA is slightly divergent and the FWHM at this position gives a good estimate of  $D_{1/e2}$ , which is actually the width at 13.5% of the intensity.<sup>19</sup>

The efficacy of the prism compressor is illustrated in Figure 2.12, below, where the uncompressed pulse is shown in blue, and the compressed pulse is shown in red. By fitting both of these data sets with Gaussians (seen as the smooth, solid blue and red curves), the pulse duration may be extracted. The fits here show that the uncompressed pulse duration is ~100 fs, while the prism compressor has shortened the pulse duration to 47 fs. Using the spectral information for the pulse ( $\lambda_c = 505.1$  nm,  $\Delta\lambda = 10.5$  nm), the transform limit is 35.7 fs, so the prisms could be adjusted further to yield a better compressed pulse. This adjustment is done iteratively, where the prism spacing is changed in one direction, the beam steering is adjusted to pass through the center of all the irises, and the OKE is collected again. If the pulse duration increases,

the prisms are moved the opposite direction. Typically, if the value for the beam diameter is correct, the worksheet will get the prism spacing right on the first try.



**Figure 2.12 Pulses With and Without Prism Compression on Road Runner** The red and blue dots are experimental data from OKE traces collected on Road Runner in the one color set up at 505 nm. The blue dots, representing the uncompressed pulse OKE response, have been fit (blue solid Gaussian fit line) to a pulse width of 101.8 fs. The red dots, representing the compressed pulse OKE response, have been fit (red solid Gaussian fit line) to a pulse width of 47.1 fs. The transform limit for this pulse is 37.2 fs, suggesting that the compressor could be further optimized.

# 2.3.2 Pump and Probe Overlap Angle

As Ziolek *et al.* have shown, the pump and probe intersection angle plays a large role in the cross-correlation width of the pulses.<sup>2</sup> The interested reader is referred to their paper for a full discussion of the pulse parameters and their effects on the measured FWHM of the cross-correlation, but the main points will be summarized here. In any pump-probe experiment, the probe beam diameter should be less than the pump beam diameter, and the optics are set up so that the beams cross at a relatively small

angle ( $\leq 10^{\circ}$ ). This study aims to address just how crucial this angle is under reasonable experimental conditions.

The authors chose values from their current experimental setup for their modeling, namely: 2 mm path length cell, 400 nm pump and probe pulses, pump beam diameter of 2 mm, and probe beam diameter of 0.2 mm. The top half of Figure 2.13 shows the results from modeling the cross-correlation of two 75 fs pulses at various intersection angles. The cross-correlation FWHM is largely unaffected by angles under 5 degrees, while the FWHM is roughly 50% larger by changing the angle to 10 degrees. The bottom half of the figure is the same modeling for two 20 fs pulses; the results of changing the angle are much more drastic. Here, even an angle of 5 degrees has affected the cross-correlation of the pulses.<sup>2</sup>

While this study has explicitly modeled pulses of the same wavelength, the importance of maintaining a small intersection angle for experiments utilizing short pulses is clear. This is why the set up for Road Runner places the sample a fair distance from the turning mirrors, since a smaller angle could be achieved if the distance to the sample was increased. As it is, the pump mirror cuts into the periphery of the probe beam ever so slightly in its current placement; any closer and the central part of the beam would be clipped.



Figure 2.13 The Effect of the Crossing Angle on the Resulting Pulse Width Modeled cross-correlation functions for pump and probe pulses centered at 400 nm, pump beam diameter 2 mm, probe beam diameter 0.2 mm, crossing at various angles in a 2 mm path length cuvette of acetonitrile. The top plot shows the results for input pulses of 75 fs, while the bottom models the response for 20 fs input pulses. Figure reproduced from reference <sup>2</sup> with permission.

# 2.3.3 Detection Wavelength and its Effects on the Observed Oscillations

Single wavelength collection on Road Runner is accomplished by passing the transmitted probe beam through a monochromator utilizing slits to give ~2 nm FWHM bandpass. Typically the monochromator is tuned to the blue and red edges at the FWHM of the raw OPA output spectrum. This tuning away from the central wavelength of the probe spectrum has been shown to affect the observed frequencies in works by Champion and coworkers.<sup>20,21</sup> In general, their observations showed that when the detuning from the central wavelength was minimal, lower wavenumber modes were

enhanced in the signals, while larger detuning resulted in enhancement of higher wavenumber modes. These observations were made for one-color experiments, and its applicability to two-color data will be discussed in more detail in Chapter 3 in the context of actual data.

## 2.4 Data Analysis Techniques

#### 2.4.1 Igor

Igor Pro (WaveMetrics, Lake Oswego, OR, USA) version 6.3 was used for the analysis of single wavelength and full spectra data contained in this thesis. The procedure for data processing and plotting full spectra data has been covered in previous McCusker group theses and will not be expanded upon here.<sup>3,22</sup> For single wavelength traces, built-in functions were used to fit the data. The Gaussian function was used to fit both XC and OKE traces; for the solvent traces (i.e. MeCN or DCM, but not MeOH), the time where the Gaussian returned to baseline was noted and used as the minimum starting point for fitting data on the molecule of interest. Mono- or biexponential fits with x offsets were used to fit data on the molecule of interest. Occasionally coherence data was fit with a tri-exponential function, which had to be added as a new user function, as this successfully minimized the residual.

The residuals from the exponential fits are further processed by the fast Fourier transform (FFT) routine to give the FFT magnitude of the frequencies. These output frequencies are in Hz, and are converted to cm<sup>-1</sup> for this thesis. To increase the resolution of the FFT, the data may be zero padded; see Appendix G: FFT Time Spacing and Frequency Resolution for more details. Any data presented in this thesis using zero padding will be mentioned explicitly.

#### 2.4.2 Linear Predictive Single Value Decomposition

The Linear Predictive Single Value Decomposition (LPSVD) analysis presented in this thesis was accomplished using MATLAB scripts acquired from Dr. Warren Beck after being modified by Dan Roscioli and originally written by Dr. Andrey Demidov and Dr. Paul Champion. The purpose of this program is to fit the data and extract the exponential components as well as the frequencies of the oscillations. An important difference here is that the damping times and the phases of these frequencies are also presented, which Igor is unable to do. The LPSVD results are presented in four graphs: the truncated data set overlaid on the full data set, the truncated data with the combined exponential and oscillatory fit, the residual of the truncated data after the exponential components have been extracted along with the oscillatory fit, and the power spectrum from the FFT of the fit. These are shown in Figure 2.14 below. The program also outputs a table of all the frequency components as well as the exponential components used to fit the data. The user has complete control over how many oscillations are used to fit the data, however, there are always at least two exponential components in the fit. One thing to note is that the power spectra from the LPSVD analysis are always smoother than those calculated in Igor for the same data set. This is because the LPSVD power spectrum comes from the FFT of the fit function, not the raw data. Further details on using the LPSVD program are presented in Appendix E: LPSVD Program Details.



## Figure 2.14 LPSVD Analysis Program Output Graphs

This is the graphing window which shows the results of the LPSVD analysis. The top left graph shows the raw data (red) and the truncated data (green) and uses numbers to show the points truncated: 62 in the beginning and 0 at the end in this case. The top right graph shows the data points of the pure oscillation (green) and the fit using 3 oscillations (blue). The bottom left graph is the truncated data (green) and the fit composed of both oscillatory and exponential components (blue). The bottom right graph is the power spectrum resulting from the FFT of the oscillatory fit curve.

# 2.5 Computational Methods

# 2.5.1 Gaussian Modeling

The starting geometries for all calculations were built using GaussView.<sup>23</sup> Geometry optimizations, frequency calculations, and single point calculations were performed using either the Gaussian '03 (G03) or Gaussian '09 (G09) software packages.<sup>24,25</sup> All calculations made use of the unrestricted B3LYP hybrid functional, composed of the LYP functional developed by Lee, Yang, and Parr and the Becke three parameter hybrid functional (B3). <sup>26–28</sup> All calculations employed the 6-311G\*\* basis set.<sup>29–32</sup> G03 calculations were carried out on the Michigan State University Chemistry

department computational server, Hydra, while G09 calculations were carried out on the High Performance Computational Center (HPCC) servers at Michigan State University.

# 2.5.2 Computational Details for Specific States

Over the course of this thesis work, the G09 software package became available to researchers at Michigan State University which is why some work was completed in G03, while some was completed in G09. This section aims to clarify how each state (ground or excited) was optimized for the molecules of interest in this thesis.

# Cr(acac)<sub>3</sub>: <sup>4</sup>A<sub>2</sub> Ground State

Ground state optimizations of Cr(acac)<sub>3</sub> in G03 were started using the crystal structure data. For these geometry optimizations, the ground state geometry was constrained to D<sub>3</sub> symmetry by freezing the dihedral angles for all methyl group protons. The system was optimized in both DCM and MeCN solvent continua, using the polarizable continuum model (pcm) and conductor-like pcm (cpcm) models, respectively.<sup>33</sup> Frequency calculations from these optimized geometries showed no negative frequencies, indicating a global minimum had been reached.

## Cr(acac)<sub>3</sub>: <sup>2</sup>E Excited State

This optimization was started from the previously optimized  ${}^{4}A_{2}$  ground state in an MeCN continuum using G03. The methyl group dihedrals remained frozen, while the total spin multiplicity of the system was changed to 2 from 4. The frequency calculations resulted in all positive frequencies for this geometry.

# <u>Cr(acac)<sub>3</sub>: <sup>4</sup>T<sub>2</sub> Excited State(s)</u>

The frequencies of the Franck–Condon  ${}^{4}T_{2}$  excited states were obtained using G09. Because the Cr(acac)<sub>3</sub> ground state structure had previously been optimized in

G03, it was re-optimized from the final G03 structure using G09. The calculations would not pass while retaining  $D_3$  symmetry, so the structure was allowed to reduce to  $C_1$ symmetry. This optimized ground state was then subjected to time-dependent density functional theory<sup>34,35</sup> to determine the ten lowest excited state energies. From these results, the three lowest energy states were chosen to for further study. Because the point group of the molecule is  $C_1$  symmetry, it can no longer support the  ${}^4T_2$ degeneracy, and so must split into three A terms.<sup>36</sup> These lowest three states are believe to be the split  ${}^{4}T_{2}$  state; this will be discussed more in Chapter 3. Each of these three states were then subjected to frequency calculations at the current geometry to give the frequencies of the  ${}^{4}T_{2}$  state in the Franck–Condon geometry. The frequency result files were expected to have, and all three did indeed exhibit, negative frequencies since this is not the stable geometry of the excited state. Attempts were also made to optimize the structure of each of these states using G09, but the optimization routine was having difficulty finding a global minimum under the conditions used; thus, this information is not currently available for this thesis.

# <u>Cr(TMHD)<sub>3</sub>: <sup>4</sup>A<sub>2</sub> Ground State</u>

The starting geometry for  $Cr(TMHD)_3$  came from the  $Cr(acac)_3$  crystal structure, whereupon the methyl groups were changed to *tert*-butyl groups, and the molecule was symmeterized (i.e. the *tert*-butyl groups were positioned at identical angles off of the acac backbone). The structure was then optimized in G03 employing the PCM model and DCM for the solvent. While the resulting geometry was formally C<sub>1</sub> symmetry, it was very close to C<sub>3</sub> symmetry; attempts to lock the dihedral angles of the *tert*-butyl

groups and optimize the structure under higher symmetry conditions were unsuccessful. The frequency results from the optimized geometry showed only positive frequencies.

As mentioned for the Cr(acac)<sub>3</sub>  ${}^{4}T_{2}$  excited states, the optimized ground state structure was submitted for re-optimization in G09. Unfortunately, this geometry optimization is not finding a global minimum, potentially due to the large variability in the rotation of methyl groups present in this molecule. Due to these complications, no data is currently available about the frequencies in the excited states of Cr(TMHD)<sub>3</sub>, for either  ${}^{2}E$  or  ${}^{4}T_{2}$  states.

APPENDICES

# Appendix A: Optics Details

All visible light mirrors (pump line and visible probe) are protected silver mirrors from Thorlabs unless otherwise noted. Part # PF10-03-P01 Desc. Ø1" (25.4 mm) round, Protected Silver Mirror.

IR (800 nm) mirrors are protected gold mirrors from Thorlabs; Part # PF10-03-M01 Desc. Ø1" (25.4 mm) round, Protected Gold Mirror.

Prisms – Newport – Part # 06LK10 Desc. Brewster Angle Dispersing Prism, Ultrafast, LaKL21, 15 mm, 370-2000 nm

Prism mount – Thorlabs – Part # KM100PM Desc. Kinematic mounting platform.

Prism clamping arm – Thorlabs – Part # PM3 Desc. Small Adjustable Clamping Arm, 6-32 Threaded Post

50:50 Beam Splitter – CVI Melles Griot – Part # BTF-VIS-50-2501M-C Desc. Standard Plate Beamsplitter, Round, optical crown glass, "visible" wavelength range, 50 R: 50 T, 1" diameter, anti-reflective coating. Thickness: 1 mm

70:30 Beam Splitter – CVI Laser Optics – Part # BTF-VIS-30-2501M-C Desc. Standard Plate Beamsplitter, Round, optical crown glass, "visible" wavelength range, 30 R: 70 T, 1" diameter, anti-reflective coating. Thickness: 1 mm

Variable ND filter wheels (both unmounted and mounted wheels) are from Thorlabs. Part # NDC-50C-4-A and NDC-50C-4M-A

Desc. (Un)mounted Continuously Variable ND Filter, Ø50 mm, OD: 0-4.0, Anti-Reflective Coating: 350-700 nm, UV Fused Silica Substrate. Thickness: 2 mm

Half wave plate – CVI Melles Griot – Part # ACWP-400-700-06-2 Desc. Air-spaced Achromatic half waveplate, air spaced quartz and MgF<sub>2</sub> components, coated for 400-700 nm light, 12 mm clear aperture, Thickness: 1 mm

Visible Economy Linear Polarizers – Thorlabs – Part # LPVISE100-A Desc. 1" linear polarizer; N-BK7 protective windows, 400-700 nm, polarizing film between windows. Thickness: 3.5 mm

800 nm Economy Linear Polarizer – Thorlabs – Part # LPNIRE100-B Desc. 1" Linear Polarizer; N-BK7 protective windows, 600-1100 nm, polarizing film between windows. Thickness: 3.5 mm

Lenses are typical BK7 glass out of the Newport lens kits available in the laser lab. Lenses are typically plano-convex with the plano side facing the incoming beam and centered so that the beam is still on its original linear path. Glan-Laser Polarizer – CVI Melles Griot – Part # CPAD-10.0-425-675 Desc. Glan-Laser double escape window linear polarizer; air spaced calcite prisms, (modified version of Glan-Taylor so less reflective losses), anti reflective coating for 425-675 nm light. 10 mm clear aperture. Thickness: 22 mm

Beam Splitter cube – Thorlabs – Part # PBS251 Desc. 1" broadband polarizing cube beamsplitter, wavelength range 420-680 nm, N-SF1 glass. Thickness: 1"

Rotation Stages – Thorlabs – Part # RP01 Desc. Manual rotation mount with continuous 360° rotation.

Single-Axis Translation Stage with Standard Micrometer – Thorlabs – Part # PT1 Desc. 3" x 4" Stage; 1" Translation Stage with Standard Micrometer, 1/4"-20 Taps.

Dovetail Optical Rails – Thorlabs – Part # RLA0300, RLA1200, RLA2400 Desc. Compact optical rails made for use with snap on rail carriers to provide rigid mechanical assemblies. Rails contain 4/20 holes over the length of the rail, but may also be clamped to the table using rail clamps. (RLA0300 is the 3" rail, 1200 is 12", 2400 is 24")

Dovetail Rail Clamps – Thorlabs – Part # RC1, RC2 Desc. Clamps made for use with dovetail rails. Used to couple optics to the rail. RC1 is a 1" clamp; RC2 is 2".

Rail Clamps – Thorlabs – Part # CL6 Desc. Wedged Table Clamp for RLA Series Rails

Amplified Silicon photodiodes are PDA36A on Wile E, and PDA55 on Road Runner. (PDA55 is no longer a valid part, they have been superseded by the PDA36A model; however, in practice these have been found to have worse signal amplitudes for the same incident light intensity.)

#### Appendix B: White Light Generation Media

This lab typically uses CaF<sub>2</sub> for the generation of white light, but the stability of this medium for wavelengths red of 650 nm is not very good. The biggest benefit to CaF<sub>2</sub> for white light generation (WLG) is its ability to generate a spectrum that extends below 400 nm.<sup>37</sup> However, on the occasion that the red part of the spectrum is of more use for the experiment, another medium should be used. Figure 2.B1 shows the intensity of white light transmitted through a solution of a  $[Ru(bpy)_3]^{2+}$  derivative, tris(4,4'-diphenyl-2,2'-bipyridine) ruthenium(II) bis(hexafluorophosphate)  $[Ru(dpb)_3](PF_6)_2$ , collected as the "I<sub>0</sub>" for full spectra, for four different media. Two different CaF<sub>2</sub> plates were tested, 4 mm and 6 mm thick, to examine the effect of thickness on stability, along with a sapphire plate, and a 4 mm thick yttrium aluminum garnet (YAG) plate. The pump wavelength for this continuum generation is 800 nm, which is the standard wavelength used in this lab for WLG, although the spectrum generated is known to have a dependence on the pump wavelength.<sup>37,38</sup> The steep drop in white light intensity around 520 nm is most likely due to the onset of  $[Ru(dpb)_3]^{2+}$ absorption, rather than a result of the material itself. Aside from the 4 mm CaF<sub>2</sub> plate, all of the media seem to generate approximately the same spectrum: a broad peak around 550 nm, followed by higher intensity, narrower peak around 710 nm. The sharp upswing around 760 nm is caused by the pump wavelength; and increase in the intensity of the white light spectrum in the vicinity of the pump wavelength has been seen in the literature before.<sup>38</sup>



**Figure 2.B1** White Light Generation Media and Their Stability in the Red These traces are the transmitted background through a sample of  $Ru(dpb)_3^{2+}$  during the set up for full spectra with various white light generation media; the absorption spectrum for this compound is shown in gray for reference. All traces from the white light media have been normalized relative to their intensity between 700 and 730 nm.

More critical than just the background spectrum of these media though, is how they behave during a delta A calculation. Negative time spectra for the media are shown in Figure 2.B2. These traces more effectively highlight this instability in the red for these different media, as the delta A calculation at negative time should be zero. The non-zero wiggles, however, show where the spectrum is highly variable and the background is not properly removed from the signal. These wiggles also appear in the positive time data, effectively obscuring significant dynamics in this region. As YAG has the best stability and therefore the least amount of wiggles, this medium is best suited for applications where wavelengths above 600 nm are of interest.



Figure 2.B2 Stability of White Light Media During Delta A Calculation

Under the same experimental conditions as, these are typical traces for negative time, highlighting the highly variable parts of the spectrum as non-zero amplitude. The YAG window (green) clearly shows the most stable performance in this part of the spectrum.

#### Appendix C: LabVIEW Data Collection and Work Up Programs

#### Wile E's Updated Data Collection Code

While the majority of the data collection code remains unaltered from previous McCusker group members who helped to write it, the specific implementation of the code needed an update in order to successfully communicate with the Soloist controller for the LMAC delay line. The primary difference being that the Soloist is looking for a reference number to be sent and retrieved at certain intervals and this number is altered after each new command, so it needs to be in a constantly running and updating structure. This necessitated the implementation of a while loop around the existing code; once the program was running, all values within the while loop would be read and scanned for changes while values outside the while loop would be ignored.

This also led to changing from a case structure to manage the different processes (home the stage, go to the starting position, start the scan, etc) to an event structure that triggered off of a button value change for each event. The advantage of the event structure is that a default case executes continuously while the while loop is running but no other event is happening. For the Soloist, this default event is sending and retrieving updated values from the controller, including the reference number. Despite these changes, the overall function of both the single wavelength and full spectra data collection programs is largely intact.

The full spectra program greatly benefitted from the addition of a built-in wait time vi which chose the appropriate wait time for the distance the stage was traveling. This meant that in a scan where late time points were added with a larger step size, that wait time did not have to be applied to the shorter steps taken in the early part of the scan.

For scans consisting of a large amount of points, these changes to wait times really added up. The proper wait times for step sizes were determined using the SCOPE utility included in the Soloist software. By monitoring the position error in time after having the delay line move commonly used step sizes, an average wait time for each step size was calculated. A vi was written with simple true/false logic to choose the correct wait time for a given step size or step size range. Immediately after the scan is started, an array is made for all of the delay line positions that will be sent to the controller during the scan. The wait time vi takes that array, computes the step size between every point in that array, and writes an array of the appropriate wait times. These arrays are both read off of an index value as the scan proceeds so that the appropriate wait time is always loaded with its corresponding new position value.

#### All Data Collection Programs

All of the data collection programs for both laser systems have been updated to accept a starting position in time, rather than steps, mm, or some other distance the particular delay line is looking for in a command. The advantage of entering the scan parameters directly in time (fs for Road Runner and ps for Wile E) is that the user can quickly and easily get the data they are after while the LabVIEW program does the appropriate unit conversions before sending the move command to the stage controller. An optimized structure to compile all of the delay positions required in a scan has helped remove redundancies when higher density early time points or low density late time points are added to the scan. The user simply inputs the information on the front panel for the starting position, step size, and number of points for higher density or late

time points and the LabVIEW program sorts all of the positions from closest to furthest and removes any duplicates from the array.

# FROG Data Collection



# Figure 2.C1 FROG Data Collection Program Front Panel

The program collects the spectrum vs. time data and plots the 2D data in the lower left plot, while the integrated intensity vs. time is shown in the lower right plot. The upper plot shows the spectrum at a given time point. Further details are given in the text.

This LabVIEW program was originally written by Dr. Michael Bishop at the National High Magnetic Field Laboratory<sup>39</sup>, but was modified to work with the Aerotech controller and delay line on Road Runner, as well as the SPEX and Hamamatsu diode array. In this way, no new instruments had to be acquired in order to collect FROG traces. The program front panel is seen in Figure 2.C1, and the details of the program are given below.

The "destination folder" specifies the user's desired file path, while the "file identifier" text box is the name of the file. Dr. Bishop added a background feature to append the timestamp to the end of this filename, and the full file path and filename are displayed in "file pathname string." Under the "delay line setup" column, the user specifies the start position (in time; just as in the regular data collection program), the step size, and the number of steps. In the "spectrometer setup" column, the user may adjust the diode array exposure time, the number of scans to average (more on this in a bit), and the start and stop "pixel" cutoffs. Typically, the exposure is left at 0.6 s, as this is the normal setting for full spectra data collection as well. The "scans to average" feature is not operational right now, but may be fixed in the future if more signal averaging is desired; the current data sets seem to be fine without it. The cutoff designations apply to "pixels" after the program runs an interpolation routine to increase the spectral resolution of the detector. While the diode array actually contains only 512 pixels, resulting in ~0.7 nm/pixel resolution, the interpolation routine decreases this number to 0.2 nm/pixel. Here the "blue W cutoff" tells the program the pixel to start with and "red W cutoff" specifies the length of pixels to keep after "blue W cutoff."

The values for "com port" and "scan mode" are never changed and default to the values shown when the program opens. The "spectrum x-axis" button toggles the x-axis of the top graph between pixel number and wavelength when setting up the baseline intensity on the spectrometer. Once the FROG scan has started, the x-axis of the top graph changes to the interpolated pixels (truncated by the blue and red cutoff numbers).

When the run button up in the toolbar is pressed, the first while loop controlling the baseline spectrum is started. The stage moves to the starting position (or optionally runs the initialization routine if the "initialize delay" button is depressed on the front panel) and the diode array pixels are read into the computer. At this point, the pump beam should be open to the sample, and this baseline reading is similar to the "dark counts" of full spectra collection; it will be subtracted off of all of the FROG spectra as they are collected at each time step in the scan. This data displays in the upper graph, updating in real time for any changes the detector sees. For the best signal-to-noise in the FROG trace, the pump and probe beams are allowed to the sample and the ND filter wheel after the sample is rotated until the leakage intensity of the probe beam is about 0.2. Then the probe is closed, and the spectrum is allowed to read a few iterations of the pump only background intensity before the "start scan" button is pressed.

"Start scan" ends the baseline spectrum while-loop and saves the last baseline reading as a "DC" file in the designated data folder. The next while loop starts, which runs the FROG data collection routine. This while loop is active until either the "stop scan" button is depressed or a spectrum is collected at all of the desired time delays. When the spectra are collected, they are passed into a sub-vi controlling the interpolation of the data, and the resulting data and associated wavelengths are truncated as specified on the front panel and then plotted in the bottom two plots. The bottom left plot is the full 2D data set, while the bottom right plot is the intensity after summing over all of the wavelengths at each time point. At the end of the scan, this

summed intensity data is sent to a pulse parameters sub-vi which evaluates the FWHM of the pulse and updates the "Int. Pulse FWHM (fs)" field.

After the scan is done (or the "stop scan" button has been pressed), the program saves two files, a .frg file and a .txt file. The .frg file contains a header with the information the FROG MATLAB script is looking for when reading the data (*vide infra*), and below is all of the 2D data from the scan where the each column is a different time delay and the rows pertain to wavelength. The .txt file contains the time points and wavelengths for the data set explicitly in the first two columns, followed by the 2D data set. Hitting the stop button located in the toolbar will avoid saving any of the data files.

#### Data Workup Programs

Over the course of this work, it became apparent that new data workup programs were necessary to fully examine the data. These new programs will be detailed here. The first update was simply adding a function to the existing single wavelength data workup program to remove a baseline offset. The main purpose of this workup program is to calculate the delta A values for the scan, but it needs to remove the scaling applied to the raw data values by the lock-in amplifier<sup>40</sup>, shown in equation 2.8, first.

$$Output = \left(\frac{Signal}{Sensitivity}\right) \times 10 V$$
(2.8)

Here, the signal is the raw difference intensity value (signal photodiode minus reference photodiode voltage), the sensitivity comes from a setting on the lock-in front panel, and 10 V is the applied scaling factor. The workup program removes this scaling while calculating the delta A values according to equations 2.9 and 2.10:

$$Delta A = log\left(\frac{I_0}{(I_0 - I)}\right)$$
(2.9)

$$I = \left(\frac{output}{10 V}\right) * sensitivity$$
(2.10)

The baseline offset correction is applied to the output values prior to this delta A calculation so that "output" here really represents "output - offset".

The front panel of the program is shown in Figure 2.C2, where the "# pts to ave" box indicates the number of negative time points to include in the offset removal. The "offset" box indicates the calculated average of these points which has been removed from the scaled data. The other inputs on the front panel relate to the delta A calculation and time zero correction, which have been previously described in Appendix A of Allison Brown's thesis.<sup>3</sup>



# **Figure 2.C2 New Data Workup Program With Baseline Correction** The new functionality here is the "# pts to ave" box which allows the user to select how many points to average for removing the baseline offset. The "offset" box displays the averaged value removed from the data.

The UFworkup program described above calculates delta A values for the average of all of the scans. As the coherence experiments required more scans with a much higher data point count than previous data collections, a new program was written to calculate the delta A value for *each scan* collected in order to look for intensity drifts or changes over the course of data collection. This new program functions in the same manner as the above mentioned program, but it reads each scan's data, removes a

baseline offset for that particular scan, calculates the delta A, and saves all of the worked up scans in a new data file as individual columns. These scans can then be plotted in Igor to look for instabilities in the data set, allowing the user to remove unstable scans from the average before working up that data further. The program front panel, seen in Figure 2.C3, looks exactly the same as the UFworkup program, however the "offset" listed here is the offset average for the last scan in the data set.



**Figure 2.C3 Examining Scan Stability With "Make Delta A's" Program** On the left is real data acquired on DCM in obviously unstable laser conditions. The traces go from red (scan 1) to blue (scan 14) and time zero is obviously shifting along with an intensity change. These instabilities are not always obvious in the average of all the scans, which makes this program immensely useful given the long scan times required in the coherence data collection.

In a similar program, the signal-to-noise value of the data set with each additional scan examines the effect of extended collection times on the quality of the data. Since a typical coherence scan consists of 495 data points with an 800 ms wait time for the delay line to settle between each move, the scans take ~11 minutes each. Originally data sets were collecting an average of 80 scans or more, but as this took over 14 hours, it was possible laser drift or instability was doing more to harm the signal-to-noise average than the increased data set length was helping. Figure2.C4 shows the front panel of the program, along with the results from a data set. The "start pt" box indicates

where in the data the solvent peak ends so that the signal-to-noise ratio is calculated for the molecule's signal only. The graph simply plots the averaged signal-to-noise value with each additional scan. For the data set shown here, the signal-to-noise drops after scan 18, indicating it may be beneficial to truncate scans 19-84 from the averaged data set. Further examination using the "Make Delta A's" program would reveal whether these scans should be truncated from the data set or not. The signal-to-noise program,



# Figure 2.C4 Calculation of the Signal to Noise of the Data Set With Each Additional Scan

The signal-to-noise program applied to a data set for  $Cr(acac)_3$  dissolved in MeCN. The initial signal-to-noise value in the stable region before scan 18 is not very high, but it drops in half by the end of the data set.

when applied to these previous data sets of 80 scans, helped determine the optimum

scan number for data collection of pure solvent or solutions. Based on the data sets

analyzed, 14 scans was adequate to reach a stable signal-to-noise value for solvent,

while a minimum of 28 scans was adequate for solutions. This helped speed up the data collection process while ensuring high data integrity.

The last new program for data workup resulted from discussions with Dr. Michael Bishop while collecting data at the National High Magnetic Field Laboratory. The data collection programs he had written for those experiments collected both the signal and phase values from the lock-in, which was different from existing protocols in the McCusker group. Dr. Bishop explained that the phasing may differ between molecules and by assuming the phase to be the same for all data sets, some of the signals may be smaller than they could be. This is a direct result from the phase sensitive detection occurring in the lock-in amplifier; the chopper input supplies a reference frequency for the signal, but the lock-in generates a sine wave which is applied to the signal by the phase sensitive detectors. A simplified diagram of this phase relationship can be seen in Figure 2.. By "phasing" the lock-in, the user is tuning the phase of the lock-in generated sine wave to achieve the best match with the phase of the signal.

The phase difference between the signal and lock-in reference sine waves is represented as  $\theta$ , and the signal and phase outputs of the lock-in are dependent on  $\theta$  as shown in equations 2.11 and 2.12.<sup>40</sup>

$$X = V_{sig} \cos \theta \tag{2.11}$$

$$Y = V_{sig} \sin \theta \tag{2.12}$$

As  $\theta$  deviates from zero, some of the signal will be thrown into the Y channel, while the signal in the X channel will decrease. By rephasing the data, however, this shifting may be reversed and all of the signal will be displayed in the X channel. That is the purpose

of the program "Rephase the Data" shown in Figure 2.. Along with rephasing the data, the phase can also be completely removed by applying the following relation:

$$V_{sig} = \sqrt{(X^2 - Y^2)}$$
(2.13)

Equation 2.13 gives the magnitude of the signal vector, which is not dependent on phase.<sup>40</sup>



# Figure 2.C5 Simplified Representation of the Signal, Reference, and Lock-in Reference waves at the Phase Sensitive Detectors

The reference box wave (red) represents the chopper frequency into the lock-in, while the middle wave (blue) represents the signal being modified by the chopper frequency. The bottom wave (green) represents the sine wave generated by the lock-in; the phase of this wave is adjusted to maximize the signal out of the phase sensitive detectors.



# Figure 2.C6 Rephasing Data Collected by Lock-in Amplification

The program works with either raw data traces (i.e. pre-delta A workup) or worked up data traces and their corresponding signal phase file. The names of the files of interest are specified in the respective boxes, along with the scan number to read. "Applied Phase" represents the  $\theta$  offset to apply to the data and the resulting data trace may be seen in the top graph, while the phaseless data is seen in the bottom graph. See the text for more details.

The program is constructed to handle either raw or worked up "X" data; if raw data is supplied, the data is passed in as rows which is the format the subsequent calculations are expecting. If the data has been worked up, the data file will be in column form, and so a transpose must be applied by pressing the "Amp Transpose" button. To specify the data files, the combination of the file path, amp name, and

phase name boxes is required. For this example. the path is "C:\Users\Eileen\[]Research[]\Data\Cr(tbut)3\15Aug26\15Aug26a" where the amplitude is contained in file "15Aug26a" (a raw data file), and the phase is in the file "15Aug26aSig ph." The amp name and phase name strings are appended to the file path, so no further information needs to be entered into the amplitude name box. However, if the worked up trace was desired, amp name should read "wu" and the amp transpose button should be pressed. The time axis spacing is taken from the amplitude file, so the phase data will plot using that x-axis, no matter which amplitude file is chosen (raw or worked up).

The "amp row" and "phase row" specify which row (or column if the amplitude is transposed) to plot in the top graph. For this example, a total of 15 scans were taken, but since the raw data file includes a row of the stage position in steps and then a row of the stage position in time, there are actually 17 total rows in the data file. LabVIEW starts the index at zero instead of one, so 16 in the "amp row" box refers to the last row in the amplitude data file. The signal phase file, however, does not contain stage positions, so the last scan number is generally used. Note: this currently assumes that the phase is identical for all scans and this may need to be modified in future versions of the program.

