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Investigation of Organometallic Reaction Mechanisms with One and Two Dimensional Vibrational Spectroscopy

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Chemical Sciences Division

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Ph.D. Thesis

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by

James Francis Cahoon

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Abstract

Investigation of Organometallic Reaction Mechanisms with One and Two Dimensional Vibrational Spectroscopy

by

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Doctor of Philosophy in Chemistry

University of California, Berkeley

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One and two dimensional time-resolved vibrational spectroscopy has been used to investigate the elementary reactions of several prototypical organometallic complexes in room temperature solution. The electron transfer and ligand substitution reactions of photogenerated 17-electron organometallic radicals CpW(CO)_3 and CpFe(CO)_2 have been examined with one dimensional spectroscopy on the picosecond through microsecond time-scales, revealing the importance of caging effects and odd-electron intermediates in these reactions. Similarly, an investigation of the photophysics of the simple Fischer carbene complex $\text{Cr(CO)}_5[\text{CMe(OMe)}]$ showed that this class of molecule undergoes an unusual molecular rearrangement on the picosecond time-scale, briefly forming a metal-ketene complex. Although time-resolved spectroscopy has long been used for these types of photoinitiated reactions, the advent of two dimensional vibrational spectroscopy (2D-IR) opens the possibility to examine the ultrafast dynamics of molecules under thermal equilibrium conditions. Using this method, the picosecond fluxional rearrangements of the model metal carbonyl Fe(CO)_5 have been examined, revealing the mechanism, time-scale, and transition state of the fluxional reaction. The success of this experiment demonstrates that 2D-IR is a powerful technique to examine the thermally-driven, ultrafast rearrangements of organometallic molecules in solution.

Chair _____ Date _____

To my parents.

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1 Introduction

The comprehensive description of a chemical reaction would contain microscopic details of each elementary step that leads from the reactant to product, including the details of bond breakage and formation, exact molecular structures, and rates of reaction, among other properties. The goal of the work described herein is to use time-resolved one and two dimensional vibrational spectroscopies to provide this type of detailed information on the chemical dynamics of organometallic complexes in solution. Pump-probe spectroscopy has been extensively used to understand these types of dynamics [1-19], and this work applies the same pump-probe methodologies as well as a relatively new technique, two dimensional infrared spectroscopy, to the photophysics and reactions of several prototypical organometallic complexes [20-26].

Three classes of organometallic compounds and reactions are examined in this document. The first class comprises transition-metal dimer complexes that contain a single metal-metal bond. Under visible light irradiation, these compounds generate odd-electron radicals, providing an ideal opportunity to examine the fundamental electron transfer (Chapters 3 and 4) and ligand substitution reactions (Chapter 5) of these types of odd-electron species. The second class of molecule is a Fischer carbene complex, $\text{Cr}(\text{CO})_5[\text{CCH}_3(\text{OCH}_3)]$. This compound exhibits unusual photochemistry, behaving similar to organic ketenes, which can be explained in light of the picosecond photophysics of the complex (Chapter 6). The third type of compound is a metal carbonyl, the prototypical complex $\text{Fe}(\text{CO})_5$, which was one of the earliest examples of a fluxional molecule [27] (fluxionality refers to the rearrangement of a molecule between two chemically indistinguishable structures). The equilibrium, picosecond fluctuations of this complex have been examined with two dimensional infrared spectroscopy (Chapter 7), revealing the time-scale, mechanism, and transition state involved in the fluxional rearrangement of the molecule.

In addition to vibrational spectroscopy, the chemical dynamics have been examined with density functional theory calculations to further elucidate the mechanisms and molecular geometries of the intermediates involved in the reactions. Taken together, the experiments and calculations provide a detailed description of the mechanisms, structures, and rates of reactions for the complexes studied. A brief introduction to the experiments, with an emphasis on the observables and information provided by each technique, is elaborated in the following sections, and a detailed description of experimental methods is provided in Chapter 2.

1.1 One dimensional vibrational spectroscopy

There is a long history of using time-resolved vibrational spectroscopy to examine the photochemistry of organometallic complexes in solution. In these types of experiments, an ultraviolet or visible light pulse is used to electronically excite a metal complex, and the subsequent reactions are probed with infrared spectroscopy. Electronic excitation typically results in the population of metal-ligand anti-bonding orbitals, and in the case of metal carbonyl complexes, causes dissociation of a CO ligand [28]. For the transition-metal dimers discussed in Chapters 3-5, visible photoexcitation populates the metal-metal anti-bonding orbitals, causing dissolution of the metal-metal bond and formation of two metal-centered radicals [29,30]. Photoexcitation of the Fischer carbene complex discussed in Chapter 6, on the other hand, does not dissociate a ligand but instead results in long-lived metal-to-ligand charge transfer (MLCT) state, in which an electron from a non-bonding metal d-orbital occupies a π^* orbital localized on the carbene ligand. As these examples suggest, organometallic complexes possess a rich and varied photochemistry, which has fueled interest in using time-resolved vibrational spectroscopy to study these complexes for several decades [31-33].

The primary irradiation wavelengths used in this work are 400 nm and 532 nm, which correspond to 71.5 kcal/mol ($25,000\text{ cm}^{-1}$) and 53.7 kcal/mol ($18,797\text{ cm}^{-1}$), respectively. These excitation energies are more than sufficient to break the metal-metal bonds of organometallic dimers (10-50 kcal/mol) [30] and still leave significant excess energy in the molecule, which is dissipated on the picosecond time scale. The time resolution of the experiments is derived from a femtosecond laser source ($1\text{ fs} = 10^{-15}\text{ s}$) which is used to generate $\sim 100\text{ fs}$ laser pulses both at the photoexcitation wavelengths and in the mid-IR spectral region. The laser source is described in more detail in Chapter 2.

1.1.1 One dimensional vibrational spectra

The chemical dynamics in this work are examined by probing the carbonyl vibrations of the reactants, intermediates, and products involved in the reactions under investigation. These vibrational modes typically fall within the $1600\text{-}2100\text{ cm}^{-1}$ region of the infrared spectrum. The relatively high frequency of these modes results in weak coupling with lower frequency vibrations of the molecules, resulting in long dephasing time constants (1-5 ps) and narrow line widths [34,35]. The CO ligands are directly bonded to the transition-metal atoms, and as a result of the π back-bonding between the metal and carbon atom, the vibrational frequencies are sensitive to changes in the electron density on the metal atoms [28]. Thus, the vibrational frequencies of the various complexes are typically well separated and unique, allowing for

conclusive identification of the chemical intermediates and examination of the chemical kinetics of each species. In addition, the transition-metal atom polarizes the CO bond, causing a strong transition dipole and absorption coefficients on the order of $10,000 \text{ M}^{-1}\text{cm}^{-1}$. These strong vibrational modes are easily detected with the experimental apparatus.

Figure 1.1 Simulated linear IR (e.g. FTIR) spectrum (A), and linear IR difference spectrum (B) for a reactant (R) with two absorptions at 2000 cm^{-1} (1.5) and 2025 cm^{-1} (1.0), which upon irradiation forms a photoproduct (P) with absorptions centered at 2005 cm^{-1} (1.0) and 2040 cm^{-1} (1.0); values in parentheses are relative intensities. All peaks represent homogeneously broadened absorptions with a line width of 5 cm^{-1} .

The experimental data are collected in the form of difference spectra, in which the absorbance of the sample without laser irradiation is subtracted from the absorbance with laser irradiation:

$$A = A_{on} - A_{off} = -\log\left(\frac{I_{on}}{I_o}\right) + \log\left(\frac{I_{off}}{I'_o}\right) = \log\left(\frac{I_{off}I_o}{I_{on}I'_o}\right), \quad (1.1)$$

where A_{on} and A_{off} as well as I_{on} and I_{off} refer to the absorbance and IR intensity, respectively, with the photochemical pump beam on and off, and I_o is the reference beam intensity. A simulation of spectra is shown in Figure 1.1. The absorbance spectrum of the reactant (A_{off}) is shown in Figure 1.1a and is identical to the spectrum that would be collected by a standard FTIR spectrometer. A

simulated difference spectrum is shown in Figure 1.1b. Negative signals result from depletion of the reactant molecules by the photochemical pump pulse and thus appear at the same positions as the peaks from the reactant in Figure 1.1a. Positive signals in Figure 1.1b correspond to the absorptions of photoproducts formed by the pump pulse. Notice that overlap between the positive and negative signals (e.g. 2000-2010 cm^{-1} in Figure 1.1b) results in cancellation between the two signals. The transient difference spectra are also collected at numerous time delays between the photochemical pump pulse and infrared detection; changes in the intensities and positions of peaks as a function of time provide a direct measurement of the chemical dynamics.

1.2 Two dimensional vibrational spectroscopy

Two dimensional infrared (2D-IR) spectroscopy [36], a technique first implemented one decade ago [37], has seen rapid progress both in experimental design [38-52] and in application to a variety of chemical [53-71] and biological [37,72-101] problems. Recently, there has been building interest in using 2D-IR to investigate the fluctuations and chemical exchange processes in systems under thermal equilibrium conditions at room temperature [20]. Ultrafast spectroscopy has long been used to monitor femto- and picosecond chemical dynamics [102], but conventional ultrafast pump-probe techniques are primarily limited to measurements on photoinitiated chemical reactions. It has now been shown, however, that 2D-IR is a fundamentally different type of technique that is ideally suited for monitoring thermally-driven reactions of systems at or close to equilibrium. Extensive work using 2D-IR by several pioneering research groups has advanced the understanding of solute-solvent complexation in weakly hydrogen-bonded systems [53-60], and fluctuations in the hydrogen-bond network of liquid water [62-71], to name just two active areas of research. There is also increasing interest in applying 2D-IR to non-equilibrium systems by inducing chemical, conformational, or temperature changes in a system and following the subsequent dynamics with 2D-IR. This method, referred to as transient 2D-IR spectroscopy (T2D-IR), is similar to many pump-probe techniques but the “probe” is a 2D-IR pulse sequence rather than a simple linear detection scheme. The T2D-IR technique has found a myriad of applications [103], such as monitoring the folding dynamics of peptides and proteins [81-90].

Chapter 7 describes the use of 2D-IR to understand the time-scale and transition state of a fluxional process: the exchange of axial and equatorial CO ligands in $\text{Fe}(\text{CO})_5$ [20]. The material in this chapter is part of a broader goal to use 2D-IR to understand the ultrafast intramolecular dynamics, rearrangements, and transition states of relatively simple chemical systems that undergo picosecond time-scale dynamics under thermal equilibrium conditions.

1.2.1 Two dimensional vibrational spectra

There exist two complementary implementations of 2D-IR, dynamic hole burning and pulsed Fourier-transform [50]. Both techniques interrogate the third-order polarization induced in the sample by three successive interactions with an electric field. The dynamic hole burning method [104] was used for the experiments described in Chapter 7. The 2D-IR spectra are collected by first exciting the sample with a narrowband ($\sim 10 \text{ cm}^{-1}$) IR laser pulse (IR-pump), which defines one frequency axis, and after a defined period of time (T_w), monitoring the change in absorption with a broadband IR laser pulse (IR-probe), which defines the second frequency axis. The spectra are constructed by collecting multiple one-dimensional horizontal slices of the spectra at different IR-pump frequencies.

Simulated 2D-IR spectra are displayed in Figure 1.2 (see Appendix A for a detailed description of the simulations). Unlike the one dimensional spectra shown in Figure 1.1, the 2D-IR spectra are sensitive to the anharmonicity of the vibrational modes. In general, the energy of the vibrational levels in a molecule can be expressed as:

$$E_{v_1, v_2, \dots, v_N} = \sum_{i=1}^N \omega_i \left(v_i + \frac{1}{2} \right) + \sum_{i=1}^j \sum_{j=1}^N \chi_{ij} \left(v_i + \frac{1}{2} \right) \left(v_j + \frac{1}{2} \right), \quad (1.2)$$

where E is the vibrational energy of the molecule, N is the number of vibrational modes in the molecule, v_i is the quantum number of vibrational mode i , ω_i is the harmonic vibrational frequency of mode i , and χ_{ij} is the anharmonic constant (anharmonicity) between vibrational modes i and j [105]. Although the one dimensional vibrational spectra are usually well understood in terms of the harmonic vibrational frequencies, ω_i , the 2D-IR spectra provide direct evidence for the diagonal, χ_{ii} , and off-diagonal, χ_{ij} , anharmonicities of the vibrational modes.

As depicted in Figure 1.2, peaks along the diagonal (blue) of the 2D-IR spectra contain similar information as a one-dimensional, FTIR spectrum; the frequencies correspond to fundamental transitions ($v = 0 \rightarrow 1$; 2000 and 2025 cm^{-1}) of individual vibrational coordinates. Shifted slightly off the diagonal along the horizontal axis appear a second set of transitions, shown in red, from the $v = 1 \rightarrow 2$ vibrational levels. The shift from the diagonal peaks reflects the diagonal anharmonicity of the vibrational potential ($\chi_{ii} = -5 \text{ cm}^{-1}$ for the simulations in Figure 1.2). Most importantly, 2D-IR reveals the correlations between different vibrational degrees of freedom through the appearance of cross peaks, or off-diagonal peaks. Cross peaks result from the correlation between two vibrational eigenstates and appear at the intersection between the frequencies of diagonal vibrational resonances. In the simplest case, the cross peaks positions are a direct measure of the anharmonic coupling between the vibrational modes. Shown in Figure 1.2 are simulations for four different values of the off-diagonal anharmonicity ($\chi_{ij} = 0, -1, -5, -15$

cm^{-1}). Not shown in this figure are cross peaks that might result from chemical exchange or energy transfer between the different vibrational modes. These types of cross peaks are discussed extensively in Chapter 7.

Figure 1.2 Simulated 2D-IR spectra for two homogeneously broadened vibrational modes centered at 2000 and 2025 cm^{-1} . The modes are of equal intensity and the same linewidth ($\Gamma = 5 \text{ cm}^{-1}$). The four horizontal panels were each simulated with progressively larger off-diagonal anharmonic couplings, $\chi_{ij} = 0, -1, -5, -15 \text{ cm}^{-1}$ (diagonal anharmonicities were constant, $\chi_{ii} = -5 \text{ cm}^{-1}$). The second set of panels, E-H, includes convolution with a Lorentzian function ($\Gamma = 10 \text{ cm}^{-1}$) along the vertical frequency axis to account the spectral resolution of the IR-pump laser pulse and thus better simulate the spectra that would be observed experimentally.

As mentioned above, the 2D-IR spectra discussed in Chapter 7 are collected with the dynamic hole burning method [50,104]. A key advantage of this technique is the ability to rapidly collect data at multiple waiting times (T_w) for one-dimensional slices of the 2D-IR spectra in order to quantitatively measure the temporal evolution of specific spectral features. However, there are some significant disadvantages of this method, most notably the reduced frequency resolution ($\sim 10 \text{ cm}^{-1}$) along the vertical, IR-pump frequency axis and reduced time resolution ($\sim 1 \text{ ps}$; see Chapter 2 for additional details). The disadvantage of the reduced frequency resolution is illustrated in Figure 1.2, panels E-H. These spectra are the same as panels A-D except for an additional convolution with the IR-pump spectral resolution along the vertical frequency axis. As can be seen from the simulations, the various diagonal and off-diagonal spectral features are no longer well separated, although all the independent features are still discernable.

The Fourier transform implementation of 2D-IR would produce spectra similar to panels

A-D. Unlike the hole-burning method, the technique is a purely time-domain method using three broadband IR laser pulses for the three electric field interactions that generate the third-order polarization signal field in the sample. In this technique, the vertical frequency axis is generated by a Fourier transform along the time delay between the first two pulses. The second frequency dimension is obtained in the same manner used for the hole-burning method (see Chapter 2). The Fourier transform technique provides better time and frequency resolution, but is not well suited to the measurement of chemical kinetics. Thus, the most comprehensive ultrafast vibrational spectrometer would incorporate both techniques [45].

2 Methods

2.1 One dimensional ultrafast vibrational spectroscopy

The ultrafast experiments are based on a commercial, Spectra-Physics laser system that generates ~ 90 fs, ~ 1 mJ laser pulses centered at 800 nm at a repetition rate of 1 kHz. The output of the commercial system is used to generate photochemical pump pulses, as described in Section 2.1.2, and mid-IR pulses, as described in Section 2.1.3. The commercial system consists of a Ti:sapphire oscillator (Spectra-Physics, Tsunami) pumped by a 5 W, diode-pumped Nd:YVO₄ continuous wave laser (Spectra-Physics, Millennia). The oscillator is used to seed a Ti:sapphire regenerative amplifier (Spectra-Physics, Spitfire), which is pumped by a 10 W, 1 kHz Q-switched, diode-pumped Nd:YLF laser (Spectra-Physics, Evolution-X; this laser has recently been replaced with an Empower-15 but this new laser was not used for the experiments described herein). The amplifier produces a 1-kHz pulse train of ~ 90 fs pulses centered at 800 nm with an average pulse energy of 0.9-1.0 mJ. Note that the laser pulses emitted from the oscillator are vertically polarized while the pulses from the amplifier are horizontally polarized.

The optics used for data collection during visible/ultraviolet-pump, IR-probe experiments have undergone numerous modifications over the past several years. The older experimental designs are described in the Ph.D. dissertations of Dr. Jennifer Shanoski [106] and Dr. Elizabeth Glascoe [107], and these designs were used for large portions of the data described in this document. This section describes only the most current design of the experimental apparatus, which dates from approximately March 2007.

2.1.1 Optical delay stage

Directly after the commercial laser system, approximately 30% of the laser output is separated with a beam splitter to generate photochemical pump pulses at the second (400 nm) or third (266 nm) harmonic of the 800 nm fundamental. Prior to generation of these harmonics, the 800 nm beam passes through a computer-controlled delay stage to generate optical delays between the photochemical pump pulses and the mid-IR laser pulses. The delay stage (Klinger, labeled TS1 in Figure 2.1) possesses a travel length of 16 cm, so one retroreflection is capable of generating delay times of ~ 1 ns. Because the photochemistry of organometallic complexes often ranges from time-scales of femtoseconds through nanoseconds or greater, the beam passes through a home-built retroreflection system, which allows the beam to pass through the delay stage four separate times (see Figure 2.1) and generates a delay time of up to ~ 4 ns.

Figure 2.1 Design of the 4-pass optical delay stage used to generate time delays of < 1 ps through 4 ns (not to scale). (A) Top-down view of the delay stage; dashed line represents a prism (CM = computer-controlled mirror; VR = vertical retroreflector; HR1 = horizontal retroreflector #1; TS1 = translation stage #1) (B) Three-dimensional depiction of the optical beam path through the 4-pass delay stage. (C) Diagram of beam misalignment into the delay stage compensated by rotation of the vertical retroreflector (VR).

The retroreflection system is partly based on a similar design by Jan Helbing and used in Peter Hamm's research group. The system (see Figure 2.1) consists of four pairs of retroreflecting mirrors with high-reflection dielectric coatings ($R \geq 99.4\%$ @ 45° angle of incidence (AOI), 800 ± 10 nm). Each pair of mirrors is mounted against a corner cube prism to ensure that the mirrors are near-perfect retroreflectors in two dimensions (note that only a portion of each mirror surface is mounted against the prism face; the laser beam reflects off the remaining free mirror surface). One pair (HR1; 76.2 mm x 25.4 mm x 7.62 mm) is mounted on the delay stage and horizontally retroreflects the laser beam, and the remaining three pairs (VR; 0.750" diameter, 0.25" thick) are mounted vertically to change the height of the beam while simultaneously retroreflecting the beam back through the delay stage. The beam path is illustrated in Figure 2.1.

The 4-pass retroreflection system is sensitive to any misalignment of the beam, which causes the beam to move spatially as the delay stage is moved to different positions. To accurately align the system, the mirror directing the beam onto the delay stage (labeled CM) is a computer-controlled mirror that permits nanometer-scale adjustments to the mirror alignment. In addition, a four-quadrant detector (New Focus, Inc. large area quadrant-cell receiver model 2911) is used to track the position and movement of the laser beam after it exits the delay stage. Although it is possible to align the delay stage manually, the process is tedious and prone to errors; thus, I wrote a feedback-controlled algorithm that iteratively moves the delay stage, tracks

the beam movement, and adjusts the mirror position until it achieves perfect alignment of the beam through the retroreflection system. The algorithm is designed to intelligently determine the magnitude and direction of movement required to improve the alignment, so the beam detector can be placed at any position close to or far downstream from the delay stage.

Table 2.1 List of optics used for the optical delay stage

Optic Label	Description / Specifications	Manufacturer
TS1	translation stage # 1, 16 cm travel	Klinger Scientific, MT-160
HR1	horizontal retroreflector, optics: $R \geq 99.4\%$, 800 ± 10 nm, 45° AOI	optics: Rocky Mountain Instrument Co.
VR	vertical retroreflector, optics: $R \geq 99.4\%$, 800 ± 10 nm, 45° AOI	optics: Rocky Mountain Instrument Co.
CM	Computer-controlled piezo-electric mirror mount	New Focus, Inc.: Motorized stability mount model 8816; Picomotor ethernet controller model 8752; Intelligent picomotor driver model 8753;

Although the algorithm can be used with the vertical retroreflector (VR) in place, it is recommended that it be used with the vertical retroreflector removed. In this case, it is critical that the manual alignment of the beam onto the computer-controlled mirror (CM) is both horizontally and vertically correct so that the retroreflecting beam will be centered upon the mirrors in the vertical retroreflector. After alignment of the beam with the VR removed, the VR can be placed back in position; if it is found that beam clips or does not properly pass through the VR, this problem results entirely from the manual misalignment of the beam onto the CM mirror and this alignment should be checked carefully. If the beam passes through the VR correctly, the alignment of the beam should again be monitored with the quadrant detector. If any misalignment of the beam is detected, the VR should be adjusted using the rotation stage on which it is mounted, which should remove any remaining drift in the laser beam position. Note that it is possible to (incorrectly) use this rotation mount to correct a misalignment of the beam into the retroreflection system, and this situation is depicted in Figure 2.1c. In this case, perfect retroreflection of the beam can be achieved, however, the beam is incident upon a different portion of the VR retroreflecting mirrors at each time delay. This situation is not desirable because: 1) the beam may clip on a portion of the mirrors at certain translation stage positions and not others, and 2) the calculation of the delay through the retroreflector is not correct. This

situation would typically occur when the beam is misaligned onto the CM mirror, causing the only beam alignment that passes through all the mirrors to become the skewed alignment shown in Figure 2.1.

2.1.2 Photochemical pump generation

After the optical delay stage described in Section 2.1.1, the 800 nm beam is used to generate photochemical pump pulses at the second (400 nm) or third (266 nm) harmonic of the 800 nm fundamental. These frequencies are generated in the standard manner by using a second-order non-linear process (sum frequency generation) in a β -barium borate (BBO) crystal. The 800 nm pulses first pass through a 0.7-mm thick, type-1 BBO crystal cut for phase-matching of 400 nm and 800 nm wavelengths ($\theta = 29.2^\circ$; $\phi = 0^\circ$).¹ The high intensity of the 800 nm pulses drives the non-linear process, generating a second-order polarization at double the fundamental frequency:

$$P_{2\omega}^{(2)}(t) = \frac{1}{(2\pi)^2} \chi^{(2)}(-2\omega; \omega, \omega) :: E(\omega)^2 e^{-i2\omega t}, \quad (2.1)$$

where $E(\omega)$ is the incident electric field of the 800 nm fundamental, $\chi^{(2)}$ is the second-order non-linear susceptibility of the BBO crystal, and $P^{(2)}$ is the induced polarization [108,109]. The non-linear process typically results in ~20% conversion of the 800 nm pulses (~200 μ J) into 400 nm pulses (~40 μ J). Note that the phase-matching conditions dictate that the generated 400 nm beam is polarized (along the extraordinary optical axis) perpendicular to the horizontally polarized (along the ordinary optical axis) 800 nm beam; thus the 400 nm beam is polarized vertically.¹

In order to generate laser pulses at the 266 nm third harmonic, the 400 nm and residual 800 nm pulses generated from the first BBO are separated and recombined onto a second type-1 BBO crystal, 0.2-mm thick and cut for phase-matching of 266 nm with the 400 and 800 nm beams ($\theta = 44.3^\circ$; $\phi = 0^\circ$).² The 800 nm beam is rotated with a half-wave plate to a vertical polarization before being overlapped with the 400 nm beam into the BBO crystal. This process generates horizontally polarized 266 nm laser pulses with an energy of ~5 μ J.

¹ BBO is a negative uniaxial birefringent crystal; the horizontally polarized 800 nm beam is polarized along the ordinary direction, $n_o = 1.66$. The vertically polarized 400 nm beam ($n_e = 1.57$; $n_o = 1.69$) is polarized ~30° from the crystal axis to produce an effective refractive index of 1.66, satisfying the phase-matching condition $n_{400\text{nm}} = n_{800\text{nm}}$.

² The vertically polarized 800 nm ($n_o = 1.66$) and 400 nm ($n_o = 1.69$) beams are polarized along the ordinary direction. The horizontally polarized 266 nm beam ($n_e = 1.61$; $n_o = 1.76$) is polarized ~45° from the crystal axis to produce an effective refractive index of 1.68, satisfying the phase-matching condition $n_{266\text{nm}} = \frac{2}{3}n_{400\text{nm}} + \frac{1}{3}n_{800\text{nm}}$.

2.1.3 Mid-infrared generation

In order to perform ultrafast vibrational spectroscopy, the 800 nm femtosecond pulses generated by the Spectra-Physics commercial laser system are converted into mid-infrared pulses in the 1700-2100 cm^{-1} region. Approximately 0.6-0.7 mJ of the 800 nm pulses is directed toward a homebuilt BBO-based optical parametric amplifier (OPA), the output of which is mixed in a AgGaS crystal to produce mid-infrared pulses at the difference frequency with a spectral width of ca. 150 cm^{-1} and pulse duration around 100 fs. The construction of this OPA has been described elsewhere [106] and is based on the design of Peter Hamm [110]. The design is capable of suppressing the 2-3% fluctuations in the 800 nm laser pulses to produce mid-IR pulses with a noise of less than 1%. This OPA was used for all the ultrafast experiments described herein and is briefly described below.

The OPA uses a 4-mm thick, type-2 BBO crystal ($\theta = 28.9^\circ$; $\phi = 30^\circ$) designed to generate near-IR light in the 1.2-2.2 μm range in two passes through the crystal. The first pass uses a vertically polarized, white-light continuum seed which is colinearly overlapped with the horizontally polarized 800 nm pump pulse, generating the difference frequency between the 800 nm pump and the signal/idler (parametric amplification). The horizontally polarized idler beam (ca. 1.7-2.2 μm) is dumped after the crystal. The vertically polarized signal beam (ca. 1.2-1.7 μm) is retroreflected and directed back through the BBO crystal and overlapped with a second horizontally polarized 800 nm pump pulse, again amplifying the difference frequency between the pump and signal/idler. After the second pass through the BBO crystal, the signal and idler are separated, recombined, and focused onto a type-1 AgGaS crystal ($\theta = 40.7^\circ$; $\phi = 45^\circ$). This crystal generates the difference frequency between the vertically polarized signal beam (now the pump beam) and horizontally polarized idler beam (now the signal). The difference frequency beam, horizontally polarized, is easily tunable from 1700-2100 cm^{-1} by angle tuning the BBO and AgGaS crystals to achieve phase matching for the desired wavelengths.

2.2 Two dimensional vibrational spectroscopy

The 2D-IR experimental setup uses the mid-infrared pulses generated as described in Section 2.1.3, and a diagram of the apparatus is illustrated in Figure 2.1. Prior to all the 2D-IR optics is a flipping mirror (FM), which allows a HeNe continuous-wave laser beam to be directed through the 2D-IR setup, facilitating alignment of the optics for the mid-IR beam. The mid-IR laser pulses from the OPA are collimated with a CaF_2 lens (L1) and then split into three beams using a wedged ZnSe substrate (WBS). The reflections ($\sim 15\%$ of the incoming beam energy) off the front and back surfaces are used as probe and reference beams, respectively. The transmitted

beam is used as the infrared pump beam and is passed through a computer-controlled Fabry-Perot interferometer (FP) based on the design used by Peter Hamm and co-workers [104,111]. The Fabry-Perot narrows the spectrum of the infrared pulse from an approximately 150 cm^{-1} full-width at half maximum (FWHM) to approximately 11 cm^{-1} FWHM (Lorentzian lineshape) and extends the temporal duration of the pulse to $\sim 1\text{ ps}$ (see Section 2.2.1 for details on the Fabry-Perot). The exact spectral width of this narrowband infrared pulse is recorded during the experiment and used in the simulation of the experimental data.

After the Fabry-Perot, the beam passes through an achromatic ($4.5\text{-}6\text{ }\mu\text{m}$) half-wave plate (WP1) held in a computer-controlled rotation stage. Using this rotation stage, the polarization of the pump beam with respect to the probe beam can be set to any arbitrary angle and is typically set to the magic angle, 54.7° , to eliminate effects from rotational diffusion. The pump beam then passes through a chopper wheel (CW) running at 500 Hz , which blocks every other pump pulse. All the experimental data presented herein are difference spectra, in which the absorption values (collected with the probe and reference beams) for the pump beam blocked are subtracted from the absorbance values without the pump beam blocked.

The pump beam next passes through a retroreflector composed of two protected-silver mirrors mounted against a corner cube prism to maintain perfect retroreflection in the two horizontal dimensions. The retroreflector is mounted on a computer controlled delay stage (TS2), which possesses a travel range of 16 cm and can generate time delays of $\sim 1\text{ ns}$. After the delay stage, the pump beam is directed toward a 10-cm focal-length off-axis parabolic mirror (PM), which focuses the beam onto the sample. The probe beam is also directed onto the PM to focus and overlap the pump and probe beams on the sample, producing spot sizes of approximately $200\text{ }\mu\text{m}$. Using a $150\text{-}\mu\text{m}$ thick, polished germanium wafer (Surface Process Group, LLC.), the pump and probe beams are cross-correlated at the sample and time zero is identified as the rising edge of the infrared pump pulse. Note that the short thickness of the Ge wafer introduces some interference effects on the cross correlation signal and it might be desirable to instead use a $500\text{ }\mu\text{m}$ or 1 mm wafer. The sample is held in a cell (Harrick Scientific) that is typically fitted with 2-mm thick non-birefringent CaF_2 windows (Crystran Ltd.) and that has a path length of $250\text{ }\mu\text{m}$ (note that MgF_2 windows should not be used due the birefringence of this material, which would alter the polarization of the beams).

Table 2.2 List of optics used in the experimental 2D-IR apparatus

Optic Label	Description / Specifications	Manufacturer
FP	Fabry-Perot: optics: ZnSe, 25 mm diameter, 3 mm thickness, $\lambda/10$ @ 633 nm, wedge ≤ 3 arc min., $R_{\text{avg}} = 85\% \pm 5\%$ inside, $R_{\text{avg}} \leq 1\%$ outside @ 4-6 μm , 0° AOI; mount: piezo-electric computer-controlled mirror mount	optics: Rocky Mountain Instrument Co., mount: Thorlabs, KC1-PZ controller: Thorlabs, MDT693A
TS2	translation stage # 2, 16 cm travel	Newport Corp., XMS-160, Linear motor stage
WBS	1° wedged beam splitter, uncoated ZnSe, 0.120 in. thick, $\sim 15\%$ reflectivity per surface	Rocky Mountain Instrument Co.
CW	chopper wheel, operating at 500 Hz	New Focus, Inc., Model 3501
WP1	waveplate #1, mid-IR achromatic (4.5-6 μm) CdS/CdSe half-waveplate mounted in computer-controlled rotation stage	waveplate: Cleveland Crystals rotation stage: Newport Corp. RGV100
WP2/3	waveplate #2, 400 nm zero-order; waveplate #3, 266 nm zero-order	CVI Melles Griot
FM	flipping mirror	New Focus, Inc.
RM	protected silver mirror mounted on computer-controlled rotation stage	Newport Corp., RGV100
PM	off-axis parabolic mirror, protected gold coating, reflected effective focal length 10.16 cm	Janos Technologies
HeNe	Helium Neon laser, 15 mW, 632.8 nm	Melles Griot, model 25-LHR-151-249
HR2	horizontal retroreflector, optics: protected silver	optics: CVI Melles Griot
L1-L4	CaF ₂ lenses, focal lengths 50, 15, 30, 30 cm, respectively	unknown
SG	Spectrograph, 150 grooves/mm, 5 micron blaze	Acton Research Corp., SpectraPro-150
WG	ZnSe wire-grid polarizer	Thorlabs, WP25H-Z
MCT	HgCdTe 2×32 pixel IR array detector	Infrared Associates, Inc.

Figure 2.2 Schematic diagram of the experimental apparatus used for two dimensional infrared spectroscopy (FM = flipping mirror; WBS = wedged ZnSe beam splitter; FP = Fabry-Perot interferometer; WP = waveplate; CW = chopper wheel; RM = rotating mirror; TS = translation stage; PM = parabolic mirror; L = lens; SG = spectrograph; MCT = HgCdTe IR array detector).

Directly after the sample, the probe beam is passed through a ZnSe wire-grid polarizer (WG) set for maximum transmission at the probe beam polarization (to eliminate scattered pump light and ensure better detection of the desired signal [112]), and the probe beam is then recollimated with a second off-axis parabolic mirror. During data collection, the probe and reference beams are sent along a parallel path through a computer-controlled spectrograph (SG) with entrance slits routinely set at $50\text{ }\mu\text{m}$ to achieve a spectral resolution of ca. 3 cm^{-1} . Spectrally dispersed probe and reference beams are detected by a 2×32 element infrared HgCdTe array detector (MCT) using a high speed signal acquisition system (Infrared Systems Development Corp.). Please refer to the Ph.D dissertation of Dr. Elizabeth Glascoe [107] for details on the array detector. Differences in optical density (ΔOD) as small as $\Delta\text{OD} = 2\times 10^{-5}$ can easily be observed within two seconds of data collection using this experimental apparatus.

In order to change the center frequency of the Fabry-Perot filter (FP), the pump beam is directed into the spectrograph, bypassing the sample, by rotating a mirror (RM) into the beam path using a computer-controlled rotation mount. The spectrum of the Fabry-Perot filter is acquired by the MCT detector and fit to a Lorentzian function in real-time using Labview software. The FP consists of two closely spaced mirrors, one of which is mounted in a computer-controlled piezoelectric mirror mount. By changing the voltage applied to the piezoelectric mounts, the spacing between the mirrors can be controlled with nanometer resolution. A feedback-controlled computer algorithm monitors the center frequency of the FP and adjusts the voltages to the piezoelectric mount to achieve the desired center frequency within $\sim 1\text{ cm}^{-1}$. Please

see Section 2.2.1 for further details on the FP. Drifts in the center frequency of the pump beam during data collection are less than 1 cm^{-1} .

The experimental apparatus described above can also be used for broadband IR-pump, IR-probe measurements simply by removing the FP from the IR pump beam path. In addition, this experimental apparatus can be used for ultraviolet/visible-pump, IR-probe experiments by blocking the IR pump beam and overlapping the ultraviolet/visible beam with the IR-probe beam at the sample. For these experiments, the polarization of the ultraviolet/visible pump beams can be controlled with zero-order half wave plates (WP2/WP3) for the 266 nm or 400 nm pump wavelengths. The ultraviolet/visible beams and IR probe beams are cross correlated at the sample using a silicon wafer. All the possible one and two dimensional pulse sequences and experiments possible with the current experimental apparatus are depicted in Figure 2.3.

Figure 2.3 Illustration of the five different pulse sequences and experiments possible with the current capabilities of the experimental apparatus. (A) one dimensional methods and (B) two dimensional methods.

2.2.1 Fabry-Perot interferometer

The Fabry-Perot interferometer (FP) is based on the same design used by Peter Hamm and converts the broadband ($\sim 150 \text{ cm}^{-1}$) mid-IR ($\sim 2000 \text{ cm}^{-1}$) ultrafast ($\sim 100 \text{ fs}$) laser pulse into a narrowband ($\sim 10 \text{ cm}^{-1}$) mid-IR pulse ($\sim 1 \text{ ps}$), which can be used as a pump pulse in the 2D-IR experiments. The Fabry-Perot interferometer is designed similar to a laser cavity, containing two parallel mirrors, but unlike most laser cavities, the mirrors are extremely close, on the order of tens of microns. The input laser beam (0° angle of incidence) undergoes multiple reflections inside the Fabry-Perot cavity and as a result of interference of the original pulse with the

reflections, the only frequencies emerging from the cavity are the allowed orders, n , of the cavity (if l is the cavity length (mirror spacing), then the allowed wavelengths, λ , are related to the cavity length and order by $\lambda = 2l/n$, giving rise to multiple resonances at fixed l corresponding to different orders n). Fabry-Perot interferometers (alternately referred to as etalons for fixed l) are typically used as filters for incoherent light sources. In this case, the bandwidth of each resonance (for fixed l and n) is primarily determined by the coefficient of finesse [113], which depends on the reflectivities of the mirrors used in the cavity. Unlike incoherent light sources, however, the femtosecond pulsed laser radiation used in the 2D-IR experiments is governed the Fourier transform relationship between time and frequency. As the femtosecond IR pulse undergoes multiple reflections inside the cavity, the original Gaussian pulse envelope acquires a new temporal envelope, which can be approximated by a single exponential function with a single time constant (corresponding to $1/e$). The exact form of the temporal envelope depends on both the cavity length and reflectivity of the mirrors inside the cavity (see Table 2.3). The Fourier transform of this temporal envelope determines the frequency bandwidth of the Fabry-Perot interferometer (assuming the cavity is perfectly aligned, i.e. exactly parallel mirrors). For a single exponential function of ~ 1 ps, the frequency profile should appear as a Lorentzian function with a linewidth of $10\text{-}15\text{ cm}^{-1}$. In practice, the exact frequency profile of the Fabry-Perot is easily measured by directing the IR-pump beam into the spectrograph.

The relationship between the Fabry-Perot cavity length (l), mirror reflectivities, and order of the cavity (n) are summarized in Table 2.3 for a cavity that is centered at 2000 cm^{-1} in order n . This table also includes the expected frequencies for the next order above ($n+1$) and below ($n-1$) the central order n . These additional resonances are observable when aligning the Fabry-Perot cavity and are useful for determining the length of the cavity and thus the expected pulse duration.

Note that the Fabry-Perot was designed to have reflectivities of 85%, and thus the ideal cavity length is $\sim 17.5\text{ }\mu\text{m}$, which (for 2000 cm^{-1}) corresponds to 7th order in the cavity and produces an IR-pump pulse with a duration of ~ 700 fs. In practice, however, the reflectivities of the mirrors are strongly wavelength dependent and sometimes far from the intended 85%, which necessitates a longer cavity length for lower reflectivities and shorter cavity length for higher reflectivities in order to achieve approximately the same temporal and spectral resolution. Note that at longer cavity lengths the approximation of the IR-pump pulse as a single exponential function becomes increasingly invalid. The current Fabry-Perot optics were ordered from Rocky Mountain Instrument Company for the $4\text{-}6\text{ }\mu\text{m}$ range, and the actual reflectivities of the mirrors vary from 0.75-0.9 over this spectra range. It might be desirable to order a new set of Fabry-Perot optics with more stringent reflectivity values for future experiments.

Table 2.3 Relationship between cavity length, orders, mirror reflectivities, and pulse duration for a Fabry-Perot interferometer centered at 2000 cm^{-1} in order n .

cavity length l (μm)	order n (centered at 2000 cm^{-1})	wavenumber (cm^{-1})		Approximate $1/e$ time constant (ps) for given reflectivity				
		$n-1$	$n+1$	0.9	0.85	0.8	0.75	0.7
15	6	1667	2333	0.9	0.6	0.4	0.3	0.3
17.5	7	1714	2286	1.1	0.7	0.5	0.4	0.3
20	8	1750	2250	1.3	0.8	0.6	0.5	0.4
22.5	9	1778	2222	1.4	0.9	0.7	0.5	0.4
25	10	1800	2200	1.6	1.0	0.7	0.6	0.5
27.5	11	1818	2182	1.7	1.1	0.8	0.6	0.5
30	12	1833	2167	1.9	1.2	0.9	0.7	0.6
32.5	13	1846	2154	2.0	1.3	1.0	0.8	0.6
35	14	1857	2143	2.2	1.4	1.0	0.8	0.7
37.5	15	1867	2133	2.4	1.5	1.1	0.9	0.7
40	16	1875	2125	2.5	1.6	1.2	0.9	0.8
42.5	17	1882	2118	2.7	1.7	1.3	1.0	0.8
45	18	1889	2111	2.8	1.8	1.3	1.0	0.9
47.5	19	1895	2105	3.0	1.9	1.4	1.1	0.9
50	20	1900	2100	3.1	2.0	1.5	1.2	1.0
52.5	21	1905	2095	3.3	2.1	1.6	1.2	1.0
55	22	1909	2091	3.4	2.2	1.6	1.3	1.1
57.5	23	1913	2087	3.6	2.3	1.7	1.3	1.1
60	24	1917	2083	3.8	2.4	1.8	1.4	1.2
62.5	25	1920	2080	3.9	2.5	1.9	1.4	1.2
65	26	1923	2077	4.1	2.6	1.9	1.5	1.3
67.5	27	1926	2074	4.2	2.7	2.0	1.6	1.3
70	28	1929	2071	4.4	2.8	2.1	1.6	1.4
72.5	29	1931	2069	4.5	2.9	2.2	1.7	1.4
75	30	1933	2067	4.7	3.0	2.2	1.7	1.5
77.5	31	1935	2065	4.9	3.1	2.3	1.8	1.5
80	32	1938	2063	5.0	3.2	2.4	1.8	1.6
82.5	33	1939	2061	5.2	3.3	2.5	1.9	1.6
85	34	1941	2059	5.3	3.4	2.5	2.0	1.7
87.5	35	1943	2057	5.5	3.5	2.6	2.0	1.7
90	36	1944	2056	5.6	3.6	2.7	2.1	1.8
92.5	37	1946	2054	5.8	3.7	2.7	2.1	1.8
95	38	1947	2053	6.0	3.8	2.8	2.2	1.9
97.5	39	1949	2051	6.1	3.9	2.9	2.3	1.9
100	40	1950	2050	6.3	4.0	3.0	2.3	2.0

2.2.2 2D-IR alignment notes

The alignment of the 2D-IR apparatus diagrammed in Figure 2.2 is heavily dependent on the accurate alignment of the HeNe tracer beam through the 2D-IR optics. If no IR light is detected on the MCT array detector even with the slits fully extended, a single element HgCdTe detector must be placed close to the output of the OPA (for instance at the FP position directly after the wedged beam splitter (WBS)) to find the mid-IR beam. Once the IR beam is found, alignment irises should be placed directly after the HeNe flipping mirror (FM) and directly before the detector, and the HeNe beam should be aligned through these two irises. With the HeNe roughly tracing the IR beam position, this tracer beam should be used to direct the beams to the MCT array detector with the slits fully extended. Once a signal is found on the MCT array, new alignment irises as close to the spectrograph as possible should be put in place for a finer alignment of the HeNe tracer beam. Note that because the IR beam is split into three beams by reflection off a wedged ZnSe window (WBS), the HeNe tracer only accurately tracks one of the three IR beams (pump, probe, or reference) after the ZnSe window; thus, each beam needs its own alignment iris and the tracer beam should be aligned through this iris before fine adjustment of the 2D-IR optics.

With the HeNe beam accurately tracing the IR beam, the 2D-IR setup can be aligned. The IR-pump beam must be aligned first because it must be directed through the translation stage (TS2) using the mirror directly before the wedged ZnSe window (WBS). This alignment must be performed with both the FP and WP1 removed. Note that the wedge in WBS requires that the beam propagate at a small angle (with respect to the optical table) prior to WBS in order to propagate and retroreflect through the delay stage (the wedge window produces an angular deviation of the beam). The alignment of the IR-pump beam should be adjusted until no drift in the HeNe beam is detected upon movement of the translation stage (TS2). After alignment of the IR-pump beam, the remaining beams can be aligned with the HeNe tracer beam by standard optical alignment procedures. Note that the beam height of the reference IR beam must change by approximately 1 cm in order to reach the top pixel row of the MCT array detector. The IR-probe beam, on the other hand, should maintain a constant height throughout the 2D-IR setup. After alignment with the tracer beams, the alignment of the IR-pump and IR-probe beams at the sample plane should be checked with a pinhole to ensure proper overlap of the two beams. It is advisable to direct the IR-pump beam into the array detector after the sample plane using a flipping mirror; this alignment only needs to be coarse in order to verify alignment of the beam through the pinhole. The rotating mirror (RM), which causes the IR-pump beam to bypass the sample, should be rotated into position and aligned using the HeNe tracer to direct the beam to the spectrograph.

With the IR-pump beam bypassing the sample and directed toward the spectrograph (SG) and MCT array detector, the Fabry-Perot (FP) can be placed in the beam path. It is advisable to begin the FP alignment with the mirrors placed far apart. The manual adjustment knobs of the FP should be adjusted until the HeNe tracer beam forms one round spot after reflection through the FP; this ensures that the FP mirrors are approximately parallel. Next, the micrometer on the FP mirror mount should be turned to slowly reduce the spacing between the mirrors. The resulting spectrum should be monitored and the manual knobs on the FP periodically adjusted to achieve a narrow lineshape with a single Lorentzian profile. Note that the FP cavity will contain resonances at different orders of the cavity spacing, and the separation between the different orders should be a minimum of 100 cm^{-1} .

2.3 Step-scan FTIR spectroscopy

Many of the photochemical reactions discussed in this document undergo chemical dynamics not only on the picosecond time-scale but also the nanosecond and microsecond time-scales. These longer time-scales are not easily accessed with the current experimental apparatus because of the long path lengths ($1\text{ }\mu\text{s} = 303\text{ m}$), which would be required to generate the long time delays. Optionally, a long time delay could be generated electronically by synchronizing the ultrafast laser system with a secondary laser as has been described by several authors [51,52,114]. Instead, we have a long-established collaboration with Heinz Frei at Lawrence Berkeley National Laboratory to use his step-scan FTIR apparatus, which provides access to these longer time-scales and a maximum time resolution of 25 ns. Frei's experimental apparatus has been described in detail elsewhere [115] and is only briefly described here. The computer programs developed to analyze the data from the step-scan apparatus are contained in Appendix B.

For experiments in the $1700 - 2100\text{ cm}^{-1}$ region, a HgCdTe detector KMPV8-1-J2 (FWHM = 37 ns, RC decay of AC amplifier = 1.4 ms) was employed. AC-coupled and DC-coupled interferometric signals were simultaneously acquired by a 40 MHz 12 bit digitizer (model PAD 1232). Samples were photolyzed with 25 ns pulses of the second harmonic of a Nd:YAG laser (DCR2A, GCR-3 optics) at 532 nm. Photolysis light was aligned in a nearly collinear geometry (10°) with the infrared beam. To prevent scattered 532 nm light from reaching interferometer and detector optics, Germanium plates (95% transmittance, anti-reflection coated) were placed in the openings of the interferometer and detector compartments. Data acquisition was triggered by a small fraction of the photolysis laser pulse detected with an EG&G Silicon photodiode (SGD-444). The sample, under Ar atmosphere, was flowed through a cell (Harrick Scientific) fitted with 1.5 mm thick CaF_2 or MgF_2 windows, giving an optical path length of 390

μm . Data were typically averaged over 15 laser-induced decays recorded for each mirror position of the Step-scan apparatus and 5-10 full time resolved Step-scan experiments were performed on each sample to ensure reproducibility and allow statistical analysis of data. Typically, changes in optical density of $\Delta\text{OD} = 5 \times 10^{-5}$ can be resolved in these experiments.

2.4 Density functional theory modeling

Extensive density functional theory (DFT) calculations have been performed to assist in the identification and characterization of the various chemical intermediates and to facilitate an understanding of the chemical dynamics. DFT calculations were typically carried out with the program package Gaussian 03 [116], and the B3LYP density function [117] or BP86 functional were used for the balance between accuracy and computational expense. Density functionals of the type used in this work have been shown to yield reliable results in calculations for transition-metal complexes [118].

Basis sets for all atoms other than transition metals consisted of the 6-31g(d), 6-31+g(d), 6-31+g(d,p) basis sets. For the transition-metal atoms, the LANL2DZ basis set, which includes a relativistic effective core potential, was used for all calculations [119]. The Hessian matrices were calculated at the stationary points in order to ensure that true minima on the potential energy hypersurfaces had been found. Harmonic vibrational frequencies (appropriately scaled for the B3LYP functional [120]) and in some cases anharmonic vibrational frequencies [121] are used in the spectral analysis of the experimental data.

3 Solvent caging and steric effects in ultrafast electron transfer reactions between metal-centered radicals

The following chapter is reproduced in part from Kling, Cahoon, *et al. J. Am. Chem. Soc.* 2004, 126, 11414-11415 [24] and Cahoon, *et al. J. Am. Chem. Soc.* 2005, 127, 12555-12565 [23].

3.1 Introduction

The 18-electron rule, one of the fundamental concepts in organometallic chemistry, predicts the greatest stability in compounds with an even number of electrons, yet the existence of odd-electron compounds both as stable species and intermediates in catalytic processes has long been recognized [122-124]. In addition to electron deficient 17-electron (17e) radicals, 19-electron (19e) species have been identified as potential intermediates in a variety of catalytic and electron transfer reactions [122-124]. One of the first 19e complexes, cobaltocene, was synthesized as early as 1953 [125,126], and many stable 19e complexes have subsequently been characterized [127-130]. While these complexes formally contain 19 valence electrons, the ‘19th’ electron is commonly localized on a ligand, allowing the metal to retain an effective 18-electron count. As a result, 19e compounds are often more accurately referred to as 18+ δ -electron complexes, where the value of δ reflects the degree of electron density residing on the metal center.

Although 18+ δ complexes are well characterized, a different class of less stable, “true” 19e complexes have been postulated as intermediates in organometallic reactions [122-124,131]. Since “true” 19e species are highly reactive, characterization has only been possible in rare instances. For example, $\text{Mn}(\text{CO})_5\text{Cl}^\bullet$ was generated by γ -irradiation of $\text{Mn}(\text{CO})_5\text{Cl}$, studied both computationally [132] and experimentally [133,134] and found to be better described as a 19 rather than 18+ δ -electron complex. In condensed phase organometallic chemistry, however, 19e species are, in general, generated by coordination of a 2-electron donor with a 17e radical:

In some instances, the 19e intermediate is predicted to be thermodynamically favorable with respect to the 17e species, yet unstable with respect to 18e counterparts [135-137]. These “true” 19e species are hence postulated as highly reactive, short-lived intermediates leading to stable even-electron products. Strong indirect evidence supports the formation of such species [138-

147], but experimental limitations previously hindered the direct observation of these intermediates and their reactions. Using transient IR spectroscopy with femtosecond time resolution, we directly observe the formation of 19e intermediates and investigate the dynamics of these short-lived species in the disproportionation of $[\text{CpW}(\text{CO})_3]_2$ with Lewis bases.

The disproportionation of $[\text{CpM}(\text{CO})_3]_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) into $\text{CpM}(\text{CO})_3^-$ and $\text{CpM}(\text{CO})_3\text{L}^+$ ($\text{L} = \text{phosphine or phosphite}$) has been well investigated and was one of the earliest photochemical reactions postulated to involve a 19e intermediate [144-147]. The currently accepted mechanism for this reaction, proposed by Tyler and co-workers [146,147], is depicted in Figure 3.1. Photoexcitation of $[\text{CpM}(\text{CO})_3]_2$ (**A**) at visible wavelengths leads to M-M bond cleavage and the formation of two 17e radicals $\text{CpM}(\text{CO})_3^\bullet$ (**B**). In the presence of Lewis bases PR_3 ($\text{R} = \text{alkyl, alkoxy, aryl or aryloxy}$), a highly reducing 19e species $\text{CpM}(\text{CO})_3\text{PR}_3^\bullet$ (**C**) is formed. Disproportionation is initiated by this 19e species: electron transfer from $\text{CpM}(\text{CO})_3\text{PR}_3^\bullet$ (**C**) to $[\text{CpM}(\text{CO})_3]_2$ (**A**) leads to formation of the cationic disproportionated product $\text{CpM}(\text{CO})_3\text{PR}_3^+$ (**D**) and a negatively charged parent dimer $[\text{CpM}(\text{CO})_3]_2^-$; successive M-M bond rupture of the negatively charged dimer yields a 17e radical $\text{CpW}(\text{CO})_3^\bullet$ (**B**) and the anionic disproportionated product $\text{CpW}(\text{CO})_3^-$ (**E**). Evidence for this mechanism includes quantum yield measurements of varying values greater than unity, which are consistent with the radical chain process in Scheme 1, and the occurrence of disproportionation when the negatively charged dimer was produced by Na metal reduction [146].

Figure 3.1 Photochemical disproportionation mechanism for $[\text{CpM}(\text{CO})_3]_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in Lewis bases PR_3 ($\text{R} = \text{alkyl, alkoxy, aryl, aryloxy}$) as proposed by Tyler [146,147]. Final disproportionated products are enclosed in boxes.

Scott et al. also found evidence for the formation of a 19e species while studying the electron transfer reactions of photo-generated $\text{CpW}(\text{CO})_3^\bullet$ radicals [143]. The rate of reduction of ferrocenium ions and benzoquinone by the $\text{CpW}(\text{CO})_3^\bullet$ radical was found to depend linearly

upon the concentration of PPh_3 , and this dependence was attributed to the formation of $\text{CpW(CO)}_3\text{PPh}_3^\bullet$, the same 19e species proposed by Tyler.

Here, we report detailed studies on the disproportionation reaction of $[\text{CpW(CO)}_3]_2$ in three Lewis bases (PR_3 ; $\text{R} = \text{OMe}, \text{Bu}, \text{Ph}$). These particular Lewis bases were chosen for their different electron-donating ability and cone-angle, enabling us to investigate steric and electronic effects on the reactivity of 19e intermediates. Using femtosecond VIS-pump, IR-probe spectroscopy we are able to resolve the complex dynamics and cage-effects involved in disproportionation and formation of 19e intermediates on an ultrafast timescale.

This chapter is organized as follows: Section 3.2 provides a brief account of our experimental techniques and theoretical approach. Section 3.3 presents the time-resolved results of pump-probe experiments and discusses the principal reaction mechanisms. Section 3.4 addresses the influence of particular Lewis bases on the disproportionation reactions. Our conclusions are summarized in Section 3.5.

