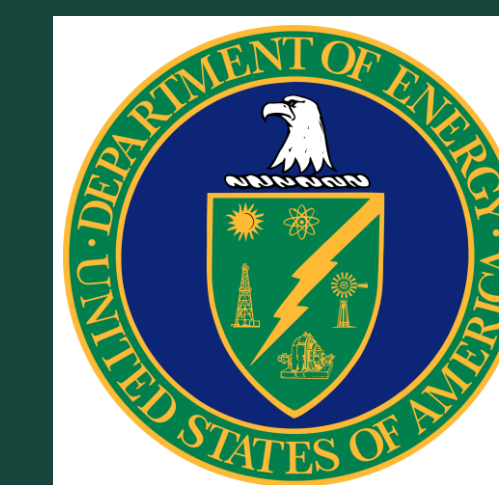


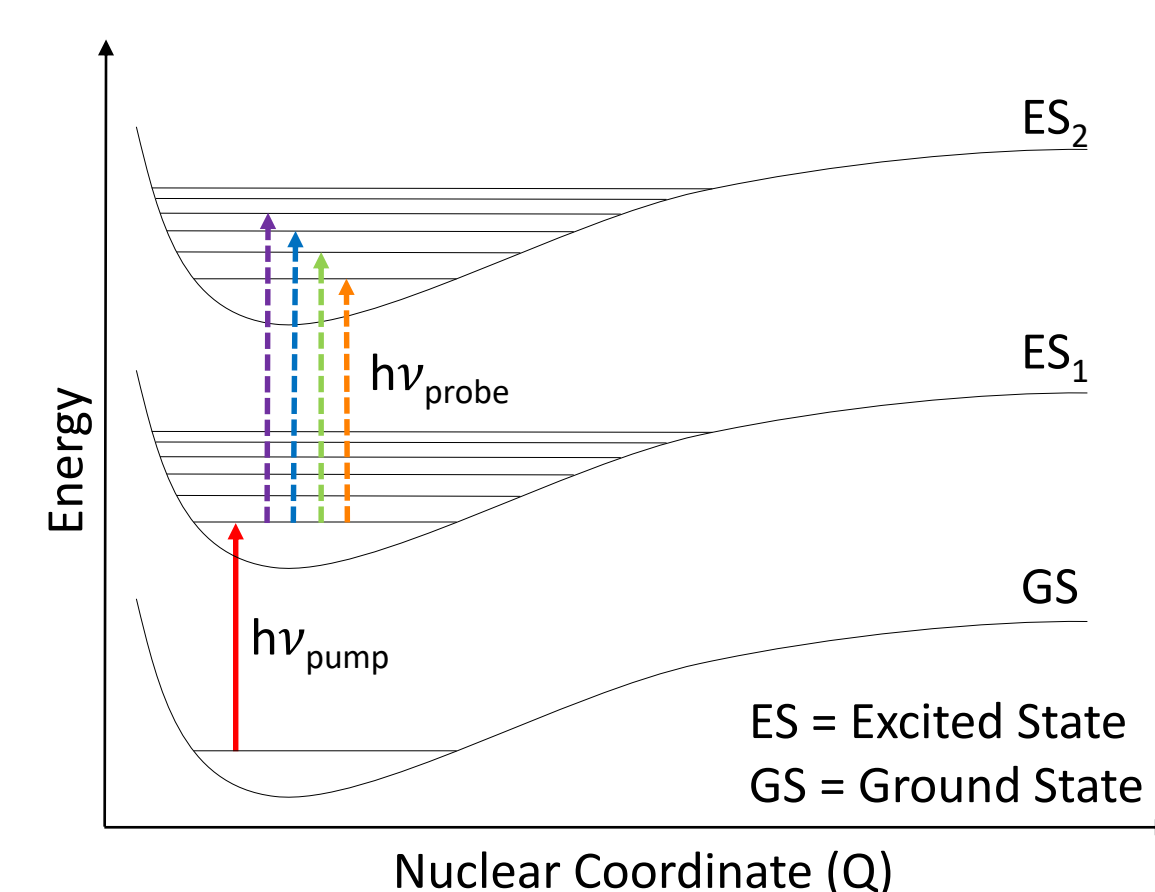
Ultrafast Investigations of Transition Metal-Based Complexes

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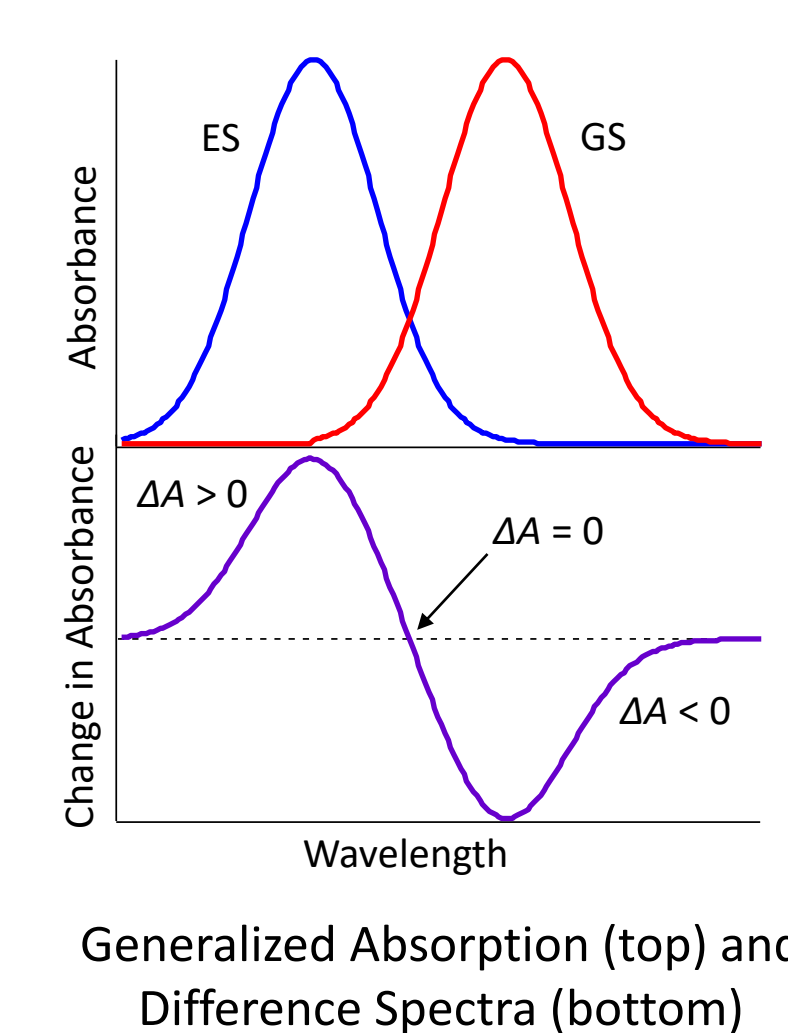
- Our group is interested in understanding the processes that occur in transition metal complexes following photoexcitation. Typical excited states that form are charge transfer (CT) and ligand field (LF) in nature.
- A CT transition represents the transfer of an electron from one moiety of a molecule to another, whereas a LF transition is localized within metal-centered orbitals.
- LF transitions are formally symmetry forbidden and therefore have low extinction coefficients, typically $100 \text{ M}^{-1}\text{cm}^{-1}$ or less, whereas CT transitions have large extinctions coefficients ranging from 10^3 to $10^4 \text{ M}^{-1}\text{cm}^{-1}$.
- In order to understand the dynamics associated with our various complexes, we utilize transient absorption (TA) spectroscopy.