The signal and phase values are ported into a built-in LabVIEW function that converts real (X) and imaginary (Y) components into polar components, r and  $\theta$ . The "applied phase" slider value on the front panel is converted from degrees to radians, and this phase shift is added to the raw  $\theta$  value before the r and " $\theta$ " (now phase shifted) values are converted back into real and imaginary components and re-plotted. Since

this program runs in a while loop, the top graph plotting the rephased data updates in real time as the phase shift is changed. The red phase trace may be scaled by updating the "phase scaling" box, making it easier to see the best phase shift. Also for convenience, the phase is fit with a linear function and the residual of that fit is shown on the front panel, along with the maximum phase value; with proper rephasing, both of these values should be minimized.

The bottom plot displays the phaseless data, computed according to Equation 2.13 above. Once the user is satisfied with the rephased data, the original signal, rephased signal, new phase values, and phaseless data are saved to a worksheet with "\_[phase shift]" appended to the amplitude file name; [phase shift] is the degree phase shift applied at the time the while loop was stopped. It is important to note that this information only saves when the square "stop" button (located below the applied phase slider) is pressed, not when the stop button in the toolbar is pressed. This was done as a convenience when the wrong data rows or filenames were chosen before the program started running so that "junk" files would not be saved.

#### Appendix D: Performing FFT Analysis in Igor

For the coherence data where a FFT is desired, several additional steps are necessary. First, the data is fit using the exponential x-offset functions, and the residual of the fit is added to the graph. This may be done automatically by navigating to the "output options" tab in the Curve Fitting window and changing the drop down by "residual" to "\_auto trace\_." This isolates the oscillatory feature for the FFT process after the population dynamics have been removed from the data. The cursors are placed on the residual trace at the first and last points of the oscillatory feature to select this range for the FFT routine. Typically, the data imported to Igor uses time in fs or ps, but the FFT routine needs to have the time in s. The simplest way to do this is to change the wave scaling ("data" menu  $\rightarrow$  "change wave scaling") of the delta A wave by inputting the appropriate values for the X axis start and delta between points in seconds. Since the section of data within the cursors is all that will undergo the FFT process, the start point is the x value of the first cursor and the delta is the tie spacing between points, typically 5E-15 seconds. From here, the FFT may be done by accessing the Analysis menu and then selecting "Fourier Transforms..." which launches a new window. Selecting "from target" under the source wave box restricts the options to those displayed in the top graph. The FFTs shown in this thesis are magnitude FFTs, where the cursors were used to denote the input range (if the input range does not satisfy the FFT requirements, a blue box will appear around the values; simply subtract one off of the B cursor to allow the routine to run). Select the box that says "display output wave" to show the FFT trace in a new graph where the x-axis is frequency in Terahertz (THz) and y-axis is the FFT magnitude. A separate excel sheet has been set

up to convert the THz numbers to wavenumbers (cm<sup>-1</sup>) and these values are noted on the graphs.

#### Appendix E: LPSVD Program Details

The main script, runsvd9.m, prompts the user to select the appropriate raw data file to open, plots the data in a separate graphing window, and then prompts the user to confirm that this is the appropriate data set. This script is looking for data files that contain only two columns: time, formatted to account for time 0, and data in delta A form. This means that the current data files acquired from the data work-up LabVIEW program have to be opened and the errors column must be removed from the file before it is resaved.

After confirming that this is the correct data, the program asks if the time scale needs to be converted from microns, if the data need to be flipped on the time scale, and if the data need to be shifted. These first two prompts (unit conversion and flipping) must have resulted from the specific way Champion and coworkers collected their data, but they are not employed with the data in this thesis. Data shifting may be used to adjust time 0 if necessary; however, this is usually adjusted before the data is opened in the program.

After the adjusted and shifted data is re-plotted in the graphing window, the program asks the user how many starting points to cut. This has typically been predetermined from working up the data in Igor, but the user may take a guess as the values may easily be changed. The starting point is chosen after the solvent XC signal goes away. The program then asks for the number of ending points to cut, which is always set to zero for the data in this thesis. After entering the starting and ending points to cut, the truncated trace is presented in green over the raw data trace in red in the graphing window and the user is prompted to confirm that these points are

acceptable. If the user enters no, the starting and ending points are chosen over again; if yes, then the script moves on and these points may not be changed without starting this analysis over from the very beginning.

With the truncation point set, the script is now ready to run the single value decomposition (SVD) fitting routine. The user is now prompted for the number of oscillations to use in the fit. For the data in this thesis, this number started at two and was increased to five or six. The results were then compared and the best fit with the fewest oscillations was chosen as the optimal fit. The next prompts set values for the optimization routine; the starting and ending orders of the Hankel matrix and the step size. Acceptable order values range from four to 394 depending on the data set. Here the starting order is always four and the ending order begins at 100 but is adjusted by watching the optimization routine. If the optimized result comes from the 95<sup>th</sup> iteration, the routine is run again with an increased ending order to ensure that this is not a local minimum. The step size used here is 1 and larger steps sizes were not tried.

The program is now set to begin the SVD routine, and asks the user if they would like to control the fit. If answered no, the routine runs automatically stepping through the Hankel orders incrementally; if yes, the routine stops after every order and waits for the user to press any key before moving on to the next order. A prompt after this deals with the speed of MATLAB and prompts the user to allow "switching of display" to speed up the calculations. This option removes the two graphs presenting the data and the current fit line (i.e. the truncated data with and without exponential components and the fit). If the user inputs "no", the graphs update every order along with the power spectrum for the current order; "yes" presents the user with a prompt to still monitor the

power spectrum of every order and the other two graphs are populated when the routine finishes the last Hankel order.

As the routine optimizes the fit, a table in the main MATLAB window updates the user on the current Hankel order and the order with the best fit so far. This best fit order number is the one used to determine if a higher ending order is necessary, as mentioned above. Once the SVD routine has finished, the program prints a calculation results section in the main MATLAB window. Here the values for the data shift, starting and ending truncation points, data points in the set, oscillations fit, and the optimal order of the Hankel matrix are presented. Below that is the table of the oscillatory and exponential components of the optimal fit. The table contains both positive and negative frequencies of the oscillatory components, owing to the double-sided nature of the FFT; only the positive frequencies will be reported here. The user is then prompted to print the graphing window, save all of the graphs and the results table, along with the options to remove frequencies and try the whole procedure again. The latter brings the user back to the truncation stage of the routine, where the starting and ending points may be adjusted as well as the number of oscillations in the fit. The option to remove frequencies has never been used, but it allows the user to adjust the left and right edges of the frequency window, in principle to determine the contributions of the major frequencies in that window.

# Appendix F: FROG Algorithm Modifications and Their Employment

# FROG Scripts

The scripts needed to work up FROG traces were written to use MATLAB's graphical user interface (GIU). For this reason, these are more intuitive to work with for users intimately familiar with LabVIEW. The first script the user needs to open is "binner". This launches the GIU for the binning program, who's main function is to turn the data into an NxN array in order to speed up the FT process in the FROG algorithm.<sup>9</sup> Along with the binned trace dimensions, the user has complete control over extracting a subset from the total 2D plot to bin, how much background subtraction to perform, and where to center the traces prior to binning.



#### Figure 2.F1 Binner Program Main Panel

This is the binner program<sup>13</sup> after the raw data trace has been loaded into the program. The top tabs, "calibration", "extract", "Background", "Centering", "Filter", and "Binning", relate to the different functions of the program. See text for more details.

As seen in Figure 2.F1, the binner program displays the full 2D trace of the data,

displayed in a colorized intensity plot where black and/or red represent low intensity
values and blue and/or white are high intensity values. The vertical axis here corresponds to the spectral domain and so the trace to the right of the 2D plot corresponds to the pulse intensity vs. frequency. Similarly, the bottom axis for the 2D plot is time, and so the trace displayed below the colorized plot is the pulse intensity vs. time. Figure 2.F2 shows the data after background subtraction has been completed.





The background subtraction was performed by iterating between subtracting a constant delay and subtracting a constant frequency. The "delay points" and "frequency points" boxes indicate how many rows/columns to average before subtracting that value from all of the data. Typically, subtracting a constant frequency has the largest impact because of the slight polarizer leakage of the probe beam. Once the pulse intensity is well isolated (i.e. near zero background outside of the pulse envelope), it is ready for binning.

On the binning tab, the user has the option to select the bin size, binned width % (whether to zero pad the trace while binning), and which axis to fit while binning the other to create an NxN array. These parameters are more thoroughly described in the "read me" file that downloads with the code, and most have been left unchanged from the default values.<sup>13</sup> The "axis fit" was set to wavelength for the data in this thesis because the wavelength axis typically had more data points in the original data set than the time axis. Empirically, this gave better binned trace results as well. A trace that has been binned along the wavelength axis can be seen in Figure 2.F3, below. The



# Figure 2.F3 Binned Trace Ready for the FROG Algorithm

The background corrected trace has now been binned along the time axis, extending the time axis from  $\sim$  -150 to 105 fs to  $\sim$ -400 to 400 fs. A slight change in the range of the wavelength axis has occurred as well to ensure the data length was a power of 2.

resulting binned trace is now ready to be saved and then imported into the program that

will run the iterative FT algorithm, "frogger".

"Frogger" is set to load with an example data set and fit results in all of the graph panels, as can be seen in Figure 2.F4. The user then opens a binned FROG trace to work up. The program makes an initial guess as to the electric field and plots that in the retrieved pulse graph. There are also graphs displaying the temporal intensity and phase of the pulse, as well as the spectral intensity and phase of the pulse. The remaining two plots show the error between the binned FROG trace and the retrieved FROG spectrum, as well as the values for the different minimization parameters.



**Figure 2.F4 The Frogger Program Just After Launching from MATLAB** This is the frogger GIU window where all of the information and errors for the retrieved pulse will be displayed.

After loading the data set, the proper pulse characteristics must be chosen. As discussed above, the electric field derives from the specific nonlinear response occurring to give the recorded signal, so the proper nonlinearity must be chosen for the result to make physical sense. The drop down menus for the "domain" and "algorithm" options are reduced to just one choice after PG is selected as the nonlinearity. The

program is now ready to solve for the electric field of the pulse and the algorithm is started by hitting the "run" button.



# Figure 2.F5 The FROG Algorithm At Convergence

The reconstructed trace closely resembles the binned FROG trace (top left) except for some intensity around the center of the pulse, which is highlighted in the Difference plot. The intensity of the temporal and spectral profiles of the pulse are shown with solid lines, while the phase is shown as a dotted line. The error values are changing out in the 4th decimal place with each iteration, showing that a minimum in the fit has been reached. The agreement of the reconstructed trace indicates this is a valid solution for the electric field.

The results, seen in Figure 2.F5, are easily saved for all of the values shown (spectral intensity and phase, temporal intensity and phase, reconstructed trace, etc) and the user may select which minimization to save, the Z error determined pulse information, the G error determined pulse information, or the current iteration's pulse information. For this thesis, the Z error was saved because the algorithm is set to a Z minimization routine. The "frogger" GUI code is not able to handle XFROG data, so a different script must be used to analyze that data.

# XFROG Script

The code provided by Prof. Trebino on his website includes a folder called "Demo" that contains a program called "PG\_XFROG\_Auto." This program encompasses both the binning and electric field retrieval steps. Since the user has more control using the GIU "binner" program from the FROG workup, the sub-routine "PG\_XFROG" responsible for the electric field retrieval in "PG\_XFROG\_Auto" was reworked to be a stand-alone program and accept the file format from the "binner" output. Other modifications were made to ensure the output graphs plotted in a single window to make data comparison easier between the original and retrieved XFROG traces. The results of a converged XFROG analysis are shown in Figure 2.F6.



# Figure 2.F6 The PG\_XFROG Program Showing the Results of a Converged Algorithm

The graph windows displays many of the same parameters seen in the "frogger" GUI, but it does not display the phase information. Also the gate pulse intensity in the time domain has been added for reference. When the MATLAB script has finished, it prints the final G error, the time-bandwidth product for the pulse, and the pulse FWHM in both fs and nm.

One major advantage of the PG\_XFROG program is that it only plots the various

spectra once the algorithm has reached convergence, so the entire process tends to be

faster than running the "frogger" program on a similar pulse. Program modifications to

the default folder location when more data is needed have also speed up the process.

The program remembers the path where the XFROG trace originated and prompts the

user to select a gate pulse from that same folder. Since the binned traces and FROG

results data are typically saved in the same location as the original FROG and XFROG

data, this makes sense. The program also now only displays files with the proper

extension for the data it needs (i.e. a binned XFROG trace ends in .bin, but the gate pulse file ends in .Ek). The updated PG\_XFROG code is included below with comments in green.

### PG\_XFROG.m

```
function PG XFROG(frog1, guess flag)
% PG XFROG.m
0
% This is a script for the automated retrieval process. This example
%is a PG XFROG problem, with a measured gate from a GRENOUILLE 8-50.
%If PG FROG is being used, simply change the gate pulse to itself. Of
%course, another geometry will also have to change the form of the
%gate, and the FROG algorithm that the program calls.
% See also: PG XFROG, binner cmd demo, calibrate, qFROG TX,
%frog wtol x, frog wtol
% By Jeff Wong (GaTech) - 2011-08-09, 2022
% === START ===
warning off
fprintf(1, 'Start PG XFROG\n');
% Find the name of measurement made by GRENOUILLE
if nargin < 1;</pre>
    [fdat,pname1]=uigetfile('*.bin.frg','Get XFROG Data File');
    frog1=[pname1 fdat];
end
[PathDir,FileName,Ext]=fileparts(frog1);
SaveName=strcat(PathDir,FileName);
% "frog1" is the "name cal bin" composed in "PG XFROG auto"
gren name = regexp(frog1, ' ', 'split');
gren dir = gren name{2};
temp cmd = sprintf('dir(''%s/*Temporal*'')',gren dir);
temp list = evalin('base',temp cmd);
gren path = sprintf('%s/%s', gren dir, temp list.name);
clear gren name gren dir temp cmd temp list
if nargin < 2;</pre>
    guess flag = 1;
end
```

```
%Gives all of the variables a "***1" name so you know it's from the
first
%pulse loaded in.
if strcmpi(frog1, '')
    % Load trace1 from GUI
    [Asiq1,tau1,freq1,dtau1,f01,df1,NumD1,NumL1,filename1] =
frogload();
else
    [Asig1, tau1, freq1, dtau1, f01, df1, NumD1, NumL1, filename1] =
frogload(frog1, 'delay');
end
% Start timer
tic:
% Initialize constant
w1=2*pi*freq1;
N = length(tau1);
G1 = Inf;
Et1B = [];
% BG Subtraction, aggressive BG subtraction may result in non-physical
% trace that the algorithm cannot retrieve.
flag20=input('Do you want to run background subtraction? (y/n)
','s');
%if flaq20 == 'y'
%Asiq1 = Asiq1 - 0.008;
%Asig1 = nonegatives(Asig1);
%end
% Take the square root of Asig for Magnitude Repel
Asig1 = sqrt(Asig1);
%% Define the initial guess method
dt1 = mean(diff(tau1));
lam01 = ltow(w1);
% UI input if input method is not provided from the parent.
method = {'Gaussian', 'Random'};
if ~(quess flag)
    fprintf(1, 'Please select initial guess from menu...\n')
    guess flag = menu('Select Initial Guess', 'Gaussian', 'Random');
end
fprintf(1, 'Using method: %s\n', method{guess flag});
% Choose between Gaussian and Random. Modification can be made if you
have
% other preferences.
switch guess flag
```

```
case 1
        % Start with Gaussian
       [Et1,t1, Ewdum,wdum]=pulsegenerator(N, @fgaussian, 75, dt1,
lam01, [0], 0, [0,0,0]);
    case 2
        % Start with Random
        [Et1,t1, Ewdum,wdum]=pulsegenerator(N, @rand, 75, dt1, lam01,
[0], 0, [0, 0, 0]);
end
%% Read the GATE Pulse from GRENOUILLE
% Only required because this is an XFROG example. Ignore this part if
vou
% are working with normal FROG. You do NOT have a known gate pulse if
working
% with normal FROG.
[t x, Et i,Et p] = readqfrog(pname1);
Et2 = sqrt(Eti) .* exp (1i * Et p);
% Find range of GREN time-axis
N = floor((max(t x))/dtau1);
t \times new = (-N:N) * dtau1;
% Resample the GREN
Et2 new = interp1(t x, Et2, t x new, 'cubic');
% Pad zeros, so that they have the same length
Et2_new = padarray(Et2 new, [0, round((length(tau1)-
length(t x new))/2)]);
    if (length(Et2 new) > length(tau1))
        Et2 new(end) = [];
    else
        Et2 new(end+1) = 0;
    end
% Rename and clean up variables
Et2 = Et2 new;
clear Et2 new t x new;
% Plotting, optional. To check the gate pulse is not under-sample
scrsz=get(groot, 'ScreenSize');
figure('OuterPosition', [scrsz(3)*0.33 scrsz(4)*0.33 scrsz(3)*0.66
scrsz(4)*0.66]);
subplot(2,3,3);plot(tau1, abs(Et2).^2);title('Gate Pulse');
clear Ewdum wdum
Et2 = center(Et2, 'max');
%% Retrieval
```

```
% Define the gate (it is known in this example), PG geometry is used
here,
\% and therefore using |E|^2
% Change the gate according to your system.
Gate = quickscale(magsq(Et2));
% The retrieval algorithm goes here. Change accordingly.
[Et1B, Et1, Esiq1, G1, Z1, EW1] = qFROG TX(Asiq1, Et1, tau1, w1, w1,
Gate, G1, Et1B);
% Should generate a sub panel of graphs from "DisplayXFROG.m" that
update as the algorithm is
% running. Original XFROG, Retrieved XFROG, Retrieved E(t), Retrieved
% E(\lambda), and G Error (of final)
% Finish the retrieval problem.
% Et1B is the output that will be used later on.
%% Plotting
% Generate the retrieved FROG trace
Ew1B = fftc(Et1B);
Asig1 = Asig1.^2;
Asig1r = abs(fft FROG(CalcEsig(Et1B,quickscale(abs(Et2).^2))).^2;
% Convert everything from angular frequency (w) into lambda (lam)
[Asiq1 lam, lam] = frog wtol(Asiq1,w1,t1);
[Asig1r lam, lam] = frog wtol(Asig1r,w1,t1);
[ELam1B, lam] = equally spaced spectrum lam(Ew1B,w1);
%Plot the 2D data
%Original Data
ax(1) = subplot(2, 3, 1);
subplot(2,3,1);imagesc(t1,lam,Asig1 lam);set(ax(1),'Tag','FROG
Trace,dum');title('Measured Trace');
h1 = get(ax(1), 'children');
%Retrieved Data
ax(2) = subplot(2, 3, 4);
subplot(2,3,4);imagesc(t1,lam,Asig1r lam);set(ax(2),'Tag','FROG
Trace,dum');title('Retrieved Trace');
h2 = get(ax(2), 'children');
linkaxes(ax); %use the same limits for both images
% Plot the retrieved pulse's 1D data
% Should appear in the same window as the 2D plots!
subplot(2,3,2);plot(t1, quickscale(abs(Et1B)));title('Probe
Temporal');
subplot(2,3,5);plot(lam, quickscale(abs((ELam1B))).^2);title('Probe
Spectral');
```

```
%% Save output
%Use if you want to manually name the file:
%datadump = input('Type a name for the saved data set. ','s');
%Auto-name the file using the input XFROG trace name
datadump = frog1;
%out name = strcat(datadump, '.mat');
%save(out name)
%Save the Temporal trace data
Ekname=[SaveName, '.Ek.dat'];
esave(t1,Et1B,Ekname);
%Save the Spectral trace data
Speckname=[SaveName, '.Speck.dat'];
esave(ltow(w1), Ew1B, Speckname);
%Save the Reconstructed trace data
AReconName=[FileName, '.Arecon.dat'];
fname = fullfile(PathDir, AReconName);
Xfrogtracesave(Asig1r lam, lam, t1, [], fname);
%Save the original trace data
AName=[FileName, '.A.dat'];
fname = fullfile(PathDir, AName);
Xfrogtracesave(Asig1 lam, lam, t1, [], fname);
TBP1 = calcTBPrms(Et1B,t1,Ew1B,w1);
FWHM fs = fwhm(magsq(Et1B),t1);
FWHM nm = fwhm(magsq(fftc(Et1B)),ltow(w1));
fprintf(1, 'G1: %e\n', G1);
fprintf(1, 'TBP1: %f\n', TBP1);
fprintf(1, 'FWHM fs: %f\n', FWHM fs);
fprintf(1, 'FWHM nm: %f\n', FWHM nm);
% Stop timer
toc
clear sb1 sb2
clear Asig1 Asig1r Asig1 lam Asig1r lam
```

```
end
```

#### Appendix G: FFT Time Spacing and Frequency Resolution

The resolution of the frequency domain is related to the number of points collected in the time domain. So to increase the resolution of the FFT for the same time point spacing (frequency range), more points need to be collected.<sup>41</sup> For the FFTs presented in this thesis, the time spacing is 5 fs and the time range is typically 2 ps or more of positive time. With these conditions, each scan takes approximately 13 minutes to collect, and a data set is typically 40 scans or more; adding on more points to each scan is not a trivial time investment. One alternative to adding more data points is to use zero padding.

Zero padding refers to the practice of adding a string of zeros to the end of the data to simulate an "infinite" data set. In principle, zero padding is simply adding null information to the time domain, but it results in interpolation of the data in the frequency domain.<sup>42</sup> An independent check of the frequencies recovered from an FFT of the non-zero padded residual with the zero padded residual (Figure 2.G1) confirms the increase in frequency resolution while leaving the overall spectrum unchanged.



**Figure 2.G1 Comparison of FFTs With and Without Zero Padding** This graph shows the FFTs of MeCN, where overlaid are the unpadded data (blue), the data with 420 points of zero padding (red), and 840 points of zero padding (green). The dominant peaks in the blue curve are maintained in the red and green traces, however their features are much sharper and more resolved.

A MATLAB script has been written to zero pad any oscillatory residual by a user determined amount, typically a factor of 10<sup>12</sup> or more. The script is explicitly placed

below with comments (green) to help guide the user through the process.

# ZeroPadding.m

```
%%MATLAB script to zero-pad the data
% Zero padding => adding zeros to the end of the "residual" (coherence
without exponential components) data in order to boost frequency
resolution
%% Clear out the old graphs
hold off
clf(subplot(2,1,1));
clf(subplot(2,1,2));
clf;
%% Bring in the data file
flag1='n';
while flag1=='n'
```

```
[fdat,pname]=uigetfile('*.*','Get data file'); %returns fdat as file
name selected and pname as path (folder) for the file
filename=fdat; %set 'filename' equal to the name and extension of the
file
fdat=[pname fdat]; % sets 'fdat' as full path to file (think
window's address bar)
fid=fopen(fdat); % figure out file format and proceed with conversion
dat=fscanf(fid,'%f %f',[2,inf]); % read data from text file and write
to 'dat'
% data needs to be tab delimited; reads in as rows
fclose(fid); % closes the open file
data=dat'; % transpose the data array; makes it into columns
Time=data(:,1); % column 1 is the time data
Resid=data(:,2); % column 4 is the IRF total signal
subplot(2,1,1),plot(Time,Resid) % plot the raw IRF file
xlabel('Time, s')
ylabel('Delta A')
title('Raw Data');
hold on
flag1=input('Is it the data file you wanted? (y/n) ', 's'); % did
you pick the wrong file? If so, fix it.
end;
%% Zero pad the Residual and the Data for time zero
ZP=input('How much to zero pad the data? ');
nptsResid=length(Resid); % tell me the length of the raw time column
ZPlength=(ZP-nptsResid);
nptsTime = nptsResid + ZPlength; % new array length
DeltaT = Time(3)-Time(2); % calculate the time spacing
% Build the new Resid data time array and fill it with corrected time
values
Timeinit=Time(2);
FinalTime=((Timeinit-DeltaT)+((ZP-1)*DeltaT));
Time0=(Timeinit-DeltaT);
TimenewT = (Time0:DeltaT:FinalTime); % initialize the new time array
(as ROW)
TimenewT(1)=0; %make the first value 0, regardless of step size to
point 2.
Timenew=TimenewT'; % make into a column
% Build the new data array and fill it in with zeros
ResidT=Resid';
```

```
PadDataT = padarray(ResidT, [0 ZPlength], 0, 'post'); % initialize a
new padded data array (as ROW)
PadData=PadDataT'; % make into a column
subplot(2,1,2), plot(Timenew, PadData); %plot new zero-padded time and
data arrays
xlabel('Time, s')
ylabel('Delta A')
title('Zero-Padded Data');
hold on
nptsTimeNew=length(Timenew);
flag11=input('Do you want to save the ouput data? (y/n) ','s');
if flag11=='y'
[newfile,pname]=uiputfile('*.*','Save the data as'); %you set the
file name for the new file and tell it where to save
 fdat=[pname newfile]; %specifies the new filename
fid=fopen(fdat,'w'); %tells it to open the file you made for writing
dout=[TimenewT; PadDataT]; %sets up the data to write to the file in
matrix form The ';' terminates a row and data is in ROWS
% THIS COMBINATION OF PASSING IN ROWS AND USING A SEMICOLON
WORKS!!!!!
 fprintf(fid, 'Time (s) \t Delta A\n'); %sets up the column headers; 'n
tells it to go to the next line
fprintf(fid, '%1.16f\t %1.16f\n', dout); %writes in the data in the
formats specified; transposes the matrix you made above
fclose(fid); %closes the file
end
```

#### **Appendix H: Time-Dependent Fast Fourier Transforms**

Traditional FFT methods assume that the oscillatory signals are stationary with time. This may not always be the case, especially if electronic state changes are happening in the midst of these vibrations, as is the case with this research. To investigate whether the vibrational energy could be seen shifting from one mode to another in time, a time-dependent fast Fourier transform (TD FFT) program was written in LabVIEW (Figure 2.). Investigation into this data analysis method was inspired by Dr. Eric Colett's research and conversations at the 2013 International Symposium on the Photochemistry and Photophysics of Coordination Compounds in Traverse City, MI. However, there have been papers on this subject in the literature for many years.

Also known as the "short-time Fourier transform", TD FFT applies a window function to the data, FTs the data within the window, and moves the window placement in time (i.e. the x-axis) and repeats the process. In this way, a 2D set of data is constructed analyzing the frequency content of the signal in time.<sup>43</sup> The window chosen for this analysis can have a large impact on the resulting signals; for the current TD FFT program, a Gaussian window is used, though the disadvantages of such a window are nicely addressed by Kraszewski *et al.*<sup>44</sup> In future iterations of this program, the window function should be a variable on the front panel, but for now, it is a built-in property of the program and not easily changed.

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# Figure 2.H1 LabVIEW TD FFT Program

The homebuilt program to analyze the frequency content of the signal with time. The 1D plot on the left is the input data, while the 2D plot on the right is the resulting TD FFT data. Here, it appears that low frequency modes become stronger at later times, suggesting IVR may be populating these modes.

The directions posted to the left on the front panel give pretty explicit directions on the use of the program, but the most important content in that list is the proper format for the data file. The data file must be in columns, with time in *seconds* and the data pre-processed to remove exponentials. The TD FFT program has no fitting routine for the exponential components in the data, and the FFT of the data with exponentials is unreliable; these components must be removed beforehand. This is easily done by using the residuals from the IGOR FFT analysis and saving the data in the proper format as a text (tab delimited) file. The two other relevant controls are the "Gaussian FWHM, fs" and "Move Gaussian in Time, fs" which control how wide the Gaussian window is and how far it is moved with each FFT iteration, respectively. Typically, only the Gaussian FWHM is adjusted when examining data, as this seems to have the largest effect on the data. The larger the window width, the finer the resolution of the frequencies, but the time axis has more uncertainty. Conversely, a narrow window will give much better resolution along the time axis, while the frequencies will be more uncertain. The "map selector" control under the z-axis values for the TD FFT plot allows the user to control the color scheme of the resulting plot.<sup>45</sup>

The program starts when the user hits the run button in the toolbar and finishes when the Gaussian window has fully moved across the data set. At the completion of the windowing routine, LabVIEW saves the results in a data file with the name "[data file]\_[Gaussian FWHM]\_[Gaussian move]" where the names in [] correspond to the values on the front panel. In this way, each Gaussian FWHM tried saves as a new uniquely named data file. The z-axis scaling may be changed by the user to highlight oscillations that are otherwise difficult to see. In the current version of the program, changing the "map selector" value only updates the graph's color scheme the next time the program is run. Unfortunately, results from this program were not as concrete as originally thought and they will not be discussed in the context of this thesis. One issue is highlighted in the example shown in Figure 2.: the exponential fit leaves the residual below baseline at long times, possibly causing the low frequency artifact at late times in the TD FFT analysis.<sup>46</sup> Obviously, altering the fit and running the TD FFT analysis on the new residual should remove the ambiguity of this feature -artifact or IVR - and the finer points of this program and its analysis are still in development. It is interesting to note, however, that the TD FFT results form a sort of counterpart to the damping times calculated for the LPSVD analysis. The degree of correlation, however, is highly dependent on the window values chosen for the TD FFT analysis.

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# 3 Cr(acac)<sub>3</sub> and Cr(TMHD)<sub>3</sub> - Pump Dependent Vibrational Coherence

#### 3.1 Introduction

The main advantage of selecting tris(2,4-pentanediono)chromium(III) (Cr(acac)<sub>3</sub>) for studies of relaxation processes is that it is electronically simple. The limited number of excited states compared to other transition metal systems like  $[Ru(bpy)_3]^{2+}$  and  $[Fe(tren(py)_3)]^{2+}$  greatly reduces the complexity of the ultrafast dynamics.<sup>1–3</sup> Aside from the electronic simplicity of Cr(III) compounds, Cr(acac)<sub>3</sub> was chosen in particular for being photochemically inert. Sheridan *et al.* contribute this stability to the pseudoaromaticity of the planar, 6-member, chelate ring, as it is orders of magnitude slower than  $[Cr(C_2O_4)_3]^{3-}$  at racemization and photoaquation.<sup>4</sup> The wealth of previous knowledge on Cr(III) compounds in the literature<sup>5,6</sup> also make this an attractive starting point for these studies.

The Tanabe-Sugano diagram for Cr(III) compounds in an octahedral field can be seen in Figure 3.1, below.<sup>7</sup> This diagram lays out the energetics of the ligand field transitions (electron transitions within the d-orbital manifold on the metal center) as a function of ligand field strength (energetic splitting between d-orbital levels),  $\Delta$ . The ground state of the molecule is <sup>4</sup>A<sub>2</sub>, which can be seen as the green line at the x-axis; all of the spin allowed transitions are shown in green, while the spin forbidden transitions are shown in blue. Absorption of a photon corresponds to a vertical transition on this diagram, and if the exact ligand field strength for the compound is known, the energies of the ligand field states may be calculated explicitly. As it is, this diagram is formulated for a ratio of C/B equal to 4.50, which is likely for most Cr(III) compounds.<sup>7</sup> Cr(acac)<sub>3</sub> has a ligand field strength of approximately 2.2 when estimated

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from transition energies for the  ${}^{4}T_{2}$  and  ${}^{2}E$  states, *vide infra.* At this position, the lowest spin allowed transition is into the  ${}^{4}T_{2}$  state, while the lowest energy excited state is the  ${}^{2}E$ . At higher excitation energies, population of the two  ${}^{4}T_{1}$  states is possible.



Figure 3.1 Tanabe-Sugano Diagram for a d<sup>3</sup> Metal Center

This diagram plots the energies of the excited states (vertical axis) as a function of the ligand field strength (horizontal axis).<sup>7</sup> The quartet states, representing the spin allowed transitions from the  ${}^{4}A_{2}$  ground state are shown in green while the doublet (spin forbidden transitions) are shown in blue. Figure adapted from information in reference 8.

The slopes of the excited state energies as a function of ligand field strength is rather telling about their orbital population. A line with relatively little change in energy as a function of  $\Delta$  indicates an intraconfigurational change (i.e. a spin flip of an electron

within an orbital). A strongly sloped line, however, is indicative of an interconfigurational change, or electron movement between the  $t_{2g}$  and  $e_g^*$  orbital sets which are split in accordance with the ligand field strength.

The ground state absorption and emission spectra for Cr(acac)<sub>3</sub> were previously collected in our group, and the results are shown in Figure 3.2.<sup>3,9,10</sup> The ground state absorption is shown in black, with the green trace scaling up the visible region of the spectrum by 50. The emission spectrum, collected at 90 K in an optical glass, is shown in blue. The band assignments for these features were previously described in detail by Schrauben<sup>9</sup>, and will be briefly summarized here. The lowest energy absorption in the visible region, centered at 560 nm, corresponds to the  ${}^{4}T_{2}$  ligand field absorption. The shoulder seen at 380 nm is caused by  ${}^{4}({}^{3}IL)$  absorption, where the  ${}^{4}({}^{3}IL)$  state represents an admixture of quartet charge transfer and triplet intraligand character. Also buried under this transition is the  ${}^{4}T_{1}$  ligand field state. The intense absorption around 335 nm is caused by a ligand to metal charge transfer (LMCT) transition. The absorptions above this band are ascribed to  $\pi$ - $\pi$ \* transitions on the basis of the Ga(acac)<sub>3</sub> reference compound absorption. The gallium analogue, with its full dmanifold, cannot exhibit d-d transitions or CT transitions, leaving only intraligand absorptions as the cause of the absorptions. The emission, with a maximum at 775 nm, results from the <sup>2</sup>E excited state.