3.2 Methods

3.2.1 Samples.

$[\text{CpW(CO)}_3]_2$, trimethyl phosphite (P(OMe)_3), *n*-tributylphosphine (PBu_3), and triphenylphosphine (PPh_3) were obtained from Aldrich, Inc. and spectroscopic grade CH_2Cl_2 was purchased from EMD Chemicals. All samples were used without further purification. Air sensitive materials were stored and handled under nitrogen atmosphere in a glove-box (Vacuum Atmospheres Company). Air and light-sensitive solutions were continuously purged with argon and rigorously secluded from all ambient light sources.

3.2.2 Data Analysis.

Kinetic data were derived from the spectral data taken at numerous picosecond pump-probe delay times. The absorbance values within distinct spectral ranges for the various chemical species were averaged at each individual time delay. Spectral ranges are as follows: CpW(CO)_3 1870-1878 cm^{-1} ; $\text{CpW(CO)}_3\text{PR}_3$ 1830-1850 cm^{-1} ($\text{R}=\text{OMe}$), 1820-1850 cm^{-1} ($\text{R}=\text{Bu}$); CpW(CO)_3^- 1750-1760 cm^{-1} ; $\text{CpW(CO)}_3\text{PR}_3^+$ 2059-2070 cm^{-1} ($\text{R}=\text{OMe}$), 2038-2052 cm^{-1} ($\text{R}=\text{Bu}$), 2048-2061 cm^{-1} ($\text{R}=\text{Ph}$). The kinetics for each species were then fit to one or more exponentials convoluted with a Gaussian (150 fs FWHM) to account for limited time resolution and accurately reflect the instrument response function. All reported errors correspond to 95% confidence intervals. Where noted, Gaussian peak fitting to the spectral data was performed to separate the contributions from two spectrally overlapped peaks, and kinetics were derived from

the area of the Gaussians.

3.2.3 Theoretical.

Density functional theory (DFT) calculations have been performed to assist in the characterization of the various intermediate species and to facilitate an understanding of the dynamical behavior. Density functionals of the type used in this work have been shown to yield reliable results in calculations for transition-metal complexes [118].

DFT calculations were carried out using the program package Gaussian03 [116], and the B3LYP hybrid method [117] was used in all calculations. It is composed of Becke's three-parameter exchange-functional [148] and the Lee-Yang-Parr non-local correlation functional [149]. Generic basis sets used consisted of the double-zeta LANL2DZ in conjunction with the relativistic effective core potential (ECP) of Hay and Wadt [119] for tungsten and 6-31G(d) (**I**), 6-31G+(d) (**II**), and 6-311+G(d,p) (**III**) basis sets for all other atoms. The Hessian matrices were calculated at the stationary points in order to ensure that true minima on the potential energy hypersurfaces had been found. Harmonic vibrational frequencies, appropriately scaled, are used in the spectral analysis of the experimental data.

Single point calculations on the optimized geometries were carried out making use of the Stuttgart effective core potential ECP60MDF [150] for tungsten with the associated basis set (8s7p6d)→[6s5p3d] plus an additional *f* polarization in conjunction with basis **II**, resulting in more than 800 contracted Gaussian-type orbitals for the largest complex. Natural bond orbital (NBO) analysis [151] has been performed wherefrom natural atomic charges were derived.

3.3 Results and discussion

3.3.1 Reactions in CH₂Cl₂.

The photochemistry of [CpW(CO)₃]₂ was monitored in the solvent CH₂Cl₂, and photolysis at 400 nm was found to yield only 17e radicals CpW(CO)₃[•]. Time resolved transient difference spectra after 400 nm photolysis of an approximately 1 mM solution of [CpW(CO)₃]₂ in neat CH₂Cl₂ are shown in Figure 3.2a. Negative absorbances result from the depletion of the parent molecule [CpW(CO)₃]₂ (**A**) while positive absorptions result from the formation of new species following laser photolysis. Two strong parent bleaches for *anti*-[CpW(CO)₃]₂ (**A**) are observed at 1909 and 1956 cm⁻¹, originating from the 2B_u and A_u carbonyl stretching modes of *anti*-[CpW(CO)₃]₂, the most stable isomer in non-polar and weakly polar solutions [152,153]. A negligible contribution from the *gauche*-isomer is observed by the weak bleach at 2012 cm⁻¹. The 17e CpW(CO)₃[•] radicals (**B**) exhibit transient absorptions at 1880 and 1995 cm⁻¹ [152,153].

Figure 3.2 Spectral data recorded for $[\text{CpW}(\text{CO})_3]_2$ in a) neat CH_2Cl_2 and b) 1.6 M $\text{P}(\text{OMe})_3$ with CH_2Cl_2 .

Photolysis of $[\text{CpW}(\text{CO})_3]_2$ can result in carbonyl loss with shorter excitation wavelengths; however, no significant absorption attributable to $\text{Cp}_2\text{W}_2(\text{CO})_5$ is observed in this experiment. $[\text{CpW}(\text{CO})_3]_2$ possesses two band maxima in the UV/Visible region at 493 and 362 nm in CCl_4 , corresponding to a weak $d\pi \rightarrow \sigma^*$ transition and strong $\sigma \rightarrow \sigma^*$ transition, respectively [30]. High energy excitation results in greater carbonyl loss while excitation into the lower energy band suppresses the carbonyl-loss pathway. In this experiment, excitation (400 nm) occurs between the two band maxima and is sufficiently low in energy to suppress a carbonyl-loss pathway. If carbonyl-loss products are generated by photolysis at 400 nm, the products are in such a low yield as to be undetectable by our experimental apparatus. Significant formation of carbonyl-loss products would be expected with higher excitation energies. Photolysis of

$[\text{CpW}(\text{CO})_3]_2$ may also result in halogen atom abstraction by the 17e radical $\text{CpW}(\text{CO})_3^\bullet$ in the presence of organic halides such as CCl_4 [154-156]. In the present study, CH_2Cl_2 is used as the solvent due to the high solubility of $[\text{CpW}(\text{CO})_3]_2$, phosphines, and phosphites in this solvent. In comparison to CCl_4 , chlorine atom abstraction is unfavorable in CH_2Cl_2 , with a second-order rate constant $k < 0.6 \text{ M}^{-1}\text{s}^{-1}$, four orders of magnitude lower than in CCl_4 ($k = 1.3 \pm 0.2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$) [154-156]. Chlorine atom abstraction would occur only to a limited extent and on a time scale of milliseconds or greater. Accordingly, no evidence for chlorine abstraction in CH_2Cl_2 was observed in our experiments on the ultrafast time scale.

In neat CH_2Cl_2 , 17e radicals (**B**) exhibit only vibrational relaxation and geminate recombination, leading to a decay of 5% within ca. 50 ps, but show no further decay on longer timescales. Geminate recombination of the 17e radicals results in formation of $[\text{CpW}(\text{CO})_3]_2$ and recovery of the bleaches for the dimer (labeled **A** in Figure 3.2), as discussed below.

3.3.2 Geminate recombination dynamics

In the initial tens of picoseconds after laser photolysis of $[\text{CpW}(\text{CO})_3]_2$ in neat CH_2Cl_2 , the nascent 17-electron radicals $\text{CpW}(\text{CO})_3^\bullet$ exhibit two dynamics, vibrational cooling and geminate recombination to reform the parent dimer. Figure 3.3 shows a kinetic plot of the 17-electron radical kinetics from spectral data in the range of 1970 to 2005 cm^{-1} . A wide spectral range is used to capture the absorption of both the vibrationally excited and cooled 17-electron radicals and hence limit the effect of vibrational cooling on the kinetics. Nevertheless, the dynamics of vibrational cooling and geminate recombination are difficult to separate and exponential fits to the data yield a rise time of $4 \pm 2 \text{ ps}$ and decay time of $52 \pm 16 \text{ ps}$. The exponential rise is attributed to vibrational cooling and exponential decay to both vibrational cooling and geminate recombination of the radicals. The kinetics thus indicate that both processes are complete within ca. 50 ps in neat CH_2Cl_2 .

Figure 3.3 Kinetic plot for the 17-electron radical $\text{CpW(CO)}_3^\bullet$ in neat CH_2Cl_2

As mentioned above, photolysis of $[\text{CpW(CO)}_3]_2$ causes depletion of this molecule, resulting in negative absorption signals, or bleaches in Figure 3.2. Within the first 50 ps following laser photolysis, geminate recombination of the photo-generated 17-electron radicals, $\text{CpW(CO)}_3^\bullet$, regenerates the $[\text{CpW(CO)}_3]_2$ molecule, causing a recovery of the bleach signal. Figure 3.4 shows the kinetics of bleach recovery in neat CH_2Cl_2 and 1.6 M P(OMe)_3 with CH_2Cl_2 . Single exponential fits to absorption data recorded at 1910 cm^{-1} yield recovery time constants of $36 \pm 2\text{ ps}$ and $21 \pm 2\text{ ps}$ for CH_2Cl_2 and $\text{P(OMe)}_3 / \text{CH}_2\text{Cl}_2$, respectively. Spectral overlap of the 17-electron radical absorption and the bleach, however, limits the reliability of these kinetic traces. The decay of 17-electron radicals and recovery of the bleach in neat CH_2Cl_2 are roughly correlated, with differences most likely due to spectral overlap and effects of vibrational cooling. Recovery of the bleach in $\text{P(OMe)}_3 / \text{CH}_2\text{Cl}_2$ gives a shorter time constant than in neat CH_2Cl_2 and suggests that geminate recombination occurs for a shorter time in the presence of P(OMe)_3 . This difference may be attributed to the formation of 19-electron intermediates from the 17-electron radical in these solutions, as discussed in the following sections.

Figure 3.4 Kinetic plots for $[\text{CpW}(\text{CO})_3]_2$ in a) neat CH_2Cl_2 and b) 1.6 M $\text{P}(\text{OMe})_3$ with CH_2Cl_2 .

3.3.3 Reactions with P(OMe)₃.

The addition of the strong Lewis base P(OMe)₃ to CH₂Cl₂ dramatically changes the intermediates and products on the ultrafast timescale, as shown by a comparison of Figure 3.2a and b. Time-resolved difference spectra after photolysis of [CpW(CO)₃]₂ in a 1.6 M solution of P(OMe)₃ in CH₂Cl₂ (“phosphite solution”) are shown in Figure 3.2b. In neat CH₂Cl₂, no significant decay of the 17e radicals (**B**) occurs after 50 ps, but in phosphite solution near complete decay of the radical is observed and four additional peaks can be seen, centered at 1770, 1850, 1967, and 2064 cm⁻¹, that are assigned to the anionic disproportionated product CpW(CO)₃⁻ (**E**), two peaks of the 19e intermediate CpW(CO)₃P(OMe)₃[•] (**C**₁), and the cationic disproportionated product CpW(CO)₃P(OMe)₃⁺ (**D**₁), respectively. Assignments are based on literature data, comparison to analogous compounds containing Mo rather than W [152,153,157-161], and extensive DFT calculations (see Table 3.1).

Neglecting the spectral trace at 20 ps, which shows effects of peak broadening due to vibrational excitation after photolysis, isosbestic points at 1865 cm⁻¹ and 1978 cm⁻¹ in Figure 3.2b indicate that the 19e intermediate (**C**₁) is directly formed from the 17e radical (**B**):

Fits to the kinetic data support this conclusion and are shown in Figure 3.5a. Kinetics for the 19e intermediate (**C**₁) were fit to an exponential decay and exponential rise, yielding 12 ± 2 ps (τ = k⁻¹) and 464 ± 101 ps respectively, with the exponential decay attributed to spectral overlap with the vibrationally hot 17e radical, which cools on this timescale, and the exponential rise attributed to the actual rise of the 19e intermediate. Kinetics for the 17e radical (**B**) were fit to two exponential decays giving 40 ± 4 ps and 417 ± 17 ps. The fast decay results from a combination of vibrational relaxation, disproportionation (as explained below), and geminate recombination. As in neat CH₂Cl₂, geminate recombination of the 17e radicals causes recovery of the bleaches for [CpW(CO)₃]₂ (labeled **A** in Figure 3.2; see Section 3.3.2 for details on the geminate recombination process). Note that the bleach centered at 1956 cm⁻¹ overlaps with a peak from the 19e species (**C**₁), causing changes in this absorption at longer time delays. The primary reaction pathway of 17e radicals in phosphite solution is the formation of 19e intermediates. Correlation of the longer time constants for the decay of 17e and rise of 19e species in addition to the isosbestic points indicate that the 19e CpW(CO)₃P(OMe)₃[•] (**C**₁) is generated from the 17e CpW(CO)₃[•] (**B**) on a 400 ps timescale.

Table 3.1 Calculated and observed vibrational frequencies (in cm^{-1}) of relevant species for the photochemistry of $[\text{CpW}(\text{CO})_3]_2$ with PR_3 (R= OMe, Bu, Ph) in CH_2Cl_2 .*

Species	calculated	observed
<i>anti</i> - $[\text{CpW}(\text{CO})_3]_2$ (A)	1892 (0.0), 1915 (0.2), 1924 (0.8), 1932 (0.0), 1968 (1.0), 2000 (0.0) ^a	1909 (s), 1956 (s)
<i>gauche</i> - $[\text{CpW}(\text{CO})_3]_2$	1902 (0.2), 1909 (0.3), 1937 (0.4), 1944 (0.0), 1970 (0.6), 2014 (0.4) ^a	2012 (w)
<i>anti</i> - $[\text{CpW}(\text{CO})_3]_2^-$	1839 (0.1), 1869 (0.8), 1881 (1.9) ^a	not observed
$\text{CpW}(\text{CO})_3^\bullet$ (17e, B)	1906 (0.6), 1907 (0.4), 1989 (0.3) ^c	1880 (s), 1995 (s)
$\text{CpW}(\text{CO})_3^-$ (18e, E)	1783 (0.7), 1784 (0.7), 1879 (0.4) ^c	1770 (w)
$\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^\bullet$ (19e, C ₁)	1867 (0.5), 1877 (0.4), 1961 (0.4) ^b	1850 (s), 1967 (m)
$\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^+$ (18e, D ₁)	1976 (0.5), 2000 (0.2), 2056 (0.3) ^b	1995 (w), 2064 (w)
$\text{CpW}(\text{CO})_3\text{PBu}_3^\bullet$ (19e, C ₂)	1821(0.8), 1857 (0.2), 1937 (0.3) ^b	1836 (m), 1943 (w)
$\text{CpW}(\text{CO})_3\text{PBu}_3^+$ (18e, D ₂)	1952 (0.5), 1978 (0.2), 2039 (0.3) ^b	2044 (w)
$\text{CpW}(\text{CO})_3\text{PPh}_3^\bullet$ (19e, C ₃)	1844 (0.7), 1864 (0.2), 1947 (0.3) ^b	1850(w)
$\text{CpW}(\text{CO})_3\text{PPh}_3^+$ (18e, D ₃)	1965 (0.5), 1981 (0.2), 2040 (0.3) ^b	2054 (w)

*calculated frequencies are scaled by the factor 0.9614[120]; ^a basis set **I**, ^b basis set **II**, ^c basis set **III**; relative intensities are given in parentheses (w = weak, m = medium, s = strong; calculated intensities are normalized with respect to the 1968 cm^{-1} mode of *anti*- $[\text{CpW}(\text{CO})_3]_2$); except for the last four rows in the table, observed frequencies are given for phosphite solutions.

Figure 3.5 Kinetic plots for a) $\text{CpW(CO)}_3\text{P(OMe)}_3^\bullet$ and $\text{CpW(CO)}_3^\bullet$, and b) $\text{CpW(CO)}_3^{\bullet-}$ and $\text{CpW(CO)}_3\text{P(OMe)}_3^+$ following 400 nm photolysis of $[\text{CpW(CO)}_3]_2$ in a 1.6 M solution of P(OMe)_3 with CH_2Cl_2 . Lines represent fits to the data (see text).

As shown in Figure 3.2b, the ionic products $\text{CpW(CO)}_3^{\bullet-}$ (E) and $\text{CpW(CO)}_3\text{P(OMe)}_3^+$ (D_1) are also formed on the ultrafast time scale. Kinetics for these species are shown in Figure 3.5, and they grow in with very similar times constants of 134 ± 27 ps for E and 140 ± 14 ps for D_1 . The similarity of these two time constants indicates that these two species are generated in a single kinetic event. Why, however, is the disproportionation reaction faster than the formation of $\text{CpW(CO)}_3\text{P(OMe)}_3$ (C_1), the alleged 19e intermediate in the disproportionation reaction? A microscopic view of the reaction can provide an answer to this question, as depicted in Figure 3.6. Homolysis of the dimer (**A**) produces two 17e radicals (**B**) enclosed by a cage of solvent molecules, represented by brackets in Figure 3.6. Coordination of P(OMe)_3 generates a 19e intermediate (C_1), which can transfer an electron to the 17e radical (**B**), forming the final

disproportionated products (**D**₁, **E**). It is important to realize that this electron transfer reaction can only occur while the electron donor (**C**₁) and acceptor (**B**) species are in close proximity, a condition which is given only within the lifetime of the solvent cage. In order to understand cage effects on the extent and rate of disproportionation, we have studied the reaction in various concentrations of P(OMe)₃, as detailed in the following section.

Figure 3.6 Mechanism of ultrafast disproportionation. Brackets represent the solvent cage

Note that due to the extremely low concentration of $[\text{CpW}(\text{CO})_3]_2$ in comparison to the other molecules, any mechanism involving this species (as in Figure 3.1) can be ruled out on the picosecond timescale. In this particular sample, over 12,000 CH_2Cl_2 molecules and 1,500 $\text{P}(\text{OMe})_3$ molecules are present for every one $[\text{CpW}(\text{CO})_3]_2$ molecule. Diffusional encounters of the 19e species with remaining $[\text{CpW}(\text{CO})_3]_2$ molecules would not occur on the picosecond timescale. Furthermore, no evidence for the formation of $[\text{CpW}(\text{CO})_3]_2^-$, an intermediate expected in the mechanism of Figure 3.1, is observed in this experiment (see Table 3.1 for predicted frequencies of this species). The concentrations used in this study also indicate at least one $\text{P}(\text{OMe})_3$ molecule will be present in the first solvation shell of the $[\text{CpW}(\text{CO})_3]_2$ molecule prior to laser photolysis, allowing the formation of 19e species to easily occur within tens of picoseconds after laser photolysis.

3.3.4 Cage effects and concentration dependence.

Changing the concentration of Lewis base $\text{P}(\text{OMe})_3$ significantly alters the dynamics of all the reactive species. The results are summarized in Figure 3.7. Homolysis of the dimer (A)

produces two 17e radicals (**B**) enclosed by a cage of solvent molecules, represented by brackets. Coordination of a phosphite generates a 19e intermediate (**C**₁), and in all concentrations of P(OMe)₃, electron transfer between the solvent caged 17e (**B**) and 19e species (**C**₁) generates the disproportionated products (**D**₁, **E**). In low concentrations of P(OMe)₃, however, there is a competing process to disproportionation: separation of the radical species. As the solvent cage breaks down, the separation of the 17e and 19e species prevents electron transfer and hence prevents formation of the disproportionated products.

Figure 3.7 Reactions of [CpW(CO)₃]₂ with P(OMe)₃. Brackets represent the solvent cage

Time constants for all the reactive species at various concentrations of P(OMe)₃ are presented in Table 3.2. The formation times of the 19e intermediate are shorter with increasing P(OMe)₃ concentration; correspondingly, the decay of the 17e radical is faster. Note that the longer time constant for the decay of the 17e radical instead of the time constant for 19e intermediate formation has been used in our analysis of the concentration dependence as these two processes are correlated and the 17e transient absorptions exhibit lower noise. The time constants for disproportionation initially increase as the concentration of P(OMe)₃ is lowered but then reach a plateau at concentrations of 2.5 M and lower.

In order to understand the observed behavior, the reactions occurring on a picosecond timescale must be analyzed in detail. Neglecting geminate recombination of the radicals, the two primary reactions are the reaction of 17e radicals with the Lewis base P(OMe)₃ to form 19e intermediates (eq. 3.1) and the reaction of 19e intermediates with 17e radicals to form the disproportionated products (eq. 3.2):

Table 3.2 Time constants ($\tau = k^{-1}$) for reactive species in $\text{PR}_3/\text{CH}_2\text{Cl}_2$ solutions of varying concentration*

R =	PR ₃ concentration in CH ₂ Cl ₂ (M)	Time-constant (ps)				
		CpW(CO) ₃ • (17e, B)	CpW(CO) ₃ PR ₃ • (19e, C)	CpW(CO) ₃ PR ₃ ⁺ (18e, D)	CpW(CO) ₃ ⁻ (18e, E)	$\frac{1}{2} \cdot \frac{\tau_{\text{radical}}}{\tau_{\text{disp}}}$ ^a
OMe	4.2	194 ± 25	174 ± 47	87 ± 12		1.11 ± 0.21
	3.6	199 ± 27	155 ± 43	114 ± 11		0.87 ± 0.15
	3.0	261 ± 7	276 ± 16 ^b	121 ± 6		1.08 ± 0.06
	2.5	279 ± 18	307 ± 116 ^b	139 ± 6	127 ± 13	1.00 ± 0.08
	2.0	363 ± 22	440 ± 26 ^b	142 ± 11		1.28 ± 0.13
	1.6	417 ± 17	464 ± 101	140 ± 14	134 ± 27	1.49 ± 0.16
Bu	2.0	315 ± 5	353 ± 62	162 ± 13	138 ± 16	0.97 ± 0.08
	1.3	463 ± 25	508 ± 206	165 ± 15	160 ± 61	1.40 ± 0.15
Ph	2.0	213 ± 32		195 ± 28		0.55 ± 0.11
	1.6	229 ± 29		226 ± 16		0.51 ± 0.07
	1.3	221 ± 18		234 ± 16		0.47 ± 0.05

*Errors correspond to 95% confidence intervals; for the 17e and 19e species, values are the longer time component of a biexponential fit (see text); ^aquotient of one-half of the time constant for CpW(CO)₃• decay and time constant for CpW(CO)₃PR₃⁺ formation (see text); ^bcalculated from Gaussian fits to the spectral data.

Figure 3.8 Dependence of the pseudo first-order rate constant for 19e intermediate formation on the concentration of Lewis base P(OMe)₃.

Because near complete decay of the radical is observed in all phosphite solutions, the rate constant k_{-1} for dissociation of the 19e intermediates to 17e radicals and phosphite is assumed sufficiently small to be neglected in the following treatment of the kinetics. In-cage disproportionation (eq. 3.2) occurs on a fast time-scale, exhibiting time constants below 150 ps in all cases. Since the 17e radical decay and 19e intermediate rise both occur on time scales approximately twice as long as disproportionation, the separation of time scales allows the 17e/19e dynamics to be modeled exclusively by reaction (eq. 3.1). Under pseudo-first order conditions, i.e. high P(OMe)₃ concentrations, the observed rate constant for (eq. 3.1), k_{obs} , depends linearly on the concentration of P(OMe)₃, with $k_{\text{obs}} = k_1[\text{P(OMe)}_3]$. A linear fit to the data is shown in Figure 3.8 and yields a value for the bimolecular rate constant of $k_1 = (1.1 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Understanding the concentration dependence of disproportionation is more complex. Both reactions (eq. 3.1) and (eq. 3.2) must be considered on time scales less than 150 ps. Since 19e intermediates are formed by reaction (eq. 3.1) but consumed by reaction (eq. 3.2), a steady-state approximation for 19e intermediates may be applied while (eq. 3.2) is sufficiently fast to maintain a low concentration of 19e species. While the steady-state assumption is not rigorously correct, it is sufficient to qualitatively interpret the experimental results. The rate equations of (eq. 3.1) and (eq. 3.2) can be solved for the concentration of disproportionated product at time t :

$$[\text{CpW(CO)}_3\text{P(OMe)}_3^+]_t = \frac{1}{2}[\text{CpW(CO)}_3^\bullet]_0(1 - e^{-2k_{\text{obs}}t}) \quad (3.3)$$

with $[\text{CpW}(\text{CO})_3^\bullet]_0$ the initial concentration of the radical species. It can be shown that (3.3) implies the relationship $\tau_{\text{disp}} = 0.5 \times \tau_{\text{rad}}$, where τ_{disp} and τ_{rad} are the time constants for disproportionation and radical decay, respectively. Within errors, this relationship is valid for the four highest concentrations of $\text{P}(\text{OMe})_3$, as illustrated by the quotient between one-half the time constant for the radical decay and the observed time constant for ultrafast disproportionation in Table 3.2. This quotient is close to unity for the four highest concentrations of $\text{P}(\text{OMe})_3$, the expected result when the steady-state approximation and equation (3.3) are applicable. Since equation (3.3) depends on only one rate constant, k_{obs} , disproportionation is limited by the depletion of 17e radicals from reaction (3.1) rather than the electron transfer of reaction (3.2) in high Lewis base concentrations.

In the two lowest concentrations of $\text{P}(\text{OMe})_3$ on the other hand, poor agreement with the steady-state prediction is observed, as indicated by the deviation from unity in the last column of Table 3.2. This discrepancy suggests that the steady-state approximation breaks down in lower concentration solutions and that the rate of electron transfer becomes important. Studies on electron transfer in proteins and in electron donor and acceptor systems predict that the rate of electron transfer will decrease exponentially with the separation of the donor-acceptor molecules [162]. In low $\text{P}(\text{OMe})_3$ concentrations therefore, separation of the radical pair may significantly slow electron transfer, limiting the rate of disproportionation. The separation of the radicals, equivalent to the breakdown of the solvent cage, can be viewed as a process that competes with disproportionation, as depicted in Figure 3.7. The distance necessary to slow electron transfer can be estimated from the time constant for disproportionation. Treating the solvent as a viscous medium and using a random walk equation for three dimensions $x(\tau) = \sqrt{6D\tau}$ in neat CH_2Cl_2 with self-diffusion coefficient $D = 1.6 \times 10^{-6} \text{ cm}^2/\text{s}$, a time constant of $\tau = 140 \text{ ps}$ corresponds to a distance $x(\tau) = 3.7 \text{ \AA}$ between two particles [163]. At distances above $3.7 \text{ \AA}$, electron transfer may be sufficiently slow to kinetically limit the build-up of electron-transfer products.

Two regimes are apparent, as shown in Figure 3.7. In the low concentration regime, diffusion limits the rate of disproportionation by separating the 17e electron acceptor and 19e electron donor. In the high concentration regime, disproportionation slows down due to depletion of the 17e radical population. The experimental results also suggest that increasing the $\text{P}(\text{OMe})_3$ concentration increases the yield of disproportionated products on a picosecond timescale. A ratio of the $\text{CpW}(\text{CO})_3\text{PR}_3^+$ peak intensity at 800 ps to the $[\text{CpW}(\text{CO})_3]_2$ bleach intensity at 1 ps may provide a relative measure of the disproportionation yield. Although the data does not allow for a quantitative analysis, qualitatively, this ratio is observed to increase with higher $\text{P}(\text{OMe})_3$ concentration. Raising the Lewis base concentration allows more electron transfer events to occur

before diffusional separation of the electron transfer species, resulting in a greater yield of disproportionated products.

3.3.5 Reactions with PBU_3 .

The photochemistry of $[\text{CpW}(\text{CO})_3]_2$ was also studied with the larger and more electron-donating Lewis base PBU_3 . The results are qualitatively similar to those in phosphite solution, although the kinetics indicate that 19e formation is slightly faster with PBU_3 . Figure 3.9 shows difference spectra of 1 mM $[\text{CpW}(\text{CO})_3]_2$ in a 2.0 M solution of PBU_3 with CH_2Cl_2 . The absorbances for $[\text{CpW}(\text{CO})_3]_2$ (**A**) and 17e $\text{CpW}(\text{CO})_3^\bullet$ (**B**) appear in the same positions as other solutions (see Table 3.1). The 19e species $\text{CpW}(\text{CO})_3\text{PBU}_3^\bullet$ (**C₂**) displays peaks at 1943 and 1836 cm^{-1} , in good agreement with DFT calculations contained in Table 3.1. The peak for $\text{CpW}(\text{CO})_3\text{PBU}_3^+$ (**D₂**) is shifted from the corresponding peak of $\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^+$ by 20 cm^{-1} to 2044 cm^{-1} , also in accord with the prediction from DFT calculations (17 cm^{-1}). $\text{CpW}(\text{CO})_3^-$ (**E**) is resolved into two separate bands at 1751 and 1771 cm^{-1} , most likely due to polarity effects from the counteranion [146].

Figure 3.9. Transient difference spectra in the CO stretching region following 400 nm photolysis of $[\text{CpW}(\text{CO})_3]_2$ in a 2.0 M solution of PBU_3 with CH_2Cl_2 .

As in phosphite solution, an isosbestic point at 1855 cm^{-1} in Figure 3.9 indicates that the 19e intermediate (**C₂**) is formed from the 17e radical (**B**). Kinetic fits to the data support this conclusion and are shown in Figure 3.10. Due to the greater separation between the 17e and 19e peaks, the kinetic data with PBU_3 exhibit less noise than those obtained for phosphite solution.

Kinetics for $\text{CpW}(\text{CO})_3^\bullet$ (**B**) were fit to two exponential decays, yielding time constants of 35 ± 2 and 315 ± 5 ps. The fast decay results from a combination of vibrational relaxation, disproportionation, and geminate recombination while the longer decay results from the formation of 19e intermediates. Kinetics for the 19e $\text{CpW}(\text{CO})_3\text{PBu}_3^\bullet$ (**C**₂), also shown in Figure 3.10, were fit to two exponential decays and one exponential rise, giving time constants of 6 ± 1 , 43 ± 14 , and 353 ± 62 ps, respectively. The decays result from overlap with the vibrationally hot and red shifted 17e radical absorbance while the exponential rise is attributed to the formation of 19e intermediates. Figure 3.10 also shows a single exponential fit (dotted line) to the 19e kinetic data omitting all points between 0 and 50 ps, which are dominated by vibrational relaxation of the 17e radical species. This fit yields a time constant of 317 ± 14 ps for the rise of the 19e species, in excellent agreement with the decay time of the 17e radical (315 ± 5 ps). Fits to the kinetic data for the disproportionated products (not shown) yield time constants of 162 ± 13 ps for $\text{CpW}(\text{CO})_3\text{PBu}_3^+$ and 138 ± 16 ps for $\text{CpW}(\text{CO})_3^-$. As in phosphite solution, the disproportionated products are formed in the same kinetic event: in-cage electron transfer between the 17e and 19e species (see Figure 3.6).

Figure 3.10 Kinetic plots for $\text{CpW}(\text{CO})_3\text{PBu}_3^\bullet$ and $\text{CpW}(\text{CO})_3^\bullet$ following 400 nm photolysis of $[\text{CpW}(\text{CO})_3]_2$ in a 2.0 M solution of PBu_3 in CH_2Cl_2 . Absorbance values for $\text{CpW}(\text{CO})_3\text{PBu}_3^\bullet$ are scaled by a factor of 2 for clarity. Lines represent fits to the data (see text).

Data were obtained at two concentrations of PBu_3 (see Table 3.2) and suggest that the same regimes and cage-effects discussed for phosphite solutions are also true for PBu_3 . The quotient in the last column of Table 3.2 indicates that in a 1.3 M concentration of PBu_3

1850 and 2054 cm^{-1} , respectively. These peak positions are in good agreement with the frequencies obtained from DFT calculations (see Table 3.1). Only one peak for the 19e species (C_3) is apparent in the spectra, most likely due to spectral overlap with the strong bleach at 1956 cm^{-1} . Figure 7 shows kinetic plots for the 17e radical (**B**) and one disproportionated product (D_3). In contrast to $\text{P}(\text{OMe})_3$ and PBU_3 , the long time component measured for 17e radical decay (**B**) matches the rise time for the disproportionated product (D_3) within errors. This agreement suggests that the decay of the 17e radical results from electron transfer to the disproportionated products and preservation of 17e/19e equilibrium rather than the formation of 19e intermediates outside the solvent cage.⁴ The dynamics were observed at various concentrations of PPh_3 (see Table 3.2) and in all cases the 17e radical did not decay completely.

Figure 3.12 Transient difference spectra in the CO stretching region following 400 nm photolysis of $[\text{CpW}(\text{CO})_3]_2$ in a 1.3 M solution of PPh_3 in CH_2Cl_2 .

Formation times for disproportionated products in PPh_3 show no significant concentration dependence (see Table 3.2), which is consistent with the results for $\text{P}(\text{OMe})_3$ at similar concentrations. As already discussed, the build-up of disproportionated products can either be limited by the separation of solvent-caged radicals or the depletion of 17e radical population. In the latter case, a strong concentration dependence should be apparent. If, on the other hand, the separation of 17e radicals limits the build-up of disproportionated products, then little

⁴ A similar decay should be present with $\text{P}(\text{OMe})_3$ and PBU_3 , but it is sufficiently low in amplitude to be masked by the larger decay resulting from 19e formation in these Lewis bases.

concentration dependence would be expected.⁵ The lack of concentration dependence in the experimental data suggests that the rate-limiting process for ultrafast disproportionation in PPh_3 at the concentrations used in this experiment is the separation of caged radicals rather than the depletion of $17e$, electron acceptor species.

Figure 3.13 Kinetic plots for $\text{CpW(CO)}_3^\bullet$ and $\text{CpW(CO)}_3\text{PPh}_3^+$ following 400 nm photolysis of $[\text{CpW(CO)}_3]_2$ in a 1.3 M solution of PPh_3 in CH_2Cl_2 .⁶ Lines represent fits to the data.

As apparent from Figure 3.12, the peak from the $19e$ species (C_3) is less intense in comparison to the other Lewis bases and, rather than growing in, maintains an almost constant intensity after vibrational cooling of the highly overlapped $17e$ radical peak (**B**). These observations suggest that the $19e$ $\text{CpW(CO)}_3\text{PPh}_3^\bullet$ is less stable than its counterparts in other Lewis bases and that the $17e/19e$ equilibrium favors $17e$ species, consistent with Scott and co-workers estimate of only $K = 6 \pm 1 \text{ L}\cdot\text{mol}^{-1}$ as the equilibrium constant ($K = k_1/k_{-1}$) for the process [143]. It is plausible to assume that while species in solution are vibrationally excited the reactants are able to overcome the barrier to $19e$ intermediate formation and reach the equilibrium concentration for the species within tens of picoseconds. No additional formation of the $19e$ species is observed on the picosecond timescale, so the decay of the $17e$ radical results

⁵ Changes in concentration alter diffusion coefficients for solutions, changing the rate of diffusion. For small concentration differences, changes in the diffusion coefficient should be negligible.

⁶ The kinetic trace for $\text{CpW(CO)}_3\text{PPh}_3^+$ begins at a negative absorbance value due to a weak bleach resulting from build-up of this product in the solution. This bleach appears after very short periods of laser photolysis most likely due to a very high quantum yield for disproportionation at high concentrations of PPh_3 .

exclusively from the disproportionation process, explaining the correlation of the two respective time constants. Since the 17e/19e equilibrium favors 17e radicals, both species should be present on longer timescales and thus may react out-of-cage. Experiments to understand the reactions on diffusion-limited timescales are currently in progress.

It is interesting to note that the 19e peak displays negligible growth while the 17e peak is still decaying. This observation might indicate that the 19e species is not an intermediate for disproportionation and that an inner sphere mechanism for electron transfer may occur. In this case, the reaction would proceed directly from the caged 17e radicals to the disproportionated products, with the coordination of a Lewis base occurring concurrently with electron transfer. In comparison, an outer sphere mechanism would first require formation of the 19e species and then transfer of the electron, as depicted in Figure 3.6. The current experimental data does not distinguish between an inner sphere mechanism without formation of 19e intermediates and an outer sphere mechanism in which electron transfer is sufficiently fast to prevent the build-up of the 19e species.

3.4 Comparison of the reactivity in different Lewis bases

3.4.1 Steric and Electronic Effects.

The stability and reactivity of 18+ δ compounds is affected by the nature of the organometallic fragment, coordinating ligand, and solvent. The organometallic species and solvent were the same in all experiments conducted, so differences in chemical dynamics result solely from the different properties of the three coordinating ligands (PR₃; R = OMe, Bu, Ph). A low energy π^* orbital in the coordinating ligand tends to enhance the stability of 18+ δ compounds since the '19th' electron can localize in the anti-bonding orbital rather than occupying a higher energy metal-centered orbital [127-129]. Reduction potentials of the lone ligand are correlated with the ligand's ability to stabilize 18+ δ compounds by accommodating the extra electron in a vacant molecular orbital [129,164,165]. A more positive reduction potential approximately indicates a smaller HOMO/LUMO energy gap and corresponds to more stable 18+ δ compounds but decreased reactivity toward electron transfer [129]. In the absence of reduction potentials for the ligands themselves,⁷ the reduction potentials (E^0) for CpFe(CO)(COMe)PR₃⁺ will be used to establish the trend for the PR₃ ligands. Reduction potentials for the CpFe(CO)(COMe)PR₃⁺⁰ couple were measured relative to acetylferrocene at 20°C and for the three relevant ligands it was

⁷ To the best of our knowledge, these values have not been published. Initial attempts to determine the reduction potentials of the phosphines suggest that decomposition of the solvent may occur before reduction is achieved; however, more rigorous attempts are called for.

found that P(OMe)_3 (-0.1344 V) $>$ PPh_3 (-0.2630 V) $>$ PBu_3 (-0.3990 V).[166] In addition to orbital considerations, electron-donating ability and cone-angle are two prototypical ligand properties which may affect the stability and reactivity of 19e intermediates. Cone-angle is the generally accepted measure of the size of coordinating ligands [167], with PPh_3 (145°) $>$ PBu_3 (132°) $>$ P(OMe)_3 (107°) [146]. The electron donating ability of phosphine and phosphite ligands can be measured by the A_1 mode CO stretching frequencies of $\text{Ni(CO)}_3\text{L}$ (L = phosphine or phosphite). Due to CO π back-bonding, lower frequencies correspond with better electron donating ability; hence, in terms of relative electron-donating ability PBu_3 (2060.3 cm^{-1}) $>$ PPh_3 (2068.9 cm^{-1}) $>$ P(OMe)_3 (2079.5 cm^{-1}) [168]. These three ligand properties, reduction potential, cone-angle, and electron donating ability, control the stability of 19e species and can be used to understand the observed reactivity.

The Lewis bases P(OMe)_3 and PBu_3 produce qualitatively similar results, while PPh_3 exhibits significantly different behavior. 19e intermediates form to a smaller extent and on a different timescale in the presence of PPh_3 , which lies between the other two ligands in terms of both electron-donating ability and reduction potential. Neither of these properties appears to be the determining factor for the kinetics and extent of 19e intermediate formation with PPh_3 . Instead, the cone-angle, which indicates that PPh_3 is the largest of the three Lewis bases (145°), is best correlated with the experimental data and implies that steric effects hinder the formation of a 19e species with PPh_3 . The cone-angles of P(OMe)_3 and PBu_3 are smaller than PPh_3 yet significantly different from one another at 107° and 132° , respectively. Despite this difference of 25° , the experimental results in P(OMe)_3 and PBu_3 are qualitatively similar, suggesting that cone-angles only become important when the steric hindrance exceeds a certain limiting value (here between 132° and 145°). This observation is in agreement with a study by Tyler in which a sudden change in reactivity was found between PPh_2Bu_3 (140°) and PPh_3 (145°) [146].

Quantitative analysis of the results in P(OMe)_3 and PBu_3 suggest that the formation of 19e species is slightly faster in PBu_3 , with a rate constant of $(1.45 \pm 0.3) \times 10^9\text{ M}^{-1}\text{s}^{-1}$ in comparison to $(1.1 \pm 0.2) \times 10^9\text{ M}^{-1}\text{s}^{-1}$ for P(OMe)_3 . The calculated rate constants may not be rigorously distinguishable, but the opposite trend would be expected if steric factors played an important role in the formation of 19e intermediates with these Lewis bases. Instead, electronic parameters appear important when the steric hinderance is below a certain limiting value. The reduction potential and electron-donating ability of PBu_3 indicate that it is less likely to accept extra electron density into a vacant molecular orbital and more likely to donate electron density to the metal center in comparison to P(OMe)_3 . Based upon the experimental data, these two properties enhance the rate of 19e intermediate formation when steric effects are no longer an

important consideration. The enhanced rate of 19e formation also causes the high concentration regime in PBu₃ to be achieved at a lower concentration (2.0 M) than was achieved with P(OMe)₃ (2.5 M; see last column of Table 3.2).

In the low concentration limit of the three Lewis bases, the differences observed in the time constants for disproportionation between the Lewis bases (Table 3.2) may be attributed to differences in the respective viscosity and diffusion constants of these solutions. Disproportionation in PPh₃, however, occurs for a significantly longer period of time in comparison to the two smaller Lewis bases. In addition to viscosity and diffusion considerations, PPh₃ may facilitate electron transfer better than the other Lewis bases, contributing to the longer period of disproportionation.

3.4.2 Atomic charge distributions.

Calculations on charge distributions in the 17e and 19e complexes were carried out to elucidate the experimental results. Data from the NBO analysis are reported in Table 3.3. The charges on the PR₃ ligand and W atom in the CpW(CO)₃PPh₃[•] complex lie between the values for the other two Lewis bases, supporting our conclusion that steric rather than electronic effects dominate the behaviour of PPh₃.

The charges of the PR₃ ligands in the 19e CpW(CO)₃PR₃[•] complexes become more positive in the order P(OMe)₃ < PPh₃ < PBu₃, in agreement with the trends in electron-donating ability and reduction potential quoted above. Because the 19e complex is neutral, the charge on the PR₃ ligand is exactly balanced by a negative charge on the CpW(CO)₃[•] portion of the species and the Cp moiety bears a considerable fraction (about one third) of this negative charge. Since the *q*(Cp) values are comparable for the three 19e complexes (see Table 3.3), the charges on the W(CO)₃ unit correspond to the aforementioned trend, with the R = Bu complex exhibiting the greatest negative charge. Within the W(CO)₃ unit, however, the most negatively charged W atom is, surprisingly, in the R = OMe complex. This result may explain why 19e intermediate formation in P(OMe)₃ is slightly slower in comparison to PBu₃. The average charges on the CO molecules are positive for the R = OMe complex and negative for the R = Bu complex, while the R = Ph species contains, on average, almost neutral CO ligands. Note that these are average values, and the individual CO values show different charges (even different in sign). The 19th electron is mostly localized in antibonding orbitals [123,124], rendering the average CO bond lengths relatively long. Accordingly, the frequencies become smaller, in agreement with experiment).

Table 3.3 Charges (in atomic units) of molecular fragments in the 17e $\text{CpW(CO)}_3^\bullet$ and 19e $\text{CpW(CO)}_3\text{PR}_3^\bullet$ (R = OMe, Bu, Ph) complexes and average CO bond lengths.

	$\text{CpW(CO)}_3^\bullet$ (B)	$\text{CpW(CO)}_3\text{P(OMe)}_3^\bullet$ (C ₁)	$\text{CpW(CO)}_3\text{PBu}_3^\bullet$ (C ₂)	$\text{CpW(CO)}_3\text{PPh}_3^\bullet$ (C ₃)
$q(\text{W})$	0.0197	-0.3529	-0.3078	-0.3152
$1/3\ q((\text{CO})_3)$	0.0472	0.0332	-0.0168	0.0076
$q(\text{W(CO)}_3)$	0.1613	-0.2530	-0.3582	-0.2923
$q(\text{Cp})$	-0.163	-0.1556	-0.1621	-0.1375
$q(\text{CpW(CO)}_3)$	0	-0.4086	-0.5203	-0.4298
$q(\text{PR}_3)$	-	0.4086	0.5203	0.4298
$r(\text{CO}) / \text{\AA}$	1.163	1.168	1.172	1.169

There is still a conceptual problem concerning whether the 19e intermediates are true 19e species or should rather be classified as 18+ δ complexes. Several definitions of δ can be found in the literature. In one theoretical study, δ is calculated as the difference in charge on ligands in cationic 18e and neutral 19e complexes [169]. Alternatively, δ can be understood in terms of the spin density, or more exactly the unpaired electron density, localized on the metal center [132,170]. Here we use $\delta = q(\text{W})$ as a meaningful definition that would yield δ values of about one third of an elementary charge.

3.5 Summary and conclusion

Figure 3.14 Proposed mechanisms for 19e intermediate formation and disproportionation in Lewis bases PR₃ (R = OMe, Bu, Ph) at varying concentrations in CH₂Cl₂. Brackets represent the solvent cage. Reactions in which both caged 17e radicals only react following breakdown of the solvent cage are omitted for clarity.⁸

The complex dynamics of 19e intermediate formation and disproportionation following 400 nm photolysis of [CpW(CO)₃]₂ in the presence of Lewis bases PR₃ (R = OMe, Bu, Ph) have been resolved on a picosecond timescale, and the results are summarized in Figure 3.14. The dynamics depend on both the identity and concentration of Lewis base, with the results separating into three distinct categories: **I** P(OMe)₃ and PBu₃ at high concentration, **II** P(OMe)₃ and PBu₃ at low concentration, and **III** PPh₃. In all cases, photolysis initially results in the formation of solvent caged 17e CpW(CO)₃• radicals (the brackets in Figure 3.14 represent the solvent cage). Coordination of a Lewis base with one 17e radical forms a 19e intermediate CpW(CO)₃PR₃•, with the equilibrium favoring 19e species in the order Bu > OMe >> Ph. In all cases,

⁸ Neglected in Scheme 5 are reactions involving separation of the 17e radicals prior to 19e formation. This scenario likely occurs for cases **II** and **III** and to a lesser extent for **I**. For cases **II** and **III**, 17e radical separation prevents disproportionation in the same manner as separation of the 17e and 19e species.

disproportionation to the 18e CpW(CO)_3^- and $\text{CpW(CO)}_3\text{PR}_3^+$ occurs by transfer of an electron from a 19e to 17e species within the same solvent cage.

For case **I**, disproportionation ceases due to the decrease in 17e radical (electron acceptor) population. In cases **II** and **III** on the other hand, disproportionation ceases due to diffusional separation of the caged radical pair [171]. Once the electron donor and acceptor have separated by several angstroms, electron transfer is sufficiently slow to limit the build-up of disproportionated products. The longest period of disproportionation is observed in case **III** (PPh_3), suggesting that PPh_3 facilitates electron over a longer separation than the other two Lewis bases.

In cases **I** and **II** (P(OMe)_3 and PBu_3), the equilibrium favors 19e species, so nearly all the 17e radicals not consumed by the in-cage disproportionation reaction are converted to 19e species. The rate of 19e formation is slightly faster with PBu_3 , an effect best attributed to the electronic properties (e.g. greater electron-donating ability) of this Lewis base. With PPh_3 (case **III**) on the other hand, the 17e/19e equilibrium favors the 17e radical, so only limited formation of a 19e species is observed. The behavior of PPh_3 is attributed to steric rather than electronic effects since its electronic parameters (electron-donating ability, reduction potential, atomic charges) lie between the other two Lewis bases. The results with the three Lewis bases indicate that steric hinderance dominates the 19e dynamics when the cone-angle of the Lewis base exceeds a certain limiting value while electronic effects dominate below this limiting value (between 132° and 145°).

The presence of the three categories (**I**, **II**, **III**) cited above provide the opportunity to manipulate the extent of ultrafast disproportionation by controlling the concentration and identity of the Lewis base. Other chemical processes, such as CO ligand substitution [172], may compete with disproportionation on longer, diffusion-limited timescales (nanosecond to milliseconds; see Chapter 5). In such a case, the primary mechanism for disproportionation may be the one proposed here, while different processes involving the 19e species occur on longer timescales. As a result, the extent of disproportionation in comparison to other processes may be affected by the identity of Lewis base and potentially controlled with the concentration. The results with different concentrations of P(OMe)_3 suggest that the yield of disproportionated products on a picosecond time-scale increases with increasing P(OMe)_3 concentration since more electron transfer events can occur before the electron donor and acceptor are separated.⁹

The results presented in this chapter confirm the formation of highly reactive 19-electron

⁹ At extremely high concentrations (e.g. with the Lewis base as solvent) the formation of two 19e species within the same solvent cage may hinder disproportionation.

species and describe a mechanism for disproportionation by in-cage electron transfer between a 17e and 19e species. In this study, disproportionation is complete within ca. 200 ps, yet the 17e and 19e species both persist beyond the time scale of the experiment (800 ps). The reactions of these radicals on longer time scales is still an unresolved question. For instance, the disproportionation mechanism proposed by Tyler (Figure 3.1) is appropriate on diffusion-limited time scales (nanoseconds to milliseconds) yet has not been directly observed using time-resolved IR spectroscopy. Experiments designed to probe the dynamics on longer time scales and distinguish the different mechanisms or processes involved in the radical chemistry are discussed in Chapters 4 and 5.

4 The role of odd-electron intermediates in the photochemical disproportionation mechanism of $[\text{CpW}(\text{CO})_3]_2$

The following chapter is reproduced in part from Cahoon, *et al. J. Mol. Struct.* (memorial issue for F. A. Cotton), 2008, 890, 328-338 [21].

4.1 Introduction

The reactivity of organometallic radicals is an important and ongoing question; odd-electron transition-metal species are used as synthetic precursors for more complex organometallic compounds and have also been shown to participate in important catalytic and electron-transfer reactions [122,123]. 17-electron (17e) metal-centered radicals are the most common transition-metal radicals and can be photochemically generated from organometallic dimers containing a single metal-metal bond; irradiation of $[\text{CpW}(\text{CO})_3]_2$, $[\text{CpFe}(\text{CO})_2]_2$, and $[\text{Mn}(\text{CO})_5]_2$ at visible or ultraviolet wavelengths produces the 17e radicals $\text{CpW}(\text{CO})_3$, $\text{CpFe}(\text{CO})_2$, and $\text{Mn}(\text{CO})_5$, respectively [122]. Despite intense study of these prototypical dimers over several decades [30,122,124], they continue to yield surprising and new results. As early as 1968, dimers of the type $[\text{CpM}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$) were observed to undergo photochemical disproportionation reactions in the presence of Lewis bases PR_3 to produce the ionic products $\text{CpM}(\text{CO})_3^-$ and $\text{CpM}(\text{CO})_3\text{PR}_3^+$ [157]. The mechanism of this unique reaction was analyzed and evidence was found for the existence of a highly reactive 19-electron (19e) radical, $\text{CpM}(\text{CO})_3\text{PR}_3$ [144,146,147]. These same dimers were also observed to participate in ligand substitution reactions to produce the products $[\text{CpM}(\text{CO})_2\text{PR}_3]_2$ or $[\text{CpM}(\text{CO})_3][\text{CpM}(\text{CO})_2\text{PR}_3]$, and again a 19e intermediate (or transition state) was postulated in these reactions [172].

As discussed in Chapter 3, we recently used time-resolved infrared spectroscopy on the femto- through microsecond time-scales to probe the photochemical reactions of the dimer $[\text{CpW}(\text{CO})_3]_2$ and directly observed the formation and the reactions of the 19e intermediate, $\text{CpW}(\text{CO})_3\text{PR}_3$, for the first time [22-24]. In the Lewis base, $\text{PR}_3 = \text{P}(\text{OMe})_3$, two main reaction pathways for 19e intermediates were found: ligand substitution and ultrafast in-cage disproportionation. The ultrafast disproportionation mechanism is displayed in Figure 4.1. Irradiation of $[\text{CpW}(\text{CO})_3]_2$ (**A**) at visible wavelengths results in metal-metal bond homolysis to form two 17e radicals, $\text{CpW}(\text{CO})_3$ (**B**). The nascent radicals are surrounded by a cage of solvent molecules, represented by brackets in Figure 4.1. Coordination of $\text{P}(\text{OMe})_3$ with **B** forms the 19e

species $\text{CpW(CO)}_3\text{P(OMe)}_3$ (C_1) and electron transfer from C_1 to B can form the disproportionated products $\text{CpW(CO)}_3\text{P(OMe)}_3^+$ (D_1) and CpW(CO)_3^- (E) while the radicals are in close proximity. The amount of ultrafast disproportionation is limited by the escape of the radicals from the solvent cage, preventing electron transfer. A delicate interplay between the formation rate of 19e species and the time-scale for diffusional separation of the radicals (approximately 140 ps for P(OMe)_3 / CH_2Cl_2 solutions) determines the precise yield of disproportionated products on the ultrafast time-scale [23]. In a given solvent, the branching ratio between reactions in- and outside of the initial solvent cage can be controlled via the reactivity of the Lewis base and the Lewis base concentration.

Figure 4.1 Ultrafast photo-induced disproportionation of $[\text{CpW(CO)}_3]_2$ with the Lewis base P(OMe)_3 [23,24]. Brackets represent the solvent cage

Figure 4.2 Ligand substitution with 19e intermediates $\text{CpW(CO)}_3\text{P(OMe)}_3$ from the photolysis of $[\text{CpW(CO)}_3]_2$ with the Lewis base P(OMe)_3 [22]. Relevant time-scales for each step in the reaction are given below the arrows.

In low concentrations of the Lewis base P(OMe)_3 , disproportionation is a minor pathway and 19e intermediates are instead found to undergo ligand substitution on the nanosecond time-scale [22]. See Chapter 5 for greater details. Briefly, as depicted in Figure 4.2, the 19e species C_1 loses a carbonyl to form the 17e species $\text{CpW(CO)}_2\text{P(OMe)}_3$ (F). Species F then dimerizes to

form the ligand substitution product $[\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3]_2$ (**G**) on the microsecond time-scale. Note that the high reactivity of the 19e intermediates prevented direct observation of their reactions in many of the earlier studies on these types of organometallic dimers.

Disproportionation may also occur on time-scales beyond the lifetime of the initial solvent cage. A reaction mechanism for disproportionation that was proposed by Tyler et al. [146,147] is shown in Figure 4.3: electron transfer from **C** to the dimer **A** produces the cationic disproportionated product **D** and a negatively charged dimer $[\text{CpW}(\text{CO})_3]_2^-$; homolysis of this dimer generates the second disproportionated product **E** and an additional 17e radical **B**. Unlike the mechanism depicted in Figure 4.1, disproportionation by Tyler's mechanism is rate-limited by diffusional encounter of the 19e species **C** and the dimer **A**. Accordingly, disproportionation by this mechanism may take place on diffusion-limited time-scales, i.e. nanoseconds to microseconds. Hereafter, this mechanism will be referred to as the "dimer mechanism."

