Hadt Lab at Caltech

Motivation

Physical Inorganic Chemistry at Caltech. Research in the Hadt lab is focused on fundamental and applied studies of transition metal electronic structure and its role across interdisciplinary areas of chemistry, biology, physics, and materials science.

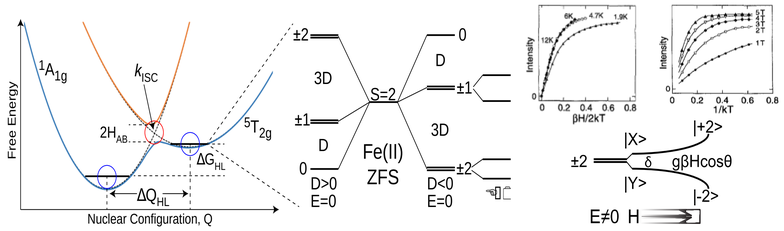
Research Interests

I. Spin-Phonon Coupling and Magnetization Dynamics in Transition Metals

Fundamental Studies and Methodology. Experimental and theoretical quantification of spin-phonon coupling in mononuclear and multinuclear transition metal complexes.

Molecular Magnetism and Spin Crossover. Understanding the role of spin-phonon coupling in the mechanisms of transition metal intersystem crossing and magnetization dynamics.

Quantum Computing. Elucidating the roles of spin-phonon coupling in the relaxation dynamics and decoherence times of molecular and solid state qubits.



(Left) Potential energy surfaces for O_h Fe(II) S=2/S=0 interconversion. ***(Right)*** *Example S=2 Fe(II) VTVH MCD curves and magnetic field dependent energies of the M_S=±2 sublevels*

II. Transition Metal-Mediated Homogeneous, Heterogeneous & Biological Catalysis

Photoredox Catalysis. Elucidating the mechanisms of Cu- and Ni-catalyzed C-X bond formation and C-H activation.

Organic Synthesis. Spectroscopic and computational elucidation of Cu- and Ni-catalyzed asymmetric reductive cross coupling reactions.

Solar Fuels Catalysis. Developing magneto-optical spectroscopies as site-selective structural probes of electrocatalytic Co and Mn oxygen evolving thin films.

Bioinorganic Chemistry. Interrogating the geometric and electronic structures of iron heme active sites, including iron-carbenes in cyt *c* and SeCys variants in P450s.

Additional Techniques

Computational Techniques

Density Functional Theory and Time-Dependent DFT

Multi-Reference Methods (CASSCF, MRCI, NEVPT2, CASPT2)

Multi-Frequency Electron Paramagnetic Resonance (Caltech)

Resonance Raman (Caltech)

Mössbauer Spectroscopy (Caltech)

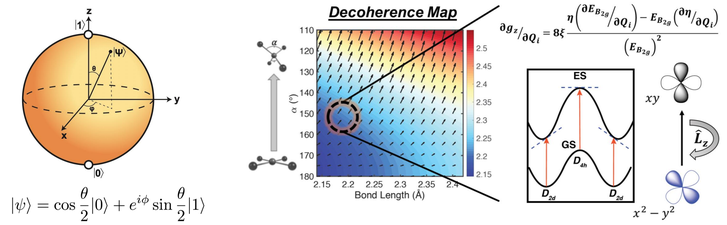
Transient Electronic Absorption/Emission (BILRC)

X-ray Absorption and Emission (Synchrotrons and XFELs)

Resonant Inelastic X-ray Scattering (Synchrotrons and XFELs)

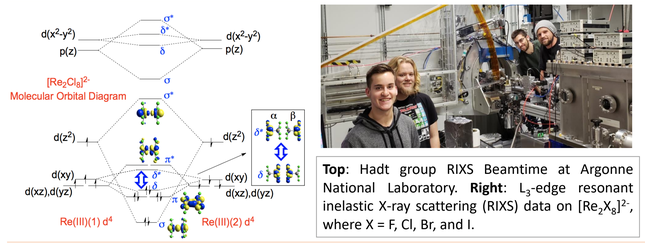
Research Summary

Investigating What Makes a Good Molecular Qubit

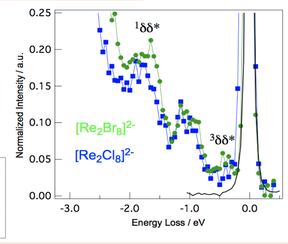


$$|\psi\rangle = \cos\frac{\theta}{2}|0\rangle + e^{i\phi}\sin\frac{\theta}{2}|1\rangle$$