The breadth of these ligand field transitions is also telling about the geometric change in the molecule associated with these states. Considering a potential energy surface diagram, a broad absorption or emission feature corresponds to two surfaces whose minima are shifted relative to one another. This shifting causes an increase in

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the Franck–Condon overlap for multiple vibrational energy levels, resulting in a broader transition. Conversely, a very narrow transition indicates two potential energy surfaces that are nested, resulting in adequate Franck–Condon overlap at just a few vibrational energy levels.



Figure 3.2 Steady State Absorption and Emission Spectra for  $Cr(acac)_3$ UV-visible absorption spectrum for  $Cr(acac)_3$  shown in black (scaled x50 in green), the  $Ga(acac)_3$  reference compound absorption in red, and  $Cr(acac)_3$  90 K emission data in blue.

Figure 3.3 shows these concepts applied to the absorption and emission spectra of  $Cr(acac)_3$ . The broad absorption band indicates that the  ${}^4T_2$  minimum is shifted from the  ${}^4A_2$  ground state minimum. The  ${}^2E$ , with its very narrow emission spectrum, should have a minimum at or very near that of the ground state. This shifting could be caused by any number of things, but here it is simplistically assumed to correlate with the metalligand bond distance.



#### Figure 3.3 Potential Energy Surface Diagram for the Lowest Energy Ligand Field States and Their Corresponding One-Electron Diagrams The minima of the potential energy surfaces here is taken as the metal-ligand bond length, where the ${}^{4}T_{2}$ surface is displaced owing to the population of the $e_{g}^{*}$ orbital. The ${}^{2}E$ state corresponds to a simple spin flip within the $t_{2g}$ orbital manifold and is expected to be the same geometry as the ground state.

Given the Tanabe-Sugano diagram and the observed absorption and emission data for this compound, one-electron pictures for the ligand field states may be developed. These are overly simplified representations of these states, but they can still be quite instructive. The ground state  $d^3$  configuration places one electron in each of the  $t_{2g}$  orbitals, as seen in Figure 3.3. The  ${}^4T_2$  energy exhibits a large change as the ligand field strength is increased, indicating an electron is moving from the filled  $t_{2g}$  set to the  $e_g$  set of orbitals. This population of an anti-bonding orbital should introduce a change in the metal-ligand bond length, considering the  $e_g$  orbitals are oriented directly along the metal-ligand bonds. This bond length change would shift the potential energy surface for the  ${}^4T_2$  relative to the ground state (along the Cr-O bond length coordinate) and result in a broad absorption feature. The  ${}^2E$ , however, is largely indifferent to the change in the ligand field strength, indicating the transition does not transfer electrons between the  $t_{2g}$  and  $e_g$  sets. This state is depicted as a single electron spin flip within

the  $t_{2g}$  set which should leave the Cr-O bond length unchanged. The highly nested potentials would give rise to a very narrow emission spectrum, which is observed experimentally.

# 3.2 Previous Time-Resolved Data on Cr(acac)<sub>3</sub>

# 3.2.1 Femtosecond Dynamics Observed with Transient Absorption and IR

Previously collected TA data on  $Cr(acac)_3$  employed a pump wavelength of 625 nm, which corresponds to generating a vibrationally cool  ${}^{4}T_{2}$  state. Observed kinetics are shown in Figure 3.4. The full experimental details are given in ref.  ${}^{10}$ ; white light generated in a CaF<sub>2</sub> plate was used as the probe. The top half of Figure 3.4 shows the full spectra collected from 460 nm to 690 nm, where early time traces are shown in red and the late time traces are shown in blue. With time the spectrum decreases in intensity, narrows, and red shifts. The kinetics of this amplitude change are shown in the bottom half of Figure 3.4, where single wavelength traces at 480 and 680 nm are fit with a monoexponential decay of ~1 ps.<sup>10</sup>





The top spectrum shows the full spectra collected after pumping at 625 nm and probing with a white light continuum. The traces go from black (negative time) to red (early time) down to dark blue (late time). The spectrum decreases in intensity, narrows, and red shifts with time. The bottom displays the single wavelength kinetics for the same sample conditions. See text for more details. Figure reproduced with permission from reference 10. © (2005) American Chemical Society.

By recording the low temperature (77 K) ns TA signal across this same spectral range, a plot of the full thermalized  ${}^{2}E$  state could be obtained. An overlay of this data with the 5 ps trace from the fs TA data confirms that the  ${}^{2}E$  is full vibrationally cooled by 5 ps. Since it is highly unlikely that the absorption spectra from the  ${}^{4}T_{2}$  and  ${}^{2}E$  excited states are highly similar, the 1 ps time constant was assigned to vibrational cooling on the  ${}^{2}E$  surface. The red shifting and narrowing of the full spectra data support this assignment as vibrational cooling; a vibrational levels in an upper state than after cooling to lower vibrational levels has occurred, causing a narrowing of the spectrum. ${}^{10}$  The intersystem crossing (ISC) from the initially populated  ${}^{4}T_{2}$  state to the  ${}^{2}E$  was hypothesized to precede vibrational relaxation on the  ${}^{4}T_{2}$  surface and happen within the 120 fs IRF of the system. ${}^{3,10}$ 

The ultrafast dynamics following photo-excitation of  $Cr(acac)_3$  have also been studied by directly monitoring the recovery of ground state vibrations using an IR probe. This work was performed by Kunttu and coworkers<sup>11,12</sup> using pump wavelengths of 345 and 400 nm and monitoring the C-O and C=C bond vibrations at 1579 cm<sup>-1</sup> and 1521 cm<sup>-1</sup>, respectively. Unlike the previously discussed TA experiments exciting the  ${}^{4}T_{2}$ ligand field state in Cr(acac)<sub>3</sub>, these experiments excite the  ${}^{4}({}^{3}IL)/{}^{4}T_{1}$  state (400 nm pump) and the  ${}^{4}LMCT$  state (345 nm pump). The data clearly show a bi-exponential decay compose primarily of a short ~ 15 ps component with smaller contributions from a longer ~800 ps component. The authors assign this long time component to ground state recovery from the  ${}^{2}E$ , which is consistent with the TA picture presented by Juban *et al.*<sup>3,10</sup> They initially assign the 15 ps component to internal conversion (IC) from the  $^{4}\mathrm{T}_{2}$  to the ground state and emphasize that this constitutes 70-85% of the decay signal.<sup>11</sup>

Re-examination of this data in conjunction with ground state vibrational cooling data has lead to a new interpretation of this data. Using an IR pump with an IR probe, Kunttu and coworkers observed two time constants for ground state vibrational decay: a 300-700 fs component and a 10-12 ps component.<sup>12</sup> The long time component was assigned to vibrational cooling on the ground state surface, while the 300-700 fs component was tentatively assigned to intramolecular vibrational redistribution (IVR) on the ground state.



Figure 3.5 Ultrafast IR Results Following 400 nm Excitation of  $Cr(acac)_3$ Utilizing a 400 nm pump, the C-O and C=C vibrations were monitored over a time window of several hundred picoseconds. The data were fit with a bi-exponential function, revealing time constants of ~15 ps and ~800 ps. See text for more details. Figure reprinted with permission from reference 11. © (2007) American Chemical Society.

By using a global fitting routine for all of the data they had collected, the rates of IC ( ${}^{4}A_{2}\leftarrow {}^{4}T_{2}$ ) and BISC ( ${}^{4}T_{2}\leftarrow {}^{2}E$ ) were further clarified. The optimized IC rate is

1.56 ps, very similar to the vibrational cooling time constant observed above in ultrafast TA, and the earlier ~15 ps component is probably a convolution of this 1.5 ps IC and 12 ps ground state vibrational cooling. The authors do acknowledge, however, that their simulations indicate a greatly reduced contribution of the fast component to ground state recovery dynamics following 600 nm excitation. At 100 ps, only 32% of the decay has occurred via the fast process, while the 400 nm pump shows 71% of the decay occurring via the fast process (345 nm shows 85%).<sup>12</sup> This observation lends credence to the absence of a fast component in the TA spectrum following a 625 nm pump pulse in Juban's data.

This dependence on excitation energy for the fast decay process indicates the presence of a BISC process that is dependent on vibrational cooling within the <sup>2</sup>E. By examining the decay of the excited state absorption, the 7-10 ps decay was assigned to the <sup>2</sup>E vibrational cooling.<sup>12</sup> The authors hypothesize that with sufficient pump energy, the system is thermally activated to BISC to the <sup>4</sup>T<sub>2</sub> manifold where it can relax to the ground state in 1.5 ps (while the ground state vibrationally cools in 10-12 ps). After the vibrational cooling on the <sup>2</sup>E surface has occurred, the population is trapped on the <sup>2</sup>E until the ground state population is recovered in 700-900 ps.<sup>12</sup>

Recent computational modeling by Ando *et al.*<sup>13</sup> suggests that this strong coupling between the <sup>2</sup>E and the <sup>4</sup>T<sub>2</sub> state is actually facilitated by potential energy surface crossings and spin orbit coupling between the <sup>2</sup>T<sub>1</sub> and the <sup>4</sup>T<sub>2</sub> states. The results show that the <sup>2</sup>T<sub>1</sub> and <sup>4</sup>T<sub>2</sub> states cross near the Franck–Condon region, and simulations suggest population transfer between these states happens around 200-250 fs, even before the molecule has reached the distorted <sup>4</sup>T<sub>2</sub> structure. Since the <sup>2</sup>T<sub>1</sub> and

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<sup>2</sup>E states are so close in energy and geometry, ultrafast IC between these states is assumed to proceed after the  ${}^{2}T_{1}$  is populated.<sup>13</sup>

The optimization of the  ${}^{4}T_{2}$  geometry confirms a distorted structure with four longer Cr-O bond lengths resulting from the  $e_{g}^{*}$  ( $d_{x}^{2}-_{y}^{2}$ ) population, and the dihedral angle between the oxygen atoms on two of the acac ligands is significantly increased from 90° to 120°. Simulations of the path between the Franck–Condon (ground state) geometry and the distorted  ${}^{4}T_{2}$  geometry indicate the low frequency modes (displacements in the primary coordination sphere, particularly the Cr-O bond length) are primarily responsible for driving this distortion.<sup>13</sup>

These data make clear the need for advanced understanding of the processes occurring between excitation and 1 ps. The works of Juban and Kunttu agree that ISC from the quartet manifold ( ${}^{4}LMCT$ ,  ${}^{4}({}^{3}IL)/{}^{4}T_{1}$ , or  ${}^{4}T_{2}$ ) to the  ${}^{2}E$  occurs within 100 fs. They also agree that the  ${}^{2}E$  decays back to the ground state in about 800 ps. ${}^{3,10,12}$  (This ground state recovery timescale has been measured as 950 ps in MeCN; see Appendix A for details.) The intervening processes are a little murkier, with each experiment having its own advantages. The IR probe results in narrower spectra, where the vibrational cooling is easier to see, but the initially formed excited state is no longer a ligand field transition. The TA results look at electronic absorptions which are broader, but kinetic complications are minimized by exciting into the lowest energetically allowed transition. Further investigations into the geometric factors driving the ultrafast ISC process could shed more light on these processes.

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### 3.2.2 Transient Absorption Utilizing 50 fs Pulses

Experiments described up to this point have employed pulses that were  $\geq$  120 fs. Previous experiments in our group, in collaboration with the Beck laboratory, employed 50 fs pump and probe pulses. As discussed in Chapter 1, the increased bandwidth with shorter pulse duration can produce a wavepacket. The results of these experiments are seen in Figure 3.6, where clear oscillations are seen in the data, lasting into multihundreds of femtoseconds, superimposed on the population dynamics. This data was collected by pumping the low energy side of the  ${}^{4}T_{2}$  absorption at 600 nm (15 nm FWHM) and monitoring the transient signals with a 600 nm probe (i.e. a one color experiment), which was either detected without spectral filtering or by using a monochromator with a 4 nm bandpass to monitor the probe at 592 nm and 608 nm.<sup>14</sup> The data shown here was collected at 592 nm, and the excited state absorption can be seen at positive time in the top plot ( $\Delta T/T$  is the same as - $\Delta A$ ). The black line is the monoexponential fit of the data and once the population dynamics (the fit) have been removed, the oscillatory residual is much clearer. This is seen in the bottom panel of Figure 3.6, where the black line here represents a cosinusoidal fit to the data composed of vibrations at 164 and 75 cm<sup>-1</sup>.<sup>14</sup>



Figure 3.6 Results from 50 fs excitation at 600 nm for  $Cr(acac)_3$ The top graph shows the entire kinetic trace resulting from 600 nm excitation and a 600 nm probe, both 50 fs in duration. The bottom plot is an expansion of the short time region where clear oscillations are seen in the data. The black line in both plots represents the fit of the data. See text for more details. Figure reproduced from reference 14 with permission of The Royal Society of Chemistry.

This vibrational coherence was assigned as wavepacket motion on the excited state, due to the low oscillator strength of the ground state absorption and the longer timescales for ground state recovery from the excited states.<sup>14</sup> The coherence signal originates near time zero, and the damping times for the two oscillations are 70 fs (164 cm<sup>-1</sup> vibration) and 1.6 ps (75 cm<sup>-1</sup> vibration). In light of the previously resolved TA
dynamics, the 70 fs time constant was loosely associated with the ISC process, indicating the coherence is originated on the  ${}^{4}T_{2}$  surface, but is maintained though the ISC crossing onto the  ${}^{2}E$  surface.<sup>14</sup>



**Figure 3.7 Vibrational Modes Possibly Facilitating Ultrafast ISC** The symmetric breathing mode, left, and the scissoring mode, right, from ground state frequency calculations in Cr(acac)<sub>3</sub>. Figure reproduced from reference 14 with permission of The Royal Society of Chemistry.

Ground state DFT calculations were carried out in an attempt to identify these vibrational modes, as they may play an important role in the reaction coordinate of this ISC process. Two modes, at 184 cm<sup>-1</sup> and 256 cm<sup>-1</sup>, were selected as likely candidates for the 164 cm<sup>-1</sup> mode observed. The population of an  $e_g^*$  orbital upon formation of the  ${}^{4}T_{2}$  state is predicted to lower these frequencies by weakening the Cr-O bonds. These modes, seen in Figure 3.7, involve displacements within the primary coordination sphere of the compound. Along with these modes, it was noted that nearly all of the low energy vibrational modes involved motions of the methyl groups or deformation of the ligand backbone.<sup>14</sup>

To test if the methyl group motion was a key factor in the ISC process, the authors synthesized a derivative using 2,2,6,6-tetramethyl-3,5-heptanedione

 $(Cr(TMHD)_3)$ , which retains the overall structure of  $Cr(acac)_3$  while exchanging the methyl groups for *tert*-butyl groups on the ligand backbone. The structure of the ground state absorption spectrum and the emission spectrum are largely the same, however the maxima are slightly red shifted from the same features in  $Cr(acac)_3$ .<sup>9,14</sup> Despite this small perturbation to the zero point energies of the electronic states, the TA signals show dramatic differences from  $Cr(acac)_3$ .

The excited state dynamics of this molecule were analyzed using the same methods as the 120 fs resolution TA studies on Cr(acac)<sub>3</sub> described above. Pumping on the low energy side of the  ${}^{4}T_{2}$  state, both full spectra and single wavelength data were collected. These results are shown in Figure 3.8, where the full spectra data exhibit more than just the narrowing and red shifting of the spectrum as was observed with Cr(acac)<sub>3</sub>. Instead, Cr(TMHD)<sub>3</sub> shows a distinct decrease in the intensity on the blue side of the spectrum, while the redder wavelengths grow in. The dynamics are confirmed by the single wavelength traces, which show this decay and rise occurring on the same timescales. The spectra become invariant after 12 ps, indicating the signal is originating from the <sup>2</sup>E state and it is vibrationally cooled at that point. The ~1.8 ps dynamics observed are assigned to the ISC from the <sup>4</sup>T<sub>2</sub> to the <sup>2</sup>E state, and encompass the vibrational cooling on the <sup>2</sup>E as well. This assignment is further substantiated by performing Gaussian deconvolution on the excited state spectra. This fitting procedure efficiently models the profiles of the full spectra traces by assuming two Gaussians, centered at 465 nm and 525 nm, start with relatively equal intensities at 300 fs, but the blue Gaussian decays as the red Gaussian grows with time. The large magnitude change in the ISC timescale for Cr(TMHD)<sub>3</sub>, coupled with the vibrational

analysis of  $Cr(acac)_3$  suggest that the methyl groups on the acac backbone play a large role in the ultrafast dynamics observed in  $Cr(acac)_3$ .<sup>9,14</sup>





The full spectra data, evolving in time from the red to blue colored trace, clearly show a decay on the blue edge of the spectrum and a concomitant rise on the red edge of the spectrum. Single wavelength data, right, confirm these processes occur with the same time constant, ~1.8 ps. Figure reproduced in part from reference 14 with permission of The Royal Society of Chemistry.

## 3.3 Current Efforts to Explore the Ultrafast Dynamics of Cr(acac)<sub>3</sub>

The work in this thesis seeks to further these coherence studies on both Cr(acac)<sub>3</sub> and Cr(TMHD)<sub>3</sub>. The experimental details are given in Chapter 2, which describes the setup for the 35 fs laser system acquired after the collaboration with Dr. Beck. This system has the flexibility to do one color or two color experiments, which will be detailed separately below.

### 3.3.1 One Color Pump Dependence

The previous coherence data on  $Cr(acac)_3$ , while instructive, resulted from creating population in the  ${}^4T_2$  state near the minimum of the potential energy surface (i.e. vibrationally cool).<sup>14</sup> The  ${}^4T_2$  absorption, however, is well isolated from other electronic states (see Figure 3.2), allowing for clean excitation of this state from 490 nm to 700 nm. In practice, the usable range is limited by the oscillator strength at these wavelengths, but the excess vibrational energy in this excited state may still be reasonably varied by ~ 4200 cm<sup>-1</sup>. The previously observed dynamics (1.1 ps cooling on the  ${}^2E$  surface) have already been shown to be invariant with pump wavelength<sup>10</sup>, so the focus of this discussion will be on the oscillatory features of the data.

The experimental setup for the one color experiment has been described in detail in Chapter 2, but it is worth noting this data was collected with a few modifications. The most noteworthy being that the probe beam contained a waveplate and Glan-Laser cube polarizer, while the pump beam did not contain these optics. The prism compressor was optimized without these optics on the probe line (i.e. GDD on the pump and probe were the same), but they were reinserted before the data was collected in order to achieve magic angle polarization. Consequently, the pump and probe are not simultaneously optimally compressed. Despite these issues, the nominal pulse widths, as characterized by cross-correlation only, are 60 fs. A cube polarizer after the sample was oriented to allow for maximum probe transmission, while rejecting the pump photons at magic angle polarization. This cube polarizer after the sample helped to mimic the experimental conditions during the collaboration with the Beck laboratory<sup>14</sup>, and has proven to be a useful technique in Paul Champion's studies.<sup>15</sup> As with any

brand new experiment to a lab, there is a bit of a learning curve while fully optimizing the experimental conditions and this was no different. The procedure for collecting coherence data has since been optimized, but the one color data will still be presented here.

#### Experimental

The pump wavelengths chosen for this study were 510, 560, and 600 nm. Since these are one color experiments, the probe beam shares the same spectral profile as the pump beam. For all of the pump wavelengths, the monochromator (10 nm bandpass) was tuned to the left edge of the pump spectrum, as shown in Figure 3.9, below. The pump wavelengths vary the vibrational energy by ~3000 cm<sup>-1</sup>, while having minimal spectral overlap with each other, i.e. pumping distinctly different vibrational levels with each pump wavelength. The experiments were performed in a 1 mm path length cuvette where the absorbance of Cr(acac)<sub>3</sub> in acetonitrile (MeCN) at the pump wavelength of interest was ~0.5. The results presented are the combination of two data sets at each pump wavelength.

The data were worked up and analyzed according to procedures detailed in Chapter 2 and appendices, which will not be repeated here. A typical data set consists of at least 40 scans, where scans showing instability or shifting (laser drift) over time were removed prior to data averaging. The resulting data set was processed in two programs, IGOR Pro and MATLAB, where traditional fast Fourier Transforms (FFT) and linear predictive single value decomposition (LPSVD) were performed, respectively.<sup>16–18</sup> While these two programs give comparable results in terms of the frequencies recovered (*vide infra*), LPSVD results are cleaner and will be reported throughout the

rest of this analysis. The best LPSVD fit was determined by examining the residual of the fit and evaluating the RMS value of the fit. For the data presented in this thesis, the best fit occurred when the RMS value stabilized and the residual no longer showed oscillatory features (data not shown).





The ground state absorption for the  ${}^{4}T_{2}$  state in Cr(acac)<sub>3</sub> (black) overlaid with the 600, 560, and 510 nm pump spectra (solid orange, turquoise, and green lines, respectively). The probe spectra after the monochromator (dashed lines), are centered approximately at the left edge of the FWHM of the pump spectrum. The blue curve is the excited state absorption at 1.5 ps, and is shown for reference.

These IGOR and LPSVD workup procedures are shown in Figure 3.10 on a typical data set for Cr(acac)<sub>3</sub>. The graphs on the left half of the figure represent the analysis process in IGOR, whereas the right graphs represent the analysis process in MATLAB using LPSVD. By comparing the frequency results of both methods, it is easy to see that the LPSVD spectrum suffers from less noise, and is better at picking up low intensity frequencies (i.e. 64 cm<sup>-1</sup>).



#### Figure 3.10 IGOR and MATLAB Data Analysis Techniques Compared

The top left graph shows the IGOR data analysis method, where the exponential components are fit explicitly (red line) and the fit residual is Fourier transformed (bottom left graph.) The major peaks are picked out from the noisy baseline and labeled. The top right graph shows the data (blue) and the LPSVD fit (red) which is comprised of cosinusoidal components with individual damping times. It is this fit that is converted into the power spectrum (bottom right graph), hence its much smoother appearance. The FT spectra show pretty close agreement, despite the difference in methodology.

Data for the molecule and the pure solvent are collected under identical experimental conditions for all pump/probe combinations in order to differentiate the impulsively stimulated Raman modes of the solvent from modes corresponding to the molecule of interest. Frequencies occurring in both the pure solvent and molecule's power spectra are neglected. For the LPSVD data shown in Figure 3.10, the 374 cm<sup>-1</sup> mode corresponds to the C-CN bending mode in MeCN, which matches the Raman frequency of 380 cm<sup>-1</sup> quite well.<sup>19</sup> The LPSVD fit of pure MeCN under these conditions (not shown) gives 384 cm<sup>-1</sup>, which matches within experimental error.

The frequency resolution and range of the FT spectrum using either method is taken from the time-domain data passed in to the analysis. The frequency resolution,  $\Delta f$ , is defined by the following equation:

$$\Delta f = \frac{1}{N \cdot \Delta t} \tag{3.1}$$

where N is the number of points acquired in the time-domain signal,  $\Delta t$  is the time spacing between points, and the product of  $N \cdot \Delta t$  is the length of time containing the time-domain signal.<sup>20</sup> For all of the experimental data collected,  $\Delta t$  was 5 fs, while N varied depending on the breadth of the solvent signal around time zero. For both methods, the frequency analysis was started after the nonresonant solvent response (see Chapter 1) around time zero had ended; the frequency resolution of most data sets is 15 cm<sup>-1</sup>. The frequency range of the results is similarly related to the time-domain signal. The last frequency is given by:

$$f_F = \frac{1}{2 \cdot \Delta t} - \frac{1}{N \cdot \Delta t} \tag{3.2}$$

such that the frequency range of the data goes from 0 to  $f_{\rm F}^{20}$  Typical values of N were 400 and over, such that the 0-3300 cm<sup>-1</sup> range is reliably covered by all data sets.

The frequency range of excited vibrational modes, however, comes from the pulse characteristics. As discussed in Chapter 1 (section 1.2.2), there are two schools of thinking on this: the first is that the pulse must have enough spectral bandwidth to coherently excite at least two vibrational levels,<sup>21,22</sup> and the second is that all vibrational modes which have periods more than two times the pulse duration will be excited.<sup>23,24</sup> To illustrate the difference between these two scenarios, consider a 35 fs laser pulse centered at 520 nm. For a transform limited pulse, the bandwidth would be 11.4 cm<sup>-1</sup>, meaning the total energy spread of the pulse at FWHM is 421.6 cm<sup>-1</sup>. Under the first condition for quantum beating, modes less than ~211 cm<sup>-1</sup> could be excited by this pulse. Alternately, examining the impulsive excitation limit, modes with periods of 70 fs and longer will be excited by this pulse, corresponding to modes less than ~477 cm<sup>-1</sup>. These two ranges bear some obvious differences, but if the energy spread of the pulse at intensities lower than FWHM is considered, the two ranges may be reconciled. The absolute limit of frequencies one could expect to observe corresponds to 1/pulse duration - 952.3 cm<sup>-1</sup> in this case - but often this limit is not reached.<sup>25</sup> It should be noted here that the solvent vibration is stimulated nonresonantly by a similar mechanism. This process, as discussed in chapter 1, is called impulsive stimulated Raman scattering (ISRS) and requires only that the pump pulse be short in relation to the vibrational period. The bandwidth of the pulse is therefore sufficient to contain multiple pairs of frequencies with a frequency difference matching the vibrational mode of interest, which drives the vibration.<sup>26</sup>

### 600 nm Excitation Results

Pumping at 600 nm creates a relatively vibrationally cool population on the  ${}^{4}T_{2}$  surface, as discussed earlier in section 3.2.2. The recorded data are shown in Figure 3.11, where the results and analyses of two data sets are shown in a stacked plot. The top plot in each set displays the raw data, along with the LPSVD fit to the data. The FT of this fit is displayed in the power spectrum below, reflecting the frequency components in the fit. These experimental conditions closely match those used in the previous coherence study<sup>14</sup>; however, the LPSVD analyses of the recorded signals show that the oscillatory feature consists of more than two vibrational modes. The power spectra shown in Figure 3.11 contain peaks at 183, ~226, 284, ~460, and 486 cm<sup>-1</sup> after neglecting the 377 cm<sup>-1</sup> mode from the solvent.

The pulse characteristics for these data sets reveal that these 470 cm<sup>-1</sup> components may be outside of the frequencies expected considering both the quantum beat and impulsive excitation pictures. The first data set was collected using 60 fs pulses centered at 599 nm with a bandwidth of 27.6 nm. This leads to an expected frequency range of 386 and 274 cm<sup>-1</sup>, respectively. The second data set was collected with a 48 fs pump pulse centered at 600.5 nm with a bandwidth of 20.9 nm. The expected frequency range here is 290 and 348 cm<sup>-1</sup>, respectively. All of these limits suggest that the higher frequency modes at ~470 cm<sup>-1</sup> should not be excited and yet they are clearly resolved in the power spectra. This suggests that these "limits" are not strict and that strong modes at higher frequencies may still be excited.





The top and third plots show the data (blue dots) and the LPSVD fit of the data (red line) collected pumping at 600 nm and probing at 592 nm for two data sets. The FT of the LPSVD fit is displayed below the data, where frequencies  $Cr(acac)_3$  (blue) and MeCN (red) are shown explicitly. The two data sets exhibit very close agreement in the results, especially for peaks at ~226, and 460 cm<sup>-1</sup>.

### 560 nm Excitation Results

Pumping at the ground state absorption maximum, which is also the energy for the best Franck–Condon overlap to the excited state, unfortunately results in data with some oscillatory features, but they are not as pronounced as the 600 nm pump data sets. The data, shown in Figure 3.12, below, exhibits only a few vibrations outside of the solvent mode. These vibrations, at 87, ~190, 223, and 568 cm<sup>-1</sup>, echo the low frequency vibrations observed utilizing the 600 nm pump.

Examining the pulse characteristics again reveals that the 568 cm<sup>-1</sup> mode is well outside of the anticipated range of frequencies excited during the wavepacket formation. The data in the top two graphs in Figure 3.12 were recorded utilizing 59 fs pulses centered at 560.3 nm (17 nm FWHM), leading to anticipated frequencies of 270 and 283 cm<sup>-1</sup>, respectively. The extreme limit from the pulse duration is 565 cm<sup>-1</sup>, putting this frequency just on the edge of the limit. It is therefore regarded as an artifact and will not be further analyzed. The low frequency component present in the Cr(acac)<sub>3</sub> data also appears in the MeCN LPSVD fit, indicating it may be an artificial component in the data. As a result, this frequency will not be investigated further in the discussion section below.

The second data set reveals frequencies that would be expected given the pulse characteristics of the pump. The better compressed 51 fs pulses were centered at 561.1 nm, with a spectral bandwidth of 15.8 nm. This leads to expected frequency ranges of 251 and 324 cm<sup>-1</sup>, respectively. The recovered frequencies of 189 and 223 cm<sup>-1</sup> fit well within this range. The frequency at 373 cm<sup>-1</sup> is attributed to MeCN, despite the overly broad feature from the solvent LPSVD fit directly.



Figure 3.12 Cr(acac)<sub>3</sub> Vibrations Resulting from 560 nm Excitation The top and third plots show the data (blue dots) and the LPSVD fit of the data (red line) collected pumping at 560 nm and probing at 552 nm for two data sets. The FT of the LPSVD fit is displayed below the data, where frequencies  $Cr(acac)_3$  (blue) and MeCN (red) are shown explicitly. The two data sets show limited frequencies with only one common mode at 190 cm<sup>-1</sup>.

### 510 nm Excitation Results

This excitation wavelength creates the most vibrationally hot wavepacket on the  ${}^{4}T_{2}$  surface. This set of pump and probe wavelengths also affords the highest signal to noise, as the ground state absorption is much lower than the excited state absorption here. Also, the exponential decay from vibrational cooling can clearly be seen in the data sets, presented in Figure 3.13. The higher signal to noise here allows for clearer oscillatory features, and the power spectra of the LPSVD fits are in close agreement. A rather broad mode is seen at ~180 cm<sup>-1</sup>, followed by a sharper peak at 456 cm<sup>-1</sup>. The bottom data set contains a higher frequency component at 551 cm<sup>-1</sup> that is reminiscent of the 568 cm<sup>-1</sup> peak present following 560 nm excitation.

As discussed for 560 nm excitation, this 551 cm<sup>-1</sup> mode, along with the narrow 883 cm<sup>-1</sup> mode, is outside of the range of frequencies expected in the wavepacket. For the top data set, the excitation pulse was 12.8 nm at FWHM centered at 510.7 nm with a measured pulse duration of 60 fs. The expected frequency ranges for this data set is 245 and 279 cm<sup>-1</sup>, respectively. This 883 cm<sup>-1</sup> mode is clearly outside of these ranges, and will be considered an artifact in the data.

As for the second data set, the expected frequency ranges are slightly different due to the shorter pulse duration. For this 510.8 nm pulse (11.5 nm FWHM), the pulse duration was measured as 46 fs, which leads to 220 and 370 cm<sup>-1</sup> for the anticipated frequency ranges, respectively. Given the agreement of the LPSVD fit with the data this is clearly a necessary component, however it will not be analyzed further in the discussion section.



**Figure 3.13** Cr(acac)<sub>3</sub> Vibrations Resulting from 510 nm Excitation The top and third plots show the data (blue dots) and the LPSVD fit of the data (red line) collected pumping at 560 nm and probing at 552 nm for two data sets. The FT of the LPSVD fit is displayed below the data, where frequencies  $Cr(acac)_3$  (blue) and MeCN (red) are shown explicitly. The two data sets exhibit strong matching in the breadth and frequency of the modes at ~178 and 456 cm<sup>-1</sup>.

# Discussion

The results from both data sets at each pump wavelength are summarized in Table 3.1, below. Each row represents the LPSVD results for the corresponding excitation wavelength, and the frequencies are grouped in columns by equivalent modes. The damping times, listed in parentheses in the table, will be analyzed in the next section detailing the two color experiments, but are listed here for reference. This table highlights the presence of the ~184 cm<sup>-1</sup> mode at all excitation wavelengths. The next mode, ~225 cm<sup>-1</sup>, is present only at 560 and 600 nm excitation, while the ~459 cm<sup>-1</sup> mode is present only for excitation on the edges of the <sup>4</sup>T<sub>2</sub> absorption. The final common mode, ~559 cm<sup>-1</sup> is present only at 510 and 560 nm excitation. Vibrations in the far right column, save for the mode at 486 cm<sup>-1</sup>, have been discounted as artifacts in the individual discussions above and will not be discussed further. As the 486 cm<sup>-1</sup> mode is past the limit of the expected frequencies and has no counterpart in any of the other data sets, it will be ignored for the remainder of the discussion.

