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Resolving Mechanistic Pathways in Bioinorganic Catalysis via Ultrafast X-ray Spectroscopy

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The most efficient and sustainable means of storing energy from raw sources involves harnessing chemical bonds. Achieving this requires the development of catalysts that are not only cost-effective but also exhibit high efficiency and selectivity. Many of these catalysts are inspired by bioinorganic systems where transition metal centers mediate complex redox transformations. Advanced X-ray spectroscopic techniques have become invaluable tools for probing relevant intermediates involved in such transformations. In particular, the use of ultrafast X-ray spectroscopy provides valuable insight not only into photophysical processes but also into ground state reactivity opening new avenues for exploration in bioinorganic chemistry.
Heterometallic systems, such as the FeMn cofactor in the ribonucleotide reductase-like enzyme R2lox, have garnered interest due to their unique chemical reactivity compared to their homo analogues. R2lox exhibits an unusually efficient light-induced decarboxylation—a rare photoactivity for natural enzymes outside of photosynthesis. This raises fundamental questions about the role of each metal site in the enzyme's reactivity, specifically the identity of the metal involved in the metal-ligand charge transfer (MLCT) that initiates the photochemical process. These questions have been addressed through element-specific femtosecond X-ray absorption spectroscopy (fs-XAS) targeting both Fe and Mn centers in R2lox enzyme and relevant synthetic model complexes. We will present our fs XAS results on Fe-Mn and Fe-Fe enzymes and discuss the photoinduced process in the light of their comparison.

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