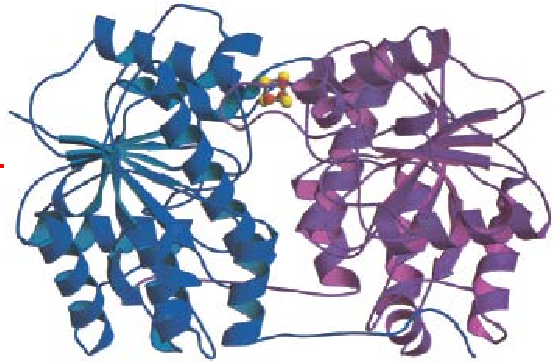
Emergency Information

- Be aware of exits in your building
  - Speaker will indicate locations for this meeting
- Fire or other emergency evacuation
  - Follow building residents out of building to the assembly area
- Earthquake
  - Remain in building: Duck, cover, and hold position until shaking stops
  - Evacuate building to assembly area outside (follow others)
  - Stay away from windows, downed power lines
- In the event of an emergency
  - Dial 911 or 9-911 from a SLAC phone; or
  - Dial 911 from your cellular phone
  - Provide SLAC address (2575 Sand Hill Road, Menlo Park, CA; cross street Saga Lane) and your building/room number

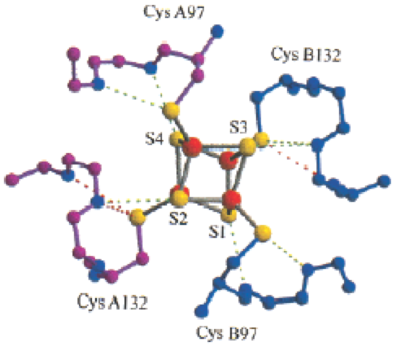
SSRL Structural Molecular Biology Program:

Low-Z X-ray Absorption Spectroscopy Summer School 2010

July 20-23, 2010



Development of S K-edge (and other low-energy edge) XAS at SSRL



Britt Hedman

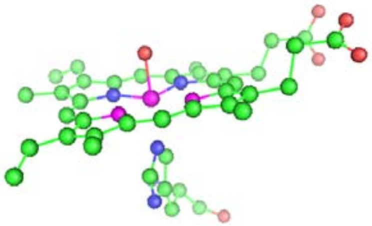
Professor and Deputy Director

Stanford Synchrotron Radiation Lightsource

SLAC, Stanford University

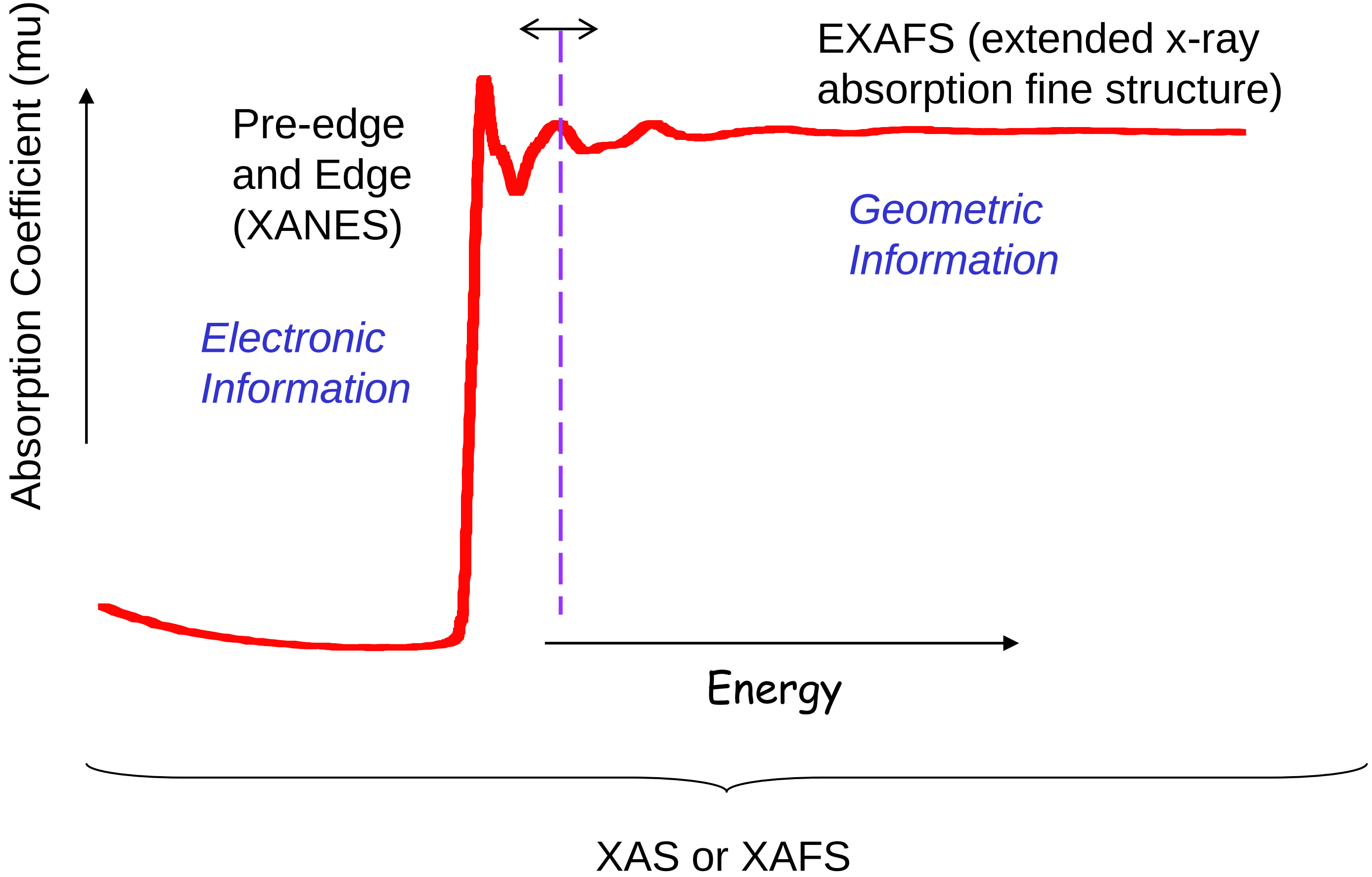
Outline

- Brief introduction to x-ray absorption spectroscopy in the “soft” 2-4 keV energy region
- Evolution of feasibility and approaches
- Experiment types
- Experiment considerations
- Science examples
- Data interpretation
- Summary



X-ray Absorption Spectroscopy (XAS) --- Regions

XAS is an element specific technique



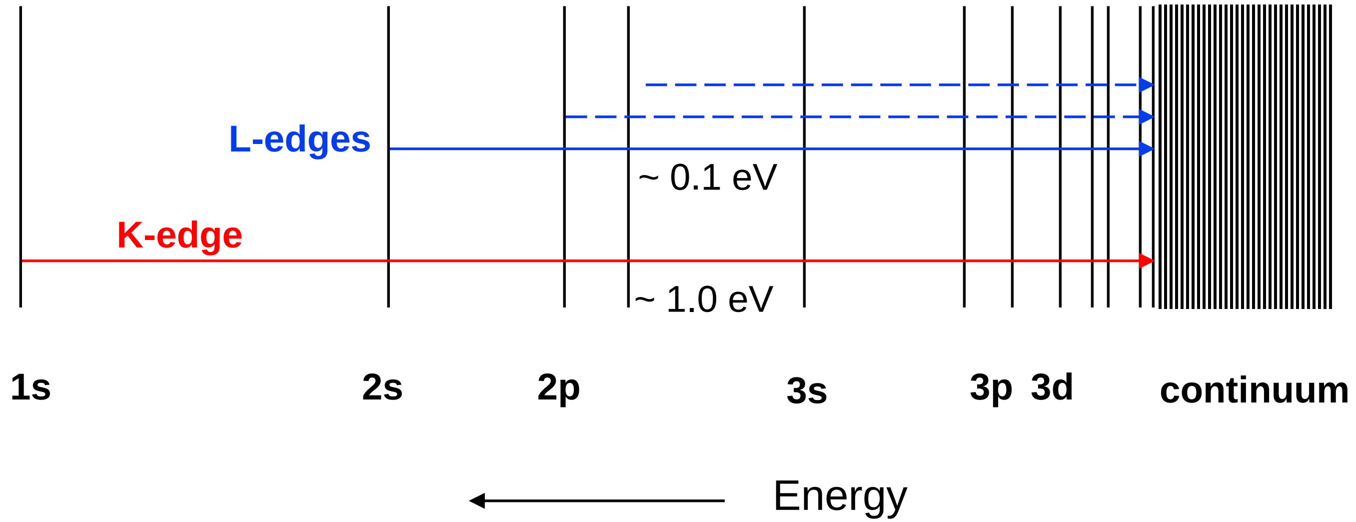
X-ray Absorption Edge Spectroscopy --- Basics