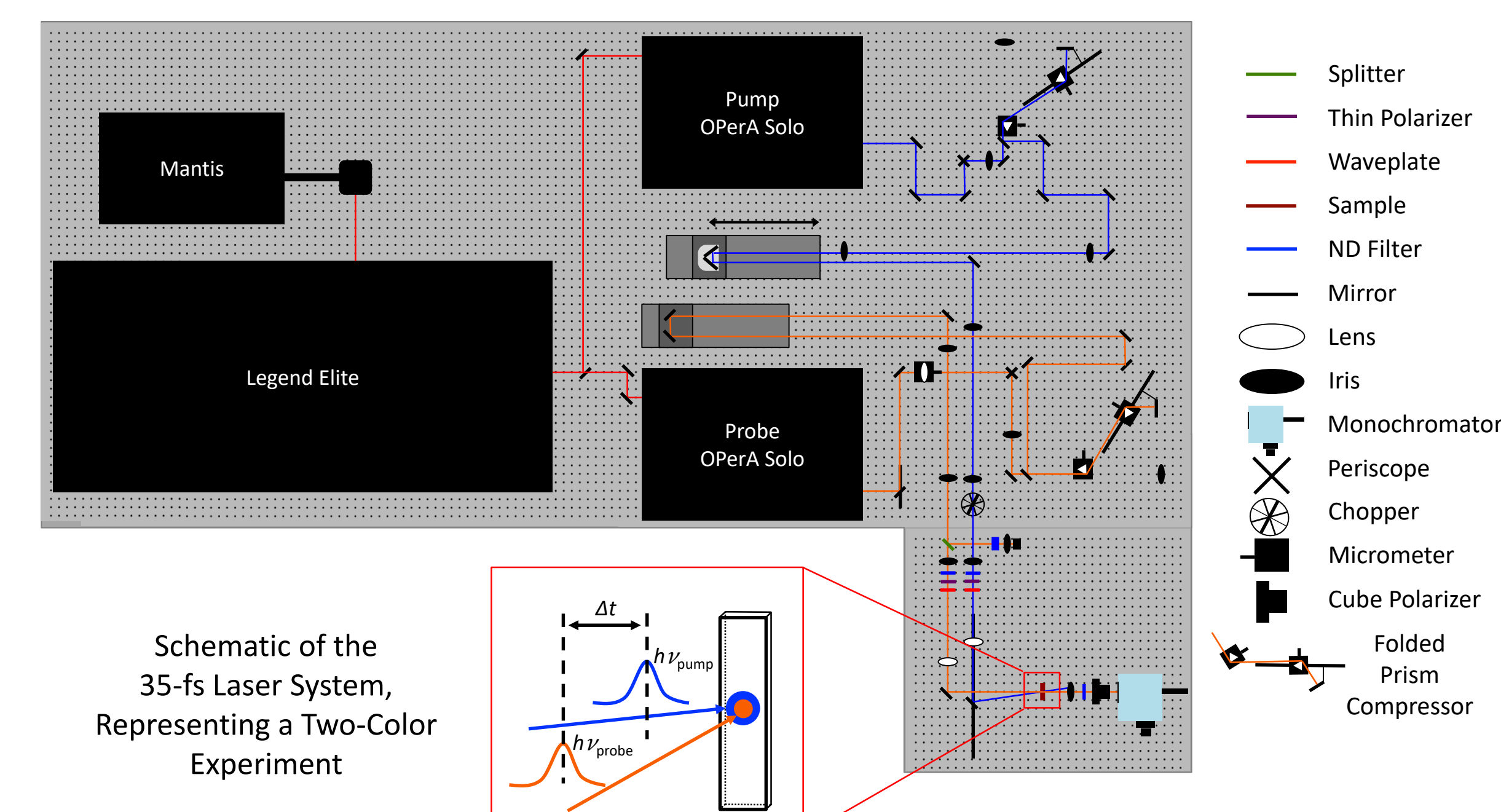
- TA spectroscopy involves exciting a small fraction of molecules with a pump pulse which is followed by a weak probe pulse to monitor changes in absorbance. The time delay between the pump and probe pulses may be changed such that a differential absorption spectrum is obtained.

Principles of Transient Absorption Spectroscopy

- The resulting spectrum represents the difference between the ground state absorption spectrum from that of the excited state, depicted to the lower right.
- When $\Delta A > 0$, excited state absorption can be seen. A bleach occurs in a region where $\Delta A < 0$ which signifies that the ground state absorbs more than the excited state. An isosbestic point occurs at $\Delta A = 0$. These are the main sources of positive and negative signals (shown to the right), but there are other possibilities as well.
- Monitoring the change in absorbance as a function of time provides information about the kinetics of excited state processes.

