

S K-edge XAS: Applications to Bio-inorganic Chemistry of Iron-Sulfur Active Sites in Enzymes and Model Systems

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Iron-sulfur active sites are ubiquitous in nature. Their varied functions include electron transport (iron-sulfur clusters), oxygen/superoxide reduction (e.g. P450, superoxide reductase), small molecule activation (nitrogenase, CO dehydrogenase), Lewis acid catalysis (nitrile hydratase), among others. The electronic structures of these sites are in most cases dominated by the Fe-S bond/s present, thus knowledge of the electronic structure and, in particular, the covalency, is related to understanding their function. Ligand K-edge x-ray absorption spectroscopy is a relatively recently developed method by our lab that specifically probes the covalency of these ligand-metal bonds. This method has been used to investigate protein active sites and their model complexes. Studies on these iron-sulfur sites have shown very significant effects of the protein environment on bonding, which contributes to the very large differences in redox properties of these sites. Also, correlation of experimental observations to results from DFT calculations have provided further insights into the nature of the Redox Active Molecular Orbitals (RAMO) involved in electron transfer, the effects of electronic relaxation and its role in ET, the effects of H-bonding on ligand-metal bond covalencies and the oxidation state of the thiolate ligands in nitrile hydratase.

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1. A. Dey, T. Glaser, M. M.-J. Couture, L. D. Eltis, R. H. Holm, B. Hedman, K. O. Hodgson and E. I. Solomon. *J. Am. Chem. Soc.* 2004, 126, 8320-8328.
2. A. Dey, T. Glaser, J. J. G. Moura, R. H. Holm, B. Hedman, K. O. Hodgson and E. I. Solomon. *J. Am. Chem. Soc.* 2004, 126, 16868-16878
3. E. I. Solomon, B. Hedman, K. O. Hodgson, A. Dey and R. Szilagy. *Coord. Chem. Rev.* "Synchrotron Radiation in Inorganic and Bio-inorganic Chemistry" thematic issue, 2005, 249, 97-129.