Experiments	Та	ble 3.1:	Summary	of Observed	Oscillations	for Cr(acac	)₃ in MeCN	Utilizing (	One (	Color
	Ex	perimer	nts							

Excitation	$O_{2}$							
Wavelength, nm	Oscillations, cm (Damping Times, fs)							
510	180 (146)		456 (628)		883 (-9000)			
510	175 (131)		456 (2000)	551 (88)				
560	193 (1140)			568 (663)	87 (96)			
500	189 (505)	223 (357)						
600	183 (360)	231 (465)	459 (1090)		486 (114)			
000		221 (250)	464 (277)		284 (385)			

As Champion and coworkers have stated, "[femtosecond coherence spectroscopy] can be thought of as a true time-domain analog of Raman spectroscopy, whereby the Fourier transform of the time-domain signal maps directly on to the traditional Raman spectrum.<sup>\*15</sup> In this regard, the ground state Raman spectrum of Cr(acac)<sub>3</sub> is a nice starting point for estimating the frequencies that might be present in the excited states of this molecule, especially considering the similar geometry of the <sup>2</sup>E state to the ground state which has been predicted to exhibit very similar vibrations to the ground state.<sup>6</sup> The resonance Raman spectrum of Cr(acac)<sub>3</sub> has been collected a number of times over the years with similar results.<sup>14,27–29</sup> One set of these results is shown in Figure 3.14, and contains ground state frequencies very close to those observed in the present excitation study. The peak at 457 cm<sup>-1</sup> has the highest intensity, followed by 232 (shoulder) and 562 cm<sup>-1</sup> at much weaker intensities. The peak at 188 cm<sup>-1</sup> is not present in the data set shown in Figure 3.14, however it has been observed in other resonance Raman spectra.<sup>14</sup> It has been noted that one advantage to this coherence spectroscopy technique is the ability to observe low wavenumbers modes that are either weak or absent in traditional Raman spectroscopy.<sup>30</sup>

To further clarify these modes and their origins, DFT frequency calculations were performed at the UB3LYP/6-311G(d,p) level employing a CPCM solvent continuum to model surrounding acetonitrile bath for the optimized ground and <sup>2</sup>E states, and the <sup>4</sup>T<sub>2</sub> state at the Franck–Condon (FC) geometry. These frequency results, listed in Appendix C: Gaussian Calculation Results, were compared to the experimental frequencies listed in Table 3.1. Details of these calculations are given in Chapter 2, however it should be noted that the molecule was optimized without symmetry restrictions and the resulting point group is formally C<sub>1</sub>, but it is very close to higher symmetry point groups through



Figure 3.14 FT Raman Spectrum for  $Cr(acac)_3$  in the Solid State The experimentally collected spectrum for  $Cr(acac)_3$  in the solid state is shown here for a Fourier Transform Raman spectrometer. Figure adapted with permission from reference 27. © (2015) Elsevier.

slight methyl group rotations. In the C<sub>1</sub> point group all of the vibrations are Raman active, allowing the results to be directly applicable to the experimental results. For the  ${}^{4}T_{2}$  calculations, the C<sub>1</sub> point group cannot support the degeneracy of this state, and so it is split into three separate states. The energies of these states in the TD DFT calculation do closely resemble the A<sub>1</sub> and E set that is predicted with a descent in symmetry.<sup>31</sup> The frequency results from these FC states contain negative frequencies consistent with these being unoptimized Franck–Condon structures. The  ${}^{2}E$  calculation, despite a similar degeneracy issue, did not suffer from this complication. Since it is the lowest energy doublet, a "ground state" DFT calculation could be performed by merely

changing the spin on the optimized ground state structure from a quartet to a doublet and re-optimizing the structure.

Considering the previous TA results which show the ISC from the  ${}^{4}T_{2}$  to the  ${}^{2}E$  is sub-100 fs, the strong agreement of the observed frequencies to the ground state Raman modes, and the low oscillator strength of ground state absorption compared to absorption out of the <sup>2</sup>E, these vibrations are assigned to the excited state. In agreement with earlier results, oscillations are present out to the end of the time-domain window at 2 ps, which indicates that the coherence is retained through the ISC process. Considering the large amount of vibrational overlap between the  ${}^{4}T_{2}$  and  ${}^{2}E$  surfaces, this efficient crossing (and retention of coherence) is not surprising. The calculations indicate that vibrational modes at 232, 457, and 562 cm<sup>-1</sup> are present in both the  ${}^{4}T_{2}$ and <sup>2</sup>E states. The 184 cm<sup>-1</sup> mode, however, is distinctly <sup>2</sup>E in character as it has no energetic match for any of the  ${}^{4}T_{2}$  calculations. The calculated 188 cm<sup>-1 2</sup>E mode looks exactly like the ground state 184 cm<sup>-1</sup> mode pictured in Figure 3.7, which comes as no surprise given the predicted frequency matching. This mode is a symmetric breathing of the acac ligands way from the Cr center, resulting in lengthened Cr-O bonds. The other modes appearing on both surfaces may facilitate the ultrafast ISC and require further examination.

The correlation between  ${}^{4}T_{2}$  and  ${}^{2}E$  modes at 559 cm<sup>-1</sup> is straightforward. For all of the modeled excited states, the motion is the same; the C-CH<sub>3</sub> bond is left rigid and a swinging of the methyl group causes the attached carbon to shift out of the plane of the acac backbone, and the oxygen is displaced out of plane in the opposite direction. The other side of the ligand performs this same motion, but out of phase. Figure 3.15

overlays the two extremes of this motion for comparison. This mode matching between the states is also seen at 459 cm<sup>-1</sup>, where all of the ligands exhibit a symmetric stretch across the acac backbone. This vibration is likely strongly coupled to the formation of the  ${}^{4}T_{2}$  state, where the bonding character of the Cr-O bonds is reduced due to population of the  $e_{q}^{*}$  orbital.



Figure 3.15 566 and 461 cm<sup>-1</sup> Modes on the <sup>2</sup>E and <sup>4</sup>T<sub>2</sub> Surfaces The 566 cm<sup>-1</sup> mode (left) corresponds to a torsion of the methyl group which forces the attached carbon atom to shift up or down from the plane of the ligand backbone. The methyl group on the opposite side of the ligand performs the same motion, but in the opposite direction. The 461 cm<sup>-1</sup> mode is a symmetric stretch across the acac backbone.

Further inspection of the ~225 cm<sup>-1</sup> mode reveals that  ${}^{4}T_{2}$ -ES<sub>1</sub> and -ES<sub>2</sub> are moving in an asymmetric version of the torsional scissor mode shown in Figure 3.7, where one ligand is mostly stationary and the other two scissor out of phase from each other with the methyl groups undergoing a large amplitude wag. The  ${}^{2}E$  mode at this frequency involves a similar methyl group wag, however this time it leverages the C=O arm of the acac in and out of the plane. These motions can be seen explicitly in Figure 3.16. In both cases, the large methyl group displacement alters the Cr-O bond lengths for both of these modes. It is conceivable that vibrational energy may transfer from one mode to the other during the state change since they both involve methyl wagging motions, but the connection is less obvious than the 559 and 459 cm<sup>-1</sup> modes above.



**Figure 3.16 233 cm<sup>-1</sup> Mode in both the**  ${}^{2}E$  and  ${}^{4}T_{2}$  **States** For the  ${}^{2}E$  (left), the arms of the acac ligand rotate about the C=CH bond on the backbone, with the arms moving out of phase from each other. For the  ${}^{4}T_{2}$  mode (right), the plane of the backbone remains intact but the ligands scissor out of phase with each other.

Ando *et. al.* discussed the importance modes involving Cr-O bond stretching in their theoretical study of the ultrafast ISC process. While simulating the reaction path to move from the Franck–Condon  ${}^{4}A_{2}$  geometry to the distorted  ${}^{4}T_{2}$  (optimized) geometry, they saw that this path was mainly described by low frequency modes corresponding to displacements in the primary coordination sphere. And as these modes move the geometry closer to the  ${}^{4}T_{2}$  minimum, it intersects a surface crossing with the  ${}^{2}T$  state at nearly degenerate energy near the Franck–Condon region before the geometry has had much opportunity to change.<sup>13</sup> Both the DFT results of this work and Ando's

computational results agree that almost all of the low wavenumber modes involve Cr-O bond stretching.

Revisiting the information in Table 1 armed with this mode coupling information is enlightening. For the 600 nm pump, where there is little excess vibrational energy in the excited state, only the 225 and 459 cm<sup>-1</sup> modes are able to couple the two states. This coupling is expected to be highly efficient when the vibrational motion and energy is the same between the  ${}^{4}T_{2}$  and  ${}^{2}E$  states, as is the case for the 459 cm<sup>-1</sup> mode. The coupling should still be quite good at 225 cm<sup>-1</sup>, where the same atoms are moving but with slight variations between the  ${}^{4}T_{2}$  and  ${}^{2}E$  states. When the excess vibrational energy in the system is increased by pumping at 560 nm, both the 225 and 568 cm<sup>-1</sup> modes are present, despite lacking the bandwidth to create a wavepacket in the 568 cm<sup>-1</sup> mode. Presumably, the 459 cm<sup>-1</sup> mode should be present as well, since it is seen in the 510 nm pump data. The signal to noise of the data collected while pumping at 560 nm was particularly low for both data sets despite coinciding with the ground state absorption maximum. It is very likely that the small amplitude of the oscillatory residuals obscured some of the components in the signal, this 459 cm<sup>-1</sup> mode being one of them. As with the 459 cm<sup>-1</sup> mode, the 559 cm<sup>-1</sup> vibration provides an efficient coupling between the  ${}^{4}T_{2}$  and  ${}^{2}E$  surfaces due to the identical motion in both states. The presence of these high frequency modes indicates that they are strongly coupled to the Franck-Condon excitation. This is especially true for the 510 nm pump, where only the 559 and 459 cm<sup>-1</sup> modes are seen, despite being well outside of the pulse bandwidth for wavepacket formation. All of these modes are alike in their deformation of the Cr-O bond, which is expected to be different in the  ${}^{4}T_{2}$  optimized structure, and so their

presence and coupling to each other are logical. The 184 cm<sup>-1</sup> mode, present at all pump wavelengths, may be a result of IVR in the <sup>2</sup>E state as it is lower in energy than all of the other vibrational modes initiated on the <sup>4</sup>T<sub>2</sub> surface. Since this mode corresponds to the symmetric breathing mode of the molecule, involving Cr-O bond length changes, it would be an efficient way to reverse the bond elongations in the <sup>4</sup>T<sub>2</sub> state and return to the original bond lengths on the <sup>2</sup>E surface.

This one-color data set has provided some valuable insights into the coupling between the  ${}^{4}T_{2}$  and  ${}^{2}E$  surfaces, but the data was not without its issues. For all of the data sets, the signal to noise was relatively low, and especially low for the 560 nm pump data. The pulses were not optimally compressed, which may have prevented deeper modulations from being observed. Residual chirp in the pump pulse has been known to wash out coherence oscillations, and negative chirp, in particular, has been used as a method to increase ground state vibrational coherence.<sup>32–36</sup> And in the one color experiment, the probe pulse is restricted to wavelengths within the pump spectrum, sometimes leading to probing where there is little excited state absorption signal (and further degrading the signal to noise). The two color experiments improve on a lot of these drawbacks.

### 3.3.2 Two Color Pump Dependence

For the two color experiments, the experimental set up followed the description in Chapter 2, where the output from each OPA was passed through a separate prism compressor which was optimized for each beam. These data were collected after acquiring thinner, minimally dispersive optics which were matched between the pump and probe beams, removing the cube polarizer after the sample, and utilizing both OKE

and FROG (see Chapter 2) for pulse characterization. As a result, the nominal pulse duration at the sample for the pump was 49 fs for 505 nm pump pulses and 33 fs for 560 and 600 nm pump pulses. The probe pulse, centered at 520 nm was more difficult to compress and was generally 45 fs at the sample position.

It was thought that the two color experiments might decrease the time duration of the nonlinear processes occurring around time zero. The one color experiments, with their phase and energy matching between the pump and the probe pulses derived from the same laser source, were prime candidates for cross-phase modulation (XPM) and self-phase modulation (SPM) while the pulses overlapped in the sample.<sup>37,38</sup> These processes should be minimized after moving to the two color experiments since the energy matching will be removed and the phase matching should be less. While the pulse compression should help minimize the nonresonant solvent response, reducing the XPM and SPM is thought to have a bigger effect. The nonresonant solvent response lasted until ~ 150 fs (*vide supra*) in the one color experiments, prohibiting signatures of the <sup>4</sup>T<sub>2</sub> state from being directly observed. If this window is minimized, the <sup>4</sup>T<sub>2</sub> signatures might become more apparent.

For this study, pump wavelengths of 505, 560, and 600 nm were used, for the same purpose as described in the one color data set *vide supra*. The sample absorbance at each pump wavelength was typically 0.3 - 0.5 for a 1mm path length cell. The major difference was the probe wavelength, which was set at 520 nm for all pump wavelengths. This coincides with the <sup>2</sup>E excited state absorption maximum and should help increase the signal to noise in the data. Figure 3.17 contains this spectral

information, displaying the spectrum for each pump and probe wavelength superimposed on the ground and excited state absorption spectra.



**Figure 3.17 Pump and Probe Spectra for Cr(acac)**<sub>3</sub> **Two Color Experiments** The ground (black) and excited state (solid blue) absorption spectra of  $Cr(acac)_3$  are shown in relation to the pump wavelengths (solid maroon, green, and red) used in this study. The probe wavelength recorded was tuned with a monochromator and the probe spectra are shown in dashed lines (purple, blue, and green).

Also in this study, the monochromator tuning was changed to assess the benefit of probing at the blue or red (FWHM) edge of the probe spectrum or at the maximum of the spectrum, utilizing slits set to 5 nm bandpass. Champion and coworkers have seen this tuning play a vital role in enhancing the low or high wavenumber modes observed in their one color experiments,<sup>15</sup> and so the concept was applied here. This tuning is responsible for the three probe spectra present in Figure 3.17; they all derive from the same 520 nm probe OPA pulse which is then filtered after passing through the monochromator before being recorded by the photodiode.

Data for both Cr(acac)<sub>3</sub> and MeCN were collected under identical conditions at every pump/probe combination in the study. The resulting data sets were worked up according to the procedures previously described for the one color data. Data for MeCN consisted of an average of at least 14 scans while data for Cr(acac)<sub>3</sub> was typically an average of 24 scans or more. The lower scan numbers compared to the one color experiments came from analyzing the signal to noise of the data as a function of each additional scan; these parameters proved optimal for achieving high signal to noise while minimizing data collection times (see Chapter 2 for more details).



Figure 3.18 Typical Data Set for  $Cr(acac)_3$  in the Two Color Pump-Probe Setup The full data set is seen in the bottom portion of the graph with the fit (red) of the long time amplitude components. The residual of the fit is seen in the top portion of the graph. The nonresonant solvent response ends around 135 fs, which is largely the same as the one color experiments.

Figure 3.18 shows a typical data set from these two color experiments. The nonresonant solvent response does not appear to be any shorter for these experiments, despite the better pulse compression. Here, the fit is started at 135 fs, which is a slight improvement from the one color results, but not as significant as was hoped. This could

mean that the timescale for XPM (or SPM) is intrinsically slow, so even though it may be reduced between the pulses, the process still takes the same amount of time. This is unfortunate, as it could still obscure processes from the  ${}^{4}T_{2}$  surface.

Before summarizing the results from this study, it is worth pointing out that for a given pump/probe combination, tuning the monochromator setting changed the shape of the nonresonant solvent response. This can be seen in the top half of Figure 3.19, where the solvent traces for one pump wavelength and three monochromator settings are displayed. Kovalenko et. al. have previously assessed these pulse shapes as arising from an electronic and Raman contribution to the signal. As monochromator wavelength is tuned, these components have different contributions and the shape of the peak changes.<sup>39</sup> This effect is particularly pronounced because the energy difference between the 514 nm probe and the 524 nm probe (371 cm<sup>-1</sup>) almost matches the 380 cm<sup>-1</sup> Raman mode of MeCN. The solvent traces collected with 600 nm excitation show the largest effect of this Raman contribution. This is because the C-H (2250 cm<sup>-1</sup>) and C≡N (2950 cm<sup>-1</sup>) stretching modes can interact with the 600 nm pump to produce anti-Stokes absorption at 510 and 528 nm<sup>39</sup>, which is very close to the The coupling of these two effects creates very large monochromator settings. amplitude oscillations in the solvent signal, as can be seen in the bottom half of Figure 3.19. The oscillations are out of phase by 180°, which is expected when monitoring at wavelengths that span the vibration of interest. This effect was previously observed in CH<sub>2</sub>Br<sub>2</sub> by Nelson and coworkers, who were monitoring the transmitted 615 nm probe at 609 and 620 nm using a monochromator.<sup>40</sup> They attribute this antiphase relationship to a "wagging" of the probe spectrum "back and forth between the red and blue as the





probe pulse arrives at the sample alternately in phase or out of phase with the coherent

vibrational motion induced by the excitation pulse."<sup>40</sup> This does not create challenges

for the data collection and assessment; it merely emphasizes the solvent vibration more than in the one color experiments.

### 600 nm Excitation Results

The results from 600 nm excitation are shown in Figure 3.20, below, where it is obvious that there are many more vibrations present than with the one color data sets. While the one color data rarely picked up oscillations below 150 cm<sup>-1</sup>, this is clearly a non-issue for the two color setup. Here, modes at ~30, 76, 85, 104, and 123 cm<sup>-1</sup> can be seen, along with higher energy vibrations at ~ 190, 260, 330, 380, and 510 cm<sup>-1</sup>. The peak around 380 cm<sup>-1</sup> is assigned to the MeCN Raman mode and is ignored.

The spectrum of the pulse used here, 22.2 nm FWHM at 599.8 nm, corresponds to a total energy of 617 cm<sup>-1</sup>. In the quantum beat picture then, wavepackets can be reasonably expected for the frequencies at or below 309 cm<sup>-1</sup>. The pulse duration was measured at 27 fs by FROG, and leads to a limit of 617 cm<sup>-1</sup> in the impulsive limit of excitation. Using the quantum beat limit leaves the 503 cm<sup>-1</sup> mode out of range, but considering the impulsive limit, this mode is reasonable. Given these two methods, the range of recovered frequencies is reasonable given the pulse characteristics.



Figure 3.20 Cr(acac)<sub>3</sub> 600 nm Pump, 520 nm Probe Results

Shown on the left are the raw data sets (blue dots) and the LPSVD fits (red) for each pump-probe combination. The FT power spectra of the fit are shown on the right. All of the fits contain at least four components, typically less than 380 cm<sup>-1</sup>.

### 560 nm Excitation Results

The data resulting from 560 nm excitation are shown below in Figure 3.21. As with the 600 nm excitation results, low frequency modes (less than 100 cm<sup>-1</sup>) are seen in at three probe wavelengths. The data also exhibit common peaks around 190, 250, 450, and 500 cm<sup>-1</sup>. The MeCN Raman mode at 380 cm<sup>-1</sup> was only visible when probing at 512 and 524 nm. This could be a result of the wagging mechanism described above, which clearly shows that the solvent oscillations are washed out when probing at 519 nm. Frequencies above the solvent mode are seen when probing at both 524 and 512 nm.

The pulses used here were compressed to 35 fs, making it possible to excite modes at 477 cm<sup>-1</sup> and under. The spectral excitation limit is closer to 332 cm<sup>-1</sup> (560 nm, 2.8 nm FWHM), which excludes the modes at ~455 and 505 cm<sup>-1</sup>. Clearly, this spectral excitation limit is too small to be reasonable given these results. Using the impulsive limit, only the ~505 cm<sup>-1</sup> mode is outside of the range, but given the breadth of the transition, this falls within a reasonable range.





The data (blue dots) and the LPSVD fit (red) are shown on the left for each pump/probe combination while the FT of the LPSVD fit is shown on the right. The frequencies resemble those seen following 600 nm excitation, including the broad low frequency components.

### 505 nm Excitation Results

The results following high energy excitation into the  ${}^{4}T_{2}$  state may be seen in Figure 3.22, where only the data probing at 514 nm show strong oscillations. This may be a direct result of both the increased pulse length and the decreased bandwidth. The pulses were only compressed to 52 fs here, and the bandwidth of the pulse was 8.8 nm FWHM centered at 504.6 nm. These characteristics lead to excitation bandwidths of 321 cm<sup>-1</sup> and 171 cm<sup>-1</sup>, respectively. This accounts for the majority of the recovered frequencies lying below 260 cm<sup>-1</sup>, and the noticeable absence of even the solvent mode at 380 cm<sup>-1</sup>. The consistent appearance of the 450 cm<sup>-1</sup> mode for 524 and 514 nm probes indicates that either there is enough bandwidth to excite this mode, or it is strongly coupled to the other modes that are excited in the wavepacket formation. This would also apply to the 507 cm<sup>-1</sup> mode present when probing at 519 nm. Despite the decreased frequency range available for wavepacket formation, the data exhibit similar frequencies at ~60, 183, and 220 cm<sup>-1</sup>.





Data (blue dots) and LPSVD fits (red) for each pump/probe combination are shown on the left, while the FT of the LPSVD fit is shown on the right. The oscillatory amplitude in the data is less, leading to few frequencies in the power spectrum. Recovered frequencies agree well with results from lower energy excitations.

# Discussion

The results of this two color study have been summarized in Table 3.2, along with the frequencies and damping times of a second data set (see Appendix A, Figures 3.A1-A3 for data). The first column shows the pump/probe wavelength being monitored and the oscillations are grouped by common frequencies in the columns to the right. The two rows surrounded by the pump/probe heading represent the two data sets collected for that combination. The last column in Table 3.2 shows the high frequency modes that appeared in some of the LPSVD analyses; they will not be discussed in this section, however, it is possible that they too are strongly coupled to the Franck–Condon modes of the molecule as they are beyond the expected frequency range for wavepacket formation.

As mentioned in the discussions of the data above, there are several new modes visible below 190 cm<sup>-1</sup> for these data sets, with average frequencies of 29, 70, and 111 cm<sup>-1</sup>. Other new modes are seen at ~250, 308, and 507 cm<sup>-1</sup>. The 190 cm<sup>-1</sup> and 456 cm<sup>-1</sup> modes, previously observed in the one color data above, are present here, too. For the same reasons discussed previously for the one color data, these frequencies are all attributed to vibrational coherence on the excited states of the system. By comparing these results to the ground state resonance Raman spectrum of Cr(acac)<sub>3</sub>, (Figure 3.14) it is clear there are ground state frequencies at 125, 231, 252, and 457 cm<sup>-1</sup>.<sup>14,27–29</sup> It is hard to say whether the low frequency modes are present in the ground state as none of the resonance Raman studies contain frequencies below 125 cm<sup>-1</sup>.

Excitation/Probe Wavelength, nm	Oscillations, cm <sup>-1</sup> (Damping Times, fs)								
505/512		57 (731)		186 (799)	258 (403) 221 (299)		447 (630)		
				200 (394)		285 (96)	455 (2810)		627 (347)
505/510		64 (-2830)			230 (576)			507 (568)	
505/519						277 (52)			782 (2890)
505/524				182 (556) 215 (199)			457 (524)		
	18 (-667)	61 (3190)		185 (346)	262 (745)		475 (490)		539 (1210)
		77 (99)		194 (611)	251 (7360)		452 (1650)	495 (446)	
560/512		72 (57)	122 (1403)	194 (1336)		339 (74)			588 (318)
F00/F40		65 (103)		198 (328)	252 (48)				
560/519									
560/524		50 (87)		189 (582) 209 (203)			461 (3400)	510 (513)	
	39 (2334)	84 (498)	104 (532)	156 (147)	247 (4519)				
600/515	28 (3440)		104 (7360)	202 (447)	266 (868)				
000/313				190 (323)		283 (89)	446 (217)	516 (228)	
		85 (87)				327 (1080)		503 (222)	
600/519		76 (-1790)				027 (1000)		000 (222)	
600/524	31 (421)	84 (261)	123 (2230)	181 (1640)	255 (-1850)				
0007021			102 (139)	184 (600)				509 (133)	823 (131)

Table 3.2: Summary of Oscillations Observed Utilizing Two Color Experiments on  $Cr(acac)_3$  in MeCN

Turning to the DFT frequency calculation results (Appendix C: Gaussian Calculation Results), it is apparent that the frequencies at ~507 and 308 cm<sup>-1</sup> must come from the  ${}^{4}T_{2}$  state as there are no corresponding frequencies in the  ${}^{2}E$  results. The  ${}^{2}E$  (ground state) contains large gaps in the frequencies in these regions, jumping from 453 to 566 cm<sup>-1</sup> (452-569 cm<sup>-1</sup>) and from 268 to 344 cm<sup>-1</sup> (257-349 cm<sup>-1</sup>), leaving no doubt that these come from the  ${}^{4}T_{2}$  state. The remaining modes at ~250, 111, and 68 cm<sup>-1</sup> are seen in both the  ${}^{4}T_{2}$  and  ${}^{2}E$  frequency results. Since the motions of the modes at 456 and 190 cm<sup>-1</sup> have previously been discussed and assigned in the context of the one color data, they will not be covered again here.

One of the biggest differences from the data collected using one color experiments is the presence of vibrations belonging to the  ${}^{4}T_{2}$  state. These modes, 299 and 510 cm<sup>-1</sup>, can be seen in Figure 3.23, where both exhibit large displacements
of the methyl groups on the acac backbone. The 299 cm<sup>-1</sup> mode induces asymmetric wagging of the methyl groups, which simultaneously shifts the whole acac backbone left to right about the metal center. This causes the Cr atom to shift positions to accommodate this sliding of the acac ligands. The 510 cm<sup>-1</sup> mode looks quite similar to the breathing mode across the ligand backbone previously seen at 461 cm<sup>-1</sup>, however



# Figure 3.23 <sup>4</sup>T<sub>2</sub> 299 and 510 cm<sup>-1</sup> Vibrational Motions

The 299 cm<sup>-1</sup> (left) vibration induces asymmetric wagging of the methyl groups, which also shifts the entire acac ligand about the Cr center. The 510 cm<sup>-1</sup> (right) is primarily a symmetric stretch across the acac backbone, but the ligand does not remain planar, as the central carbon and hydrogen shift up and down out of the plane as the methyl groups stretch and compress.

the acac backbone does not remain planar during this motion. Instead, the central carbon and hydrogen atom on the backbone oscillate up and down out of the plane as the methyl groups stretch and compress.

The mode at ~245 cm<sup>-1</sup> is almost the same motion on both the  ${}^{4}T_{2}$  and  ${}^{2}E$  surfaces. This mode is essentially the 254 cm<sup>-1</sup> scissor mode seen in Figure 3.7 above. A side by side comparison of the  ${}^{2}E$  and  ${}^{4}T_{2}$  motions is shown in Figure 3.24, where the differences are easily seen. The  ${}^{4}T_{2}$  vibration scissors all of the methyl groups on the



Figure 3.24 Scissoring Mode at 254 cm<sup>-1</sup> on the  ${}^{4}T_{2}$  and  ${}^{2}E$  Excited States The  ${}^{4}T_{2}$  excited states show a completely symmetric scissoring mode at 253 cm<sup>-1</sup> where all of the methyl groups swing toward the oxygens in unison. This motion is slightly modified on the  ${}^{2}E$  surface, where only one acac ligand swings the methyl groups toward the oxygens while the other two swing the methyl groups away from the oxygen. There is also some slight deformation of the acac ring in the  ${}^{2}E$ vibration, specifically in the central carbon and hydrogen atoms.

backbone in phase together, as denoted by the displacement vectors pointing towards the oxygen atoms on all ligands. For the  ${}^{2}E$  vibration, however, two of the ligands swing their methyl groups away from the Cr metal center as the third ligand swings them toward the metal center. The overall motion remains the same, but the phase between the ligands is different. Closer inspection of the ground state 254 cm<sup>-1</sup> mode shown in Figure 3.7 shows the same phase relationship as the  ${}^{2}E$  vibration shown here.

The remaining low frequency modes at ~68, 111 cm<sup>-1</sup> are composed of methyl group rotations about the C-C bond on the acac backbone. Typically, one set of methyl groups on a single acac ligand is rotating while the others are almost stationary. This is illustrated in Figure 3.25, where the methyl groups are eclipsed at the extremes of the

rotation. The  $\sim$ 30 cm<sup>-1</sup> mode, while seen at multiple pump/probe combinations, will not be discussed here given the resolution of the experiment. It is possible that it is real, but the 15 cm<sup>-1</sup> resolution from the time domain delay spacing and the total time delay window in relation to the period of the vibration (less than two full periods over the entire time window) make this frequency suspect.



**Figure 3.25 Low Frequency Methyl Group Rotation at 70 and 104 cm**<sup>-1</sup> The methyl groups on one ligand rotate approximately 180° about the C-C bond as evidenced by the ghost atoms (the opposite extreme of the rotation) in an eclipsed geometry to the original position. This is seen for both the  ${}^{4}T_{2}$  and  ${}^{2}E$  excited states.

Now that the of the oscillations has been assigned, a closer examination of their pump wavelength dependence is possible. Consistent with the one color results, the ~190 and 456 cm<sup>-1</sup> modes are seen at all pump wavelengths. The new frequencies at ~70, 250, and 507 cm<sup>-1</sup> are also seen at all pump wavelengths. Only the frequencies at ~111 and 298 cm<sup>-1</sup> seem to have a subtle pump wavelength dependence, where the 111 cm<sup>-1</sup> is prevalent at 600 and 560 nm excitation, while the 308 cm<sup>-1</sup> mode is seen for both 505 nm and 600 nm excitation. Almost all of the vibrations show up at every pump

wavelength, indicating that overall, there is not a strong pump dependence despite the large increase in extra vibrational energy to the system.

This lack of pump wavelength dependence can be understood as the excitation of vibrational overtones at higher pump wavelengths. Takeuchi *et al.* explored this concept in their studies of 10-hydrozxybenzo[h]quinoline.<sup>41</sup> They point out that oscillatory period depends on the energy difference between the coherently excited



#### Figure 3.26 Illustrations of Multimode and Progression Excitation Schemes

The two shaded Gaussians represent two different excitation pulses with different center wavelengths while the narrow lines represent vibrational modes which could be excited by these pulses. Scenario A, multimode excitation, results in completely different frequencies being excited when the pump wavelength is changed. Scenario B, progression excitation, merely excites overtones of the same vibration at a higher pump energy. Figure reprinted with permission from reference 41. © (2005) American Chemical Society.

vibrations. Therefore, two scenarios are possible when changing excitation The pump pulse could create a wavepacket of different vibrational wavelengths. modes, where the oscillatory period corresponds to the difference between these two modes. Or, the pump pulse could create a wavepacket on an overtone or combination progression where the spacing between the levels corresponds to the vibrational mode. For their study, they varied the pump energy by 1800 cm<sup>-1</sup>, but saw the same four bands in the 200-700 cm<sup>-1</sup> region of the Fourier Transform spectrum, which they concluded came "from a coherent excitation of the overtone/combination regression relevant to each vibrational mode."<sup>41</sup> This is believed to be the case for Cr(acac)<sub>3</sub> as well, where increasing the vibrational energy by >3000cm<sup>-1</sup> had no effect on the observed oscillations. This trend simply became clearer with the better signal to noise afforded in the two color experiments. Also, the presence of modes outside of the pump pulse bandwidth indicates a strong coupling between these modes throughout the  ${}^{4}T_{2}$ excited state.

The better signal to noise of these data sets allows for a more confident analysis of the associated damping times (see Table 3.2). Since the wavepackets are generated between two electronic states (see Chapter 1), electronic coherence is possible, but these dephasing times are typically sub-70 fs.<sup>42,43</sup> The majority of the damping times observed here are longer than this, so the oscillations are assigned as vibrational coherence. Pure vibrational dephasing times occur on the ps timescale, ranging from 2-10 ps depending on the molecule and the vibration.<sup>22,41</sup> Vibrational dephasing times on a sub-ps timescale, indicate the mode is modulated in some way, such as undergoing a surface crossing in this case.

With these benchmarks in mind, the damping times in Table 3.2 are broadly reclassified as sub-1 ps, longer than 1 ps, or a mixture for each vibrational mode (column). The two modes associated with the  ${}^{4}T_{2}$  state, 308 and 507 cm<sup>-1</sup>, exhibit damping times in the sub-1 ps range, save for one instance for the 308 cm<sup>-1</sup> mode. The LPSVD fit for this data (600 nm pump, 519 nm probe) was altered to examine the robustness of this damping time, but despite changing the number of oscillations in the data or where the fitting routine started, this damping remained 1 ps or greater. It is attractive to believe the 308 cm<sup>-1</sup> mode has a sub-1 ps damping time as it is associated with the  ${}^{4}T_{2}$  state which undergoes ISC in less than 120 fs. Treating the 1 ps damping time as an outlier leaves an average dephasing time of ~78 fs for this mode, which is consistent with the previously published vibrational coherence data for Cr(acac)<sub>3</sub>.<sup>14</sup>

The damping time of the 507 cm<sup>-1</sup> is clearly modulated by the ISC event, however the damping time is not as fast as the 308 cm<sup>-1</sup> also associated with the  ${}^{4}T_{2}$ . Here, the average damping time is ~350 fs; roughly four times the damping time of the 308 cm<sup>-1</sup> mode. Interestingly, the 190 cm<sup>-1</sup> also shows sub-1 ps damping times, save for two outliers. Removing these two points yields an average damping time of 425 fs. Given the uncertainty of this damping time (78 cm<sup>-1</sup>) and the presence of  ${}^{4}T_{2}$  vibrations at ~170 and 206 cm<sup>-1</sup>, it is possible that this is a mode on the  ${}^{4}T_{2}$  surface and not exclusive to the  ${}^{2}E$ .

