X-ray Spectroscopy
A Critical Look at the Past
Accomplishments and Future Prospects

James Penner-Hahn      jeph@umich.edu
Room 243
Monday – Wednesday 3-5 PM and by appointment

Lecture plan
1. Basic Physical Principles
2. Practical aspects of x-ray absorption
3. Data analysis
4. Near edge structure
5. Spatially and temporally resolved methods
6. Exotic x-ray spectroscopies

Grading
• Participation – 20%
• Draft research proposal – 30%
• Final research proposal – 50%
  • Original
  • Feasible
  • Well presented

Proposal forms and guidelines at
http://www-ssrl.slac.stanford.edu/users/user_admin/
xray_vuv_proposal_guide.html

Proposal body – not more than 5 pages

A. DESCRIPTION OF EXPERIMENT
   I. Background
   II. Previous results
   III. Proposed Experiments
IV. Literature cited

B. PREVIOUS EXPERIENCE WITH THE
TECHNIQUES AND FACILITY

C. DETAILED SAFETY CONCERNS

D. EQUIPMENT DEVELOPMENT SCHEDULE

E. RESOURCES FOR PROGRAM PROJECT

Techniques for studying metal sites in proteins

• UV-visible spectroscopy
• EPR spectroscopy  Require open d shell
• Magnetic susceptibility
• MCD
• NMR spectroscopy  Requires I=1/2 nucleus
• X-ray crystallography  Requires crystals

• X-ray spectroscopy
Absorption of x-rays by Pb

Electron binding energies of the elements

X-ray absorption spectroscopy
Information Content of EXAFS

- Bond length ± 0.02 Å (accuracy)
- Bond length ±0.005 Å (precision)
- Coordination number (lower limit) ± 1
- Ligation type (Z) ± 10

\[ R_{\text{max}} < \sim 4 \text{ Å} \]

Dependence of XANES on Oxidation State

Mn(V)=O has intense pre-edge transition, not seen in Mn(III) analog

Depolarization of X-ray Absorption Spectroscopic Evidence for a Unique Nickel Site in Chromatium thiomarinol Carbon Monoxide Dehydrogenase

X-ray Fluorescence

X-ray fluorescence lines

X-ray fluorescence spectra give element sensitivity

Advantages of XAFS
- Direct structural determination for:
  - Any form of matter
  - Any isotope
  - Any spin state
- Direct determination of oxidation state

Disadvantages of XAFS
- Bulk spectroscopy (average structure)
- Little angular information
- Gives only local structural information
- Limited sensitivity
- Requires synchrotron x-ray source
Bremsstrahlung radiation

Synchrotrons produce intense, tunable x-ray beams
MetE (cobalamin independent MetSyn) contains Zn

Zn is tightly bound
Zn is required for activity
Is Zn involved in reaction, or does it play a structural role?

The Zn site in MetE has ZnS$_2$(O/N)$_2$ ligation.

Addition of homocysteine changes ligation to ZnS$_3$(O/N).

Changes in ligation are due to homocysteine binding to Zn

Combination of Zn + Se EXAFS consistent with only a small distortion from tetrahedral geometry in substrate-bound enzyme
EXAFS shows that CN does not remain bound

Structures of cyanocuprates in THF

Solution speciation of CuI+PhLi

Crystalline phenyl:copper species

Titration of CuI+ n PhLi shows isosbestic behavior up to 1.2 equivalents

Titration of CuI+ n PhLi shows isosbestic behavior from 1.2-2.0 equivalents
EXAFS data support XANES speciation