Molecular oxygen, O₂, is a powerful oxidant, which is kinetically sluggish under ambient conditions. The ability of living cells to overcome this barrier using transition metal enzymes lead to the explosion of aerobic life. We are interested in understanding mechanisms of O₂ activation in biology and their applications from fundamental and industrial chemistry to climate control and biomedical solutions. Working with metalloenzymes, their synthetic analogs, and subcellular organelles, we use a range of spectroscopic, electrochemical, and engineering approaches to resolve structures and mechanisms of highly reactive bio-inorganic complexes and associated electron transfer steps.

**Enzymes use transition metals** to overcome spin restrictions of triplet O₂, which oxidizes the metal/protein complex in a concerted, multi-e⁻ step. The resulting highly oxidized species, in turn, initiate chemical reactions with specific substrates. Protein moiety tunes reactivity of the metal through coordination environment and accessibility.

**Methane Monoxygenase**, an enzyme in methanotrophic bacteria, uses a pair of Fe⁵⁺ ions to accomplish an unrivaled conversion of methane to methanol. This reaction is of major interest for liquid fuels production from natural gas and as an initial step in the industrial synthesis. Using time-resolved laser spectroscopy, we observed this reaction in real time and resolved the mechanism that puzzled the field for the last two decades. Many more analogous enzymes with unresolved mechanisms are awaiting their turn.

**Enzymatic O₂ activation** always starts with reduction, followed by metal oxidation yielding formal Fe₅=O state (top path), which activates the substrate SH to transient S⁺ radical. By reversing the reaction under large positive electrode potential we can generate Fe⁵=O directly from water, circumventing the need for O₂ (bottom path) and opening intriguing possibilities for applied catalysis and new analytical methods.

**Mitochondria are power plants of the cell**: semi-autonomous organelles, which capture the energy of e⁻ current from food to O₂ to make ATP. A choreographed chain of enzymatic redox reactions takes place in the impermeable inner mitochondrial membrane, which isolates mitochondria from the cytosol. It makes detection of functional changes in whole mitochondria in such metabolic disorders as diabetes, Alzheimer’s disease, etc., difficult. We are developing a fundamentally new method to study intact mitochondria. It is based on dynamic redox equilibrium of natural metabolites, membrane transport, and electrochemistry on specifically modified electrodes. We establish chemically-mediated e⁻ current from fiber electrodes into mitochondrial enzymes and further to oxygen, mimicking natural metabolic pathways as an artificial “respiration in a tube”.

**Selected Publications**


