Magnetic Spectroscopy Across Scales: Investigating Biological Energy Systems and Synthetic Magnetic Architectures

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Magnetic spectroscopy techniques serve as a powerful tool to probe the electronic structure of complex systems across multiple length scales. In the first part of this talk, I will present the elucidation of structure-function correlation in a complex biomolecular energy system called respiratory oxidases using magnetic circular dichroism (MCD) spectroscopy in the ultraviolet-visible-near infrared (IR) energy regime. In the second part of the talk, I will present our efforts to synthesize a novel class of magnetic thin films using f-block element-based molecules and unravelling their properties using an existing end station at the Advanced Light Source (ALS) that is modified for simultaneous X-ray MCD (XMCD) and FT-IR spectral measurements.

Aerobic organisms use O_2 to drive the membrane-bound electron transport chain for ATP synthesis. The $4e^-$ reduction of $O_2 \rightarrow H_2O$ underlying this process is catalyzed by the superfamily of respiratory oxidases called heme–copper oxidases (HCO). The HCO active site consists of a heme ligated by a histidine (His) and a Cu ligated by three His, one of them covalently linked to a tyrosine (Tyr). Reaction with O_2 results in O–O bond cleavage forming a $Fe^{IV}{=}O$ intermediate P_M. Further e^-/H^+ transfers to the active site form subsequent intermediates ($P_M \rightarrow F \rightarrow O_H \rightarrow E_H \rightarrow R$), each coupled to pumping a H^+ across the membrane for ATP synthesis.

A major challenge in studying HCOs is the presence of additional redox centers in the enzyme, low spin heme and binuclear Cu_A (in some HCOs), with intense spectroscopic features precluding the study of the oxidation/protonation states of Cu and Tyr. We have leveraged MCD, a site-selective magnetic spectroscopy method, to investigate the Fe/Cu/Tyr site in HCOs. We studied P_M in UbO (an HCO that lacks the Cu_A center) from *E. coli* by low temperature MCD where we observe a unique feature from its $Fe^{IV}{=}O$ center. Variable-temperature variable-field (VTVH) MCD on this excited state feature enabled us to study the ground state of P_M determining that it is a three-spin exchange-coupled system: $Fe^{IV}{=}O$ (S=½), Cu^{II} (S=½), $Tyr^{\bullet}$ (S=½), which for the first time gave direct experimental evidence for the presence of Cu^{II} and $Tyr^{\bullet}$ in P_M. The experimental characterization of P_M provides novel insight into how the reduction of P_M is coupled to H^+ pumping thus elucidating structural contributions to the biological function of HCOs.[a]

Transitioning from biological systems to synthetic magnetic architectures, molecular materials offer significant potential for microelectronics and quantum information science where the goal is to harness individual molecules for functional applications. Achieving this goal requires precise control over molecular assemblies and a fundamental understanding of the interplay between spin and electronic structure.

A key challenge is the atomically precise arrangement of molecules into large-scale, ordered 2D patterns, a prerequisite for utilizing surface science tools to characterize a single species of surface-bound molecules with uniform configuration relative to the substrate and neighboring molecules. To address this, we are preparing thin films of f-block element-based molecules which can be considered as an intermediate between bulk and individual molecules. These thin films are characterized at an existing XMCD beamline end station at ALS (9 T maximum magnetic field) that is modified to enable simultaneous FT-IR measurements. In the future, we aim to deposit these magnetic molecules on a graphene-metal moiré, serving as a template for near-perfect self-organized assembly. This system will provide a conceptual testbed for exploring single-molecule data storage and computation, leveraging individual molecular spins for quantum applications.[b]

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