Figure 4.3 Photochemical disproportionation mechanism for $[\text{CpM}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$) in Lewis bases PR_3 ($\text{R} = \text{alkyl, alkoxy, aryl, aryloxy}$) as proposed by Tyler [146,147]

In this paper, we present time-resolved infrared results for the photochemistry of $[\text{CpW}(\text{CO})_3]_2$ with the Lewis base PPh_3 . Unlike $\text{P}(\text{OMe})_3$, we *do* observe significant disproportionation on diffusion-limited time-scales, but we find no evidence for the dimer mechanism (Figure 4.3). Instead, the disproportionation kinetics can be explained by a mechanism similar to Figure 4.1: electron transfer between an encounter-complex of the 19e species **C** and the 17e radical **B**. From here on this mechanism is referred to as the "radical mechanism". We present evidence for a similar (but minor) electron transfer pathway in high

concentrations of the Lewis base P(OMe)_3 and give explanations for the large difference in reactivity between P(OMe)_3 and PPh_3 . We also compare our results to the literature and suggest that the dimer mechanism may be a viable mechanism under certain reaction conditions (e.g. low intensity continuous irradiation) whereas the radical mechanism is operating for the experimental conditions described herein.

This chapter is organized as follows: Section 4.2 provides a brief account of our methods and theoretical approach, Section 4.3 presents the time-resolved results and addresses the possible disproportionation mechanisms. Our conclusions are summarized in Section 4.4.

4.2 Methods

4.2.1 Samples

$[\text{CpW(CO)}_3]_2$, trimethyl phosphite (P(OMe)_3), and triphenylphosphine (PPh_3) were obtained from Sigma-Aldrich Co. and spectroscopic grade CH_2Cl_2 was purchased from EMD Chemicals. All samples were used without further purification. Air sensitive materials were stored and handled under nitrogen atmosphere in a glove-box (Vacuum Atmospheres Company). Air and light-sensitive solutions were continuously purged with argon and rigorously secluded from all ambient light sources.

4.2.2 Data Analysis.

Kinetic data were derived from the spectral data at numerous times after photolysis. The absorbance values within distinct spectral ranges for the various chemical species were averaged at each individual time delay. The ranges for each species were as follows: CpW(CO)_3^- 1750–1800 cm^{-1} , $\text{CpW(CO)}_2\text{P(OMe)}_3$ 1815–1816 cm^{-1} , $\text{CpW(CO)}_3\text{P(OMe)}_3$ 1850–1860 cm^{-1} , $\text{CpW(CO)}_3(\text{P(OMe)}_3)_2^+$ 1980–2000 cm^{-1} , $\text{CpW(CO)}_2\text{P(OMe)}_3^-$ 1700–1730 cm^{-1} . Kinetic traces were then fit to various functions as noted in the text, and in all cases the functions included a floating parameter for time zero and a floating parameter for a constant vertical offset necessary to account for a small nonzero baseline in the experimental data. All reported errors correspond to 95% confidence intervals except where noted.

4.2.3 Theoretical.

Density functional theory (DFT) calculations have been performed to assist in the characterization of the various intermediate species and to facilitate an understanding of the dynamical behavior. Density functionals of the type used in this work have been shown to yield reliable results in calculations for transition-metal complexes [118].

DFT calculations were carried out using the program package Gaussian 03 [116], and the B3LYP hybrid method [117] was used in all calculations. It is composed of Becke's three-parameter exchange-functional [148] and the Lee-Yang-Parr non-local correlation functional [149]. Generic basis sets used consisted of the double-zeta LANL2DZ in conjunction with the relativistic effective core potential (ECP) of Hay and Wadt [119] for tungsten and 6-31G(d) (**I**) or 6-31G+(d) (**II**) basis sets for all other atoms. The Hessian matrices were calculated at the stationary points in order to ensure that true minima on the potential energy hypersurfaces had been found. Harmonic vibrational frequencies, appropriately scaled [120], are used in the spectral analysis of the experimental data. The electronic energies of all the optimized structures are within ca. 10 kcal/mol. For these open-shell complexes, the changes in energy are within a reasonable margin of error for these types of calculations. Thus, we do not use the energetics but rather the vibrational frequencies and molecular geometries for the interpretation of the experimental results.

4.3 Results and discussion

4.3.1 Dynamics in neat CH₂Cl₂

Figure 4.4 Spectral data on the microsecond time scale for 532 nm photolysis of [CpW(CO)₃]₂ (**A**) in neat CH₂Cl₂.

The dynamics of 17-electron (17e) radicals CpW(CO)₃[•] (**B**) were measured in the neat solvent CH₂Cl₂ and are depicted in Figure 4.4. Although chlorine atom abstraction by the radicals may occur in halogenated solvents such as CCl₄, this process occurs only to a limited extent in

CH₂Cl₂—no peaks attributable to CpW(CO)₃Cl, the product from Cl atom abstraction of CH₂Cl₂ by **B**, are observed on the time scale of this experiment [155]. The only dynamics apparent in Figure 4.4 involve dimerization of the radicals **B** to reform the parent dimer **A** in both the *anti* and *gauche* conformations. The *gauche* isomer is formed in a nonequilibrium concentration, causing the rise of the product peak at 2010 cm⁻¹. On a longer time scale, this isomer should isomerize to reform *anti*-**A**.

A simple analysis of the dimerization reaction indicates that the kinetics for **B** should follow the equation:

$$[\mathbf{B}] = \frac{1}{k_6 t + [\mathbf{B}]_0^{-1}}, \quad (4.1)$$

where t is time, k_6 is the rate constant for recombination of the 17-electron (17e) radicals **B** (see eq. 4.6), and $[\mathbf{B}]_0$ is the concentration of the radicals at time $t = 0$. In the absence of an extinction coefficient for the transient radical **B**, we used an estimated extinction coefficient of 9000 M⁻¹cm⁻¹, a typical value for CO absorptions in metal-carbonyl complexes. A fit of the kinetics for **B** at 1995 cm⁻¹ to eq. 4.1 is shown in Figure 4.5 and yields values of $k_6 = (8.5 \pm 0.1) \times 10^9$ M⁻¹s⁻¹ and $[\mathbf{B}]_0 = 0.021 \pm 0.001$ mM. The value for k_6 is consistent with previous studies, which have shown that radicals of this type recombine at slightly below the diffusion-controlled rate [173]. The value for k_6 determined from this experiment in neat CH₂Cl₂ is used in the analysis of the disproportionation kinetics presented below for PPh₃ / CH₂Cl₂ solutions.

Figure 4.5 Kinetic data on the microsecond time scale, averaged over the spectral range 1990–1999 cm⁻¹, for the 17e radical CpW(CO)₃ in neat CH₂Cl₂.

4.3.2 Reactions with PPh₃: Spectral Data.

The time-resolved infrared results for 1.0 mM [CpW(CO)₃]₂ (**A**) with 1.0 M PPh₃ in CH₂Cl₂ after photolysis at 532 nm are presented in Figure 4.6. Negative absorptions, or bleaches, result from the depletion of reactant molecules while positive absorptions correspond to the formation of intermediates and products after photolysis. Peak assignments are based on literature values [23,24,152]. Two bleaches from the *anti* conformation of [CpW(CO)₃]₂ (*anti*-**A**) are observed at 1907 and 1954 cm⁻¹ and two peaks from the 17e radical CpW(CO)₃ (**B**) are observed at 1994 and 1881 cm⁻¹. A portion of the 17e radicals **B** dimerize to reform **A** in both the *anti* and *gauche* conformations:

Formation of *anti*-**A** results in recovery of the bleach at 1954 cm⁻¹ while the bleach at 1907 cm⁻¹ maintains an approximately constant intensity due to spectral overlap with the peak from **B** at 1881 cm⁻¹. The formation of *gauche*-**A**, on the other hand, causes the rise of an absorption at 2010 cm⁻¹ in Figure 4.6. Isomerization of the *gauche* isomer to the more stable *anti* isomer may occur, although the free energy of activation has been estimated at 16.2 ± 0.5 kcal/mol [174]. Isomerization would thus take place on the time-scale of milliseconds to seconds and is not observed in these experiments on the microsecond time-scale.

Figure 4.6 Time-resolved IR spectra in the CO stretching region on the microsecond time-scale for 1.0 M PPh₃ in 1 mM [CpW(CO)₃]₂ (**A**)

The 17e radicals (**B**) that do not dimerize to reform **A** are in equilibrium with 19e species $\text{CpW(CO)}_3\text{PPh}_3$ (**C**₂), which exhibit an absorption at 1855 cm^{-1} . This assignment is based on our previous ultrafast studies on this dimer complex and is in accord with the DFT calculations contained in Table 4.1. The 17e and 19e radicals disproportionate to form the ionic products CpW(CO)_3^- (**E**) and $\text{CpW(CO)}_3\text{PPh}_3^+$ (**D**₂). Peaks from **E** appear at 1768 and 1795 cm^{-1} and a single peak from **D**₂ appears at 2055 cm^{-1} in Figure 4.6. It has been proposed that on the microsecond time-scale, disproportionation might occur via the mechanism depicted in Figure 4.3 (dimer mechanism) and discussed in Section 4.1. The central feature of this mechanism is electron transfer from the 19e species **C** to the dimer **A** to form the products **D** and $[\text{CpW(CO)}_3]_2^-$; however, we find no absorption attributable to $[\text{CpW(CO)}_3]_2^-$ (see Table 4.1 for the calculated frequencies of this species). This finding does not conclusively discard the dimer mechanism (Figure 4.3) since $[\text{CpW(CO)}_3]_2^-$ may be a short-lived intermediate, which never builds-up sufficient concentration to be detected in our experiment.

Table 4.1 Calculated and observed CO vibrational frequencies (in cm^{-1}) of relevant species for the photochemistry of $[\text{CpW}(\text{CO})_3]_2$ with Lewis bases PR_3 ($\text{R} = \text{OMe}, \text{Ph}$).^a

Species	Calculated	Observed
<i>anti</i> - $[\text{CpW}(\text{CO})_3]_2$ (A)	1892 (0.0), 1915 (0.2), 1924 (0.8), 1932 (0.0), 1968 (1.0), 2000 (0.0) ^b	1907, 1954
<i>gauche</i> - $[\text{CpW}(\text{CO})_3]_2$	1902 (0.2), 1909 (0.3), 1937 (0.4), 1944 (0.0), 1970 (0.6), 2014 (0.4) ^b	2010
<i>anti</i> - $[\text{CpW}(\text{CO})_3]_2^-$	1839 (0.1), 1842 (0.0), 1862 (0.0), 1869 (0.8), 1881 (1.9), 1940 (0.0) ^b	not observed
$\text{CpW}(\text{CO})_3^-$ (18e, E)	1785 (0.6), 1786 (0.7), 1880 (0.4) ^c	1768, 1795
$\text{CpW}(\text{CO})_3$ (17e, B)	1906 (0.6), 1907 (0.4), 1987 (0.3) ^c	1881, 1994
$\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3$ (19e, C ₁)	1867 (0.5), 1877 (0.4), 1961 (0.4) ^c	1854, 1967
$\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^+$ (18e, D ₁)	1976 (0.5), 2000 (0.2), 2056 (0.3) ^c	1995, 2064
$\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3$ (17e, F ₁)	1847 (0.6), 1910 (0.3) ^c	1815, 1916
$\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^-$ (18e, I)	1753 (0.6), 1815 (0.4) ^c	1714
$\text{CpW}(\text{CO})_2(\text{P}(\text{OMe})_3)_2^+$ (18e, H)	1913 (0.5), 1972 (0.1) ^c	1990
<i>anti</i> - $[\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3]_2$ (G ₁)	1839 (0.0), 1871 (0.7), 1882 (0.2), 1920 (0.0) ^b	1835, 1868
<i>gauche</i> - $[\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3]_2$ (G ₁)	1847 (0.2), 1862 (0.6), 1875 (0.0), 1928 (0.2) ^b	
$\text{CpW}(\text{CO})_3\text{PPh}_3$ (19e, C ₂)	1844 (0.7), 1864 (0.2), 1947 (0.3) ^c	1855
$\text{CpW}(\text{CO})_3\text{PPh}_3^+$ (18e, D ₂)	1965 (0.5), 1981 (0.2), 2040 (0.3) ^c	2055
$\text{CpW}(\text{CO})_2\text{PPh}_3$ (17e, F ₂)	1830 (0.6), 1901 (0.3) ^c	not observed

^a calculated frequencies are scaled by the factor 0.9614[120]; ^b basis set **I**, ^c basis set **II**; calculated intensities are normalized to the 1968 cm^{-1} mode of *anti*- $[\text{CpW}(\text{CO})_3]_2$; for the first four rows in the table, observed frequencies are given for PPh_3 solutions.

We propose here an alternative disproportionation mechanism (radical mechanism), which we will test against the dimer mechanism: the disproportionated products are directly formed by electron transfer from the 19e species **C** to the 17e radical **B**, similar to Figure 4.1:

Unlike Figure 4.1, however, the radical pair is formed by diffusional encounter of species **B** and **C** rather than by homolysis of the metal-metal bond in **A**. In order to distinguish these two possible disproportionation mechanisms (the dimer and the radical mechanisms), we performed concentration dependent studies. The rate and extent of disproportionation by the dimer mechanism depends on the concentration of dimer **A**, but disproportionation by the radical mechanism should be independent of the dimer concentration. In addition, we varied the initial concentration of the 17e radical **B** by changing the 532 nm laser intensity. As will be shown in our kinetic analysis of the data, the two mechanisms are expected to depend on the concentration of radicals **B** in a different manner. For all the concentration dependent studies, we used a PPh₃ concentration of 85 mM. This low concentration prevented a significant amount of disproportionation from occurring on the picosecond time-scale.

First, data collected with different dimer concentrations lends some insight into the disproportionation mechanism. Data collected at a concentration of 1.5 mM **A** and at a concentration one-third lower, 0.5 mM **A**, are shown in Figure 4.7a and b, respectively. Note that the concentration of **A** for the data presented in Figure 4.7a (1.5 mM) is the same concentration used in the detailed studies by Tyler et al. and discussed in Section 4.1 [146]. The initial radical **B** concentration (at 1 μs) in the experiments with the two concentrations of **A** was kept constant by using a higher laser intensity for the 0.5 mM solution.¹⁰ Qualitative comparison between Figure 4.7a and b reveals no significant difference between the two data sets. This initial result lends support to the radical mechanism, which is expected to be independent of the dimer **A** concentration.

¹⁰ The bleach intensity increased approximately linearly with the laser intensity, indicating that the laser intensity was not so high as to cause two photon absorption.

Figure 4.7 Time-resolved IR spectra in the CO stretching region on the microsecond time-scale for 85 mM PPh_3 in various concentrations of $[\text{CpW}(\text{CO})_3]_2$ (A) and with different laser photolysis fluences. (a) 1.5 mM A and 0.2 mJ, (b) 0.5 mM A and 1.6 mJ, (c) 1.5 mM A and 0.8 mJ.

Additional insight into the mechanism is provided by data collected at the same concentration of dimer **A** (here 1.5 mM) but with different initial concentrations of the 17e radical **B** (Figure 4.7c shows the data for an approximately 2.5 times greater concentration of **B** as compared to Figure 4.7a). For a higher **B** concentration the disproportionation yield is significantly enhanced (as can be seen by the larger relative intensity of the disproportionation peaks (**D**₂, **E**) in Figure 4.7c as compared to Figure 4.7a; note the change in the ordinate scale). As both the dimer and the radical mechanism predict this type of behavior, further conclusions require a detailed kinetic analysis that is given in the following section.

4.3.3 Reactions with PPh₃: Kinetic Analysis.

In the kinetic modeling of the experimental data, we will first make a few simplifying yet physically reasonable assumptions. We assume that the concentrations of the dimer [CpW(CO)₃]₂ (**A**) and the Lewis base PPh₃ remain constant within the time-scale of the experiment. For the data presented in Figure 4.7a, laser photolysis depletes less than 3% of the dimer molecules within the volume of sample irradiated by one laser pulse and depletes less than 5% of the total dimer concentration during the course of the experiment.¹¹ The concentration of PPh₃ is far greater than the dimer concentration and so is negligibly changed by the photochemical reactions. Furthermore, in agreement with the kinetic analysis by Scott et al. [143], the 17e and 19e species are assumed to be in equilibrium with the equilibrium constant K_{eq} :

and the equilibrium lies far on the side of the 17e species ($K_{eq} = 6 \pm 1 \text{ M}^{-1}$) [143].

The two alternative pathways that may yield disproportionation on diffusion-limited time-scales, the radical and the dimer mechanisms, are represented in eqs. 4.4 and 4.5, respectively:

¹¹ This number represents an upper limit based on a 1.0 quantum yield and neglecting any recombination of the 17e radicals. For data presented in Figure 4.7b and c, a greater portion of the dimer molecules within the sample volume may be consumed. This effect is not included in the yield analysis of the experimental data but would only increase the discrepancy between the dimer mechanism and experimental data, thus strengthening the arguments made in the section.

Figure 4.8 (a) Kinetic data for $\text{CpW}(\text{CO})_3^-$ and fits to the kinetic model predicted by the dimer (red line) and radical mechanisms (blue line). Error bars represent one standard deviation. (b) Plot of same data as in (a) but with the ordinate as $1/(\Delta\text{mOD} - A)$, which will yield a straight line for the radical mechanism (see text for details).

Eq. 4.6 describes the dimerization of two 17e radicals to reform the parent dimer **A**:

From eqs. 4.3, 4.5, and 4.6 and the assumptions given above, we can now derive an equation for the concentrations of the disproportionated products **D**₂ and **E** for the *dimer mechanism*:

$$[\mathbf{D}_2] = [\mathbf{E}] = \frac{k_5}{k_6} [\text{PPh}_3] [\mathbf{A}] K_{\text{eq}} \ln(k_6 [\mathbf{B}]_0 t + 1), \quad (4.7)$$

where t is time and $[\mathbf{B}]_0$ is the concentration of the 17e radicals **B** at time $t = 0$. A similar analysis may be performed for the *radical mechanism* using eqs. 4.3, 4.4 and 4.6:

$$[\mathbf{D}_2] = [\mathbf{E}] = \frac{k_4 K_{\text{eq}} [\text{PPh}_3]}{k_4 K_{\text{eq}} [\text{PPh}_3] + k_6} \left(\frac{-1}{(k_4 K_{\text{eq}} [\text{PPh}_3] + k_6)t + [\mathbf{B}]_0^{-1}} + [\mathbf{B}]_0 \right), \quad (4.8)$$

A comparison of eqs. 4.7 and 4.8 shows that the two disproportionation mechanisms are expected to exhibit different kinetic behavior. The dimer mechanism should show logarithmic behavior (eq. 4.7) while the radical mechanism should be consistent with a function of the form $-1/t$ (eq. 4.8). The experimental kinetic data for the anionic disproportionated product **E** from Figure 4.7a is shown in Figure 4.8a and fits to eqs. 4.7 and 4.8 are displayed as the red and blue lines, respectively (see Section 4.3.4 for a more thorough description of the fitting procedure and the fitting parameters for the cationic and anionic disproportionated products (**D**₂, **E**) for all concentrations of **A** and **B**). Even when taking the noise in the data into account, examination of these fits shows that the functional form of eq. 4.8 provides a better fit to the experimental data.

If disproportionation follows the radical mechanism, in a plot of $1/(\Delta\text{mOD} - A)$ versus time t , where A is the long-time limit of the disproportionation concentration (the asymptote in Figure 4.8a), the data will follow a straight line. Such a representation of the data is given in Figure 4.8b together with the best fits from the radical (blue line) and the dimer mechanism (red line). Within experimental noise, the data appear to follow the linear behavior predicted by the radical mechanism. The values of fits to the data presented in Figure 4.8 are given Section 4.3.4. Starting from the analysis of a particular set of **A** and **B** concentrations, we can now predict the yield of disproportionated product that would be expected from each mechanism as the dimer concentration and initial radical concentrations are varied. In Table 4.2 we compare the experimental data for the relative absorption of species **E** at distinctly chosen concentrations of **A** and **B** with the values predicted by the two mechanisms from eqs. 4.7 and 4.8. The data are normalized to data set (a) because this data set is used to establish the best fit parameters. For data set (b), the dimer concentration has been decreased by one-third, and because disproportionation by the dimer mechanism depends on the presence of dimer molecules, this mechanism predicts a sharp decrease in the disproportionation yield. The radical mechanism, on the other hand, predicts a slight increase in the disproportionation yield because there was a slight increase in the initial concentration of the radical **B**. The experimental data are clearly in agreement with the prediction of the radical mechanism since the disproportionation yield marginally increases in comparison to data set (a). For data set (c), the laser photolysis power was significantly increased to augment the initial concentration of the radical **B**. The dimer mechanism predicts a small increase in the disproportionation yield while the radical mechanism predicts a far more dramatic increase. Again, the radical mechanism provides a better prediction of the observed yield.

Table 4.2 Relative yield of disproportionated product observed experimentally and predicted from the kinetic models for the radical and dimer mechanisms for different $[\text{CpW}(\text{CO})_3]_2$ (**A**) concentrations and laser photolysis fluences. Data sets (a), (b), and (c) correspond to the data displayed in Figure 4.7, and changes in yield are normalized to data set (a).

Data set	Experiment	Radical mechanism	dimer mechanism
(a)	1.0	1.0	1.0
(b)	1.1 ± 0.2	1.1	0.3
(c)	2.2 ± 0.2	3.2	1.2

4.3.4 Fits to the kinetic analysis

The kinetic equations for disproportionation by the dimer and radical mechanisms are shown in eqs. 4.7 and 4.8, respectively, and details of the fits of the experimental data to these equations are presented here. For disproportionation by the dimer mechanism, the model uses values of $k_6 = 8.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ as determined in Section 1, $K_{eq} = 6 \text{ M}^{-1}$ [143], $[\text{PPh}_3] = 85 \text{ mM}$, and $[\text{A}] = 1.5 \text{ mM}$ or 0.5 mM depending on the experiment. The floating parameters for the fit are thus k_5 , the rate constant for radical to dimer electron transfer, and $[\text{B}]_0$, the concentration of the radical **B** at time $t = 0$. Note that the long-time limit of this equation is not physically reasonable and occurs because we have assumed a constant concentration of **A**. For short times and limited depletion of **A**, however, this equation is valid. The best fit of this equation to kinetic data for $\text{CpW}(\text{CO})_3^-$ (**E**) at a 1.5 mM concentration of **A** and low **B** concentration is shown as the red line in Figure 4.8a and yields values of $k_5 = (2.5 \pm 0.2) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ and $[\text{B}]_0 = 0.8 \pm 0.2 \text{ mM}$. The best fit parameters for both disproportionated products $\text{CpW}(\text{CO})_3\text{PPh}_3^+$ (**D**₂) and $\text{CpW}(\text{CO})_3^-$ (**E**) at all the concentrations of **A** and **B** used in this study are summarized in Table 4.3.

Table 4.3 Parameters for the kinetic fits of disproportionated products with varying concentrations of the dimer $[\text{CpW}(\text{CO})_3]_2$ (**A**) and the 17e radical $\text{CpW}(\text{CO})_3^\bullet$ (**B**)*

	radical mechanism		dimer mechanism	
	k_4 ($\text{M}^{-1}\text{s}^{-1}$)	$[\text{B}]_0$ (mM)	k_5 ($\text{M}^{-1}\text{s}^{-1}$)	$[\text{B}]_0$ (mM)
(a) 1.5 mM A, low B				
$\text{CpW}(\text{CO})_3\text{PPh}_3^+$ (D ₂)	$(8 \pm 1) \times 10^8$	0.022 ± 0.005	$(1.4 \pm 0.1) \times 10^6$	12 ± 7
$\text{CpW}(\text{CO})_3^-$ (E)	$(2.0 \pm 0.2) \times 10^9$	0.013 ± 0.002	$(2.5 \pm 0.2) \times 10^6$	0.8 ± 0.2
(b) 0.5 mM A, low B				
$\text{CpW}(\text{CO})_3\text{PPh}_3^+$ (D ₂)	$(3.3 \pm 0.3) \times 10^8$	0.021 ± 0.002	$(5.8 \pm 0.4) \times 10^5$	ca. 1645
$\text{CpW}(\text{CO})_3^-$ (E)	$(2.0 \pm 0.2) \times 10^9$	0.016 ± 0.002	$(2.9 \pm 0.1) \times 10^6$	1.2 ± 1.0
(c) 1.5 mM A, high B				
$\text{CpW}(\text{CO})_3\text{PPh}_3^+$ (D ₂)	$(1.9 \pm 0.5) \times 10^8$	0.29 ± 0.07	$(1.0 \pm 0.2) \times 10^6$	ca. 370000
$\text{CpW}(\text{CO})_3^-$ (E)	$(6.7 \pm 1.5) \times 10^8$	0.13 ± 0.04	$(3.6 \pm 0.5) \times 10^6$	ca. 930

*errors represent 95% confidence intervals

For fits of the experimental kinetic data to the model for the radical mechanism, values for k_6 , K_{eq} , and $[\text{PPh}_3]$ were used as given above. The floating parameters for this fit were thus k_4 , the rate constant for radical to radical electron transfer, and $[\text{B}]_0$. The best fit of this equation to kinetic data for $\text{CpW}(\text{CO})_3^-$ (**E**) at a 1.5 mM concentration of **A** and low **B** concentration is shown as the blue line in Figure 4.8 and yields values of $k_4 = (2.0 \pm 0.2) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $[\text{B}]_0 = 0.013 \pm 0.002$. Unlike the fits for the dimer mechanism, the value of $[\text{B}]_0$ determined for the radical mechanism falls within the expected range based upon the experimental conditions. The best fit parameters for both disproportionated products $\text{CpW}(\text{CO})_3\text{PPh}_3^+$ (**D**₂) and $\text{CpW}(\text{CO})_3^-$ (**E**) at all the concentrations of **A** and **B** used in this study are summarized in Table 4.3.

4.3.5 Disproportionation mechanism with PPh_3

Our experimental results and the kinetic modeling for the photochemical disproportionation of $[\text{CpW}(\text{CO})_3]_2$ (**A**) with PPh_3 provide the following evidence for the reaction mechanism. First, we find no spectroscopic evidence for $[\text{CpW}(\text{CO})_3]_2^-$, a key intermediate in the dimer disproportionation mechanism. Second, the kinetics of disproportionation are more consistent with the kinetic model derived for the radical mechanism than for the dimer mechanism. Third, changes in the yield of disproportionated products with changing concentrations of dimer **A** and radical **B** show poor agreement with the dimer mechanism but are consistent with the radical mechanism - specifically, when the dimer concentration was reduced by one-third, the disproportionation yield increased, the opposite result predicted from the dimer

mechanism but the correct result according to the radical mechanism. Based on these findings, we conclude that on diffusion-limited time-scales disproportionation in PPh_3 is more appropriately described with the radical mechanism. In Section 4.3.8, we provide alternative explanations for evidence in the literature in favor of the dimer mechanism.

Figure 4.9 Photochemical disproportionation mechanism for $[\text{CpW}(\text{CO})_3]_2$ with the Lewis base PPh_3 . Brackets represent the solvent cage

The complete mechanism for photochemical disproportionation of $[\text{CpW}(\text{CO})_3]_2$ (A) with the Lewis base PPh_3 on ultrafast and diffusion-limited time-scales is summarized in Figure 4.9. Photolysis of A at visible wavelengths produces two 17e radicals B surrounded by a cage of solvent molecules, represented by brackets in Figure 4.9. These radicals may follow two different pathways; coordination of PPh_3 with one 17e radical may form a 19e radical C_2 and cause disproportionation inside the initial solvent cage within hundreds of picoseconds after photoexcitation. Alternatively, the 17e radicals B may escape the solvent cage. A portion of the 17e radicals B which escape the initial solvent cage will recombine at a diffusion-limited rate to reform the dimer A (not shown in Figure 4.9). The remaining radicals, as depicted in Figure 4.9, may react with PPh_3 to form a 19e radical C_2 . These 19e radicals may then encounter remaining 17e radicals at a diffusion controlled rate and form an encounter complex analogous to the solvent caged complex directly after photolysis. The 17e and 19e radicals in the encounter complex can then disproportionate to form the final products D_2 and E.

4.3.6 Reactions with $\text{P}(\text{OMe})_3$

The photochemistry of $[\text{CpW}(\text{CO})_3]_2$ (A) with a relatively low concentration of Lewis

base P(OMe)₃ (85 mM in CH₂Cl₂) is presented in Chapter 5. As discussed in the Introduction, we directly observed spontaneous CO loss from the 19e species CpW(CO)₃P(OMe)₃ (**C**₁) to form the 17e species CpW(CO)₂P(OMe)₃ (**F**₁) (refer to Figure 4.2 and Chapter 5). Species **F**₁ subsequently dimerizes to form the ligand substitution product [CpW(CO)₂P(OMe)₃]₂ (**G**). Here, we present results at a higher concentration (1 M) of the Lewis base P(OMe)₃. While ligand substitution is still the primary reaction at this higher concentration, we also find evidence for a new radical-to-radical electron transfer reaction.

Nano- and microsecond time-resolved results for a 1 M concentration of P(OMe)₃ in CH₂Cl₂ with 1.5 mM **A** are presented in Figure 4.10. Similar to Figure 4.6, peaks from the *anti* isomer of **A** appear at 1901 and 1955 cm⁻¹, and peaks from the 17e radical CpW(CO)₃ (**B**) appear at 1880 and 1994 cm⁻¹. Two peaks from the 19e species CpW(CO)₃P(OMe)₃ (**C**₁) are apparent at 1854 cm⁻¹ and 1967 cm⁻¹ [23,24]. The 19e species **C**₁ loses a carbonyl on the nanosecond time-scale to form the 17e species **F**₁, with peaks at 1815 and 1916 cm⁻¹ (see Chapter 5) [22,175]. The net reaction from the 17e **B** to 17e **F**₁ is an associative ligand substitution, a reaction commonly observed with organometallic radicals [172,176]. The spontaneous loss of a carbonyl from the 19e complex is also consistent with the reactivity observed after electrochemical reduction of similar types of complexes [141,177,178]. Kinetics for this process are depicted in Figure 4.11a and exhibit single exponential behavior according to the following equation:

$$[\mathbf{C}_1] = [\mathbf{C}_1]_0 e^{\frac{-k_{\text{diss}}}{1+(K_{\text{eff}}[\text{P(OMe)}_3])^{-1}} t}, \quad (4.9)$$

where $[\mathbf{C}_1]_0$ is the initial concentration of **C**₁, k_{diss} is the rate constant for CO dissociation from **C**₁, K_{eff} is the effective **B**/**C**₁ equilibrium constant, $[\text{P(OMe)}_3]$ is the Lewis base concentration, and t is time. The time constant from a monoexponential fit to the kinetics of **C**₁ (see Figure 4.11a) gives $\tau = 81 \pm 8$ ns. In agreement with eq. 4.9, we find this time to be shorter compared to an 85 mM P(OMe)₃ concentration ($\tau = 280 \pm 9$ ns) [22]. As expected, the rise of **F**₁ is directly correlated with the decay of **C**₁ and gives a time constant of $\tau = 70 \pm 5$ ns.

Figure 4.10 Time-resolved IR spectra in the CO stretching region on the (a) nanosecond and (b) microsecond time-scales for 1 M P(OMe)₃ in 1.5 mM A.

Figure 4.11 Kinetic data for (a) the 19e species $\mathbf{C}_1$ and 17e species $\mathbf{F}_1$ on the nanosecond time-scale and (b) the ionic products $\mathbf{H}$ and $\mathbf{I}$ on the microsecond time-scale. Lines represent monoexponential fits to the data (see text) and data for $\mathbf{H}$ is scaled by a factor of four for clarity.

On the microsecond time-scale, peaks from the ligand substitution product $\mathbf{G}$, resulting from dimerization of the 17e species $\mathbf{F}_1$, appear at 1835 and 1868 cm^{-1} . To our surprise, we also observed two additional peaks at 1990 and 1714 cm^{-1} , labeled $\mathbf{H}$ and $\mathbf{I}$ in Figure 4.10b, respectively. Kinetics for these peaks are displayed in Figure 4.11b and monoexponential fits to these kinetic traces yield rise times of $43 \pm 7\text{ }\mu\text{s}$ and $45 \pm 5\text{ }\mu\text{s}$ for $\mathbf{H}$ and $\mathbf{I}$, respectively. We propose that these peaks arise from the ionic products $\text{CpW(CO)}_2\text{(P(OMe)}_3)_2^+$ ($\mathbf{H}$) and $\text{CpW(CO)}_2\text{P(OMe)}_3^-$ ($\mathbf{I}$). DFT calculations for the harmonic frequencies of these species are contained in Table 4.1. The calculations predict a shift in CO stretching frequency from the 17e

radical $\text{CpW(CO)}_2\text{P(OMe)}_3$ (**F**₁) to the new ionic product $\text{CpW(CO)}_2\text{P(OMe)}_3^-$ (**I**) of 94 cm^{-1} , which is in good agreement with the experimental shift of 101 cm^{-1} . Similarly, a shift from the disproportionated product $\text{CpW(CO)}_3\text{P(OMe)}_3^+$ (**D**₁) to the new ionic product $\text{CpW(CO)}_2(\text{P(OMe)}_3)_2^+$ (**H**) of 84 cm^{-1} is predicted, in reasonable agreement with the experimental shift of 74 cm^{-1} .

The simplest explanation for the formation of **H** and **I** is electron transfer between two 17e radicals $\text{CpW(CO)}_2\text{P(OMe)}_3$ (**F**₁) with concomitant coordination of a second Lewis base to the electron donor, as shown in eq. 4.10:

Although it is conceivable for electron transfer between the radicals to occur without coordination of the Lewis base, this reaction would produce the 16-electron (16e) cation $\text{CpW(CO)}_2\text{P(OMe)}_3^+$, which is coordinatively unsaturated and likely subject to back electron transfer, reproducing the 17e radicals. In addition, we have found no spectroscopic evidence for the formation of a 16e cation. Thus, it is more probable that photoproducts **H** and **I** are formed by concerted electron transfer and coordination of P(OMe)_3 . This trimolecular process should only produce an appreciable yield in high concentrations of P(OMe)_3 , which explains the absence of these products at a lower 85 mM concentration [22]. This result emphasizes the importance of radical-to-radical electron transfer in the formation of ionic products with $[\text{CpW(CO)}_3]_2$. Note that the formation of $\text{CpW(CO)}_2\text{P(OMe)}_3^-$ (**I**) cannot be explained by electron transfer from the 19e species **C**₁ to the dimer **A** because this reaction would produce CpW(CO)_3^- (**E**) rather than **I**.

4.3.7 Comparison of Lewis base reactivity

The time-resolved infrared results presented herein indicate that the formation of ionic products in the photochemistry of $[\text{CpW(CO)}_3]_2$ (**A**) with Lewis bases results from electron transfer between radical species. The results also show that on diffusion-limited time-scales, ligand substitution is the primary reaction channel for the 19e species $\text{CpW(CO)}_3\text{PR}_3$ when $\text{R} = \text{OMe}$ but disproportionation is the primary reaction when $\text{R} = \text{Ph}$. A natural question arises: what causes the difference in reactivity between these two Lewis bases?

Figure 4.12 DFT optimized structures for the 19e species (**C**) and ligand substitution 17e species (**F**) with the Lewis bases P(OMe)_3 and PPh_3 . Hydrogen atoms are omitted.

At first glance, CO loss from the sterically crowded 19e species $\text{CpW(CO)}_3\text{PPh}_3$ (C_2) would appear to be a favorable process in comparison to CO loss from the less sterically crowded 19e species $\text{CpW(CO)}_3\text{P(OMe)}_3$ (C_1), yet this is not the result observed experimentally. Cone-angle is the generally accepted size of a coordinating ligand, and the Lewis base PPh_3 possesses a cone angle of 145° while P(OMe)_3 is dramatically smaller at only 107° [167]. Thus, the 19e species with $\text{R} = \text{Ph}$ would be expected to experience far greater steric strain than the $\text{R} = \text{OMe}$ counterpart.

The DFT optimized structures of the 19e species (C) as well as the CO loss 17e species (F) for both $\text{R} = \text{OMe}$ and $\text{R} = \text{Ph}$ are illustrated in Figure 4.12. Perhaps the most striking result is that upon CO loss the W–P bond distance decreases by $0.23 \text{ \AA}$ for $\text{R} = \text{OMe}$ while the bond distance decreases by only $0.03 \text{ \AA}$ for $\text{R} = \text{Ph}$. Qualitatively, the driving force for CO loss with $\text{R} = \text{OMe}$ appears to be a stronger W–P bond while this driving force does not exist for $\text{R} = \text{Ph}$. In addition, the 17e CO-loss radical with the less sterically demanding Lewis base P(OMe)_3 achieves a W–P bond distance $0.09 \text{ \AA}$ shorter than with the more sterically hindered PPh_3 counterpart. This result further supports that CO loss is more favorable with the smaller P(OMe)_3 Lewis base.

A comparison of the 19e structures for both $\text{R} = \text{OMe}$ and $\text{R} = \text{Ph}$ in Figure 4.12a and c shows that the sterically encumbered $\text{R} = \text{Ph}$ system achieves, surprisingly, a W–P bond distance $0.11 \text{ \AA}$ shorter than the $\text{R} = \text{OMe}$ analog. In addition, the C–W–C bond angle for opposite CO groups is approximately 45° larger with $\text{R} = \text{Ph}$. Based on these calculations alone, it is difficult to determine the reason for these differences in molecular structure. To provide additional insight, we performed calculations on analogous 19e species with $\text{R} = \text{Me}$ and $\text{R} = \text{Bu}$ ($\text{Me} = \text{CH}_3$; $\text{Bu} = (\text{CH}_3)_3\text{CH}_4$), and the structures are shown in Figure 4.13. The Lewis bases PMe_3 and PBu_3 have nearly identical electronic properties but are of extremely different sizes; any differences in structure between the two 19e species are the result of steric effects. The W–P bond distance with $\text{R} = \text{Bu}$ is $0.21 \text{ \AA}$ shorter than with $\text{R} = \text{Me}$, and the C–W–C bond angle of opposite CO groups is 44° larger than with $\text{R} = \text{Me}$. These phosphines thus reproduce the same trend as observed with $\text{R} = \text{OMe}$ and Ph ; the bulkier Lewis base distorts the structure of the CO groups, and apparently, this steric effect permits a shorter W–P bond distance in the 19e species. The similarity of the Me/Bu structures with OMe/Ph structures suggest that the differences observed between $\text{R} = \text{OMe}$ and $\text{R} = \text{Ph}$ are attributable to steric effects.

Figure 4.13 DFT optimized structures for 19e species with the Lewis bases PMe_3 and $\text{P}^\bullet\text{Bu}_3$. Hydrogen atoms on the Lewis bases are omitted for clarity.

4.3.8 Comparison to mechanistic conclusions from previous studies

The dimer mechanism for disproportionation is often cited in the literature, yet the time-resolved infrared measurements presented in this paper provide no evidence in support of the dimer mechanism when the reaction is initiated by intense pulsed laser irradiation. Instead, disproportionation appears to proceed by the radical mechanism: electron transfer between the 19e and 17e radicals. When Tyler and co-workers originally proposed the dimer mechanism more than twenty years ago [146,147], the novel aspect of the mechanism was the possibility of a 19e radical which serves as a strong reductant and initiates electron transfer; this aspect has clearly been proven correct. We have demonstrated, however, that the 17e radical rather than the dimer appears to be the electron acceptor for the reaction conditions present in our experiments. The idea that disproportionation proceeds by a mechanism involving electron transfer from a radical to the parent dimer has been well addressed in the literature and originated from Brown and co-workers studies on Co and Mn carbonyl dimers [179-182]. There is considerable evidence for this type of mechanism; thus, we suggest that electron transfer from the 19e species to the parent dimer is a viable though less favorable reaction pathway in comparison to electron transfer from the 19e species to 17e radical. In cases where 17e radicals are in extremely low concentrations or are rendered poor electron acceptors (e.g. due to substitution of CO for a more electron donating ligand), electron transfer from the 19e species to the parent dimer is the more likely reaction pathway. In the following section, we discuss the experimental evidence for the dimer mechanism and the conditions which may favor this mechanism.

The dimer mechanism as shown in Figure 4.3 produces a new 17e radical **B** for every radical consumed in the disproportionation reaction; thus, disproportionation according to this mechanism is a self-sustaining chain process which continues until termination by radical-radical recombination (eq. 4.6). In contrast, the radical mechanism we propose does not predict a chain mechanism because no additional radicals are generated by the disproportionation reaction. Tyler and co-workers advanced two main arguments to support disproportionation by electron transfer to the dimer. Note that Tyler's papers mainly address the photochemistry of $[\text{CpMo}(\text{CO})_3]_2$ rather than the W analog studied here, but, as stated in their paper [146], they performed experiments on the W analog which led them to believe that in all cases the reactivity of the two dimers is the same.

First, in order to show that the anionic dimer $[\text{MeCpMo}(\text{CO})_3]_2^-$ is a key intermediate which begins the radical chain mechanism (MeCp rather than Cp was used in their studies for solubility purposes), Tyler and co-workers directly produced this species by sodium metal

reduction of the dimer $[\text{MeCpMo}(\text{CO})_3]_2$ in the presence of the Lewis base $\text{PPh}_2(\text{CH}_3)$ and observed significant formation of the disproportionated product $(\text{MeCp})\text{Mo}(\text{CO})_3^-$ [146]. In the absence of Lewis base, they reported only small amounts of $(\text{MeCp})\text{Mo}(\text{CO})_3^-$. While this experiment does indicate that the anionic dimer would decompose to an anion and radical, the results may also be explained in light of our new results. Decomposition of the anionic dimer produces the 17e radical **B** in addition to the anion; a portion of the chemically generated 17e radicals will coordinate with the Lewis base $\text{PPh}_2(\text{CH}_3)$ to form 19e radicals. These 17e and 19e radicals may then disproportionate according to the radical mechanism. The radical mechanism does not, however, explain the quantum yields observed in these experiments, as discussed below.

The second major evidence for the dimer mechanism is a quantum yield greater than one for the disproportionation reactions of $[(\text{MeCp})\text{Mo}(\text{CO})_3]_2$ with a variety of phosphine and phosphite Lewis bases [146]. A quantum yield greater than one is a clear indication of a chain process and supports the dimer mechanism. Specifically, quantum yields greater than one were reported for PPh_2CH_3 , $\text{P}(\text{OMe})_3$, and the bidentate ligand bis(1,2-diphenylphosphino)ethane (dppe). It is important to point out that these earlier photochemical studies were performed under continuous photolysis conditions which may change the reaction conditions in two important ways in comparison to the time-resolved experiments. First, continuous photolysis provides a lower power and light intensity compared to pulsed laser excitation. The relatively intense laser light may produce a high concentration of radicals which heavily favors radical-to-radical electron transfer and radical-radical termination. In this scenario, the dimer mechanism may occur at the low radical concentrations produced by continuous photolysis but be shut down at the higher concentrations produced by laser excitation. This scenario is also supported by previous studies of Tyler and co-workers which showed that an increase in light intensity leads to a decrease in disproportionation quantum yields [142], suggesting that radical-radical termination reactions prevail at higher light intensities. Note that a radical concentration sufficiently low to disfavor radical-radical chemistry would likely be undetectable (less than ~ 0.002 mM) given the signal-to-noise ratio in time-resolved IR experiments.

The second important difference between continuous and pulsed laser excitation is the possibility that an intermediate could absorb another photon. Our time-resolved infrared experiments allow only a single photon absorption since this one photochemical event defines time zero for the experiment. In contrast, a continuous photolysis experiment may allow the 19e species $\text{CpW}(\text{CO})_3(\text{PPh}_2\text{CH}_3)$ to absorb a photon and quickly lose a carbonyl to form the 17e

species $\text{CpW(CO)}_2(\text{PPh}_2\text{CH}_3)$ [22].¹² Such a photochemical reaction will quickly deplete the solution of 17e radicals CpW(CO)_3 and prevent disproportionation by the radical mechanism. The remaining radical species in solution, most likely both $\text{CpW(CO)}_2(\text{PPh}_2\text{CH}_3)-(\text{PPh}_2\text{CH}_3)$ and $\text{CpW(CO)}_3(\text{PPh}_2\text{CH}_3)$, may undergo electron transfer to the dimer to produce disproportionated products. The rate for electron transfer to the dimer is in all likelihood far slower than electron transfer to the 17e radical CpW(CO)_3 , but this slower process will occur when the CpW(CO)_3 radicals are quickly eliminated or reduced to a low concentration given the reaction conditions. Similar arguments may be made for the Lewis bases P(OMe)_3 and dppe.

4.4 Summary and conclusions

We have studied the photo-induced disproportionation reactions of $[\text{CpW(CO)}_3]_2$ with the Lewis bases P(OMe)_3 and PPh_3 on diffusion-limited time-scales using time-resolved infrared spectroscopy. Intense pulsed laser irradiation of $[\text{CpW(CO)}_3]_2$ homolytically cleaves the metal-metal bond to produce two 17e radicals CpW(CO)_3 , and coordination of Lewis bases PR_3 to these radicals forms the 19e species $\text{CpW(CO)}_3\text{PR}_3$. A detailed analysis of the experimental data indicates that the subsequent formation of ionic products such as $\text{CpW(CO)}_3\text{PR}_3^+$ and CpW(CO)_3^- proceeds by electron transfer from the 19e radicals to 17e radicals. This result is contrary to the currently accepted dimer mechanism for disproportionation which predicts electron transfer from the 19e radical to the parent dimer (Figure 4.3). Disproportionation by the dimer mechanism likely occurs only when the 17e radicals are in extremely low concentration and thus not available to serve as the electron acceptor. This condition may arise in continuous photolysis experiments at low light intensities or in cases in which the 17e radicals are nearly all converted to 19e species.

The results presented in this paper offer the first evidence that radical-to-radical electron transfer is an important process on diffusion-limited time-scales for the photochemistry of organometallic dimers containing a single metal-metal bond. We believe these results are not only applicable to the dimers $[\text{CpM(CO)}_3]_2$ ($\text{M} = \text{Mo}, \text{W}$), but also to the dimers $[\text{CpM(CO)}_2]_2$ ($\text{M} = \text{Fe}, \text{Ru}$), $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}, \text{Re}$), and $\text{M}_2(\text{CO})_8$ ($\text{M} = \text{Co}, \text{Rh}$) which have been observed to form similar ionic products in the presence of Lewis bases.

¹² Typically, photon energies in the visible region would not be sufficient to induce carbonyl loss in organometallic compounds; however, in the case of 19e species, our results with P(OMe)_3 indicate the W-CO bonds are significantly weakened so CO loss from excitation in the visible region is reasonable.

5 Photochemical ligand substitution reactions of 17-electron, metal-centered radicals

The following chapter is reproduced in part from Cahoon, *et al. J. Am. Chem. Soc.* 2006, 128, 3152-3153 [22] and from a manuscript submitted to *Organometallics* for publication [25].

5.1 Introduction

One of the fundamental concepts in organometallic chemistry is the 18-electron (18e) rule, which predicts the greatest stability for compounds with an 18e count on the transition-metal atom. Although the majority of organometallic chemistry can be understood in terms of 18e or even-electron complexes, there are many of chemical transformations that proceed through less well understood odd-electron intermediates. For instance, 17-electron (17e) organometallic radicals can be generated by homolysis of the metal-metal single bond in organometallic dimers such as $[\text{CpFe}(\text{CO})_2]_2$, $[\text{CpM}(\text{CO})_3]_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), and $[\text{M}(\text{CO})_5]_2$ ($\text{M} = \text{Re}, \text{Mn}$) [29,30,33,122-124,183]. In the presence of electron-donating ligands such as phosphines, these complexes undergo a variety of photoinduced electron transfer and substitution reactions, yet the exact mechanism for these reactions is not fully understood. In particular, it has been proposed that the 17e radicals will coordinate with a Lewis base PR_3 to form a 19e radical:

The photoinduced reactions of metal-metal dimers has been explained in terms of these 19e intermediates, yet until recently no spectroscopic method had succeeded in directly identifying this type of radical complex.

Complexes with a formal 19e count on the metal atom are not uncommon in organometallic chemistry. For example, the first 19e complex, cobaltocene, was isolated more than fifty years ago [125,126] and a variety of similar complexes have since been identified [127-130]. The descriptor “19-electron” comes with some qualification—the ‘19th’ or unpaired electron is usually localized on a ligand rather than the transition-metal atom [129,130]. These complexes are thus more accurately given the name 18+ δ -electron complexes, where the value of δ reflects the degree of unpaired electron density residing on the metal center. Although cobaltocene is better described as an 18+ δ complex, the 19e intermediates produced from photogenerated 17e radicals are expected to be of a different class, with values of δ close to unity. These “true” 19e complexes are highly reactive and thus extremely short-lived, hindering their characterization by

a standard spectroscopic method [123].

19e radicals have been postulated as intermediates in both the photochemical disproportionation and ligand substitution reactions of organometallic dimers containing a single metal-metal bond [30,147,172,183]. The involvement of 19e intermediates in disproportionation reactions is discussed in detail in Chapters 3 and 4. In this chapter, the importance of these intermediates in ligand substitution reactions is examined. Ligand substitution reactions are ubiquitous in organometallic chemistry as a method of introducing new ligands into metal complexes. These simple reactions can typically be classified in three distinct categories: dissociative, interchange, or associative [184]. In the dissociative mechanism, a ligand is first lost from the metal complex, followed by the coordination of a new ligand to the metal. In the other extreme, the associative mechanism, the new ligand first binds to the metal complex and only then does a second ligand dissociate from the metal. Most ligand exchange reactions do not correspond to one of the two extremes and instead are better described by the interchange mechanism, in which the entering and leaving ligands are simultaneously forming and breaking their bonds to the metal complex. In the following sections, we present direct spectroscopic evidence that the photoinduced ligand exchange reactions of both $[\text{CpW}(\text{CO})_3]_2$ and $[\text{CpFe}(\text{CO})_2]_2$ occur by a purely associative mechanism involving a 19e radical intermediate.

5.2 Materials and methods

5.2.1 Samples

$[\text{CpFe}(\text{CO})_2]_2$, $[\text{CpW}(\text{CO})_3]_2$, and trimethyl phosphite ($\text{P}(\text{OMe})_3$) were obtained from Sigma-Aldrich Co. and spectroscopic grade *n*-hexane and cyclohexane was purchased from EMD Chemicals. All samples were used without further purification. Air sensitive materials were stored and handled under nitrogen atmosphere in a glove-box (Vacuum Atmospheres Company). Air and light-sensitive solutions were held under a positive pressure of argon and rigorously secluded from all ambient light sources.

5.2.2 Data analysis.

Kinetic data were derived from the spectral data at numerous times after photolysis. The absorbance values within distinct spectral ranges for the various chemical species were averaged at each individual time delay. The ranges for species involved in the photochemistry of $[\text{CpFe}(\text{CO})_2]_2$ were as follows: $\text{CpFe}(\text{CO})_2$ (**R₁**) 1930-1942 cm^{-1} , 2006 cm^{-1} (2 M $\text{P}(\text{OMe})_3$ solution), 1935 cm^{-1} (300 mM solution); $\text{CpFe}(\text{CO})_2\text{P}(\text{OMe})_3$ (**R₂**) 1895-1909 cm^{-1} , 1968-1970 cm^{-1} (picosecond data), 1970 cm^{-1} (nanosecond data); $\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3/\text{CpFe}(\text{CO})[\text{P}(\text{OMe})_3]_2$

(**R₃/R₄**) 1890-1915 cm⁻¹; Cp₂Fe₂(CO)₃P(OMe)₃ (**D₂**) 1726-1740 cm⁻¹; [CpFe(CO)P(OMe)₃]₂ (**D₃**) 1708-1726 cm⁻¹; ³Cp₂Fe₂(CO)₃ 1815-1830 cm⁻¹. Spectral ranges for the photochemistry of [CpW(CO)₃]₂ are as follows: CpW(CO)₃ 1865-1875 cm⁻¹; CpW(CO)₃P(OMe)₃ 1850-1860 cm⁻¹, CpW(CO)₂P(OMe)₃ 1815 cm⁻¹; CpW(CO)₃⁻ 1750-1780 cm⁻¹; CpW(CO)₃P(OMe)₃⁺ 2045-2085 cm⁻¹. Time constants for chemical reactions were determined by fitting the kinetics to a sum of exponentials using the Levenberg-Marquardt method. All given errors correspond to a 95 % confidence interval.

5.2.3 DFT methods

Density functional theory (DFT) calculations have been performed to assist in the characterization of the various intermediate species and to facilitate an understanding of the dynamical behavior. Density functionals of the type used in this work have been shown to yield reliable results in calculations for transition-metal complexes [118]. DFT calculations were carried out using the program package Gaussian 03 [185], and the B3LYP hybrid method [117] was used in all calculations. It is composed of Becke's three-parameter exchange-functional [148] and the Lee-Yang-Parr non-local correlation functional [149]. Generic basis sets used consisted of the double-zeta LANL2DZ in conjunction with the relativistic effective core potential (ECP) of Hay and Wadt [119] for tungsten and iron and 6-31G(d) or 6-31G+(d) basis sets for all other atoms. The Hessian matrices were calculated at the stationary points in order to ensure that true minima on the potential energy hypersurfaces had been found. Harmonic vibrational frequencies, appropriately scaled by 0.9614 [120], are used in the spectral analysis of the experimental data.

One-dimensional slices of the potential energy surfaces that correspond to CO loss and P(OMe)₃ coordination for the complexes CpFe(CO)₂P(OMe)₃ and CpFe(CO)P(OMe)₃, respectively, were calculated by performing successive partial geometry optimizations and energy calculations at fixed Fe–CO and Fe–P distances (see Section 5.7.3). This method is qualitatively effective at describing reaction pathways and dynamics of transition-metal compounds in solution [3,10,11,186,187].

5.3 Substitution reactions of CpW(CO)₃

5.3.1 Dynamics in P(OMe)₃ solution

The ultrafast dynamics of CpW(CO)₃[•] (**B**) with three Lewis bases PR₃ (R = OMe, Bu, Ph) are presented in Chapter 3 and provide direct evidence for the formation of 19e radicals CpW(CO)₃PR₃[•] (**C**) on a picosecond time scale [23,24]. As depicted below, irradiation of [CpW(CO)₃]₂ (**A**) at visible wavelengths results in metal-metal bond homolysis and formation of

two 17e radicals **B**. Coordination of a strong Lewis base PR_3 with **B** generates 19e radicals **C** that are in an equilibrium with **B**.

Although some 17e and 19e radicals disproportionate by an in-cage mechanism on a picosecond time scale (see Chapter 3), the majority of the 19e species **C** persist beyond 1 ns. This study resolves the 19e dynamics on longer time-scales.

Figure 5.1 Time-resolved IR spectra in the CO stretching region on a) nanosecond and b) microsecond time scales[188] for 1.5 mM $[\text{CpW(CO)}_3]_2$ and 85 mM P(OMe)_3 in CH_2Cl_2 .