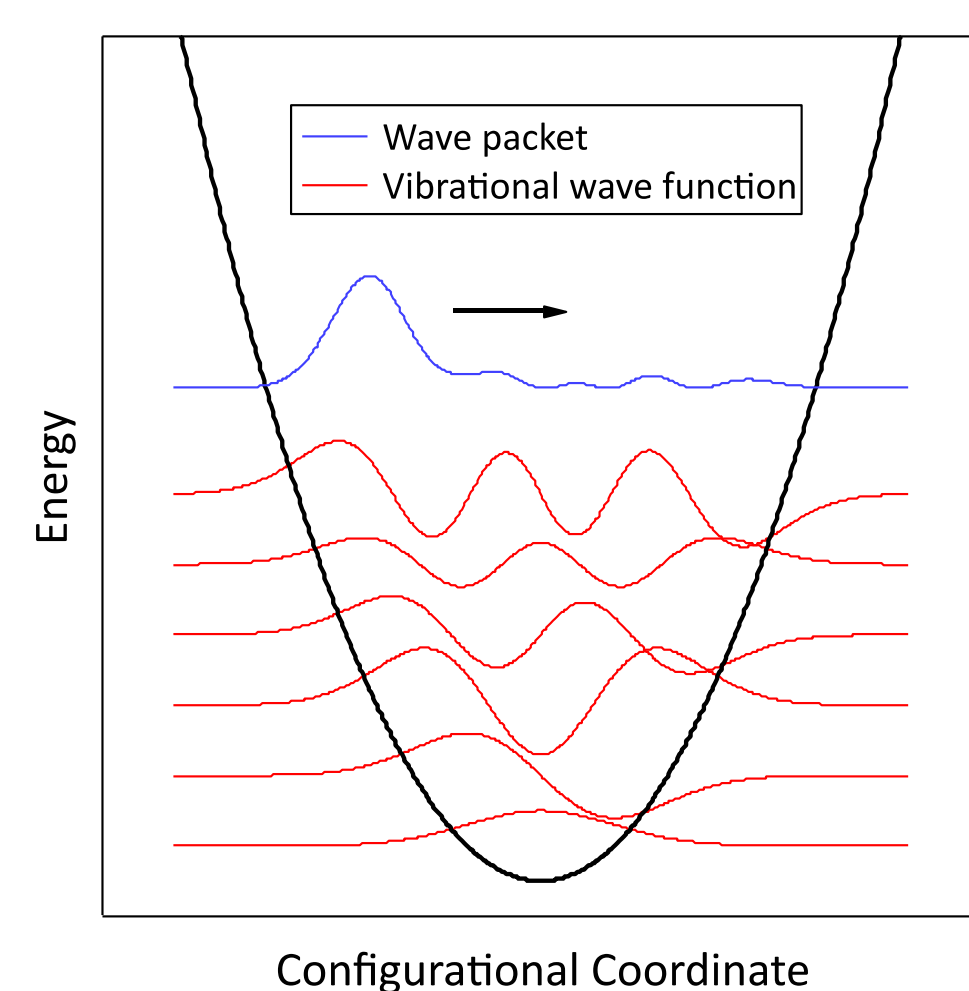
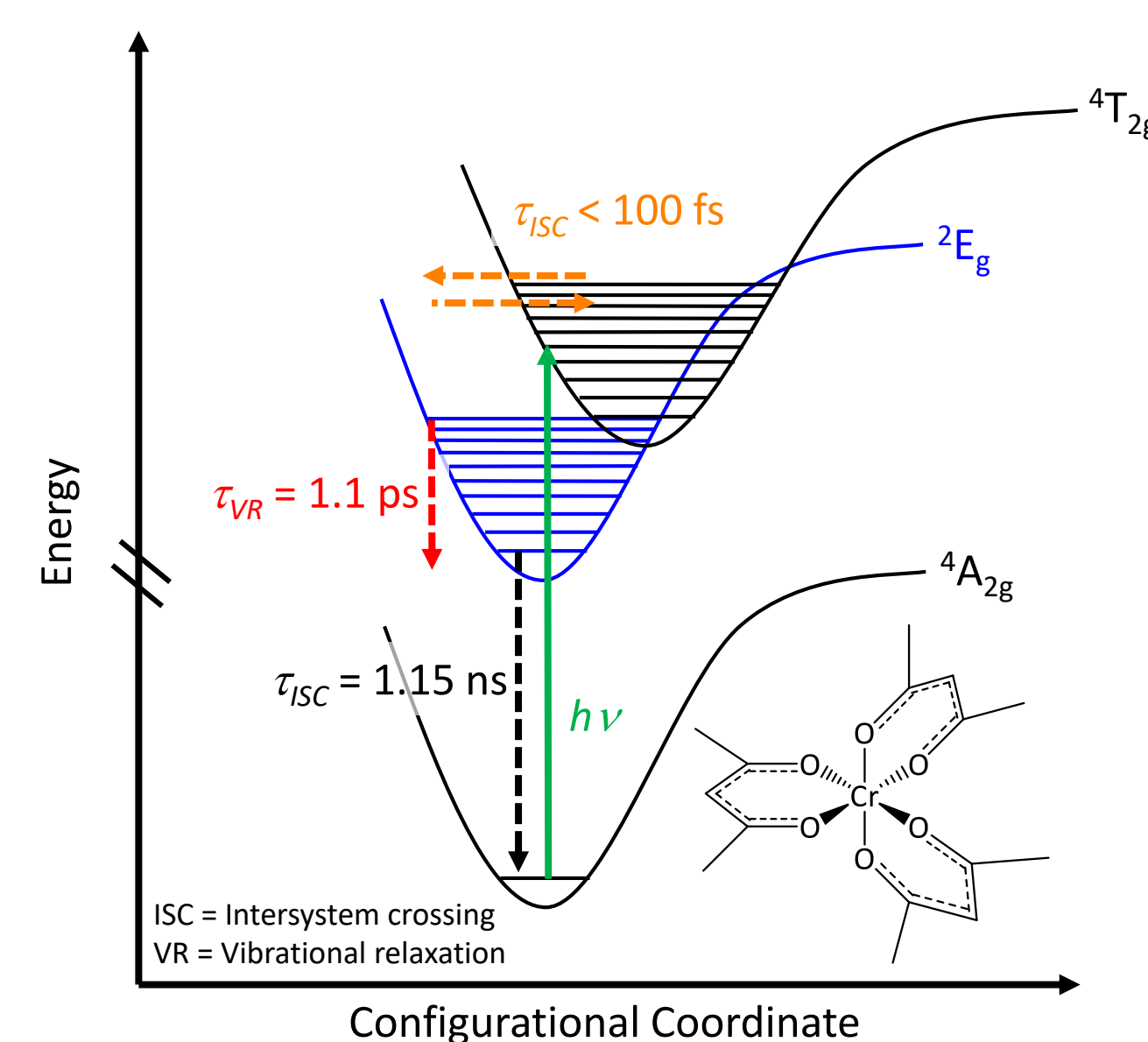


- There are two ultrafast laser systems in the McCusker group. The first laser system produces approximately 135 fs pulses (with a delay of up to 13 ns), and the second, as shown to the right, produces 35 fs pulses (with delays up to 1.2 ns). A moveable stage on the pump line is used to alter the arrival time between the pump and probe pulses.
- Our group is equipped to conduct several types of measurements, including anisotropy, coherence, and variable-temperature. These can be performed with one-color, two-color, or white light continuum set-ups.
- In a typical two-color experiment (shown to the right), the regenerative amplifier output is split and routed into separate pump and probe optical parametric amplifiers. Folded prism compressors allow for temporal compression.