The remaining modes, which have been attributed to vibrations on both the  ${}^{4}T_{2}$  and  ${}^{2}E$  states have a mixture of damping times ranging from 48 fs to 7 ps. It is difficult to say if these dephasing times are modulated by the surface crossing or not. Most

likely these modes are created with the initial wavepacket, but are not intimately involved in the ISC process, which accounts for the large range in dephasing times.

Liebel *et al.* describe the behavior of vibrations around surface crossings as either tuning modes or coupling modes. Tuning modes are necessary to guide the wavepacket to the surface crossing while coupling modes are the modes spanning this surface crossing. The result is coupling modes are strongly affected by the surface crossing but the tuning modes are not.<sup>44</sup> Under this description, the observed modes at 190, 308, and 507 cm<sup>-1</sup> could be coupling modes responsible for driving the ISC process. The remaining modes seem likely to be tuning modes, whose movement of the methyl groups or expansion of the Cr-O bond lengths serve to move the wavepacket to the surface crossing.

#### 3.4 Cr(acac)<sub>3</sub> Concluding Comments

Using sub-50 fs pump pulses at different energies throughout the  ${}^{4}T_{2}$  absorption, many important vibrational modes were identified. All of these involved motions in the primary coordination sphere of Cr(acac)<sub>3</sub>, with a majority relying on motions of the methyl groups in particular. Two modes were explicitly assigned to the  ${}^{4}T_{2}$  state - 308 and 507 cm<sup>-1</sup> - and identified as coupling modes between the states based on their rapid damping times. The mode at 190 cm<sup>-1</sup>, reminiscent of the mode observed in the study by Schrauben *et al.*, also exhibits a short damping time indicative of involvement in the ISC process. Modes at 70, 111, 233, 250, 456, 566 cm<sup>-1</sup> showed similar motions between the  ${}^{4}T_{2}$  and  ${}^{2}E$  states and could be facilitating the rapid ISC between the states owing to their energetic and vibrational matching. The static nature of the observed vibrations at all pump wavelengths, particularly those outside of the pump pulse

bandwidth, indicates that these modes are strongly coupled to the  ${}^{4}T_{2}$  absorption and the subsequent energy redistribution driving the system towards the surface crossing.

#### 3.5 Cr(TMHD)<sub>3</sub> Vibrational Coherence

Since the Cr(acac)<sub>3</sub> results point to a heavy reliance on the methyl group motion to facilitate the ultrafast ISC and previous TA studies on Cr(TMHD)<sub>3</sub> show this ISC is drastically slowed when the methyl groups are replaced with *tert*-butyl groups (*vide supra*), two color pump dependence studies were carried out on this system as well. Following the same two color experimental setup described for Cr(acac)<sub>3</sub>, data sets were collected for Cr(TMHD)<sub>3</sub> in dichloromethane (DCM). Unfortunately the solubility in MeCN was low and sufficient optical densities could not be achieved at the desired pump wavelengths. As a control, solutions of Cr(acac)<sub>3</sub> in DCM were checked at select pump/probe combinations and the results (Appendix A: Supplemental Data, Figure 3.A4 and Table 3.4) agreed with that for solutions in MeCN. Therefore, the results for Cr(TMHD)<sub>3</sub> may be compared directly with those of Cr(acac)<sub>3</sub> in MeCN.

A significant difference, however, is the increased stimulated Raman scattering in DCM. Not only are there more Raman peaks observed in the pure solvent spectra, their amplitude, particularly at 292 cm<sup>-1</sup>, is much higher than most of the Raman peaks from Cr(TMHD)<sub>3</sub> (*vide infra*). A typical spectrum from pure DCM is seen in Figure 3.27, where the three peaks agree well with the literature values of 285, 703, and 3053 cm<sup>-1</sup> collected in the solid state.<sup>45</sup> These modes have been assigned to the CCl<sub>2</sub> scissor mode, the symmetric CCl<sub>2</sub> stretch, and the asymmetric CH<sub>2</sub> stretch, respectively.<sup>19</sup> There must be substantial coupling between these modes, as the pump characteristics never have enough energy to excite the mode at 3053 cm<sup>-1</sup> and yet it is an important

component of the LPSVD fit of the solvent response for many pump-probe combinations.



Figure 3.27 Raman Peaks From  $CH_2CI_2$  Observed in Two Color Experiments The signal to noise for these solvent peaks is especially high compared to MeCN. The peaks agree with the literature values for DCM which are listed at 285, 703, and  $3053 \text{ cm}^{-1}$ .

The two color experiments were carried out for largely the same pump/probe combinations as Cr(acac)<sub>3</sub>, except the bluest pump wavelength was shifted to 525 nm due to laser instability. This still affords 2380 cm<sup>-1</sup> of additional vibrational energy across the 600, 560, and 525 nm excitation range. Also, since the 519 nm probe did not prove exceptionally useful in the Cr(acac)<sub>3</sub> studies, these data were recorded only at 515 and 525 nm probes. Data sets again consisted of at least 14 scans for the solvent and at least 24 scans for Cr(TMHD)<sub>3</sub> (and Cr(acac)<sub>3</sub>). The absorbance was between 0.4 and 0.5 at the pump wavelength using a 1 mm path length cuvette. Typical results for DCM and Cr(TMHD)<sub>3</sub> scans are shown below in Figure 3.28. A strong rise in the transient absorption signal with time can be seen when probing at 525 nm for all pump wavelengths. The data collected while probing at 515 nm shows much less of an

amplitude change. These results are consistent with the full spectral data for Cr(TMHD)3, presented in Figure 3.8 above. The subsequent discussion will focus on the oscillatory features of this data only.





The top graph shows a typical data set for  $Cr(TMHD)_3$  in DCM. The oscillations are much more apparent here, but as can be seen in the bottom graph of pure DCM, they are largely due to the solvent.

#### 600 nm Excitation Results

Similar to Cr(acac)<sub>3</sub>, the 600 nm pump creates a relatively vibrationally cool  ${}^{4}T_{2}$  state, while the 516 and 525 nm probes monitor signals near the maximum of the  ${}^{2}E$  excited state spectrum. The data its corresponding LPSVD fit are shown in Figure 3.29. For reference, the pure DCM power spectra are plotted with the data for that probe wavelength. These DCM peaks are easily the largest peaks in the spectrum, particularly the 282 cm<sup>-1</sup> mode, and so the vertical scales have been truncated on the power spectra to make the Cr(TMHD)<sub>3</sub> peaks more visible. There is a distinct possibility the ISRS in DCM is so pronounced because the pump bandwidth is 575 cm<sup>-1</sup>, leading to an immense number of frequency combinations available to drive the 282 cm<sup>-1</sup> mode.

Here, there are common modes at ~200 and 485 cm<sup>-1</sup>, but the spectra also exhibit peaks at 72, 122, 339, and 559 cm<sup>-1</sup>. The features are broader and less defined that the signals seen in Cr(acac)<sub>3</sub>, perhaps suggestive of the underlying physical process, or the result of the strong Raman contribution from the solvent in the data. The LPSVD program tries to find and optimize subtle oscillations superimposed on a very large signal, which makes the subtle oscillations difficult to distinguish from noise.

The pump pulse characteristics (36 fs, 600.2 nm with 20.7 nm FWHM) lead to a excitation limit of 287 cm<sup>-1</sup> in the quantum beat picture and 463 cm<sup>-1</sup> in the impulsive limit. For the quantum beat picture, this precludes the direct formation of wavepackets for the modes at 339, 492, and 559 cm<sup>-1</sup>. The impulsive limit relaxes this restriction some, but the presence of modes above these limits suggests these vibrations are strongly coupled to the Franck–Condon transition.



**Figure 3.29** Cr(TMHD)<sub>3</sub> in DCM Following 600 nm Excitation Results from exciting on the low energy side of the  ${}^{4}T_{2}$  absorption in Cr(TMHD)<sub>3</sub> while probing near the  ${}^{2}E$  absorption maximum. The peaks are broader than those seen for Cr(acac)<sub>3</sub> in MeCN, and the predominant feature is the 282 cm<sup>-1</sup> DCM mode. The 516 and 525 nm probes share common modes at 200 and 485 cm<sup>-1</sup>.

#### 560 nm Excitation Results

The 560 nm pump is slightly to the blue side of the  ${}^{4}T_{2}$  absorption maximum in Cr(TMHD)<sub>3</sub> because of the small red shift observed for both the ground state absorption and stead state emission features compared to Cr(acac)<sub>3</sub> (*vide supra*). The vibrational modes observed probing at 512 nm and 526 nm are seen in Figure 3.30, below, and have fairly well resolved peaks. Once again, the ISRS in DCM is very strong and



dominates the signal. The peaks at 88, 136, 210, and 323 cm<sup>-1</sup> echo those observed following 600 nm excitation.

**Figure 3.30 Cr(TMHD)**<sub>3</sub> in DCM Following 560 nm Excitation Results from exciting near the  ${}^{4}T_{2}$  absorption maximum and probing near the  ${}^{2}E$  absorption maximum for Cr(TMHD)<sub>3</sub>. The results from probing at 515 nm show peaks with a lot more definition, while the 525 nm probe results exhibit less definition when compared to Figure 3.29.

The spectral characteristics of the pump pulse (557.9 nm center, 18.2 nm FWHM) give an energy window of 585 cm<sup>-1</sup>, while the 32 fs pulse duration sets the impulsive limit at 515 cm<sup>-1</sup>. While the quantum beat picture suggests the modes observed at 323 and 383 cm<sup>-1</sup> cannot be excited with the initial wavepacket (292 cm<sup>-1</sup>)

limit), the impulsive limit disagrees. As the ~330 cm<sup>-1</sup> mode was also observed at 600 nm excitation, it is probable that this mode is coupled with the formation of the initial wavepacket.

#### 525 nm Excitation Results

The data collected utilizing 525 nm excitation was subject to more pump scatter than other data sets because of the direct spectral overlap of the pump and probe wavelengths. This baseline offset was removed prior to LPSVD analysis and the results, as shown in Figure 3.31, below, resemble other data sets without this issue. The vibrational modes observed with a 524 nm probe very strongly resemble the 524 nm probe data following 560 nm excitation. The vibrations present with the 514 nm probe, however, suggest the presence of higher frequency modes.

Here the pulse duration is 40 fs, reducing the window of impulsively excited frequencies to modes at 417 cm<sup>-1</sup> or less. The quantum beat picture limits the prepared wavepacket to frequencies less than 221 cm<sup>-1</sup> (525 nm center wavelength, 12.2 nm FWHM). For either case, the frequencies at 513 and 1141 cm<sup>-1</sup> are outside of this window. Obviously the mode at 1141 cm<sup>-1</sup>, which is beyond even the maximum limit given by the pulse duration (834 cm<sup>-1</sup>), is an artifact from the fit. The mode at 513 cm<sup>-1</sup>, however, supports frequencies observed at other pump wavelengths where the pulse restrictions are not so severe. It is likely that this mode is real and strongly coupled to the formation of the wavepacket in the Franck–Condon region.



**Figure 3.31** Cr(TMHD)<sub>3</sub> in DCM Following 525 nm Excitation Results from pumping on the higher energy side of the  ${}^{4}T_{2}$  absorption in Cr(TMHD)<sub>3</sub> while monitoring the excited state absorption near the  ${}^{2}E$  maximum. The data show low frequency modes similar to those observed following 560 nm excitation. The decreased pulse bandwidth reduces the DCM contributions and leads to better

resolution of the other frequencies present.

#### Discussion

The results from the data sets at the pump/probe combinations listed above have been compiled in Table 3.3. The left column gives the pump/probe information, where the data is ordered from high energy pump/probe to low energy pump/probe. The oscillations for each combination are shown in rows, where like frequencies are in the same column; the damping times for these vibrations are listed in parentheses next to the vibration. The oscillations at ~158, and 260 cm<sup>-1</sup> will not be addressed in this analysis because of their inconsistent presence at pump/probe combinations. This leaves common modes at ~67, 119, 207, 334, 399, and 495 cm<sup>-1</sup> for further analysis.

Color Pump-Probe Setup										
Excitation/Probe Wavelength, nm	Oscillations, cm <sup>-1</sup> (Damping Times, fs)									
525/512			148 (191)		247 (314)		432 (13500)		914 (1560)	
		117 (274)		216 (558)		344 (-18868)		513 (111)	1141(3500)	
525/524		133 (694)					402 (41)			
	41 (394)	120 (428)		202 (185)			383 (3100)			
560/512		109 (476)	167 (203)			323 (40300)	383 (1850)			
	52 (-7467)	106 (648)		194 (286)	265 (-4814)		396 (1275)			
560/524	88 (459)	136 (426)		210 (349)						
		141 (1258) 110 (379)		202 (306)		334 (1590)			613 (34)	
600/515		122 (180)		212 (140)		339 (84)		492 (572)		
	81 (-581)	116 (380)	181 (1966)	211 (233)		336 (256)		503 (232)		
600/524	72 (170)			197 (230)				485 (50)	559 (13300)	
		103 (303)	160 (204)	216 (539)				481 (391)		

Table 3.3: Summary of Observed Oscillations for  $Cr(TMHD)_3$  in DCM Utilizing a Two Color Pump-Probe Setup

The ground state resonance Raman spectrum for this compound is known and contains peaks at very similar frequencies to the  $Cr(acac)_3$  structure.<sup>46</sup> This is not surprising given the structures of the compounds and the frequencies discussed for  $Cr(acac)_3$ . Of the  $Cr(acac)_3$  vibrations discussed above, the ~70 and 111 cm<sup>-1</sup> modes - involving only the rotation of the methyl groups about the C-C bond - would be most significantly affected by the change from a methyl to *tert*-butyl group. Unfortunately, the  $Cr(TMHD)_3$  Raman spectrum stops at 150 cm<sup>-1</sup> and these changes, if present, are not visible.

As with Cr(acac)<sub>3</sub>, DFT calculations were performed to gain more insight into the excited state vibrations for this compound; full computational details are given in Chapter 2. The ground state was successfully optimized utilizing Gaussian '03 software<sup>47</sup> by freezing the dihedral angles of the methyl groups within the *tert*-butyl groups on the ligand backbone. This optimized structure was ported into Gaussian

'09<sup>48</sup> for re-optimization of the ground state before performing the TD-DFT and excited state frequency calculations. However, the ground state structure has not optimized after over a month of computational time. This is most likely due to the unrestricted methyl groups, where their many degrees of freedom generate a very shallow potential minimum which prevents the program from finding a global minimum.

The results from the Gaussian '03 ground state frequency calculation (UB3LYP, 6-311g(d,p), pcm dichloromethane continuum model) are given in Appendix C: Gaussian Calculation Results. These calculations were done for IR intensity and not Raman intensity, but in C<sub>1</sub> symmetry, all of the vibrations are Raman active. This allows the frequencies and their motions to be more generally applied to these results. Comparing these computational results to the experimental Raman spectrum gives a close match for frequencies up to 450 cm<sup>-1</sup>.<sup>46</sup> Between 450 and 775 cm<sup>-1</sup>, the agreement between the calculation and the experimental spectrum is not very good; there are large gaps where no frequencies are listed and yet an experimental peak is observed. However, past 775 cm<sup>-1</sup> the agreement becomes quite good again. These computational results serve as a good starting point, but should be reinvestigated to obtain better agreement with the experimental Raman spectrum.

Applying these results to the common frequencies in Table 3.3, it becomes clear that all of these vibrations have a close match in the ground state frequencies except for the 67 cm<sup>-1</sup> mode, which falls in a large gap in the frequencies. Excited state calculations should be performed explicitly, but tentatively this 67 cm<sup>-1</sup> mode is assigned to a vibration in the  ${}^{4}T_{2}$  state. The remaining frequencies, despite their close match to ground state modes, are assigned to vibrational coherence in an excited state. The

extinction coefficient for the ground state absorption maximum in  $Cr(TMHD)_3$  is only modestly higher than that for  $Cr(acac)_3$ , precluding the observation of vibrational coherence from the ground state surface. Following the same arguments laid out for  $Cr(acac)_3$ , the narrow emission spectrum indicates that the <sup>2</sup>E state is nested with the ground state potential energy surface and their frequencies are most likely similar.

Upon inspection of the vibrational modes of the ground state, it becomes clear that the *tert*-butyl groups experience the same types of motions as the methyl groups, albeit to a lesser extent. This is entirely consistent with the *tert*-butyl groups being bulkier overall. And while the individual methyl groups still rotate a fair amount, this motion is offset by their attachment to the tertiary carbon before linking into the ligand backbone. It also appears that there may be less deformation of the primary coordination sphere, though the magnitude of the Cr-O bond length change is difficult to gauge from the vibrational motions alone. The ground state vibration modes at 118, 195, 332, 397, and 508 cm<sup>-1</sup> can be seen explicitly in Figure 3.32, below.

The vibration at 118 cm<sup>-1</sup> resembles the out of phase scissor-type mode previously seen in Cr(acac)<sub>3</sub>, where the downward bend on one ligand's *tert*-butyl groups coincides with the neighboring *tert*-butyl groups flexing backwards. While this motion translated into an outward flexing of the ligand backbone for acac, particularly the oxygen atoms, this motion is greatly diminished for TMHD. The 195 cm<sup>-1</sup> mode rotates the entire *tert*-butyl group while also leveraging the ligand backbone up and down out of the plane. This mode causes some of the largest Cr-O bond length changes for all of the vibrations discussed here.



### Figure 3.32 Ground State Vibrational Modes in Cr(TMHD)<sub>3</sub>

Cr(TMHD)<sub>3</sub> ground state vibrational modes of the five commonly observed vibrations in the two color coherence data. The amplitudes of the *tert*-butyl group motions are on par with the methyl group motions, however, the motions do not translate as efficiently into ligand backbone deformations as they did for acac.

The mode at 332 cm<sup>-1</sup> is a symmetric stretch across the ligand backbone, similar to the motion observed at 461 cm<sup>-1</sup> in Cr(acac)<sub>3</sub>. As with the other modes for Cr(TMHD)<sub>3</sub>, however, the magnitude of the ligand displacement is reduced compared to Cr(acac)<sub>3</sub>. The vibrational mode at 397 cm<sup>-1</sup> consists of a pucker, where the methyl groups in plane with the ligand backbone flex up, the central carbon on the ring is forced down, and the oxygens swing up. The final vibration at 508 cm<sup>-1</sup> is another symmetric stretch across the ligand backbone, where the central carbon and proton are nearly stationary while the Cr-O bonds undergo a larger bond length change than in the 332 cm<sup>-1</sup> mode.

Assuming *that* the Cr-O bond lengths will try to lengthen to accommodate the population of an anti-bonding orbital upon formation of the  ${}^{4}T_{2}$ , it is tempting to think that the modes at 195 and 508 cm<sup>-1</sup> will be the most important of those listed above as they appear to elicit the largest Cr-O bond length changes. Their presence at all of the pump/probe combinations listed in Table 3.3 bolsters this argument. The damping times for these modes are also indicative of their role in the ISC process. The mode at 399 cm<sup>-1</sup>, corresponding to the puckering of the acac backbone, exhibits damping times over 1 ps except for one case following 525 nm excitation. It is likely that this mode, without significant Cr-O bond length changes or tert-butyl group displacement, is unaffected by the surface crossing and relaxes with the traditional dephasing time. The mode at 332 cm<sup>-1</sup> exhibits a mix of damping times, indicating that it is modulated by, but not directly driving, the ISC process. The remaining modes at 67, 119, 207, and 495 cm<sup>-1</sup> exhibit damping times less than 600 fs for the majority of the LPSVD results. This strong modulation implies that these modes are driving the ISC event, and similar to

Cr(acac)<sub>3</sub>, these modes involve large movements of the *tert*-butyl groups which change the Cr-O bond distance or the flexing of the ligand backbone directly. As the motions are somewhat similar to those observed in Cr(acac)<sub>3</sub>, but the timescale for ISC is so much slower, this implies that the *magnitude* of the motions is the driving factor. In this case, the *tert*-butyl groups mitigate the amount of Cr-O bond displacement. This strengthens the argument laid out by Ando *et al.* that Cr-O bond length changes drive the system towards the ISC event.

#### 3.6 Cr(TMHD)<sub>3</sub> Concluding Comments

Despite increasing the excess vibrational energy by over 2300 cm<sup>-1</sup>, there does not seem to be a pump dependence to the oscillations retrieved from the data for  $Cr(TMHD)_3$ . Of the vibrational modes that were observed, only a low frequency mode at ~67 cm<sup>-1</sup> was readily assigned to  ${}^4T_2$  vibrational motion. However, excited state frequency calculations were not available for this compound, limiting the analysis of these vibrations. By inspecting the ground state frequencies, it can be seen that the deformation of the primary coordination sphere appeared to be less, and the Cr-O bond lengths were not as affected in the active vibrations. This is consistent with the previous conclusions for Cr(acac)<sub>3</sub> that this deformation is vital to the ultrafast ISC and is greatly facilitated by large amplitude motions of the methyl groups and Cr-O bonds.

#### 3.7 Future Work

Any subsequent researchers should strongly investigate alternative procedures to optimize the ground and excited states of  $Cr(TMHD)_3$  using DFT methods. This would allow for a direct comparison to the frequencies established for  $Cr(acac)_3$ . Another possibility would be to optimize the structures using complete active space self-

consistent field theory (CAS SCF) in collaboration with Dr. Ben Levine (Michigan State University) and to model the excited state wavepacket motion using these methods. The wavepacket motion/path modeling performed by Ando *et al.* was done using CAS SCF methods. Under the assumption that DFT methods will work to optimize the pertinent structures for Cr(TMHD)<sub>3</sub>, the frequency calculations should be re-run to calculate the Raman intensity, not the IR intensity. These results could then be compared to the ground state Raman spectrum, which would be a better indicator of their accuracy.

Experimentally, it could be enlightening to collect full spectra data utilizing a white light continuum probe to monitor the coherence in these systems. Provided the IRF and the resolution on the diode array is good enough, the phases between probe wavelengths may be investigated and the "classic turning points" of the potential(s) identified.<sup>21,22</sup> This may reveal better wavelengths for probing the  ${}^{4}T_{2}$  oscillations, particularly in the case of Cr(TMHD)<sub>3</sub> where a bit of a spectral signature is detected blue of the  ${}^{2}E$  excited state absorption.

The data collected on Cr(TMHD)<sub>3</sub> may become clearer if the Raman modes from DCM were subtracted from the data prior to performing the LPSVD analysis. This would remove some of the largest amplitude features that are not relevant to the molecular vibrations of interest, leaving room for a finer analysis of the smaller amplitude frequencies present. This may reveal the presence of the 164 and 256 cm<sup>-1</sup> modes at more pump/probe combinations so that they may be added to the analysis.

It may also prove enlightening to zero pad the data prior to LPSVD analysis to increase the resolution in the frequency-domain. Chergui and coworkers have related

slight decreases in the oscillatory frequency with increasing excitation energy to the (an)harmonicity of the potential energy surface they are probing.<sup>21</sup> With the current resolution of this experiment at 15 cm<sup>-1</sup>, this kind of information is not available.

APPENDICES

## Cr(acac)<sub>3</sub> Two Color Data in MeCN





These data exhibit common modes at ~190, 250, and 460 cm<sup>-1</sup>, consistent with the other data set from 505 nm excitation. These modes correspond to both the  ${}^{2}E$  and  ${}^{4}T_{2}$  states. The pulse duration here was 45 fs, and the spectral bandwidth 10.8 nm.





The 517 nm probe exhibits a very broad spectrum, indicating the damping times are heavily modulated (truncated) by the electronic state change. The pulse duration was 32 fs, and the spectrum of the pulse was 17.7 nm FWHM, centered at 558.5 nm.



#### Figure 3.A3 Cr(acac)<sub>3</sub> in MeCN with 600 nm Excitation

The data collected when probing at 525 nm show clearer oscillations than have been observed for most pump probe combinations. The common modes include the sharp feature at 188 cm<sup>-1</sup>, and a broader peak at 512 cm<sup>-1</sup>, corresponding to the <sup>2</sup>E and <sup>4</sup>T<sub>2</sub>, respectively. The pulse duration was 36 fs, and the spectrum of the pulse was 23.6 nm at FWHM, centered at 600.3 nm.

#### Cr(acac)<sub>3</sub> Two Color Data in DCM

Excitation/Probe Wavelength, nm				Oscillation	s, cm⁻¹ (Dam	oing Times, fs)			
525/512	25 (84)				441 (984)	514 (356)			
525/512			192 (247)	395 (-2396)	463 (710)				
525/524									
	5 (574)			330 (2480)	432 (1290)	489 (559)	594 (2000)		
560/512			172 (144)	262 (6401)				633 (2762)	1228 (1222)
560/524			182 (800)	303 (0491)				033 (2702)	1230 (1232)
			178 (459)	405 (1450)		533 (2230)		680 (6990)	849 (413)
300/324									
600/515									
000/515		85 (-3310)	179 (1384)	291 (82)	447 (826)		556 (520)		
600/524	25 (380)		191 (1640)		435 (344)	495 (302)			

 Table 3.4:
 Summary of Observed Oscillations for Cr(acac)3 in DCM Utilizing Two Color Experiments

The strong Raman active modes in DCM result in peaks of the same magnitude as molecular vibrations of interest for the Chromium compounds. Given that these "artifacts" are so strong, they may be able to completely obscure other vibrational modes at much lower intensities. Despite these issues, the common modes found for Cr(acac)3 in DCM are a pretty close match to those found in MeCN. The one exception is the presence of a mode around 356 cm-1, but this may have been obscured by the 380 cm<sup>-1</sup> mode of MeCN previously. This strong agreement allows for direct comparisons between the Cr(TMHD)<sub>3</sub> data in DCM and the Cr(acac)<sub>3</sub> data collected in MeCN. The data summarized in Table 3.4 are presented below.



**Figure 3.A4** Cr(acac)<sub>3</sub> in DCM Following Excitation at 525, 560, and 600 nm A summary of these results is presented in Table 3.4, above. At all excitation wavelengths, the peaks are much sharper compared to the data collected in MeCN. The stronger DCM modes at 282 and 707 cm<sup>-1</sup> may be obscuring other oscillations in the data, but overall the agreement to MeCN results is quite good.

Figure 3.A4, (cont'd)



Figure 3.A4 (Cont'd)



#### Cr(TMHD)<sub>3</sub> Two Color Data in DCM



#### Figure 3.A5 Cr(TMHD)<sub>3</sub> in DCM Following 600 nm Excitation

The data (blue dots) and the LPSVD fit (red line) are shown in the plots on the left, while the power spectra of the fits are shown on the right. The DCM power spectra are shown explicitly to emphasize the strength of these modes. Except for the mode at 326 cm<sup>-1</sup>, the two data sets show a strong agreement. The pulse duration was 35 fs and the spectrum was centered at 598.1 nm (21 nm FWHM).



#### Figure 3.A6 Cr(TMHD)<sub>3</sub> in DCM Following 560 nm Excitation

The data (blue dots) and the LPSVD fit (red line) are shown in the plots on the left, while the power spectra of the fits are shown on the right. Here there is strong mode agreement at 110 and 196 cm<sup>-1</sup> modes, while other frequencies at 141, 265, 334, and 396 cm<sup>-1</sup> are present. The pulse spectrum was centered at 560.4 nm (18.1 nm FWHM) and was measured as 37 fs by FROG.



#### Figure 3.A7 Cr(TMHD)<sub>3</sub> in DCM Following 525 nm Excitation

The data (blue dots) and the LPSVD fit (red line) are shown in the plots on the left, while the power spectra of the fits are shown on the right. The modes at 1111 and 914 cm<sup>-1</sup> are beyond the pump pulse capabilities and are treated as artifacts of the fits. The spectra have a common mode at ~145 cm<sup>-1</sup>, while also exhibiting overlapping peaks at ~415 cm<sup>-1</sup>. The pulse spectrum was centered at 525.7 nm (12.1 nm FWHM), and measured 36 fs by FROG.

#### Appendix B: Ground State Recovery in Cr(acac)<sub>3</sub> and Cr(TMHD)<sub>3</sub>

Previous data on Cr(acac)<sub>3</sub> and Cr(TMHD)<sub>3</sub> were not able to fully quantify the ground state recovery timescales in these compounds because of instrument limitations. The experimental setup for these data sets used a delay line capable of delays out to ~1 ns. The timescale for ground state recovery for both of these compounds was guesstimated to be about 1 ns, but this could not be proven. With the installation of a 13 ns delay line on Wile E (see Chapter 2), these ground state recovery timescales could be characterized.



**Figure 3.B1 Ground State Recovery Dynamics for Cr(acac)**<sub>3</sub> in MeCN and DCM The ground state recovery dynamics for Cr(acac)<sub>3</sub> in DCM (blue) and MeCN (green) are shown here along with their fits. The two time constants are statistically different, which indicates a solvent dependence on ground state recovery despite the ligand field nature of the excited state. These data were collected by pumping at 560 nm and probing at 520 nm.

In Figure 3.B1 above, the ground state recovery (GSR) dynamics of Cr(acac)<sub>3</sub> in

DCM and MeCN are overlaid after normalizing to the excited state maximum. The

timescale for GSR in DCM averaged 1.15 ns for two data sets probing at five different

wavelengths. The timescale for GSR in MeCN, however, averaged 950 ps over two data sets probing at four different probe wavelengths. The ligand field nature of the excited state should keep the excited electron well shielded from the solvent, so it is not intuitive that there should be a solvent dependence. Yet these time constants are statistically different and indicate this solvent dependence requires further exploration.

The GSR dynamics for  $Cr(TMHD)_3$  in DCM are shown in Figure 3.B2 for a 560 nm pump and 530 nm probe. The average lifetime for this data set is 870 ps after probing at four different wavelengths. The shorter timescale for GSR compared to  $Cr(acac)_3$  in DCM is entirely consistent with the red-shifted emission maximum discussed above. Since the potentials are nested, a drop in their energy difference should lead to a higher rate of nonradiative decay and thus a shorter lifetime.<sup>49</sup>



Figure 3.B2 Ground State Recovery Dynamics for  $Cr(TMHD)_3$  in DCM The data shown here were collected using a 560 nm pump and a 530 nm probe. A monoexponential fit to the data yields a lifetime of ~870 ps, averaged over the data set.
### Appendix C: Gaussian Calculation Results

 $Cr(acac)_3$  Ground State Optimization

# opt ub3lyp/6-311g(d,p) scrf=(cpcm,solvent=acetonitrile) scf=(maxcycle=1000)

04			
Cr	0.00034300	-0.00139100	0.00022800
С	-2.48659800	-1.20198400	1.01090300
С	-2.51317700	-2.17477400	0.00101500
С	2.75419400	-0.19455000	-1.01258100
С	2.28874100	-1.54527800	1.01296500
С	3.14212400	-1.08304200	0.00061100
С	-1.20774800	2.48041500	-1.01332400
С	0.19776000	2.75304600	1.01018200
С	-0.62920600	3.26103800	-0.00206000
С	-1.54613100	-2.29000200	-1.00825900
0	1.58496700	0.30407700	-1.13972600
0	1.05992000	-1.21967700	1.13903100
0	-1.58553000	-0.30555600	1.13924700
0	-1.05719700	1.21810800	-1.13935100
0	0.52768300	1.52556900	1.13780800
0	-0.52762200	-1.52957400	-1.13565800
С	2.81026700	-2.50026700	2.05551200
Н	3.86069900	-2.74664300	1.90707600
Н	2.67950200	-2.05719300	3.04665800
Н	2.21661600	-3.41828200	2.03175300
С	3.75319800	0.23686200	-2.05519400
Н	4.73568600	-0.20684000	-1.90020700
Н	3.38282500	-0.04275500	-3.04541700
Н	3.84170300	1.32662400	-2.03971800
С	-1.67130600	-3.37597400	-2.04557900
Н	-2.55331700	-3.99662800	-1.89405300
Н	-1.71516600	-2.92147500	-3.03920500
Н	-0.77728300	-4.00506600	-2.01771000
С	-3.57937000	-1.16755500	2.04800800
Н	-4.32147700	-1.95035500	1.89752900
Н	-3.13603300	-1.27560400	3.04176300
Н	-4.07224800	-0.19184200	2.01893000
С	0.76663900	3.68269500	2.05100400
Н	0.46358000	4.71728400	1.89623700
Н	0.44094600	3.35524000	3.04224300
Н	1.85809800	3.61882300	2.03260300
С	-2.08171300	3.13011100	-2.05495400
Н	-2.17858700	4.20473300	-1.90672400
Н	-1.66245300	2.93839500	-3.04654600

Н	-3.07371300	2.67071400	-2.02991200
Н	-0.83430200	4.32199000	-0.00239700
Н	4.16391200	-1.43468700	0.00077300
Н	-3.33102300	-2.88107500	0.00055100

Optimization information found in file:

"CrAcac3\_D3\_Opt\_G09\_UB3LYP\_6311gdp\_cpcmMeCN6.log"

Cr(acac)<sub>3</sub> Ground State Frequencies

Stoichiometry C15H21CrO6(4) Framework group C1[X(C15H21CrO6)] Deg. of freedom 123 Full point group C1 NOp 1 Largest Abelian subgroup C1 NOp 1 Largest concise Abelian subgroup C1 NOp 1 Standard orientation:

\_\_\_\_\_

Center	Atom	ic At	omic	Coordinates	(Angstroms)
Number	Nun	nber	Туре	X Y	Z
1	24	0	0.000343	-0.001391	0.000228
2	6	0	-2.486598	-1.201984	1.010903
3	6	0	-2.513177	-2.174774	0.001015
4	6	0	2.754194	-0.194550	-1.012581
5	6	0	2.288741	-1.545278	1.012965
6	6	0	3.142124	-1.083042	0.000611
7	6	0	-1.207748	2.480415	-1.013324
8	6	0	0.197760	2.753046	1.010182
9	6	0	-0.629206	3.261038	-0.002060
10	6	0	-1.546131	-2.290002	-1.008259
11	8	0	1.584967	0.304077	-1.139726
12	8	0	1.059920	-1.219677	1.139031
13	8	0	-1.585530	-0.305556	1.139247
14	8	0	-1.057197	1.218108	-1.139351
15	8	0	0.527683	1.525569	1.137808
16	8	0	-0.527622	-1.529574	-1.135658
17	6	0	2.810267	-2.500267	2.055512
18	1	0	3.860699	-2.746643	1.907076
19	1	0	2.679502	-2.057193	3.046658
20	1	0	2.216616	-3.418282	2.031753
21	6	0	3.753198	0.236862	-2.055194
22	1	0	4.735686	-0.206840	-1.900207
23	1	0	3.382825	-0.042755	-3.045417
24	1	0	3.841703	1.326624	-2.039718
25	6	0	-1.671306	-3.375974	-2.045579
26	1	0	-2.553317	-3.996628	-1.894053
27	1	0	-1.715166	-2.921475	-3.039205
28	1	0	-0.777283	-4.005066	-2.017710
29	6	0	-3.579370	-1.167555	2.048008
30	1	0	-4.321477	-1.950355	1.897529
31	1	0	-3.136033	-1.275604	3.041763
32	1	0	-4.072248	-0.191842	2.018930
33	6	0	0.766639	3.682695	2.051004

1	0	0.463580	4.717284	1.896237
1	0	0.440946	3.355240	3.042243
1	0	1.858098	3.618823	2.032603
6	0	-2.081713	3.130111	-2.054954
1	0	-2.178587	4.204733	-1.906724
1	0	-1.662453	2.938395	-3.046546
1	0	-3.073713	2.670714	-2.029912
1	0	-0.834302	4.321990	-0.002397
1	0	4.163912	-1.434687	0.000773
1	0	-3.331023	-2.881075	0.000551
	1 1 6 1 1 1 1	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

\_\_\_\_\_

D2PCM: C-PCM CHGder 2nd derivatives, FixD1E=F FixD2E=F DoIter=F DoCFId=F I1PDM=0

Calling FoFJK, ICntrl= 100127 FMM=F ISym2X=0 I1Cent= 0 IOpCIX= 1 NMat=1 NMatS=1 NMatT=0.