Figure 5.1 shows time-resolved transient difference spectra in the CO stretching region on nanosecond (Figure 5.1a) and microsecond (Figure 5.1b) time scales for 1.5 mM **A** and 85 mM P(OMe)_3 in CH_2Cl_2 . Irradiation at 532 nm with a Nd:YAG laser generated the radical species in equation 5.1, and subsequent reactions were probed with step-scan FTIR spectroscopy. Negative absorptions in Figure 5.1 originate from the bleaching of reactant species while positive

absorptions correspond to products formed after photolysis. Peak assignments are based on literature data [23,24,152] or DFT calculations and are tabulated in Table 5.1.

On the nanosecond time scale, two strong parent bleaches appear at 1901 and 1955 cm^{-1} from the *anti*-isomer of **A**. A weak product absorption from the *gauche*-isomer of **A** is also apparent at 2010 cm^{-1} , indicating that within 25 ns a small portion of the 17e $\text{CpW}(\text{CO})_3^\bullet$ radicals **B** have dimerized to regenerate **A**.¹³ Peaks from **B** appear at 1880 and 1994 cm^{-1} while a single peak from the 19e species **C** is visible at 1855 cm^{-1} . The 17e and 19e species (**B**, **C**) are in quasi-equilibrium ($K_{\text{eff}} \cong 3.4 \text{ M}^{-1}$) and decay concomitantly,¹⁴ with monoexponential fits to **C** (see Figure 5.2) and **B** giving decay times of $277 \pm 18 \text{ ns}$ and $288 \pm 10 \text{ ns}$, respectively. Peaks from the disproportionated products $\text{CpW}(\text{CO})_3^-$ (**G**) and $\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^+$ (**F**) are observed at 1775 and 2065 cm^{-1} and grow in with rise times of 199 ± 36 and $265 \pm 78 \text{ ns}$, respectively. The intensity of these peaks indicate that the disproportionation yield is low and the reaction is a minor pathway (< 20%) at this concentration of $\text{P}(\text{OMe})_3$ (85 mM).

Surprisingly, in addition to the products from disproportionation, two new peaks labeled **D** grow in at 1815 and 1916 cm^{-1} . Kinetic fits to the data yield rise times of $280 \pm 9 \text{ ns}$ (Figure 5.2) and $274 \pm 18 \text{ ns}$, respectively. The correlation of these time constants with the decay of 17e and 19e species in addition to an isosbestic point at 1838 cm^{-1} indicate that species **D** is formed from the 19e species **C**. Based on the kinetics and peak positions, **D** is assigned to the 17e radical $\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^\bullet$. DFT calculations predict a shift in CO stretching frequency from **B** to **D** of 60 and 77 cm^{-1} for the lower and higher frequency modes, respectively, which are in excellent agreement with the experimentally observed shifts of 65 and 78 cm^{-1} . The major reaction of 19e species $\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^\bullet$ (**C**) on the nanosecond time scale is thus found to be spontaneous loss of a carbonyl group to form the 17e species **D**.

Assuming **B** and **C** are in quasi-equilibrium and the only subsequent reaction of these

¹³ note that in the presence of organic halides such as CCl_4 , Cl atom abstraction by **B** may occur; however, spectral data in neat CH_2Cl_2 discussed in Chapter 4 indicate that Cl atom abstraction does not occur on the time scale of the experiment

¹⁴ Since the concentrations of radical species **B** and **C** are not constant, the two species cannot be in dynamic equilibrium. The reaction quotient Q , however, maintains a constant value over the lifetimes of these radical species so that they appear in quasi-equilibrium. Assuming the same oscillator strength for the peaks at 1885 cm^{-1} (**C**) and 1994 cm^{-1} (**B**), an "effective" equilibrium constant can be defined and is found to have a value of $K_{\text{eff}} = 3.4 \pm 0.4 \text{ M}^{-1}$. Further assuming $K_{\text{eff}} \cong K_{\text{eq}}$ and using the thermodynamic relation $\Delta G^\circ = -RT \ln(K_{\text{eq}})$, where ΔG° is the change in standard Gibbs energy, K_{eq} the equilibrium constant, R the ideal gas constant, and T the absolute temperature, the value for K_{eff} gives $\Delta G^\circ = -2.4 \pm 0.3 \text{ kcal/mol}$. Thus the 19e species **C** is estimated to be 2–3 kcal/mol lower in energy than the 17e species **B**, likely due to an increase in bond order of 0.5 between the two species.

radicals involves formation of **D**, the dynamics of **C** (or **B**) should exhibit a monoexponential decay, as shown in Figure 5.2, according to the following kinetic equation:

$$[\mathbf{C}] = [\mathbf{C}]_0 e^{\frac{-k_{\text{diss}}}{1+(K_{\text{eff}}[\text{P(OMe)}_3])^{-1}} t} \quad (5.2)$$

where $[\mathbf{C}]_0$ is the initial concentration of **C**, K_{eff} is the effective **B/C** equilibrium constant, and k_{diss} is the rate constant for CO dissociation from **C**. A time constant of 280 ± 9 ns implies a value of $k_{\text{diss}} = (1.6 \pm 0.3) \times 10^7 \text{ s}^{-1}$. Using simple transition state theory, the rate constant suggests a barrier of 7.6 ± 0.3 kcal/mol for spontaneous loss of CO from the 19e species **C**.¹⁵

Figure 5.2 Kinetic data and monoexponential fits (solid lines) for $\text{CpW(CO)}_3\text{P(OMe)}_3^\bullet$ (**C**) and $\text{CpW(CO)}_2\text{P(OMe)}_3^\bullet$ (**D**) on the nanosecond time scale. Kinetics for **D** are scaled by 0.3 for clarity.

¹⁵ Assuming simple transition state theory, $k_{\text{diss}} = (k_B T/h) \exp(-\Delta G^\ddagger/k_B T)$, where k_B is the Boltzmann constant, h Planck's constant, T ambient temperature, and $\Delta G^\ddagger$ the free energy of activation.

Table 5.1 Observed and DFT calculated frequencies of relevant species in the nanosecond / microsecond photochemistry of $[\text{CpW}(\text{CO})_3]_2$ with the Lewis base $\text{P}(\text{OMe})_3$

species	calculated*	observed
anti- $[\text{CpW}(\text{CO})_3]_2$ (A)	1892 (0.0), 1915 (0.2), 1924 (0.8), 1932 (0.0), 1968 (1.0), 2000 (0.0) ^a	1901 (s), 1955(s)
gauche- $[\text{CpW}(\text{CO})_3]_2$ (A)	1902 (0.2), 1909 (0.3), 1937 (0.4), 1944 (0.0), 1970 (0.6), 2014 (0.4) ^a	2010 (w)
$\text{CpW}(\text{CO})_3^\bullet$ (17e, B)	1906 (0.6), 1907 (0.4), 1987 (0.3) ^b	1880 (s), 1994 (s)
$\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^\bullet$ (19e, C)	1867 (0.5), 1878 (0.4), 1961 (0.4) ^b	1855 (m)
$\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^\bullet$ (17e, D)	1847 (0.6), 1910 (0.3) ^b	1815 (s), 1916 (m)
anti- $[\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3]_2$ (E)	1839 (0.0), 1871 (0.7), 1882 (0.2), 1920 (0.0) ^a	1835 (m), 1868 (m)
gauche- $[\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3]_2$ (E)	1847 (0.2), 1862 (0.6), 1875 (0.0), 1929 (0.2) ^a	
$\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^+$ (18e, F)	1977 (0.5), 2000 (0.2), 2057 (0.3) ^b	2065 (w)
$\text{CpW}(\text{CO})_3^-$ (18e, G)	1785 (0.6), 1786 (0.7), 1880 (0.4) ^b	1775 (w)
$\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^-$ (18e)	1753 (0.6), 1815 (0.4) ^b	1715 (w)
$\text{CpW}(\text{CO})_3\text{Cl}$ (18e)	1966 (0.3), 1985 (0.5), 2046 (0.2) ^a	not observed
anti- $[\text{CpW}(\text{CO})_3]_2^-$	1839 (0.1), 1842 (0.0), 1862 (0.0), 1869 (0.8), 1881 (1.9), 1940 (0.0) ^a	not observed

*calculated frequencies are scaled by the factor 0.9614[120]; ^a basis set 6-31g(d), ^b basis set 6-31+g(d); relative intensities are given in parentheses (w = weak, m = medium, s = strong; calculated intensities are normalized with respect to the 1968 cm^{-1} mode of *anti*- $[\text{CpW}(\text{CO})_3]_2$).

This result emphasizes the difference between even and odd-electron species; dissociation of a carbonyl from even-electron transition metal complexes typically requires ca. 40 kcal/mol of energy [189], yet the process appears to be thermodynamically favorable in the case of this 19e species. The lability of the metal-CO bond in **C** most likely arises from the population of a metal-to-ligand anti-bonding orbital by the “19th” electron, which weakens the metal-CO bonds [124]. Numerous studies have shown that the ligand substitution reactions of 17e radicals such as $\text{CpM}(\text{CO})_3^\bullet$ ($\text{M} = \text{Cr}, \text{W}$), $\text{CpFe}(\text{CO})_2^\bullet$, $\text{M}(\text{CO})_5^\bullet$ ($\text{M} = \text{Mn}, \text{Re}$), or $\text{V}(\text{CO})_6^\bullet$ proceed by an associative mechanism [122,172,176,183], but this study is the first evidence that a 19e species is an intermediate rather than a transition state in the ligand substitution reaction [190]. In contrast to this observation, nanosecond time resolved studies on the similar dimer $[\text{CpFe}(\text{CO})_2]_2$ monitored the ligand substitution of $\text{CpFe}(\text{CO})_2^\bullet$ with $\text{P}(\text{OMe})_3$ but found no evidence for a 19e intermediate [176]. The intermediates were likely present but too low in concentration to be detected, and the reactions of the iron radical are discussed in detail in Section 5.4.

On the microsecond time scale (see Figure 5.1b), the 17e radical **D** decays while new absorptions appear at 1835 and 1868 cm^{-1} which are assigned to the ligand substitution dimer $[\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3]_2$ (**E**) based on DFT calculations and literature values for the Mo containing analog of **E** [158]. The decay of **D** and the rise of **E** are correlated, as evident by the isosbestic point at 1831 cm^{-1} in Figure 5.1b; thus, the only reaction on the microsecond time scale is the dimerization of **D** to form **E**.

In summary, the primary reaction of 19e intermediates (**C**) on diffusion-limited time scales is the spontaneous loss of CO to form ligand substitution products:

This type of reactivity is likely to be typical for 17e/19e radicals in Lewis bases, and experiments on the similar dimer $[\text{CpFe}(\text{CO})_2]_2$ are discussed in Section 5.4.

5.3.2 Disproportionation side-reactions of $[\text{CpW}(\text{CO})_3]_2$

Disproportionation of $[\text{CpW}(\text{CO})_3]_2$ (**A**) in the presence of Lewis bases PR_3 forms the products $\text{CpW}(\text{CO})_3\text{PR}_3^+$ (**F**) and $\text{CpW}(\text{CO})_3^-$ (**G**), which are observed in low yield in Figure 5.1. The dynamics leading to the formation of these species are discussed in detail in Chapters 3 and 4. We also observe one additional peak at 1715 cm^{-1} , labeled * in Figure 5.1b. This peak is tentatively assigned to $\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^-$. DFT calculations (see Table 5.1) predict a shift in

CO stretching frequency from $\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^\bullet$ (**D**) to $\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^-$ of 94 cm^{-1} , which is in excellent agreement with the experimentally observed shift of 100 cm^{-1} . Electron transfer from the 19e species $\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^\bullet$ (**C**) to **D** would form this new species as well as the cationic disproportionated product $\text{CpW}(\text{CO})_3\text{P}(\text{OMe})_3^+$ (**F**). Although no change in the peak for **F** is observable on the microsecond time scale, DFT calculations indicate that this peak possesses half the oscillator strength of the peak from $\text{CpW}(\text{CO})_2\text{P}(\text{OMe})_3^-$, so no change in intensity would likely be observable within experimental noise.

5.4 Substitution reactions of $\text{CpFe}(\text{CO})_2$

5.4.1 Introduction

Although the study described in Section 5.3 proved the importance of 19e intermediates for understanding the reactivity of tungsten metal-centered radicals, the applicability of the results for other transition-metal atoms was still in question. Notably, the photoinduced reactions of $[\text{CpFe}(\text{CO})_2]_2$ in the presence of the phosphite $\text{P}(\text{OMe})_3$ were investigated with nanosecond time-resolved IR spectroscopy by Dixon and co-workers, and under the experimental conditions they used, the data provided no evidence for a 19-electron intermediate [139,176]. In the study described herein, we present a comprehensive study of the photochemistry of the iron complex in phosphite solution from the picosecond through the microsecond time-scales. We present direct evidence for the involvement of two different 19e intermediates in the associative ligand substitution reaction of the $[\text{CpFe}(\text{CO})_2]_2$ complex.

In this study, the $\text{CpFe}(\text{CO})_2$ radicals were generated by visible irradiation (400 and 532 nm) of the dimer $[\text{CpFe}(\text{CO})_2]_2$, and the final product was the disubstituted dimer, $[\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3]_2$. This final product was formed by dimerization of the monocarbonyl 17e radicals $\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3$. Although irradiation primarily results in homolysis of the Fe–Fe bond, for short wavelength excitation it also causes photodissociation of a CO ligand from the complex [29]. We focus on the reactions of the metal-centered radicals. The reactions of CO-loss products are briefly discussed in Section 5.5.2.

In this study, we provide conclusive evidence that the ligand exchange reaction of photogenerated 17e radicals $\text{CpFe}(\text{CO})_2$ proceeds through a purely associative mechanism involving the 19e intermediate $\text{CpFe}(\text{CO})_2\text{P}(\text{OMe})_3$:

The net reaction is the exchange of a CO for P(OMe)₃ in the 17e complex CpFe(CO)₂, forming the new monocarbonyl 17e complex CpFe(CO)P(OMe)₃. This reactivity is identical to the results reported in Section 5.3 for the tungsten analogs of these complexes. Surprisingly however, the 17e complex CpFe(CO)P(OMe)₃ is not the final radical formed during the reaction, and we observe a second 19e intermediate CpFe(CO)[P(OMe)₃]₂, which forms by coordination of a second phosphite to the 17e radical. The results show that iron-centered radicals easily undergo ligand addition and dissociation reactions which change the formal electron count on the metal between 17 and 19 electrons. Together with the previously reported results for tungsten complexes, the experiments suggest that 19e intermediates and associative substitution mechanisms are common for metal-centered radicals.

This Section is organized as follows. Materials and methods are described in Section 5.2. The picosecond experimental data is presented in Section 5.5 and the nanosecond/microsecond data in Section 5.6. Section 5.7 presents an analysis of the experimental data in light of DFT calculations to build a coherent picture of the ligand substitution dynamics. Our conclusions are summarized in Section 5.8 and the full photochemical mechanism for [CpFe(CO)₂]₂ in P(OMe)₃/*n*-hexane solution is presented in Figure 5.13 of Section 5.8.

5.5 Picosecond experimental results

5.5.1 Dynamics of iron-centered radicals

Figure 5.3a displays spectra collected on the picosecond time-scale for [CpFe(CO)₂]₂ in *n*-hexane solution after photoexcitation at 400 nm. Picosecond data for this complex in hexane solution has been reported previously and our experimental results are in accord with those reported earlier [191-193]. Peaks from the 17-electron radical CpFe(CO)₂, labeled **R**₁, appear at 1935 and 2007 cm⁻¹. At early time delays, the peaks are broad and red-shifted as a result of vibrational energy imparted by excess energy of the 400 nm photon. The radicals cool within tens of picoseconds after photoexcitation; as a result, nearly all the peaks discussed in this section exhibit either a rise or decay on a time-scale of ca. 10 ps. In Figure 5.3a, the radicals **R**₁ do not exhibit significant dynamics after ca. 50 ps. The positive-going peaks that are not assigned to **R**₁ in Figure 5.3a result from CO photodissociation from the reactant and are discussed in Section 5.5.2.

Figure 5.3b displays picosecond data of [CpFe(CO)₂]₂ similar to Figure 5.3a but with 2.0 M P(OMe)₃ in *n*-hexane. The addition of the polar phosphite to the *n*-hexane solution results in significant inhomogeneous broadening of all the absorption lines in comparison to Figure 5.3a, a common effect for organometallic complexes placed in polar solution [194]. Peaks from the

radical are again labeled **R**₁ in Figure 5.3b and appear at approximately the same positions as Figure 5.3a. Unlike data in *n*-hexane solution, however, the peaks from **R**₁ decay nearly to the baseline within 500 ps. The kinetics for the **R**₁ peak at 1935 cm⁻¹ are displayed in Figure 5.4a. The data were well fit to a single exponential decay with a time constant of 137 ± 4 ps. The second peak from **R**₁ at 2007 cm⁻¹ exhibits similar kinetics and was well fit with a time constant of 153 ± 8 ps (not shown in Figure 5.4a).

Figure 5.3 Picosecond time-resolved IR spectra for [CpFe(CO)₂]₂ in (A) neat *n*-hexane solution and (B) *n*-hexane with 2.0 M P(OMe)₃.

Two new peaks, labeled **R**₂ in Figure 5.3b, grow in on a hundreds of picosecond time scale. Kinetics for the **R**₂ peak at 1904 cm⁻¹ are also shown in Figure 5.4a. The kinetics of **R**₂ are well fit to an exponential rise with a time constant of 154 ± 8 ps for the peak at 1904 cm⁻¹ and 131 ± 11 ps for the peak at 1970 cm⁻¹ (not shown). Note that these fits also included an exponential decay of ca. 10 ps, which corresponds to vibrational relaxation of radical **R**₁. The agreement of the ca. 150 ps time constants for the decay of **R**₁ and rise of **R**₂ is a clear indication that **R**₁ forms **R**₂ within several hundred picoseconds. Data were also collected for a lower concentration of the phosphite ligand (300 mM). The kinetics of **R**₁ and **R**₂ at this lower

concentration are shown in Figure 5.4b, analogous to the data in Figure 5.4a (again, the data exhibited dynamics on a ca. 10 ps time scale from vibrational relaxation). The dynamics at this lower concentration, a decay of 583 ± 49 ps for $\mathbf{R}_1$ and a rise of 701 ± 32 ps for $\mathbf{R}_2$, were approximately four times slower than at the higher concentration. The rate of conversion from $\mathbf{R}_1$ to $\mathbf{R}_2$ strongly depends on the concentration of phosphite. This dependence demonstrates that $\mathbf{R}_2$ is formed by the reaction of $\mathbf{R}_1$ with phosphite. We assign $\mathbf{R}_2$ to the 19-electron intermediate $\text{CpFe(CO)}_2\text{P(OMe)}_3$ on the basis of DFT calculations, which are discussed in detail in Section 5.7.

Figure 5.4 Picosecond kinetics of iron radicals in *n*-hexane/phosphite solutions with (A) 2.0 M P(OMe)_3 and (B) 300 mM P(OMe)_3 . Solid lines are exponential fits to the experimental data.

Note that in the presences of phosphines and phosphites, it is well-known metal–metal bonded dimers like $[\text{CpFe(CO)}_2]_2$ may undergo disproportionation reactions to form ionic products [138], and these reactions can occur on both the picosecond [23,24] and microsecond [21] time-scales (see Chapters 3 and 4). We did not observe these products in our experiments because the Fe dimer does not form ionic products as readily as other metals, such as Mo or W, and because the non-polar solvent, hexane, does not favor the formation and stabilization of

disproportionation products [138,147,195].

5.5.2 Dynamics of CO-loss products

Several positive-going peaks appear in Figure 5.3 that are assigned to CO-loss products based on literature values [139,193,196-198]. In both neat *n*-hexane and phosphite solutions, a peak appears at ca. 1823 cm^{-1} which is assigned to the bridging CO stretching mode of the CO-loss species $^3\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ in a triplet spin state. The identity and spin state of this species has been definitively established [196-198]. This absorption grows in with a time constant of 22 ± 1 ps in neat *n*-hexane, 22 ± 1 ps in 2.0 M $\text{P}(\text{OMe})_3$, and 20 ± 1 ps in 300 mM $\text{P}(\text{OMe})_3$. The invariability of the time constant in different solutions shows that this species has little or no interaction with the phosphite molecule. It is difficult to determine the reason for the rise time of this peak, and several possible explanations have been proposed in the literature [139,193,199]. Unfortunately, our experiments provide no additional insight into this process. Surprisingly, we find no evidence that this triplet CO-loss product is solvated by $\text{P}(\text{OMe})_3$ on a picosecond time scale, even in the high 2.0 M concentration. The triplet CO-loss product is stable throughout the 800 ps time window of the data.

Figure 5.5 Picosecond kinetics of the CO-loss feature D_2 at 1736 cm^{-1} in *n*-hexane/phosphite solutions of 2.0 M and 300 mM $\text{P}(\text{OMe})_3$. Solid lines are biexponential fits to the data. Data at 300 mM have been offset by $-0.5\text{ }\Delta\text{mOD}$ for clarity.

A small peak marked with an asterisk is present at 1905 cm^{-1} in Figure 5.3a. This peak has been observed in previous ultrafast experiments [193] and may result from an additional CO-loss product in a singlet spin state, $^1\text{Cp}_2\text{Fe}_2(\text{CO})_3$. The exact identity or structure of this intermediate is not known with any certainty. This small peak is not discernable in phosphite solutions (Figure 5.3b) most likely because it is masked by the absorption of the 17-electron radical $\text{CpFe}(\text{CO})_2$ (**R**₁), centered at 1935 cm^{-1} , which is broader in phosphite solution.

In the phosphite solutions, a peak also grows in at 1736 cm^{-1} which is labeled **D**₂ in Figure 5.3b. The kinetics of this peak at phosphite concentrations of 2.0 M and 300 mM are shown in Figure 5.5 with biexponential fits to each data set. The kinetics each exhibit a low amplitude, ca. 10 ps decay, which most likely corresponds to spectral overlap with the absorption tail of a vibrationally excited molecule that cools on this time-scale. The kinetics also exhibit a longer time-scale exponential rise that corresponds to the rise of the peak labeled **D**₂. The fits to the data give time constants of $248 \pm 13\text{ ps}$ for the 2.0 M solution and a time constant greater than 800 ps for the 300 mM solution. The strong dependence of the rate with concentration indicates that this peak results from a reaction with $\text{P}(\text{OMe})_3$, and so one possible assignment is to the monosubstituted dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OMe})_3$. The absorption of this species is reported in the literature at $\sim 1752\text{ cm}^{-1}$ in hexane [200], cyclohexane [201], or methylcyclohexane [202] solution. Even allowing for shifts in frequency from different solvents, the literature value is only in borderline agreement with the peak we observe experimentally (1736 cm^{-1}). Note that $\text{P}(\text{OMe})_3$ is a liquid at room temperature and the hexane/ $\text{P}(\text{OMe})_3$ mixture is significantly different from the alkane solvent alone. The identity of the precursor to **D**₂ is also not clear from the experimental data; we would expect to observe a peak that decays on the same time scale as the rise of **D**₂. One possible explanation is that **D**₂ forms by reaction of $\text{P}(\text{OMe})_3$ with the species marked by an * in Figure 5.3a, and these dynamics are masked in phosphite solution by the broad absorptions of the radicals **R**₁ and **R**₂. It is also possible that **D**₂ arises from a different chemical species. The relatively low vibrational frequency is suggestive of a bridging CO ligand, and it has been proposed in the literature that dimers with a bridging CO ligand and no metal-metal bond might exist in solution [139,203-205]. Such a complex might form by a reaction between the 17e radical $\text{CpFe}(\text{CO})_2$ and 19e radical $\text{CpFe}(\text{CO})_2\text{P}(\text{OMe})_3$. Despite several attempts, we were unable to use DFT calculations to optimize any molecule with a structure similar to those that have been proposed in the literature. In the absence of a more likely candidate, we only weakly assert that the peak at 1736 cm^{-1} arises from $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OMe})_3$.

5.6 Nanosecond/microsecond experimental results

5.6.1 Dynamics of iron-centered radicals

Figure 5.6 presents time-resolved IR spectra after 532 nm laser excitation on the nano- and microsecond time-scales (Figure 5.6a and Figure 5.6b, respectively) for $[\text{CpFe}(\text{CO})_2]_2$ in *n*-hexane/phosphite solutions with 85 mM $\text{P}(\text{OMe})_3$. Peaks labeled **R**₂ appear at the same positions as observed in the picosecond data (see Figure 5.3b) and discussed in Section 5.5.1. Note that the CO-loss products apparent in the picosecond data and discussed in Section 5.5.2 do not appear in Figure 5.6 because longer wavelength excitation (532 nm) was used in this data. The wavelength-dependent photochemistry of $[\text{CpFe}(\text{CO})_2]_2$ has been well-addressed, and the absence of appreciable CO-loss products with 532 nm excitation is consistent with literature reports [29,32,139,206].

The peaks labeled **R**₂ in Figure 5.6 undergo dynamics on a hundreds of nanoseconds to microsecond time-scale. The higher frequency peak of **R**₂ at 1970 cm^{-1} decays to less than one-quarter its initial intensity within 2 μs . The kinetics of this peak are displayed in Figure 5.7, and the decay is well fit to a single exponential function with a time constant of $1.3 \pm 0.2 \mu\text{s}$. At first glance, the lower frequency peak of **R**₂ at 1904 cm^{-1} appears to decay only to one-half the initial intensity within 2 μs ; however, the dynamics of this peak are more complex upon closer inspection. Figure 5.8a shows an enlargement of the peak at a time delay of 200 ns. The peak is asymmetric in shape and is not well fit to a single Voigt function. Instead, as shown in Figure 5.8, the peak is well fit only with three Voigt functions. For the purposes of discussion, we assume that these three Voigt functions correspond to three different radical species, labeled **R**₂, **R**₃, and **R**₄—this assignment is justified by the DFT calculations discussed in Section 5.7. At a time delay of 200 ns, the peak primarily consists of an absorption from **R**₂ centered at 1904 cm^{-1} . As the **R**₂ peak decays, the absorptions from **R**₃ and **R**₄ grow in at 1910 and 1899 cm^{-1} , respectively. Figure 5.8b shows the same spectral region at a delay of 5 μs , and the spectrum is well fit to **R**₃ and **R**₄ without need for a third peak corresponding to **R**₂. Taken together, the spectra and kinetics clearly suggest that **R**₂ decays into **R**₃ and **R**₄ on a time scale of 1-2 μs . Note that the spectra in Figure 5.8 also exhibit a weak absorption from the 17e radical $\text{CpFe}(\text{CO})_2$ (**R**₁) at ca. 1935 cm^{-1} . The presence of this peak suggests that even though the reactions heavily favor **R**₃/**R**₄, an equilibrium exists between all the radical species **R**₁ through **R**₄.

Figure 5.6 Time-resolved IR spectra for $[\text{CpFe}(\text{CO})_2]_2$ after 532 nm excitation in 85mM $\text{P}(\text{OMe})_3/n$ -hexane solution on the nanosecond to early microsecond time scales.

Figure 5.7 Kinetics of radical species $\mathbf{R}_2$ in 85 mM $\text{P}(\text{OMe})_3/n$ -hexane on the early microsecond time-scale. Solid line is an exponential fit to the experimental data.

In order to help identify $\mathbf{R}_2$, $\mathbf{R}_3$, and $\mathbf{R}_4$, data were collected at a higher 200 mM concentration of $\text{P}(\text{OMe})_3$, and the spectra appeared similar to the data presented in Figure 5.6. The decay of the radical $\mathbf{R}_2$ at 1970 cm^{-1} is quantitatively similar to the data in Figure 5.7, and the kinetics were well fit to a single exponential decay with a time constant of $1.6 \pm 0.1\text{ }\mu\text{s}$. Within experimental error, the time constants measured in 85 and 200 mM $\text{P}(\text{OMe})_3$ are identical, so the rate of reaction ($k = 7 \pm 2 \times 10^5\text{ s}^{-1}$) from $\mathbf{R}_2$ to $\mathbf{R}_3/\mathbf{R}_4$ appears to be independent of the phosphite concentration. There is, however, evidence that the higher concentration of phosphite changes the relative amount of species $\mathbf{R}_3$ and $\mathbf{R}_4$. Figure 5.8c shows the peaks from species $\mathbf{R}_3$ and $\mathbf{R}_4$ at a time delay of $5\text{ }\mu\text{s}$ in the 200 mM $\text{P}(\text{OMe})_3/n$ -hexane solution. Compared to the 85 mM data in Figure 5.8b, the higher phosphite concentration produced a higher relative population of $\mathbf{R}_4$.

compared to R_3 . This difference clearly indicates that the peaks labeled R_3 and R_4 are from two separate chemical species (not two different vibrations of the same molecule). The difference can be explained if the two species are in equilibrium; the addition of phosphite shifts the equilibrium further toward R_4 . The identity of these peaks is discussed in Section 5.7.1.

Figure 5.8 Enlargement of the overlapped R_2 , R_3 , and R_4 peaks in 85 mM $P(OMe)_3/n$ -hexane solutions at a time delay of (A) 200 ns and (B) 5 μs , and 200 mM $P(OMe)_3/n$ -hexane solution at a time delay of 5 μs (C). Solid black lines are the experimental data, dashed gray lines are the best fit to the data, and dashed black lines are individual Voigt functions used to fit the data.

5.6.2 Formation of final product $[\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3]_2$

Figure 5.9 shows time-resolved IR spectra on the microsecond time-scale for $[\text{CpFe}(\text{CO})_2]_2$ in 85mM $\text{P}(\text{OMe})_3/n$ -hexane solution. The two peaks from R_3 and R_4 are clearly visible and slowly decay on a hundreds of microsecond time-scale, although the relative amplitude of the two peaks remains approximately constant. Figure 5.10 shows kinetics for these species integrated over the area of both peaks from 1890-1915 cm^{-1} . The kinetics are well fit to a biexponential function with a short time constant of $\sim 2 \mu\text{s}$ (corresponding to the decay of the R_2 ; see Figure 5.7) and a long time constant of $164 \pm 20 \mu\text{s}$. There is only one positive-going peak in the spectra of Figure 5.9 which grows in on this longer time-scale. The peak, labeled D_3 , appears at 1716 cm^{-1} and is attributed to the dimer $[\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3]_2$ (D_3) on the basis of literature values [139,202]. This species is expected to be stable and is the final photoproduct observed in the time-resolved experiments. The kinetics for D_3 are also shown in Figure 5.10, and the data is well fit to a single exponential rise with a time constant of $163 \pm 37 \mu\text{s}$. The kinetics are a clear indication that species R_3/R_4 decay into the final product D_3 on a time scale of 100-200 μs .

Figure 5.9 Time-resolved IR spectra on the microsecond time-scale for $[\text{CpFe}(\text{CO})_2]_2$ after 532 nm excitation in 85mM $\text{P}(\text{OMe})_3/n$ -hexane solution

Figure 5.10 Microsecond kinetics of radicals $\mathbf{R}_3/\mathbf{R}_4$ and dimer $\mathbf{D}_3$ species in 85 mM $\text{P(OMe)}_3/n$ -hexane solution. Solid line is a single exponential fit for $\mathbf{D}_3$ and a biexponential fit for $\mathbf{R}_3/\mathbf{R}_4$. (see text)

5.7 Discussion and DFT results

In this section, the experimental results are analyzed in the context of DFT calculations in order to build a complete picture of the ligand substitution mechanism. This section is divided into three parts. In Sections 5.7.1-5.7.2, we identify the molecular and electronic structures, respectively, of radical intermediates ($\mathbf{R}_1$ - $\mathbf{R}_4$), and in Section 5.7.3 present an explanation for the reactivity in terms of the relative energetics of the complexes. Based on this analysis, we present the complete mechanism for the ligand substitution reaction in $\text{P(OMe)}_3/n$ -hexane solution in Section 5.8, Figure 5.13.

5.7.1 Identification and molecular structures of radical intermediates $\mathbf{R}_1$ - $\mathbf{R}_4$

The experimental results presented in Sections 5.5 and 5.6 follow the homolysis of the Fe-Fe bond in $[\text{CpFe(CO)}_2]_2$ ($\mathbf{D}_1$) through the formation of the final ligand substitution product, $[\text{CpFe(CO)P(OMe)}_3]_2$ ($\mathbf{D}_3$). In the course of the reaction, the experimental results have identified four different radical species, $\mathbf{R}_1$ through $\mathbf{R}_4$, which participate in the reaction. The first radical formed, $\mathbf{R}_1$, has been identified in the literature [32,191-193] and assigned is to the 17-electron radical CpFe(CO)_2 . The remaining radical species are discussed below.

It has been proposed that $\mathbf{R}_1$ may form a 19-electron species $\text{CpFe(CO)}_2\text{P(OMe)}_3$ by coordination of a phosphite ligand [183], however, previous time-resolved IR studies on the dimer $\mathbf{D}_1$ in 14 mM $\text{P(OMe)}_3/n$ -heptane solution by Dixon and co-workers did not provide any evidence for a 19-electron species [139,176]. That study monitored the conversion of the 17e radical CpFe(CO)_2 ($\mathbf{R}_1$) to the monosubstituted 17e radical CpFe(CO)P(OMe)_3 , which possesses a peak at 1907 cm^{-1} [176]. In our experiments, we used a significantly higher concentration of

phosphite and found three separate absorptions, centered at 1899, 1904, and 1910 cm^{-1} , in this spectral region. As a result, the correspondence between our experiments and the previous report is not initially clear.

Figure 5.11 DFT optimized structures for two 17-electron and two 19-electron radicals involved in the photochemical ligand substitution of $[\text{CpFe(CO)}_2]_2$. Energies relative to $\mathbf{R}_1$ and calculated harmonic vibrational frequencies (scaled by 0.9614[120]) for CO ligands are provided to the right of each structure, and the Fe–P bond distances ($\text{\AA}$) for each structure are labeled.

Table 5.2 Experimentally observed, calculated, and literature $\nu(\text{CO})$ frequencies (cm^{-1}) for various species involved in the photochemistry of $[\text{CpFe}(\text{CO})_2]_2$.

Compound	Experiment ^a	DFT ^e	Literature
$[\text{CpFe}(\text{CO})_2]_2$ (D ₁)	1794, 1961, 2005 ^b	–	1794, 1961, 2006 ^f
$\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OMe})_3$ (D ₂)	1736 ^c	–	1753, 1947, 1966 ^f
$[\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3]_2$ (D ₃)	1716 ^d	–	1716 ^f
$\text{CpFe}(\text{CO})_2$ (R ₁)	1935, 2007 ^b	1956, 2011	1938, 2004 ^g
$\text{CpFe}(\text{CO})_2\text{P}(\text{OMe})_3$ (R ₂)	1904, 1970 ^c	1933, 1982	–
$\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3$ (R ₃)	1910 ^d	1927	1907 ^h
$\text{CpFe}(\text{CO})[\text{P}(\text{OMe})_3]_2$ (R ₄)	1899 ^d	1916	–

^a this work; ^b neat *n*-hexane solution; ^c 2.0 M $\text{P}(\text{OMe})_3$ /*n*-hexane solution; ^d 85 mM $\text{P}(\text{OMe})_3$ /*n*-hexane solution; ^e B3LYP functional, frequencies scaled by 0.9614[120]; ^f reference [200], hexane solution; ^g reference [32], cyclohexane solution; ^h reference [176], 14 mM $\text{P}(\text{OMe})_3$ /*n*-heptane solution.

In order to identify the radicals in our study, we have performed DFT calculations on possible 17e and 19e iron-centered radical species involved in the reaction. The observed and calculated vibrational frequencies are summarized in Table 5.2, and the molecular structures for the radicals are depicted in Figure 5.11. DFT calculations have been shown reliable for predicting the energetics, vibrational frequencies, electronic structure, and molecular geometries of organometallic radicals [21-24,132,170,207-209]. Figure 5.11a shows the 17e radical $\text{CpFe}(\text{CO})_2$ (**R**₁) which serves as the reference point for the reported energies of all other radical species. We have performed calculations on the 19e radical $\text{CpFe}(\text{CO})_2\text{P}(\text{OMe})_3$ (Figure 5.11b), and interestingly, this molecule is predicted to be 4.9 kcal/mol more stable than the 17e analog **R**₁. The vibrational frequencies of the 19e species were calculated to be 23 (asymmetric CO stretch) and 29 cm^{-1} (symmetric CO stretch) lower than the corresponding modes in the 17e species **R**₁. These shifts are in reasonably good agreement with the shifts observed experimentally between the **R**₁ and **R**₂ peaks, 30 and 37 cm^{-1} (see Figure 5.3). In addition, the rate of formation of **R**₂ depends on the concentration of $\text{P}(\text{OMe})_3$ (refer to Figure 5.4), a result which would be expected for the formation of the 19e species from the 17e radical $\text{CpFe}(\text{CO})_2$. Taken together, the calculated energetics, frequency shifts, and concentration dependence strongly indicate the peaks labeled **R**₂ (1904 and 1970 cm^{-1}) are best attributed to the 19e species $\text{CpFe}(\text{CO})_2\text{P}(\text{OMe})_3$.

Although the experimental results are the first direct evidence for the existence of the 19e species $\text{CpFe}(\text{CO})_2\text{P}(\text{OMe})_3$, there has been indirect evidence that this type of intermediate is

involved in the disproportionation reactions of the parent dimer complex $[\text{CpFe}(\text{CO})_2]_2$ [138,195]. In addition, there is indirect evidence for the formation of a similar 19e species $\text{CpFe}(\text{CO})_3$ both from photochemical studies of the dimer under CO atmosphere [205,210] and electrochemical studies involving the reduction of 18e cations [178]. If the Cp ring is replaced by an indenyl ring, a stable intermediate, $(\text{indenyl})\text{Fe}(\text{CO})_2\text{L}$ ($\text{L} = \text{CO}, \text{PPh}_3$), has been isolated, although it was assumed that the indenyl ring is bonded η^3 rather than η^5 to the metal center, producing a 17e rather than 19e count on the metal [211].

These results provide compelling evidence that **R**₂ corresponds to the 19e species, and our studies on the tungsten analog of this complex in Section 5.3 [22] as well as studies on electrochemically generated 19e species [137,141,177,178,212-214] suggest that this complex may spontaneously lose a CO ligand. Figure 5.11 shows the calculated structure of the monocarbonyl 17e radical $\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3$, which is the complex remaining after loss of a CO ligand from the 19e radical **R**₂. Based on the experimental data, we know **R**₂ decays into the peaks labeled **R**₃ and **R**₄ on a time-scale of 1 μs (refer to Figure 5.7 and Figure 5.8). It is likely that one of these two absorptions results from the monocarbonyl 17e radical, but the identity of the other is unclear. A suitable explanation is that the second absorption results from a 19e species with two phosphite ligands, $\text{CpFe}(\text{CO})[\text{P}(\text{OMe})_3]_2$, as shown in Figure 5.11d. This molecule would form upon coordination of a second phosphite ligand to the monocarbonyl 17e radical. The 19e species is predicted to be ca. 1.5 kcal/mol more stable than the monosubstituted 17e radical and has a CO vibrational frequency 11 cm^{-1} lower in energy. This calculated frequency difference agrees perfectly with the difference of 11 cm^{-1} observed experimentally between the **R**₃ and **R**₄ peaks, 1899 and 1910 cm^{-1} , respectively. In addition, the **R**₃ and **R**₄ radicals are isoenergetic within the margin of error for DFT calculations [186,187], so it is reasonable that the species are in equilibrium and that the absorptions would appear with approximately equal intensity (note that the ratio of the intensities for **R**₃/**R**₄ from the calculations is 1.16). Thus, we assign **R**₃ (1910 cm^{-1}) to the 17e radical $\text{CpFe}(\text{CO})\text{P}(\text{OMe})_3$ and **R**₄ (1899 cm^{-1}) to the 19e radical $\text{CpFe}(\text{CO})[\text{P}(\text{OMe})_3]_2$. This assignment is further supported by the observation of an enhancement of the **R**₄ population at higher $\text{P}(\text{OMe})_3$ concentration, which shifts the **R**₃/**R**₄ equilibrium toward the species with two $\text{P}(\text{OMe})_3$ ligands (refer to Figure 5.8).

The formation of a 19e intermediate with two phosphite ligands (**R**₄) is a rather surprising result because unfavorable steric interactions between the two bulky phosphite ligands might be expected to prevent the coordination of the second phosphite molecule. One explanation for the result is to consider that $\text{P}(\text{OMe})_3$ is a rather small ligand in comparison to other phosphine and phosphite ligands. The cone angle, the generally accepted measure for the size of a coordinating

ligand, is only 107° for P(OMe)_3 in comparison to significantly larger values for other phosphines, such as PBu_3 (132°) and PPh_3 (145°) [167]. We have reported that steric effects play a major role in determining the dynamics of 19e radicals for the analogous tungsten system (see Chapter 3) [21,23]. We thus expect that a 19e radical with two Lewis bases is less likely to form in the presence of a larger Lewis bases. The molecular structure of $\text{CpFe(CO)[P(OMe)}_3\text{]}_2$ (**R₄**) shown in Figure 5.11 already shows some evidence of possible steric effects—the bond distances between the Fe atom and the two P atoms are not equal. One phosphite molecule is bound 2.23 Å from the metal while the second phosphite is 2.37 Å from the Fe atom. These two bond distances are both longer than the Fe–P bond distance (2.17 Å) of the 17e species **R₃** (refer to Figure 5.11c). These differences suggest that steric effects prevent the second phosphite molecule from bonding to the iron atom as tightly as the first phosphite, and furthermore, the second phosphite weakens the bond between the metal atom and first phosphite molecule. Rather surprisingly, the Fe–P bond distance of the 19e species **R₂** with one phosphite and two carbonyls (Figure 5.11b) is 2.47 Å, which is 0.1 Å longer than the Fe–P bond of any of the other radicals. We attribute this long bond distance to an electronic effect which likely arises from the strong π back-bonding of the CO ligands to the metal. This result emphasizes the importance of both steric and electronic effect for understanding the reactivity of these metal-centered radicals.

5.7.2 Electronic structure of radical intermediates **R₁**–**R₄**

The experimental and DFT results provide strong evidence for the existence of the two distinct 19e radicals shown in Figure 5.11b and Figure 5.11d. The label “19-electron” implies that the unpaired electron is nearly entirely localized on the metal atom. It is common, however, for organometallic radicals to exhibit a shift of the spin density to a ligand, avoiding a 19e count on the metal [129,130,169,209]. These type of complexes are often labeled $18+\delta$ compounds, where δ refers to the amount of radical character localized on the metal, and they sometimes exhibit a structural distortion of the ligand to better accommodate the unpaired electron. For instance, it has been proposed that the cyclopentadienyl ($\text{Cp} = \text{C}_5\text{H}_5$) rings in radicals like **R₂** and **R₄** could bear most of the unpaired electron, causing the Cp ring to slip to an η^4 rather than η^5 configuration [210]. The molecular structures in Figure 5.11, however, show no evidence for ring slip or any other distortion of the Cp ligands.

For a more quantitative analysis of the electronic structure, we have used NBO calculations [151] to report the charge and spin residing on different fragments of these complexes. These types of calculations have been shown reliable in comparison to experimental data on 19e complexes [132,170,207,208]. The results are tabulated in Table 5.3 and show little

variation between the four radicals **R**₁-**R**₄. In all cases the Fe atom bears the majority of the spin, with a value around 1.0 in all cases, so it is apparent that these complexes are well described as metal-centered radicals. All the radical complexes also exhibit a relatively large degree of spin polarization, which causes an appreciable amount of β spin density on various fragments of the complexes in addition to the α spin density associated with the unpaired electron [186,187]. Spin polarization effects have been reported previously for these types of complexes [132,170,207,208].

Interestingly, the charge on the metal atom also changes very little between the radicals, becoming only slightly positive for the 17e radicals and slightly negative for the 19e radicals, with a total change of less than one-quarter of an atomic charge. The relatively small changes indicate that the transition from a 17e to 19e radical does not appreciably affect the electron density surrounding the metal atom. This result agrees well with previous DFT studies on transition-metal radicals; a collective change in the electron distributions of numerous molecular orbitals helps to preserve the net electron density on the metal [132,170,207,208]. Nevertheless, the ‘19th’, unpaired electron is localized on the iron atom; thus, we consider the complexes are appropriately labeled 19e, metal-centered radicals and not 18+ δ compounds.

5.7.3 Reactivity and energetics

The 19e radical **R**₂ forms by coordination of a phosphite molecule to the 17e radical **R**₁. As discussed above, the 19e species is calculated to be 4.9 kcal/mol more stable than the 17e radical. The relative stability of 19e compared to 17e species been rationalized by the formation a bond between the metal and coordinating ligand which has a bond order of one-half, providing additional stabilization to the complex [124]. We performed partial optimization calculations for different Fe–P bond lengths in the 19e complex **R**₂ to better understand the coordination of P(OMe)₃ to **R**₁. The results showed that the coordination of P(OMe)₃ was energetically downhill for all the calculated bond lengths (2.47-5.47 Å), suggesting that the formation of the 19e species **R**₂ is a near barrierless, diffusion-limited reaction.

Table 5.3 Calculated values for the net spin and charge residing in the cyclopentadienyl (Cp) ring, CO ligands, P(OMe)₃ ligands, and metal atom for radicals **R**₁-**R**₄.

	CpFe(CO) ₂ 17e (R ₁)	CpFe(CO) ₂ P(OMe) ₃ 19e (R ₂)	CpFe(CO)P(OMe) ₃ 17e (R ₃)	CpFe(CO)[P(OMe) ₃] ² 19e (R ₄)
Spin				
Fe	1.09 α	0.90 α	1.10 α	0.93 α
Cp	0.01 β	0.09 α	0.01 β	0.08 α
CO	0.08 β	0.10 β	0.07 β	0.11 β
P(OMe) ₃	-	0.11 α	0.02 β	0.10 α
Charge				
Fe	+0.16	-0.03	+0.08	-0.08
Cp	-0.28	-0.26	-0.34	-0.30
CO	+0.12	+0.11	-0.04	0.00
P(OMe) ₃	-	+0.18	+0.30	+0.38

The formation of **R**₃/**R**₄ from **R**₂ has two possible mechanisms. The first case is the reaction depicted in eq. 5.4: **R**₂ loses a CO ligand forming **R**₃, and subsequently, **R**₃ coordinates with P(OMe)₃ to form **R**₄ (i.e., **R**₂→**R**₃→**R**₄). In the second case, there is concerted coordination of **R**₂ with a P(OMe)₃ molecule from the bath and loss of a CO group, directly forming **R**₄. Subsequently, **R**₄ dissociates a P(OMe)₃ ligand, forming **R**₃ (i.e., **R**₂→**R**₄→**R**₃). In the latter case, an increase in the concentration of P(OMe)₃ should increase that rate of conversion from **R**₂ to **R**₃/**R**₄; however, we observed no change in this rate at different concentrations (refer to Section 5.6.1). This result supports the former mechanism: loss of CO from **R**₂ followed by coordination of P(OMe)₃.

The energy profile for this mechanism calculated by the method of partial optimization [186,187] is depicted in Figure 5.12. The left hand side of the figure depicts the change in the energy of **R**₂ as the Fe–CO bond distance is lengthened while the remaining degrees of freedom in the system are optimized. Loss of the CO ligand produces the 17e radical **R**₃, and this complex is calculated to be 13.3 kcal/mol less stable than **R**₂. The ~1-2 μs time constant observed experimentally seems to result from the large energy difference between **R**₂ and **R**₃ rather than a high energy transition state. Experimentally, the reaction heavily favors the formation of **R**₃ despite the relative instability of this complex compared to **R**₂. This result suggests that the back-reaction, coordination of CO with **R**₃, does not occur to an appreciable extent. The absence of the back-reaction might be a kinetic effect stemming from the rapid diffusion of the CO ligand in solution. This explanation is consistent with the previous reports that the yield of ligand substitution products is reduced in solutions under CO atmosphere [204].

The right hand side of Figure 10 depicts the change in the energy of **R**₃ as Fe–P distance is shortened while the remaining degrees of freedom in the system are allowed to fully optimize. Adding a P(OMe)₃ ligand to **R**₃ leads to the formation of **R**₄, which is predicted to be only 1.6 kcal/mol more stable than **R**₃. Again, there is a negligible barrier connecting the two radicals. These computational results suggest that **R**₃ and **R**₄ would be in rapid equilibrium, which is in accord with the experimental result in Section 4.1 showing the simultaneous growth of **R**₃ and **R**₄ as **R**₂ slowly loses a CO ligand.

The final product observed in the experimental data is the disubstituted dimer [CpFe(CO)P(OMe)₃]₂ (**D**₃), which forms on a time-scale of 100-200 μs from the radicals **R**₃ and **R**₄. The most straightforward mechanism for the formation of **D**₃ is dimerization of **R**₃; however, we cannot rule out an additional contribution from the dimerization of **R**₄ with concerted loss of P(OMe)₃ ligands.

Figure 5.12 DFT partial optimizations following the reaction coordinate connecting radicals **R**₂, **R**₃, and **R**₄. Left-hand side corresponds to lengthening of the Fe–CO bond during dissociation of a CO ligand from **R**₂, forming **R**₃. Right-hand side corresponds to shortening of the Fe–P bond distance as the radical **R**₃ coordinates with a second P(OMe)₃ molecule, forming **R**₄.

5.8 Summary and conclusions

With the assignment of radicals **R**₁ through **R**₄ presented in the preceding section, we can build a complete picture of the ligand substitution dynamics, as depicted in Figure 5.13. Photoexcitation of the reactant dimer [CpFe(CO)₂]₂ (**D**₁) results in homolysis of the Fe–Fe bond and formation of two 17e radicals CpFe(CO)₂ (**R**₁) within 1 ps. On a hundreds of picoseconds time-scale, which is nearly diffusion-limited, the Lewis base P(OMe)₃ coordinates with 17e radicals **R**₁ to form the 19e radicals CpFe(CO)₂P(OMe)₃ (**R**₂). The 17e/19e species (**R**₁/**R**₂) are in an equilibrium which heavily favors the 19e species. Next, **R**₂ spontaneously loses a CO ligand in 1–2 μs to form the 17e radical CpFe(CO)P(OMe)₃ (**R**₃). The monocarbonyl 17e radical **R**₃ rapidly establishes an equilibrium with its 19e counterpart, CpFe(CO)[P(OMe)₃]₂ (**R**₄). The final step of the reaction is the dimerization of **R**₃ to form the final product [CpFe(CO)P(OMe)₃]₂ (**D**₃), which occurs with a time constant of 100–200 μs.

Figure 5.13 The total mechanism of photochemical ligand substitution with $[\text{CpFe}(\text{CO})_2]_2$ (center row), as well as side reactions resulting from photoinduced CO loss (top and bottom rows). Note that the side reactions are only observed in the experiments performed with shorter wavelength (400 nm) excitation.

The experimental results also identify two side reactions which result from photodissociation of CO ligands from the reactant dimer $[\text{CpFe}(\text{CO})_2]_2$ (**D**₁), shown in the top and bottom rows of Figure 5.13. These side reactions are appreciable only with the shorter wavelength excitation (400 nm) used in the picosecond data (refer to Section 5.5.2). One photoproduct is the triplet CO-loss species $^3\text{Cp}_2\text{Fe}_2(\text{CO})_3$, and the second is best attributed to the monosubstituted dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{P(OMe)}_3$ (**D**₂).

The time-resolved IR data provides direct evidence for the associative ligand substitution mechanism of $[\text{CpFe}(\text{CO})_2]_2$, which involves two 17e and two 19e metal-centered radicals. The facile change in electron count on photogenerated iron-centered radicals ($17\text{e} \rightarrow 19\text{e} \rightarrow 17\text{e} \rightarrow 19\text{e}$) is surprising but comparable to earlier results reported for tungsten radicals [21-24]. The observation of similar reactivity for the two different metals is a strong indication of the generality of the reaction mechanism.

6 Photochemistry of Fischer-carbene complexes

6.1 Introduction

Fischer carbene transition-metal complexes have been developed as reagents for a large variety of reactions that form new carbon–carbon bonds and which exploit the chemistry of the formal double bond between the metal and carbene carbon [215,216]. The carbon atom is electrophilic and readily undergoes nucleophilic addition reactions, resulting, for example, in benzannulation between unsaturated alkoxy-carbenes and alkynes [217]. These types of thermal reactions are a long-standing area of investigation; however, Fischer carbenes are also useful for an entirely different set of unique but poorly understood photoinduced reactions.

Louis Hegedus and coworkers discovered that photoexcitation of Fischer carbenes, such as $\text{Cr}(\text{CO})_5\text{CR}_1(\text{R}_2)$, leads to products consistent with the reactivity expected from ketenes [218–220]. For example, the carbenes readily react with imines after visible photoexcitation to form β -lactams, the four-membered ring common to all penicillin antibiotics, as shown in Figure 6.1. This reactivity led Hegedus to propose that photoexcitation results in some type of metal-ketene structure in which a carbonyl has inserted into the metal–carbene bond to form the ketene moiety. Nevertheless, there is no direct evidence for a metal-ketene structure despite previous attempts in cryogenic matrices and with microsecond time-resolved spectroscopy [221,222].

Figure 6.1 Photochemical reaction of Fischer-carbenes with imines observed by Hegedus and co-workers.

Here, the picosecond dynamics of the group 6 Fischer carbene $\text{Cr}(\text{CO})_5[\text{CCH}_3(\text{OCH}_3)]$ (**A**) are investigated after visible photoexcitation. We show the first conclusive evidence that a metal-ketene is formed and that it is extremely short-lived, relaxing back to **A** within tens of picoseconds, as depicted in equation 1:

6.2 Experimental results and discussion

Figure 6.2 shows time resolved IR difference spectra in the region of the CO stretch vibrations for **A** dilute in cyclohexane. Negative signals, referred to as bleaches, result from absorptions depleted by the 400 nm excitation pulse and correspond to the absorptions of **A**. Positive signals result from new absorptions present after photoexcitation, and Figure 6.2 shows two positive peaks centered at 1777 cm^{-1} and 1992 cm^{-1} . The latter absorption is intense and broad at the earliest time delay of 1 ps and completely masks one additional bleach from **A**.

Figure 6.2 Time-resolved IR difference spectra probing the CO stretch vibrations of $\text{Cr}(\text{CO})_5[\text{CCH}_3(\text{OCH}_3)]$ dilute in cyclohexane following photexcitation at 400 nm. Note that the scale on the horizontal axis is discontinuous and the peak on the left-hand side has been scaled by a factor of 4.

Figure 6.3 Kinetic measurements of the metal-ketene CO vibration in cyclohexane and methanol solution. Solid lines represent a fit of the experimental data to the sum of an exponential rise and decay.