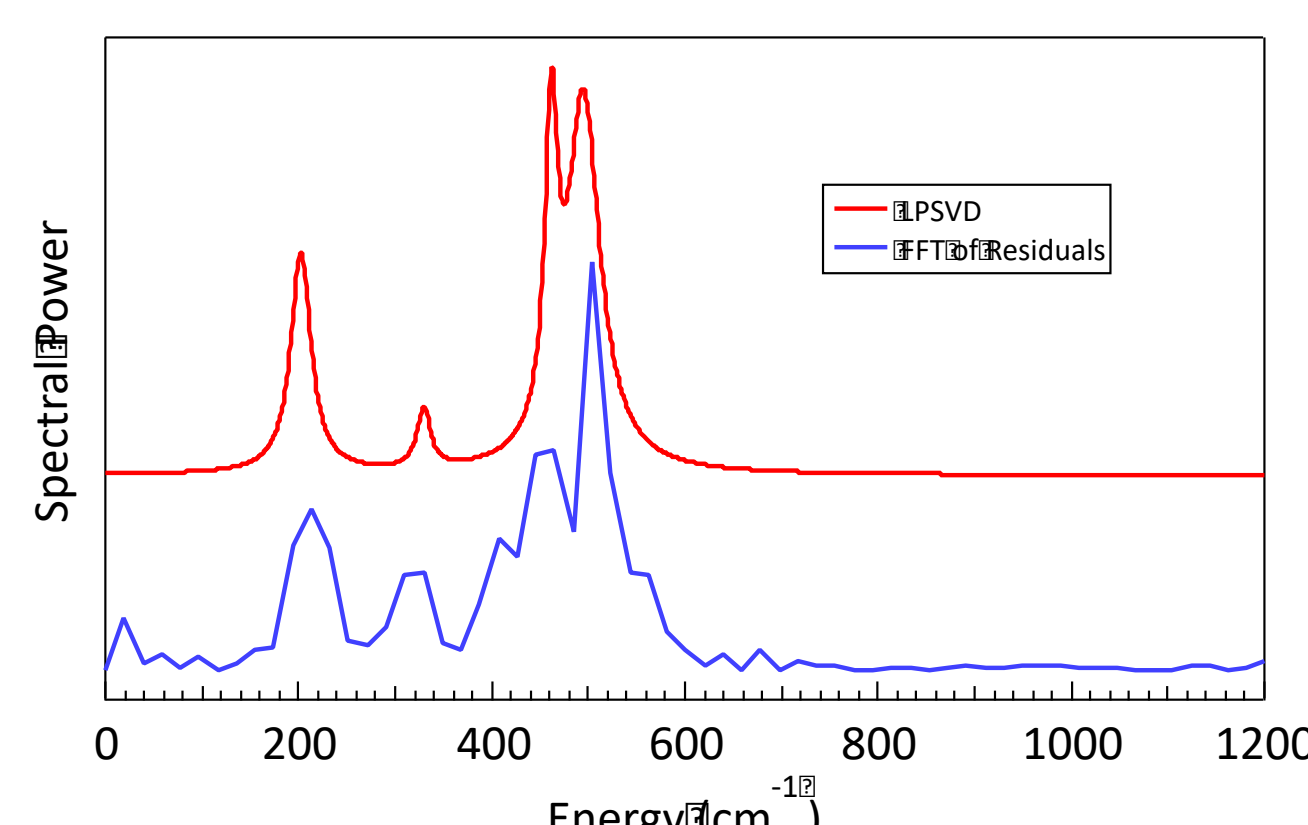
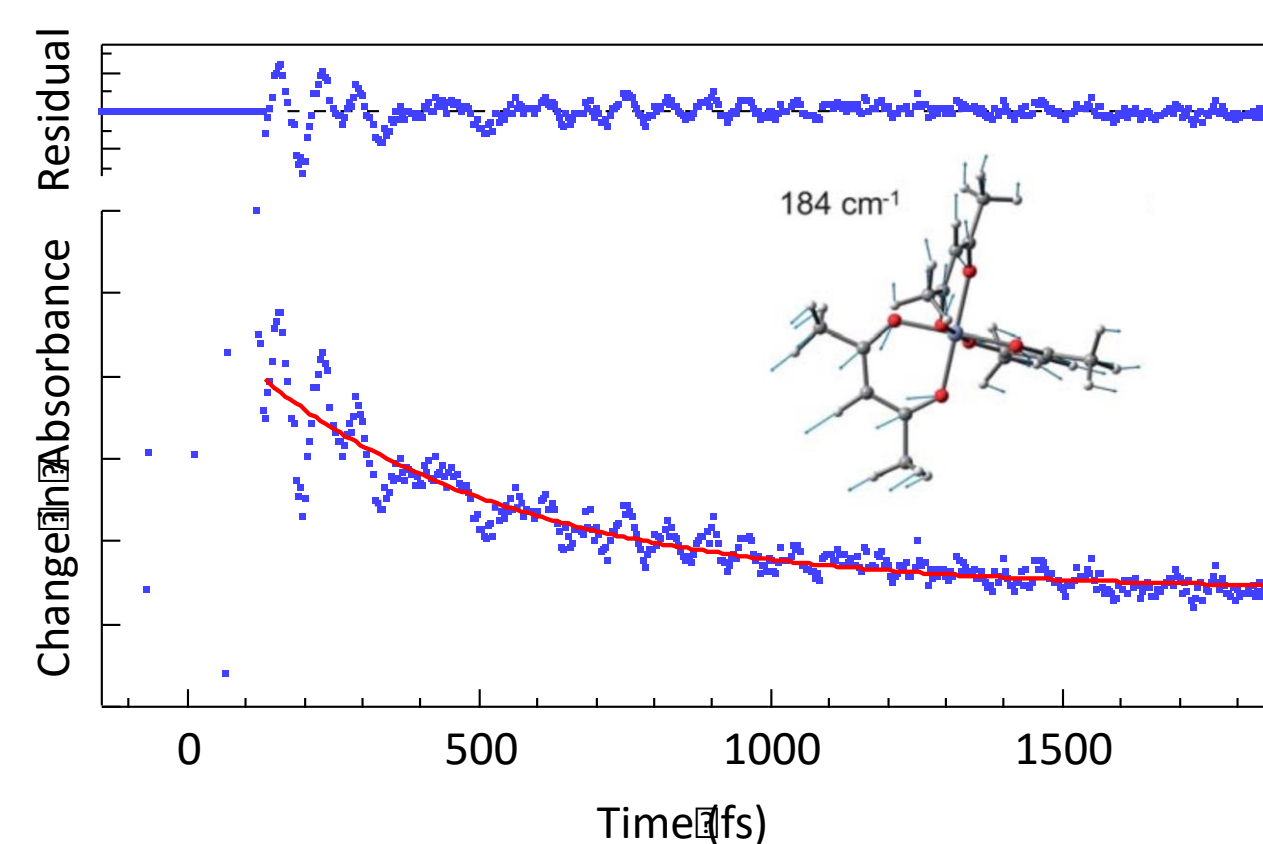


Coherence: Bridging Structure and Dynamics

- The goal of these experiments is to parse out features of the often ill-defined or poorly understood configurational coordinates pertinent to photophysical processes.
- The electronic simplicity and photochemical stability of $\text{Cr}(\text{acac})_3$ (acac = acetylacetonate) make it well-suited for these endeavors. Specifically, we seek to understand what drives the intersystem crossing (ISC) process between the initially populated excited state (${}^4T_{2g}$) and the lowest energy excited state (2E_g) in this system.
- Previous studies have characterized excited state kinetics and show that ISC to the lowest energy excited state occurs on the sub-100 fs timescale.



- In $\text{Cr}(\text{acac})_3$ and its derivatives, coherent oscillations in TA traces are observed upon photoexcitation with sub-50 fs pulses.
- Ultrashort, high bandwidth pulses are able to produce vibrational coherence by simultaneously exciting multiple vibrational levels. The superposition of each wave function yields a localized wave packet that migrates across the potential energy surface. Movement of the wave packet causes oscillations in the absorption signal.



- Subtraction of exponential kinetic components, as seen at left with $\text{Cr}(\text{acac})_3$, leaves oscillatory residuals which can be interpreted with fast Fourier transform (FFT) analysis.
- Linear Predictive Singular Value Decomposition (LPSVD) is also used to fit data to a summation of damped cosines.

$$S(t) = \sum A_i \cos(\omega_i t + \phi_i) \exp(-\gamma_i t)$$
- Both FFT and LPSVD techniques can extract the frequency of the activated vibrations. LPSVD can also determine the rate at which individual normal modes are damped, which indicates their relevance.
- Once important vibrational modes are identified, they are characterized by ground and excited state frequency calculations (via DFT).
- Through this method, a scissoring mode with large amplitude methyl group motions was identified as an active mode for ISC. To hinder this motion, *t*-butyl groups were substituted on the acac backbone and shown to reduce the ISC rate by at least an order of magnitude. Similar coherence measurements performed on this *t*-butyl derivative should help extend our understanding of the reaction coordinate.
- Detailed knowledge of the configurational coordinate should further elucidate the link between structure and dynamics.