- An edge results when a core electron absorbs energy equal to or greater than its binding energy
- Therefore XAS is an element specific technique
- Edges are labeled according to the shell the core electron originates from

Cu K-edge ~9000 eV
Cu L-edges ~930 eV
Cu M-edges ~70-120 eV

Fe K-edge ~7000 eV
Fe L-edges ~720 eV
Fe M-edges ~50-100 eV

S K-edge ~2472 eV
S L-edges ~200 eV

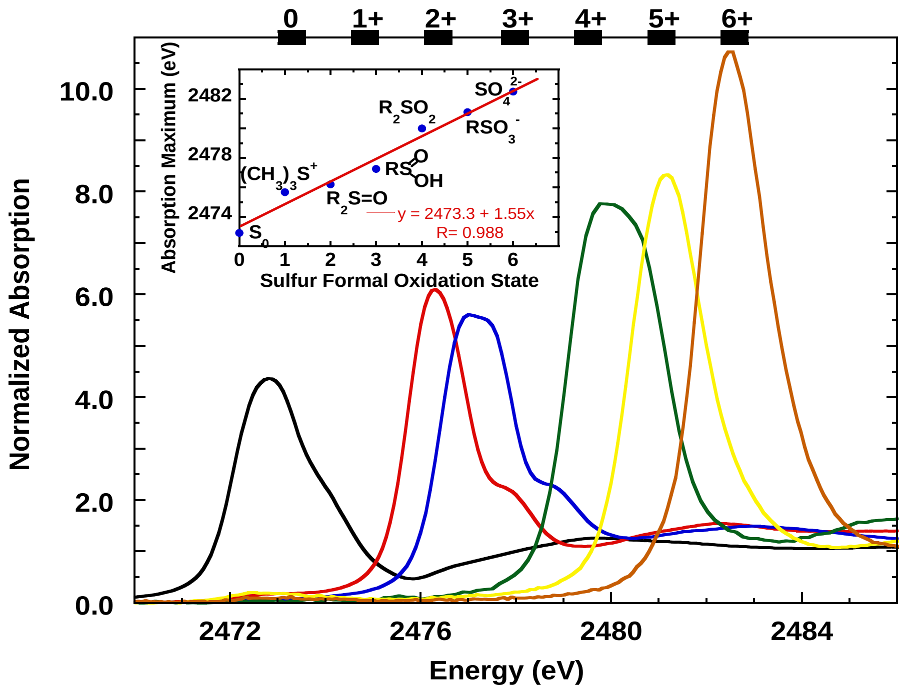


XAS Edges: What Information Can You Get?

Metal/element K-edge:	1s ground state oxidation state spin state (in some cases) covalency (indirect) site symmetry coordination number
Metal L-edge:	2p ground state metal d-character in unoccupied 3d-orbitals differential covalency (in some cases) measure of backbonding (in certain cases)
Ligand K-edge:	1s ground state probes metal or site as "reporter" absorber direct probe of ligand 3p character in unoccupied 3d set - covalency
Polarized XAS:	unique and/or enhanced electronic and structural information

Soft X-ray Absorption Spectroscopy (XAS)

- 1st row transition metal K-edges in the ~5-11 keV range ⇨ metalloproteins most commonly studied by ***metal*** XAS; also some higher-row metal K-edges
- XAS in the **2-3 keV** region allows study of ***ligand*** elements, such as S and Cl
- High monochromator energy resolution & low core hole life time broadening effects ⇨ high delineation of oxidation state and other electronic effects



- Edge shifts >13 eV observed for inorganic S
- Energy resolution is excellent (~0.5 eV) and reproducibility in the <0.1 eV range
- Cl and/or S as ***ligand*** can be used as reporter element for metal sites