Full mass-weighted force constant matrix:

Low frequencies --- -3.8391 -0.0027 0.0031 0.0037 4.4112 9.5376 Low frequencies --- 26.3456 28.8051 40.3304

Diagonal vibrational polarizability:

217.8675780 234.2381222 209.7730361 Harmonic frequencies (cm\*\*-1), IR intensities (KM/Mole), Raman scattering activities (A\*\*4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

Frequency	Frequency	Reduced	Force	IR
#	(cm <sup>-1</sup> )	Masses	Constants	Intensity
1	26.2166	3.9858	0.0016	3.2651
2	28.7735	4.1205	0.002	3.5714
3	40.3279	4.2434	0.0041	7.9486
4	48.1097	2.5121	0.0034	0.686
5	51.4403	3.0963	0.0048	0.2003
6	52.0062	3.2187	0.0051	0.1854
7	68.0942	1.2427	0.0034	3.4372
8	82.9715	1.1281	0.0046	3.0263
9	83.5244	1.1379	0.0047	3.1226
10	86.4019	1.079	0.0047	0.4086
11	97.0658	1.0474	0.0058	0.1293
12	99.6314	1.0642	0.0062	0.0177
13	161.3313	2.8076	0.0431	0.0395
14	163.2805	2.6929	0.0423	0.0835
15	164.5812	2.6541	0.0424	0.1353
16	173.5317	6.2745	0.1113	1.1729
17	175.0744	6.5556	0.1184	1.1163
18	185.029	7.202	0.1453	0.0002

19	188.0776	5.6957	0.1187	0.8625
20	223.9761	6.158	0.182	0.2097
21	224.1975	5.902	0.1748	0.1204
22	235.5933	7.1114	0.2326	0.0559
23	241.6162	5.701	0.1961	3.5632
24	242.2123	5.6188	0.1942	3.7896
25	253.0701	3.3816	0.1276	1.0896
26	254.305	3.4075	0.1298	1.2306
27	257.0314	3.1887	0.1241	0.0274
28	349.2832	7.4674	0.5368	2.4538
29	354.041	10.2077	0.7539	65.3938
30	354.5317	10.3433	0.766	65.7619
31	422.213	4.6867	0.4922	6.9978
32	422.4446	4.6587	0.4898	10.8648
33	423.1174	4.6225	0.4876	22.5902
34	449.3861	6.292	0.7486	183.5549
35	449.6824	6.3023	0.7509	181.7024
36	452.7984	5.7575	0.6955	0.5265
37	569.8092	2.8991	0.5546	0.2625
38	570.2753	2.8987	0.5554	0.2501
39	571.7161	2.9212	0.5626	0.0112
40	589.5869	4.6479	0.9519	63.1408
41	590.3822	4.6536	0.9557	63.2337
42	605.68	5.0519	1.0919	95.1482
43	675.0585	4.1237	1.1072	59.9826
44	675.2989	4.1233	1.1079	59.0579
45	680.3143	4.1274	1.1255	0.1896
46	683.0274	2.9449	0.8095	14.8856
47	683.2657	2.9289	0.8056	13.3149
48	683.9185	2.9324	0.8081	14.0529
49	800.055	1.1368	0.4287	30.3761
50	800.2164	1.1371	0.429	26.8039
51	803.0105	1.1356	0.4315	28.2682
52	947.3801	4.8275	2.5528	72.3929
53	948.3212	4.8154	2.5515	12.7933
54	948.4176	4.8179	2.5533	12.5415
55	962.6191	2.9726	1.6229	16.188
56	962.6887	2.9758	1.6249	15.8991
57	963.2125	2.888	1.5787	0.3454

Full frequency results available in file:

"CrAcac3\_D3\_freq\_G09\_UB3LYP\_6311gdp\_cpcmMeCN.log"

Cr(acac)<sub>3</sub> Time Dependent Single Point Calculation

# td=(nstates=10) ub3lyp/6-311g(d,p) scrf=(cpcm,solvent=acetonitrile) scf=(tight,maxcycle=1000)

04			
Cr	-0.00030800	-0.00092400	-0.00048000
С	2.51039100	-1.15225700	-1.01089300
С	2.55555700	-2.12397200	-0.00089000
С	-2.75017800	-0.25067700	1.01120400
С	-2.25505300	-1.59415900	-1.01216100
С	-3.11840600	-1.14902700	-0.00058000
С	1.15508400	2.50520800	1.01338700
С	-0.25387800	2.74788400	-1.01179700
С	0.56105300	3.27326900	0.00148700
С	1.59257800	-2.25563600	1.01043400
0	-1.59205700	0.27321600	1.13804700
0	-1.03367300	-1.24178700	-1.13861400
0	1.59244200	-0.27296500	-1.13882000
0	1.03070900	1.24006900	1.13942600
0	-0.55733200	1.51354900	-1.13973900
0	0.55942800	-1.51518500	1.13762100
С	-2.75559300	-2.56196600	-2.05314100
Н	-3.80027300	-2.83128500	-1.90369700
Н	-2.63502100	-2.11777700	-3.04507400
Н	-2.14173900	-3.46658200	-2.02787000
С	-3.75886500	0.16076100	2.05253300
Н	-4.73145500	-0.30442200	1.89779900
Н	-3.38310200	-0.10881600	3.04349900
Н	-3.87109500	1.24831000	2.03492000
С	1.74163700	-3.33634200	2.05011000
Н	2.63570200	-3.93932200	1.89776800
Н	1.77902000	-2.87839200	3.04241500
Н	0.86040800	-3.98338400	2.02621000
С	3.60152600	-1.09663800	-2.04868600
Н	4.35932300	-1.86460600	-1.89947500
Н	3.15968900	-1.21297900	-3.04217600
Н	4.07505700	-0.11139200	-2.01954500
С	-0.84060600	3.66520400	-2.05352700
Н	-0.56068100	4.70621400	-1.89785100
Н	-0.50510600	3.34549600	-3.04405700
Н	-1.93039300	3.57719000	-2.03797700
С	2.01458100	3.17333100	2.05543800
Н	2.08786400	4.24998200	1.90802800
Н	1.59990200	2.97165200	3.04695800
Н	3.01654100	2.73607800	2.02972400

Н	0.74350100	4.33827900	0.00205300
Н	-4.13239200	-1.52242600	-0.00075400
Н	3.38655200	-2.81471000	-0.00025000

Excitation Energies and Oscillator Strengths

Excited State	1: 4.017-A	2.5101 eV	493.94 nm	f=0.0003	<s**2>=3.785</s**2>
82A -> 97A	-0.10661				
82A -> 98A	0.12034				
83A -> 97A	-0.12427				
83A -> 98A	-0.10244				
85A -> 97A	-0.18763				
86A -> 98A	0.18125				
87A -> 97A	0.42861				
88A -> 98A	0.41403				
92A -> 97A	0.48325				
92A -> 98A	0.13908				
93A -> 97A	-0.14611				
93A -> 98A	0.46682				
This state for c	optimization and	d/or second	-order corre	ction.	
Total Energy, E	E(TD-HF/TD-K	S) = -2080.	48803091		

Copying the excited state density for this state as the 1-particle RhoCl density.

Excited State	2: 4.015-A	2.5813 eV	480.31 nm	f=0.0003	<s**2>=3.781</s**2>
82A -> 98A	-0.12051				
83A -> 97A	-0.11879				
84A -> 97A	0.11665				
85A -> 98A	-0.12355				
86A -> 97A	0.12545				
87A -> 97A	0.11609				
87A -> 98A	0.32020				
88A -> 97A	0.32094				
88A -> 98A	-0.12297				
90A -> 97A	-0.54057				
92A -> 97A	0.28338				
92A -> 98A	0.29719				
93A -> 97A	0.30226				
	0.00220				
93A -> 98A	-0.28981				
93A -> 98A	-0.28981				
93A -> 98A Excited State	-0.28981 3: 4.015-A	2.5826 eV	480.07 nm	f=0.0003	<s**2>=3.781</s**2>
93A -> 98A Excited State 82A -> 97A	-0.28981 3: 4.015-A 0.11805	2.5826 eV	480.07 nm	f=0.0003	<\$**2>=3.781
93A -> 98A Excited State 82A -> 97A 83A -> 98A	-0.28981 3: 4.015-A 0.11805 -0.12174	2.5826 eV	480.07 nm	f=0.0003	<s**2>=3.781</s**2>
93A -> 98A Excited State 82A -> 97A 83A -> 98A 84A -> 98A	-0.28981 3: 4.015-A 0.11805 -0.12174 -0.11430	2.5826 eV	480.07 nm	f=0.0003	<s**2>=3.781</s**2>
93A -> 98A Excited State 82A -> 97A 83A -> 98A 84A -> 98A 85A -> 97A	-0.28981 3: 4.015-A 0.11805 -0.12174 -0.11430 0.12087	2.5826 eV	480.07 nm	f=0.0003	<s**2>=3.781</s**2>
93A -> 98A Excited State 82A -> 97A 83A -> 98A 84A -> 98A 85A -> 97A 86A -> 98A	-0.28981 3: 4.015-A 0.11805 -0.12174 -0.11430 0.12087 0.12766	2.5826 eV	480.07 nm	f=0.0003	<s**2>=3.781</s**2>
93A -> 98A Excited State 82A -> 97A 83A -> 98A 84A -> 98A 85A -> 97A 86A -> 98A 87A -> 97A	-0.28981 3: 4.015-A 0.11805 -0.12174 -0.11430 0.12087 0.12766 -0.31374	2.5826 eV	480.07 nm	f=0.0003	<s**2>=3.781</s**2>
93A -> 98A Excited State 82A -> 97A 83A -> 98A 84A -> 98A 85A -> 97A 86A -> 98A 87A -> 97A 87A -> 98A	-0.28981 3: 4.015-A 0.11805 -0.12174 -0.11430 0.12087 0.12766 -0.31374 0.11819	2.5826 eV	480.07 nm	f=0.0003	<s**2>=3.781</s**2>
93A -> 98A Excited State 82A -> 97A 83A -> 98A 84A -> 98A 85A -> 97A 86A -> 98A 87A -> 97A 87A -> 98A 87A -> 98A 88A -> 97A	-0.28981 3: 4.015-A 0.11805 -0.12174 -0.11430 0.12087 0.12766 -0.31374 0.11819 0.12136	2.5826 eV	480.07 nm	f=0.0003	<s**2>=3.781</s**2>
93A -> 98A Excited State 82A -> 97A 83A -> 98A 84A -> 98A 85A -> 97A 86A -> 98A 87A -> 97A 87A -> 97A 87A -> 98A 88A -> 97A 88A -> 98A	-0.28981 3: 4.015-A 0.11805 -0.12174 -0.11430 0.12087 0.12766 -0.31374 0.11819 0.12136 0.33060	2.5826 eV	480.07 nm	f=0.0003	<s**2>=3.781</s**2>

92A -> 97A-0.2910992A -> 98A0.2882293A -> 97A0.2855893A -> 98A0.30993	
Excited State4:4.755-A91A ->94A-0.3538292A ->95A0.3493392A ->96A0.1459193A ->95A-0.1419193A ->96A0.3429688B ->92B-0.3251589B ->93B-0.3209490B ->91B0.59269	3.0057 eV 412.49 nm f=0.0008 <s**2>=5.403</s**2>
Excited State5:4.776-A91A ->95A0.3191591A ->96A0.1471092A ->94A-0.4158592A ->95A0.1726692A ->96A-0.2096293A ->95A-0.2100993A ->96A-0.1787688B ->91B0.4535488B ->92B-0.2109688B ->93B0.1157289B ->91B0.2366789B ->92B0.1158089B ->92B-0.3572490B ->93B-0.13355	3.0243 eV 409.96 nm f=0.0003 <s**2>=5.452</s**2>
Excited State 6: 4.776-A 91A -> 95A -0.14831 91A -> 96A 0.31849 92A -> 95A -0.20430 92A -> 96A -0.17698 93A -> 94A -0.41175 93A -> 95A -0.18375 93A -> 95A 0.21529 88B -> 91B -0.23702 88B -> 92B 0.11197 88B -> 93B 0.20996 89B -> 91B 0.45342 89B -> 92B 0.21100 89B -> 93B -0.12155	3.0246 eV 409.92 nm f=0.0003 <s**2>=5.452</s**2>

90B -> 92B 0.13167 90B -> 93B -0.35762	
Excited State 7: 4.035-A 82A -> 97A -0.10100 83A -> 98A -0.10052 85A -> 98A -0.16317 86A -> 97A -0.16415 87A -> 98A 0.37111 88A -> 97A -0.37409 92A -> 97A -0.15861 92A -> 98A 0.52252 93A -> 97A -0.52728 93A -> 98A -0.15657	3.1045 eV 399.37 nm f=0.0000 <s**2>=3.821</s**2>
Excited State8:4.019-A78A -> 97A-0.1272684A -> 97A0.1506487A -> 98A-0.2099288A -> 97A-0.2021590A -> 97A-0.7898992A -> 97A-0.1830693A -> 97A-0.2608093A -> 98A0.18744	3.2177 eV 385.32 nm f=0.0012 <s**2>=3.787</s**2>
Excited State 9: 4.019-A 78A -> 98A 0.12700 84A -> 98A -0.15218 87A -> 97A 0.20333 88A -> 98A -0.20384 90A -> 98A 0.79209 92A -> 97A 0.25339 92A -> 97A 0.25339 92A -> 97A -0.18727 93A -> 97A -0.18227	3.2206 eV 384.98 nm f=0.0011 <s**2>=3.787</s**2>
Excited State 10: 4.278-A 91A -> 94A 0.18210 92A -> 95A -0.27472 92A -> 96A -0.11494 93A -> 95A 0.11407 93A -> 96A -0.27568 87B -> 91B 0.12887 88B -> 92B 0.24758 89B -> 93B 0.24781	3.7921 eV 326.95 nm f=0.0329 <s**2>=4.326</s**2>

90B -> 91B	0.78576
90B -> 96B	0.15191

SavETr: write IOETrn= 770 NScale= 10 NData= 16 NLR=1 NState= 10 LETran= 190.

Time-Dependent Single Point Information found in file:

"CrAcac3\_D3\_TDsp3\_G09\_UB3LYP\_6311gdp\_cpcmMeCN.log"

# Cr(acac)<sub>3</sub> <sup>2</sup>E State Optimization

# opt=modredundant ub3lyp/6-311g(d,p) scrf=(cpcm,solvent=acetonitrile) scf=(fermi,maxcycle=1000)

02			
Cr	0.00000000	0.00000000	0.00000000
C	0.73268400	2.66145500	0.99687500
C	0.00000000	3.32125300	0.00000000
C	-1.93854500	-1.96525000	-0.99687500
C	-2.67122900	-0.69620400	0.99687500
С	-2.87629000	-1.66062700	0.00000000
C	2.67122900	-0.69620400	-0.99687500
C	1.93854500	-1.96525000	0.99687500
C	2.87629000	-1.66062700	0.00000000
C	-0.73268400	2.66145500	-0.99687500
0	-0.80079800	-1.40278100	-1.12639000
0	-1.61524300	0.00787900	1.12639000
0	0.81444500	1.39490200	1.12639000
0	1.61524300	0.00787900	-1.12639000
0	0.80079800	-1.40278100	1.12639000
0	-0.81444500	1.39490200	-1.12639000
С	-3.74835600	-0.43525700	2.01885600
Н	-4.64227700	-1.03349600	1.84341500
Н	-3.35903400	-0.65235600	3.01816400
Н	-4.01198800	0.62604200	2.00154700
С	-2.25112200	-3.02854300	-2.01885600
Н	-3.21617300	-3.50358200	-1.84341500
Н	-2.24447300	-2.58283100	-3.01816400
Н	-1.46382600	-3.78750400	-2.00154700
С	-1.49723400	3.46380100	-2.01885600
Н	-1.42610500	4.53707800	-1.84341500
Н	-1.11456000	3.23518600	-3.01816400
Н	-2.54816200	3.16146300	-2.00154700
С	1.49723400	3.46380100	2.01885600
Н	1.42610500	4.53707800	1.84341500
Н	1.11456000	3.23518600	3.01816400
Н	2.54816200	3.16146300	2.00154700
С	2.25112200	-3.02854300	2.01885600
Н	3.21617300	-3.50358200	1.84341500
Н	2.24447300	-2.58283100	3.01816400
Н	1.46382600	-3.78750400	2.00154700
С	3.74835600	-0.43525700	-2.01885600
Н	4.64227700	-1.03349600	-1.84341500
Н	3.35903400	-0.65235600	-3.01816400
Н	4.01198800	0.62604200	-2.00154700

3.81400400	-2.20201600	0.00000000
-3.81400400	-2.20201600	0.00000000
0.00000000	4.40403200	0.00000000
F		
F		
F		
6 F		
7 F		
8 F		
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	3.81400400 -3.81400400 0.00000000 F F F 5 7 F 5 F F F F F F F F F F F F F	3.81400400 -2.20201600 -3.81400400 -2.20201600 0.00000000 4.40403200 F F F F F F F F F F F F F F F F F F

Optimization information found in file:

"CrAcac3\_D3F\_2E\_opt\_UB3LYP\_6311gdp\_fermi\_cpcmMeCN.log"

## Cr(acac)<sub>3</sub> <sup>2</sup>E State Frequencies

Stoichiometry C15H21CrO6(2) Framework group D3[O(Cr),3C2(.CH),X(C12H18O6)] Deg. of freedom 20 Full point group D3 Largest Abelian subgroup C2 NOp 2 Largest concise Abelian subgroup C2 NOp 2 Standard orientation:

Center	Atomic	At	omic	Coordinates	(Angstroms)
Number	Numbe	er	Туре	X Y	Z
1	24	0	0.000000	0.000000	0.000000
2	6	0	0.732684	2.661455	0.996875
3	6	0	0.000000	3.321253	0.000000
4	6	0	-1.938545	-1.965250	-0.996875
5	6	0	-2.671229	-0.696204	0.996875
6	6	0	-2.876290	-1.660627	0.000000
7	6	0	2.671229	-0.696204	-0.996875
8	6	0	1.938545	-1.965250	0.996875
9	6	0	2.876290	-1.660627	0.000000
10	6	0	-0.732684	2.661455	-0.996875
11	8	0	-0.800798	-1.402781	-1.126390
12	8	0	-1.615243	0.007879	1.126390
13	8	0	0.814445	1.394902	1.126390
14	8	0	1.615243	0.007879	-1.126390
15	8	0	0.800798	-1.402781	1.126390
16	8	0	-0.814445	1.394902	-1.126390
17	6	0	-3.748356	-0.435257	2.018856
18	1	0	-4.642277	-1.033496	1.843415
19	1	0	-3.359034	-0.652356	3.018164
20	1	0	-4.011988	0.626042	2.001547
21	6	0	-2.251122	-3.028543	-2.018856
22	1	0	-3.216173	-3.503582	-1.843415
23	1	0	-2.244473	-2.582831	-3.018164
24	1	0	-1.463826	-3.787504	-2.001547
25	6	0	-1.497234	3.463801	-2.018856
26	1	0	-1.426105	4.537078	-1.843415
27	1	0	-1.114560	3.235186	-3.018164
28	1	0	-2.548162	3.161463	-2.001547
29	6	0	1.497234	3.463801	2.018856
30	1	0	1.426105	4.537078	1.843415
31	1	0	1.114560	3.235186	3.018164
32	1	0	2.548162	3.161463	2.001547
33	6	0	2.251122	-3.028543	2.018856

34	1	0	3.216173	-3.503582	1.843415
35	1	0	2.244473	-2.582831	3.018164
36	1	0	1.463826	-3.787504	2.001547
37	6	0	3.748356	-0.435257	-2.018856
38	1	0	4.642277	-1.033496	-1.843415
39	1	0	3.359034	-0.652356	-3.018164
40	1	0	4.011988	0.626042	-2.001547
41	1	0	3.814004	-2.202016	0.000000
42	1	0	-3.814004	-2.202016	0.000000
43	1	0	0.000000	4.404032	0.000000

Density matrix has only Abelian symmetry.

D1PCM: C-PCM CSMder 1st derivatives, ID1Alg=0 FixD1E=F Dolter=F I1PDM=0. D2PCM: C-PCM 2nd derivatives, FixD2E=F I1PDM=0. Density matrix has only Abelian symmetry.

Full mass-weighted force constant matrix:

Low frequencies --- -15.8024 -15.6578 -14.2954 3.8237 12.3267 23.4380

Low frequencies --- 39.8430 43.0139 55.5326

Diagonal vibrational polarizability:

195.5380719 489.3866137 122.3142559 Harmonic frequencies (cm\*\*-1), IR intensities (KM/Mole), Raman scattering activities (A\*\*4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

Frequency	Frequency	Reduced	Force	IR
#	(cm <sup>-1</sup> )	Masses	Constants	Intensity
1	14.1955	4.2528	0.0005	3.0079
2	24.5212	3.7339	0.0013	2.195
3	54.3444	2.2111	0.0038	3.4837
4	70.849	1.3973	0.0041	5.4499
5	70.8913	1.4021	0.0042	0.2125
6	79.6604	2.5257	0.0094	0.1138
7	82.2029	2.1936	0.0087	1.5807
8	82.9877	1.262	0.0051	1.2146
9	89.3912	1.594	0.0075	0.3768
10	90.2828	1.3524	0.0065	5.7928
11	101.3376	1.1325	0.0069	0.9342
12	102.3798	1.1402	0.007	0.3256
13	151.6753	3.7085	0.0503	1.007
14	167.0352	3.506	0.0576	0.4526
15	172.0613	2.6805	0.0468	0.7639
16	177.3487	4.6637	0.0864	1.3013
17	177.3705	3.6402	0.0675	0.8746
18	188.4336	7.7021	0.1611	0.0011
19	189.35	6.3673	0.1345	0.8031

20	219.6094	6.7574	0.192	0.087
21	230.2767	6.7763	0.2117	0.0049
22	233.0061	6.8219	0.2182	0.0331
23	244.4329	5.2855	0.1861	3.27
24	244.6959	5.7798	0.2039	3.3914
25	255.7133	3.3177	0.1278	1.7567
26	256.1452	3.2932	0.1273	2.0242
27	268.9053	2.9619	0.1262	0.0048
28	344.361	7.3168	0.5112	4.0771
29	354.1519	10.5116	0.7768	44.8675
30	370.2263	9.0198	0.7284	4.8262
31	422.6002	4.684	0.4929	32.3346
32	422.9382	4.6181	0.4867	8.4591
33	423.0541	4.6963	0.4952	10.2498
34	447.317	6.1315	0.7229	173.9364
35	449.8913	6.3237	0.7541	191.9691
36	453.9905	5.71	0.6934	0.2541
37	566.6775	2.9154	0.5516	0.8817
38	568.6168	2.8961	0.5517	0.1133
39	570.5048	2.9114	0.5583	0.0166
40	582.802	4.4088	0.8823	42.3951
41	593.2067	4.6246	0.9588	79.7196
42	598.2976	4.7755	1.0072	86.377
43	671.0597	4.0643	1.0784	58.6495
44	671.1865	4.0664	1.0793	57.7572
45	678.5575	4.1407	1.1233	0.2269
46	683.2759	2.9045	0.799	4.8433
47	683.495	2.9445	0.8105	15.2602
48	684.0093	2.9464	0.8122	15.7981
49	787.3624	1.1392	0.4161	18.0136
50	789.6423	1.1393	0.4186	39.2743
51	790.1191	1.1395	0.4191	33.4402
52	947.5512	4.7727	2.5247	61.3333
53	947.646	4.7191	2.4969	13.6225
54	949.0658	4.7691	2.5453	8.5107
55	961.8511	2.9736	1.6209	11.4881
56	963.0219	2.8851	1.5765	0.837
57	963.1202	2.9258	1.599	15.9825

Full frequency results in file:

"CrAcac3\_D3F\_2E\_freq\_UB3LYP\_6311gdp\_fermi\_cpcmMeCN.log"

Center Number	Ate N	omic Iumber	For X	ces (Hartrees/B Y	 ohr) Z
	 21	0 0002	 17328	0 000566690	
2	6	0.0002	5059	0.001581506	-0.004022550
3	6	-0.00024	7525	0.000501772	-0.000014982
4	6	-0.00186	39549	0.002368515	0.004047175
5	6	0.00003	88657	-0.002924625	-0.003909978
6	6	0.00069	91220	0.000234374	-0.000041111
7	6	0.00286	6799	0.000526434	0.003818593
8	6	-0.00248	38045	0.001454008	-0.003791447
9	6	-0.00011	16839	-0.000707959	-0.000004651
10	6	-0.0009	82843	-0.002796053	0.003762642
11	8	-0.0130	75614	-0.003607814	0.004388731
12	8	-0.0117	92550	-0.005396529	-0.003987986
13	8	0.0110	63766	-0.007713992	-0.004350367
14	8	0.0030	64149	0.012419743	0.004142903
15	8	0.0012	78428	0.012619253	-0.004092329
16	8	0.0092	63793	-0.009022700	0.004004488
17	6	-0.0011	17564	-0.000363875	0.000284871
18	1	-0.0002	27560	-0.000297635	-0.000246556
19	1	0.0000	10000	0.000061109	0.000042998
20	1	0.0000	27094	-0.000021160	0.000018128
21	6	-0.0011	60519	-0.000474187	-0.000280050
22	1	-0.0003	71727	0.000082859	0.000262364
23	1	0.0000	57098	-0.000039153	-0.000042005
24	1	0.0000	20059	0.000042424	-0.000033654
25	6	0.0009	25469	-0.000649822	-0.000264050
26	1	0.0001	21028	-0.000389801	0.000254464
27	1	0.0000	11898	0.000053341	-0.000035508
28	1	-0.0000	35182	-0.000002755	-0.000038806
29	6	0.0009	32462	-0.000818866	0.000281981
30	1	0.0004	09686	-0.000050204	-0.000258184
31	1	-0.0000	70118	-0.000018446	0.000051761
32	1	0.0000	11968	0.000031689	0.000022363
33	6	0.0002	58634	0.001145552	0.000256157
34	1	-0.0001	50502	0.000328834	-0.000230743
35	1	0.0000	39138	-0.000043670	0.000040543
36	1	-0.0000	33357	-0.000025274	0.000034304
37	6	0.0001	37372	0.001156944	-0.000273131
38	1	0.0002	53025	0.000274713	0.000237793
39	1	-0.0000	54616	-0.000029863	-0.000042001
40	1	0.0000	19552	-0.000043103	-0.000029141
41	1	0.0000	03893	0.000030583	0.000003624

Crl	acac	). <sup>4</sup> Τ.	FS.	Franck_	Condon	Fron	ulancias	
	acac	J3 I2		I TAHUK-		1164	lacincies	2

 42
 1
 -0.000028629
 -0.000022083
 0.000007375

 43
 1
 -0.000034840
 -0.000020771
 0.000086646

Cartesian Forces: Max 0.013075614 RMS 0.003155708 NDeriv= 129 NFrqRd= 0 NDerD0= 0 MskFDP= 0 MskDFD= 0 MskDF0= Re-enter D2Num: IAtom= 43 IXYZ=3 IStep= 2. Maximum difference in off-diagonal FC elements: I= 25 J= 1 Difference= 4.3062875163D-04 Max difference between analytic and numerical forces: I=127 Difference= 3.1412442524D-05 Full mass-weighted force constant matrix: Low frequencies --- -770.2123 -758.1657 -40.3135 -34.5176 -34.0272 -11.6055 Low frequencies --- -4.0443 -0.6309 0.5555 \*\*\*\*\*\* 5 imaginary frequencies (negative Signs) \*\*\*\*\*\* Diagonal vibrational polarizability:

0

1123.2614067 483.0419417 486.7422454 Harmonic frequencies (cm\*\*-1), IR intensities (KM/Mole), Raman scattering activities (A\*\*4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

Frequency	Frequency	Reduced	Force	IR
#	(cm <sup>-1</sup> )	Masses	Constants	Intensity
1	-770.212	13.5559	4.738	2825.685
2	-758.166	13.4877	4.5679	2752.145
3	-25.427	4.6021	0.0018	8.6182
4	-14.0682	4.1445	0.0005	1.5664
5	-7.2951	4.2034	0.0001	1.7158
6	33.1099	3.555	0.0023	0.4775
7	35.8004	3.6454	0.0028	0.285
8	42.5759	3.1836	0.0034	0.0368
9	72.6455	1.1267	0.0035	2.5713
10	86.8611	1.1163	0.005	2.7793
11	90.67	1.1433	0.0055	2.813
12	91.4955	1.0418	0.0051	0.5979
13	98.9477	1.0288	0.0059	0.252
14	103.5755	1.0468	0.0066	0.218
15	125.5881	5.8989	0.0551	8.7518
16	128.4504	6.4766	0.063	8.0457
17	144.2863	6.1342	0.0752	3.1472
18	158.5739	2.8659	0.0425	0.3185
19	159.7143	2.8313	0.0426	0.4816
20	161.8606	7.5122	0.116	0.0427
21	162.7888	2.9246	0.0457	0.5364
22	206.9017	8.4444	0.213	15.6084

23	207.979	8.3433	0.2126	15.7512
24	209.4458	7.8057	0.2017	2.6394
25	234.9917	4.1769	0.1359	0.0586
26	235.3882	4.2719	0.1395	0.1305
27	253.0619	2.878	0.1086	0.0021
28	299.4995	4.8586	0.2568	82.6918
29	300.4866	4.8515	0.2581	81.3317
30	321.2731	5.4221	0.3297	13.907
31	362.814	3.6976	0.2868	88.8394
32	363.4545	3.7129	0.289	88.8225
33	415.556	5.8394	0.5941	36.7146
34	425.5819	6.2081	0.6625	34.0675
35	426.3067	6.1958	0.6634	34.382
36	461.1155	5.6699	0.7103	0.0144
37	548.2537	4.2837	0.7593	44.8762
38	549.8997	4.3197	0.7696	46.1517
39	567.4792	2.8379	0.5384	0.0426
40	568.2269	2.8369	0.5397	0.0291
41	569.301	2.8521	0.5446	0.0127
42	588.2433	4.3817	0.8933	84.7496
43	657.9989	3.6229	0.9242	162.4704
44	658.6434	3.6413	0.9307	163.9383
45	675.3655	3.0149	0.8102	3.1003
46	676.3566	3.0247	0.8152	1.779
47	676.8748	2.8251	0.7626	7.3374
48	681.0294	4.203	1.1485	0.011
49	799.167	1.1488	0.4323	16.3954
50	800.1284	1.1471	0.4327	18.4035
51	802.1226	1.1397	0.4321	23.8632
52	919.6471	4.8073	2.3955	178.0899
53	920.2345	4.7792	2.3845	176.7851
54	947.4635	4.8488	2.5646	82.088
55	954.3888	3.5973	1.9305	3.6474
56	954.6977	3.5716	1.918	4.0252
57	960.875	2.8609	1.5563	0.0492