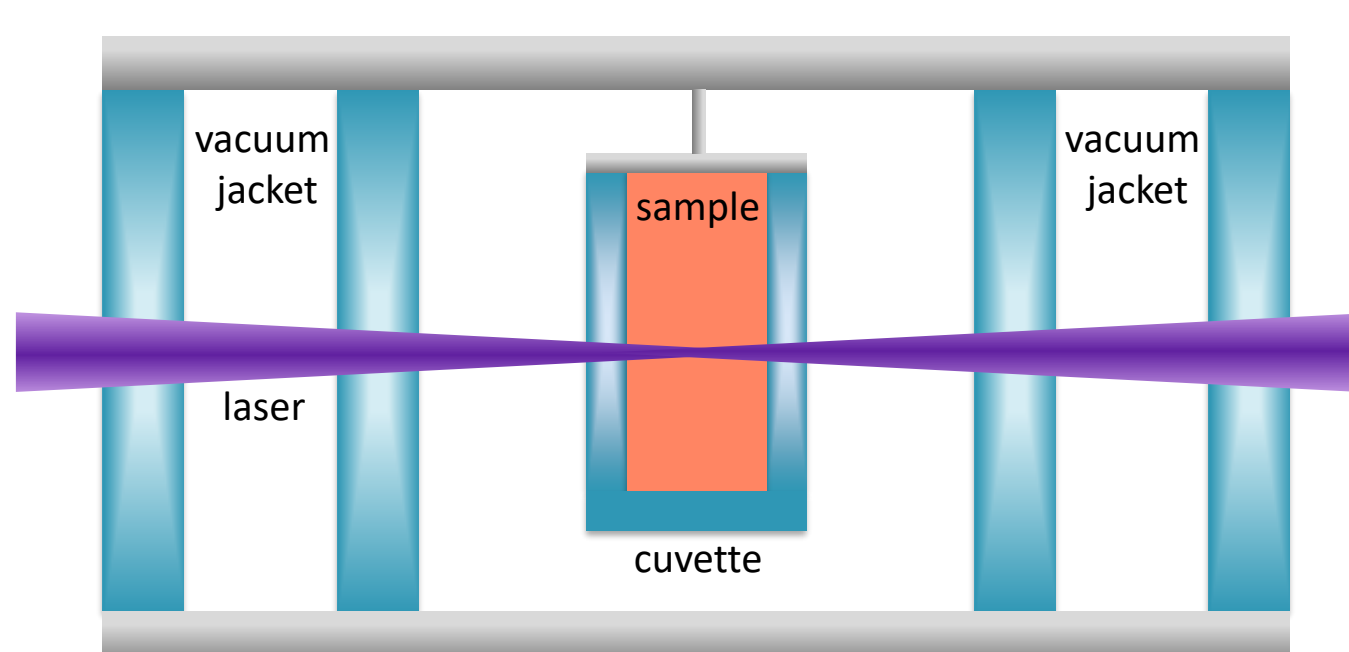
Ultrafast Variable-Temperature Spectroscopy

- The goal of this experiment is to directly measure kinetics as a function of temperature. In so doing, the activation energy (E_a) for a specific process can be found from the Arrhenius equation.

$$k_{nr} = A \exp\left\{\frac{E_a}{k_B T}\right\}$$

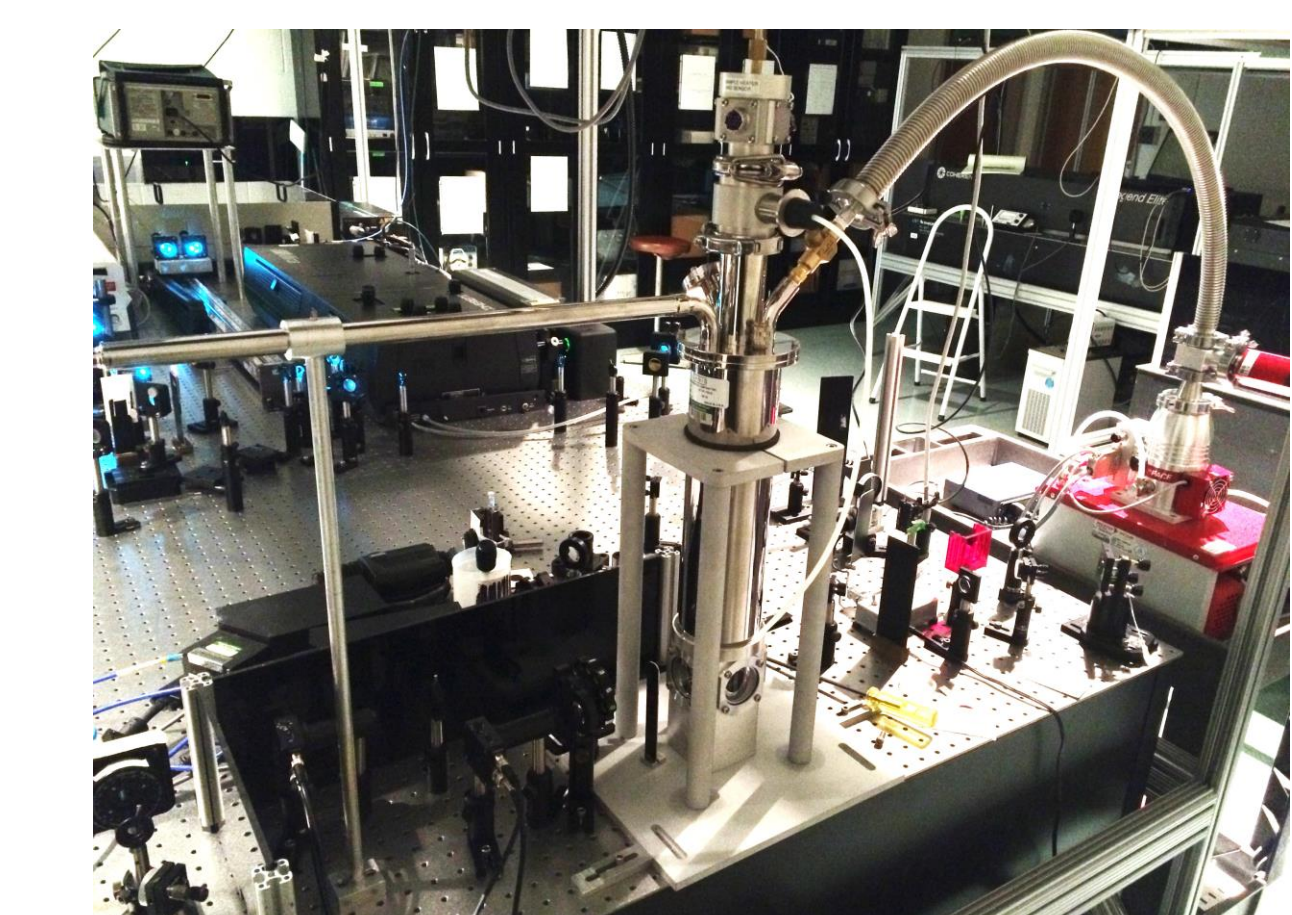
- From these Arrhenius parameters, we hope to determine the Marcus parameters, specifically the reorganization energy (λ), of Fe(II) complexes between the lowest energy excited state and the ground state.

$$k_{nr} = \frac{2\pi}{\hbar} |H_{ab}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left\{-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda k_B T}\right\}$$