Excellent Results from Very Early in-Vacuum Experiments…

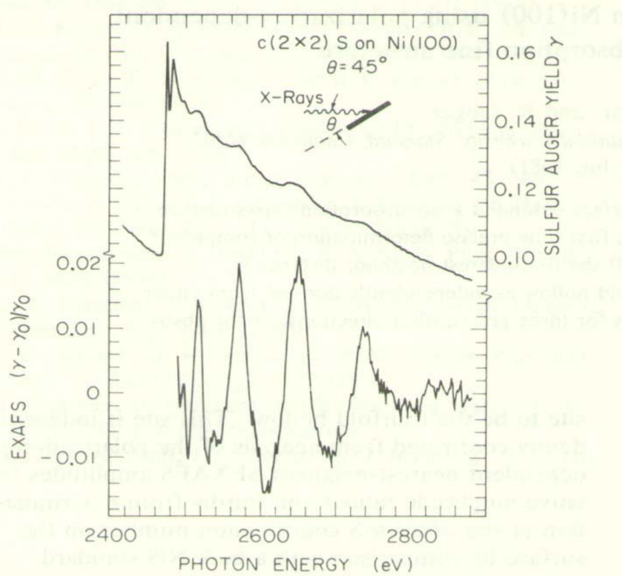


FIG. 1. Sulfur *K*-edge SEXAFS spectrum for $c(2\times2)$ (half monolayer) S on Ni(100) recorded at 45° x-ray incidence. The SEXAFS oscillations after background subtraction are shown in the lower half.

- Sulfur K-edge SEXAFS of half monolayer on Ni
- Brennan, Stöhr, Jaeger, *Phys Rev B* **24**, 4871 (1981)

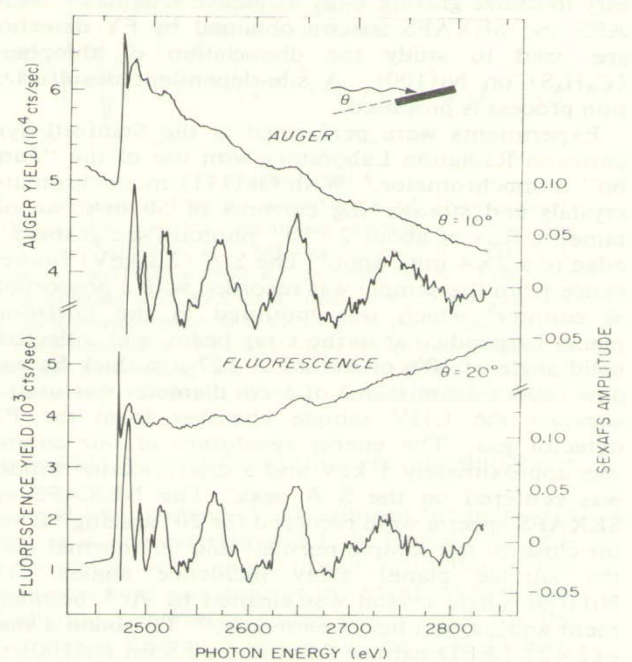


FIG. 1. Auger-electron-yield (Ref. 10) and x-ray-fluorescence-yield SEXAFS spectra above the S *K* edge for $c(2\times2)$S on Ni(100) corresponding to half a S monolayer. Both spectra were recorded at grazing x-ray incidence. Underneath each spectrum the SEXAFS oscillations after background subtraction are shown enlarged.

- Comparison of same data with measurements using fluorescence detection
- Sette, Pearton, Poate, Rowe, Stöhr, *Phys Rev Lett* **56**, 2637 (1986)

Sulfur K-edges - In Vacuum or in “Air” – or He?

Approximate transmission in air and helium

	Sulfur		Vanadium	Iron
	2470 eV		5460 eV	7100 eV
1 cm	70%	99.9%	97%	98%
2 cm	50%	99.9%	75%	87%
10 cm	<1%	99.4%	55%	78%

- *6 micron polypropylene window ~80% transmission at S K-edge*
- *5 mils (125 micron) Be ~45% transmission at sulfur*

