Resonant Diffraction: Or how learned to stop worrying and love variable energy X-rays

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Complex systems that inspire questions about basic chemistry

N₂ + 8H⁺ + 6e⁻ $\rightarrow$ 2NH₃ + H₂

Questions
How do substrates engage?
Role of individual metals?
Spin state dependent?
How is redox stabilized or delocalized?

Derive functional models to probe these questions

Fe-Mo cofactor (FeMoco)

Synthesize clusters to test iso/mixed valency and redox trapping

**Goal:** systematically synthesize iso/mixed-valent clusters

**Test** what are observable changes
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Resonant Diffraction Anomalous Fine Structure (DAFS)

Elemental *identification* at given crystallographic sites
Only at *synchrotron* light sources

Variable $h\nu = f^0 + f' + if''$

Permits *site-specific* element ID and oxidation state determination

7.09 keV
7.11 keV
7.13 keV
7.15 keV
Synthesize clusters to test iso/mixed valency and redox trapping

**Goal**: systematically synthesize iso/mixed-valent clusters

**Test**: what are observable changes

*Fe* K-edge: photoionization of a *Fe*\((1s)\) electron
Resonant Diffraction: resolving our nearest neighbors

\[ \Delta = 17\% \]
Resonant Diffraction: resolving our nearest neighbors

\[ \Delta = 4\% \]
Analyzing the structure factors of a sample as a function of X-ray energy enables the identification of specific elements at given crystallographic sites.

Only possible at tunable synchrotron light sources – NSF ChemMatCARS!

\[ f^0 = f + \Delta f' + \Delta f'' \]

Contour Map at Mn k-edge (6539 keV)

Contour Map at Fe k-edge (7112 keV)

Powers, et al. JACS 2013, 135, 12289
Merits of DAFS versus Neutron Diffraction

Anomalous X-ray scattering (DAFS):  
- Short collection time
- Small crystal size

Neutron diffraction:  
- Longer collection times
- Large single crystal size required
- Protons on ligand inhibit data collection for molecular species

Neutron Scattering Cross Section

![Graph showing Neutron Scattering Cross Section with elements Z = 27, Z = 26, and Z = 25 highlighted.](image)
Identification of specific elements at given crystallographic sites

Proposed the canted beamline would extend the energy range down to 3 keV, providing access to the entire series of $3d \rightarrow 4d$ transition metals, including Sc, Ti, V, K, and Ca, which are not accessible on the existing beamline.

Only at synchrotron light sources

- Proposed Pilatus 2M detector for optimizing data collection time for low energy experiments
- PILATUS3 X 2M
  - Large active area detector; 254x289mm$^2$ (8 Mb/frame)
  - Readout time ~0.95 ms/frame
- Low energy resonant diffraction (3 keV - 16 keV)
- Absolute configuration determination (need long wavelength X-ray)

Bio-inorganic

Catalysis

Material Science

Resonant Diffraction/Diffraction Anomalous Fine Structure (DAFS)