The second positive peak at 1777 cm^{-1} is broad and weak at 1 ps and reaches its maximum intensity by 10 ps. The kinetics of this absorption are shown in Figure 6.3 and are well fit to the sum of an exponential rise and exponential decay with time constants of 4 ± 1 and 34 ± 2 ps, respectively. Although this absorption is the only peak exhibiting a rise time, all the peaks in Figure 6.2 decay on this same time-scale of ~ 34 ps; kinetic fits to the data give a decay of 34 ± 2 for the 1992 cm^{-1} absorption and a recovery time of 33 ± 2 ps for the bleach of **A**. In order to understand the origin and dynamics of these peaks, we turn to DFT calculations on the structures and vibrational frequencies of possible intermediates involved in the photochemistry of **A**.¹⁶

Figure 6.4 Molecular orbital diagram for a model Fischer carbene complex. Adapted from reference [223].

A recent DFT study of chromium carbene complexes by Fernandez et al. showed that the lowest lying triplet state possesses a metal-ketene structure [223], suggesting that this state is responsible for the unique photochemistry of the compounds. A molecular orbital diagram for this complex is displayed in Figure 6.4, adapted from reference [223]. The highest occupied molecular orbital (HOMO) is a non-bonding d-orbital and the lowest unoccupied molecular orbital (LUMO) is a π^* orbital localized on the carbene ligand. Given this electronic structure, a

¹⁶ DFT calculations were performed at the BP86 level using the basis sets 6-31+g(d,p) for C, O, and H and LANL2DZ for Cr with the program Gaussian 03.

HOMO to LUMO transition would result in metal-to-ligand charge transfer (MLCT) state in which the triplet spin state is the lowest in energy.

Figure 6.5 DFT calculated energetics as a function of the carbene-chromium-carbonyl C–Cr–C bond angle for the S_0 and T_1 electronic levels involved in the photoexcitation of $\text{Cr}(\text{CO})_5[\text{CCH}_3(\text{OCH}_3)]$ (**A**), with all displayed energy values relative to **A**. Arrows represent the dynamics observed in the experimental data. Numbered insets show the calculated molecular structures at various points on the electronic potential energy surfaces, and the associated bond angles are given in the lower corners of the insets. Data points for T_1 correspond to the structure shown in inset 2. Solid horizontal bars represent the energy of singlet (S_1 , S_2) and triplet (T_1 , T_2 , T_3) excited states within the energy of a 400 nm photon ($h\nu = 71.5$ kcal/mol), represented by the dashed horizontal line.

The results of DFT calculations on the singlet (S_0) and triplet (T_1) ground states of **A** are summarized in Figure 6.5. Two nearly isoenergetic triplet geometries with a metal-ketene structure are shown in insets 1 and 2 of Figure 6.5, and harmonic frequency calculations give stretching frequencies for the ketene ($\text{C}=\text{C}=\text{O}$) groups of 1749 and 1772 cm^{-1} , respectively. These calculated vibrational frequencies are in close agreement with the 1777 cm^{-1} absorption we observe experimentally and are a strong indication that this absorption arises from a transient metal-ketene complex in a triplet spin state. Unfortunately, we cannot definitively ascertain which triplet structure we observe experimentally. The calculated terminal CO stretch frequencies of

both metal-ketenes also agree reasonably well with the absorption at 1992 cm^{-1} in Figure 6.2. One of the two triplet structures is also displayed in Figure 6.6a, and the spin density from the DFT calculations is overlaid on this structure in Figure 6.6b. The calculations clearly confirm that the unpaired electrons are localized in a metal d-orbital and an anti-bonding orbital centered on the carbene ligand.

Triplet spin states are relatively common in the photochemistry of transition-metal complexes because of the high spin-orbit coupling associated with the metal center, which provides efficient coupling between different spin states [224,225]. Here we observe the ketene vibration of the triplet complex form in $\sim 4\text{ ps}$ after photoexcitation. Time-dependent DFT calculations show that there are five electronic levels accessible with the energy of a 400 nm photon (71.5 kcal/mol): three triplet states (T_1 , T_2 , T_3) and two singlet states (S_1 , S_2), as shown in Figure 6.5. Because spin-allowed absorption cross sections are typically larger than for spin-forbidden excitations, it is likely that photoexcitation promotes **A** to a singlet electronic state (S_1 or S_2), and the molecule subsequently relaxes to the lowest triplet state (T_1). We attribute the 4 ps rise time of the 1777 cm^{-1} metal-ketene absorption as the time for the photoexcited molecule to relax from higher lying excited states and reach the minimum on the T_1 potential energy surface (PES). In contrast, the peak at 1992 cm^{-1} shows no rise time but is broad at early time delays. The breadth of this peak likely results from a distribution of photoexcited **A** molecules which have not yet formed the metal-ketene structure but already possess terminal CO absorptions in this spectral region.

Figure 6.6 DFT calculated structures for the metal-ketene. (A) Triplet metal metal ketene, (B) triplet metal ketene with overlaid spin density (blue), and (C) metal-ketene in a singlet spin state and solvated by methanol.

Within the first 4 ps, the structure of the photoexcited **A** molecules changes significantly in order to form the ketene moiety. Figure 6.5 shows one-dimensional relaxed PES scans along the carbene-chromium-carbonyl C–Cr–C bond angle for both the S_0 and T_1 levels. This bond angle changes by 43° between S_0 structure **A** (inset 4) and T_1 metal-ketene structures (insets 1 and 2), and the distance between the carbene carbon and carbonyl carbon shortens from 2.75 to 1.63 Å. The metal-ketene subsequently decays in ~ 34 ps. Because the recovery of the bleach for **A** agrees well with this decay, the triplet apparently relaxes back to **A** and the S_0 electronic level on this time-scale.

The difference in the spin-state and geometry between T_1 and S_0 might cause the triplet state to be long-lived, persisting for hundreds of picoseconds or more [225]. Instead the metal-ketene relaxes in tens of picoseconds, and this fast relaxation likely occurs due to a crossing between the two electronic states in the vicinity of the minimum on the T_1 PES. Although we were not able to locate an exact crossing point, the PES scans in Figure 6.5 approach one another at C–Cr–C bond angles close to 45° , and the S_0 structure (see inset 3) closely resembles the metal-ketene structures. Thus it is reasonable to expect a crossing close to the T_1 minimum which facilitates fast relaxation to S_0 .

The photoinduced reactions of Fischer carbenes observed by Hegedus likely occur as a result of the triplet metal-ketene, yet the short lifetime (~ 34 ps) does not lend itself to an efficient bimolecular reaction. Fernandez et al. proposed that the triplet could undergo a solvent-induced spin-crossover with polar, electron donating solvents and form stable, and potentially long-lived, singlet metal-ketene complexes [223]. This solvated metal-ketene could be responsible for the reactivity of the Fischer carbenes. To explore this possibility, we collected data in methanol solution, and the kinetics of the ketene absorption are shown in Figure 6.3. Surprisingly, the data appear identical to the data collected in cyclohexane solution. Figure 6.6c shows the molecular structure of a the metal-ketene solvated with a methanol molecule; however, the experimental data shows no evidence for the formation of this type of species even though the calculations predict that this species is ca. 15 kcal/mol more stable than the triplet complexes.

The experiments presented herein show the first conclusive evidence for the photoinduced formation of triplet metal-ketenes from Fischer carbenes, and the ketene relaxes back to the starting material within tens of picoseconds. Although the experiments did not conclusively determine the role of the metal-ketenes in the reported photochemistry of Fischer carbenes (see Figure 6.1), it is likely that the ketenes play a prominent role. The previous reports on the photochemistry of these complexes have involved continuous wave photolysis of the complexes over several hours. It is likely that long-lived metal ketenes are formed in low yield

(too low to be detected with the current experimental apparatus), but these low yields are sufficient to build-up large concentrations under the continuous photolysis conditions used for synthetic chemistry.

7 Determining transition state geometries in liquids using 2D-IR: Fluxionality in $\text{Fe}(\text{CO})_5$

The following chapter is reproduced in part from Cahoon, *et al. Science*. 2008, 319, 1820-1823 [20].

7.1 Introduction

Transition states determine many properties of chemical reactions, yet there are limited experimental methods to directly probe the details of transition state geometries and symmetries in liquids. Molecular structures primarily reflect local minima on a potential energy surface and chemical reactions occur only during brief excursions up and over transition states on these surfaces. The excursions are short-lived, greatly complicating any measure of their properties. Most methods with sufficient time resolution rely on photoinitiation of a chemical reaction and provide information on the intermediates formed during the course of the reaction rather than direct information on transition state structures [102].

Here, we demonstrate that ultrafast two dimensional infrared (2D-IR) spectroscopy provides evidence for the transition state involved in a simple thermal chemical reaction, the fluxionality of $\text{Fe}(\text{CO})_5$. Fluxionality refers to the rearrangement of a molecule between chemically indistinguishable structures. These reactions produce no net change in molecular structure, yet they are important for understanding the basic chemical behavior and reactivity of molecules in solution.

$\text{Fe}(\text{CO})_5$, an organometallic complex with five CO ligands arranged in a trigonal bipyramidal geometry, is a textbook example for fluxionality. In the late 1950s, nuclear magnetic resonance (NMR) spectroscopy revealed that this molecule rapidly exchanges its CO ligands between axial and equatorial sites. The ^{13}C NMR spectrum of ^{13}C labeled $\text{Fe}(\text{CO})_5$ exhibits only a single peak at all accessibly measured solution temperatures, indicating that ^{13}C nuclei shift between axial and equatorial positions faster than NMR spectroscopy is able to distinguish these two chemical environments [27,226,227]. Careful analysis of IR, Raman, and NMR spectra of $\text{Fe}(\text{CO})_5$ and various derivatives suggests that the exchange process possesses a low barrier and occurs on a time-scale of picoseconds [227-229]. Nevertheless, the dynamics in solution have not been quantified.

From a general perspective, fluxional processes are simple chemical reactions in which a molecule briefly rearranges to a new symmetry and geometry as it crosses a transition state and

then returns to its original geometry as it completes the reaction. We show for $\text{Fe}(\text{CO})_5$ that during this process energy is exchanged between the vibrational modes of the reactive ligands. Quantification of this energy exchange provides direct information on the time-scale, transition state, and consequently, mechanism of the reaction.

2D-IR spectroscopy has recently received much attention for its ability to monitor thermal reactions and chemical exchange on the femtosecond and picosecond time-scales. Conventionally, ultrafast timing of chemical reactions is achieved by photoinitiating the reactions with a short, intense laser pulse which electronically excites the molecules and typically leaves them with significant excess energy [102]. In comparison, 2D-IR spectroscopy only requires vibrational excitation with an ultrafast IR laser pulse and allows the investigation of an entirely different class of thermally activated reactions in liquids at or close to equilibrium. Although similar to one-dimensional IR-pump, IR-probe experiments (1D-IR), 2D-IR spectroscopy separates the contributions to the 1D-IR spectrum into two frequency dimensions, which provides information on the correlations, anharmonicities, and exchange dynamics between all vibrational modes encompassed by the bandwidth of the laser pulses [194,230,231]. This additional information is necessary to monitor thermal chemical reactions with ultrafast precision.

For example, Fayer and coworkers recently reported direct dynamics measurements of carbon-carbon single-bond rotation [61], and in similar experiments several groups have observed the complexation and dissociation of solute-solvent complexes [57-59]. These experiments use 2D-IR spectroscopy to vibrationally tag a specific, localized vibrational mode and monitor its shift in frequency as the system undergoes chemical dynamics. Here we demonstrate a conceptually different experiment on $\text{Fe}(\text{CO})_5$. We are imparting vibrational energy into a specific but delocalized vibrational mode and monitoring how that energy is distributed between the delocalized modes as the molecule crosses a transition state. Quantification of this energy exchange provides direct information on the time-scale, transition state, and consequently, mechanism of the reaction.

7.2 Experimental results and analysis

$\text{Fe}(\text{CO})_5$ has two IR active vibrational modes involving the stretch of the CO ligands. For the D_{3h} symmetry of $\text{Fe}(\text{CO})_5$, these absorptions correspond to a doubly degenerate e' band and an a_2'' band, respectively at 1999 and 2022 cm^{-1} in *n*-dodecane solution (Figure 7.1A). Density functional theory (DFT) vibrational frequency calculations¹⁷ yield CO displacements for the a_2''

¹⁷ DFT calculations were performed at the BP86 level using the basis sets 6-31+g(d) for C and O and LANL2DZ for Fe with the program Gaussian 03.

and e' modes as illustrated in Figure 7.1B. The e' mode involves nearly exclusive vibration of the three equatorial CO groups whereas the a_2'' mode involves vibration of the axial CO groups.

Figure 7.1 (A) Room-temperature (25 °C) FTIR spectrum (solid line) of $\text{Fe}(\text{CO})_5$ in *n*-dodecane and spectrum at 100 °C (dashed line) (B) Depiction of the approximate eigenvectors for the a_2'' and doubly degenerate e' vibrational modes of $\text{Fe}(\text{CO})_5$.

In principal, fluxionality can cause the coalescence and collapse of the two IR absorptions into a single peak, analogous to the coalescence of line shapes observed in NMR spectra. The frequency of exchange must be comparable to the frequency separation of the absorption bands, which is ca. 1 ps^{-1} for these absorptions. The Fourier transform (FT) IR spectrum at 100 °C shows some evidence of coalescence relative to the room temperature spectrum (Figure 7.1A), but it is unclear if the changes in line shape are the result of exchange or homogenous broadening (see Figure 7.5 and Section 7.3). The boiling point (103 °C) and thermal instability of $\text{Fe}(\text{CO})_5$ prevent acquisition of spectra at sufficiently high temperatures to conclusively observe IR coalescence. Nevertheless, several examples of this phenomenon have been reported and attributed to fast exchange [60,232,233], yet the true physical origin of the effect has been debated in some instances [234]. The 2D-IR spectra reported below, however, show strong evidence for the time-scale of fluxionality and exchange in room-temperature solution and highlight the advantage of 2D-IR as a more general method of observing IR exchange, analogous to the advantages of 2D-NMR over conventional NMR spectroscopy [235].

The experiment proceeds as follows. First, a narrowband IR laser pulse selectively excites one of the two vibrational bands in $\text{Fe}(\text{CO})_5$, promoting it from the $v = 0$ to $v = 1$ vibrational level. Second, a fixed time elapses (referred to as the waiting time, T_w) to allow the

molecule to exchange axial and equatorial ligands. Third, a broadband IR laser pulse probes the sample, and the resulting absorption spectrum reflects how the vibrational energy imparted by the first pulse has been redistributed between the vibrational modes. The relative polarization between the two laser pulses is set to the magic angle (54.7°) to avoid effects from rotational diffusion. This setup, based on a pump-probe style experiment [104], gives a time resolution of ca. 1 ps and eliminates many of the coherence transfer effects which are observed in heterodyne-detected photon echo 2D-IR experiments [230].

2D-IR spectra of $\text{Fe}(\text{CO})_5$, normalized to the strongest peak at each T_w , are displayed in Figure 7.2 for T_w of 2 ps, 7.5 ps, and 20 ps, and spectra acquired at additional T_w are provided in Figure 7.7. The vertical axis represents the frequency of the narrowband IR pulse used to selectively excite vibrational modes, and the horizontal axis represents the change in absorbance resulting from this excitation after the waiting time T_w . Interpretation of this type of spectrum has been discussed extensively [194]. Negative signals are shown in blue and appear along the diagonal at (2022, 2022) and (1999, 1999), which correspond to the 0-1 transition frequencies for the a_2'' and e' modes, respectively. Shifted down in frequency along the horizontal axis from the diagonal are positive peaks shown in red, corresponding to the 1-2 transition frequencies. These peaks are shifted off the diagonal by the anharmonicity of the vibrational potential. Note that the 0-1 peaks result both from bleaching of the ground state and stimulated emission from the excited state whereas the 1-2 peaks result from only $v = 1$ to $v = 2$ transitions [109]. Unlike 2D-IR experiments on solute-solvent complexes [57,59], all vibrational modes in these spectra share one common ground state level, and as a result, the exchange dynamics apparent in both the 0-1 and 1-2 signals only reflect dynamics in the excited vibrational states. The following analysis uses kinetic data from the 0-1 signal because these absorption line shapes are narrower and clearly defined on the diagonal and off-diagonal.

A significant shift in the peak intensities is observed between $T_w = 2$ and 7.5 ps (Figure 7.2B). The most noticeable change is the increase in intensity at the cross peak positions, labeled as triangles in panels A to C. Several factors affect the relative intensities of peaks in 2D spectra, and cross peaks typically arise from anharmonic coupling between vibrational modes. In order to predict the intensity of anharmonic cross peaks between the a_2'' and e' modes, DFT anharmonic frequency calculations [121] were performed, giving an anharmonicity of 0.6 cm^{-1} between the two modes. Because the anharmonic shift is much smaller than the vibrational line widths, the contribution of these peaks to the 2D spectra is present but relatively minor. Vibrational relaxation may also contribute to changes in the peak intensities [236]; however, vibrational relaxation of the CO stretches occurs on a much longer time scale (ca. 150 ps, Figure 7.6) than

the values of T_w in Figure 7.2 and does not affect the interpretation of the spectra, as discussed further in Section 7.4.

Figure 7.2 Contour plots of experimental 2D-IR spectra (top row) for $\text{Fe}(\text{CO})_5$ in *n*-dodecane at room temperature (18 °C) acquired at waiting times of $T_w = 2$ ps (A), 7.5 ps (B), and 20 ps (C). Simulated 2D-IR data for the same waiting times are shown in the bottom row; panels D, E, and F, respectively. The data are normalized to the maximum absorption at each T_w , which corresponds to the negative absorption (blue) of the e' vibrational mode (see Figure 7.6 for the absolute magnitude of this absorption), and contour lines represent a 10% change in absorption intensity. Diagonal peaks are marked by circles and off-diagonal peaks by triangles in panels A to C. Arrows in panel B represent vibrational energy exchange. Simulations (panels D to F) include energy exchange from a pseudo-rotation with a time constant of 8 ps, and details of the simulation parameters are provided in the SOM.

The change in intensity at the diagonal and cross peak positions is attributed to vibrational energy transfer between the CO normal modes as $\text{Fe}(\text{CO})_5$ crosses the transition state. Panels D to F of Figure 7.2 show simulated 2D-IR spectra using DFT calculated anharmonic parameters (including the cross anharmonicity of 0.6 cm^{-1}) and assuming energy exchange (as described below) between the vibrational modes. The simulated spectra qualitatively reproduce the experimental data, indicating that the changes in peak intensity do result from vibrational energy transfer.

Figure 7.3 (A) Ratio of 2D-IR off-diagonal to diagonal peak intensity at room temperature (18 °C) as a function of the waiting time T_w for selective excitation of the e' band (squares) and a_2'' band (diamonds). Ratios are calculated from Lorentzian fits to one-dimensional horizontal slices of the 2D-IR spectra using the intensities for peaks marked by circles and diamonds in Fig. 2. Solid lines are simulations assuming energy exchange due to the pseudo-rotation; a single time constant of 8 ± 0.6 ps gives the best fit for both curves. (B) The distribution of the number of transition state crossings as a function of the waiting time T_w for a fluxional process with a kinetic time constant of 8 ps

The most straightforward manner to see the energy exchange in the experimental data is to plot the ratio of off-diagonal (triangles) to diagonal (circles) peak intensities for the two horizontal slices of the 2D-IR spectra at $\omega_{\text{pump}} = 1999$ and 2022 cm^{-1} . Data were collected for a range of waiting times T_w between 2 and 40 ps, and Figure 7.3A displays these ratios as a function of T_w . For excitation of the a_2'' band, the ratio rises to an asymptotic value of 2, and for excitation of the e' band to an asymptotic value of 0.5.

In order to quantitatively understand the vibrational energy transfer and asymptotic values shown in Figure 7.1A, the details of the molecular rearrangement must be considered. R. Stephen Berry proposed a pseudo-rotation mechanism for this type of trigonal bipyramidal complex: the D_{3h} equilibrium structure rearranges to a transition state with C_{4v} symmetry and then returns to the D_{3h} structure [228,237]. In the process, the two axial ligands are exchanged with two equatorial ligands at the transition state and the molecule appears to have rotated by 90° . We have modeled this mechanism with DFT calculations of the intrinsic reaction coordinate [238],

with the results shown in Figure 7.4A. The calculations give an electronic energy barrier of 2.13 kcal/mol.

In order to model the vibrational energy transfer observed in the 2D-IR spectra, we first assume the delocalized normal modes of $\text{Fe}(\text{CO})_5$ can be expressed as linear combinations of the individual, localized CO stretch displacements (7.1):

$$|n\rangle = \sum_{j=1}^5 |\text{CO}_j\rangle \langle \text{CO}_j | n \rangle \quad (7.1)$$

where $|n\rangle$, $n = 1 \dots 5$, represents the five harmonic normal modes composed of CO stretches and $|\text{CO}_j\rangle$, $j = 1 \dots 5$ represents the displacement vector of the j th CO group. Neglecting changes in this displacement vector as the CO groups change position (i.e. neglecting changes in the local mode force constants and wavefunctions), the initial normal mode $|n_i\rangle$ before rearrangement of the molecule can be expressed as a superposition of the normal modes $|n_f\rangle$ after rearrangement as in eq. 7.2,

$$|n_i\rangle = \sum_{n_f=1}^5 |n_f\rangle \sum_{j=1}^5 \langle n_f | \text{CO}_j \rangle \langle \text{CO}_j | n_i \rangle, \quad (7.2)$$

where the individual CO groups $|\text{CO}_j\rangle$ retain their label j as they rearrange. This analysis was performed assuming the pseudo-rotation mechanism by projecting the initial CO normal modes, including the two IR inactive a_1' modes, onto the C_{4v} transition state and then onto the rearranged D_{3h} structure using the DFT calculated vibrations. The results are summarized schematically in Figure 7.4B, where the states $|n\rangle$ are labeled by their corresponding symmetries, and coefficients, as calculated from eq. 7.2, are provided in front of these labels. Note that the irreducible representations and projections for the vibrations would be different for transition states with different symmetries.

In order to model vibrational energy transfer, we need the probability that the initial vibration $|n_i\rangle$ will transfer energy into a final normal mode $|n_f\rangle$, which is given by eq. 7.3,

$$P_{n_i \rightarrow n_f} = \left| \sum_{j=1}^5 \langle n_f | \text{CO}_j \rangle \langle \text{CO}_j | n_i \rangle \right|^2, \quad (7.3)$$

and these values are given in the far right column of Figure 7.4B as percentages. Based on these values, we have simulated energy transfer in $\text{Fe}(\text{CO})_5$ using a simple deterministic rate law governed by one rate constant k , the rate of crossing the barrier in the fluxional reaction. The rate of transferring energy from one initial mode into a final vibrational mode is given by eq. 7.4,

$$k_{n_i \rightarrow n_f} = P_{n_i \rightarrow n_f} \times k, \quad (7.4)$$

and the kinetics for energy transfer among all the normal modes have been calculated using standard finite difference methods [239].

Figure 7.4 (A) Depiction of the mechanism and energetics of a pseudo-rotation plotted as a function of the bond angle (C–Fe–C) between one axial and one equatorial CO ligand which exchange during the pseudo-rotation. Circles are DFT calculated energies along the intrinsic reaction coordinate, which gives a barrier height of 2.13 kcal/mol. Symmetry labels for the molecule as it passes over the barrier are provided above the structures. (B) The splitting of the vibrational modes, denoted by their symmetry labels, as the molecule crosses the transition state. The irreducible representation, Γ_{CO} , for vibrations of the CO groups is given at the top of each column. The individual vibrational modes in the starting structure becomes a superposition of vibrational modes in the transition state and then again in the final rearranged structure, with the coefficients given for each mode in the superposition. The mixing is limited to those modes which are allowed to mix by symmetry. The final distribution of energy after one cross over the transition state is shown on the far right in percentages.

Based on this analysis, 2D-IR data were simulated with energy transfer included as shown in Figure 7.2 panels D to F. In addition, the ratios of off-diagonal to diagonal peak intensity, which directly reflect the relative populations of the e' and a_2'' vibrational modes, were simulated using this model. The best agreement with the experimental data at room temperature (18 °C) was achieved with a time constant of 8.0 ± 0.6 ps, or equivalently $k = 1/8 \text{ ps}^{-1}$, and details of the procedure used to simulate and fit the data are provided in Section 7.5.2. The results of the simulation are shown as solid lines through the data in Figure 7.3A. The good agreement of the simulations with the experimental data suggests that this model is sufficient to describe the vibrational energy exchange.

Both the simulations and experimental data show that the initial vibrational excitation rapidly reaches an equilibrium between the two IR active vibrational modes. Because there are two degenerate e' modes and only one a_2'' mode, this equilibration causes the off-diagonal to diagonal ratios in Figure 7.3A to asymptotically approach the values $2 e' : 1 a_2''$. If the molecules crossed the transition state only once, we would expect the asymptotic values would instead reflect the percentages in Figure 7.4B. This case would be expected for reactions in which the product is thermodynamically stable compared to the reactant. In this experiment, however, the reactant and product are energetically equivalent and the barrier to the transition state is low, allowing the molecules to cross the transition state multiple times.

We have estimated the distribution of transition state crossings as a function of the waiting time T_w using Gillespie's Monte-Carlo algorithm to model the reaction as a stochastic process within the Markov approximation [239,240]. The distribution is displayed in Figure 7.3B and shows that within 8 ps, approximately 25% of the molecules have crossed the transition state two or more times. Multiple crossings allow the fast exchange of energy between the vibrational modes and cause complete equilibration of the energy within a few crosses of the transition state. The rate of equilibration depends both on the rate of the fluxional reaction and the details of the energy redistribution, which are determined by the transition state symmetry and, hence, mechanism of the rearrangement.

Although the pseudo-rotation has been widely accepted as the most likely mechanism for fluxionality in trigonal bipyramidal complexes like $\text{Fe}(\text{CO})_5$, other possibilities have not been ruled out [241]. The analysis of 2D-IR data described above requires the assumption of a mechanism and a transition state geometry in order to simulate the energy transfer process. To explore alternative pathways, we simulated data for a different fluxional mechanism in which one axial CO and two equatorial CO groups execute a twist motion, resulting in the exchange of one axial and one equatorial ligand. This mechanism predicts different energy exchange dynamics

than the pseudo-rotation mechanism, the details of which are provided in Section 7.5.3. We found that reasonable agreement with the experimental data at room temperature (18 °C) could be achieved only with a much shorter time constant of 3.5 ± 0.4 ps for the twist rearrangement. The difference in time constant between the twist and pseudo-rotation mechanisms demonstrates that the experiment is sensitive to the mechanism, but because of fast multiple crossings, the data at room-temperature alone do not definitively support just one mechanism. Experiments at different temperatures, however, provide the additional data necessary to rule out the twist mechanism.

2D-IR data were collected at two additional temperatures and a kinetic analysis based on a pseudo-rotation was performed at all three temperatures, giving time constants of 8.0 ± 0.6 ps at room temperature (18 °C), 6.3 ± 0.8 ps at 50 °C, and 4.6 ± 0.4 ps at 90 °C. An Arrhenius plot of the data (Figure 7.9) gives a straight line with an activation energy of 1.6 ± 0.3 kcal/mol. This result is in reasonable agreement with the barrier for the pseudo-rotation mechanism calculated by DFT (2.13 kcal/mol). In contrast, our DFT calculations on the twist mechanism, detailed in the Section 7.5.3, indicate that the barrier for this type of rearrangement is at least one order of magnitude greater than the pseudo-rotation mechanism.

The Arrhenius plot not only further confirms the pseudo-rotation mechanism, but also demonstrates that the energy transfer results from a barrier crossing process and not intramolecular vibrational relaxation (IVR) caused by anharmonic coupling between the modes. IVR typically occurs on a time scale of picoseconds and could potentially compete with fluxionality as the cause of energy exchange between the e' and a_2'' modes. The rate of IVR depends on the strength of the coupling as well as the existence of liquid phonons (instantaneous normal modes of the solvent) at the frequency of the energy mismatch between the modes (22.8 cm^{-1}), which serve to receive or supply the energy difference [242,243]. At higher temperatures, an increase in the population of low frequency phonons around 22.8 cm^{-1} may increase the rate of IVR. Because this frequency is low compared to the thermal energy in these experiments ($200\text{--}260\text{ cm}^{-1}$), the population will increase relatively little with temperature. Between 18 and 90 °C, we would expect the IVR rate to increase by $\sim 26\%$ (see Section 7.6 for a description of this estimate), yet we observe a change in rate three times greater over this temperature range. IVR is also not supported by the DFT calculations, which predict a weak coupling between these modes (0.6 cm^{-1}) in comparison to other documented examples of IVR [230,244]. The 2D-IR data thus strongly support a fluxionality mechanism in which $\text{Fe}(\text{CO})_5$ exchanges CO groups and vibrational energy through the C_{4v} transition state of the pseudo-rotation mechanism on a time-scale of 8 ps.

In extending the present technique to other systems, the interpretation of the data should

be especially straightforward in cases where the system crosses the transition state only once. Even in more complex cases, we anticipate broad applications toward solution phase transition state characterization of both thermal and photoinitiated reactions.

7.3 FTIR analysis

7.3.1 Data analysis

Fits to the FTIR and 2D-IR experimental data were performed using the Nelder-Mead simplex algorithm to iteratively find the best fit parameters by the method of least squares [245]. For fits of the 2D-IR data (e.g. Figure 7.3A), errors were calculated with a bootstrap fitting method in which the experimental data was simulated 500 times using a Monte Carlo method to sample each data point within a Gaussian distribution determined by the standard deviation calculated from five or more repeated measurements. Each simulation was then fit as described in Section 7.5.2 using the simplex algorithm. The resulting distribution of best fit parameters was fit to a Gaussian distribution, and cited errors are two standard deviations corresponding to this Gaussian distribution. The errors represent uncertainty resulting from noise in the experimental data and are not meant as an estimate of any systematic error in the analysis.

The IR pump-probe data (Figure 7.6A) was fit to single exponential function convoluted with a Gaussian function (full-width at half maximum (FWHM) of 200 fs) to accurately reflect the instrument response function. The Levenberg-Marquet least squares algorithm was used to find the best fit parameters, and the cited error corresponds to one standard deviation.

7.3.2 Temperature-dependent FTIR spectra

The coalescence of absorption lines in nuclear magnetic resonance (NMR) spectroscopy has been observed for many compounds, yet the coalescence of absorptions in linear IR spectra has been observed in only a handful of instances. Most recently, Hochstrasser and coworkers reported IR spectra of acetonitrile dilute in methanol, a system which undergoes hydrogen bond exchange on the picosecond time-scale [60]. At low temperatures (-17 °C), the CN stretch on acetonitrile gives rise to two peaks corresponding to hydrogen-bonded and non-hydrogen bonded molecules. At high temperatures (80 °C), however, these two peaks coalesce in both the linear and 2D-IR spectra due to fast hydrogen bond exchange. In a very different system, Kubiak and coworkers observed the coalescence of FTIR absorptions on trinuclear ruthenium clusters which undergo rapid intramolecular electron transfer between the metal centers [232,246]. The electron transfer causes a coalescence of the absorptions for the CO groups on the metal centers, and this effect was used to extract the rates of intramolecular electron transfer in these systems. The rapid

fluctuation of hydrogen bonds or transfer of electrons are both distinctly different physical processes than fluxionality, yet all three can significantly affect the IR spectra under the proper conditions.

The only example of IR coalescence resulting from fluxionality (of which we are aware) is for the complex $\text{Fe}(\text{CO})_3(\eta^4\text{-1,5-cyclooctadiene})$, the linear IR spectrum of which has been reported several times [233,247-251]. Grevels, McClung, and coworkers modeled the changes in lineshape with temperature in terms of exchange and were able to extract rate constants for the exchange process by systematically fitting the spectra at multiple temperatures. Nevertheless, it has been debated whether the changes in lineshape can be equally well explained by other physical processes [234]. Here we report an analysis on the linear IR spectra of $\text{Fe}(\text{CO})_5$ which highlights the limitations of linear IR spectroscopy and the advantage of 2D-IR spectroscopy as a more general method of observing IR exchange.

FTIR spectra in the CO stretching region of $\text{Fe}(\text{CO})_5$ were measured at several temperatures between 25 and 150 °C and are shown in Figure 7.5A normalized to the intensity of the ν vibrational mode of $\text{Fe}(\text{CO})_5$. Above 100 °C, the sample was not stable due both to the boiling point (103 °C) and thermal instability of $\text{Fe}(\text{CO})_5$. Nevertheless, the sample temperature was ramped at a sufficient rate (ca. 10 °C per minute) to collect FTIR spectra at 125 and 150 °C before decomposition of the sample. We were unable to collect a spectrum at 175 °C. The FTIR spectra show progressive changes as the temperature is raised, with the most notable change the increase in absorption intensity between the two vibrational bands. This effect is typical for absorption bands beginning to show coalescence but may also be due to an increase in the homogeneous line width resulting from an increase in the rate of vibrational dephasing with temperature.

In order to quantitatively understand the changes in line shape, the FTIR spectra at each temperature were fit to two Lorentzian functions, with the best fit curves shown in Figure 7.5B. The FTIR spectra were also simulated in the presence of fast exchange following the method outlined by Grevels, McClung, and co-workers for purely homogeneous broadening [233]. DFT calculations were used to supply the fixed parameters necessary for the simulation procedure. The best fit simulations were achieved using an iterative procedure (refer to Section 7.3.1) in which all variables (center frequencies, dephasing rates, intensities, and exchange rate) were adjustable, and these curves are shown in Figure 7.5C. The iterative routine typically produced exchange rate constants on the order of 0.1 ps^{-1} , but we do not cite exact numbers or errors due to the potentially large systematic error in this procedure.

Figure 7.5 Temperature dependent FTIR spectra of $\text{Fe}(\text{CO})_5$ in *n*-dodecane (A), the best fits of the data to two Lorentzian functions (B), and the best fits of the data including the effects of coalescence due to exchange of the carbonyl groups by a pseudo-rotation mechanism (C). All spectra are normalized to the peak of the e' vibrational mode.

Comparing the Lorentzian fits (Figure 7.5B) with the exchange simulations (Figure 7.5C), both models appear to adequately reproduce the experimental data. It is useful to note that the Lorentzian fits are equivalent to an exchange simulation with an exchange rate constant of zero. The similarity of the two simulations highlights the difficulty in using linear IR spectroscopy alone to understand the exchange dynamics underlying these lineshapes. The changes with temperature are subtle, and without data over a broad range of temperatures sufficient to show complete coalescence of the two bands into one, it is not possible to extract accurate information on the exchange dynamics.

Despite the limitations of linear IR spectroscopy, 2D-IR spectroscopy, even at one single temperature, provides direct information on the exchange dynamics and gives conclusive evidence that exchange is a real and importance process on the IR time-scale. The 2D-IR data indicate that exchange occurs on a time-scale less than 10 ps, which is sufficiently rapid to contribute to the changes in FTIR lineshape in Figure 7.5A. Thus, the most physically reasonable method to quantitatively understand the line shapes are through models which include effects of exchange (Figure 7.5B). These results also imply that the analysis given by Grevels et al. for the line shapes of $\text{Fe}(\text{CO})_3(\eta^4\text{-1,5-cyclooctadiene})$ is physically sound and could be further confirmed with 2D-IR spectroscopy.

7.4 Effects of vibrational relaxation

In this work we analyze changes in the 2D-IR spectra of $\text{Fe}(\text{CO})_5$ in terms of fluxionality, however, vibrational relaxation processes may also give rise to dynamics in 2D-IR spectra and these possibilities are addressed below. For clarity, we separately address two different processes:

population relaxation of quanta in the CO stretch vibrational modes and population transfer between the CO stretch vibrational modes.

7.4.1 Population Relaxation

The CO stretches of organometallic complexes typically relax on a time-scale of many tens of picoseconds to hundreds of picoseconds [244,252-254]. For $\text{Fe}(\text{CO})_5$, the e' and a_2'' modes relax on a time-scale of ca. 150 ps by transferring energy into the lower frequency modes of the molecule and ultimately into the solvent, which is a standard paradigm for vibrational relaxation in the condensed phase [242,255]. Figure 7.6A shows kinetic data for the e' vibrational mode from broadband IR-pump, IR-probe experiments on $\text{Fe}(\text{CO})_5$ in *n*-hexane. The data are well fit to a single exponential decay with a time constant of 154 ± 7 ps. The a_2'' vibrational mode decays on a similar time-scale of 156 ± 10 ps. It is not surprising that the two vibrational modes exhibit nearly identical population relaxation times because these modes efficiently exchange energy on a much faster time-scale than population relaxation.

This relaxation process causes a decay in the amplitude of the 2D-IR spectra with increased T_w . The 2D-IR spectra in Figure 7.2 are normalized with respect to the maximum absorption at each T_w (the e' diagonal absorption) and this normalization eliminates the decay in amplitude from population relaxation. The kinetics of the e' diagonal absorption used for normalization are shown in Figure 7.6B in order to provide a quantitative measure of the decay in the signal amplitude. The magnitude of the absorption rises on a time-scale limited by the laser pulse and then initially decays due to energy transfer out of this mode as a result of fluxionality. The longer decay is the same decay observed in Figure 7.6A and results from population relaxation of the CO stretches into lower frequency vibrations. Note that on the time-scale of fluxionality (8 ps), approximately 5% of the vibrational energy initially imparted in the CO stretch vibrations has undergone population relaxation to the lower frequency vibrational modes.

Figure 7.6 (A) Vibrational population relaxation kinetics of the e' CO vibrational mode at 2000 cm^{-1} from broadband IR pump-probe data of $\text{Fe}(\text{CO})_5$ in n -hexane. Solid line represents a single exponential fit to the data with a time constant of $154 \pm 7\text{ ps}$. (B) Kinetics of the negative diagonal peak for the e' vibrational mode of $\text{Fe}(\text{CO})_5$ in n -dodecane from 2D-IR data at room temperature (18°C).

In order to understand the 2D-IR data in terms of fluxionality, we analyze the ratio of the off-diagonal to diagonal intensity for the negative signals of the a_2'' and e' vibrational modes as a function of waiting time. If population relaxation of these two modes occurred on a time-scale competitive with the energy transfer process and if the rates of vibrational relaxation were different for the two modes, then this ratio would not necessarily eliminate effects from population relaxation. Fortunately, neither of these two cases is true for $\text{Fe}(\text{CO})_5$, and the ratio is thus a convenient measure of the energy transfer process and can be modeled without needing to include the effects of population relaxation.

Because population relaxation of the CO stretching modes populates lower frequency modes in the molecule, this process can cause additional changes in the cross peaks of the CO stretches if the lower frequency modes are strongly coupled to the CO vibrations. Rubitsov and coworkers recently reported this effect in a small organic molecule and stressed its potential importance for enhancing cross peak intensities at long T_w [236]. We do not observe this effect in $\text{Fe}(\text{CO})_5$ for two reasons. First, the CO stretches in $\text{Fe}(\text{CO})_5$ relax on a relatively long 150-ps time-scale (Figure 7.6A) while the lower frequency modes for organometallic complexes have been shown to relax by transferring energy to the solvent on a shorter time-scale of ca. 50 ps or less [253,256]. The fast relaxation of the low frequency modes in comparison to the high frequency CO stretches prevents vibrational energy from building up in them; thus, the modes do not have sufficient population to strongly contribute to the 2D-IR spectra. Second, as discussed

by Rubitsov, this effect can be observed in 2D-IR spectra as a shift in the cross peak positions. Cross peaks resulting from the anharmonicity between vibrational modes appear in pairs, with one positive and one negative peak. The separation between these two peaks is determined by the magnitude of the anharmonic coupling between the vibrational modes and the line width of the absorptions. In the case discussed by Rubitsov, vibrational relaxation populates new vibrational modes with smaller magnitude anharmonic coupling and this difference manifests itself as a decrease in the separation between the negative and positive peak pair. In contrast, we do not observe any change in this separation in the 2D-IR spectra of $\text{Fe}(\text{CO})_5$. Figure 7.7 shows 2D-IR spectra at seven different waiting times, and the separation between the positive and negative signals of the two cross peaks is preserved at all T_w , a strong indication that lower frequency modes are not contributing to the spectra. This observation is especially apparent through a comparison of panels E and G of Figure 7.7, which depict spectra collected at T_w separated by 25 ps but which appear nearly identical. In addition, the negative and positive signals of the two cross peaks appear at exactly the same horizontal positions (probe frequency) as the diagonal peaks vertically displaced from them. This observation is a firm indication that the separation of the negative and positive signals of each cross peak result from the diagonal anharmonicity of the vibrational modes (just like the vertically displaced diagonal peaks) rather than off-diagonal anharmonic coupling between different vibrational modes. Thus, it seems clear that the cross peaks result solely from vibrational energy transfer between the CO stretching vibrations of $\text{Fe}(\text{CO})_5$ and vibrational relaxation into lower frequency modes is not important for understanding the dynamics observed in the spectra.

Figure 7.7 2D-IR spectra of $\text{Fe}(\text{CO})_5$ acquired at waiting times of $T_w = 2$ ps (A), 5 ps (B), 7.5 ps (C), 10 ps (D), 15 ps (E), 20 ps (F), and 40 ps (C). The data are normalized to the maximum absorption at each T_w , which corresponds to the negative absorption (blue) of the e' vibrational mode (see Figure 7.6 for the absolute magnitude of this absorption), and contour lines represent a 10% change in absorption intensity. The spectra shown in Fig. 2 are reproduced here for easy comparison.

7.4.2 Population transfer

There are only a handful of examples of fast vibrational energy transfer between the carbonyl vibrations of organometallic complexes in the literature [194,230,244,254,257-259]. A rigorously documented example is $\text{Rh}(\text{CO})_2(\text{acac})$ (RDC; $\text{acac} = \text{C}_5\text{H}_7\text{O}_2$) which has been studied with ultrafast spectroscopy by several groups [194,230,244,259]. Tokmakoff and coworkers analyzed the 2D-IR spectra of RDC and thoroughly analyzed both coherence transfer and population transfer between the symmetric and asymmetric stretches of the two carbonyls [230]. Note that this 2D-IR study used a fully coherent three-pulse Fourier transform technique in which the transfer of a coherence between vibrational modes during the two coherence times affects the 2D-IR spectra. In contrast, the pump-probe 2D-IR spectroscopy used here on $\text{Fe}(\text{CO})_5$ does not show the effects of coherence transfer because the bandwidth of IR pump pulse is sufficiently narrow that a vibrational population cannot be created following a coherence transfer event; thus, the coherence transfer does not affect the third-order polarization signal acquired by frequency-resolved heterodyne detection of the IR probe pulse. This pump-probe technique is, however, sensitive to population transfer in exactly the same manner as the fully coherent three-pulse

Fourier transform 2D-IR spectroscopy.

Tokmakoff and coworkers observed population transfer between the symmetric and asymmetric stretch of RDC on a time-scale of 3 ps, an effect which had also been observed earlier with IR-pump, IR-probe measurements [244]. It is difficult to determine whether fluxionality might be relevant to this system without further investigation, but we assume the energy transfer is purely a result of IVR. The question arises if this time-scale of a few picoseconds is general to organometallic complexes such as $\text{Fe}(\text{CO})_5$ or if RDC is a case of unusually efficient IVR. The anharmonicity between the symmetric and asymmetric stretches of RDC was experimentally measured to be 26 cm^{-1} [194] whereas the calculated anharmonicity for the e' and a_2'' modes of $\text{Fe}(\text{CO})_5$ is a drastically smaller 0.6 cm^{-1} . Note that the anharmonicity of RDC has also been calculated from DFT giving a value of 20.3 cm^{-1} [260], which is in good agreement with experiment. Because the third-order and higher anharmonic terms in the nuclear potential energy are responsible for IVR processes, the small magnitude of the coupling between the modes in $\text{Fe}(\text{CO})_5$ suggests that energy transfer should be significantly slower in comparison to RDC [242].

There are two key differences between RDC and $\text{Fe}(\text{CO})_5$, which provide simple and intuitive reasons for the differences in the anharmonicities of the CO vibrations for these molecules. First, the symmetric and asymmetric stretches of RDC are exactly localized on the same two CO ligands whereas the e' and a_2'' modes of $\text{Fe}(\text{CO})_5$ are each localized on different sets of CO ligands. Using the squares of the coefficients of the local mode projection of these vibrations as described in eq. 7.1, the DFT calculations indicate that the e' and a_2'' modes are each greater than 99.9% localized on the equatorial and axial CO ligands, respectively. The difference in spatial overlap of the vibrational modes helps to explain why the anharmonicity for the IR active CO stretches in these two systems is different by more than an order of magnitude. Second, the metal and ligand bonding in RDC and $\text{Fe}(\text{CO})_5$ provide some additional insight additional into the differences of these systems. In RDC, the σ -bonding of the two equivalent carbonyls to the metal occurs through the same set of metal orbitals of d , s , and p character. In $\text{Fe}(\text{CO})_5$ on the other hand, the σ -bonding of the axial and equatorial carbonyl groups occurs through different metal d -orbitals, primarily d_{z^2} for the axial CO groups and $d_{x^2-y^2} / d_{xy}$ for the equatorial CO groups [261]. The axial and equatorial CO groups both participate in π back-bonding with the same metal d_{xz} / d_{yz} orbitals, which provides a weaker mechanism for coupling than would be provided by direct σ -bonding with the same set of metal orbitals as is the case in RDC.

Despite the differences in the bonding and vibrational modes of RDC and $\text{Fe}(\text{CO})_5$, we are still left to consider a system-bath interaction in which the bath serves to couple the two

modes and also accepts the energy difference, or mismatch, between the CO stretch modes. For RDC, Tokmakoff and coworkers propose that the acac ring in the molecule serves as the “bath” to couple the two vibrational modes, and there is clearly no equivalent for Fe(CO)₅. The lowest calculated vibrational frequency in Fe(CO)₅ is 53 cm⁻¹, well above the energy mismatch (22.8 cm⁻¹) between the e' and a₂'' modes. Instead, the solvent, *n*-dodecane, must serve as the bath in this system. Recent studies have suggested that solvent-assisted IVR, another term which could be used for population transfer with participation of the solvent, is an extremely physically localized process. Pate and coworkers analyzed the IVR dynamics of the acetylenic C–H stretch of a series of progressively larger terminal acetylenes and, as one conclusion, determined that solvent-induced energy relaxation only occurs in close physical proximity to the excited vibrational state [262]. These results suggest that solvent-assisted IVR is less likely to occur in Fe(CO)₅ because the e' and a₂'' vibrational modes are localized on different sets of CO groups. While this consideration does not preclude the energy transfer mechanism, it does indicate the process would be slower than if the vibrations were delocalized over the same set of CO groups.

The considerations outlined in the preceding paragraphs do not definitively prove that solvent-assisted IVR is not occurring in Fe(CO)₅. Rather, these considerations are only meant to provide a qualitative argument that IVR in this system is likely to occur on a longer time-scale than has been observed previously in RDC and on a longer time-scale than fluxionality. We have found that we can fully simulate and understand the 2D-IR data without including IVR. In addition, we have examined the temperature dependence of vibrational energy exchange and found that it is in better agreement with fluxionality than IVR, as detailed in Section 7.6.

7.5 Simulations

7.5.1 2D-IR spectra

The 2D-IR spectra in Figure 7.2 were simulated assuming purely Lorentzian line shapes as given by Lorentzian fits to the room-temperature FTIR spectrum shown in Figure 7.1A. This FTIR spectrum is well fit to two Lorentzian functions centered at 1999 and 2022 cm⁻¹ with FWHM of 6.3 cm⁻¹ and 4.0 cm⁻¹, respectively, indicating that the a₂'' and e' peaks are primarily homogeneously broadened. As a result, the 2D-IR spectra should not exhibit any changes attributable to spectral diffusion since these effects result from the sampling of frequencies within an inhomogeneously broadened distribution of frequencies. For off-diagonal contributions to the spectra, harmonic scaling of the intensities and line widths was assumed. Anharmonic parameters were included in the simulations as calculated by DFT anharmonic frequency calculations [121] for the anharmonicities of each individual mode ($\chi_{a_2''} = -6.0$ cm⁻¹; $\chi_{e'} = -6.0$ cm⁻¹) and between

the different modes ($\chi = 0.6 \text{ cm}^{-1}$) and between the two degenerate e' modes ($\chi = -7.9 \text{ cm}^{-1}$). All peaks resulting from vibrational anharmonicity were included in the simulations appropriately scaled relative to the diagonal peaks to account for their relative contribution to the third-order polarization signal.

Vibrational energy exchange was also included in the simulation of the 2D-IR spectra, causing changes in relative intensities of the diagonal and off-diagonal peaks as a function of the waiting time T_w . The kinetics of the vibrational energy exchange were simulated using eq. 7.4 and standard finite difference methods [239], and the kinetic simulation included convolution with the experimental time resolution of 1 ps. Based on the energy transfer predicted by this kinetic model, the relative intensities of the diagonal and off-diagonal peaks were scaled up or down as appropriate and the intensities of all anharmonic peaks were recalculated accordingly. Spectra were generated by calculating the intensity on a two dimensional grid with a spacing of 0.5 cm^{-1} between each point. The data were then convoluted with the experimental spectral resolution along both frequency axes in order to allow direct comparison between the simulation and experimental data.

7.5.2 Kinetics of vibrational energy exchange

The kinetics of the energy exchange process were simulated using eq. 7.4 and standard finite difference methods [239]. The population of each vibrational mode beginning from time zero was updated in time steps of 50 fs assuming vibrational energy transfer into each mode at a rate defined by eq. 4. In order to account for the degeneracy of the e' vibrational modes, the energy between these two modes was equilibrated (i.e. divided equally) between the modes after each time step of the simulation. The result of this kinetic simulation was then convoluted with a single-sided exponential decay of 1 ps in order to accurately reflect the instrument response function and the time resolution of the 2D-IR experiment. This simulation was performed for different mechanisms by changing the values for $P_{n_i \rightarrow n_f}$ in eq. 7.4 as appropriate for the mechanism under consideration.

In order to determine the fluxionality rate constant k (see eq. 7.4) which best reproduces the experimental data, an iterative procedure was used to produce the best fit to the data. The simulations of vibrational energy exchange produce two data sets comparable to the experimental data, one in which the vibrational energy is initially in the a_2'' mode and a second in which the vibrational energy is initially in the e' mode. These two data sets asymptotically approach, at long T_w , values of $2 \text{ e}' : 1 \text{ a}_2''$ regardless of the mechanism (due to multiple crossings), and a plot of these ratios is directly comparable to the experimental data of the off-diagonal to diagonal ratios

(refer to Figure 7.3A). In order to find the rate constant k which best fits the experimental data for a given mechanism, an iterative fitting procedure was used in which k was varied until the best agreement with the data was achieved. This fitting procedure also includes a small scaling factor and offset for the simulation curves in order to account for the fact that the experimental off-diagonal to diagonal ratio is affected by relative absorption intensities and line widths. The scaling factor and offset for each curve along with one rate constant k (total of five parameters) were iterated to achieve the best fit with the experimental data. The reported time constants are equivalent to k^{-1} .

7.5.3 Twist mechanism

In order to verify that the 2D-IR method employed in this study is sensitive to the mechanism and transition state of the reaction, we have simulated the data for a twist type rearrangement of the CO ligands in $\text{Fe}(\text{CO})_5$, as shown in Figure 7.8. This particular twist rearrangement involves the motion of three adjacent CO groups, with one axial CO becoming equatorial, one equatorial CO becoming axial, and one equatorial CO shifting positions but remaining equatorial. As in the Berry pseudo-rotation mechanism, the reactant and product are chemically identical, and the mechanism is distinguished only by the transition state of the reaction, which defines the motion between reactant and product and defines which CO groups are exchanged during the process. We were unable to locate a transition state corresponding to this mechanism using DFT calculations; however, we were able to project the vibrations in the reactant directly onto the vibrations in the product as described by eq. 7.2, where the rearrangement of CO groups explicitly assumes the mechanism and transition state of the reaction. The coefficients for the projection are given in Figure 7.8, where the vibrational normal modes are labeled by their corresponding symmetries, analogous to Figure 7.4. The squares of these coefficients, as given by eq. 7.3, are given as percentages in the far right column of Figure 7.8 and represent the probability of vibrational energy transferring into the vibrational modes. Since this mechanism proceeds through a transition state of lower symmetry than the Berry pseudo-rotation, the vibrational energy transfer is not limited by symmetry considerations, and it is necessary to explicitly show energy transfer from each mode into all five other vibrational modes. The room-temperature experimental 2D-IR data was fit for this mechanism by the procedure described above (Section 7.5.2), and the best fit was achieved with a time constant of 3.5 ± 0.4 ps.

Figure 7.8 The splitting of vibrational modes and vibrational energy as predicted for a twist rearrangement of the CO groups in $\text{Fe}(\text{CO})_5$

In order to provide a rough estimate of the electronic energy barrier for a twist rearrangement of the CO ligands in $\text{Fe}(\text{CO})_5$, we constrained the structure to an approximate guess of the transition state geometry and performed a DFT geometry optimization and energy calculation with the constraints. The bond angles (C–Fe–C) between each exchanging CO group and the CO group it replaces were constrained to half the total change in bond angle required to complete the rearrangement. Thus for the three exchanging CO groups, the axial CO which

becomes equatorial was constrained to 45° , the equatorial CO which becomes axial was also constrained to 45° , and the equatorial CO which remains equatorial was constrained to 60° . These constraints produced a structure similar to the C_1 structure depicted in Figure 7.8. For the DFT calculations, all C–Fe–C bond angles were fixed while all other parameters (bond lengths, Fe–C–O bond angles) were optimized. The calculated energy of the constrained structure is 38.97 kcal/mol higher than the D_{3h} structure of $\text{Fe}(\text{CO})_5$.

In order to provide an approximate benchmark of the accuracy of this constrained DFT calculation, we performed a similar calculation for the C_{4v} transition state of the pseudo-rotation mechanism. For this mechanism, all C–Fe–C bond angles for the exchanging CO groups move by a total of 30° with respect to the one CO group that does not exchange. The exchanging CO groups were thus fixed at 15° from their original position as appropriate. All parameters other than the C–Fe–C bond angles were optimized and the resulting structure was 2.32 kcal/mol higher in energy than the D_{3h} structure of $\text{Fe}(\text{CO})_5$. Thus, for the pseudo-rotation mechanism, the calculation with constrained bond angles overestimated the barrier height by only 0.19 kcal/mol in comparison to our previous calculation on the fully optimized transition state structure. Given the accuracy of this method for the pseudo-rotation mechanism, it appears reasonable to assume that the true barrier for the twist rearrangement would be at least one order of magnitude (21 kcal/mol) greater than the calculated barrier for the pseudo-rotation mechanism (2.13 kcal/mol). Unfortunately, our calculations attempting to locate a true stationary point on the electronic potential energy surface of $\text{Fe}(\text{CO})_5$ corresponding to the twist rearrangement consistently relaxed to a lower energy stationary point.