Soft XAS – It Started (as usual) with Farrel Lytle…

542 Nuclear Instruments and Methods in Physics Research 226 (1984) 542-548 North-Holland, Amsterdam

MEASUREMENT OF SOFT X-RAY ABSORPTION SPECTRA WITH A FLUORESCENT ION CHAMBER DETECTOR

F.W. LYTLE and R.B. GREEGOR
The Boeing Company, Seattle, WA 98124, USA
D.R. SANDSTROM and E.C. MARQUES
Washington State University, Pullman, WA 99164, USA
Joe WONG and C.L. SPIRO
General Electric Corporate Research and Development, Schenectady, NY 12301, USA
G.P. HUFFMAN and F.E. HUGGINS
us Steel Corporation, Monroeville, PA 15146, USA

Received 19 December 1983 and in revised form 29 February 1984

No vacuum – He gas, Si(111), "Stern-Heald-Lytle" detector, showed a path for soft-energy experiments that could enable bio expts!

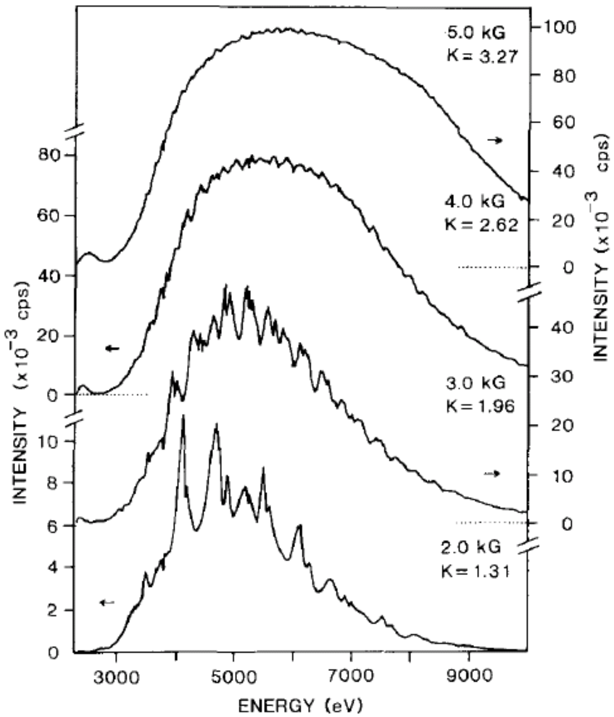
Soft XAS – Making a Wiggler Be an Undulator!

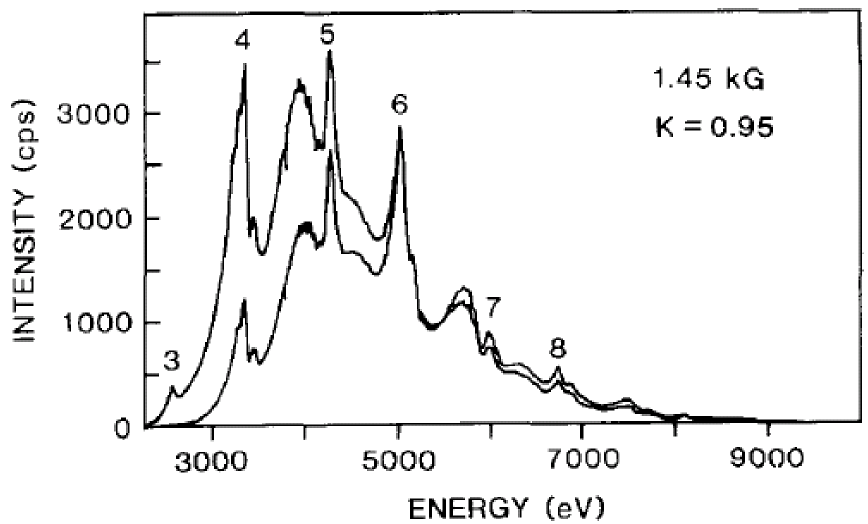
Nuclear Instruments and Methods in Physics Research A246 (1986) 797-800

SULFUR K-EDGE X-RAY ABSORPTION STUDIES USING THE 54-POLE WIGGLER AT SSRL IN UNDULATOR MODE

Britt HEDMAN [1,2], Patrick FRANK [2], James E. PENNER-HAHN [1,2], A. Lawrence ROE [2], Keith O. HODGSON [1,2], Robert M.K. CARLSON [3], George BROWN [1], John CERINO [1], Robert HETTEL [1], Teresa TROXEL [1], Herman WINICK [1] and John YANG [1]