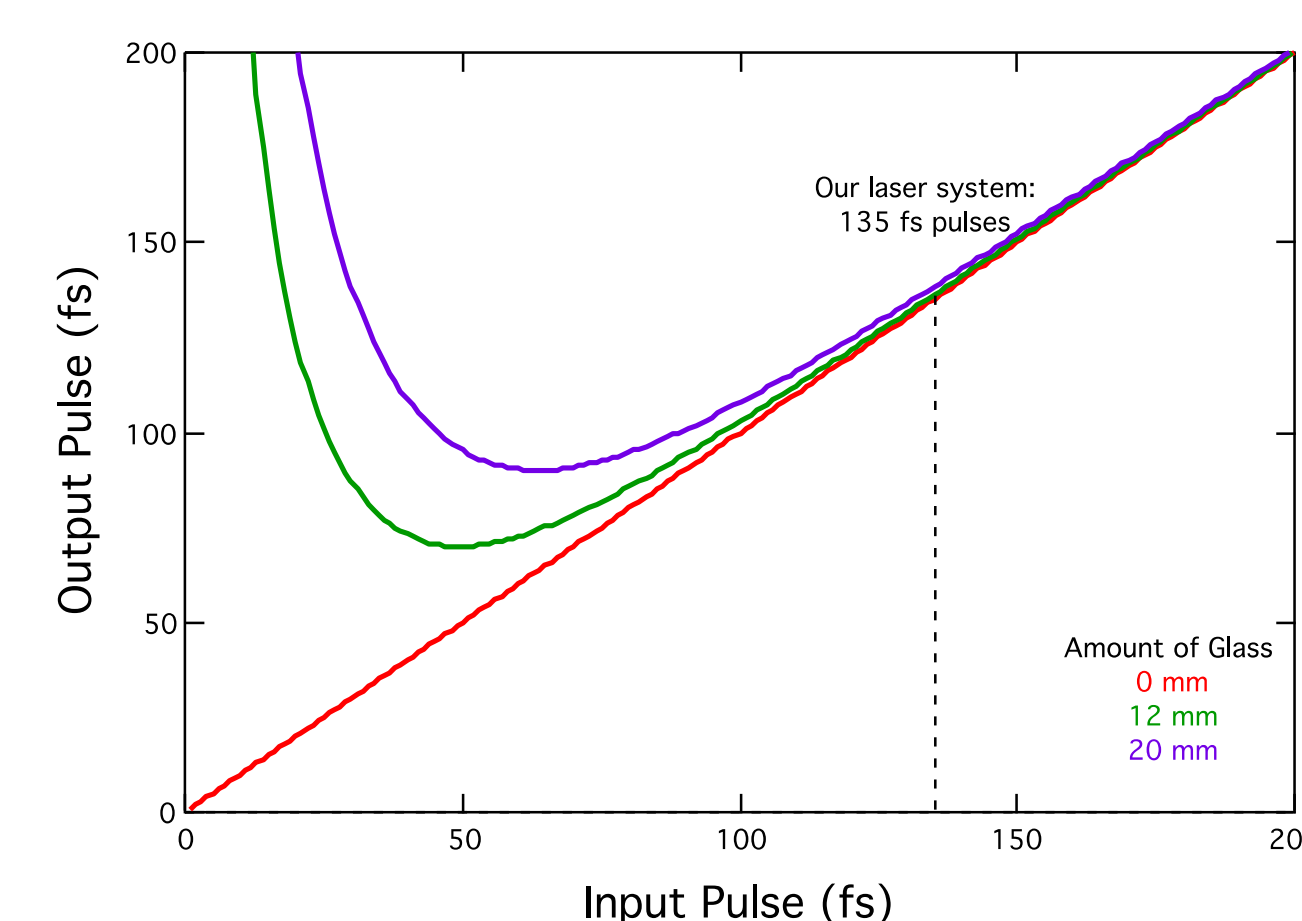
- Glass is known to broaden the duration of a laser pulse due to dispersion. Although the effect is negligible for ps and longer pulses, with fs pulses, the broadening can be hugely detrimental.

- The laser system used in conjunction with the cryostat for these experiments, however, has pulses on the order of 135 fs. Based on the amount of glass the pulse is propagating, the effect should be minimal on this system.

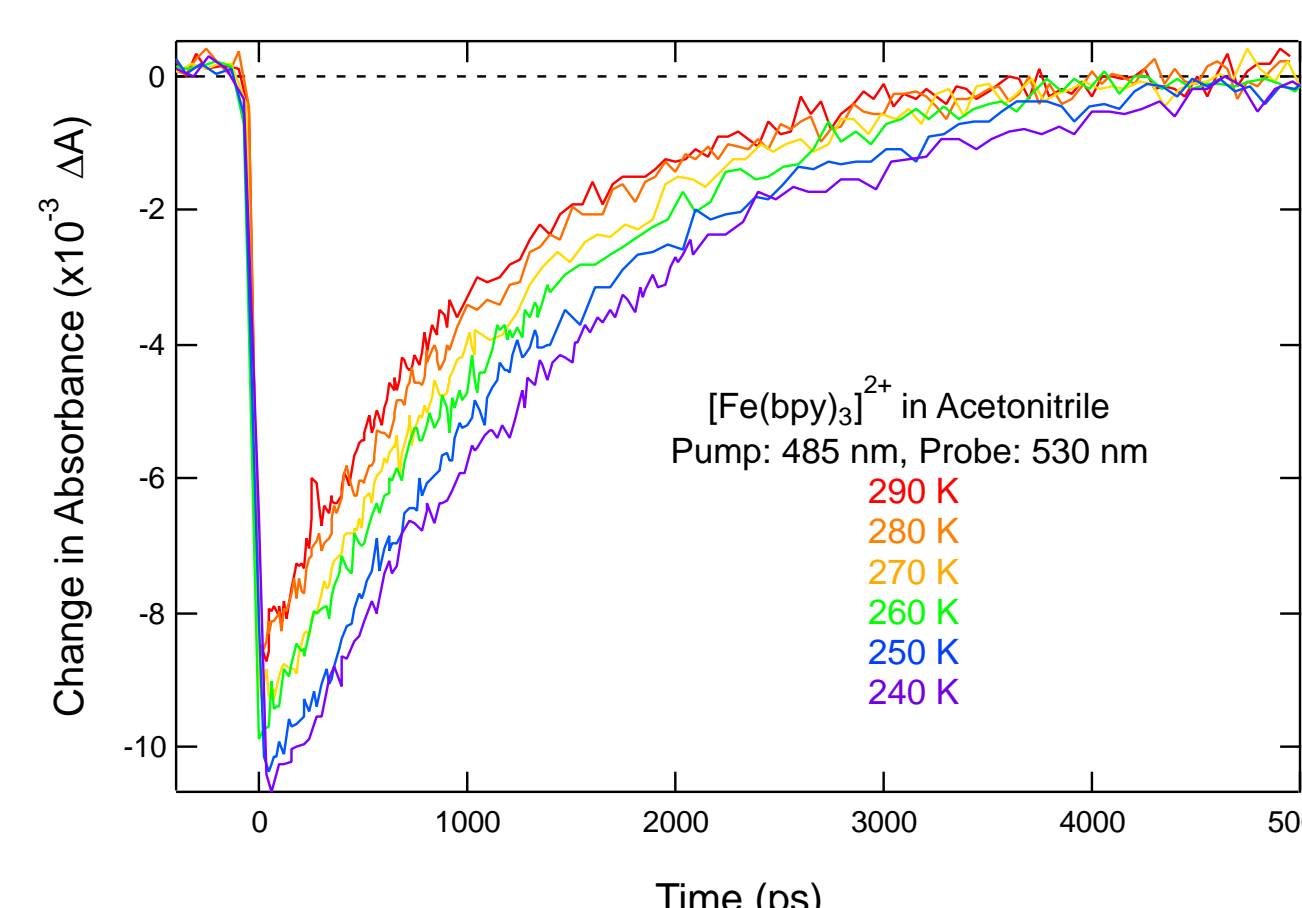


- Work on this project is ongoing. Thus far, data has been collected only in acetonitrile. In order to separate inner- and outer-sphere reorganization energies (the sum of which equals the total reorganization energy), data will be collected in a series of solvents.