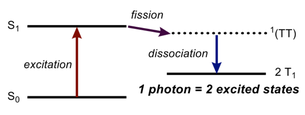
Detecting the "Undetectable": $^3[\delta \rightarrow \delta^*]$ in $[Re_2X_8]^{2-}$

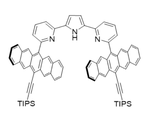


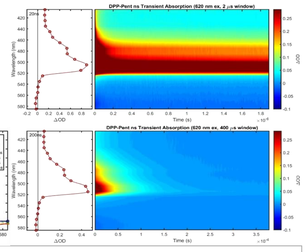
Top: Hadt group RIXS Beamtime at Argonne National Laboratory. **Right**: L_3-edge resonant inelastic X-ray scattering (RIXS) data on $[Re_2X_8]^{2-}$, where X = F, Cl, Br, and I.



Singlet Fission in Bipentacene Complexes



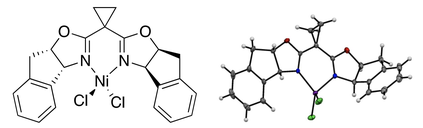




Singlet fission is a process by which one singlet excited state is converted into two lower energy triplet states via singlet correlated triplet pairs – magnetic fields perturb this interconversion.

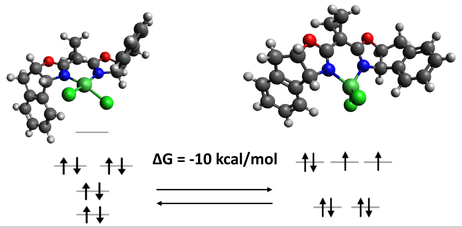
Nanosecond transient absorption spectra of a bipentacene dipyridyl pyrrole system showing the decay of a long-lived triplet photoinduced absorption.

Ultrafast Magneto-Optical Studies of Transition Metal ISC Dynamics



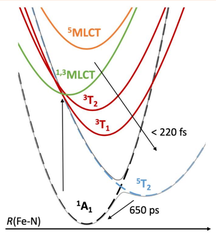
J. Am. Chem. Soc. 2018, 140, 139−142

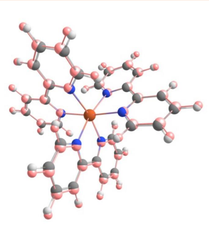
Structure of asymmetric Ni-catalyzed reductive cross-coupling catalyst **nickel(II) bis(chloride)** from the Reisman group.

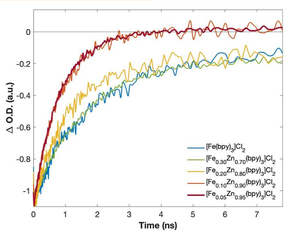


Calculated energy difference between the tetrahedral (high spin) and square planar (low spin) conformations. This structural and spin-state change can be photo-triggered and monitored using ultrafast spectroscopies.

Ultrafast Molecular Magnetism in Thin Films

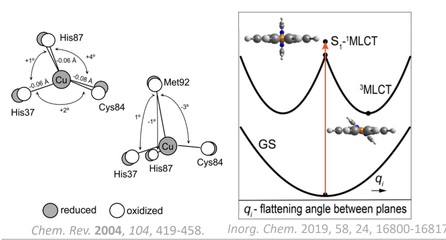




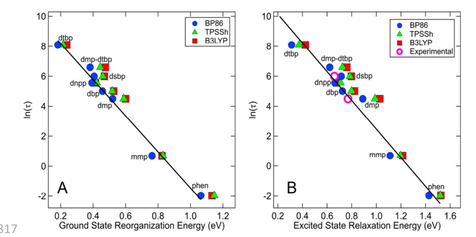


Left: Ultrafast state transitions in $[Fe(bpy)_3]^{2+}$ observed after photoinduced excitation. **Center:** Relative distortion along the symmetric stretching mode from quintet $[Fe(bpy)_3]^{2+}$ **Right:** Normalized transient absorption spectra of a 2.5 mM thin films probed at 370 nm.

