Caltech
Student-Faculty Programs

Session D Abstracts

Less is more: Data-driven quality evaluation of electron diffraction for intelligent unit cell identification
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Mentors: Hosea Nelson and Dmitry Eremin

Recent advances in artificial intelligence and machine learning have enabled scientists to process and rationalize an unprecedented volume of experimental data. However, this surge in data poses significant challenges to data collection practices. The quality of data acquired and processed becomes the priority, paving the road to autonomous and intelligent data acquisition. One field in particular is undergoing this evolution. Microcrystal electron diffraction (MicroED), a method used to determine 3D molecular structures. Not only have numerous structures been solved using microED, but even new chemical matter has been recently discovered. However, the growing volume of the acquired data presents a technical bottleneck.

To address this, the Nelson lab is developing MILEDD (Machine Learning Leveraging Electron Diffraction Database), a platform designed to streamline and accelerate data processing using AI and ML tools.

My SURF project focuses on improving the acquisition pipeline to ensure higher data quality to be deposited to MILEDD. To achieve this goal, I am using computational methods to filter existing microED data and to determine the minimal number of frames and angular range necessary to accurately determine crystal unit cells. These tools will help automate and optimize not just unit cell identification but also pushing MicroED closer to its full scientific potential.

Photophysics and photochemistry of a thioxanthone dimer
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Organic photoredox catalysis has emerged as a powerful tool to drive a myriad of challenging chemical transformations. A notable organic photoredox catalyst is thioxanthone, which is competent for energy transfer, single-electron transfer, and hydrogen atom transfer reactivity through its triplet excited state. Thioxanthone, however, suffers from a low triplet quantum yield (TQY), particularly in polar solvents, which are often necessary in synthetic applications, making it less attractive compared to ruthenium and iridium based polypyridyl complexes. A potential strategy to enhance TQY is through H-dimerization, where multiple chromophores are stacked in an offset side-by-side arrangement. In this work, H-dimerization is successfully exploited as a strategy to achieve near unity (97.5%) TQY in a molecular thioxanthone dimer ("TXXanth") in benzene. The ultrafast excited state dynamics and reactivity of TXXanth were then probed with a range of femtosecond and nanosecond transient absorption measurements and a suite of complementary photophysical techniques.

Circular dichroism action spectroscopy for precise enantiomeric excess measurement
Linus Z. Murphy
Mentors: Mitchio Okumura and Leah Stevenson

We developed a novel method of measuring enantiomeric excess in organic samples via a technique known as Circular Dichroism Action Spectroscopy (CDAS). CDAS is a specialized form of Action Spectroscopy, a spectroscopic method that measures the Mass Spectrometric (MS) signal of a sample after the sample is photodissociated at a parametrized wavelength. By circularly polarizing the photodissociation laser pulse, chiral samples will photodissociate more or less depending on if the

strongest absorbing bonds are circularly aligned with the laser pulse polarization. By repeatedly performing this technique and averaging the resulting MS signals, a reliable measure of enantiomeric excess can be determined. This technique has potential applications in the search for extraterrestrial biology, as it is largely portable in interplanetary probes and reliable for a variety of chiral chemical systems. We partially constructed a CDAS system with a 266 nm 1kHz pulse diode laser.

Developing stopping criteria for C–H oxidation regioselectivity prediction
Carolyn Ruan
Mentors: Sarah E. Reisman and Anjali Gurajapu

Accurate regioselectivity prediction models for C–H oxidation are crucial towards derisking C–H activation steps in synthetic campaigns and synthesis planning, ultimately reducing reliance on slow, resource-intensive experiments and enabling more efficient drug design and material development. Furthermore, generating the dataset for a successful model may require significant time and laboratory resources for the purification, characterization, and precise assignment of the functionalization site. Recent work in the Reisman Lab has used active learning-based acquisition functions with random forest models to reduce the number of data points needed to perform accurate prediction for C(sp3)–H functionalization. This project aims to develop a stopping criterion for the active learning loop to minimize the number of required experiments for training while maintaining model performance. Various molecular properties, random forest model and acquisition function performance metrics, and sequential machine learning models are investigated as stopping properties.