- As yet, the activation energies have been found for four Fe(II) complexes. Future studies will include the ground state recovery measurement of other Fe-based chromophores.



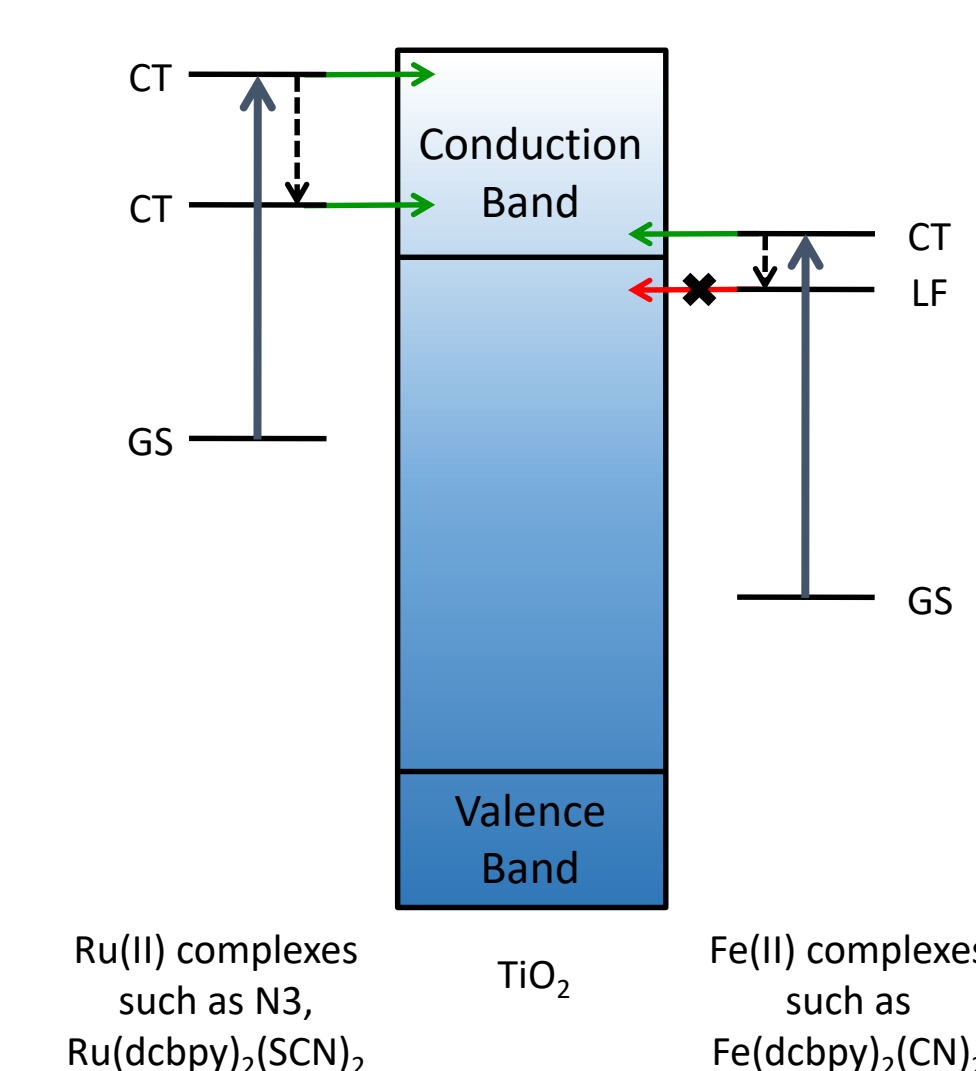
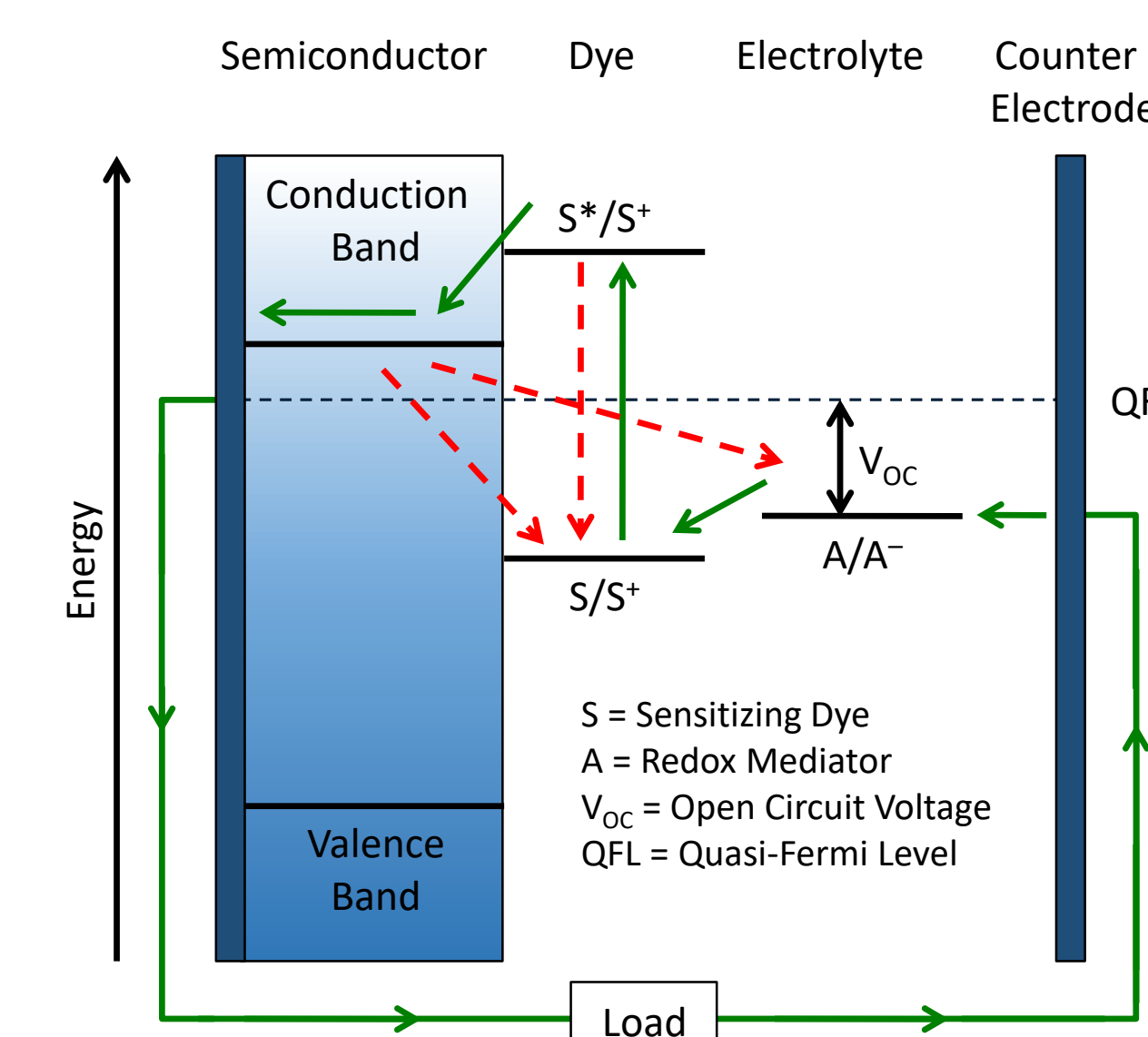
- The set-up achieves continuous flow of the cryogenic liquid, utilizing a 35 L Dewar, the cryostat, and a transfer line between the two. A turbomolecular pump is used to bring the cryostat to vacuum pressures before any cryogen transfer occurs. The temperature is monitored and controlled by a heating unit mounted to the sample within the cryostat. The rest of the experiment is a standard ultrafast TA measurement.