Structural Control of Transition Metal Excited State Dynamics



Chem. Rev. **2004**, *104*, 419-458. *Inorg. Chem.* 2019, 58, 24, 16800-16817



Proteins impose unique geometric and electronic structures on redox-active metal sites, resulting in finely tuned functional properties and **entatic** states.

Correlation between excited state lifetime and ground state reorganization energy (A) and excited state relaxation energy (B).

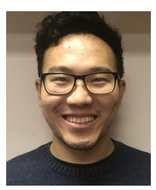
Current Group & Research Directions

Magnetism and Spectroscopy of Artificial Photosynthetic Cobalt Oxide Thin Films - *Ruben Mirzoyan*

Despite decades of research on Oxygen Evolution Reactivity (OER), the mechanism of the O-O bond forming step is still under debate. Intramolecular electron transfer parameters and magnetic coupling between Co atoms in catalytic Co-oxide thin films could be established, providing insight on the mechanism by which heterogeneous OER catalysts operate.

Effects on Spin Crossover in Photomagnetic Compounds - *Nick Higdon*

Photomagnetic compounds exhibit a magnetic change upon irradiation below a critical temperature, an effect known as Light Induced Excited State Spin Trapping. My project focuses utilizing advanced spectroscopies coupled with structural perturbations and computations to probe kinetic aspects affecting T_c and the spin relaxation of photomagnetic materials, focusing on the role of zero-field splitting and spin-phonon interactions in the rate of spin crossover.



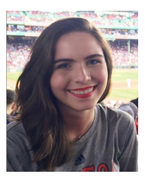
Dynamics of Spin Equilibria in Nickel and Cobalt Complexes - *Jaron Tong*

Investigation of spin equilibria is complicated by the diversity of processes that can accompany spin change. Cobalt quinoid and nickel phosphine halide are two model complexes for intramolecular electron transfer coupled spin crossover (SCO) and geometric distortion coupled SCO. We aim to identify important factors underpinning the mechanisms of these processes, applying these added insights from spin chemistry to understanding base metal catalysts.

Bipentacene Coordination Complexes as a Platform for Studying Singlet Fission - *Ryan Ribson (joint with Agapie Group)*

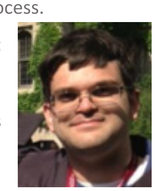
We are currently targeting the synthesis of molecular bipentacene complexes capable of ligating metal ions, enabling coordination chemistry-controlled inter-chromophore morphology (DPP-Pent, PentPhOH). Ultrafast optical and magneto-optical spectroscopies will identify singlet fission pathways in these systems and may elucidate important mechanistic information about this process.

Electron Dynamics in Exchange-Coupled Dimers - *Alexandra Barth*



In biological systems, metal dimers and higher nuclearity clusters are abundantly used as electron-transfer agents. Targeting mixed valence Fe(II)Fe(III) and Mn(III)Mn(IV) dimers, we aim to investigate the intersection between ultrafast electron transfer dynamics and magnetic coupling and to determine mechanisms for large, photo-triggered spin state changes.

Extending Bioinorganic Concepts to Transition Metal Dynamics: Developing a Quantitative Methodology - *Gautam Stroscio*



Development of computational methodologies for probing geometric and electronic structural effects on the excited state dynamics and decoherence times of first-row transition metal complexes, particularly those with potential applications as photosensitizers or qubits.

Electronic Structure and Spin Dynamics in Bioinorganic Chemistry – *Alec Follmer*

Metalloenzymes carry out some of the most critical processes in biology (e.g. electron transport, metabolism, etc). These enzymes manipulate the electronic structure of their cofactors in ways that are not completely understood. By monitoring electron dynamics through ultrafast magnetic and optical spectroscopies, we can clarify the complex relationship between structure and function in bioinorganic reactivity.

Investigating the Mechanisms of Transition Metal Mediated Photoredox Catalysis – *David Cagan*

Recent discoveries present nickel complexes as effective photoredox cross-coupling catalysts. However, the mechanisms and nature of the electronic transitions responsible for the critical bond-forming step are not well understood. We are leveraging ultrafast spectroscopy and advanced computational modeling to elucidate these excited state dynamics.