INNER-SHELL SPECTROSCOPY (ISS)

Techniques and Capabilities

- **High flux beamline** dedicated to core level spectroscopy optimized for biological and chemical samples
- Ultra dilute samples (down to 1 μmol/L or )
- Complex heterogeneous systems (real sample under real condition)
- Three techniques offered in standard mode (can be performed simultaneously)
  - Conventional fluorescence XAFS (~30s per sample per condition)
  - X-ray Emission Spectroscopy (XES) to probe chemical environment of absorber atom
  - X-ray Energy Loss Spectroscopy to probe reactivity and structural environment of light elements
- **The approach:** Build to increase scientific output
  - High flux wigglar beamline (10^14 ph/sec) with wide energy range (4.9KeV-36KeV) will allow fast change of scan-range
  - Optimizing detection system, beamline optics, and data-acquisition system allows highly efficient detection and minimizes sample damage
- Complete environment control from sample preparation to measurement broadens the applicability to a wide range of technologically and scientifically relevant sample systems and reduces risk for failure.

Low-concentration XAS

The adsorption of Hg to B. subtilis and S. oneidensis MR-1 biomass was investigated to understand the interaction of Hg with bacterial cell surfaces. A wide range of Hg²⁺ concentration (120 nM to 350 μM) was measured at a fixed bacterial cell density and pH. The Hg L₂ edge XAS analysis showed that Hg complexes entirely with sulhydryl groups at the nanomolar and low micromolar concentrations, and with carboxyl sites at high micromolar concen-trations. The sulhydryl interaction would not be observed at Hg concentrations measurable at a dipole XAS beamline.

XES

Detection efficiency in combination with high flux beamline buys unprecedented sensitivity to chemical information.

**Example:** Methane monoxygenase (MMO) is an ideal systems for time-resolved, dispersive XES studies. MMO is a common methane hydroxylation enzyme with an enzymatic cycle composed of structurally distinct, short-lived states. The transformations can be monitored on ms time scale in a stop-flow arrangement, as a function of spin state at the iron (Kβ main line), and changes in ligand/substrate binding (valence core region).

XELS

XELS offers an enticing approach to collect spectroscopic information in the hard X-ray regime otherwise restricted to conventional soft X-ray spectroscopy. Since a hard X-ray probe is used, XELS is compatible with many in situ sample environments, opening soft X-ray spectroscopy to operating batteries, controlled atmosphere environments, and more. In the example shown, C K edge spectra from graphite are shown from a study of polyaromatic hydrocarbons for which the size of an individual molecule exceeds the Auger escape depth. This molecule can only be measured by XELS.

High-resolution XANES

- Use a crystal analyzer to measure XANES spectra below the core-hole lifetime.
- Enhanced resolution of XANES features and more precise determination of edge position and absorber valance.
- This is a standard tool at ISS – all XANES measurements will be measured at high resolution.

High heat-load optics

- Management of the high heat load of the wigglar source is essential to meet the 10^14 ph/sec. flux target. This represents the central technical challenge of the beamline.
- Preliminary finite element analysis show that a directly cooled first mirror can support >6 kW total power while suffering tolerable slope errors.
- Preliminary FEA shows that a directly-cooled, “hockey puck” style mono crystal can support >2 kW with slope errors small compared to the Si(111) width.