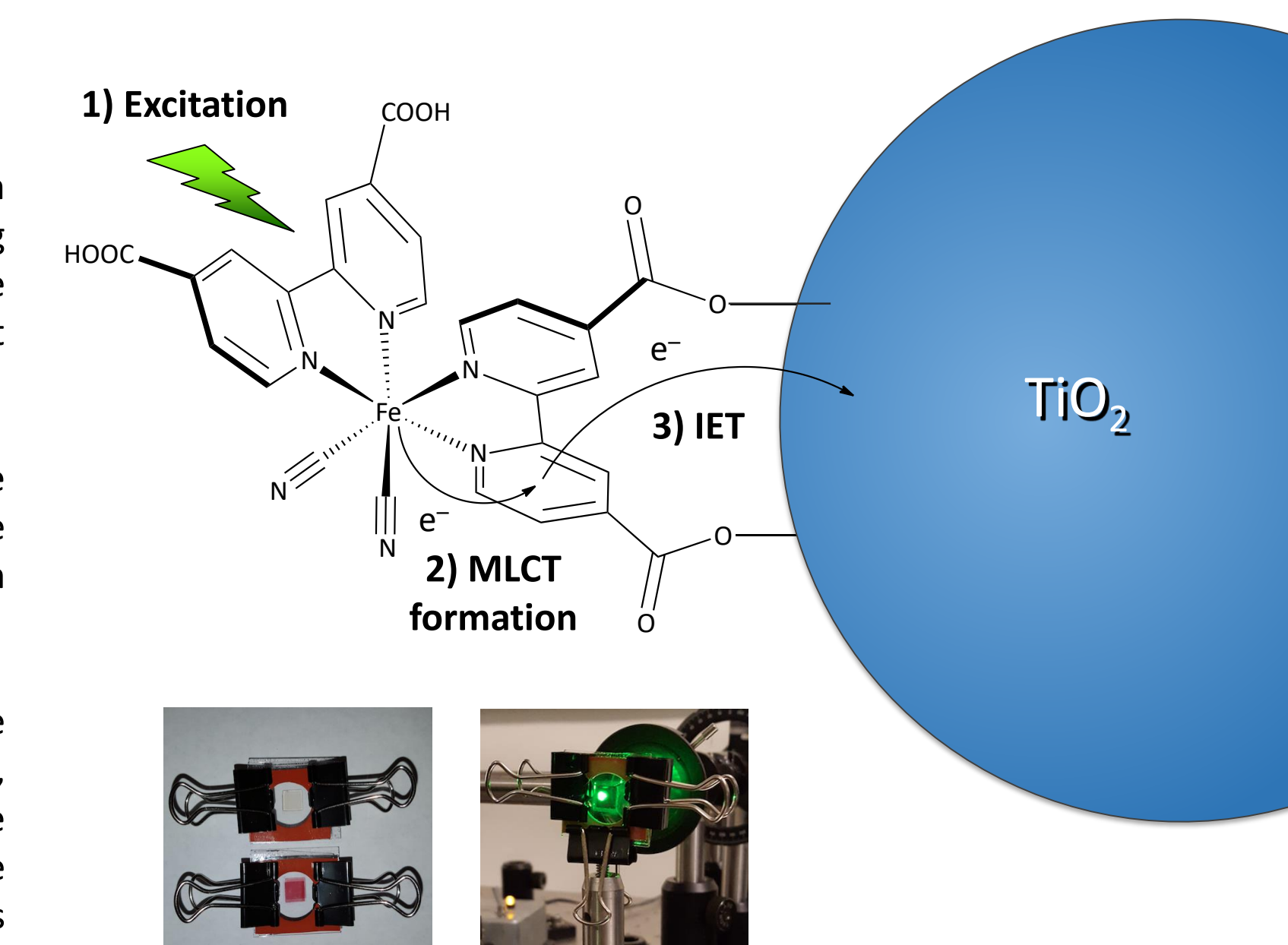
The Effect of Dispersion on Ultrashort Pulses. <http://www.newport.com> (accessed Feb 20, 2013).

Probing Interfacial Electron Transfer

- Dye-sensitized solar cells (DSSCs) capture solar energy using a sensitizer adsorbed to a wide band gap semiconductor.
- Photoexcitation generates a metal-to-ligand charge transfer (MLCT) excited state in the dye, which injects an electron into the conduction band of the semiconductor.
- The injected electron travels to the back electrode and through the circuit to the counter electrode.
- A redox mediator in the electrolyte completes the circuit by shuttling the electron from the counter electrode to the oxidized dye.
- Processes shown in green are favorable, while those in red short circuit the cell, decreasing the overall efficiency.
- At present, our research focuses on the competition between injection and relaxation of the excited state.



- While the most widely studied solar cells incorporate ruthenium as the dye metal center, ruthenium is rare.
- Iron represents an abundant alternative and has been shown to produce a photocurrent in a dye covalently bound to nanocrystalline titanium dioxide (TiO_2).
- Unfortunately, ultrafast deactivation (on a sub-ps timescale) from an injecting charge transfer (CT) state to a metal-centered ligand field (LF) state significantly hindered the injection yield.
- Initial strategies to boost the injection yield with iron complexes involve modifying the anchoring groups (based on theoretical findings) and the semiconductor substrates to improve the driving force and coupling between the TiO_2 acceptor states and dye donor states.



- Data from probing in the visible region correspond to the loss of the injecting excited state or the formation of the oxidized dye as an indirect measurement of interfacial electron transfer (IET).
- Signal from electrons injected into the semiconductor can be observed in the near-IR region, though contributions from other species may still exist.
- Probing in the mid-IR region allows for the direct detection of electron injection, where conduction band electrons have strong absorptions, but care must be taken to discriminate for signals corresponding to vibrational transitions.
- In order to better understand the processes and sources contributing to the observed signal following photoexcitation, it is worthwhile to conduct studies of individual components (e.g. dye in solution or bare TiO_2) as well as studies which systematically build up complexity to operational DSSCs, while probing in the visible, near-IR, and mid-IR regions.
- Our goal is to expand on initial reports and use our knowledge of synthetic design, steady-state characterization, and electron injection detection to improve the efficiency of Fe(II)-based solar cells.