

# Spin-Polarization and Spectroscopic Validation of the Through-Bond Electron Transfer Mechanism of Redox Metalloproteins

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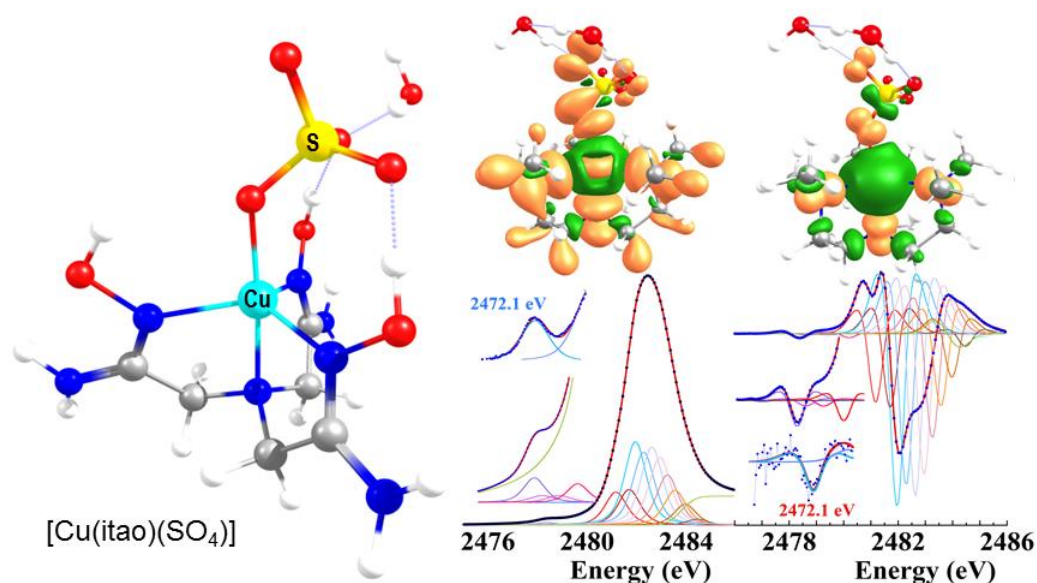
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Abstract: Sulfur K-edge XAS spectra of the monodentate sulfate complexes  $[M^{II}(\text{itao})(\text{SO}_4)(\text{H}_2\text{O})_{0,1}]$  and  $[\text{Cu}(\text{Me}_6\text{tren})(\text{SO}_4)]$  exhibit well-defined pre-edge transitions at 2479.4 eV, 2479.9 eV, 2478.4 eV, and 2477.7 eV, respectively (M = Co, Ni, Cu), despite having no direct metal-sulfur bond. The sulfur K-edge XAS of  $[\text{Cu}(\text{itao})(\text{SO}_4)]$  uniquely exhibits a weak transition at 2472.1 eV, an extraordinary 8.7 eV below the first inflection of the rising K-edge.



Ground state and time-dependent Density Functional Theory (TDDFT) calculations indicate electron transfer from coordinated sulfate to paramagnetic late transition metals, which produces spin polarization that differentially mixes the spin-up ( $\alpha$ ) and spin-down ( $\beta$ ) spin-orbitals, producing negative spin density at sulfate sulfur. Sulfur 3p character then mixes into ligand anti-bonding sigma

orbitals. This process produced the 2472.1 eV transition. This evidence of spin-radical mixing from Cu(II) through sulfur and across an H-bond bridge into distant sigma-bond molecular orbitals of the itao ligand, provides the first direct spectroscopic confirmation of the through-bond electron transfer mechanism of redox-active metalloproteins.