Full frequency results in file:

"51\_CrAcac3\_D3\_TDFCes1\_G09\_UB3LYP\_6311gdp\_cpcmMeCN\_6.log"

Center	At	omic Fa	orces (Hartrees/B	 ohr)
Number	Ν	lumber X	Y	Z
	24	0 002378924	0.003251585	 -0 000125624
2	6	0.002070024	-0.000529046	-0.004638033
3	6	-0.000261477	0.000652969	-0.000759144
4	6	-0 003043454	0.001790016	0.005169513
5	6	0.000040404	-0.003560672	-0.004790014
6	6	0.000893076	0.000741812	0.000814783
7	6	0.001667462	0.001436193	0.002849101
8	6	-0.007368265	0.00123681	-0.002665600
q	6	0.002000200	-0 000128694	0.002000000
10	6	-0.00000000000	-0.000120004	0.000701000
10	8	-0.003070230	-0.002030140	0.003200000
12	8	-0.0138852/7	-0.00202+373	-0.00050505051
12	8	0.013003247	-0.003773003	-0.00200077
1/	0 8	0.013040713	-0.000+0.00200	0.004331330
15	0 8	0.004030210	0.010013470	-0.000040313
16	0 8	0.000394712		0.003490022
10	6	-0.0010109333	-0.000400324	0.000044107
18	1		-0.000304399	-0.000122000
10	1	-0.00022080-		-0.000240249
19	1	-0.00000000000	0.000040930	0.000003428
20	с С	-0.000004920	0.000000795	0.000042759
21	1	-0.001391790	0.000031347	-0.000300039
22	1	-0.000440338		0.000331300
23	1	0.000070310		0.000001903
24	I C	0.000029000	0.000029635	-0.0000466004
25	0	0.000843927		-0.000153884
20	1	0.000096143		0.000193629
21	1	0.000005100		-0.000018417
28	I C			-0.000063414
29	0		-0.000999390	0.000464650
30	1	0.000474636	-0.000076790	-0.000326880
31	1	-0.000132988		0.000020638
32		-0.000014388	0.000062871	0.000015818
33	6	0.000293525	0.000906871	0.000339578
34	1	-0.000118906	0.000244809	-0.000169114
35	1	0.000024594	-0.000093505	0.000038422
36	1	-0.000018368	-0.000069958	0.000034601
37	6	0.000059283	0.001160461	-0.000515366
38	1	0.000240170	0.000265702	0.000234281
39	1	-0.000078194	-0.000111726	-0.000035857
40	1	0.000008956	6 -0.000106078	-0.000020841

Cr(acac)<sub>3</sub> <sup>4</sup>T<sub>2</sub> ES<sub>2</sub> Franck–Condon Frequencies

41	1	0.000124921	0.000040870	-0.000086416
42	1	-0.000033842	0.000125419	-0.000101427
43	1	0.000139221	0.000204816	0.000204008

Cartesian Forces: Max 0.015756385 RMS 0.003302774 NDeriv= 129 NFrqRd= 0 NDerD0= 0 MskFDP= 0 MskDFD= 0 MskDF0= Re-enter D2Numr: IAtom= 43 IXYZ=3 IStep= 2. Maximum difference in off-diagonal FC elements: I= 2 J= 1 Difference= 2.0907428113D-02 Max difference between analytic and numerical forces: I= 2 Difference= 8.1943078482D-05 Full mass-weighted force constant matrix: Low frequencies ----2167.0242 -161.0212 -44.4312 -35.6243 -33.1860 -19.0162 Low frequencies --- -13.9655 0.4136 1.6321 4 imaginary frequencies (negative Signs) \*\*\*\*\*\* \*\*\*\*\* Diagonal vibrational polarizability:

0

121.4717556 331.6327864 334.5315922 Harmonic frequencies (cm\*\*-1), IR intensities (KM/Mole), Raman scattering activities (A\*\*4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

Frequency	Frequency	Reduced	Force	IR
#	(cm⁻¹)	Masses	Constants	Intensity
1	-2167.0204	9.6516	26.704	840.9415
2	-155.5764	7.2931	0.104	10.3866
3	-33.4224	4.5187	0.003	8.8939
4	-21.1479	4.4563	0.0012	2.2749
5	25.6469	4.3414	0.0017	1.2007
6	35.6952	3.3622	0.0025	0.321
7	43.3537	3.196	0.0035	0.0445
8	46.0268	3.6624	0.0046	0.6558
9	71.0852	1.1242	0.0033	2.3538
10	83.7103	1.1009	0.0045	2.4267
11	89.4854	1.1596	0.0055	4.4456
12	92.3799	1.0469	0.0053	0.8112
13	100.498	1.0433	0.0062	0.5425
14	102.5824	1.1037	0.0068	1.5461
15	109.1961	4.8863	0.0343	13.2648
16	132.5392	5.8602	0.0607	8.9201
17	153.1845	3.7319	0.0516	1.4269
18	155.8156	2.7387	0.0392	2.1365
19	16.2099	2.8071	0.0425	0.2804
20	164.3605	5.0298	0.0801	0.6217
21	174.7507	6.7929	0.1222	7.461
22	206.7838	6.8947	0.1737	23.1944

23	209.8929	7.4473	0.1933	0.6547
24	217.9602	7.5137	0.2103	7.7766
25	233.6366	4.6196	0.1486	1.4119
26	253.144	2.8657	0.1082	0.164
27	280.1321	3.5158	0.1626	48.1992
28	295.997	4.4539	0.2299	78.5832
29	309.1275	5.0038	0.2817	19.6423
30	328.3854	3.9003	0.2478	21.9234
31	392.3375	4.1394	0.3754	63.2157
32	414.8776	5.8495	0.5932	38.1312
33	421.9145	5.7992	0.6082	7.8017
34	433.1555	6.055	0.6693	47.7396
35	461.8671	5.6687	0.7125	0.1112
36	510.849	4.663	0.717	121.469
37	535.146	4.3532	0.7345	42.5631
38	555.4657	3.4754	0.6318	72.5056
39	567.9235	2.8386	0.5394	0.2575
40	569.4568	2.8362	0.5419	0.0522
41	576.7309	3.2418	0.6353	55.4134
42	584.0202	4.146	0.8332	79.4147
43	664.7032	3.29	0.8565	72.3566
44	672.2625	3.5303	0.94	47.3913
45	673.1968	3.0149	0.805	24.3398
46	676.9728	3.0583	0.8258	22.6162
47	681.4291	4.2205	1.1547	4.4245
48	747.1275	2.061	0.6778	14.0182
49	776.9436	2.5291	0.8995	105.8726
50	800.4544	1.137	0.4292	32.6154
51	805.1386	1.3409	0.5121	95.6439
52	871.7398	2.0637	0.924	35.3473
53	940.3703	4.3966	2.2907	33.5854
54	947.2403	4.8463	2.562	83.5445
55	953.8618	3.959	2.1223	2.068
56	960.8199	2.8633	1.5574	0.3778
57	980.5215	2.4589	1.3929	75.642

Full Frequency results in file:

"55\_CrAcac3\_D3\_TDFCes2\_G09\_UB3LYP\_6311gdp\_cpcmMeCN\_5.log"

Center	At	omic Forces (Hartrees/Bohr)			
Number	Ν	lumber X	Ϋ́Υ	Z	
1	24	-0.002714742	-0.004122521	-0.000046339	
2	6	0.001273674	0.003402512	-0.003651481	
3	6	-0.002002891	0.000147989	0.002004351	
4	6	-0.000471955	0.002280159	0.002714019	
5	6	-0.001173742	-0.002052645	-0.002977726	
6	6	0.000224649	-0.000397955	-0.000889704	
7	6	0.003821955	-0.000607484	0.004959694	
8	6	-0.002416109	0.002652568	-0.005125266	
9	6	-0.000582462	-0.001039620	-0.000849988	
10	6	0.001811188	-0.003290638	0.003764545	
11	8	-0.009869092	-0.002481289	0.005043911	
12	8	-0.009164719	-0.006905889	-0.006292110	
13	8	0.009556618	-0.007819743	-0.003235689	
14	8	0.003341828	0.015558780	0.002819062	
15	8	-0.000212497	0.016186610	-0.003503943	
16	8	0.008010197	-0.011638298	0.005236608	
17	6	-0.001194472	-0.000309581	0.000560539	
18	1	-0.000232299	-0.000302876	-0.000256546	
19	1	0.000089193	0.000106273	0.000041419	
20	1	0.000089781	0.000003765	0.000012518	
21	6	-0.000793084	-0.000421883	-0.000330429	
22	1	-0.000236286	0.000054277	0.000172324	
23	1	0.000095892	-0.000011605	-0.000039231	
24	1	0.000064244	0.000029645	-0.000033363	
25	6	0.001217859	-0.000774003	-0.000528429	
26	1	0.000174105	-0.000481838	0.000342459	
27	1	-0.000031012	0.000121419	-0.000012076	
28	1	-0.000074887	0.000021090	-0.000039261	
29	6	0.000615834	-0.000608687	0.000078306	
30	1	0.000277686	-0.000037786	-0.000174059	
31	1	-0.000044624	-0.000008678	0.000024810	
32	1	-0.000011830	-0.000006058	0.000036324	
33	6	0.000362339	0.001480663	0.000269225	
34	1	-0.000161883	0.000421436	-0.000312476	
35	1	0.000051306	-0.000061137	-0.000006253	
36	1	-0.000024340	-0.000030006	0.000050165	
37	6	0.000077979	0.001249978	-0.000102095	
38	1	0.000235523	0.000292337	0.000249253	
39	1	-0.000046878	-0.000009059	0.000001033	
40	1	-0.000010788	-0.000017260	-0.000052051	

Cr(acac)<sub>3</sub> <sup>4</sup>T<sub>2</sub> ES<sub>3</sub> Franck–Condon Frequencies

41	1	-0.000123419	0.000003585	0.000100512
42	1	-0.000023074	-0.000120268	0.000093455
43	1	0.000225238	-0.000456281	-0.000116018

Cartesian Forces: Max 0.016186610 RMS 0.003333712 NDeriv= 129 NFrqRd= 0 NDerD0= 0 MskFDP= 0 MskDFD= 0 MskDF0= Re-enter D2Numr: IAtom= 43 IXYZ=3 IStep= 2. Maximum difference in off-diagonal FC elements: I= 31 J= 1 Difference= 1.9636044146D-02 Max difference between analytic and numerical forces: I= 2 Difference= 8.7459572511D-05 Full mass-weighted force constant matrix: Low frequencies --- -154.6618 -44.7489 -36.1738 -33.0693 -18.4061 -16.6625 Low frequencies --- -2.0377 0.1448 12.2391 3 imaginary frequencies (negative Signs) \*\*\*\*\*\* \*\*\*\*\* Diagonal vibrational polarizability:

0

387.0160192 158.1267646 349.7548627 Harmonic frequencies (cm\*\*-1), IR intensities (KM/Mole), Raman scattering activities (A\*\*4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

Frequency	Frequency	Reduced	Force	IR
#	(cm <sup>-1</sup> )	Masses	Constants	Intensity
1	-149.8352	7.9434	0.1051	4.6834
2	-33.6827	4.5904	0.0031	8.7123
3	-16.7687	4.3651	0.0007	2.1972
4	21.5635	4.2386	0.0012	1.1522
5	35.2963	3.4715	0.0025	0.5718
6	41.6333	3.219	0.0034	1.2271
7	44.1268	3.3063	0.0038	1.0272
8	74.6448	1.1373	0.0037	3.9609
9	86.007	1.1202	0.0049	2.8663
10	89.8131	1.1436	0.0054	3.0747
11	90.9557	1.0399	0.0051	0.4093
12	96.6092	1.0251	0.0056	0.0106
13	103.6217	1.1244	0.0071	1.8828
14	105.6699	4.4387	0.0292	14.6871
15	131.2359	6.0376	0.0613	1.7702
16	153.7542	2.9864	0.0416	2.2314
17	155.5129	3.9665	0.0565	0.5409
18	160.6081	2.7243	0.0414	0.5672
19	163.6143	4.5172	0.0712	0.7203
20	173.5606	6.4944	0.1153	4.6642
21	208.6461	7.5508	0.1973	2.2309
22	211.2271	6.3978	0.1682	15.3486

23	218.5326	0.7052	0.1887	7.7177
24	246.8184	3.6346	0.1305	4.5719
25	253.5211	2.8914	0.1095	0.0402
26	285.1337	3.5959	0.1722	26.9849
27	297.0941	4.4466	0.2312	81.2436
28	308.5585	5.1356	0.2881	23.5642
29	344.5261	5.1444	0.3598	14.3617
30	392.5418	4.2013	0.3814	53.6338
31	414.4057	5.9082	0.5978	35.9193
32	419.2758	5.5708	0.577	5.9365
33	430.8188	6.1042	0.6675	23.482
34	461.8454	5.668	0.7124	0.218
35	496.9239	5.921	0.8614	203.2983
36	534.991	4.114	0.6938	28.6242
37	546.7318	4.2293	0.7448	84.8744
38	567.7088	2.8237	0.5362	0.0652
39	569.3938	2.8479	0.544	0.0481
40	571.7911	2.9901	0.576	15.3764
41	584.2736	4.1885	0.8424	80.0203
42	662.9227	3.5202	0.9115	95.1469
43	671.9139	3.4653	0.9218	43.6442
44	675.5913	2.8823	0.7751	8.6461
45	676.5269	3.0854	0.832	24.9282
46	668.2721	4.2163	1.153	2.2582
47	731.177	2.3692	0.7463	35.3519
48	775.6787	2.8968	1.0269	92.1412
49	798.7288	1.1506	0.4325	38.9857
50	803.7035	1.3577	0.5167	101.9407
51	848.4491	1.5321	0.6498	22.6894
52	938.8627	4.4646	2.3187	43.4268
53	947.2227	4.8478	2.5627	83.4048
54	954.1186	4.0522	2.1734	2.4758
55	960.7874	2.8662	1.5589	0.4556
56	975.6518	2.5425	1.4259	45.1092

Full frequency results in file:

"54\_CrAcac3\_D3\_TDFCes3\_G09\_UB3LYP\_6311gdp\_cpcmMeCN\_5.log"

# Cr(TMHD)<sub>3</sub> Ground State Optimization

# opt ub3lyp/6-311g(d,p) s	<pre>scrf=(solvent=dichloromethane,pcm)</pre>
scf=(tight,maxcycle=1000)	

04			
Cr	-0.00626800	-0.00228800	-0.00119800
С	-2.56845500	-1.04887500	-1.01880800
С	-3.31517300	-0.43775700	0.00184800
С	1.68029200	2.19006500	1.02112400
С	0.36821600	2.74488400	-1.00632400
С	1.28371700	3.07623600	0.00618900
С	1.07442200	-2.55639900	1.00285500
С	2.19819200	-1.67442300	-1.02214300
С	2.04565900	-2.63497300	-0.00866600
С	-2.74967400	0.34378400	1.02283800
0	1.27020800	0.98911900	1.12676700
0	-0.20607800	1.61342300	-1.11372000
0	-1.30219000	-0.97026000	-1.12790600
0	0.22390700	-1.61509000	1.11070000
0	1.48523200	-0.62489300	-1.13068900
0	-1.50543400	0.59193500	1.13215700
С	-0.03543300	3.75552000	-2.09845500
С	2.67608900	2.60759800	2.12161700
С	-3.61408600	0.98734200	2.12541900
С	-3.23940100	-1.89128000	-2.12195200
С	3.27144500	-1.81723600	-2.11960200
С	0.95074600	-3.63785000	2.09471400
Н	2.70938500	-3.48050700	-0.00935700
Н	1.70161900	4.06662400	0.00638000
Н	-4.38102600	-0.57626300	0.00210200
С	4.18062900	-0.56967500	-2.05114800
Н	4.91999400	-0.60388200	-2.85672800
Н	3.59063200	0.34169600	-2.15238400
Н	4.71777500	-0.52688700	-1.09897000
С	2.54132800	-1.84576100	-3.48134600
Н	3.27205400	-1.87601400	-4.29506000
Н	1.90280200	-2.73024900	-3.56580000
Н	1.91604000	-0.96028600	-3.59986000
С	4.13589600	-3.08102800	-1.98211400
Н	4.68884900	-3.09752700	-1.03903600
Н	3.53823000	-3.99411200	-2.04837400
Н	4.86800200	-3.10705400	-2.79414500
С	1.98360000	-4.76881200	1.96977600
Н	1.88423900	-5.31050400	1.02528900
Н	3.00839800	-4.39602100	2.04854000

Н	1.83200400	-5.48870200	2.77914000
С	1.12347600	-2.93944700	3.46255300
Н	0.40567600	-2.12587000	3.57114100
Н	0.96838400	-3.66016500	4.27087400
Н	2.13044800	-2.52442400	3.56699800
С	-0.47186700	-4.23439900	2.00003600
Н	-0.62760000	-4.95684800	2.80664900
Н	-1.22358000	-3.44848100	2.07994900
Н	-0.61767200	-4.75288000	1.04764100
С	-3.39333300	2.51543500	2.05950700
Н	-3.93829800	3.00595000	2.87149900
Н	-2.33339400	2.75482100	2.15092600
Н	-3.75641100	2.92449100	1.11188500
С	-3.10605600	0.45475200	3.48442400
Н	-3.64908900	0.94014000	4.30077300
Н	-3.26368300	-0.62477000	3.56702100
Н	-2.04044800	0.65462400	3.60036100
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Optimization information found in file:

"CrTBut3\_opt\_UB3LYP\_6311gdp\_tight\_CH2Cl2.log"

Cr(TMHD)<sub>3</sub> Ground State Frequencies

Stoichiometry C33H57CrO6(4) Framework group C1[X(C33H57CrO6)] Deg. of freedom 285 Full point group C1 Largest Abelian subgroup C1 NOp 1 Largest concise Abelian subgroup C1 NOp 1 Standard orientation:

\_\_\_\_\_

Center	Ato	omic Ate	omic	Coordinates	(Angstroms)
Number	Ν	umber	Туре	X Y	Z
1	24	0	-0.006103	-0.002530	-0.001252
2	6	0	-2.550578	-1.091745	-1.018463
3	6	0	-3.307402	-0.493123	0.002232
4	6	0	1.643222	2.218033	1.020770
5	6	0	0.321827	2.750462	-1.006585
6	6	0	1.231592	3.097477	0.005914
7	6	0	1.117482	-2.538131	1.002742
8	6	0	2.226194	-1.637366	-1.022197
9	6	0	2.089929	-2.600516	-0.008806
10	6	0	-2.754694	0.297576	1.023245
11	8	0	1.253711	1.010423	1.126265
12	8	0	-0.233211	1.609592	-1.113704
13	8	0	-1.285948	-0.992164	-1.127415
14	8	0	0.251433	-1.611316	1.110432
15	8	0	1.495606	-0.600221	-1.130614
16	8	0	-1.514895	0.566459	1.132164
17	6	0	-0.099874	3.754303	-2.098035
18	6	0	2.632421	2.652020	2.120725
19	6	0	-3.629488	0.927127	2.125602
20	6	0	-3.207312	-1.945479	-2.121326
21	6	0	3.301654	-1.761938	-2.119593
22	6	0	1.011709	-3.621541	2.094419
23	1	0	2.767765	-3.434813	-0.009577
24	1	0	1.632601	4.094853	0.006097
25	1	0	-4.370829	-0.649287	0.002577
26	6	0	4.190065	-0.499533	-2.050529
27	1	0	4.929955	-0.521260	-2.856047
28	1	0	3.585118	0.402029	-2.151488
29	1	0	4.726332	-0.448237	-1.098273
30	6	0	2.572170	-1.801889	-3.481377
31	1	0	3.303383	-1.819713	-4.295014
32	1	0	1.948353	-2.696776	-3.566280
33	1	0	1.932329	-0.926811	-3.599596
34	6	0	4.186858	-3.011401	-1.982578

35	1	0	4.739760	-3.019331	-1.039347
36	1	0	3.604387	-3.934214	-2.049510
37	1	0	4.919495	-3.024873	-2.794430
38	6	0	2.063515	-4.734985	1.969820
39	1	0	1.973596	-5.278279	1.025300
40	1	0	3.081875	-4.344990	2.048891
41	1	0	1.923852	-5.457341	2.779133
42	6	0	1.172135	-2.920361	3.462340
43	1	0	0.440898	-2.118781	3.570629
44	1	0	1.028636	-3.643591	4.270548
45	1	0	2.172034	-2.488693	3.567301
46	6	0	-0.400672	-4.241855	1.999173
47	1	0	-0.544709	-4.966565	2.805915
48	1	0	-1.165517	-3.468618	2.078408
49	1	0	-0.537263	-4.762990	1.046854
50	6	0	-3.432806	2.458523	2.060031
51	1	0	-3.985556	2.940214	2.872033
52	1	0	-2.376773	2.714621	2.151645
53	1	0	-3.802117	2.862044	1.112438
54	6	0	-3.113452	0.402383	3.484647
55	1	0	-3.664333	0.879005	4.300895
56	1	0	-3.254052	-0.679505	3.567026
57	1	0	-2.051156	0.619016	3.600953
58	6	0	-5.125997	0.603100	1.992753
59	1	0	-5.544493	0.979744	1.055494
60	1	0	-5.316932	-0.471894	2.049001
61	1	0	-5.672435	1.078639	2.812109
62	6	0	-4.733157	-2.070979	-1.985191
63	1	0	-5.021417	-2.548834	-1.044941
64	1	0	-5.230789	-1.099348	-2.045745
65	1	0	-5.118796	-2.689538	-2.800579
66	6	0	-2.869516	-1.289428	-3.479219
67	1	0	-1.790407	-1.188101	-3.598733
68	1	0	-3.260866	-1.902853	-4.296172
69	1	0	-3.317835	-0.294391	-3.557041
70	6	0	-2.574188	-3.353953	-2.061928
71	1	0	-2.964847	-3.972051	-2.875615
72	1	0	-1.489675	-3.290972	-2.155677
73	1	0	-2.808653	-3.850907	-1.115838
74	6	0	-1.632048	3.931423	-1.999609
75	1	0	-1.983640	4.588109	-2.800818
76	1	0	-2.136223	2.968301	-2.086285
77	1	0	-1.914647	4.381602	-1.043241
78	6	0	0.257399	3.132164	-3.466756
79	1	0	-0.088784	3.784761	-4.273674
80	1	0	1.339461	3.008413	-3.571587

81	1	0	-0.210077	2.153375	-3.577480
82	6	0	0.577851	5.128385	-1.975325
83	1	0	0.329368	5.624900	-1.033472
84	1	0	1.666072	5.054683	-2.050680
85	1	0	0.234180	5.774102	-2.788376
86	6	0	1.925801	2.460038	3.481698
87	1	0	1.579068	1.432147	3.592141
88	1	0	2.618225	2.691286	4.296518
89	1	0	1.061586	3.124948	3.572252
90	6	0	3.858222	1.714124	2.042299
91	1	0	4.555639	1.944666	2.853029
92	1	0	3.550047	0.671542	2.126909
93	1	0	4.388157	1.839742	1.093401
94	6	0	3.102426	4.109960	1.995657
95	1	0	3.628558	4.290833	1.054418
96	1	0	2.270136	4.815259	2.067701
97	1	0	3.797146	4.335993	2.809612

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D1PCM: PCM CHGder 1st derivatives, ID1Alg=0 FixD1E=F Dolter=F I1PDM=0. D2PCM: PCM 2nd derivatives, FixD2E=F I1PDM=0.

Full mass-weighted force constant matrix:

Low frequencies --- -5.0145 -0.4812 -0.4373 -0.4069 4.1410 6.9898 Low frequencies --- 18.4737 20.4902 23.0544

Diagonal vibrational polarizability:

116.4688699 116.7047242 105.3680123 Harmonic frequencies (cm\*\*-1), IR intensities (KM/Mole), Raman scattering activities (A\*\*4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

Frequency	Frequency	Reduces	Force	IR
#	(cm⁻¹)	Masses	Constants	Intensity
1	18.2755	3.3669	0.0007	0.227
2	20.4312	3.6713	0.0009	0.3943
3	23.0143	3.4814	0.0011	0.4944
4	25.2674	3.6597	0.0014	0.0755
5	25.9923	3.8296	0.0015	0.1586
6	27.4391	3.7309	0.0017	0.0776
7	29.9929	3.264	0.0017	0.4019
8	31.9933	3.4654	0.0021	0.8365
9	33.4997	2.8659	0.0019	0.0009
10	35.6147	2.8771	0.0022	0.1619
11	38.5039	2.8689	0.0025	0.1735
12	41.9633	2.867	0.003	0.1688
13	100.8995	3.5794	0.0215	0.0181
14	101.1567	3.5947	0.0217	0.0168

15	101.8567	3.5771	0.0219	0.0169
16	105.6548	3.5855	0.0236	0.0005
17	117.5628	3.6654	0.0298	0.0088
18	118.0998	3.7118	0.0305	0.0002
19	128.2623	4.7313	0.0459	0.7587
20	128.6817	4.628	0.0452	0.8362
21	144.9243	5.5638	0.0688	1.8776
22	147.696	4.1286	0.0531	0.5747
23	148.6459	4.149	0.054	0.5084
24	162.4987	4.0419	0.0629	0.0046
25	173.6687	3.6551	0.065	0.0005
26	194.9265	3.6374	0.0814	0.4016
27	195.9064	3.724	0.0842	0.4301
28	225.207	1.1404	0.0341	0.0763
29	226.4832	1.1203	0.0339	0.0669
30	231.2644	1.1144	0.0351	0.1208
31	232.8817	1.1647	0.0372	0.038
32	234.9977	1.1466	0.0373	0.1526
33	238.1153	1.1911	0.0398	0.058
34	243.5331	3.2124	0.1123	0.872
35	244.3063	3.0345	0.1067	0.8628
36	245.2233	3.1794	0.1126	0.0366
37	257.5745	1.9962	0.078	2.7301
38	260.7001	1.3002	0.0521	0.3092
39	263.1375	1.4323	0.0584	0.2531
40	268.9919	1.4946	0.0637	0.1721
41	273.8445	1.0972	0.0485	1.9672
42	276.6702	1.1605	0.0523	1.6744
43	280.8726	1.0609	0.0493	0.9038
44	287.4233	2.4105	0.1173	0.0712
45	289.2685	2.6036	0.1284	0.0166
46	290.0132	1.7499	0.0867	1.3807
47	291.3943	1.8141	0.0908	1.2234
48	300.9694	2.3285	0.1243	0.6676
49	301.6888	2.5719	0.1379	0.4976
50	307.561	1.9257	0.1073	2.7508
51	308.8207	2.954	0.166	4.672
52	313.1395	1.5352	0.0887	1.7888
53	315.1697	1.2367	0.0724	0.1306
54	316.6857	1.1976	0.0708	0.443
55	318.6556	1.7092	0.1023	0.4894
56	320.5557	1.1025	0.0667	0.2236
57	323.6215	1.0909	0.0673	0.1217

58	327.0698	1.1273	0.071	0.26
59	332.8058	3.038	0.1983	10.9424
60	333.4395	2.8544	0.187	10.7044
61	335.4487	2.7995	0.1856	1.0575
62	339.9574	3.342	0.2276	3.1423
63	340.8428	3.5224	0.2411	5.9462
64	350.8306	2.8121	0.2039	3.2993
65	357.3407	4.0279	0.303	38.2188
66	358.3249	3.9609	0.2996	37.169
67	380.6851	2.3223	0.1983	0.0307
68	382.2625	2.3148	0.1993	0.0137
69	384.2575	2.3252	0.2023	0.0055
70	394.9038	2.527	0.2322	1.7213
71	397.4567	2.6327	0.245	5.6323
72	398.811	2.6079	0.2444	5.0955
73	425.1591	3.085	0.3286	3.5672
74	426.791	3.096	0.3323	2.1907
75	430.5251	3.0104	0.3288	0.6984
76	436.1022	3.2217	0.361	47.3761
77	437.4707	3.2119	0.3622	43.9997
78	449.1244	3.3607	0.3994	15.7752
79	486.7284	3.4449	0.4808	5.9195
80	487.1537	3.4635	0.4843	10.0042
81	488.1145	3.5823	0.5029	30.2129
82	508.8166	2.9875	0.4557	84.4536
83	509.1458	2.9671	0.4532	73.5988
84	509.7069	2.9579	0.4528	60.3285
85	616.446	5.7066	1.2777	4.3061
86	616.6079	5.7072	1.2785	3.1649
87	628.87	6.4745	1.5086	29.6565
88	633.4348	5.4608	1.291	140.5741
89	633.8612	5.506	1.3034	141.1427
90	640.5657	5.4596	1.3199	0.0798
91	734.4712	6.859	2.18	0.1044
92	734.7538	6.8622	2.1827	0.1532
93	735.55	6.8851	2.1948	0.0461
94	741.9074	5.099	1.6536	18.7563
95	742.2771	5.0825	1.6499	8.4784
96	742.3258	5.0709	1.6464	7.2031
97	783.9681	1.5679	0.5678	2.0078
98	785.2257	1.6209	0.5888	1.475
99	785.5607	1.6237	0.5904	0.9113
100	814.2106	2.6838	1.0483	29.194

101	815.0004	2.5271	0.989	29.2484
102	815.5555	2.5401	0.9954	29.7115
103	823.3595	2.7219	1.0872	0.9982
104	823.8905	2.723	1.089	1.0276
105	824.1743	2.7198	1.0885	0.5062
106	876.2946	2.4966	1.1295	78.2135
107	877.0469	2.496	1.1312	64.2808
108	877.2474	2.493	1.1304	31.2945
109	933.0998	1.7754	0.9108	0.1305
110	933.245	1.7823	0.9146	3.304
111	933.3714	1.7826	0.915	1.8531
112	934.329	1.7924	0.9219	2.196
113	935.8002	1.7873	0.9222	0.7332
114	936.0061	1.7861	0.9219	2.8752
115	941.9181	1.7369	0.9079	4.6597
116	942.9179	1.7442	0.9137	4.792
117	943.4478	1.7425	0.9138	3.5097
118	944.4368	1.6413	0.8625	0.5298
119	945.1549	1.6301	0.858	0.2779
120	946.539	1.6459	0.8688	0.8523
121	965.4229	1.2038	0.661	0.0405
122	966.9366	1.2039	0.6632	0.0504
123	967.0493	1.2036	0.6632	0.0345
124	967.2392	1.2081	0.6659	0.1307
125	967.4571	1.2004	0.662	0.0356
126	968.9027	1.2015	0.6645	0.0557
127	981.8449	4.6293	2.6294	10.7047
128	981.9576	4.6382	2.635	10.3943
129	982.8075	4.6238	2.6314	0.3104

Full frequency results in file:

"CrTBut3\_freq\_UB3LYP\_6311gdp\_tight\_CH2Cl2\_3.log"

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#### 4 Magnetic Field Dependence of Intersystem Crossing in Cr(III) Compounds

#### 4.1 Introduction

External magnetic fields have been shown to alter the rates and mechanisms of reactions involving electron spins, including triplet-triplet annihilation, intersystem crossing (ISC), and electron transfer.<sup>1–3</sup> These magnetic field effects have received interest since the late 1960s, primarily focusing on radical pairs, separate but correlated spins in unique orbitals on the molecule; the application of an external field can change the rate of spin evolution and therefore the rate at which these two spins can recombine into a singlet state.<sup>3</sup> This rate dependence on magnetic field arises from the Zeeman splitting of the initial spin states, as can be seen in Figure 4.1. The Zeeman splitting is given by:

$$E = \beta \cdot g \cdot H \cdot m_s \tag{4.1}$$

in which  $\beta$  is the Bohr magneton (0.4668 cm<sup>-1</sup>T<sup>-1</sup>), *g* is the effective g factor, *H* is the magnetic field strength (in Tesla, T), and *m<sub>s</sub>* is the spin quantum number.<sup>4</sup> Shown in Figure 4.1 are the Zeeman splittings of a singlet and triplet state with an applied magnetic field, in which the Zeeman splitting is a perturbation on the initial energy of the state. The singlet, with m<sub>s</sub> = 0, shows no dependence on the magnetic field, as would be expected from Equation 4.1. The triplet state, however, is composed of m<sub>s</sub> = -1, 0, 1 values. As for the singlet, the energy of the triplet's m<sub>s</sub> = 0 level shows no field dependence, however, the m<sub>s</sub> = 1, -1 states do show a field dependence where the m<sub>s</sub> = -1 level is stabilized with increasing field strength. As long as the energy gap between the states involved is small compared to the mechanism mixing them (i.e. spin-orbit coupling or hyperfine

coupling), state mixing is allowed. When the Zeeman splitting produces an energy gap larger than the magnitude of this mixing, the states may no longer communicate and the rate of the process is affected.<sup>5</sup>



# Figure 4.1 Schematic of Radical Ion Pair Energy Levels as a Function of Magnetic Field

The radical ion pair depicted here involves exchange between a singlet (S) and triplet (T) state, however the T state is split in a magnetic field into individual  $m_s$  levels by Zeeman splitting. The coupling between the states is represented by 2J, and where the splitting is larger than 2J, the states may no longer couple to produce the singlet product. Reprinted with permission from reference 3. © (1989) American Chemical Society.