7.6 Arrhenius plot

2D-IR data were collected at 18 °C (room temperature), 50 °C, and 90 °C, and the off-diagonal to diagonal ratios at all three temperatures were fit using the procedure outlined in Section 7.5.2 to the pseudo-rotation mechanism, giving time constants of 8.0 ± 0.6 ps, 6.3 ± 0.8 ps, and 4.6 ± 0.4 ps, respectively. An Arrhenius plot of these data is shown in Figure 7.9, and gives a straight line with a slope corresponding to an activation energy of 1.6 ± 0.3 kcal/mol.

The temperature dependence of the 2D-IR data is consistent with our interpretation that the vibrational energy exchange between the e' and a_2'' modes results from the physical exchange of carbonyl groups in $\text{Fe}(\text{CO})_5$. Nevertheless, solvent-assisted intramolecular vibrational relaxation (IVR) can also cause vibrational energy exchange (see Section 7.4.2) and may also exhibit temperature dependence. IVR is caused by anharmonic coupling between vibrational modes, and the solvent assists this process by receiving or supplying the difference in energy

between the modes. The ability of the solvent to mitigate the energy mismatch relies on the presence of liquid phonons (instantaneous normal modes of the solvent) at the frequency of the energy mismatch (22.8 cm^{-1}), and the occupation number of the phonons at this frequency is linearly proportional to the rate of the transition [242,243]. The phonon occupation number, n , is expressed by the well know relation [263] eq. 7.5,

$$n = [\exp(E_p / k_b T) - 1]^{-1}, \quad (7.5)$$

where E_p is the phonon energy, k_b is the Boltzmann constant, and T is temperature. Based on this expression, the occupation number for phonons at 22.8 cm^{-1} should increase by 26% between 18 °C and 90 °C, and thus the rate of IVR should also increase by 26%. We instead observe a $74\% \pm 20\%$ increase in the rate over this temperature range.

Figure 7.9 Arrhenius plot for the rate of fluxionality at 18 °C, 50 °C, and 90 °C as determined by 2D-IR experiments at these temperatures. Line is a linear fit to the data points, giving a slope and corresponding activation energy of $1.6 \pm 0.3 \text{ kcal/mol}$.

IVR may also exhibit a temperature dependence through the other factors which enter into a calculation of the IVR rate, such as the anharmonic matrix elements connecting the vibrational modes and the phonon density of states. It has been suggested that both of these properties tend to reduce the rate of IVR at higher temperatures and in some cases, overcome the contribution of the phonon occupation number. As a result, the rate of vibrational relaxation has been observed to decrease at higher temperatures in some circumstances [243]. Given these considerations, it seems reasonable to expect that an increase of 26% based eq. 7.5 is an upper estimate for the change in the rate of IVR with temperature, and the temperature dependence we observe in the 2D-IR data is not consistent with this estimate.

8 Conclusions

The basic understanding of elementary steps in a chemical reaction is an important prerequisite for developing sophisticated synthetic chemistry methods. Organometallic chemistry has been extensively developed over the past half-century, yet a variety of fundamental questions concerning, for example, the reactivity of odd-electron species (Chapters 3-5) or picosecond intramolecular rearrangements (Chapters 6-7), have remained. As demonstrated by the investigation of several prototypical complexes, time-resolved vibrational spectroscopy is uniquely suited for developing a detailed knowledge of both photoinduced and thermally driven reactions of organometallic complexes in room-temperature solution.

The experiments on odd-electron radicals formed by irradiation of the metal-metal dimers $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{CpW}(\text{CO})_3]_2$ provided several insights into the reactions of these complexes. Foremost, the experiments confirmed the existence of highly reactive and short-lived 19-electron complexes, which are unusual because they violate the well-known 18-electron rule. The 19-electron complexes undergo either electron transfer or ligand substitution reactions (sometimes both) on a variety of time-scales. For example, solvent caging effects lead to electron transfer on the 100 ps time-scale (Chapter 3) while ligand substitution reactions occur on the nanosecond time-scale (Chapter 5). Electron transfer reactions also occur on a microsecond time-scale, limited by the rate of diffusion (Chapter 4). The experiments are important not only because they definitively established the mechanisms of these reactions, but also because the results are likely applicable to the entire class of organometallic dimers which contain a single metal-metal bond.

Similar to the photoinduced reactions of the metal dimers, the reactions of Fischer carbene complexes have been examined for several decades, yet a clear explanation for the photochemistry of the complexes remained elusive. For instance, it is known that under visible irradiation in the presence of imines, the complexes generate a β -lactam, but the intermediates leading to this product were unknown. The picosecond experiments described in Chapter 6 revealed that photoexcitation of the complexes results in an unusual metal-ketene complex in a triplet spin state. This metal-ketene forms within a few picoseconds after photoexcitation and relaxes back to the carbene within tens of picoseconds. The short life-time of the complex explains why the reactions of Fischer carbenes were not well understood and highlights the importance of time-resolved studies on the picosecond time-scale for a thorough understanding of organometallic reaction mechanisms.

Although ultrafast spectroscopy has been extensively used to study chemical dynamics,

most methods relied on photoinitiation of the chemical reaction to achieve temporal precision. The recent development of two dimensional infrared spectroscopy (2D-IR), however, provides the capacity to monitor thermally driven chemical reactions with ultrafast precision. This technique was used to monitor the picosecond fluxional rearrangement of the classic metal carbonyl complex $\text{Fe}(\text{CO})_5$. This molecule is a textbook example of fluxionality, yet the rearrangement of the molecule had not yet been directly observed. The 2D-IR data provided direct evidence for not only the time-scale, but also the mechanism and transition state involved in the fluxional process. The success of this experiment resolved a question which had existed for several decades and highlighted the importance of 2D-IR for understanding the picosecond, thermally-driven intramolecular dynamics of organometallic complexes in solution.

The projects described in this work encompass several different classes of organometallic complexes and reactions. Each project resulted in a detailed understanding of the chemical reactions through a combination of time-resolved spectroscopy and quantum chemical calculations. Taken together, the projects further the knowledge of organometallic chemistry and demonstrate the importance of further studies using time-resolved vibrational spectroscopy

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Appendix A: Simulation programs

A.1 Linear IR coalescence

The following program was written to simulate spectral coalescence in linear (first-order) infrared spectroscopy (e.g. FTIR spectra). The program is based on the analysis of coalescence in the presence of purely homogeneous (Lorentzian) broadening as developed by Grevels, McClung, et. al. [233]. Thus, this program is appropriate for solute molecules that interact weakly with the solvent (e.g. transition-metal carbonyl complexes in alkane solvents) but is not appropriate for molecules that interact strongly with the solvent (e.g. metal carbonyls in polar solvents such as CH_2Cl_2 , MeOH, etc.) The article by Grevels, McClung, and co-workers [233] does include an analysis of spectral coalescence in the presence of inhomogeneous (Gaussian) broadening, so this program could be modified to incorporate those effects.

A.1.1 Variables

The program relies on the input variables “peakparameters,” “ThetaMatrices,” and “Nmatrix.” For “peakparameters,” each column corresponds to a different peak, and row 1 is the dephasing time constant (ps), row 2 is the center frequency, and row 3 is the integrated intensity. “ThetaMatrices” is a cell array in which each cell is an n by n matrix, where n is the number of peaks. The individual matrixes are defined as described in reference [233] to account for the different permutations involved in chemical exchange. Similarly, “Nmatrix” is an n by n matrix defined as in reference [233].

A.1.2 Matlab code

```
newtimeconstant = input('What is the timeconstant (ps) for the kinetics ');
if length(newtimeconstant)==0
    timeconstant=initialkinetictimeconstant;
else
    timeconstant=newtimeconstant;
    initialkinetictimeconstant=newtimeconstant;
end
peakparameters=initialpeakparameters;
nmbpeaks=length(peakparameters(1,:));

Zmatrix=zeros(nmbpeaks,nmbpeaks);
for j=1:length(ThetaMatrices)
    clear ThetaMatrix;
    ThetaMatrix=ThetaMatrices{j};
    tempZmatrix=(Nmatrix*ThetaMatrix*Nmatrix').^2;
    % Average the values for the two e bands; specific to Fe(CO)5
    % tempZmatrix(:,1:2)=repmat(mean(tempZmatrix(:,1:2),2),1,2);
    % tempZmatrix(1:2,:)=repmat(mean(tempZmatrix(1:2,:),1),2,1);
```



```

% -----
Zmatrix=Zmatrix+tempZmatrix;
clear tempZmatrix;
end
Zmatrix=Zmatrix/length(ThetaMatrices);

xdata=waves;
unitmatrix=zeros(nmbrpeaks,nmbrpeaks);
for j=1:nmbrpeaks
    unitmatrix(j,j)=1;
end
Kmatrix=(1/timeconstant)*(Zmatrix-unitmatrix);
Amatrix=zeros(nmbrpeaks,nmbrpeaks);
for j=1:nmbrpeaks
    clear i;
    Amatrix(j,j)=-1*i*peakparameters(2,j)*0.02998*2*pi+1/peakparameters(1,j);
end
Amatrix=Amatrix-Kmatrix;
[Smatrix,eigenvalues]=eig(Amatrix,'nobalance');
Pvector=peakparameters(3,:);
xdatamatrix=zeros(length(eigenvalues(1,:)),length(eigenvalues(:,1)));
for j=1:length(xdata)
    for k=1:length(xdatamatrix(:,1))
        xdatamatrix(k,k)=xdata(j)*0.02998*2*pi;
    end
    ydata(j)=real(Pvector*Smatrix*(eigenvalues+i*xdatamatrix)^(-
1)*inv(Smatrix)*ones(length(Kmatrix(:,1)),1));
end

figure;
maximum=max(ydata);
h = plot(xdata,ydata/maximum,'r');
hold on;
plot(xdata,ydata/maximum,'r');
maximum=max(abs(ydata));
h = plot(xdata,abs(ydata)/maximum,'r');
hold on;
maximum=max(abs(data));
plot(waves,data/maximum,'k');
axis([1960 2060 0 1.05]);
titlename=strcat('Simulated FTIR: exchange time ',num2str(timeconstant),' ps;
dephasing time ',num2str(dephasingtimeconstant),' ps');
title(titlename);
clear Amatrix Kmatrix Pvector dephasingtimeconstant j k nmbrpeaks timeconstant;
clear xdatamatrix;

clear Amatrix Kmatrix Pvector Smatrix ThetaMatrix Zmatrix eigenvalues h j k
maximum nmbrpeaks peakparameters;
clear timeconstant unitmatrix xdata xdatamatrix ydata newtimeconstant;

```

A.2 Two dimensional spectral simulations

The following program was written to simulate two dimensional infrared spectra in the presence of purely homogeneous (Lorentzian) broadening. Two sets of input parameters are required for the simulations: first are the peak positions, linewidths (full-width at half maximum, Γ_{01}), and integrated intensities of the fundamental $v=0 \rightarrow v=1$ transitions, all three of which can

be derived from Lorentzian fits to the linear (first-order) FTIR spectra. The second set of required input parameters are the anharmonicities of the vibrational modes, including both the diagonal and off-diagonal anharmonicities. These values can be calculated from a DFT anharmonic frequency calculation [121], as implemented in Gaussian 03 (note that such a calculation should use stringent convergence criteria, e.g. using the keywords `opt=tight`, `int=ultrafine`, `scf=tight` in Gaussian 03). Based on these two sets of parameters, the program will calculate the two dimensional infrared spectra, including the diagonal $v=0 \rightarrow v=1$ and $v=1 \rightarrow v=2$ transitions (the latter of which are shifted off the diagonal by twice the diagonal anharmonicity value, χ_{aa} , and this shift is typically denoted Δ_{aa} , where $\Delta_{aa} = 2\chi_{aa}$) as well as the cross peak transitions (shifted from one another by the off-diagonal anharmonicity, $\chi_{ab} = \Delta_{ab}$). Although this program requires anharmonicity values to calculate the position of various peaks in the 2D spectra, the program assumes the harmonic approximation in regard to changes in the linewidths and intensities of the transitions, e.g., $\mu_{01} = \sqrt{2} \mu_{12}$ and $\Gamma_{01} = \Gamma_{12}$. Based on studies by Tokmakoff and co-workers, this approximation appears to be valid for transition-metal carbonyls [264]. Each peak in the 2D spectrum is scaled as appropriate for multiple interactions with the transition dipoles of the molecule: the diagonal $v=0 \rightarrow v=1$ transitions are scaled by $(\mu_{01})^4$, the diagonal $v=1 \rightarrow v=2$ transitions are scaled by $(\mu_{01})^2(\mu_{12})^2$, and the off-diagonal cross peaks are scaled by $(\mu_{01})^2(\mu_{01})^2$ in which the first and second $(\mu_{01})^2$ terms have different values corresponding to the transition dipoles of two different vibrational modes. Note that the absolute magnitude of the transition dipoles are not known from the FTIR spectra; the integrated intensities from the FTIR spectra only provide the relative values of $(\mu_{01})^2$ for the various vibrational modes. As a result, all the transition dipole values used in the simulation program are the integrated intensities of each peak normalized to the peak with the maximum integrated intensity, which provides the correct relative intensity of each peak. In addition, each peak is scaled by the number of Feynman pathways contributing to the third-order polarization signal, which leads to a scaling factor of one-half for the $v=1 \rightarrow v=2$ diagonal transitions and one-half for the cross peak transitions [109,265].

A.2.1 Variables

The Matlab code below relies on three variables, “diagonalpeakparameters,” “anharmonicities,” and “transfermatrix”. These variables are each an n by n matrix, where n is the number of peaks in the linear, FTIR spectrum. For “diagonalpeakparameters,” each column corresponds to a different peak, and row 1 is the linewidth, row 2 is the center frequency, and row 3 is the integrated intensity. For “anharmonicities,” the diagonal terms are the diagonal anharmonicities of the vibrational modes, and the off-diagonal terms are the cross

anharmonicities. For “transfermatrix”, the off-diagonal values are the probability of dipole transfer between vibrational modes and the diagonal terms are the probability of dipole transfer out of each vibrational mode.

A.2.2 Matlab code

simulate2D.m

```
% Requires the variables "transfermatrix",
% "diagonalpeakparameters", "anharmonicities"

% Normalizes the integrated intensities to the maximum peak
diagonalpeakparameters(3,:)=diagonalpeakparameters(3,+)/max(diagonalpeakparameters(3,:));

% Choose the 2D grid of data points for plotting spectra
xspectralpoints=[1965:1:2050];
yspectralpoints=[1965:1:2050];

% Choose the resolution for calculation of spectra
yresolution=0.25;
xresolution=0.25;
xdata=[1965:xresolution:2050];
ydata=[1965:yresolution:2050];

% length of IRpump pulse in picoseconds
IRpumplength=1;

% The resolution of the spectrograph
ProbeResolution=1.5;

nmbrpeaks=length(diagonalpeakparameters(1,:));

% Choose the timeconstant (single exponential) if the peaks
% have kinetics. Input "0" if you want to calculate spectra
% with no kinetics.
timeconstant = input('What is the timeconstant for the kinetics? ');
if length(timeconstant) == 0
    timeconstant = 0;
end
if timeconstant == 0
    timeconstant = 0;
    calckinetics = 'n';
    timesplotted=0;
    tempsimulatedkinetics=zeros(nmbrpeaks,nmbrpeaks);
    for i=1:nmbrpeaks
        tempsimulatedkinetics(i,i)=1;
    end
    simulatedkinetics{1}=tempsimulatedkinetics;
    clear tempsimulatedkinetics;
else
    calckinetics = 'y';
end
if calckinetics == 'y'
    timesplotted = input('Which times would you like to plot? ');
    if length(timesplotted) == 0
        timesplotted = 7.5;
    end
end
nmbrpopulationpeaks=length(transfermatrix(:,1));
convolute = input('Do you want to convolute with the IR pump bandwidth? (y/n)');
```

```

', 's');
if length(convolute)==0
    convolute='n';
end
if convolute=='y'
    lorentzianwidth = input('What is the IR pump Lorentzian FWHM? ');
    if length(lorentzianwidth)==0;
        lorentzianwidth=10;
    end
end
end

if calckinetics=='y'
    % Calculates kinetics by finite difference using this time step (ps)
    timeresolution = 0.050;
    %
    simulatedpumptimes = [0 : timeresolution : 5*IRpumplength];
    simulatedpump = (1/IRpumplength).*exp(-1.*simulatedpumptimes/IRpumplength);
    simulatedkinetictimes = [0 : timeresolution : 50];
    temppopulations=zeros(nmbrpopulationpeaks,nmbrpopulationpeaks);
    for i=1:nmbrpopulationpeaks
        temppopulations(i,i)=1;
    end
    % % Averages populations in e band, specific to Fe(CO)5
    % temppopulations(1:2,:)=repmat(mean(temppopulations(1:2,:),1),2,1);
    %
    populations{1}=temppopulations;
    clear temppopulations;
    for i=2:length(simulatedkinetictimes)
        populations{i}=populations{i-1}*exp(-
1*timeresolution/timeconstant)+transfermatrix*(1-exp(-
1*timeresolution/timeconstant))*populations{i-1};
    % % Averages populations in e band
    % temppopulations=populations{i};
    % temppopulations(1:2,:)=repmat(mean(temppopulations(1:2,:),1),2,1);
    % populations{i}=temppopulations;
    %
    end
    % convolutes IRpump and simulation
    for i=1:nmbrpopulationpeaks
        for j=1:nmbrpopulationpeaks
            clear temppopulations;
            for k=1:length(simulatedkinetictimes)
                temppopulations(k)=populations{k}(i,j);
            end
            temppopulations=conv(temppopulations,simulatedpump);
            temppopulations=temppopulations(1:length(temppopulations)-
length(simulatedpump)+1);
            for k=1:length(simulatedkinetictimes)
                populations{k}(i,j)=temppopulations(k);
            end
        end
    end
    end
    for i=1:length(timesplotted)
        tempsimulatedkinetics=zeros(nmbrpopulationpeaks,nmbrpopulationpeaks);
        indexoftimes = find(simulatedkinetictimes == timesplotted(i));
        simulatedkinetics{i}=populations{indexoftimes};
        clear tempsimulatedkinetics populationsindex indexoftimes;
    end
end

for m=1:length(timesplotted)
    clear tempsimulatedkinetics;
    tempsimulatedkinetics = simulatedkinetics{m};
end

```

```

spectrum=zeros(length(xdata),length(ydata));
nmb peaks=length(diagonalpeakparameters(1,:));
for i=1:length(ydata)
    for j=1:length(xdata)
        for n=1:nmb peaks
            % contribution from diagonal peaks
            spectrum(j,i)=spectrum(j,i)-
temp simulated kinetics(n,n)*lorentzian(xdata(j),diagonalpeakparameters(1:3,n))*1
orentzian(ydata(i),diagonalpeakparameters(1:3,n));
            % contribution from diagonal anharmoncity

spectrum(j,i)=spectrum(j,i)+temp simulated kinetics(n,n)*lorentzian(xdata(j),[dia
gonalpeakparameters(1,n) diagonalpeakparameters(2,n)+2*anharmonicities(n,n)
diagonalpeakparameters(3,n)])*lorentzian(ydata(i),diagonalpeakparameters(1:3,n)
);

            % contribution from off-diagonal anharmonicity
            if calckinetics=='y'
                % This loop goes through all possible exchanges for
                % peak n
                for p=1:nmb peaks
                    if p==n
                        else
                            % contribution from 0 to 1 transition
                            spectrum(j,i)=spectrum(j,i)-
temp simulated kinetics(p,n)*lorentzian(xdata(j),[diagonalpeakparameters(1,p)
diagonalpeakparameters(2,p)
diagonalpeakparameters(3,p)])*lorentzian(ydata(i),[diagonalpeakparameters(1,p)
diagonalpeakparameters(2,n) 1]);
                            % contribution from 1 to 2 transition

spectrum(j,i)=spectrum(j,i)+temp simulated kinetics(p,n)*lorentzian(xdata(j),[dia
gonalpeakparameters(1,p) diagonalpeakparameters(2,p)+2*anharmonicities(p,p)
diagonalpeakparameters(3,p)])*lorentzian(ydata(i),[diagonalpeakparameters(1,p)
diagonalpeakparameters(2,n) 1]);
                        end
                    % This loop goes through all the cross peaks resulting
                    peak n and from the exchange of diagonal peak n to peak p
                    for q=1:nmb peaks
                        if p==q
                            else
                                spectrum(j,i)=spectrum(j,i)-
0.5*temp simulated kinetics(p,n)*lorentzian(xdata(j),[diagonalpeakparameters(1,q)
diagonalpeakparameters(2,q)
diagonalpeakparameters(3,q)])*lorentzian(ydata(i),diagonalpeakparameters(1:3,n)
);

spectrum(j,i)=spectrum(j,i)+0.5*temp simulated kinetics(p,n)*lorentzian(xdata(j),
[diagonalpeakparameters(1,q) diagonalpeakparameters(2,q)+anharmonicities(q,p)
diagonalpeakparameters(3,q)])*lorentzian(ydata(i),diagonalpeakparameters(1:3,n)
);

                                end
                            end
                        end
                    end
                for k=1:nmb peaks
                    if calckinetics=='y'
                        else
                            if k==n
                                else
                                    spectrum(j,i)=spectrum(j,i)-
0.5*lorentzian(xdata(j),diagonalpeakparameters(1:3,k))*lorentzian(ydata(i),diag
onalpeakparameters(1:3,n));
                                end
                            end
                        end
                    end
                end
            end
        end
    end
end

```

```

spectrum(j,i)=spectrum(j,i)+0.5*lorentzian(xdata(j),[diagonalpeakparameters(1,k)
) diagonalpeakparameters(2,k)+anharmonicities(k,n)
diagonalpeakparameters(3,k)])*lorentzian(ydata(i),diagonalpeakparameters(1:3,n)
);
        end
    end
end
    end
end
spectra{m} = spectrum;
clear spectrum nmbrpeaks;
end

if convolute=='y'
    for m=1:length(timesplotted)
        spectrum=spectra{m};
        nmbrwidths=2;
        a = [lorentzianwidth 0 10];
        lorentzianxdata=[-
1*nmbrwidths*lorentzianwidth:yresolution:nmbrwidths*lorentzianwidth];
        lorentzianydata=lorentzian(lorentzianxdata,a);
        for i=1:length(spectrum(:,1))
            convolutedspectrum(i,:)=conv(spectrum(i,:),lorentzianydata);
        end

spectrum=convolutedspectrum(:,round((nmbrwidths*lorentzianwidth)/yresolution)+1
:end-round((nmbrwidths*lorentzianwidth)/yresolution));
        minimum = min(min(spectrum));
        maximum = max(max(spectrum));
        minimum = abs(minimum);
        maximum = abs(maximum);
        limit = max([minimum maximum]);
        spectra{m} = spectrum/limit;
        clear convolutedspectrum spectrum minimum maximum;
    end
    clear a lorentzianxdata lorentzianydata;
end

for m=1:length(timesplotted)
    spectrum=spectra{m};
    nmbrwidths=3;
    a = [10 ProbeResolution 0];
    gaussianxdata=[-
1*ProbeResolution*nmbrwidths:xresolution:ProbeResolution*nmbrwidths];
    gaussianydata=gaussian(gaussianxdata,a);
    for i=1:length(spectrum(1,:))
        convolutedspectrum(:,i)=conv(spectrum(:,i),gaussianydata);
    end

spectrum=convolutedspectrum(length([0:xresolution:ProbeResolution*nmbrwidths]):
end-length([0:xresolution:ProbeResolution*nmbrwidths])+1,:);
        minimum = min(min(spectrum));
        maximum = max(max(spectrum));
        minimum = abs(minimum);
        maximum = abs(maximum);
        limit = max([minimum maximum]);
        spectra{m} = spectrum/limit;
        clear convolutedspectrum spectrum minimum maximum;
    end

for m=1:length(timesplotted)
    spectrum=spectra{m};

```

```

newspectrum=zeros(length(xdata),length(yspectralpoints));
newspectrum2=zeros(length(xspectralpoints),length(yspectralpoints));
for i=1:length(yspectralpoints)
    matches = find(ydata==yspectralpoints(i));
    newspectrum(:,i)=spectrum(:,matches);
end
for i=1:length(xspectralpoints)
    matches = find(xdata==xspectralpoints(i));
    newspectrum2(i,:)=newspectrum(matches,:);
end
minimum = min(min(newspectrum2));
maximum = max(max(newspectrum2));
minimum = abs(minimum);
maximum = abs(maximum);
limit = max([minimum maximum]);
spectra{m} = newspectrum2/limit;
clear spectrum newspectrum newspectrum2 minimum maximum matches;
end

```

lorentzian.m

```

%Lorentzian function where the parameters are:
% a(1)    FWHM
% a(2)    peak position
% a(3)    Peak volume & sign
function g=lorentzian(X,a)
g=a(3)*(a(1)/(2*pi))*(1./((X-a(2)).^2+(a(1)/2).^2));

```

gaussian.m

```

%Gaussian function where the parameters are:
% a(1)    amplitude
% a(2)    FWHM
% a(3)    peak position
function g=gaussian(X,a)
g=(10*a(1)/(a(2)*(8*log(2)).^(-1/2)*(2*pi).^5))*exp(-(X-
a(3)).^2/(2*(a(2)*(8*log(2)).^(-1/2))^2));

```

plotsimulation.m

```

figure;
spectrum=spectra{m};

% Uncomment one of the following depending on how you want to plot data
% -----
% steps = 0.1;
% [C,h] = contourf(xspectralpoints,yspectralpoints,spectrum',[-1:steps:0-
steps] [0+steps:steps:1]);
% % [C,h] = contourf(xspectralpoints,yspectralpoints,spectrum',[-1:steps:1]);
% linevalue=1;
% customjet=load('customjet_2.txt');
% colormap(customjet);
% -----
steps = 0.025;
[C,h] = contour(xspectralpoints,yspectralpoints,spectrum', [-1:steps:1]);
linevalue=2;
colormap(jet);
% -----
% steps = 0.05;
% [C,h] = contour3(xspectralpoints,yspectralpoints,spectrum', [-1:steps:1]);
% linevalue=2;

```

```

% colormap(jet);
% -----

caxis([-1 1]);
% axis equal;
axis([1970 2045 1970 2045]);
h=gca;
set(get(h,'children'),'linewidth',linevalue)
set(h,'ticklength',[0.015 0.015])
set(h,'ytick',[1980:10:2040],'xtick',[1980:10:2040],'xticklabel',{'1980' ''
'2000' '' '2020' '' '2040'},'yticklabel',{'1980' '' '2000' '' '2020' ''
'2040'});
set(h,'layer','top');
set(h,'linewidth',1.0)
set(h,'ticklength',[0.015 0.015])
hold on;
plot([1970 2045],[1970 2045],'k');
colorbar;
titlename=strcat('Simulated Spectra: ',num2str(timesplotted(m)),' ps');
title(titlename);

```

A.3 DFT calculations with Gaussian 03

The projects described in Chapters 3 through 7 require extensive modeling with DFT calculations, and the simulations described in this Appendix also require several input parameters which can be accurately calculated with DFT. The majority of the calculations were performed with Gaussian 03, and the following programs are designed to extract and calculate the required information from the output file of a Gaussian 03 run.

A.3.1 Extract values from Gaussian output files

gaussianextraction.m

```

% This program is designed to extract relevant geometry, energy, and
% frequency parameters from the output file of Gaussian 03.

clear atomicnumbers bondangles inputorientation nmbratoms optimizationenergies
standardorientation;
gaussianfile = input('Gaussian output file name? ','s');

done='n';
filestring=[];
counter=0;
while done=='n'
    counter=counter+1;
    if counter==1
        newgaussianfile=gaussianfile;
    else
        stringcounter = num2str(counter);
        newgaussianfile=[gaussianfile(1:end-4) '_' stringcounter '.out'];
    end
    fin = fopen(newgaussianfile,'r');
    clear newgaussianfile;
    if fin < 0
        break;
    else
        newfilestring = fread(fin);
    end
end

```



```

% -----

% -----
% Extract the standard orientation. For multiple job steps, it only
% extracts the first input orientation.
matches=findstr(filestring,'Standard orientation:');
if length(matches)>0
    geometryindex=findstr(filestring(matches(1):end),'-----
-----');
    linesindex=findstr(filestring(matches(1)-1+geometryindex(2):matches(1)-
1+geometryindex(3)),char([10 32]));
    linesindex=linesindex+matches(1)+geometryindex(2)-2;
    standardorientationdata=zeros(nmbratoms,6);
    for i=1:nmbratoms

standardorientationdata(i,:)=str2num(filestring(linesindex(i)+1:linesindex(i+1)
));
        end

standardorientation=reshape(standardorientationdata(:,4:end)',nmbratoms*3,1);
else
    standardorientation=inputorientation;
end
clear matches nmbrlines geometryindex linesindex standardorientationdata;
% -----

% -----
% Extract the Frequencies, Intensities, and x,y,z coordinates for
% vibrations from the Gaussian output

frequencies=zeros(1,1);
intensities=zeros(1,1);
vibcoordinates=zeros(nmbratoms*3,1);

matches=findstr(filestring,'Frequencies ---');
if length(matches)>0
    hpmodes='true';
    lpmodes='fals';
    endoffline = findstr(filestring(matches(1)-7:matches(1)-7+200),char([10
32]));
    nmbrcharacters=endoffline(1);
    runningcounter=matches(1)-7;
else
    hpmodes='fals';
    clear matches;
    matches=findstr(filestring,'Frequencies --');
    if length(matches)>0
        lpmodes='true';
        nmbrcharacters=matches(2)-matches(1);
    else
        lpmodes='fals';
    end
end

if hpmodes=='true'
    counter=1;
    linecounter=0;
    matchcounter=2;
    done='n';
    while done=='n'

```

```

tempfilestring(1,:)=filestring(runningcounter:runningcounter+nmbcharacters);
    if length(findstr(tempfilestring(1,:), 'Harmonic frequencies'))>0
        break;
    elseif length(findstr(tempfilestring(1,:), 'Coord Atom Element:'))>0
        runningcounter=runningcounter+21;
    elseif length(findstr(tempfilestring(1,:), '
                                '))>0
        endofline = findstr(tempfilestring(1,:), char([10 32]));
        runningcounter=runningcounter+endofline;
    elseif tempfilestring(1,end-1:end)==char([10 32])

organizedfilestring(counter,1:length(tempfilestring))=tempfilestring;
    runningcounter=runningcounter+nmbcharacters;
    counter=counter+1;
else
    clear endofline;
    endofline = findstr(tempfilestring(1,:), char([10 32]));
    clear tempfilestring;
    nmbcharacters=endofline(1);

tempfilestring(1,:)=filestring(runningcounter:runningcounter+nmbcharacters);

organizedfilestring(counter,1:length(tempfilestring))=tempfilestring;
    runningcounter=runningcounter+nmbcharacters;
    counter=counter+1;
end
end
organizedfilestring=double(organizedfilestring);
tempfrequencydata=organizedfilestring(:,24:end-2);
organizedfilestring=char(organizedfilestring);
tempfrequencydata=char(tempfrequencydata);

frequencydata=zeros(length(tempfrequencydata(:,1)),length(str2num(tempfrequency
data(1,:)))));
    for i=1:length(tempfrequencydata(:,1))
        tempdata=str2num(tempfrequencydata(i,:));
        frequencydata(i,1:length(tempdata(1,:)))=tempdata;
    end
    for i=1:length(matches)
        frequencies=[frequencies frequencydata(1+(nmbratoms*3+4)*(i-1),:)] ;
        intensities=[intensities frequencydata(4+(nmbratoms*3+4)*(i-1),:)] ;
        vibcoordinates=[vibcoordinates frequencydata(5+(nmbratoms*3+4)*(i-
1):5+nmbratoms*3-1+(nmbratoms*3+4)*(i-1),:)] ;
    end
    frequencies=frequencies(2:nmbratoms*3-6+1);
    intensities=intensities(2:nmbratoms*3-6+1);
    vibcoordinates=vibcoordinates(:,2:nmbratoms*3-6+1);
elseif lpmodes=='true'
    for i=1:length(matches)
        tempfilestring=filestring(matches(i)-1:matches(i)+nmbcharacters-1);
        endofline = findstr(tempfilestring,char([10 32]));
        tempfilestring=tempfilestring(1:endofline(5+nmbratoms)+1);
        clear endofline;
        endofline = findstr(tempfilestring,char([10 32]));
        frequencies = [frequencies str2num(tempfilestring(14:endofline(1)-1))];
        intensities = [intensities
str2num(tempfilestring(endofline(3)+16:endofline(4)-1))];
        tempdata = str2num(tempfilestring(endofline(5)+1:endofline(end)));
        vibcoordinates = [vibcoordinates
reshape(tempdata(:,3:5)',nmbratoms*3,1)];
        vibcoordinates = [vibcoordinates
reshape(tempdata(:,6:8)',nmbratoms*3,1)];
        vibcoordinates = [vibcoordinates
reshape(tempdata(:,9:11)',nmbratoms*3,1)];

```

```

end
frequencies=frequencies(2:nmbratoms*3-6+1);
intensities=intensities(2:nmbratoms*3-6+1);
vibcoordinates=vibcoordinates(:,2:nmbratoms*3-6+1);
else
    clear frequencies intensities vibcoordinates;
end
clear matches;
% -----

% -----
% Extract the energies and geometries at each optimization point

matches=findstr(filestring,'Optimization completed');
morematches=findstr(filestring,'Optimization stopped');
matches=[matches morematches];

if length(matches)>0
    matches=sort(matches);
    if hpmodes == 'true' | lpmodes == 'true'
        nmbroptimizations=length(matches)-1;
    else
        nmbroptimizations=length(matches);
    end

    SCFmatches = findstr(filestring(1:matches(1)),'SCF Done:');

    % tempoptimizationenergy = filestring(SCFmatches(1)+22:SCFmatches(1)+40);
    % changed for [CpFe(CO)2]2:
    tempoptimizationenergy = filestring(SCFmatches(1)+26:SCFmatches(1)+40);

    optimizationenergies(1)=str2num(tempoptimizationenergy);

    % % specific to Fe(CO)5
    % if IRC == 'true'
    %     anglematches = findstr(filestring(1:matches(1)),'C5-Fel-C6=');
    %     tempbondangle = filestring(anglematches(1)+10:anglematches(1)+17);
    %     bondangles(1)=str2num(tempbondangle);
    % end
    % % -----
--

    if nmbroptimizations > 0
        clear optimizationenergies;
        for j=1:nmbroptimizations
            clear tempoptimizationenergy tempbondangle SCFmatches anglematches;
            SCFmatches = findstr(filestring(1:matches(j)),'SCF Done:');

            % tempoptimizationenergy =
            filestring(SCFmatches(end)+22:SCFmatches(end)+40);
            % changed for [CpFe(CO)2]2:
            tempoptimizationenergy =
            filestring(SCFmatches(end)+26:SCFmatches(end)+40);
            % -----

            optimizationenergies(j)=str2num(tempoptimizationenergy);

            %
            % specific to Fe(CO)5
            % if IRC == 'true'
            %     anglematches = findstr(filestring(1:matches(j-1)),'C5-
            Fel-C6=');
            %     tempbondangle =

```

```

filestring(anglematches(end)+10:anglematches(end)+17);
%             bondangles(j)=str2num(tempbondangle);
%             end
%             % -----
-----
%
%             % specific to carbenes
%             clear anglematches tempbondangle;
%             anglematches =
findstr(filestring(matches(j):length(filestring)), 'A(4,1,12)');
%             tempbondangle =
filestring(anglematches(1)+matches(j)+20:anglematches(1)+matches(j)+35);
%             bondangles(j)=str2num(tempbondangle);
%             clear anglematches tempbondangle;
%             % data = [data' [bondangles optimizationenergies]'];
%             % -----
-----
%
%             % specific to [CpFe(CO)2]2
%             if gaussianfile(1:40)=='cpfecopome3_doublet_b3lyp_631+gd_scan_p'
%             clear bondmatches tempbondlength;
%             bondmatches =
findstr(filestring(matches(j):length(filestring)), 'R(15,31)');
%             tempbondlength =
filestring(bondmatches(1)+matches(j)+20:bondmatches(1)+matches(j)+35);
%             bondlengths(j)=str2num(tempbondlength);
%             clear bondmatches tempbondlength;
%             elseif
gaussianfile(1:38)=='cpfecopome3_doublet_b3lyp_631+gd_scan'
%             clear bondmatches tempbondlength;
%             bondmatches =
findstr(filestring(matches(j):length(filestring)), 'R(11,31)');
%             tempbondlength =
filestring(bondmatches(1)+matches(j)+20:bondmatches(1)+matches(j)+35);
%             bondlengths(j)=str2num(tempbondlength);
%             clear bondmatches tempbondlength;
%             elseif
gaussianfile(1:38)=='cpfecopome32_doublet_b3lyp_631+gd_scan'
%             clear bondmatches tempbondlength;
%             bondmatches =
findstr(filestring(matches(j):length(filestring)), 'R(13,29)');
%             tempbondlength =
filestring(bondmatches(1)+matches(j)+20:bondmatches(1)+matches(j)+35);
%             bondlengths(j)=str2num(tempbondlength);
%             clear bondmatches tempbondlength;
%             end
%             % -----
--

        end
        optimizationenergies = optimizationenergies';
        %     bondangles = bondangles';
        bondlengths=bondlengths';
    end
    % -----
    optimizationenergieskcalmol=optimizationenergies(:)*627.509391;
end;

% -----
% Extract NBO charges and spins
if NBO=='true'
    nbomatch=findstr(filestring,'Summary of Natural Population Analysis');

```

```

        nboindexstart=findstr(filestring(nbomatch(1):end),'-----
        -----');

nboindexend=findstr(filestring(nbomatch(1):end),'=====
=====');
    linesindex=findstr(filestring(nbomatch(1)-1+nboindexstart(1):nbomatch(1)-
1+nboindexend(1)),char([10 32]));
    linesindex=linesindex+nbomatch(1)+nboindexstart(1)-2;
    chargedata=zeros(nmbratoms,6);
    nboatoms=zeros(nmbratoms,2);
    for i=1:nmbratoms
        chargedata(i,:)=str2num(filestring(linesindex(i)+9:linesindex(i+1)));
        nboatoms(i,1:2)=filestring(linesindex(i)+7:linesindex(i)+8);
    end
    nboatomnumbers=chargedata(:,1);
    nbocharges=chargedata(:,2);
    clear chargedata linesindex;

    alphamatch=findstr(filestring,'Alpha spin orbitals');
    alphaindexstart=findstr(filestring(alphamatch(1):end),'-----
    -----');
    alphaindexend=findstr(filestring(alphamatch(1):end),'Summary of Natural
Population Analysis');
    linesindex=findstr(filestring(alphamatch(1)-
1+alphaindexstart(1):alphamatch(1)-1+alphaindexend(1)),char([10 32]));
    linesindex=linesindex+alphamatch(1)+alphaindexstart(1)-2;
    counter=0;
    atomcounter=1;
    indexcounter=0;
    moredata='y';
    alphaspinadatotal=zeros(nmbratoms,1);
    while moredata=='y'
        indexcounter=indexcounter+1;

tempdata=filestring(linesindex(indexcounter)+1:linesindex(indexcounter+1));
        previousatomcounter=atomcounter;

atomcounter=str2num(filestring(linesindex(indexcounter)+15:linesindex(indexcoun
ter)+16));
        if atomcounter==previousatomcounter
            counter=counter+1;
            tempdata=str2num(tempdata(36:end));
            tempdata=tempdata(1,1);
            alphaspindata{atomcounter}(counter,1)=tempdata;
            clear tempdata;
        else

alphaspindatatotal(previousatomcounter,1)=sum(alphaspindata{previousatomcounter
}(:,1));
            if previousatomcounter==nmbratoms
                break;
            end
            counter=1;
            tempdata=str2num(tempdata(36:end));
            tempdata=tempdata(1,1);
            alphaspindata{atomcounter}(counter,1)=tempdata;
            clear tempdata;
        end
    end
    clear chargedata linesindex;

    betamatch=findstr(filestring,'Beta spin orbitals');
    betaindexstart=findstr(filestring(betamatch(1):end),'-----
    -----');

```

```

-----');
    betaindexend=findstr(filestring(betamatch(1):end),'Summary of Natural
Population Analysis');
    linesindex=findstr(filestring(betamatch(1)-
1+betaindexstart(1):betamatch(1)-1+betaindexend(1)),char([10 32]));
    linesindex=linesindex+betamatch(1)+betaindexstart(1)-2;
    counter=0;
    atomcounter=1;
    indexcounter=0;
    moredata='y';
    betaspindatatotal=zeros(nmbratoms,1);
    while moredata=='y'
        indexcounter=indexcounter+1;

tempdata=filestring(linesindex(indexcounter)+1:linesindex(indexcounter+1));
        previousatomcounter=atomcounter;

atomcounter=str2num(filestring(linesindex(indexcounter)+15:linesindex(indexcoun
ter)+16));
        if atomcounter==previousatomcounter
            counter=counter+1;
            tempdata=str2num(tempdata(36:end));
            tempdata=tempdata(1,1);
            betaspindata{atomcounter}(counter,1)=tempdata;
            clear tempdata;
        else

betaspindatatotal(previousatomcounter,1)=sum(betaspindata{previousatomcounter}(
:,1));
            if previousatomcounter==nmbratoms
                break;
            end
            counter=1;
            tempdata=str2num(tempdata(36:end));
            tempdata=tempdata(1,1);
            betaspindata{atomcounter}(counter,1)=tempdata;
            clear tempdata;
        end
    end
    clear linesindex;

spindatatotal=zeros(nmbratoms,1);
spindatatotal=alphaspindatatotal-betaspindatatotal;

%     % specific to [CpFe(CO)2]2
%     if length(gaussianfile)==36
%         if gaussianfile(1:32)=='cpfeco2_doublet_b3lyp_631+gd_nbo'
%             Cpcharge=sum(nbocharges(1:10));
%             Cpspin=sum(spindatatotal(1:10));
%             COcharge=sum(nbocharges(11:14));
%             COspin=sum(spindatatotal(11:14));
%             Fecharge=nbocharges(15);
%             Fespin=spindatatotal(15);
%             fprintf(['The Cp charge is ' num2str(Cpcharge) ' and spin is '
num2str(Cpspin) char([10])]);
%             fprintf(['The CO charge is ' num2str(COcharge) ' and spin is '
num2str(COspin) char([10])]);
%             fprintf(['The Fe charge is ' num2str(Fecharge) ' and spin is '
num2str(Fespin)]);
%         end
%     end
%     if length(gaussianfile)==41
%         if gaussianfile(1:37)=='cpfeco2pome3_doublet_b3lyp_631+gd_nbo'

```

```

%           Cpcharge=sum(nbocharges(1:10));
%           Cpspin=sum(spindatatotal(1:10));
%           COcharge=sum(nbocharges(11:14));
%           COspin=sum(spindatatotal(11:14));
%           Pcharge=sum(nbocharges(15:30));
%           Pspin=sum(spindatatotal(15:30));
%           Fecharge=nbocharges(31);
%           Fespin=spindatatotal(31);
%           fprintf(['The Cp charge is ' num2str(Cpcharge) ' and spin is '
num2str(Cpspin) char([10])]);
%           fprintf(['The CO charge is ' num2str(COcharge) ' and spin is '
num2str(COspin) char([10])]);
%           fprintf(['The P(OMe)3 charge is ' num2str(Pcharge) ' and spin is
' num2str(Pspin) char([10])]);
%           fprintf(['The Fe charge is ' num2str(Fecharge) ' and spin is '
num2str(Fespin)]);
%       end
%   end
%   if length(gaussianfile)==40;
%       if gaussianfile(1:36)=='cpfecopome3_doublet_b3lyp_631+gd_nbo'
%           Cpcharge=sum(nbocharges(1:10));
%           Cpspin=sum(spindatatotal(1:10));
%           COcharge=sum(nbocharges(11:12));
%           COspin=sum(spindatatotal(11:12));
%           Pcharge=sum(nbocharges(13:28));
%           Pspin=sum(spindatatotal(13:28));
%           Fecharge=nbocharges(29);
%           Fespin=spindatatotal(29);
%           fprintf(['The Cp charge is ' num2str(Cpcharge) ' and spin is '
num2str(Cpspin) char([10])]);
%           fprintf(['The CO charge is ' num2str(COcharge) ' and spin is '
num2str(COspin) char([10])]);
%           fprintf(['The P(OMe)3 charge is ' num2str(Pcharge) ' and spin is
' num2str(Pspin) char([10])]);
%           fprintf(['The Fe charge is ' num2str(Fecharge) ' and spin is '
num2str(Fespin)]);
%       end
%   end
%   if length(gaussianfile)==41
%       if gaussianfile(1:37)=='cpfecopome32_doublet_b3lyp_631+gd_nbo'
%           Cpcharge=sum(nbocharges(1:10));
%           Cpspin=sum(spindatatotal(1:10));
%           COcharge=sum(nbocharges(11:12));
%           COspin=sum(spindatatotal(11:12));
%           Pcharge=sum([nbocharges(13:28) ' nbocharges(30:45)']);
%           Pspin=sum([spindatatotal(13:28) ' spindatatotal(30:45)']);
%           Fecharge=nbocharges(29);
%           Fespin=spindatatotal(29);
%           fprintf(['The Cp charge is ' num2str(Cpcharge) ' and spin is '
num2str(Cpspin) char([10])]);
%           fprintf(['The CO charge is ' num2str(COcharge) ' and spin is '
num2str(COspin) char([10])]);
%           fprintf(['The P(OMe)3 charge is ' num2str(Pcharge) ' and spin is
' num2str(Pspin) char([10])]);
%           fprintf(['The Fe charge is ' num2str(Fecharge) ' and spin is '
num2str(Fespin)]);
%       end
%   end
%   % -----
end
% -----

```



```

% % -----
% % specific to [CpFe(CO)2]2
% if length(gaussianfile)>=42
%     if gaussianfile(1:40)=='cpfeco2pome3_doublet_b3lyp_631+gd_scan_p' |
gaussianfile(1:38)=='cpfeco2pome3_doublet_b3lyp_631+gd_scan' |
gaussianfile(1:38)=='cpfecopome32_doublet_b3lyp_631+gd_scan'
%         phosphiteenergy=-686.7911209;
%         phosphiteenergykcalmol=phosphiteenergy*627.509391;
%         radicalenergy=-543.668587;
%         radicalenergykcalmol=radicalenergy*627.509391;
%         COenergy=-113.3152256;
%         COenergykcalmol=COenergy*627.509391;
%         if gaussianfile(1:40)=='cpfeco2pome3_doublet_b3lyp_631+gd_scan_p'
%             optimizationenergies=optimizationenergies-phosphiteenergy-
radicalenergy;
%             optimizationenergieskcalmol=optimizationenergieskcalmol-
phosphiteenergykcalmol-radicalenergykcalmol;
%             elseif gaussianfile(1:38)=='cpfeco2pome3_doublet_b3lyp_631+gd_scan'
%                 optimizationenergies=optimizationenergies-phosphiteenergy-
radicalenergy;
%                 optimizationenergieskcalmol=optimizationenergieskcalmol-
phosphiteenergykcalmol-radicalenergykcalmol;
%                 elseif gaussianfile(1:38)=='cpfecopome32_doublet_b3lyp_631+gd_scan'
%                     optimizationenergies=optimizationenergies-2*phosphiteenergy-
radicalenergy+COenergy;
%                     optimizationenergieskcalmol=optimizationenergieskcalmol-
2*phosphiteenergykcalmol-radicalenergykcalmol+COenergykcalmol;
%             end
%             figure;
%             plot(bondlengths,optimizationenergieskcalmol,'ko');
%             hold on;
%             plot(bondlengths,optimizationenergieskcalmol,'k');
%             gaussianfile=strrep(gaussianfile,'_','-');
%             title(gaussianfile);
%         end
%     end
% % % -----

clear tempfrequencydata organizedfilestring frequencydata tempdata
tempfilestring matches counter;
clear ans i nmbrcharacters fin endoffline done matchcounter linecounter
runningcounter hpmodes lpmodes;
clear searchstring tempoptimizationenergy nmbroptimizations nmbrjobsteps IRC
SCFmatches j;
clear filestring;

```

A.3.2 Normal and local mode analysis

The programs described below will calculate the projection of delocalized harmonic normal modes onto a specific set of local coordinates, e.g. a set of CO ligands. The local modes can then be projected onto a different set of similar local modes to calculate the degree of dipole transfer during an exchange process.

localmodeprojection.m

```

% This program will project the vibrational motion of the normal
% vibrational modes into the local motion of individual linear groups (e.g. CO
groups)

```

```

% that are specified in the variable "local groups" where each row is a
% new group and column 1 is the first atom number (as specified in the
% Gaussian file) and column 2 the second atom number in the group

unitvectors=zeros(length(localgroups(:,1))*3,1);
for i=1:length(localgroups(:,1))
    unitvectors((i-1)*3+1:(i-1)*3+3,1)=standardorientation((localgroups(i,2)-
1)*3+1:(localgroups(i,2)-1)*3+3,1)-standardorientation((localgroups(i,1)-
1)*3+1:(localgroups(i,1)-1)*3+3,1);
    unitvectors((i-1)*3+1:(i-1)*3+3,1)=unitvectors((i-1)*3+1:(i-
1)*3+3,1)/sqrt(sum(unitvectors((i-1)*3+1:(i-1)*3+3,1).^2));
end

projvibcoordinates=zeros(length(localgroups(:,1)),length(vibcoordinates(1,:)));
for i=1:length(vibcoordinates(1,:))
    for j=1:length(localgroups(:,1))
        projvibcoordinates(j,i)=dot(vibcoordinates((localgroups(j,2)-
1)*3+1:(localgroups(j,2)-1)*3+3,i),unitvectors((j-1)*3+1:(j-1)*3+3,1))-
dot(vibcoordinates((localgroups(j,1)-1)*3+1:(localgroups(j,1)-
1)*3+3,i),unitvectors((j-1)*3+1:(j-1)*3+3,1));
    end

projvibcoordinates(1:end,i)=projvibcoordinates(1:end,i)/sqrt(sum(projvibcoordin
ates(1:end,i).^2));
end
clear i j unitvectors;

```

vibmodetransfer.m

```

% This program will take the projection of vibrational normal modes onto
% local groups for one molecular geometry (projvibcoordinates1) and
% calculate the coefficients for the projection of the motion of each
% decomposed normal mode onto the local modes of a second geometry
% (projvibcoordinates2) for which the vibrational modes have also been
% decomposed into motion along the same local groups as for first geometry.
% NOTE: the atom numbering used in geometry 1 and geometry 2 (i.e. the
% order in which the local groups were specified MUST be the same or the
% output of this program will be nonsense. The output is in the variable
% vibtransfer1to2

for i=1:length(projvibcoordinates1(1,:))
    for j=1:length(projvibcoordinates1(:,1))

vibtransfer1to2(j,i)=dot(projvibcoordinates1(:,i),projvibcoordinates2(:,j));

vibtransfer2to1(j,i)=dot(projvibcoordinates2(:,i),projvibcoordinates1(:,j));
    end
end
clear i j;

```

Appendix B: Data analysis programs

B.1 One dimensional transient vibrational spectroscopy

The following programs were written to analyze the data collected with the visible-pump, IR-probe experimental apparatus. The programs average data files, plot the spectra, and extract kinetic traces, as well as offering several error analysis and background subtraction options.