Understanding and quantifying pseudocapacitance through measurements of entropy
Nora K. Kristufek
Mentors: Nicholas P. Stadie and Brent T. Fultz

Fast-charging, energy-dense batteries are crucial to reduce the reliance on fossil fuels and to expand renewable energy use[1]. Faradaic materials have high energy density but charge slowly due to complete ion desolvation and electron transfer[1][2]. On the other hand, capacitive materials charge quickly but have low energy density due to using electrostatic adsorption without desolvation or electron transfer [2]. Pseudocapacitive materials, which exhibit partial desolvation and partial electron transfer, could offer a promising solution to the drawbacks of each—but their behavior is poorly understood, and no standard, quantitative metric exists to define a material as pseudocapacitive[3][4][5]. We propose an entropy-based metric in order to quantitatively distinguish between capacitive, faradaic, and pseudocapacitive mechanisms, measured using two temperature-dependent electrochemical methods [5][6][7]. First, we measure the lithiation entropy as a function of lithiation state for five materials of interest using an isothermal half-cell against lithium metal: zeolite-templated carbon (ZTC) being capacitive, graphite and lithium iron phosphate (LFP) being faradaic, and Nb_2O_5 and p-HBC being considered as pseudocapacitive [3]. Then we examine the desolvation entropy for the electrolyte using a non-isothermal, symmetrical H-cell (lithium metal against lithium metal) [7]. Combining these two metrics across all of the above-mentioned materials (consisting of all three mechanism types), we report the unique desolvation entropy for each, providing a quantitative scale for

Characterization of high-pressure high-temperature synthetic nanodiamond precursors
David V. Welt
Mentors: Jonathan S. Owen, Theodor Agapie, Augustin Braun, Daybis Tencio, and Johnson Dalmieda

High-pressure high-temperature (HPHT) synthesis is a promising method for growing nanodiamonds with good purity and crystallinity. However, in order to improve control over the synthesis process, the mechanism of nanodiamond growth from starting materials must be better understood. This project used mass spectrometry, 1H-NMR and DOSY spectroscopy, powder X-ray diffraction, and UV-visible absorbance and photoluminescence spectroscopy to characterize the mixtures of intermediate compounds from HPHT syntheses. Samples were run at intermediate temperatures and pressures to study the product mixtures close to the decomposition point of the starting material. Adamantane was present in some of the samples, and TiF_3 was present in all samples, supporting the loss of hydrogen fluoride as part of the reaction mechanism. The presence of adamantanol in some

samples indicated that the standard sample preparation in air allows for oxygen incorporation that may impact the process of diamond growth or introduce variability between otherwise consistent samples. Additional components corresponding to broad NMR signals and high molecular weight MALDI peaks were further investigated by optical spectroscopy. Improving synthetic control via mechanistic understanding may allow us to better tailor synthetic processes to produce nanodiamonds well-suited to incorporating nitrogen vacancy centers, which are promising for applications in quantum sensing.

Elucidating the mechanism of nitrogenase model compound-catalyzed carbon-sulfur bond cleavage

Alex S. Xu
Mentors: Jonas C. Peters and John Ovian

Recent reports of carbon-sulfur bond cleavage in nitrogenase-related enzymes have spurred an ongoing effort to better understand inorganic cofactor-catalyzed carbon-sulfur bond cleavage. One way in which the reaction can be better understood is through the use of model compounds such as the tris-phosphineborane iron (B(C6H4PiPr2)3Fe, denoted here as "TPBFe") platform developed by the Peters group. This complex was designed to mimic the [Fe8S9C] cluster, the same cluster found in both nitrogenases and their related enzymes. In this study, we elucidate the mechanism of the TPBFe-catalyzed carbon-sulfur cleavage reaction through a kinetic Hammett study *via* NMR spectroscopy. We find the mechanism to most closely resemble…[*as the study has not yet been completed, this is as far as I can go in my abstract*]. Future areas for inquiry include developing a viable catalytic cycle for the reaction followed by condition screening for optimal turnover.

Probing SmI_2-mediated inner sphere electron transfer to Mo^{IV} imido complexes in an electrocatalytic nitrogen reduction system

Bao T. Nguyen
Mentors: Jonas C. Peters and Hoimin Jung

The reduction of nitrogen to ammonia with well-defined molecular transition metal catalysts is of great interest for opportunities to better understand mechanisms of N_2 reduction and for offering a possible alternative to the energy-intensive Haber-Bosch process. Recent work by our group has demonstrated the electrocatalytic reduction of N_2 with SmI_2 and a molybdenum catalyst with high Faradaic efficiency. A proposed key step of the mechanism is an inner sphere electron transfer (ISET) step between SmI_2 and a protonated Mo^{IV} imido species, which allows for a milder applied potential that mitigates competing acid reduction. Herein, we describe the synthesis of functional analogs of the protonated Mo^{IV} imido species as well as attempts to probe possible interactions between Sm and these complexes to better understand the nature of the proposed ISET step in our reported electrocatalytic system.