

Nitrogen K-edge Spectroscopy as a Probe of FeMoco.

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Nitrogen K-edge XAS is a potentially powerful probe of speciation and electronic structure of metal-nitrogen complexes through $1s \rightarrow 2p$ transitions. In addition it also offers the prospect of local structure determination through N K-edge EXAFS. N K-edges occur at ~ 400 eV, in the soft x-ray region. That they have been little used reflects the technical difficulties of working at these low x-ray energies, as well as the preponderance of N in many materials and solvents.

We are applying N-edge XAS and EXAFS to the nitrogenase cofactor FeMoco isolated in nitrogen-free solvents as well as a series of Fe-N inorganic complexes. Our motivation is to be able to (1) identify and characterize nitrogen bound intermediates of FeMoco and (2) unambiguously demonstrate whether a central atom proposed for the center of FeMoco is indeed a catalytic nitrogen. These measurements exploit the technical capabilities of ABEX, a facility for biological soft x-ray spectroscopy current being developed at the Advanced Light Source, Berkeley.

Our initial results are encouraging. Although quantitation of the x-ray fluorescence suggests our current samples still contain a small percentage of the N solvent N-methyl formamide, the FeMoco N K-edge is structured and shows sensitivity to cluster oxidation state and x-ray photoreduction (figure 1 – top). Similarly, Fe-N compounds, such as the imido complex $p\text{-H}_3\text{CPhNFe}(\text{PPh}_2\text{CH}_2)\text{BPh}$, produce detailed edge structure which is dependent on Fe oxidation state (figure 1 – bottom). These measurements are being supported by appropriate DFT analyses.

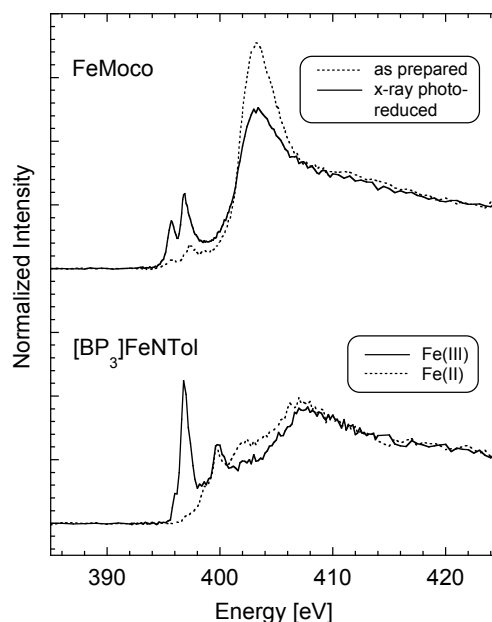


Figure 1: N K-edge spectra from (top) FeMoco and (bottom) Fe(III) and Fe(II) $p\text{-H}_3\text{CPhNFe}(\text{PPh}_2\text{CH}_2)\text{BPh}$ - ($[\text{BP}_3]\text{FeNTol}$).