B.1.1 Average data files

avgdata.m

```
inputfile = input('Data info filename? ','s');
if length(inputfile)==0;
    inputfile='datinfo.txt';
end
fin = fopen(inputfile,'r');
if fin < 0
    error(['Could not open ',inputfile,' for input']);
end

filebody = fgetl(fin);
specinfo = fscanf(fin,'%f');
nmbrfiles = length(specinfo);

%-----%
% Input all of the data collected into time and wave cell arrays %
% Note, that the data is usually not symmetric! %
%-----%
for k=1:nmbrfiles
    filename = strcat(filebody,num2str(specinfo(k,1)));
    fin = fopen(filename,'r');
    for i=1:4
        header = fgetl(fin);
    end
    inputdata = fscanf(fin,'%g %g %g',[3 inf]);
    if k>1
        AllData=[AllData inputdata]; %concatenate files
    else
        AllData=inputdata;
    end;
end;
AllData=AllData';
AllData(:,2)=round(AllData(:,2)*10)/10; %Round wavenumbers to 1 digit

AllData=sortrows(AllData,2); %Sort data according to
wavelengths
j=1;
k=1;
for i=1:length(AllData(:,2))-1
    if AllData(i,2)==AllData(i+1,2);
        k=k+1;
    else
        Waves(j,1)=AllData(i,2);
        Waves(j,2)=k; %This particular wavenumber is
```

```

k-times in the data
    TimeArray{j}=AllData(sum(Waves(1:j-1,2))+1:sum(Waves(1:j-1,2))+k,:);
    j=j+1; %TimeArray is a cell array with
each cell being a different time slice
    k=1;
end;
end;
Waves(j,1)=AllData(i,2);
Waves(j,2)=k;
TimeArray{j}=AllData(sum(Waves(1:j-1,2))+1:sum(Waves(1:j-1,2))+k,:);
nmbrwvs=length(Waves(:,1)); %Number of unique wavenumbers

AllData=sortrows(AllData,1); %Sort data according to times
j=1;
k=1;
for i=1:length(AllData(:,1))-1
    if AllData(i,1)==AllData(i+1,1);
        k=k+1;
    else
        Times(j,1)=AllData(i,1);
        Times(j,2)=k; %This particular time is k-times
in the data
        WaveArray{j}=AllData(sum(Times(1:j-1,2))+1:sum(Times(1:j-1,2))+k,:);
        j=j+1; %WaveArray is a cell array with
each cell being a different spectral slice
        k=1;
    end;
end;
Times(j,1)=AllData(i,1);
Times(j,2)=k;
WaveArray{j}=AllData(sum(Times(1:j-1,2))+1:sum(Times(1:j-1,2))+k,:);
nmbrtms=length(Times(:,1)); %Number of unique times

%-----%
% Now average the data over the individual scans (use spectral data to do so)
%
%-----%

% devpm = input('# of standard deviations (1-3)? ');
% if length(devpm)==0;
%     devpm=3;
% end
devpm=3;

% This is a simple outlier treating and averaging routine
for i=1:nmbrtms;
    snglscns=WaveArray{i};
    % Assign wavenumbers to individual arrays and calculate the mean and
    % standard deviation
    for j=1:nmbrwvs;
        somedata='n';
        specindex = find(Waves(j,1) == snglscns(:,2));
        WaveDataUnchecked=sort(snglscns(specindex,3));
        m=1;
        % Remove all values of 100.00 in the raw data (recorded value when
        % IR intensity is too low)
        for k=1:length(WaveDataUnchecked)
            if WaveDataUnchecked(k)==100.00
            else
                WaveData(m)=WaveDataUnchecked(k);
                m=m+1;
                somedata='y';
            end
        end
    end
end

```

```

        end
        if somedata=='y'
            if length(WaveData)<=2
                message=strcat('Warning: Two or less data points were used
for',' ',num2str(Waves(j,1)));
                disp(message);
            end
            % Take only the center part of the data as a reference for the
            % outlier treatment (depending on the number of scans)
            if length(WaveData)>100
                WaveHelp=WaveData(round(length(WaveData)*0.1):end-
round(length(WaveData)*0.1));
            elseif length(WaveData)>10
                WaveHelp=WaveData(2:end-2);
            else
                WaveHelp=WaveData;
            end;
            AveHelp=0;
            StdHelp=0;
            AveHelp=mean(WaveHelp);
            StdHelp=std(WaveHelp);
            n=1;
            for k=1:length(WaveData)
                if (WaveData(k)>=AveHelp-devpm*StdHelp) &
(WaveData(k)<=AveHelp+devpm*StdHelp)
                    FinalData(n)=WaveData(k);
                    n=n+1;
                end;
            end;
            AveWaves(j)=mean(FinalData);
            StdWaves(j)=std(FinalData);
        else
            AveWaves(j)=200;
            StdWaves(j)=1000;
            % message=strcat('Warning: No data available for ',
            % num2str(Waves(j,1)), ' (200.00 used instead)');
            % disp(message);
        end
        clear('WaveData');
        clear('FinalData');
    end;
    AveData(:,i)=AveWaves(:);
    StdData(:,i)=StdWaves(:);
    clear('AveWaves');
    clear('StdWaves');
end;

%-----%
% Negative time spectra filtering (FFT lowpass) and subtraction %
%-----%

subtraction = input('Subtract negative time slices (first 5 points) ? (y/n)
','s');
if length(subtraction)==0
    subtraction='n';
end
if (subtraction=='y') | (subtraction=='Y')
    clear negtime;
    negtime=zeros(nmbrwvs,1);
    for i=1:5
        negtime=negtime+AveData(:,i);
    end;
    negtime=negtime/5;

```

```

filtering = input('Lowpass filter negative time slices? (y/n) ','s');
if length(filtering)==0;
    filtering='Y';
end;
if (filtering=='y') | (filtering=='Y')
    cutoff=nmbwvs/5;
    for i=1:nmbwvs
        sum=1;
        for j=1:cutoff-1
            sum=sum+2*cos(2*pi*j*(i-1)/nmbwvs);
        end;
        u(i)=sum/nmbwvs;
    end;
    for i=1:nmbwvs
        sum=0;
        for j=1:nmbwvs
            k=mod(i-j,nmbwvs);
            sum=sum+negtime(j)*u(k+1);
        end;
        filtered(i)=sum;
    end;
    negtime=filtered';
end;
end;

%-----%
% Time and wavelength data are now put into the array %
%-----%

Output(2:nmbwvs+1,2:nmbwvs+1)=AveData;
Output(2:end,1)=Waves(:,1);
Output(1,:)=[0 Times(:,1)'];
[p,q]=size(Output);

if (subtraction=='y') | (subtraction=='Y')
    for i=2:q;
        Output(2:p,i) = Output(2:p,i)-negtime(:);
    end;
    Output(2:p,2)=negtime;
end;

%-----%
% Correction of baseline drift (last 20 timeslices are used) %
%-----%

basedrift = input('Correct baseline drift? (y/n) ','s');
if length(basedrift)==0;
    basedrift='n';
end;
if (basedrift=='y') | (basedrift=='Y')
    Waves(:,1) '
    leftwavenumber = input('left anchor / wavenumbers ');
    rightwavenumber = input('right anchor / wavenumbers ');
    specindex = find(leftwavenumber <= Waves(:,1) & Waves(:,1) <=
rightwavenumber);
    leftbase=mean(Output(specindex(1)+1,q-20:q-1));
    rightbase=mean(Output(specindex(end)+1,q-20:q-1));
    starttime = input('correct from / ps (e.g. 0) ');
    j=find(Output(1,2:q)==starttime);
    for i=1:nmbwvs
        newbase=leftbase+(Waves(i,1)-Waves(1,1))*(rightbase-
leftbase)/(Waves(nmbwvs,1)-Waves(1,1));
    end;
end;

```

```

        Output(i+1,j:q)=Output(i+1,j:q)-newbase;
    end;
end;

%-----%
% Fourierfilter all data (or filter for window signal correction only)? %
%-----%

filterall = input('Remove high-frequency noise in all data? (y/n) ','s');
if length(filterall)==0
    filterall='n';
end
filterall2 = filterall;
if (filterall=='n') | (filterall=='N')
    windowssignal = input('Correct for window signal? (y/n) ','s');
    if (windowssignal=='y') | (windowssignal=='Y')
        clear filterall;
        filterall = input('Remove high-frequency noise for correction? (y/n)
', 's');
    else
        windowssignal='n';
    end
end
if (filterall=='y') | (filterall=='Y')
    OutputFFT = Output;
    for n=1:nmbrrtms
        specscan=OutputFFT(2:end,n+1);
        cutoff=nmbrrwvs/5;
        for i=1:nmbrrwvs
            sum=1;
            for j=1:cutoff-1
                sum=sum+2*cos(2*pi*j*(i-1)/nmbrrwvs);
            end;
            u(i)=sum/nmbrrwvs;
        end;
        for i=1:nmbrrwvs
            sum=0;
            for j=1:nmbrrwvs
                k=mod(i-j,nmbrrwvs);
                sum=sum+specscan(j)*u(k+1);
            end;
            filtered(i)=sum;
        end;
        OutputFFT(2:end,n+1)=filtered';
    end;
    if (filterall2=='y') | (filterall2=='Y')
        clear Output;
        Output = OutputFFT;
    end
else
    OutputFFT = Output;
end;

%-----%
% Correction for window signal (assuming it is a linear offset) %
%-----%

if (filterall2=='y') | (filterall2=='Y')
    windowssignal = input('Correct for window signal? (y/n) ','s');
    if length(windowssignal)==0;
        windowssignal='n';
    end
end
end

```

```

if (windowSignal=='y') | (windowSignal=='Y')
    clear specindex leftbase newbase rightbase leftwavenumber rightwavenumber
    starttime leftwave rightwave j k m;
    leftwavenumber = input('left anchor range, e.g. [2002 2007]? ');
    rightwavenumber = input('right anchor range, e.g. [2002 2007]? ');
    starttime = input('begin correction (ps)? ');
    endtime = input('end correction (ps)? ');
    starttimeindex=find(Output(1,2:end)>=starttime);
    starttimeindex=starttimeindex+1;
    j=starttimeindex(1);
    endtimeindex=find(Output(1,2:end)>=endtime);
    endtimeindex=endtimeindex+1;
    k=endtimeindex(1);
    if leftwavenumber==rightwavenumber
        oneanchor = 'y';
    else
        oneanchor = 'n';
    end
    if length(leftwavenumber)==1
        specindex = find(leftwavenumber <= Output(:,1) & Output(:,1) <=
rightwavenumber(1));
        specindexleft = specindex(1);
        leftwave = Output(specindexleft,1);
        for m=1:k-j+1
            leftbase(m) = OutputFFT(specindexleft,j+m-1);
        end
    else
        specindexleft = find(leftwavenumber(1) <= Output(:,1) & Output(:,1) <=
leftwavenumber(2));
        leftwave = (Output(specindexleft(1),1)+Output(specindexleft(end),1))/2;
        for m=1:k-j+1
            leftbase(m) = mean(OutputFFT(specindexleft(:),j+m-1));
        end
    end
    if length(rightwavenumber)==1
        clear specindex;
        specindex = find(leftwavenumber(1) <= Output(:,1) & Output(:,1) <=
rightwavenumber);
        specindexright = specindex(end);
        rightwave = Output(specindexright,1);
        for m=1:k-j+1
            rightbase(m) = OutputFFT(specindexright,j+m-1);
        end
    else
        specindexright = find(rightwavenumber(1) <= Output(:,1) & Output(:,1) <=
rightwavenumber(2));
        rightwave = (Output(specindexright(1),1)+Output(specindexright(end),1))/2;
        for m=1:k-j+1
            rightbase(m) = mean(OutputFFT(specindexright(:),j+m-1));
        end
    end
    for m=1:k-j+1
        for i=1:nmbwvs
            if oneanchor=='y'
                newbase(1)=leftbase(m);
            else
                slope = (rightbase(m)-leftbase(m))/(rightwave-leftwave);
                newbase(1)=leftbase(m)+slope*(Output(i+1,1)-leftwave);
            end
            Output(i+1,j+m-1) = Output(i+1,j+m-1)-newbase(1);
            clear newbase slope;
        end;
    end;
end;

```



```

end;

%-----
% Write files
%-----

StdDev = zeros(nmbrwvs+1,nmbrtms+1);
StdDev(2:nmbrwvs+1,2:nmbrtms+1)=StdData;
StdDev(2:end,1)=Waves(:,1);
StdDev(1,:)= [0 Times(:,1)'];
if length(specinfo) == 1
    filebody2 = strcat(filebody,num2str(specinfo(1)));
else
    filebody2 = strcat(filebody,num2str(specinfo(1)),'-
',num2str(specinfo(end)));
end
outputfileboolean = input('Write output and std dev (y/n)? ','s');
if length(outputfileboolean)==0
    outputfileboolean='y';
end
if (outputfileboolean == 'y') | (outputfileboolean == 'Y')
    filenamedata=strcat('data_',filebody2,'.dat');
    filenamestd=strcat('data_',filebody2,'.std');
    save(filenamedata,'Output','-ascii');
    save(filenamestd,'StdDev','-ascii');

end;

```

B.1.2 Plotting data

plotdata.m

```

filename = input('What is the data filename? ','s');
if length(filename) > 0;
    Output = load(filename);
end;
specpositions = Output(2:end,1);
timepositions = Output(1,2:end);
nmbrtimes = length(timepositions);
nmbrspecs = length(specpositions);
disp(timepositions');
whichtimes = input('Which times [10,20,...]? ');
nmbrplots = length(whichtimes);
if nmbrplots==0;
    whichtimes = [1,5,10,50,100,400,700];
    nmbrplots = length(whichtimes);
end;
for i=1:nmbrplots;
    whichslices(i) = find(whichtimes(i)==timepositions);
end;
whichslices = whichslices+1;

% -----
% This section checks for data values of 100.00 or 200.00 and removes them
% from the plotted data
datachecked=zeros(nmbrspecs,2*nmbrplots);
speccounter=zeros(nmbrplots);
speccounter(:)=1;
figure;
baddata='n';
color=['bgrcmyk'];

```

```

m=1;
for i=1:nmbrplots
    for j=1:nmbrspecs
        if Output(j+1,whichslices(i))==200.00 |
Output(j+1,whichslices(i))==100.00
            baddata='y';
        else
            datachecked(speccounter(i),2*i-1)=Output(j+1,1);
            datachecked(speccounter(i),2*i)=Output(j+1,whichslices(i));
            speccounter(i)=speccounter(i)+1;
        end
    end
    plot(datachecked(1:speccounter(i)-1,2*i-1),datachecked(1:speccounter(i)-
1,2*i),color(m));
    hold on;
    m=m+1;
    if m==8
        m=1;
    end
end
if baddata=='y'
    disp('Warning: Data reading 100.00 or 200.00 has been removed from these
plots');
end
% -----

for j=1:nmbrplots;
    lgnd = sprintf('%4.0f',(Output(1,whichslices(j))));
    lgnds{j}=[lgnd, ' ps'];
    legend(lgnds);
end;
xlabel('wavenumbers / cm^{-1}');
ylabel('\Delta mOD');
% titlename = input('Title for spectral graph: ','s');
% title(titlename);
clear whichtimes nmbrplots whichslices lgnd lgnds titlename baddata
clear speccounter datachecked baddata;

```

intpeaks.m

```

filename = input('What is the data filename? ','s');
if length(filename) > 0;
    Output = load(filename);
end;

filename = input('What is the std dev filename? ','s');
if length(filename) > 0;
    StdDev = load(filename);
end;

Waves = Output(2:end,1)';
Times = Output(1,2:end);
NmbrTms = length(Times);
nmbrwvs = length(Waves);
again = 'y';
clear filebody;
intindex=0;
while again == 'y';
    intindex=intindex+1;
    leftedge = input('left edge (wavenumbers)? ');
    rightedge = input('right edge (wavenumbers)? ');
    intpeak=zeros(NmbrTms,1);

```

```

intstd=zeros(NmbrTms,1);
if leftedge==rightedge
    specindex=find(Waves==leftedge);
    for i=1:NmbrTms
        intpeak(i)=Output(specindex(1)+1,i+1);
        intstd(i)=StdDev(specindex(1)+1,i+1);
    end
else
    specindex = find(leftedge <= Waves & Waves <= rightedge);
    for i=1:NmbrTms
        for j=specindex(1):specindex(end)
            if j<=nmbrwvs
                intpeak(i) = intpeak(i)+Output(j+1,i+1)*(Waves(j+1)-
Waves(j));
                intstd(i) = intstd(i)+StdDev(j+1,i+1)*(Waves(j+1)-
Waves(j));
            else
                intpeak(i) = intpeak(i)+Output(j+1,i+1)*(Waves(j)-Waves(j-
1));
                intstd(i) = intstd(i)+StdDev(j+1,i+1)*(Waves(j)-Waves(j-
1));
            end;
        end;
    end;
    intpeak=intpeak/(Waves(specindex(end))-Waves(specindex(1)));
    intstd=intstd/(Waves(specindex(end))-Waves(specindex(1)));
end;
outkinetics=[Times' intpeak];
outstd=[Times' intstd];
if intindex==1
    filebody = input('What is the root filename? (do not include .dat
extension) ','s');
    if length(filebody) == 0
        filebody = filebody2;
    end
end
if leftedge==rightedge
    filename=strcat('kin_',filebody,'_',num2str(leftedge),'.dat');
    fid = fopen(filename,'w');
    fprintf(fid,'%g\t %g\n',outkinetics);
    fclose(fid);
    filename=strcat('kin_',filebody,'_',num2str(leftedge),'.std');
    fid = fopen(filename,'w');
    fprintf(fid,'%g\t %g\n',outstd);
    fclose(fid);
else
    filename=strcat('kin_',filebody,'_',num2str(leftedge),'-
',num2str(rightedge),'.dat');
    fid = fopen(filename,'w');
    fprintf(fid,'%g\t %g\n',outkinetics);
    fclose(fid);
    filename=strcat('kin_',filebody,'_',num2str(leftedge),'-
',num2str(rightedge),'.std');
    fid = fopen(filename,'w');
    fprintf(fid,'%g\t %g\n',outstd);
    fclose(fid);
end
figure;
plot(Times',intpeak);
xlabel('t / ps');
ylabel('int. absorbance / a.u. ');
titlename=strcat(num2str(leftedge),'cm to ',num2str(rightedge),'cm');
title(titlename);

```

```

        again = input('Would you like to integrate another spectral range? (y/n)
        ','s');
        clear leftedge rightedge specindex intpeak intstd outkinetics outstd
        filename;
    end;

```

B.2 Two dimensional vibrational spectroscopy

The following programs are designed to average, analyze, and plot the two dimensional infrared data and include the ability to select and plot data with different polarizations. These programs work for plotting 2D-IR data and transient 1D-IR data, but have not been fully tested for transient 2D-IR data analysis.

B.2.1 Average data files

```

% -----
% "avg2d" program written by James Cahoon, Version 11, updated 5/25/08

% Changes Version 10: Program now analyzes the noise in
% the data and throws away data outside a standard deviation threshold.

% This program is designed to average, 1D-IR, T1D-IR, 2D-IR, and T2D-IR data
% collected at one or multiple polarization angles, one or multiple UVpump-
% IRprobe
% and IRpump-IRprobe delay times, and one or multiple IRpump frequencies. The
% data is written as a binary Matlab file (.mat), which contains several
% variables:
% 1) sorteddata: contains the actual experimental data organized as cell
%    arrays of cell arrays. Each cell array row and column organizes the
%    data, as follows:
%    first cell array:
%        rows: IRpump-IRprobe delay time
%        columns: UVpump-IRprobe delay time
%    second cell array
%        rows: Polarizations
%        columns: IR-pump frequencies
%    third cell array
%        row 1, column 1: absorbance data
%        row 1, column 2: standard deviation data
%    fourth array (not a cell array, contains the actual data)
%        column 1: wavenumbers
%        column 2: absorbance data or standard deviation data
% 2) IRtimes: contains the IR-pump-IRprobe delay times
% 3) UVtimes: contains the UV-pump-IRprobe delay times
% 4) datafilename: string with the data filename, not including .mat
%    extension
% 5) polarizations: each row contains the different polarization conditions
%    with which data was collected. For T2D-IR data, the first column is the
%    IRpump-IRprobe relative polarization and the second column is UV-pump-
%    IRprobe relative polarization
% 6) waves: contains the wavenumbers collected

% This program assumes that the data filenames are contained in the file
% "datinfo.txt" and goes through all files specified by it

% This program does NOT plot the data, calculate kinetics, or calculate
% anisotropy data. These functions are performed by a separate matlab

```

```

% program "analyze2d" which relies on all the variables created by this
% program and written in the binary matlab file "datafilename.mat"
% -----

clear;

% -----
% Parameters used by program which you may want to adjust as needed

% determines number of standard deviations outside of which data must be
% to be determined as an outlier and deleted
stddevthresh = 3;

% determines the number of standard deviations for oscillations in the
% data less than 2 cm-1 apart in order for data set to be removed
stddevthreshoscillations = 1;

% determines the number of data points needed before noise analysis will
% throw away outliers (e.g. at least three for some statistics)
dataptsthresh = 3;

% determines how to round the IR time delays, for
% 10 fs set to 100
% 5 fs set to 200
% 1 fs set to 1000
timerounding = 100;

% determines the name of the input file
inputfile='datinfo.txt';
% -----

fin = fopen(inputfile,'r');
if fin < 0
    error(['Could not open ',inputfile,' for input']);
end

outputfileboolean = input('Write output binary file (.mat)? ','s');
if length(outputfileboolean)==0
    outputfileboolean='y';
end

oscillationanalysis = input('Perform error analysis on oscillations? ','s');
if oscillationanalysis == 'y'
    minimization = input('Scale individual data sets to mean? (requires chi.m,
simps.m, scaleddata.m) ','s');
    if length(minimization) == 0
        minimization = 'y';
    end
else
    oscillationanalysis = 'n';
    minimization = 'n';
end

filebody = fgetl(fin);
specinfo = fscanf(fin,'%f');
nmbrfiles = length(specinfo);

counterpolar=0;

% This for loop goes through all the files as specified by the datinfo
% file
for filenmbr=1:nmbrfiles

```

```

% -----
% This section determines the properties of this particular file, e.g.
% are there multiple IRpump frequencies, how many lines are there
% between specification of polarization / pump freqs, etc
filename = strcat(filebody,num2str(specinfo(filenbr,1)));
fin = fopen(filename,'r');
for i=1:4
    header = fgetl(fin);
end
counter=0;
polarizationcounter=0;
line=fgetl(fin);
if line(1:12)=='IR Frequency';
    counterfreq=0;
    IRfreqindex=1;
    yesIRfreqs='y';
    clear line;
    line=fgetl(fin);
else
    yesIRfreqs='n';
    counterfreq=1;
    IRfreqindex=1;
end
if line(1:20)=='IR Pump Polarization' | line(1:20)=='UV Pump Polarization';
    polarizationdone = 'n';
    if line(1:20)=='UV Pump Polarization'
        UVpumpprobe='y';
    else
        UVpumpprobe='n';
    end
    if length(find(line=='-'))>0
        if line(30:49)=='IR Pump Polarization' | line(31:50)=='IR Pump
Polarization';
            T2D='y';
            UVpumpprobe='n';
        else
            T2D='n';
        end
    else
        T2D='n';
    end
else
    T2D='n';
    polarizationdone='y';
    nmbrcolumns = length(str2num(line));
    counter=counter+1;
    polarizationcounter=polarizationcounter+1;
end
done = 'n';

while done == 'n'
    clear line;
    if polarizationdone=='n'
        polarizationcounter=polarizationcounter+1;
    end
    line = fgetl(fin);
    if counter == 0
        nmbrcolumns = length(str2num(line));
    end
    if length(line)<3
        done='y';
    elseif line(1:20)=='IR Pump Polarization' | line(1:20)=='UV Pump
Polarization';

```

```

        if polarizationdone=='n'
            polarizationcounter=polarizationcounter-1;
        end
        polarizationdone='y';
    elseif line(1:12)=='IR Frequency';
        done='y';
    else
        counter=counter+1;
    end
end
% nmbrpolarizationsections gives the number of sections of length
% polarizationcounter between the IR frequencies
nmbrpolarizationsections=counter/polarizationcounter;
fclose(fin);
fin = fopen(filename,'r');
for i=1:4
    header = fgetl(fin);
end
done = 'n';
if filenmbr==1
    IRfreqs(1,1:2)=[10000 10000];
    tempfreq(1,1:2)=[20000 20000];
    if T2D=='y'
        polarizations(1,1)=500;
        polarizations(1,2)=600;
    else
        polarizations(1,1)=500;
    end
end
counterpolarizationsections = 0;
% -----

% -----
% This section reads the data out of the file while simultaneously
% organizing it by polarization and IRpump frequency (if applicable)
while done=='n'
    clear line;
    line = fgetl(fin);
    if length(line)<5
        break;
    end
    if yesIRfreqs=='y' & counterpolarizationsections==0
        clear index;
        tempfreq(1,1) = str2num(line(15:20));
        index = find(tempfreq(1,1)-1 <= IRfreqs(:,1)+1 & IRfreqs(:,1)-1 <=
tempfreq(1,1)+1);
        if length(index)==0
            newIRfreq='y';
            counterfreq=counterfreq+1;
            IRfreqindex=counterfreq;
            tempfreq(1,2) = 0;
            IRfreqs(IRfreqindex,1) = tempfreq(1,1);
            clear line;
            line = fgetl(fin);
            if T2D=='y'
                tempUVpolarization = str2num(line(22:find(line=='-')-1));
                temp polarization = str2num(line(find(line=='-')+24:end));
            else
                temp polarization = str2num(line(22:end));
            end
        elseif length(index)==1;
            IRfreqindex=index(1,1);
            clear line;

```

```

        line = fgetl(fin);
        if T2D=='y'
            tempUVpolarization = str2num(line(22:find(line=='-')-1));
            temp polarization = str2num(line(find(line=='-')+24:end));
        else
            temp polarization = str2num(line(22:end));
        end
    end
else
    if T2D=='y'
        tempUVpolarization = str2num(line(22:find(line=='-')-1));
        temp polarization = str2num(line(find(line=='-')+24:end));
    else
        temp polarization = str2num(line(22:end));
    end
end
data = fscanf(fin,'%g %g %g',[nmbrcolumns polarizationcounter]);
line = fgetl(fin);
data = data';

% -----
% Rounds the IR time delays to nearest time step as determined by the
% variable "timerounding" (see comments at top of file)
data(:,1) = round(timerounding*data(:,1))/timerounding;
% -----

clear line;
if T2D == 'y'
    IRpolarizationindex = find(temp polarization(1,1)-1 <=
polarizations(:,1) & polarizations(:,1) <= temp polarization(1,1)+1);
    if length(IRpolarizationindex)==0
        polarizationindex=[];
    else
        UVpolarizationindex = find(tempUVpolarization(1,1)-1 <=
polarizations(:,2) & polarizations(:,2) <= tempUVpolarization(1,1)+1);
        if length(UVpolarizationindex)==0
            polarizationindex=[];
        else
            polarizationindex=IRpolarizationindex(find(UVpolarizationindex==IRpolarizationi
ndex));
        end
    end
    clear IRpolarizationindex UVpolarizationindex;
else
    polarizationindex = find(temp polarization(1,1)-1 <=
polarizations(:,1) & polarizations(:,1) <= temp polarization(1,1)+1);
    end
    newpolarization='n';
    if length(polarizationindex)==0
        newpolarization='y';
        counterpolar=counterpolar+1;
        polarizationindex=counterpolar;
        polarizations(polarizationindex,1)=temp polarization;
        if T2D=='y'
            polarizations(polarizationindex,2)=tempUVpolarization;
        end
    else
        end
    counterpolarizationsections=counterpolarizationsections+1;
    if yesIRfreqs=='y' &
counterpolarizationsections==nmbrpolarizationsections
        counterpolarizationsections=0;
    end
end

```



```

line = fgetl(fin);
tempfreq(1,2) = str2num(line(15:20));
IRfreqs(IRfreqindex,2) = tempfreq(1,2);
if newpolarization=='n'
    tempdata = alldata{polarizationindex(1),IRfreqindex};
    tempdata = tempdata';
    tempdata = [tempdata data'];
    tempdata = tempdata';
    tempdata = sortrows(tempdata,1);
    alldata{polarizationindex(1),IRfreqindex} = tempdata;
    clear tempdata;
else
    data = sortrows(data,1);
    alldata{polarizationindex(1),IRfreqindex}=data;
end
else
    if newpolarization=='y' | newIRfreq=='y'
        newpolarization = 'n';
        newIRfreq = 'n';
        data = sortrows(data,1);
        alldata{polarizationindex(1),IRfreqindex}=data;
    else
        tempdata = alldata{polarizationindex(1),IRfreqindex};
        tempdata = tempdata';
        tempdata = [tempdata data'];
        tempdata = tempdata';
        tempdata = sortrows(tempdata,1);
        alldata{polarizationindex(1),IRfreqindex} = tempdata;
        clear tempdata;
    end
end
end
nmbrpolarizations=length(polarizations(:,1));
% -----

% -----
% Rounds IRpump frequencies to the nearest 0.1 cm-1
if yesIRfreqs=='y'
    IRfreqs=round(IRfreqs*10)/10;
end
% -----

% -----
% This section organizes data by IR time delays into the new variable
% alldatatimesorted where each row is a new IR time delay
done='n';
% For 2D-IR, timecounter is IR time delay; For T2D-IR, timecounter is
% UV time delay
timecounter=0;
while done=='n'
    tempdata=alldata{1,1};
    if length(tempdata)==0;
        break;
    end
    timecounter=timecounter+1;
    IRtimes(timecounter)=tempdata(1,1);
    clear tempdata;
    for i=1:length(IRfreqs(:,1))
        for j=1:nmbrpolarizations
            tempdata=alldata{j,i};
            clear index;
            index = find(tempdata(:,1)==IRtimes(timecounter));
            if length(index)==0

```

```

        tempcell{j,i} = 0;
    else
        tempcell{j,i} = tempdata(index(1):index(end),:);
        if T2D=='y'
            tempcell{j,i}=sortrows(tempcell{j,i},2);
        end
        alldata{j,i} = tempdata(index(end)+1:end,:);
        clear tempdata;
    end
end
end
if T2D=='y'
    alldatetimesorted{1,timecounter}=tempcell;
    clear tempcell;
else
    alldatetimesorted{timecounter,1}=tempcell;
    clear tempcell;
end
end
if T2D=='y'
    UVtimes=IRtimes;
    nmbrUVtimes=length(UVtimes);
    alldata=alldatetimesorted;
    clear IRtimes alldatetimesorted;
    for k=1:nmbrUVtimes
        timecounter=0;
        done='n';
        while done=='n'
            clear tempdata;
            tempdata=alldata{1,k}{1,1};
            if length(tempdata)==0;
                done='y';
                break;
            end
            timecounter=timecounter+1;
            IRtimes(timecounter)=tempdata(1,2);
            clear tempdata;
            for i=1:length(IRfreqs(:,1))
                for j=1:nmbrpolarizations
                    tempdata=alldata{1,k}{j,i};
                    clear index;
                    index = find(tempdata(:,2)==IRtimes(timecounter));
                    if length(index)==0
                        tempcell{j,i} = 0;
                    else
                        tempcell{j,i} = tempdata(index(1):index(end),:);
                        alldata{1,k}{j,i} = tempdata(index(end)+1:end,:);
                        clear tempdata;
                    end
                end
            end
            end
            alldatetimesorted{timecounter,k}=tempcell;
            clear tempcell;
        end
    end
else
    nmbrUVtimes=1;
end
nmbrIRtimes=length(IRtimes);
% -----
% -----
% This section organizes the data by wavenumbers and accrues data from

```

```

different
% files in the variable 'alldatafiles'.
for n=1:nmbrUVtimes
    for m=1:nmbrIRtimes
        clear tempdata;
        tempdata=alldatatimesorted{m,n};
        for k=1:nmbrpolarizations;
            for i=1:length(IRfreqs(:,1))
                clear secondtempdata;
                secondtempdata = tempdata{k,i};
                if T2D=='y'
                    wavecolumn=3;
                    datacolumn=6;
                else
                    wavecolumn=2;
                    datacolumn=3;
                end
                secondtempdata = sortrows(secondtempdata,wavecolumn);
                wavecounter=0;
                nmbrwaveavgs=0;
                done='n';
                while done=='n';
                    wavecounter=wavecounter+1;
                    if length(secondtempdata(:,3))==0;
                        clear secondtempdata;
                        break
                    elseif filenmbr > 1
                        if wavecounter == nmbrwaves+1
                            break
                        end
                    end
                    if filenmbr==1
                        waves(wavecounter)=secondtempdata(1,wavecolumn);
                        nmbrwaves = length(waves);
                    else
                        nmbrwaves = length(waves);
                    end
                    clear index;
                    index = find(secondtempdata(:,wavecolumn) >=
(waves(wavecounter)-0.05) & secondtempdata(:,wavecolumn) <=
(waves(wavecounter)+0.05));
                    if filenmbr==1

alldatafiles{m,n}{k,i}(wavecounter,1)=waves(wavecounter);
                    nmbrdatapts{m,n}{k,i}(wavecounter,1)=0;
                    end
                    if wavecounter == 1
                        clear nmbraddedpts;
                        nmbraddedpts =
length(secondtempdata(index(1):index(end),datacolumn));

alldatafiles{m,n}{k,i}(wavecounter,1:length(alldatafiles{m,n}{k,i}(wavecounter,
:))+nmbraddedpts)=[alldatafiles{m,n}{k,i}(wavecounter,:)
secondtempdata(index(1):index(end),datacolumn)'];
                    if T2D == 'y'

alldatafiles2DIR{m,n}{k,i}(wavecounter,1:length(alldatafiles{m,n}{k,i}(wavecounter,
:))+nmbraddedpts)=[alldatafiles{m,n}{k,i}(wavecounter,:)
secondtempdata(index(1):index(end),datacolumn-1)'];

alldatafilesT1DIR{m,n}{k,i}(wavecounter,1:length(alldatafiles{m,n}{k,i}(wavecounter,
:))+nmbraddedpts)=[alldatafiles{m,n}{k,i}(wavecounter,:)
secondtempdata(index(1):index(end),datacolumn-2)'];

```

```

end

nmbrdatapts{m,n}{k,i}(wavecounter,1)=length(alldatafiles{m,n}{k,i}(wavecounter,
:))-1;
secondtempdata =
secondtempdata(index(end)+1:end,:);
else
alldatafiles{m,n}{k,i}(wavecounter,1:length(alldatafiles{m,n}{k,i}(wavecounter,
:)))=[alldatafiles{m,n}{k,i}(wavecounter,1:length(alldatafiles{m,n}{k,i}(waveco
unter,:))-nmbraddedpts) secondtempdata(index(1):index(end),datacolumn)'];
if T2D == 'y'

alldatafiles2DIR{m,n}{k,i}(wavecounter,1:length(alldatafiles{m,n}{k,i}(wavecou
nter,:))+nmbraddedpts)=[alldatafiles{m,n}{k,i}(wavecounter,:)
secondtempdata(index(1):index(end),datacolumn-1)'];

alldatafilesT1DIR{m,n}{k,i}(wavecounter,1:length(alldatafiles{m,n}{k,i}(wavecou
nter,:))+nmbraddedpts)=[alldatafiles{m,n}{k,i}(wavecounter,:)
secondtempdata(index(1):index(end),datacolumn-2)'];
end
secondtempdata =
secondtempdata(index(end)+1:end,:);

nmbrdatapts{m,n}{k,i}(wavecounter,1)=nmbrdatapts{m,n}{k,i}(1,1);
end
end
end
clear tempdata;
end
% -----

clear alldatetimesorted;
% now goes back to the top and begins with the next file
end
tempalldatafiles=alldatafiles;
% -----

% -----
% This section performs an error analysis on the data, throwing away data
% deemed outside the acceptable standard deviations. It averages the
% remaining data and calculates standard deviations. It also checks if there
% are readings of 100.00 in the data and removes them. If there is no
% good data at all for a particular wavenumber, it places a 200.00 in the
% data file. This 200.00 is then removed by the program "analyze2d" when
% plotting the data
nmbrarraypositions=length(waves)/32;
averagedalldatafiles=alldatafiles;

if T2D=='y'
nmbriterations=3;
else
nmbriterations=1;
end

for r=1:nmbriterations
if r==2
clear alldatafiles averagedalldatafiles;
alldatafiles=alldatafiles2DIR;
clear alldatafiles2DIR;
averagedalldatafiles=alldatafiles;

```

```

        oscillationanalysis == 'n';
elseif r==3
    clear alldatafiles averagedalldatafiles;
    alldatafiles=alldatafilesT1DIR;
    clear alldatafilesT1DIR;
    averagedalldatafiles=alldatafiles;
    oscillationanalysis == 'n';
end
for n=1:nmbrUVtimes
    for m=1:nmbrIRtimes
        for k=1:nmbrpolarizations;
            for i=1:length(IRfreqs(:,1))

                % -----
                % this section identifies data points well outside the
                % deviation of data
                standard
                clear allstddata allmeandata;
                allstddata=zeros(nmbrwaves,2);
                allmeandata=zeros(nmbrwaves,2);
                allstddata(:,1)=alldatafiles{m,n}{k,i}(:,1);
                allmeandata(:,1)=alldatafiles{m,n}{k,i}(:,1);
                for j=1:nmbrwaves
                    nmbrpts = length(alldatafiles{m,n}{k,i}(j,2:end));
                    clear tempdata stddev;
                    tempdata = alldatafiles{m,n}{k,i}(j,2:nmbrpts);
                    clear delindex;
                    delindex = find(tempdata==100 | tempdata==-100);
                    tempdata(delindex)=[];
                    nmbrpts = length(tempdata);
                    if nmbrpts==0
                        tempdata = 200
                    elseif nmbrpts >= dataptsthresh
                        stddata=std(tempdata);
                        meandata=mean(tempdata);
                        delindex = find(tempdata < meandata-
stddevthresh*stddata | tempdata > meandata+stddevthresh*stddata);
                        tempdata(delindex) = [];
                        allstddata(j,2)=std(tempdata);
                        allmeandata(j,2)=mean(tempdata);
                    else
                        allstddata(j,2)=std(tempdata);
                        allmeandata(j,2)=mean(tempdata);
                    end
                end
                averagedalldatafiles{m,n}{k,i}=[];
                averagedalldatafiles{m,n}{k,i}{1,1}=allmeandata;
                averagedalldatafiles{m,n}{k,i}{1,2}=allstddata;
                % -----
                % -----
                % this section identifies data sets with large oscillations
                % between adjacent wavenumbers (< 2 cm-1) and removes them
                if oscillationanalysis == 'y'
                    clear allstddata allmeandata;
                    allstddata=zeros(nmbrwaves,2);
                    allmeandata=zeros(nmbrwaves,2);
                    allstddata(:,1)=alldatafiles{m,n}{k,i}(:,1);
                    allmeandata(:,1)=alldatafiles{m,n}{k,i}(:,1);
                    if nmbrarraypositions>1

```

```

clear arrayoscillations;
index=0;
baddataindex=[];
for j=1:nmbrdatapts{m,n}{k,i}(1,1)
    clear arrayoscillations
    arrayoscillations = [];
    clear tempdata;
    tempdata = alldatafiles{m,n}{k,i}(:,1+j);
    clear delindex;
    baddata = 'n';
    delindex = find(tempdata==100 | tempdata==
100);

    if length(delindex) > 0
        baddata = 'y';
        baddataindex=[baddataindex j];
    end
    if baddata == 'n'
        index=index+1;
        for q=2:nmbrarraypositions
            for p=1:nmbrarraypositions-1
                if abs(waves(32*q)-waves(32*q-
p))<1.8 & abs(waves(32*q)-waves(32*q-p))>0.1
                    arrayoscillations =
[arrayoscillations abs((tempdata([32*q:-1*(p+1):32*q-31*(p+1)])-tempdata([32*q-
p:-1*(p+1):32*q-31*(p+1)-p])))]';
                end
            end
        end
        avgarrayoscillations(index) =
mean(arrayoscillations);
    end
end
if length(avgarrayoscillations)>0
    stdoscillations=stddevthreshoscillations*std(avgarrayoscillations);
    meanoscillations=mean(avgarrayoscillations);
    baddataindex=[baddataindex
find(avgarrayoscillations > meanoscillations+stdoscillations)];
    if nmbrdatapts{m,n}{k,i}(1,1)-
length(baddataindex) < dataptsthresh
        else
            alldatafiles{m,n}{k,i}(:,1+baddataindex)=[];
            if minimization == 'y'
                for
j=1:length(alldatafiles{m,n}{k,i}(1,2:end));
                    % variable contains scaling factors
and
                    % offset for each data set
                    scalefactors{m,n}{k,i}(1:2,j)=[1
0.0001]';
                    avgdata =
averagedalldatafiles{m,n}{k,i}{1,1}(:,2);
                    data =
                    low = [0.5 -0.2];
                    high = [2 0.2];
                    options = foptions;
                    deltachi = 2000;
                    oldchi = 1000;
                    searchparam = [1 0.001]';
                    nmbrparam = 1:2;
                    while deltachi > 0.01*oldchi

```

```

searchparam=simps('chi',searchparam,nmbrparam,options,low,high,avgdata,data);
scaleddataset =
scaleddata(data,searchparam);
newchi=sum((scaleddataset-
avgdata).^2);
deltachi = oldchi-newchi;
oldchi = newchi;
end

scalefactors{m,n}{k,i}(1:2,j)=searchparam;
alldatafiles{m,n}{k,i}(:,1+j) =
scaleddataset;
clear scaleddataset searchaparam;
end
end

allstddata(:,2)=std(alldatafiles{m,n}{k,i}(:,2:end)');
allmeandata(:,2)=mean(alldatafiles{m,n}{k,i}(:,2:end)');
averagedalldatafiles{m,n}{k,i}{1,1}=allmeandata;
averagedalldatafiles{m,n}{k,i}{1,2}=allstddata;
end
end
end
end
% -----
-----

end
end
end
if r==1
sorteddata=averagedalldatafiles;
elseif r==2
sorteddata2DIR=averagedalldatafiles;
elseif r==3
sorteddataT1DIR=averagedalldatafiles;
end

end
% -----
% -----
% This section puts all the data into the proper format, clears variables
% which are not to be saved, and saves the .mat data file
clear alldatetimesorted alldatafiles averagedalldatafiles;
if yesIRfreqs=='n'
clear IRfreqs;
IRfreqs='NA';
end
IRtimes=IRtimes';
if T2D=='y'
UVtimes=UVtimes';
elseif UVpumpprobe=='y'
UVtimes=IRtimes;
clear IRtimes;
end
waves=waves';
sorteddata=sorteddata;

```

```

clear newtempdata index i plotthedata fin line nmbrfiles nmbrwaveavgs;
clear k timecounter ans counter whichtime done counterfreq;
clear wavecounter inputfile tempfreq header alldata filename;
clear nmbrcolors data minimum maximum limit;
clear counterpolar j newpolarization nmbrpolarizations
nmbrpolarizationsections;
clear nmbrIRtimes polarizationcounter polarizationdone polarizationindex
polarizationline;
clear temp polarization yesIRfreqs nmbrcolumns m;
clear averagedata averagedstd databyfiles filenmbr tempdata tempstd
counterpolarizationsections newIRfreq;
clear IRfreqindex allmeandata allstddata arrayoscillations avgarrayoscillations
baddata;
clear baddataindex dataptsthresh delindex meandata meanoscillations
nmbrarraypositions nmbrpts nmbrwaves;
clear p q secondtempdata stddata stddevthresh stddevthreshoscillations
stdoscillations timerounding;
clear averagedalldatafiles avgdata deltachi high low newchi nmbraddedpts
nmbrdatapts nmbrparam;
clear oldchi options oscillationanalysis scalefactors searchparam
tempalldatafiles;
clear minimization T2D UVpumpprobe n nmbrUVtimes tempUVpolarization r
nmbriterations wavecolumn;
clear datacolumn;

if length(specinfo) == 1
    datafilename = strcat(filebody,num2str(specinfo(1)));
else
    datafilename = strcat(filebody,num2str(specinfo(1)),'-
',num2str(specinfo(end)));
end
datafilename=strcat('data_',datafilename);
clear filebody specinfo;

if outputfileboolean=='y'
    clear outputfileboolean;
    save(datafilename);
else
    clear outputfileboolean;
end
end
% -----

```

B.2.2 Analyzing and plotting data

analyze2d.m

```

inputfile = input('What is the data filename? ','s');
if length(inputfile)==0;
else
    load(inputfile);
end

if length(polarizations(1,:))==2
    T2D='y';
    UVpumpprobe='n';
    nmbrUVtimes=length(UVtimes);
    whichdataset=input('Which data set do you want to analyze? (t2d,2d,t1d)
','s');
    if length(whichdataset)==0
        whichdataset='t2d';
    end
end

```



```

elseif whichdataset=='2d'
    sorteddata=sorteddata2DIR;
elseif whichdataset=='t1d'
    sorteddata=sorteddataT1DIR;
end
else
    T2D='n';
end

if T2D == 'n'
    UVpumpprobe='n';
    variables=who;
    for i=1:length(variables)
        if length(variables{i})==7
            if variables{i}(1:7)=='UVtimes';
                IRtimes=UVtimes;
                UVpumpprobe='y'
            end
        end
    end
end

nmbrpolarizations = length(polarizations(:,1));
nmbrIRtimes = length(IRtimes);
nmbrwaves=length(waves);
if length(IRfreqs(1,1))<2
    nmbrIRfreqs=length(IRfreqs(:,1));
else
    nmbrIRfreqs=0;
end

if nmbrIRfreqs>3
    calc2Dspectra = input('Do you want to plot 2D spectra? (y/n) ','s');
    if length(calc2Dspectra)==0
        calc2Dspectra = 'y';
    end
else
    calc2Dspectra = 'n';
end

if calc2Dspectra == 'n'
    writefile = input('Do you want to write an output file (.dat .std)? ','s');
    if length(writefile) == 0
        writefile = 'n';
    end
else
    writefile = 'n';
end

if nmbrIRfreqs>1 & calc2Dspectra == 'n';
    display(IRfreqs(:,1));
    chooseIRfreq = input('Which IR pump freq do you want to analyze? ');
    IRfreqindex = find(IRfreqs(:,1)>chooseIRfreq-1.1 &
    IRfreqs(:,1)<chooseIRfreq+1.1);
else
    IRfreqindex = 1;
end

if T2D=='y' & calc2Dspectra == 'n';
    if nmbrUVtimes==1 & nmbrIRtimes==1
        UVorIR='NA';
    elseif nmbrUVtimes==1
        UVorIR='IR';
    end
end

```

```

elseif nmbrIRtimes==1
    UVorIR='UV';
end
end

if nmbrpolarizations == 2
    calcmagicangle = input('Do you want to calculate the magic angle signal?
(y/n) ','s');
    if calcmagicangle == 'y'
        polarizationmode = 'magic';
        polarizationtitle = ' Polarization: magic angle';
        calcanisotropy = 'n';
        calcparallel = 'n';
    end
    if calcmagicangle == 'n'
        calcanisotropy = input('Do you want to calculate the anisotropy? (y/n)
','s');
        if calcanisotropy == 'y'
            polarizationmode = 'anis';
        end
        elseif calcmagicangle == 'y'
            calcanisotropy = 'n';
        end
        if calcanisotropy == 'n' & calcmagicangle == 'n'
            calcmagicangle='y';
            calcparallel = input('Which polarization do you want to plot? (pl,pd)
','s');
            if calcparallel == 'pl'
                polarizationmode = 'pl';
                polarizationtitle = ' Polarization: parallel';
            elseif calcparallel == 'pd'
                polarizationmode = 'pd';
                polarizationtitle = ' Polarization: perpendicular';
            end
        else
            calcparallel = 'n';
        end
    elseif nmbrpolarizations == 1
        calcanisotropy = 'n';
        calcmagicangle = 'n';
        calcparallel = 'n';
        polarizationmode = '';
        if polarizations(1,1) == 54.7;
            polarizationmode = 'magic';
            polarizationtitle = ' Polarization: magic';
        elseif polarizations(1,1) == 0;
            polarizationtitle = ' Polarization: parallel';
        elseif polarizations(1,1) == 90;
            polarizationtitle = ' Polarization: perpendicular';
        else
            polarizationtitle = '';
        end
    elseif nmbrpolarizations == 4
        calcanisotropy = 'n';
        calcmagicangle = 'n';
        calcparallel = 'n';
        polarizationmode = '';
        polarizationtitle = '';
    end

    if calc2Dspectra == 'n'

```

```

if nmbrpolarizations == 1
    if T2D=='y'
        if UVorIR=='IR';
            times=IRtimes;
        elseif UVorIR=='UV'
            times=UVtimes;
        else
            times=IRtimes;
        end
    else
        times=IRtimes;
    end
    nmbrtimes=length(times);
    Output = zeros(nmbrwaves+1,nmbrtimes+1);
    Output(2:end,1) = waves;
    Output(1,2:end) = times';
    StdDev = zeros(nmbrwaves+1,nmbrtimes+1);
    StdDev(2:end,1) = waves;
    StdDev(1,2:end) = times';
    calcanisotropy = 'n';
    calcmagicangle = 'n';
    calcparallel = 'n';
    for i=1:nmbrtimes
        if T2D=='y'
            if UVorIR=='UV'
                Output(2:end,i+1) = sorteddata{1,i}{1,IRfreqindex}{1}(:,2);
                StdDev(2:end,i+1) = sorteddata{1,i}{1,IRfreqindex}{2}(:,2);
            elseif UVorIR=='IR'
                Output(2:end,i+1) = sorteddata{i,1}{1,IRfreqindex}{1}(:,2);
                StdDev(2:end,i+1) = sorteddata{i,1}{1,IRfreqindex}{2}(:,2);
            elseif UVorIR=='NA'
                Output(2:end,i+1) = sorteddata{i,1}{1,IRfreqindex}{1}(:,2);
                StdDev(2:end,i+1) = sorteddata{i,1}{1,IRfreqindex}{2}(:,2);
            end
        else
            Output(2:end,i+1) = sorteddata{i,1}{1,IRfreqindex}{1}(:,2);
            StdDev(2:end,i+1) = sorteddata{i,1}{1,IRfreqindex}{2}(:,2);
        end
    end
end

if nmbrpolarizations == 2

    if T2D=='y'
        clear IRtimes;
        if UVorIR=='IR';
            IRtimes=IRtimes;
        elseif UVorIR=='UV'
            IRtimes=UVtimes;
        else
            IRtimes=IRtimes;
        end
    end

    if calcanisotropy == 'y'
        anisotropydata=zeros(nmbrwaves,nmbrIRtimes);
        anisotropystd=zeros(nmbrwaves,nmbrIRtimes);
        for i=1:nmbrIRtimes
            if T2D=='y'
                if UVorIR=='UV'
                    data=sorteddata{1,i};
                elseif UVorIR=='IR'
                    data=sorteddata{i,1};
                end
            end
        end
    end
end

```

```

        elseif UVorIR=='NA'
            data=sorteddata{i,1};
        end
    else
        data=sorteddata{i,1};
    end
    if T2D=='y'
        if polarization(1,1)==polarization(2,1)
            if polarizations(1,2)==0

[tempparalleldata,tempperpendiculardata]=deal(data{1:2,IRfreqindex});
                elseif polarizations(1,2)==90

[tempperpendiculardata,tempparalleldata]=deal(data{1:2,IRfreqindex});
                end
                elseif polarization(1,2)==polarization(2,2)
                    if polarizations(1,1)==0

[tempparalleldata,tempperpendiculardata]=deal(data{1:2,IRfreqindex});
                        elseif polarizations(1,1)==90

[tempperpendiculardata,tempparalleldata]=deal(data{1:2,IRfreqindex});
                            end
                            end
                        else
                            if polarizations(1,1)==0

[tempparalleldata,tempperpendiculardata]=deal(data{1:2,IRfreqindex});
                                elseif polarization(1,1)==90

[tempperpendiculardata,tempparalleldata]=deal(data{1:2,IRfreqindex});
                                    end
                                    end
                                end
                                parallelstd=paralleldata{2};
                                paralleldata=paralleldata{1};
                                perpendicularstd=perpendiculardata{2};
                                perpendiculardata=perpendiculardata{1};
                                anisotropydata(:,i) = (1.00*paralleldata(:,2)-
perpendiculardata(:,2))./(1.00*paralleldata(:,2)+2*perpendiculardata(:,2));
                                anisotropystd(:,i) = (parallelstd(:,2)-
perpendicularstd(:,2))./(parallelstd(:,2)+2*perpendicularstd(:,2));
                                end
                                Output = zeros(nmbrwaves+1,nmbrIRtimes+1);
                                Output(2:end,1) = waves;
                                Output(1,2:end) = IRtimes';
                                StdDev = zeros(nmbrwaves+1,nmbrIRtimes+1);
                                StdDev(2:end,1) = waves;
                                StdDev(1,2:end) = IRtimes';
                                Output(2:end,2:end) = anisotropydata;
                                StdDev(2:end,2:end) = anisotropystd;
                            end
                        end

if calcmagicangle == 'y'
    magicangledata=zeros(nmbrwaves,nmbrIRtimes);
    magicanglestd=zeros(nmbrwaves,nmbrIRtimes);
    paralleldata=zeros(nmbrwaves+1,nmbrIRtimes+1);
    parallelstd=zeros(nmbrwaves+1,nmbrIRtimes+1);
    perpendiculardata=zeros(nmbrwaves+1,nmbrIRtimes+1);
    perpendicularstd=zeros(nmbrwaves+1,nmbrIRtimes+1);
    for i=1:nmbrIRtimes
        if T2D=='y'
            if UVorIR=='UV'
                data=sorteddata{1,i};

```

```

elseif UVorIR=='IR'
    data=sorteddata{i,1};
elseif UVorIR=='NA'
    data=sorteddata{i,1};
end
else
    data=sorteddata{i,1};
end
if T2D=='y'
    if polarization(1,1)==polarization(2,1)
        if polarizations(1,2)==0

[temppparalleldata,temppperpendiculardata]=deal(data{1:2,IRfreqindex});
        elseif polarizations(1,2)==90

[temppperpendiculardata,temppparalleldata]=deal(data{1:2,IRfreqindex});
        end
        elseif polarization(1,2)==polarization(2,2)
            if polarizations(1,1)==0

[temppparalleldata,temppperpendiculardata]=deal(data{1:2,IRfreqindex});
            elseif polarizations(1,1)==90

[temppperpendiculardata,temppparalleldata]=deal(data{1:2,IRfreqindex});
            end
        end
    else
        if polarizations(1,1)==0

[temppparalleldata,temppperpendiculardata]=deal(data{1:2,IRfreqindex});
        elseif polarization(1,1)==90

[temppperpendiculardata,temppparalleldata]=deal(data{1:2,IRfreqindex});
        end
    end
    temppparallelstd=temppparalleldata{2};
    temppparallelstd=temppparallelstd(:,2);
    temppparalleldata=temppparalleldata{1};
    temppparalleldata=temppparalleldata(:,2);
    temppperpendicularstd=temppperpendiculardata{2};
    temppperpendicularstd=temppperpendicularstd(:,2);
    temppperpendiculardata=temppperpendiculardata{1};
    temppperpendiculardata=temppperpendiculardata(:,2);

%Checks if the parallel or perpendicular data have any readings
%of 200
clear checkindex gooddataindex;
checkindex = find(temppparalleldata(:,1)==200);
gooddataindex = [1:1:length(temppparalleldata(:,1))];
gooddataindex(:,checkindex) = [];
for j=1:length(checkindex)
    clear firstindex lastindex;
    firstindex = find(gooddataindex(1,:) < checkindex(j));
    firstindex = gooddataindex(firstindex(end));
    lastindex = find(gooddataindex(1,:) > checkindex(j));
    lastindex = gooddataindex(lastindex(1));
    if length(firstindex)==0
        firstindex=lastindex;
    end
    if length(lastindex)==0
        lastindex=firstindex;
    end
    temppparalleldata(checkindex(j),1) =

```

```

(temppparalleldata(firstindex)+temppparalleldata(lastindex))/2;
    end
    clear checkindex gooddataindex;
    checkindex = find(temppperpendiculardata(:,1)==200);
    gooddataindex = [1:1:length(temppperpendiculardata(:,1))];
    gooddataindex(:,checkindex) = [];
    for j=1:length(checkindex)
        clear firstindex lastindex;
        firstindex = find(gooddataindex(1,:) < checkindex(j));
        firstindex = gooddataindex(firstindex(end));
        lastindex = find(gooddataindex(1,:) > checkindex(j));
        lastindex = gooddataindex(lastindex(1));
        if length(firstindex)==0
            firstindex=lastindex;
        end
        if length(lastindex)==0
            lastindex=lastindex;
        end
        temppperpendiculardata(checkindex(j),1) =
(temppperpendiculardata(firstindex,1)+temppperpendiculardata(lastindex,1))/2;
    end
    %

    magicangledata(:,i) =
1.00*temppparalleldata(:,1)+2*temppperpendiculardata(:,1);
    magicanglestd(:,i) =
temppparallelstd(:,1)+2*temppperpendicularstd(:,1);
    paralleldata(2:end,i+1)=temppparalleldata(:,1);
    parallelstd(2:end,i+1)=temppparallelstd(:,1);
    perpendiculardata(2:end,i+1)=temppperpendiculardata(:,1);
    perpendicularstd(2:end,i+1)=temppperpendicularstd(:,1);
    clear temppparalleldata temppperpendiculardata
temppperpendiculardata temppparalleldata;
    clear temppparallelstd temppperpendicularstd temppperpendicularstd
temppparallelstd;
    end
    Output = zeros(nmbrwaves+1,nmbrIRtimes+1);
    Output(2:end,1) = waves;
    Output(1,2:end) = IRtimes';
    StdDev = zeros(nmbrwaves+1,nmbrIRtimes+1);
    StdDev(2:end,1) = waves;
    StdDev(1,2:end) = IRtimes';
    Output(2:end,2:end) = magicangledata;
    StdDev(2:end,2:end) = magicanglestd;
    if calcparallel == 'pl'
        Output(2:end,2:end) = paralleldata(2:end,2:end);
        StdDev(2:end,2:end) = parallelstd(2:end,2:end);
    end
end
end

if UVpumpprobe=='y'

%-----%
% Negative time spectra filtering (FFT lowpass) and subtraction
%
%-----%

subtraction = input('Subtract negative time slices (first 5 points) ?
(y/n) ','s');
if length(subtraction)==0