These radical pairs are primarily systems with low total spin (i.e. singlets, doublets, and triplets) based on organic compounds, but recently transition metal systems have gained traction for their access to higher spin multiplicities.<sup>6</sup> Many of these studies focus on photochemical processes such as quenching,<sup>7</sup> ligand loss, or photoaquation<sup>8</sup>; however, some have focused on the photophysics between states within a single transition metal compound.<sup>7-9</sup> Ferraudi and coworkers have studied the of Cr(III) rate of emission in а series polypyridine compounds

tris(2,2'bipyridine)chromium(III) tris(perchlorate) and tris(1,10phenanthroline)chromium(III) tris(perchlorate) - and found a 10% increase in the rate with applied fields of 5 T.<sup>8</sup> Aside from this simple decrease in the lifetime of the doublet emissive state, the emission spectra as a function of field showed an intensity shift from 725 nm to 690 nm, indicating the population of a different state. These compounds can be represented by the same d<sup>3</sup> Tanabe-Sugano diagram presented in Chapter 3 (Figure 3.1) for tris(2,4-pentanediono)chromium(III),  $Cr(acac)_3$ , where the lowest energy states are closely spaced  ${}^{2}T_{1}$  and  ${}^{2}E$  states. The nominal D<sub>3</sub> symmetry of the Cr(III) polypyridyls forces the  ${}^{2}T_{1}$  excited state to split into E and A<sub>2</sub> states in zero field, and the Zeeman splitting with applied field causes these states to split further. The increase in emission at 690 nm is assigned to intensity stealing from the <sup>2</sup>E excited state after the  ${}^{2}T_{1}$  state splits in the field. The overall effect of the field then is to increase the coupling between the excited and ground states, which causes a decrease in the lifetime (increase in the rate).<sup>8</sup>

While  $Cr(acac)_3$  is roughly octahedral in symmetry and should not suffer from this same geometric splitting in zero field, it is anticipated that application of large magnetic fields might perturb the ISC dynamics in this compound. Using very simplistic modeling, the splitting of the ground and excited states for  $Cr(acac)_3$  with applied fields up to 25 T is shown in Figure 4.2. This model assumes the  ${}^4T_2$  and  ${}^2E$  initial energies are given by their absorption and emission maxima, respectively, does not account for any splitting in zero field from geometric considerations, and assumes g = 2 for the g factor. The Zeeman splittings have been calculated according to Equation 4.1, giving a reduction in

the  ${}^{4}T_{2}$ - ${}^{2}E$  energy gap of 46.7 cm<sup>-1</sup> at 25 T. Whether this perturbation is enough to measurably affect the rate of ISC is unknown.



Figure 4.2 Proposed Zeeman Splitting of  $Cr(acac)_3$  in Fields up to 25 T The ground (black),  ${}^4T_2$  (green), and  ${}^2E$  (blue) states of  $Cr(acac)_3$  and their proposed Zeeman splitting in fields up to 25T. This model assumes g = 2 for all states and the  ${}^4T_2$  and  ${}^2E$  states are located at their absorption and emission maxima in zero field, respectively.

Investigation of this possible effect utilizes ultrafast laser spectroscopy with sub-50 fs pulses in high (>15 T) magnetic fields in fluid solutions, which is a very new combination in this area of research. For fields of this magnitude, experiments were carried out at the National High Magnetic Field Laboratory (NHMFL) to make use of the specially designed Split Florida-Helix magnet, capable of producing fields up to 25.2 T. The two compounds investigated in this study are  $Cr(acac)_3$  and tris(2,2,6,6-tetramethyl- $3,5-heptanediono)chromium(III), <math>Cr(TMHD)_3$ , which have been well characterized in zero field time resolved measurements. As discussed in Chapter 3, following excitation into the  ${}^4T_2$  state,  $Cr(acac)_3$  undergoes sub-100 fs ISC to the  ${}^2E$  state, where vibrational cooling is proceeds on a 1.1 ps timescale. Following the same  ${}^{4}T_{2}$  excitation, Cr(TMHD)<sub>3</sub> exhibits a much slower ISC process, occurring in ~1.8 ps followed by vibrational cooling. Any field induced modulations to this ISC timescale should be easy to measure. Cr(acac)<sub>3</sub> therefore forms the control for monitoring the behavior of vibrational cooling in the presence of a large magnetic field. It is simplistically assumed that vibrational cooling will be field independent because it involves the oscillation of the electric dipole of the molecule, but not the spin of electrons in the molecule. These experiments seek to confirm that vibrational cooling is a field independent process and that the application of high magnetic fields can modulate the ISC timescale in simple Cr(III) compounds.

### 4.2 Methods

The experiments performed in this chapter are TA experiments akin to those described in Chapters 2 and 3, except that the sample is housed within a very large magnet capable of producing fields up to 25 T. Optical windows allow the beams to pass through the magnet to the sample and on to the photodiodes where detection takes place in the standard fashion. Section 4.2.1 details the specifics of the TA experiment built at the magnet lab, while section 4.2.2 discusses the magnet, the Split-Florida Helix.

### 4.2.1 Optical Components

This data was collected at the National High Magnetic Field Laboratory in Tallahassee, FL with the help of Dr. Stephen McGill and Dr. Michael Bishop. The laser experimental setup included a Vitara oscillator (Coherent, 80 MHz, 511 mW out at 800

nm) coupled to a Legend Elite Duo (Coherent, 1 kHz, 4.6 W at 800 nm) regenerative amplifier capable of producing 4 W at the output with 35 fs pulses. A portion of the output beam is routed into an OPerA Solo optical parametric ampifier (OPA) to produce visible light output at 520 nm (~300 mW output). The OPA output power is attenuated externally with a variable neutral density (ND) filter wheel before passing through a 90° periscope to rotate the polarization from vertical to horizontal. This horizontal polarization is necessary for the prism compressor on the beam line, which uses a one prism configuration.<sup>10</sup> The prism compressor output passes through a thin wedge (1.5 mm fused silica, 2-3°) to generate the pump, probe, and reference beams. The transmitted beam is used as the pump beam, the front surface reflection is used as the probe beam, and the rear surface reflection is used as the reference beam. The pump beam was passed over a delay line (Aerotech, PRO165LM with Ensemble controller) capable of ~800 ps delays before passing through a wire-grid polarizer, waveplate, and optical chopper (NewFocus, 3501, 217 Hz) just prior to the final turning mirror. A 1 m focal length lens placed after this mirror is used to focus the pump beam onto the sample located inside the bore of the magnet. The probe beam passes through a 1 mm piece of fused silica to balance the chirp caused by the wedge on the pump beam. The probe beam is routed over a distance roughly equal to the pump beam and is passed through a wire grid polarizer and thin waveplate so that the pump and probe beam polarizations are at magic angle. The probe beam is reflected toward the sample at a small angle (vertical offset) from the pump and passes through the center of the same 1 m lens to focus on the sample. The transmitted probe beam is attenuated with a variable ND filter wheel before passing through a monochromator (Mini-chrom, DMC1-

03) equipped with 300 µm slits (2 nm bandpass) and focused with a lens into the photodiode (Thor Labs, PDA55). The reference beam reflection is directed towards the reference photodiode by a single mirror and passes through a variable ND filter wheel before the photodiode (Thor Labs, PDA55). This reference detection takes place near the pump delay line in order to minimize the number of open beams near the magnet. The signals are recorded using lock-in amplification with SRS830 lock-in amplifiers connected to the computer using a GPIB interface. The data are collected using LabVIEW programs written by Drs. McGill and Bishop, which function in largely the same way as the coherence LabVIEW program previously described in Chapter 2. The data sets consist of an average of at least three scans.

Sample solutions were prepared using a home-built UV-Vis instrument coupled to an Ocean Optics USB 2000 spectrometer. Spectra were collected after data collection to ensure sample integrity. Typical sample absorptions were 0.3-0.4 at the pump wavelength in a 1 mm path length cell.

The pulse compression was checked each day by alternately routing the prism compressor output to an SHG FROG setup which included a plate of fused silica to compensate for the dispersion of the lens, waveplates, polarizers, and the wedge. FROG trace collection was accomplished using a custom-built LabVIEW program<sup>11</sup> previously described in Chapter 2, and subsequently characterized using the MATLAB FROG code available from Professor Trebino.<sup>12</sup> Typical pulse durations for these experiments were ~45 fs.

#### 4.2.2 Magnet Capabilities and Probe Design

The magnet used for these experiments is the Split Florida-Helix, a specially designed split resistive magnet capable of producing 25.2 T fields while accommodating four elliptical viewing/scattering ports in the mid-plane region for optical experiments. Each port is a cone shape with a 45° horizontal spread and an 11.4° vertical spread, allowing for maximum versatility with various transmissive and reflective experiments.<sup>13</sup> For the ultrafast experiments described here, the pump and probe beams enter through one port and exit out the port on the opposite side; the two side ports are not used. The vacuum plates on the faces of the ports were removed to minimize the dispersion in the experiment.

A cross section of the magnet can be seen in Figure 4.3. The vertical channel running through the center of the magnet is called the bore. In this cross sectional view, two of the viewing ports are shown with their apex meeting at the central bore of the magnet; this is the sample position inside the magnet. The vertical gold bars, wrapped in shades of orange/brown, above and below these ports represent the five resistive coils generating the magnetic field. In this arrangement, the field is perpendicular to the probe beam propagation through the sample.

The sample cuvette is lowered into the bore of the magnet, and thus the optical beam path, by a custom-designed probe. This probe, at the most basic level, is a long rod with a special cuvette holder secured to the end capable of holding three sample cuvettes in a vertical arrangement. This allows for a quick vertical adjustment of the probe to change the sample without affecting the pump-probe overlap in the cuvette. Further details about the probe are given in Appendix A. The data presented here were

collected at constant fields, typically with a 0 T data set collected prior to ramping the field and after ramping the field.



# Figure 4.3 The 25 Tesla Split Florida-Helix Magnet

While the entire inner workings of the magnet are shown here, only a few components will be highlighted. The central, vertical tube is the bore of the magnet where the probe was loaded and the cuvette height adjusted so that it was centered on the opening of the ports. The cones tapering toward the central tube from the right and left are the viewing ports which were used to pass the beams through the sample. See text for details. Figure reproduced with permission from reference 14. © National High Magnetic Field Laboratory.

#### 4.3 NHMFL Studies

#### 4.3.1 Dynamics of Cr(acac)<sub>3</sub> in Acetonitrile and Dichloromethane in High Fields

Previous studies on Cr(acac)<sub>3</sub> confirming that the vibrational cooling timescale is 1.1 ps were performed in acetonitrile (MeCN), so the initial magnet studies reproduced these conditions.<sup>15</sup> Since the experiments were restricted to one color, the pump pulse was tuned to 525 nm, producing a vibrationally hot  ${}^{4}T_{2}$  state, while the probe was tuned to 521 nm, corresponding to the  ${}^{2}E$  absorption maximum. The data, collected over an ~3 ps window and at fields of 0, 5, 15, and 25 T, are shown below in Figure 4.4. The inset, which shows an expanded view of the change in absorbance with field, shows



**Figure 4.4 The Dynamics of Cr(acac)**<sub>3</sub> in MeCN in Fields From 0 T to 25 T Shown in the large plot are the full scale dynamics of the solvent window and Cr(acac)<sub>3</sub> dynamics; the inset focuses on the signals from Cr(acac)<sub>3</sub>. The amplitude of the signals are small, but all of the data fit well to a 1.1 ps decay as expected for vibrational cooling on the <sup>2</sup>E surface.

that the kinetics are identical in fields up to 15 T. The 25 T trace, however, does not appear to have the same amplitude, despite the fit of the data being the same.

Because of the minimal amplitude change in the signal, the exponential fit results in a large error; however, if the fit is fixed at 1.1 ps, the residuals are reasonable, as shown in Figure 4.5.



Figure 4.5 Cr(acac)<sub>3</sub> in MeCN with 1.1 ps Fit

Shown here is the data collected at 15 T (525 nm pump, 530 nm probe) with a fixed 1.1 ps exponential decay. The residuals, shown at the top of the figure, show a good agreement for this fit, despite the lack of significant amplitude change. This agrees with the zero field vibrational cooling timescale for  $Cr(acac)_3$ .

A closer examination of the nonresonant solvent response around time zero reveals there are some changes with field to the shape and amplitude of these peaks. A comparison to the data collected on pure MeCN at the same magnetic fields reveals these same changes. The trace at 0 T is just slightly different than the traces at 5 and 15 T, while the trace at 25 T shows the most marked difference of the grouping. This can be seen in Figure 4.6, below, in which the largest difference in the 25 T trace occurs on the positive side of the differential signal. This is in agreement with the solvent signals observed in the presence of Cr(acac)<sub>3</sub>, where the 25 T solvent response had

less amplitude in the positive spike than at other fields. Unfortunately, the cause of this field dependence for the solvent response is not known at this time; it is possible that the probe becomes less stable at higher fields and the transient absorption experiment is sensitive enough to register this small change in the sample position at high fields.



**Figure 4.6 Acetonitrile Cross Correlation Signals from 0 to 25 T** The MeCN signal shows little variation with field up to 15 T but shows a dramatic difference in the signal at 25 T. This is consistent with the data collected on  $Cr(acac)_3$  solutions and suggests an intrinsic field dependence on the solvent signal.

The data collected in dichloromethane (DCM) look largely the same as the data in MeCN. The oscillations in the data are from the impulsive stimulated Raman scattering in DCM; an FFT of the raw solvent trace (Appendix B, Figure 4.B1) cleanly returns a 280 cm<sup>-1</sup> frequency component which matches the literature value of 281.5 cm<sup>-1</sup> very well.<sup>16</sup> While the data have better agreement between all of the fields in this case, the fits are subject to the same errors from a lack of significant amplitude change in the system. As with the MeCN data, these traces may also be fit with a fixed 1.1 ps exponential decay to give quite reasonable residuals (Appendix B, Figure 4.B2). Closer examination of the dynamics occurring around time zero reveals that the data show close agreement until 25 T. This shifting at full field is consistent with the data on pure DCM (Appendix B, Figure 4.B3) and reproduces the shifting observed for MeCN in a 25 T field.



Figure 4.7 The Dynamics of  $Cr(acac)_3$  in DCM in Fields From 0 to 25 T The traces at different fields have better amplitude matching between different magnetic fields than those seen in MeCN. The oscillations in the data are from DCM and match the ground state -CCl<sub>2</sub> scissor mode.

For both of these data sets, the ISC process was not visible in the recovered kinetics. Given the results from 35 fs pump pulses in Chapter 3, this observation is not surprising. And, loosely assuming the ISC perturbation works in the same fashion as the Cr(III) polypyridyls, the ISC would be faster in applied fields because of the increased coupling between the initial and final states. Despite the small amplitude changes observed in these data sets, they uniformly show a 1.1 ps decay which corresponds to the vibrational cooling timescale in zero field, indicating that vibrational cooling is indeed independent of field.

## 4.3.2 Dynamics of Cr(TMHD)<sub>3</sub> in Dichloromethane in High Fields

The data for Cr(TMHD)<sub>3</sub> was collected over a larger time delay window in order to resolve the ~1.8 ps ISC process previously observed in this compound.<sup>17</sup> The probe, at 524 nm, is tuned to the <sup>2</sup>E absorption maximum and should be well positioned to observe the formation of the <sup>2</sup>E state. Indeed, this increase in absorption is seen in all fields from 0 T to 25 T; however, these dynamics appear uniform at all fields (Figure 4.8). The amplitude change observed in these data sets is enough to obtain reasonable, unrestricted fits for all fields. The recovered time constants agree with the previously observed 1.8 ps component within error (Appendix B, Figure 4.B4).



Figure 4.8 Dynamics of Cr(TMHD)<sub>3</sub> in DCM at Fields From 0 to 25 T The rise in the change in absorbance is associated with the transfer of population to the <sup>2</sup>E from the <sup>4</sup>T<sub>2</sub> excited state. The kinetic fits of all traces agree within error to the 1.8 ps ISC timescale observed in zero field.

The solvent response also appears more uniform for all fields, in contrast to the dynamics observed for  $Cr(acac)_3$ . The shape of the solvent response appears as a negative spike rather than a derivative signal as a result of the increased step size in the experiment. Scans using smaller step sizes show the derivative solvent signal around time zero as expected (not shown).

The agreement of the fits for this data set to that collected in zero field indicates that the 25 T field was not enough to perturb the ISC dynamics in Cr(TMHD)<sub>3</sub>. Simplistically, the Zeeman splitting in this system may be viewed in the same way as was illustrated in Figure 4.2 for Cr(acac)<sub>3</sub>, despite the slight shifting in absorbance and emission maxima for this compound.<sup>17</sup> The Zeeman splitting would reduce the  ${}^{2}\text{E}{}^{-4}\text{T}_{2}$  energy gap by ~45 cm<sup>-1</sup>, while causing a separation between the ms levels of 70 cm<sup>-1</sup> at full field. Given that the thermal energy in the system ( $k_BT$ ) is 207 cm<sup>-1</sup>, it is not surprising that the Zeeman splitting did not have a large effect on the system. It should be stressed, however, that the proposed Zeeman splitting is based on a number of simplistic assumptions about geometry and the g factor that may not be accurate for this system, especially the splittings in the excited states.

The Cr(TMHD)<sub>3</sub> data set was only collected once due and so the results need to be verified with subsequent data sets; however, the initial results indicate that the applied magnetic fields are not successfully modulating the ISC dynamics observed in this system. It may also be argued that since the 1.8 ps component was previously assigned to *both* ISC and vibrational cooling processes, that the vibrational cooling timescale outweighs the ISC process in this time constant. As vibrational cooling has

been shown to be independent of field in  $Cr(acac)_3$ , this would explain the field independence of the kinetics observed in  $Cr(TMHD)_3$ .

### 4.4 Concluding Comments

The experiments performed at the magnet lab had an interesting set of limitations which made for less than ideal experimental conditions. The largest factor in the stability of these data sets resulted from ongoing maintenance in the building, manifesting as instability in the room temperature and thus, the laser output. Unfortunately, these circumstances could not be prevented and efforts were made to obtain the best laser stability possible under such conditions. Another factor affecting the quality of the data was the use of a wedge to form the probe and reference beams. The reflection off the wedge typically produced a probe pulse with a power of 0.056 µJ for a pump pulse of 3 µJ. Values for experiments performed in our research lab at Michigan State University typically utilize pump powers of 5 µJ and probe powers at 1/10<sup>th</sup> of the pump power, or 0.5 µJ. These lower pump powers result in less excited state population and the extremely low probe powers could be responsible for the minimal excited state signals observed. Changing the slit settings on the monochromator to a wider setting did not significantly increase the signals observed. The primary advantage of the wedge is that any double pulses produce will not trace the same vector as the primary beam direction (i.e. the back reflection used as the reference), which is not the case with traditional beam splitters. It is possible that better signals could have been achieved through the use of anti-reflection coated beam splitters instead of the wedge.

Another key difference in the experimental set-up is the use of one lens to focus both the pump and the probe on the sample. Not only did the 1 m focal length produce a wider beam waist at the focal point, it is unlikely that the beam size of the pump and probe beams are significantly different. The lens position was optimized by observing the excited state signal at positive time as a function of lens position, but it is difficult to ensure that the tightest focus at the sample was achieved. The long focal length was necessary due to the breadth of the magnet, as well as safety concerns for the field strength immediately outside of the magnet. While every effort was made to use nonmagnetic optical mounts and bases, all optics were kept at least two feet from the surface of the magnet as a precaution. With these restraints in mind, a 1 m focal length lens gave the tightest focus for these parameters.

Coupled to the issue of beam spot sizes and focal planes is the changing of the probe rod position each time the set of samples was changed. The improved probe adjustment set-up greatly reduced variations in sample position between cuvettes in the same holder, but when the entire probe rod was removed and replaced, it was not guaranteed to maintain the same position as before. The "best probe alignment" ensured that the probe was centered within the bore when viewed from below the magnet and that the back reflection off the cuvette was not following the incoming pump beam (i.e. the cuvette was slightly canted in the bore). Care was taken to aim this back reflection to the same location each time the sample was changed to ensure the canting remained uniform between cuvettes.

Given these issues and the results from the data sets collected, it has been successfully shown that vibrational cooling is a field independent process. The

vibrational cooling timescales for Cr(acac)<sub>3</sub> in both MeCN and DCM agree well with data collected in zero field, and are consistent for multiple data sets. The lack of any ISC signatures in these kinetic traces precludes any modulation of the ISC timescale for Cr(acac)<sub>3</sub>. Initial experimental observations for Cr(TMHD)<sub>3</sub> indicate that the application of fields up to 25 T does not result in a measurable difference in the time constant for ISC. This should be verified in future experiments, which would also benefit from moving to a two color experimental set-up. This would allow the pump to be tuned to the ground state absorption maximum, while the probe could be tuned to the <sup>2</sup>E maximum. These conditions should increase the signal-to-noise of the data set and hopefully provide larger amplitude changes in the observed signals.

It may also be possible to expand these experiments variable temperature data sets, along with changing the applied field. The magnet is capable of variable temperature measurements, but a new probe designed to work with a cryostat will be needed. The reduction in temperature would reduce the thermal energy in the system, potentially magnifying the effect of the Zeeman splitting on the ISC kinetics. APPENDICES

#### Appendix A: Probe Design

The results presented in this chapter are the product of two trips to the NHMFL one in July of 2014 and one in January of 2015 - both of which proved to be a useful learning experience for all parties involved. The trip in July helped to resolve many unexpected data collection issues, as this was the second time transient absorption experiments had been performed in the Split Florida-Helix. The data collection programs were refined, the delay line programming improved, and the cuvette holder went under a redesign.

This first iteration of a probe for transient absorption experiments consisted of a cage-like apparatus being attached to the top of the magnet to hold the probe in place during experiments. This holder, depicted in Figure 4.A1 B, consisted of four arms, spaced around a circle 90° apart with two vertically spaced tension screws in each arm. The top screws were used to tilt the probe rod (Figure 4.A1, A) as necessary to ensure it was centered in the bore of the magnet, while the bottom screws were optimized initially for centering in the bore and then not significantly adjusted when the probe was reinserted into the magnet. The cuvette holder at the end of the probe (Figure 4.A1, B and C), pinches the sides of the cuvette in a narrow track and is mounted to the bottom of the probe rod with a set screw. While this design allowed for optimal use of the cuvette face, it required the probe rod to be removed from the magnet each time a new sample was necessary.

When removing the probe from the magnet, only two of the top tension screws and two of the bottom tension screws of the probe holder were loosened. It was hoped that by not adjusting two of the screws, a probe position close to the previous position



## Figure 4.A1 Initial Probe Design

Panel A displays the entire probe rod, where the thicker spacers near the top help secure the rod in the probe holder above the magnet. Panels B and C detail the cuvette holder design, where narrow tracks help hold the sides of the cuvette and ensure it stays upright in the probe. Panel D shows the tension screw apparatus used to align the probe inside the bore of the magnet; the bottom screws aligned the bottom of the rod, while the top screws tilted the top of the rod.

might be obtained. However, in practice, the cuvette was most likely in a different

position. The aluminum spacers seen at the top of the rod were prone to deformation,

and required successively more adjustments of the tension screws to obtain a

reasonable alignment in the bore as the experiments progressed throughout the week.

To circumvent some of these issues, a new probe was designed which would

allow for three cuvettes to be loaded vertically at one time and for the probe position to

be largely maintained between sample changes. The new probe design can be seen in Figure 4.A2, below, where the probe rod now contains an outer "sleeve" to allow the inner rod to move up and down without adjusting the tilt of the rod overall. The probe holder was changed from the cage-like apparatus to two plates with x-y axis adjustments on them. These plates were sandwiched on the top and bottom of the optical table above the magnet to achieve the same fixed position and adjustment settings as the cage-like apparatus in the previous version. The x-y plate below the optical table (Figure 4.A2 C) fits snuggly around the probe rod and is optimized for probe centering in the bore; for all successive sample changes, this position is not adjusted. The top x-y plate is adjusted as necessary after the samples were changed, though this was hardly necessary. The opening of the x-y plate is fairly snug around the probe rod, but the tension clamp at the top of the probe rod locks the probe arm in its vertical position. The range of motion allowed by this set-up is really quite minimal and greatly reduced alterations in the probe position when changing the cuvettes.

To move to a different cuvette, the top tension clamp was loosened and the inner rod was adjusted and reclamped. As before, the cuvette was canted slightly to ensure the back reflection of the pump did not trace the original beam path. The ability to switch samples by a simple vertical adjustment of the probe was a phenomenal improvement over the initial probe design and greatly reduced the time required to get a new sample in place for the experiment. The experiments detailed in this chapter were collected with this new, three sample probe.



# Figure 4.A2 Improved Probe Design

Panels A,B,C detail the x,y micrometer adjustment design for precise probe rod alignments. The new probe rod, seen in panels D and F, allows for the inner rod to be adjusted while the outer rod maintains the alignment within the bore. Panel E displays the new three cuvette design, so that three samples may be monitored with a single probe alignment.





**Figure 4.B1 FFT of the Oscillatory Component in the DCM Signal** The oscillatory feature observed in the DCM signal was processed in IGOR to give the FFT of the signal as described in chapter 2. The 280 cm<sup>-1</sup> agrees well with the expected 282 cm<sup>-1</sup> -CCl<sub>2</sub> scissoring mode for DCM.





Typical data for  $Cr(acac)_3$  in DCM is shown here for 15 T (518.5 nm pump, 514 nm probe) with a fixed exponential fit of 1.1 ps, corresponding to the vibrational cooling observed in zero field. The residuals of this fit, seen at the top of the figure, reflect the validity of this fit.









The data collected for  $Cr(TMHD)_3$  exhibited enough amplitude change to be individually fit. The data shown here for 16 T agrees well with the data collected at other fields and exhibits a 1.7 ps rise, which agrees well with the expected ~1.8 ps ISC process in zero field.

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#### 5 Outlook and Future Work

A significant portion of the work carried out for the studies presented in this dissertation was invested in the experimental aspects presented in Chapter 2: acquiring a new 35 fs laser system, implementing pulse compression techniques to maintain the 35 fs pulse duration at the sample, successfully characterizing pulses at the sample, and reworking the existing 120 fs pulse laser system to achieve 13 ns delays. These efforts have resulted in the lab's ability to perform transient absorption experiments with ultrashort pulses, not only for vibrational coherence measurements presented in this document, but also for anisotropy experiments on Ru(II) polypyridyls and other transition metal compounds. The 120 fs laser system can successfully characterize ground state recovery dynamics between 1-10 ns, a time span that was previously immeasurable in this lab. Preliminary investigations of the solvent dependence on ground state recovery in tris(2,4-pentanediono)chromium(III), Cr(acac)<sub>3</sub>, (Chapter 3, Appendix B) indicate that this could be a rich new area of study for transition metal complexes that few research labs have the ability to explore.

The data collection and work up programs have also benefitted from the experience and information gained over the course of this work. New programs/attributes include: the automatic adjustment to the appropriate wait time based on the step size during data collection, the collection of both X (data) and Y (phase) channels from the lock-in amplifier, a program to rephase the data should the phasing change over the course of an experiment, the use of two lock-in amplifiers to simultaneously collect the reference photodiode signal and the differential signal at every time delay, frequency resolved optical gating experiments and data workup, linear

predictive single value decomposition data processing, and time-dependent fast Fourier transforms (TD FFT). The availability of these programs greatly enhances the capabilities of this lab.

The ability to reliably collect vibrational coherence data opens the door to studies on other substituted Cr(acac)<sub>3</sub>-type compounds. Many derivatives have been previously synthesized by Dr. Joel Schrauben over the course of his PhD work in this group and are available for study.<sup>1</sup> A summary of these molecules is presented in Figure 5.1, where both the R and R' positions are available for substitution. Transient



**Figure 5.1 Cr(acac)**<sub>3</sub> **Derivatives Available for Future Coherence Studies** Synthesized and initially characterized on the 120 fs laser system, these compounds are available for future studies and represent a variety of substituents.

absorption experiments utilizing 120 fs pulses revealed that substitution at the -R position is largely ineffective for altering the intersystem crossing (ISC) and potentially, the ground state recovery timescales in these compounds.<sup>1</sup> In light of the vibrational

motions observed in Cr(acac)<sub>3</sub> in Chapter 3, it may prove interesting to investigate these compounds utilizing 35 fs pulses in conjunction with computational studies to see if the key vibrations are significantly affected by the substituent. The scissoring motions at 235 and 255 cm<sup>-1</sup> (see Chapter 3) may be limited by the steric bulk introduced in this R position, potentially altering the other modes observed during ISC if they are strongly coupled to these vibrations. The ground state recovery timescales of these compounds may now be quantified utilizing the 13 ns delay line, which could bring to light some differences for this series of compounds.

As for substituents in the -R' positions, the 120 fs data show some variation from Cr(acac)<sub>3</sub> dynamics, but not all of the substituents exhibit as pronounced of an effect as tris(2,2,6,6-tetramethyl-3,5-heptanediono)chromium(III) (Cr(TMHD)<sub>3</sub>, R'=t-butyl).<sup>1</sup> А common theme among this series though, is the presence of two features: one in the blue that decays and one in the red that grows in as a function of time. The particular dynamics for each system are different, and some have disparate timescales for the decay and rise features (i.e. 700 fs and 7 ps) which bear further investigation.<sup>1</sup> The protocols in place for setting the polarization of the pump and probe beams when the initial data on these molecules were collected is now suspect after polarization experiments performed over the course of this thesis. It is possible that the fast decay dynamics observed in bluer wavelengths for these compounds are the result of residual solvent signals or anisotropy in the data. Those processes would account for the tenfold difference in decay and rise times for these data sets. With the current optimized experimental set-ups, these systems would benefit from a re-characterization to verify that these short decay times are not the result of artifacts in the data. If these disparate

time scales are in fact real, further investigation into the vibrational modes active in these systems could be enlightening.

Aside from a wealth of additional compounds that would benefit from vibrational coherence experiments, the data presented in this dissertation may benefit from a more thorough analysis using the TD FFT program described in Chapter 2, Appendix H. This program was used to investigate data sets on a few occasions with no concrete results, but an improvement in the window function could increase the utility of this program. Kraszewski and coworkers have detailed the impact of the window function on the results of these kinds of analyses and have successfully shown that a smoothed rectangular function gives more accurate results without artificially weighting parts of the data within the window.<sup>2</sup> Successful use of this program would give a pseudo-two dimensional view of the data to view the transfer of vibrational energy with time. The primary advantage of this analysis is that it requires no extra steps during data collection and can monitor the exchange of vibrational energy between the low frequency modes observed in the experiment.

An alternative approach would be to collect transient 2DIR (t-2DIR) data to resolve which vibrational modes are active and coupling as a function of time. Dr. Kevin Kubarych has succinctly summarized the benefits of two types of transient 2DIR experiments, which yield different information about the system. "[Triggered-exchange 2DIR] provides vibrational mode correlation in optically triggered processes by mapping reactant vibrations to product vibrations, thus avoiding ambiguities associated with one-dimensional transient absorption methods. [Transient-2DIR] extends to transient species the structurally sensitive information inherent to 2DIR, such as normal-mode

coupling and vibrational energy transfer rates with a temporal dynamic range spanning multiple time scales."<sup>3</sup> While these experiments directly probe the relationship between vibrational modes, they are currently used in the mid-IR to observe modes between 1,700 and 2100 cm<sup>-1</sup>, typically.<sup>3–6</sup> If IR sources between 100-600 cm<sup>-1</sup> were available for this experiment, a direct measurement of the TD FFT 2D "spectra" would be possible.

Another experimental technique, 2D electronic spectroscopy (2DES), while not directly probing IR transitions, may be able to resolve these vibrations at low frequencies. In a recent paper by Greg Scholes and coworkers, 2DES is applied to methylene blue and the population dynamics are removed from the resulting 2D spectra to give the coherent oscillations in the data, which is then Fourier transformed to give the frequencies.<sup>7</sup> By coupling this data with traditional pump probe spectra collected with a broad-band white light probe, they are able to observe the frequencies of the Franck–Condon active vibrations in this molecule and associate them with the geometry change observed in the excited state of methylene blue. By inspecting the amplitudes of the observed frequencies, they were able to refine the important displacement coordinates for the ground and excited state surfaces.

The works of Scholes, Ando, Tahara, and others highlight the importance of computational modeling to interpret the results of observed vibrational coherences and surface crossings.<sup>7–9</sup> Geometry optimizations have been performed by these authors using both density functional theory and complete active space self-consistent field (CAS-SCF) methods. The primary advantage of CAS-SCF is the ability to model the wavepacket dynamics. In light of this, a collaboration with Dr. Ben Levine at Michigan
State University seeks to model these dynamics for further insights into the vibrations and the connection between geometric changes and photophysical processes in these Cr(III) compounds.

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