```

```

        subtraction='n';
    end
    if (subtraction=='y') | (subtraction=='Y')
        clear negtime;
        negtime=zeros(nmbrwaves,1);
        negtimesindex = find(Output(1,1:end)<-5);
        nmbrnegtimes = length(negtimesindex);
        for i=1:nmbrnegtimes
            negtime=negtime+Output(2:end,negtimesindex(i));
        end;
        negtime=negtime/nmbrnegtimes;
        %         filtering = input('Lowpass filter negative time slices?
(y/n) ','s');
        %         if length(filtering)==0;
        %             filtering='Y';
        %         end;
        %         if (filtering=='y') | (filtering=='Y')
        %             cutoff=nmbrwaves/5;
        %             for i=1:nmbrwvs
        %                 sum=1;
        %                 for j=1:cutoff-1
        %                     sum=sum+2*cos(2*pi*j*(i-1)/nmbrwvs);
        %                 end;
        %                 u(i)=sum/nmbrwvs;
        %             end;
        %             for i=1:nmbrwvs
        %                 sum=0;
        %                 for j=1:nmbrwvs
        %                     k=mod(i-j,nmbrwvs);
        %                     sum=sum+negtime(j)*u(k+1);
        %                 end;
        %                 filtered(i)=sum;
        %             end;
        %             negtime=filtered';
        %         end;
        for i=2:length(Output(1,:));
            Output(2:end,i) = Output(2:end,i)-negtime(:);
        end;
    end;

%-----%
% Correction for window signal (assuming it is a linear offset)
%

nmbrwvs=nmbrwaves;
windowssignal = input('Correct for window signal? (y/n) ','s');
if length(windowssignal)==0;
    windowssignal='n';
end
if (windowssignal=='y') | (windowssignal=='Y')
    OutputFFT = Output;
    clear specindex leftbase newbase rightbase lefwavenumber
    rightwavenumber starttime leftwave rightwave j k m;
    lefwavenumber = input('left anchor range, e.g. [2002 2007]? ');
    rightwavenumber = input('right anchor range, e.g. [2002 2007]? ');
    starttime = input('begin correction (ps)? ');
    endtime = input('end correction (ps)? ');
    starttimeindex=find(Output(1,2:end)>=starttime);
    starttimeindex=starttimeindex+1;
    j=starttimeindex(1);
    endtimeindex=find(Output(1,2:end)>=endtime);
    endtimeindex=endtimeindex+1;

```

```

        k=endtimeindex(1);
        if leftwavenumber==rightwavenumber
            oneanchor = 'y';
        else
            oneanchor = 'n';
        end
        if length(leftwavenumber)==1
            specindex = find(leftwavenumber <= Output(:,1) & Output(:,1) <=
rightwavenumber(1));
            specindexleft = specindex(1);
            leftwave = Output(specindexleft,1);
            for m=1:k-j+1
                leftbase(m) = OutputFFT(specindexleft,j+m-1);
            end
        else
            specindexleft = find(leftwavenumber(1) <= Output(:,1) &
Output(:,1) <= leftwavenumber(2));
            leftwave =
(Output(specindexleft(1),1)+Output(specindexleft(end),1))/2;
            for m=1:k-j+1
                leftbase(m) = mean(OutputFFT(specindexleft(:),j+m-1));
            end
        end
        if length(rightwavenumber)==1
            clear specindex;
            specindex = find(leftwavenumber(1) <= Output(:,1) & Output(:,1)
<= rightwavenumber);
            specindexright = specindex(end);
            rightwave = Output(specindexright,1);
            for m=1:k-j+1
                rightbase(m) = OutputFFT(specindexright,j+m-1);
            end
        else
            specindexright = find(rightwavenumber(1) <= Output(:,1) &
Output(:,1) <= rightwavenumber(2));
            rightwave =
(Output(specindexright(1),1)+Output(specindexright(end),1))/2;
            for m=1:k-j+1
                rightbase(m) = mean(OutputFFT(specindexright(:),j+m-1));
            end
        end
        for m=1:k-j+1
            for i=1:nbrwvs
                if oneanchor=='y'
                    newbase(1)=leftbase(m);
                else
                    slope = (rightbase(m)-leftbase(m))/(rightwave-
leftwave);
                    newbase(1)=leftbase(m)+slope*(Output(i+1,1)-leftwave);
                end
                Output(i+1,j+m-1) = Output(i+1,j+m-1)-newbase(1);
                clear newbase slope;
            end;
        end;
    end;
end;
%-----%
end

if nbrpolarizations == 4
    Display('Needs to be programmed');
end

```



```

end;

filenamedat = strcat(datafilename, '-', polarizationmode, '.dat');
filenamestd = strcat(datafilename, '-', polarizationmode, '.std');
if writefile == 'y'
    save(filenamedat, 'Output', '-ascii');
    save(filenamestd, 'StdDev', '-ascii');
end
clear filenamedat filenamestd;

if calc2Dspectra == 'y';

    if nmbrIRtimes > 1
        display(IRtimes);
        whichtime = input('Which IR time do you want to plot (only one)? ');
        whichtimeindex = find(whichtime==IRtimes);
    elseif nmbrIRtimes == 1
        whichtime = IRtimes(1,1);
        whichtimeindex = 1;
    end

    if T2D=='y'
        if nmbrUVtimes > 1
            display(UVtimes);
            whichUVtime = input('Which UV time do you want to plot (only one)? ');
            whichUVtimeindex = find(whichUVtime==UVtimes);
        elseif nmbrUVtimes==1
            whichUVtime = UVtimes(1,1);
            whichUVtimeindex = 1;
        end
    else
        whichUVtimeindex = 1;
    end

    data=sorteddata{whichtimeindex,1};

    if nmbrpolarizations == 2
        Output=zeros(nmbrwaves+1,nmbrIRfreqs+2);
        paralleldata=zeros(nmbrwaves+1,nmbrIRfreqs+2);
        perpendiculardata=zeros(nmbrwaves+1,nmbrIRfreqs+2);
        parallelstd=zeros(nmbrwaves+1,nmbrIRfreqs+2);
        perpendicularstd=zeros(nmbrwaves+1,nmbrIRfreqs+2);
        for i=1:nmbrIRfreqs
            clear data;
            data=sorteddata{whichtimeindex,whichUVtimeindex};
            if T2D=='y'
                if polarization(1,1)==polarization(2,1)
                    if polarizations(1,2)==0
                        [tempparalleldata,tempperpendiculardata]=deal(data{1:2,i});
                        elseif polarizations(1,2)==90
                            [tempperpendiculardata,tempparalleldata]=deal(data{1:2,i});
                            end
                        elseif polarization(1,2)==polarization(2,2)
                            if polarizations(1,1)==0
                                [tempparalleldata,tempperpendiculardata]=deal(data{1:2,i});
                                elseif polarizations(1,1)==90
                                    [tempperpendiculardata,tempparalleldata]=deal(data{1:2,i});
                                    end
                                end
                            end
                        end
                    end
                end
            end
        end
    end
end

```

```

        end
    else
        if polarizations(1,1)==0
            [tempparalleldata,tempperpendiculardata]=deal(data{1:2,i});
        elseif polarization(1,1)==90
            [tempperpendiculardata,tempparalleldata]=deal(data{1:2,i});
        end
    end
    if T2D=='y'
        datacolumn=2;
    else
        datacolumn=1;
    end
    tempparallelstd=tempparalleldata{2};
    tempparallelstd=tempparallelstd(:,datacolumn);
    tempparalleldata=tempparalleldata{1};
    tempparalleldata=tempparalleldata(:,datacolumn);
    tempperpendicularstd=tempperpendiculardata{2};
    tempperpendicularstd=tempperpendicularstd(:,datacolumn);
    tempperpendiculardata=tempperpendiculardata{1};
    tempperpendiculardata=tempperpendiculardata(:,datacolumn);

    %Checks if the parallel or perpendicular data have any readings
    %of 200
    clear checkindex gooddataindex;
    checkindex = find(tempparalleldata(:,1)==200);
    gooddataindex = [1:1:length(tempparalleldata(:,1))];
    gooddataindex(:,checkindex) = [];
    for j=1:length(checkindex)
        clear firstindex lastindex;
        firstindex = find(gooddataindex(1,:) < checkindex(j));
        firstindex = gooddataindex(firstindex(end));
        lastindex = find(gooddataindex(1,:) > checkindex(j));
        lastindex = gooddataindex(lastindex(1));
        if length(firstindex)==0
            firstindex=lastindex;
        end
        if length(lastindex)==0
            lastindex=firstindex;
        end
        tempparalleldata(checkindex(j),1) =
        (tempparalleldata(firstindex)+tempparalleldata(lastindex))/2;
    end
    clear checkindex gooddataindex;
    checkindex = find(tempperpendiculardata(:,1)==200);
    gooddataindex = [1:1:length(tempperpendiculardata(:,1))];
    gooddataindex(:,checkindex) = [];
    for j=1:length(checkindex)
        clear firstindex lastindex;
        firstindex = find(gooddataindex(1,:) < checkindex(j));
        firstindex = gooddataindex(firstindex(end));
        lastindex = find(gooddataindex(1,:) > checkindex(j));
        lastindex = gooddataindex(lastindex(1));
        if length(firstindex)==0
            firstindex=lastindex;
        end
        if length(lastindex)==0
            lastindex=lastindex;
        end
        tempperpendiculardata(checkindex(j),1) =
        (tempperpendiculardata(firstindex,1)+tempperpendiculardata(lastindex,1))/2;
    end
    %

```

```

        magicangledata(:,i) =
1.00*tempparalleldata(:,1)+2*tempperpendiculardata(:,1);
        magicanglestd(:,i) =
tempparallelstd(:,1)+2*tempperpendicularstd(:,1);
        paralleldata(2:end,i+2)=tempparalleldata(:,1);
        parallelstd(2:end,i+2)=tempparallelstd(:,1);
        perpendiculardata(2:end,i+2)=tempperpendiculardata(:,1);
        perpendicularstd(2:end,i+2)=tempperpendicularstd(:,1);
        clear tempparalleldata tempperpendiculardata tempperpendiculardata
tempparalleldata;
        clear tempparallelstd tempperpendicularstd tempperpendicularstd
tempparallelstd;
    end
end

```

```

    if calcparallel == 'pl'
        Output(2:end,3:end) = paralleldata(2:end,3:end);
    elseif calcparallel == 'pd'
        Output(2:end,3:end) = perpendiculardata(2:end,3:end);
    elseif calcmagicangle == 'y'
        Output(2:end,3:end) = magicangledata;
    end
end

if nmbrpolarizations == 1
    Output=zeros(nmbrwaves+1,nmbrIRfreqs+2);
    rawdata=zeros(nmbrwaves+1,nmbrIRfreqs+2);
    rawstd=zeros(nmbrwaves+1,nmbrIRfreqs+2);
    baddata = 'n';
    if T2D=='y'
        datacolumn=2;
    else
        datacolumn=2;
    end
    for i=1:nmbrIRfreqs
        clear data tempdata tempdatastd;
        data=sorteddata{whichtimeindex,whichUVtimeindex};
        tempdata = data{1,i};
        tempdatastd=tempdata{2};
        tempdatastd=tempdatastd(:,datacolumn);
        tempdata=tempdata{1};
        tempdata=tempdata(:,datacolumn);
        %Checks if the parallel or perpendicular data have any readings
        %of 200
        clear checkindex gooddataindex;
        checkindex = find(tempdata(:,1)==200);
        if baddata == 'n'
            if length(checkindex)>0
                baddata = 'y';
            end
        end
        gooddataindex = [1:1:length(tempdata(:,1))];
        gooddataindex(:,checkindex) = [];
        for j=1:length(checkindex)
            clear firstindex lastindex;
            firstindex = find(gooddataindex(1,:) < checkindex(j));
            firstindex = gooddataindex(firstindex(end));
            lastindex = find(gooddataindex(1,:) > checkindex(j));
            lastindex = gooddataindex(lastindex(1));
            if length(firstindex)==0
                firstindex=lastindex;
            end
        end
    end
end

```

```

        if length(lastindex)==0
            lastindex=firstindex;
        end
        tempdata(checkindex(j,1),1) =
(tempdata(firstindex)+tempdata(lastindex))/2;
    end
    clear checkindex gooddataindex;
    %
    rawdata(2:end,i+2)=tempdata(:,1);
    rawstd(2:end,i+2)=tempdatastd(:,1);
    clear tempdata tempdatastd;
    clear tempparallelstd tempperpendicularstd tempperpendicularstd
tempparallelstd;
    end
    Output(2:end,3:end) = rawdata(2:end,3:end);
    if baddata == 'y'
        display('Warning, data reading 100 or 200 has been removed and
replaced by interpolation');
    end
end

if nmbrpolarizations == 4
    % Needs to be programmed
end

Output(2:end,3:end)=-1*Output(2:end,3:end);

nmbrcolors=101;
minimum = min(min(Output(2:end,3:end)));
maximum = max(max(Output(2:end,3:end)));
minimum = abs(minimum);
maximum = abs(maximum);
absolutemaximum = max([minimum maximum]);
normalize = input('Do you want to normalize the spectra? ','s');
if length(normalize) == 0
    normalize = 'y';
end
if normalize == 'y';
    steps = input('What contour step size (e.g. 0.1)? ');
    if length(steps) == 0
        steps = 0.1;
    end
    figure;
    [C,h] =
contourf(waves,IRfreqs(:,1),Output(2:end,3:end)/absolutemaximum, [[-1:steps:0-
steps] [0+steps:steps:1]]);
    % [C,h] =
contourf(waves,IRfreqs(:,1),Output(2:end,3:end)/absolutemaximum, [[-
1:steps:1]]);
    caxis([-1 1]);
else
    steps = round(10*(absolutemaximum/10))/10;
    % figure;
    [C,h] = contourf(waves,IRfreqs(:,1),Output(2:end,3:end)', [-
1*absolutemaximum : steps : absolutemaximum]);
    caxis([-1*absolutemaximum absolutemaximum]);
end
if T2D=='y'
    space=' ';
    title(strcat('Tw = ',num2str(whichtime),'ps',space,space,'
t=',num2str(whichUVtime),'ps',space,polarizationtitle));
    clear space;
else

```

```

        title(strcat('Tw = ',num2str(whichtime),'ps',polarizationtitle));
    end
    axis equal;
    % load custom colormap if desired
    customjet=load('customjet_2.txt');
    colormap(customjet);
    % standard colormap, jet, is below
    % colormap(jet);
    % -----
    % colorbar;
    set(h,'linewidth',1.0)
    if datafilename(1:10) == 'data_feco5'
        axis([1970 2045 1970 2045]);
        hold on;
        plot([1970 2045],[1970 2045],'k');
        set(h,'linewidth',1.0)
        h=gca;
        set(h,'ticklength',[0.015 0.015])

set(h,'ytick',[1980:10:2040],'xtick',[1980:10:2040],'xticklabel',{'1980' ''
'2000' '' '2020' '' '2040'},'yticklabel',{'1980' '' '2000' '' '2020' ''
'2040'});
        elseif datafilename(1:10) == 'data_ru3co'
            axis([1990 2080 1990 2080]);
        end
    end
end

```

B.3 Step-scan FTIR spectroscopy

The experimental step-scan FTIR apparatus is operated with OPUS software (Bruker Optik GmbH). In order to analyze the data off-site with Matlab, the programs below were written to convert the Opus files into a standard text file format which can then be analyzed in Matlab.

B.3.1 OPUS programs

B.3.1.1 Convert Opus file to text format

OPUS2TXT.MTX

VARIABLES SECTION

```

STRING <outputpath> = 'D:\Chemistry\Data\Heinz_Raw_Data\4_06\060414\414_';
NUMERIC <outputfilename> = 1;
STRING <inputpath> = 'D:\Chemistry\Data\Heinz_Raw_Data\temp';
STRING <inputfilename> = 'tmp.1';
FILE <data>;
FILE <extractionfile>;

```

PROGRAM SECTION

```

UserDialog ('0', STANDARD, EDIT:<outputpath>', FILE:[<extractionfile>], BLANK,
BLANK, BLANK, BLANK, BLANK, BLANK, BLANK, BLANK, BLANK, BLANK, BLANK);
PostrunExtract ([<extractionfile>], {EXS=1, EXE=1, ENT=636, ENE=1, ECO=0,
XTP=<inputpath>', XTN='tmp.1', XTI=0, EAB=0, ELF=0});
StartLoop (1900, 0);
<inputfilename> = 'tmp.<outputfilename>';
[<data>] = LoadFile ('<inputpath>\<inputfilename>', WARNING|ABORT);
SaveAs ([<data>], {DAP=<outputpath>', OEX='0', SAN=<outputfilename>',

```

```
COF=64, INP='C:\OPUS\METHODS', IFP='C:\OPUS\METHODS', INM='DEFAULT',
IFN='DEFAULT', DPA=5, DPO=5, SEP=',', YON='0', ADP='1'});
Unload ([<data>], {});
Delete ('<inputpath>\<inputfilename>');
<outputfilenumber> = <outputfilenumber>+1;
EndLoop (0);
```

B.3.1.2 Convert multiple Opus files to text format

OPUS2TXT_MULTI.MTX

VARIABLES SECTION

```
STRING <outputpath> = 'D:\Chemistry\Data\Heinz_Raw_Data\4_06\060414\414_';
NUMERIC <outputfilenumber> = 0;
STRING <inputpath> = 'D:\Chemistry\Data\Heinz_Raw_Data\temp';
STRING <inputfilename> = 'tmp.1';
FILE <data>;
FILE <extractionfile>;
NUMERIC <nmbrfiles> = 1;
NUMERIC <filenmbr> = 1;
STRING <finaloutputpath> = '';
STRING <extractionfilename> = '';
STRING <firstfileroot> = 'D:\Chemistry\Data\Heinz_Raw_Data\4_06\060414\060414';
```

PROGRAM SECTION

```
UserDialog ('0', STANDARD, EDIT:<outputpath>', EDIT:<nmbrfiles>',
EDIT:<filenmbr>', EDIT:<firstfileroot>', BLANK, BLANK, BLANK, BLANK, BLANK,
BLANK, BLANK, BLANK, BLANK, BLANK);
StartLoop (<nmbrfiles>, 0);
<extractionfilename> = '<firstfileroot>.<filenmbr>';
[<extractionfile>] = LoadFile ('<extractionfilename>', WARNING|ABORT);
PostrunExtract ([<extractionfile>], {EXS=1, EXE=1, ENT=636, ENE=1, ECO=0,
XTP=<inputpath>', XTN='tmp.1', XTI=0, EAB=0, ELF=0});
Unload([<extractionfile>],{});
<outputfilenumber> = 1;
<finaloutputpath> = '<outputpath><filenmbr>';
<filenmbr> = <filenmbr>+1;
StartLoop (1900, 1);
<inputfilename> = 'tmp.<outputfilenumber>';
[<data>] = LoadFile ('<inputpath>\<inputfilename>', WARNING);
If (MACROERROR, .EQ., TRUE);
EndLoop(1);
Else ();
SaveAs ([<data>], {DAP=<finaloutputpath>', OEX='0', SAN=<outputfilenumber>',
COF=64, INP='C:\OPUS\METHODS', IFP='C:\OPUS\METHODS', INM='DEFAULT',
IFN='DEFAULT', DPA=5, DPO=5, SEP=',', YON='0', ADP='1'});
Unload ([<data>], {});
Delete ('<inputpath>\<inputfilename>');
<outputfilenumber> = <outputfilenumber>+1;
EndLoop (1);
Endif ();
EndLoop (0);
```

B.3.2 Matlab programs

B.3.2.1 Convert AC and DC data into absorbance values

This Matlab program, “acdc2abs.m,” converts the AC and DC scans from the step-scan

FTIR experiments (already converted into text files by the programs in Section B.3.1) into absorbance values.

acdc2abs.m

```
% This program will use a folder containing files for AC spectra and
% folder containing files for DC spectra to generate one file containing the
% absorption spectra in mOD for all time slices. All files must be taken
% with the same time step. You can specify multiple AC and DC folder pairs
% which are to be converted to mOD by including them in the "acdcinfo.txt"
file
% with the root foldername on the first line followed by the AC and then
% DC folder number, e.g.:

% 0710_          (the root foldername)
% 1              (the AC folder number)
% 2              (the DC folder number)
% 3              (next pair of AC and DC
% 4              folders to be averaged)
% ...           (and so on)

% This program would then generate two files called "data_heinz_0710_1" and
% "data_heinz_0710_3" which are written in the folder in which you place
% this file.
%
% The program averages all the DC spectra in the DC folder to generate one
% DC spectrum which is used for all the AC spectra time slices. The
% inputted scaling factors are used to correct for different signal
% amplifications during the experiment and must be changed based on the
% experiment performed.

% load the file specifying the folders with the raw data to be converted

% Change AC and DC scaling factors here.
ACscale = 1;
DCscale = 15.8;

inputfile = input('AC/DC info filename? ','s');
if length(inputfile)==0
    inputfile = 'acdcinfo.txt';
end
fin = fopen(inputfile,'r');
if fin < 0
    error(['Could not open ',inputfile,' for input']);
end
% Give timestep in nanoseconds, e.g. for a microsecond input 1000
timestep = input('What is the time step (in ns)? ');
% You can change the number of negative time slices here. For
% consistency, first time slice with absorption changes should be given as
% time zero even though it is actually some undetermined positive time.
% Thus in a kinetics fitting routine time zero should always be a floating
% parameter.
if timestep == 250
    nmbrnegtimes = 100;
elseif timestep == 25
    nmbrnegtimes = 97;
elseif timestep == 1000
    nmbrnegtimes = 1;
elseif timestep == 50
    nmbrnegtimes = 98;
end
foldername = fgetl(fin);
```

```

specinfo = fscanf(fin,'%f');
fclose(fin);
nmbrfiles = length(specinfo)/2;
% Below is the maximum number of time slices the data may contain.
nmbrtimes = 1900;
% The outer for loop goes through the AC/DC pairs
for k=1:nmbrfiles
    ACfoldername = strcat(foldername,num2str(specinfo(2*k-1)));
    DCfoldername = strcat(foldername,num2str(specinfo(2*k)));
    filename = strcat('data_heinz_',ACfoldername,'.dat');
    DCfilename = strcat(DCfoldername,'\1');
    DCdata1 = load(DCfilename);
    nmbrwaves = length(DCdata1(:,2));
    % The variable ABSdata is the array which will contain the spectral data
    % for all the time slices
    ABSdata = zeros(nmbrwaves+1,nmbrtimes+1);
    ABSdata(2:end,1) = DCdata1(:,1);
    DCdata = zeros(nmbrwaves,nmbrtimes);
    DCdataavg = zeros(nmbrwaves,nmbrtimes);
    % ACdata contains all the AC data for the different time slices
    % ACdata1 is a temporary variable which contains the AC data for
    % only one time slice. Analogous variables are present for DC data.
    ACdata = zeros(nmbrwaves,nmbrtimes);
    DCdata(:,1) = DCdata1(:,1);
    ACfilename = strcat(ACfoldername,'\1');
    ACdata1 = load(ACfilename);
    ACdata(:,1) = ACdata1(:,2);
    clear DCfilename DCdata1 ACfilename ACdata1;
    % loops through the number of times and loads all the individual AC and
    % DC data files and places them in the larger arrays.
    nmbrACTimes=1;
    nmbrDCTimes=1;
    for i=2:nmbrtimes
        DCfilename = strcat(DCfoldername,'\ ',num2str(i));
        fid = fopen(DCfilename,'r');
        if fid < 0
            else
                nmbrDCTimes = nmbrDCTimes+1;
                DCdata1 = fscanf(fid,'%g,%g',[2 inf]);
                DCdata1 = DCdata1';
                fclose(fid);
                DCdata(:,i) = DCdata1(:,2);
                clear DCfilename DCdata1 fid;
            end
        ACfilename = strcat(ACfoldername,'\ ',num2str(i));
        fid = fopen(ACfilename,'r');
        if fid < 0
            % Assumes AC file will always have more time slices than DC file
            break;
        else
            nmbrACTimes = nmbrACTimes+1;
            ACdata1 = fscanf(fid,'%g,%g',[2 inf]);
            ACdata1 = ACdata1';
            fclose(fid);
            ACdata(:,i) = ACdata1(:,2);
            clear ACfilename ACdata1 fid;
        end
    end
    ACdata = ACdata(:,1:nmbrACTimes);
    DCdata = DCdata(:,1:nmbrDCTimes);
    ABSdata = ABSdata(:,1:nmbrACTimes+1);
    ABSdata(1,2:end) = [-nmbrnegtimes*timestep : timestep : (nmbrACTimes-
nmbrnegtimes-1)*timestep];

```



```

DCdataavg = repmat((mean(DCdata(:,1:nmbrDCtimes)'))',1,nmbrACtimes);
% The absorbance is calculated here. Units are mOD.
warning off MATLAB:divideByZero;
ABSdata(2:end,2:end) = -1000*real(log10((ACdata(:,:)*ACscale+...
abs(DCdataavg(:,:))*DCscale)./(abs(DCdataavg(:,:))*DCscale)));
save(filename,'ABSdata','-ascii');
clear ABSdata DCdata DCdataavg ACdata nmbrwaves ACfoldername...
DCfoldername DCdataavg counter nmbrAC nmbrDC;
end

```

B.3.2.2 Average data files

This program, “avgheinz.m,” will average the absorbance data generated from the programs in Section B.3.2.1.

avgheinz.m

```

% This program will average separate files collected on Heinz's
% step-scan FTIR which have been analyzed with the program called
% "acdc2abs.m". The files to be averaged are specified in the file
% "datainfo.txt" and containing the root folder name on the first
% line followed by the file numbers to be averaged, e.g.:
%
% data_heinz_0710_      (the root folder name)
% 1                    (first file to be averaged)
% 3                    (second file to be averaged)
% ...                  (and so on)
%
% The program then write two files, one called "data_heinz_0710_1&3.dat"
% containing the averaged data, and one called "data_heinz_0710_1&3.std"
% containing the standard deviation data.
%
% This program can also time average the data (note that time averaging
% begins with time zero and no averaging is done for negative times) and
% the output depends on the number of averages specified, e.g.:
% When the number of time slices to be averaged is 2:
% The 25 ns slice is actually the average of the 25 and 50 ns slices. The
% 50 ns slice is the average of the 50 ns and 75 ns slices. The 75 ns
% slice is the average of the 75 and 100 ns slices. The last time slice is
% different, so that the 2450 ns slice is the average of the 2450 and 2425
% ns time slices; hence the last and second to last time slices are the same.
% When the number of time slices to be average is 3:
% The 25 and 50 ns slices are the same and are the average of the 25, 50,
% and 75 ns slices. The 75 ns slice is the average of itself, the one
% before, and the one after; 50, 75, 100. And so on for the intermediate
% time slices. The last and second to last time slices are the same.
% And so on with this trend when more time slices are to be averaged.
%
% Time averaged files include the additional "timeavg_#", where number
% indicates the number of time slices that have been averaged. So, for
% example: "data_heinz_0710_1&3_timeavg_2.dat" indicates that every time
% slice is the average of two time slices. In the special case that you
% want to average all time slices, simply input "all" for the number of
% time slices to be averaged and then input the time slice at which you
% would like to begin the averaging (in order to omit the early
% fluctuations due to detector response)
%
% Retain data only between the upper and lower limits specified here
lowerlimit = 1650;
upperlimit = 2150;

```

```

inputfile = input('Data info filename? ', 's');
if length(inputfile) == 0
    inputfile = 'datinfo.txt';
end
fin = fopen(inputfile, 'r');
if fin < 0
    error(['Could not open ', inputfile, ' for input']);
end
inputtimeavg = input('Do you wish to time average the data, (y/n)? ', 's');
if length(inputtimeavg) == 0;
    inputtimeavg = 'n';
end
if inputtimeavg == 'y'
    nmbravgstring = input('How many time slices would you like to average at
once, (3,4,...,all)? ', 's');
    if nmbravgstring(1) == 'all'
        beginavg = input('At which time slice would you like to begin averaging,
(25,50,1000,etc)? ');
    else
        nmbravgs = str2num(nmbravgstring);
    end
end
filebody = fgetl(fin);
specinfo = fscanf(fin, '%f');
nmbrfiles = length(specinfo);
if nmbrfiles > 1
    filename = strcat(filebody, num2str(specinfo(1,1)), '&');
    RawData = load(strcat(filebody, num2str(specinfo(1,1)), '.dat'));
    spectralindex = find(RawData(:,1) >= lowerlimit & RawData(:,1) <=
upperlimit);
    nmbrwaves = length(spectralindex);
    nmbrtimes = length(RawData(1,:))-1;
    Data1(1,:) = RawData(1,:);
    Data1(2:nmbrwaves+1,:) = RawData(spectralindex(1):spectralindex(end),:);
    OutputTemp = zeros(nmbrwaves+1, nmbrtimes+1);
    StdDevTemp = zeros(nmbrwaves+1, nmbrtimes+1);
    OutputTemp(2:end,1) = Data1(2:end,1);
    StdDevTemp(2:end,1) = Data1(2:end,1);
    OutputTemp(1,2:end) = Data1(1,2:end);
    StdDevTemp(1,2:end) = Data1(1,2:end);
    Output = OutputTemp;
    StdDev = StdDevTemp;
    DataArray = zeros(nmbrwaves, nmbrtimes, nmbrfiles);
    DataArray(:, :, 1) = Data1(2:end, 2:end);
    clear Data1 RawData;
    for i=2:nmbrfiles
        RawData = load(strcat(filebody, num2str(specinfo(i,1)), '.dat'));
        Data1(1,:) = RawData(1,:);
        Data1(2:nmbrwaves+1,:) =
RawData(spectralindex(1):spectralindex(end),:);
        DataArray(:, :, i) = Data1(2:end, 2:end);
        clear Data1 RawData;
        if i < nmbrfiles
            filename = strcat(filename, num2str(specinfo(i,1)), '&');
        else
            if inputtimeavg == 'y'
                filenameedata =
strcat(filename, num2str(specinfo(i,1)), '_timeavg_', nmbravgstring, '.dat');
                filenameestd =
strcat(filename, num2str(specinfo(i,1)), '_timeavg_', nmbravgstring, '.std');
            else
                filenameedata = strcat(filename, num2str(specinfo(i,1)), '.dat');
                filenameestd = strcat(filename, num2str(specinfo(i,1)), '.std');
            end
        end
    end
end

```

```

        end
    end
    end;
    OutputTemp(2:end,2:end) = mean(DataArray,3);
    StdDevTemp(2:end,2:end) = 1.96*std(DataArray,0,3);
else
    RawData = load(strcat(filebody,num2str(specinfo(1,1)),'.dat'));
    spectralindex = find(RawData(:,1) >= lowerlimit & RawData(:,1) <=
upperlimit);
    nmbrwaves = length(spectralindex);
    nmbrtimes = length(RawData(1,:))-1;
    Data1(1,:) = RawData(1,:);
    Data1(2:nmbrwaves+1,:) = RawData(spectralindex(1):spectralindex(end),:);
    OutputTemp = zeros(nmbrwaves+1,nmbrtimes+1);
    StdDevTemp = zeros(nmbrwaves+1,nmbrtimes+1);
    OutputTemp(2:end,1) = Data1(2:end,1);
    StdDevTemp(2:end,1) = Data1(2:end,1);
    OutputTemp(1,2:end) = Data1(1,2:end);
    StdDevTemp(1,2:end) = Data1(1,2:end);
    Output = OutputTemp;
    StdDev = StdDevTemp;
    OutputTemp = Data1;
    filenamedata =
strcat(filebody,num2str(specinfo(1,1)),'_timeavg_',nmbravgstring,'.dat');
    clear Data1 RawData;
end

counter=1;
if inputtimeavg == 'y'
    % if you wish to average all the time slices
    if nmbravgstring(1) == 'all'
        beginavgindex = find(OutputTemp(1,:) == beginavg);
        Output(2:end,beginavgindex:end) =
repmat(mean(OutputTemp(2:end,beginavgindex:end),2),1,nmbrtimes+2-
beginavgindex);
        StdDev(2:end,beginavgindex:end) =
repmat(mean(StdDevTemp(2:end,beginavgindex:end),2),1,nmbrtimes+2-
beginavgindex);
        Output(2:end,2:beginavgindex-1) =
repmat(mean(OutputTemp(2:end,2:beginavgindex-1),2),1,beginavgindex-1);
        StdDev(2:end,2:beginavgindex-1) =
repmat(mean(StdDevTemp(2:end,2:beginavgindex-1),2),1,beginavgindex-1);
    else
        % The time averaging will start with time zero, which is found below.
        timezeroindex = find(OutputTemp(1,:) == 0);
        timezeroindex = timezeroindex(2);
        nmbravgtimes = length(OutputTemp(1,timezeroindex:end));

        % if the number of slices to average is even:
        if round(nmbravgs/2) == nmbravgs/2
            for i=timezeroindex:(nmbrtimes+1);
                if i <= (nmbravgs/2+timezeroindex-1)
                    Output(2:end,i) =
mean(OutputTemp(2:end,timezeroindex:timezeroindex+nmbravgs-1),2);
                    StdDev(2:end,i) =
mean(StdDevTemp(2:end,timezeroindex:timezeroindex+nmbravgs-1),2);
                elseif i >= (nmbrtimes+1-nmbravgs/2+1)
                    Output(2:end,i) = mean(OutputTemp(2:end,nmbrtimes+1-
nmbravgs+1:nmbrtimes+1),2);
                    StdDev(2:end,i) = mean(StdDevTemp(2:end,nmbrtimes-
nmbravgs+2:nmbrtimes+1),2);
                else
                    Output(2:end,i) = mean(OutputTemp(2:end,i-

```

```

nmbravgs/2+1:i+nmbravgs/2),2);
        StdDev(2:end,i) = mean(StdDevTemp(2:end,i-
nmbravgs/2+1:i+nmbravgs/2),2);
        counter = counter+1;
    end
end
for i=2:timezeroindex-1
    if i <= (nmbravgs/2+1)
        Output(2:end,i) = mean(OutputTemp(2:end,2:2+nmbravgs-1),2);
        StdDev(2:end,i) = mean(StdDevTemp(2:end,2:2+nmbravgs-1),2);
    elseif i >= (timezeroindex-1-nmbravgs/2+1)
        Output(2:end,i) = mean(OutputTemp(2:end,timezeroindex-1-
nmbravgs+1:timezeroindex-1),2);
        StdDev(2:end,i) = mean(StdDevTemp(2:end,timezeroindex-1-
nmbravgs+1:timezeroindex-1),2);
    else
        Output(2:end,i) = mean(OutputTemp(2:end,i-
nmbravgs/2+1:i+nmbravgs/2),2);
        StdDev(2:end,i) = mean(StdDevTemp(2:end,i-
nmbravgs/2+1:i+nmbravgs/2),2);
        counter = counter+1;
    end
end

% if the number of slices is odd:
else
    for i=timezeroindex:nmbtimes+1
        if i <= (nmbravgs/2+timezeroindex-3/2)
            Output(2:end,i) =
mean(OutputTemp(2:end,timezeroindex:timezeroindex+nmbravgs-1),2);
            StdDev(2:end,i) =
mean(StdDevTemp(2:end,timezeroindex:timezeroindex+nmbravgs-1),2);
        elseif i >= (nmbtimes+1-nmbravgs/2+3/2)
            Output(2:end,i) = mean(OutputTemp(2:end,nmbtimes+1-
nmbravgs+1:nmbtimes+1),2);
            StdDev(2:end,i) = mean(StdDevTemp(2:end,nmbtimes-
nmbravgs+2:nmbtimes+1),2);
        else
            Output(2:end,i) = mean(OutputTemp(2:end,i-(nmbravgs-
1)/2:i+(nmbravgs-1)/2),2);
            StdDev(2:end,i) = mean(StdDevTemp(2:end,i-(nmbravgs-
1)/2:i+(nmbravgs-1)/2),2);
        end
    end
    for i=2:timezeroindex-1
        if i <= (nmbravgs/2+2-3/2)
            Output(2:end,i) = mean(OutputTemp(2:end,2:2+nmbravgs-1),2);
            StdDev(2:end,i) = mean(StdDevTemp(2:end,2:2+nmbravgs-1),2);
        elseif i >= (timezeroindex-nmbravgs/2+1/2)
            Output(2:end,i) = mean(OutputTemp(2:end,timezeroindex-1-
nmbravgs+1:timezeroindex-1),2);
            StdDev(2:end,i) = mean(StdDevTemp(2:end,timezeroindex-1-
nmbravgs+1:timezeroindex-1),2);
        else
            Output(2:end,i) = mean(OutputTemp(2:end,i-(nmbravgs-
1)/2:i+(nmbravgs-1)/2),2);
            StdDev(2:end,i) = mean(StdDevTemp(2:end,i-(nmbravgs-
1)/2:i+(nmbravgs-1)/2),2);
        end
    end
end
end
else

```

```

        Output = OutputTemp;
        StdDev = StdDevTemp;
    end
    clear OutputTemp StdDevTemp;

    if inputtimeavg == 'y'
        OutputTemp = Output;
        StdDevTemp = StdDev;
        timezeroindex = find(Output(1,2:end) == 0);
        firsttime = round(nmbravgs/2);
        OutputNegative = OutputTemp(:,firsttime+1:nmbravgs:timezeroindex);
        OutputPositive = OutputTemp(:,timezeroindex+firsttime+1:nmbravgs:end);
        StdDevNegative = StdDevTemp(:,firsttime+1:nmbravgs:timezeroindex);
        StdDevPositive = StdDevTemp(:,timezeroindex+firsttime+1:nmbravgs:end);
        clear Output StdDev;
        Output = [OutputTemp(:,1) OutputNegative OutputPositive];
        StdDev = [StdDevTemp(:,1) StdDevNegative StdDevPositive];
    end

    save(filenameedata,'Output','-ascii');
    if nmbrfiles > 1
        save(filenameestd,'StdDev','-ascii');
    end
    clear i inputfile fin filebody specinfo nmbrfiles nmbrwaves nmbrtimes
    spectralindex;
    clear DataArray filename filenameedata filenameestd inputtimeavg beginavg
    nmbravgtimes timezeroindex;
    clear nmbravgstring nmbravgs OutputTemp StdDevTemp beginavgindex lowerlimit
    upperlimit;

```

B.3.2.3 Data plotting

The Matlab programs below are designed to plot both the spectra and the kinetics from data files which have been averaged with the program in Section B.3.2.2. The program “plotdata.m” will plot the spectra at a variety of time delays as specified by the user. The program “intpeaks.m” will generate a kinetic trace from the spectral data – in addition to plotting the data it will also generate a new data file giving the absorbance value as a function of time delay. The program also has the capacity to scale each individual data file before generating the standard deviations for the kinetics. This function is intended to be used when an analysis of the shape of the kinetic curve (and not the absolute magnitude) is desired.

plotdata.m

```

filename = input('What is the data filename? ','s');
if length(filename) > 0;
    Output = load(filename);
end;
specpositions = Output(2:end,1);
nmbrspecs = length(specpositions);
timelabel = input('What is the time label, (ps,ns,us)? ','s');
if length(timelabel) == 0
    timelabel = 'ns';
    OutputNew = Output;
elseif timelabel == 'us'
    OutputNew = Output;
    OutputNew(1,2:end) = Output(1,2:end)/1000;

```

```

else
    OutputNew = Output;
end
timepositions = OutputNew(1,2:end);
nmbrtimes = length(timepositions);
disp(timepositions');
whichtimes = input('Which times [10,20,...]? ');
nmbrplots = length(whichtimes);
if nmbrplots==0;
    clear whichtimes nmbrplots;
    if timelabel == 'ns'
        whichtimes = [25,100,500,1000,1500,2000,2450];
    elseif timelabel == 'us'
        whichtimes = [1,5,10,20,40,60,90];
    elseif length(timelabel) == 0
        timelabel = 'ps'
        whichtimes = [1,5,10,50,100,400,700];
    end;
    nmbrplots = length(whichtimes);
end;
for i=1:nmbrplots;
    whichslices(i) = find(whichtimes(i)==timepositions);
end;
whichslices = whichslices+1;

% -----
% This section checks for data values of 100.00 or 200.00 and removes them
% from the plotted data
datachecked=zeros(nmbrspecs,2*nmbrplots);
speccounter=zeros(nmbrplots);
speccounter(:)=1;
figure;
baddata='n';
color=['bgrcmk'];
m=1;
for i=1:nmbrplots
    for j=1:nmbrspecs
        if OutputNew(j+1,whichslices(i))==200.00 |
OutputNew(j+1,whichslices(i))==100.00
            baddata='y';
        else
            datachecked(speccounter(i),2*i-1)=OutputNew(j+1,1);
            datachecked(speccounter(i),2*i)=OutputNew(j+1,whichslices(i));
            speccounter(i)=speccounter(i)+1;
        end
    end
    plot(datachecked(1:speccounter(i)-1,2*i-1),datachecked(1:speccounter(i)-
1,2*i),color(m));
    hold on;
    m=m+1;
    if m==8
        m=1;
    end
end
if baddata=='y'
    disp('Warning: Data reading 100.00 or 200.00 has been removed from these
plots');
end
% -----

for j=1:nmbrplots;
    lgnd = sprintf('%4.0f',(OutputNew(1,whichslices(j))));
    if timelabel == 'ns'

```

```

        lgnds{j}=[lgnd, ' ns'];
        legend(lgnds);
    elseif timelabel == 'us'
        lgnds{j}=[lgnd, ' us'];
        legend(lgnds);
    elseif timelabel == 'ps'
        lgnds{j}=[lgnd, ' ps'];
        legend(lgnds);
    end
end;
xlabel('wavenumbers / cm-1');
ylabel('\Delta mOD');
% titlename = input('Title for spectral graph: ','s');
% title(titlename);
clear whichtimes nmbrplots whichslices lgnd lgnds titlename baddata color
filename OutputNew;
clear speccounter datachecked baddata timelabel i j m nmbrspecs nmbrtimes
specpositions timepositions;

```

intpeaks.m

```

% This program will integrate peaks areas for data collected in Heinz's
% lab. It will optionally scale and offset the individual data files in
% order to improve the standard deviations of the individual data points.
% This option only affects the standard deviations, not the averaged value
% of the data points and accounts for long time fluctuations in the
% photochemical pump intensity.

% If you choose to scale the data, the program relies on the .m files chi.m,
% simps.m, and scaledata.m and also requires that the individual data files
% are present in the active directory

datafilename = input('What is the data filename? ','s');
dividingfactor = input('Divide times by? ');
if length(dividingfactor) == 0;
    dividingfactor = 1;
end
scaledata = input('Scale and offset individual data files to improve standard
deviation? (requires chi.m, simps.m, scaledata.m) ','s');
if length(scaledata) == 0;
    scaledata = 'n';
end

timeaveraging = findstr(datafilename,'timeavg');
if length(timeaveraging)>0
    dataistimeavg = 'y';
    fileindex3 = find(datafilename == '.');
    nmbrtimeavgs = str2num(datafilename(timeaveraging+8:fileindex3-1));
else
    dataistimeavg = 'n';
    nmbrtimeavgs = [];
end

if scaledata == 'y'
    fileindex = find(datafilename == '.');
    fileindex2 = find(datafilename == '&');
    if length(fileindex2) == 0
        Output = load(datafilename);
        nmbrtimes = length(Output(1,:))-1;
        nmbrwaves = length(Output(:,1))-1;
    else
        fileindex3 = find(datafilename == '.');
    end
end

```

```

        timeaveraging = findstr(datafilename,'timeavg');
        if length(timeaveraging)>0
            fileindex3=timeaveraging-1;
        end
        filebody = datafilename(1:fileindex(3)-1);
        specinfo = zeros(1,length(fileindex2)+1);
        specinfo(1) = str2num(datafilename(fileindex(3)+1:fileindex2(1)-1));
        specinfo(end) = str2num(datafilename(fileindex2(end)+1:fileindex3-1));
        for i=1:length(specinfo)-2
            specinfo(1,i+1) =
str2num(datafilename(fileindex2(i)+1:fileindex2(i+1)-1));
        end
        % Retain data only between the upper and lower limits specified here
        lowerlimit = 1650;
        upperlimit = 2150;
        nmbrfiles = length(specinfo);
        RawData = load(strcat(filebody,'_',num2str(specinfo(1)),'.dat'));
        spectralindex = find(RawData(:,1) >= lowerlimit & RawData(:,1) <=
upperlimit);
        nmbrwaves = length(spectralindex);
        nmbrtimes = length(RawData(1,:))-1;
        Data1(1,:) = RawData(1,:);
        Data1(2:nmbrwaves+1,:) =
RawData(spectralindex(1):spectralindex(end),:);
        Output = zeros(nmbrwaves+1,nmbrtimes+1);
        StdDev = zeros(nmbrwaves+1,nmbrtimes+1);
        Output(2:end,1) = Data1(2:end,1);
        StdDev(2:end,1) = Data1(2:end,1);
        Output(1,2:end) = Data1(1,2:end);
        StdDev(1,2:end) = Data1(1,2:end);
        DataArray = zeros(nmbrwaves+1,nmbrtimes+1,nmbrfiles);
        DataArray(:, :, 1) = Data1(:, :);
        clear Data1 RawData;
        for i=2:nmbrfiles
            RawData = load(strcat(filebody,'_',num2str(specinfo(i)),'.dat'));
            Data1(1,:) = RawData(1,:);
            Data1(2:nmbrwaves+1,:) =
RawData(spectralindex(1):spectralindex(end),:);
            DataArray(:, :, i) = Data1(:, :);
            clear Data1 RawData;
        end;
        Output(2:end,2:end) = mean(DataArray(2:end,2:end,:),3);
        StdDev(2:end,2:end) = 1.96*std(DataArray(2:end,2:end,:),0,3);
    end
elseif scaledata == 'n'
    fileindex2 = [];
    fileindex3 = find(datafilename == '.');
    Output = load(datafilename);
    nmbrtimes = length(Output(1,2:end));
    nmbrwaves = length(Output(2:end,1));
    stddatafilename = strcat(datafilename(1:fileindex3),'std');
    StdDev = load(stddatafilename);
end

Waves = Output(2:end,1)';
Times = Output(1,2:end)/dividingfactor;
again = 'y';
clear filebody;
intindex=0;
while again == 'y';
    intindex=intindex+1;
    leftedge = input('left edge (wavenumbers)? ');

```



```

rightedge = input('right edge (wavenumbers)? ');
if length(fileindex2) == 0
    intpeak=zeros(nmbrrtimes,1);
    if leftedge==rightedge
        specindex=find(Waves>=leftedge-0.5 & Waves<=leftedge+0.5);
        specindex=specindex(1);
        exactwave=Waves(specindex);
        exactwave=round(10*exactwave)/10;
        for i=1:nmbrrtimes
            intpeak(i)=Output(specindex(1)+1,i+1);
        end
    else
        specindex = find(leftedge <= Waves & Waves <= rightedge);
        for i=1:nmbrrtimes
            for j=specindex(1):specindex(end)
                if j<=nmbrwaves
                    intpeak(i) = intpeak(i)+Output(j+1,i+1)*(Waves(j+1)-
Waves(j));
                else
                    intpeak(i) = intpeak(i)+Output(j+1,i+1)*(Waves(j)-
Waves(j-1));
                end;
            end;
        end;
        % intpeak=intpeak/(Waves(specindex(end))-Waves(specindex(1)));
        intpeak=-1*intpeak;
    end;
    outkinetics=[Times' intpeak];
else
    if leftedge==rightedge
        specindex=find(Waves>=leftedge-0.5 & Waves<=leftedge+0.5);
        specindex=specindex(1);
        exactwave=Waves(specindex);
        exactwave=round(10*exactwave)/10;
        avgdata = zeros(1,length(DataArray(1, :, 1))-
1,length(DataArray(1,1, :)));
        for k=1:nmbrrfiles
            for i=1:nmbrrtimes
                avgdata(1,i,k) = DataArray(specindex,i+1,k);
            end;
        end;
    else
        specindex = find(leftedge <= DataArray(:,1,1) & DataArray(:,1,1) <=
rightedge);
        avgdata = zeros(1,length(DataArray(1, :, 1))-
1,length(DataArray(1,1, :)));
        for k=1:nmbrrfiles
            for i=1:nmbrrtimes
                for j=specindex(1):specindex(end)
                    if j<=nmbrwaves
                        avgdata(1,i,k) =
avgdata(1,i,k)+DataArray(j,i+1,k)*(Waves(j)-Waves(j-1));
                    else
                        avgdata(1,i,k) =
avgdata(1,i,k)+DataArray(j,i+1,k)*(Waves(j-1)-Waves(j-2));
                    end;
                end;
            end;
        end;
        % avgdata=avgdata/(Waves(specindex(end))-Waves(specindex(1)));
        % avgdata=-1*avgdata;
    end
end

```

```

    intpeak = mean(avgdata,3)';
    % This section performs a minimization to determine the best offset
    % and scaling factor using the program simps.m. This section also
    % calls on chi.m and scaleddata.m
    if scaleddata == 'y'
        nmbparam = 1:2;
        param = zeros(2,nmbrfiles);
        % change the limits for the scaling factor and offsets; first is
the scaling factor
        % and second is the offset
        low = [0.1 -0.05];
        high = [5 0.05];
        options = foptions;
        scaleddatasets=(zeros(1,length(Times)-1,nmbrfiles));
        for i=1:nmbrfiles
            searchparam = [1 0.001]';
            deltachi = 2000;
            oldchi = 1000;
            clear data;
            % data contains the raw data for this time slice
            data = avgdata(1,2:end,i)';
            % This is the minimization part of the program
            while deltachi > 0.01*oldchi

param(:,i)=simps('chi',searchparam,nmbparam,options,low,high,intpeak(2:end),da
ta);

                searchparam = param(:,i);
                scaleddatasets(1,:,i) = scaleddata(data,param(:,i));
                newchi=sum((data-scaleddatasets(1,:,i)).^2);
                deltachi = oldchi-newchi;
                oldchi = newchi;
            end
            clear searchparam data;
        end
        avgdata(:,2:end,:) = scaleddatasets(:, :, :);
    end
    intstd = std(avgdata,0,3)';
    %   intstd = 1.96*std(avgdata,0,3)';
    outkinetics=[Times' intpeak];
    outstd=[Times' intstd];
end

%   if dataistimeavg == 'y'
%       timezeroindex = find(outkinetics(:,1) == 0);
%       firsttime = round(nmbrtimeavgs/2);
%       outkineticsnegative =
outkinetics(firsttime:nmbrtimeavgs:timezeroindex-1,:);
%       outkineticspositive =
outkinetics(timezeroindex+firsttime:nmbrtimeavgs:end,:);
%       clear outkinetics;
%       outkinetics = [outkineticsnegative' outkineticspositive']';
% %       outstdnegative = outstd(1:nmbrtimeavgs:timezeroindex-1,:);
% %       outstdpositive = outstd(timezeroindex:nmbrtimeavgs:end,:);
% %       clear outstd;
% %       outstd = [outstdnegative' outstdpositive']';
%   end

    if intindex==1
        filebody = datafilename(12:end-4);
    end
    if leftedge==rightedge
        filename=strcat('kin_',filebody,'_',num2str(exactwave),'.dat');
        fid = fopen(filename,'w');

```

```

        fprintf(fid,'%g\t %g\n',outkinetics');
        fclose(fid);
        if length(fileindex2) == 0
            else
                filename=strcat('kin_',filebody,'_',num2str(exactwave),'.std');
                fid = fopen(filename,'w');
                fprintf(fid,'%g\t %g\n',outstd');
                fclose(fid);
            end
        else
            filename=strcat('kin_',filebody,'_',num2str(leftedge),'-
',num2str(rightedge),'.dat');
            fid = fopen(filename,'w');
            fprintf(fid,'%g\t %g\n',outkinetics');
            fclose(fid);
            if length(fileindex2) == 0
                else
                    filename=strcat('kin_',filebody,'_',num2str(leftedge),'-
',num2str(rightedge),'.std');
                    fid = fopen(filename,'w');
                    fprintf(fid,'%g\t %g\n',outstd');
                    fclose(fid);
                end
            end
        figure;
        if length(fileindex2) == 0
            plot(outkinetics(:,1),outkinetics(:,2),'ko');
            hold on;
            plot(outkinetics(:,1),outkinetics(:,2),'k');
        else
            errorbar(Times',intpeak,intstd,'ko');
            hold on;
            %         for i=1:nbrfiles
            %             plot(Times',avgdata(1,:,i),'^r');
            %             hold on;
            %         end
        end
        xlabel('t / ps');
        ylabel('int. absorbance / a.u. ');
        if leftedge==rightedge
            titlename=strcat(num2str(exactwave));
            title(titlename);
        else
            titlename=strcat(num2str(leftedge),'cm to ',num2str(rightedge),'cm');
            title(titlename);
        end
        again = input('Would you like to integrate another spectral range? (y/n)
','s');
        if length(again)==0
            again = 'y';
        end
        if again == 'y'
            clear i j k exactwave leftedge rightedge specindex intpeak intstd
            outkinetics outstd filename avgdata avgdatascaled;
        else
            clear i j k exactwave leftedge rightedge specindex intpeak intstd
            filename avgdata;
        end
    end;
end;

```

chi.m

```

% a parameters
% X the averaged data set
% Y the data set from one scan

function [chivalue,b] = chi(a,X,Y)
b=[];
scaleddataset = zeros(length(Y),1);
scaleddataset(:,1) = scaleddata(Y,a);
chivalue = sum((scaleddataset-X).^2);

```

scaleddata.m

```

% the function for the scale data
function g=scaleddata(X,a)
g=a(1)*(X+a(2));

```