[1] *Stanford Synchrotron Radiation Laboratory, SLAC, Bin 69, PO Box 4349, Stanford, CA 94305, USA*
[2] *Department of Chemistry, Stanford University, Stanford, CA 94305, USA*
[3] *Chevron Oil Field Research Company, PO Box 446, La Habra, CA 90631, USA*

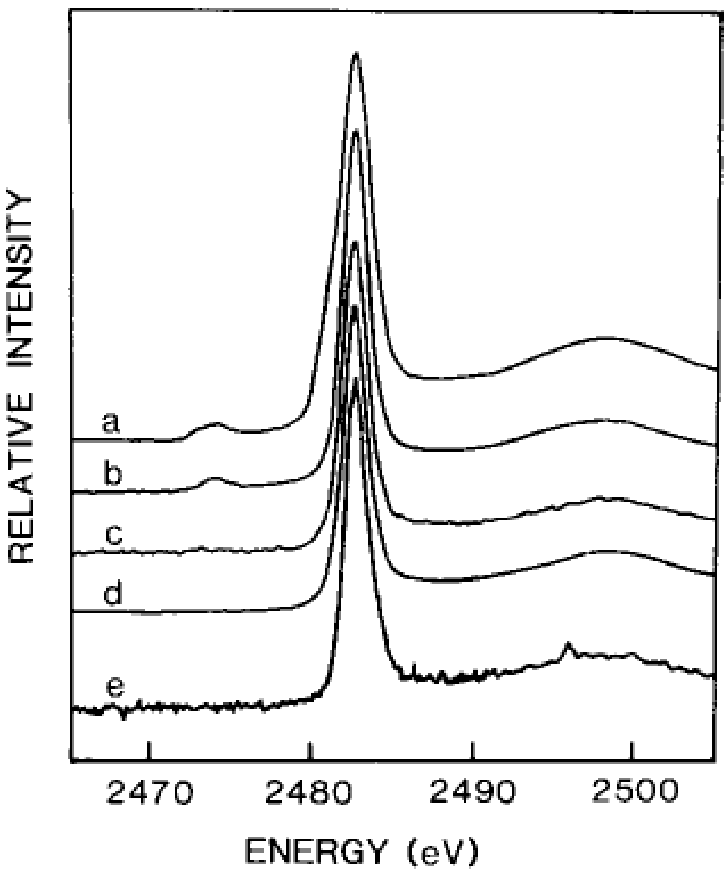




Low field; 3rd harmonic; no C filters –> beautiful source for non-vacuum soft energy XAS from 1986 onwards...

Soft XAS – Early Biology (Inorganic Chemistry)

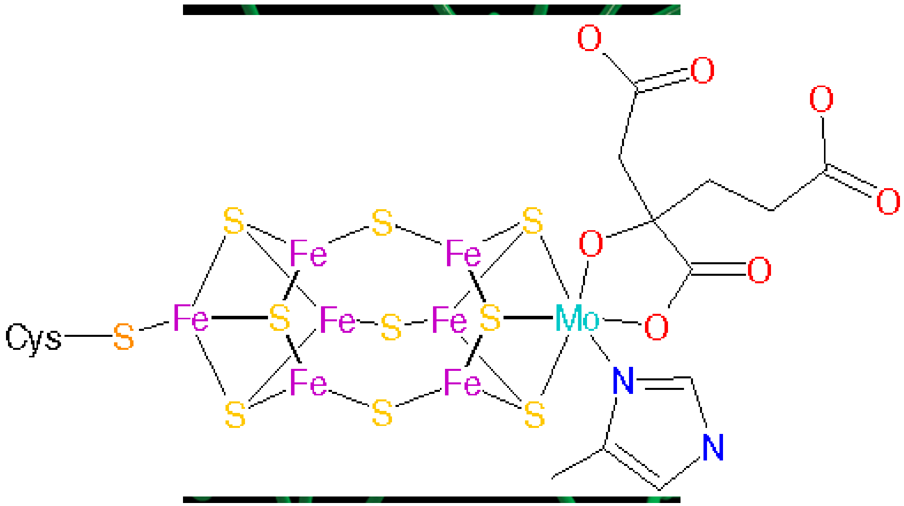
- Gave a wealth of results in various areas – biology, chemistry and materials science



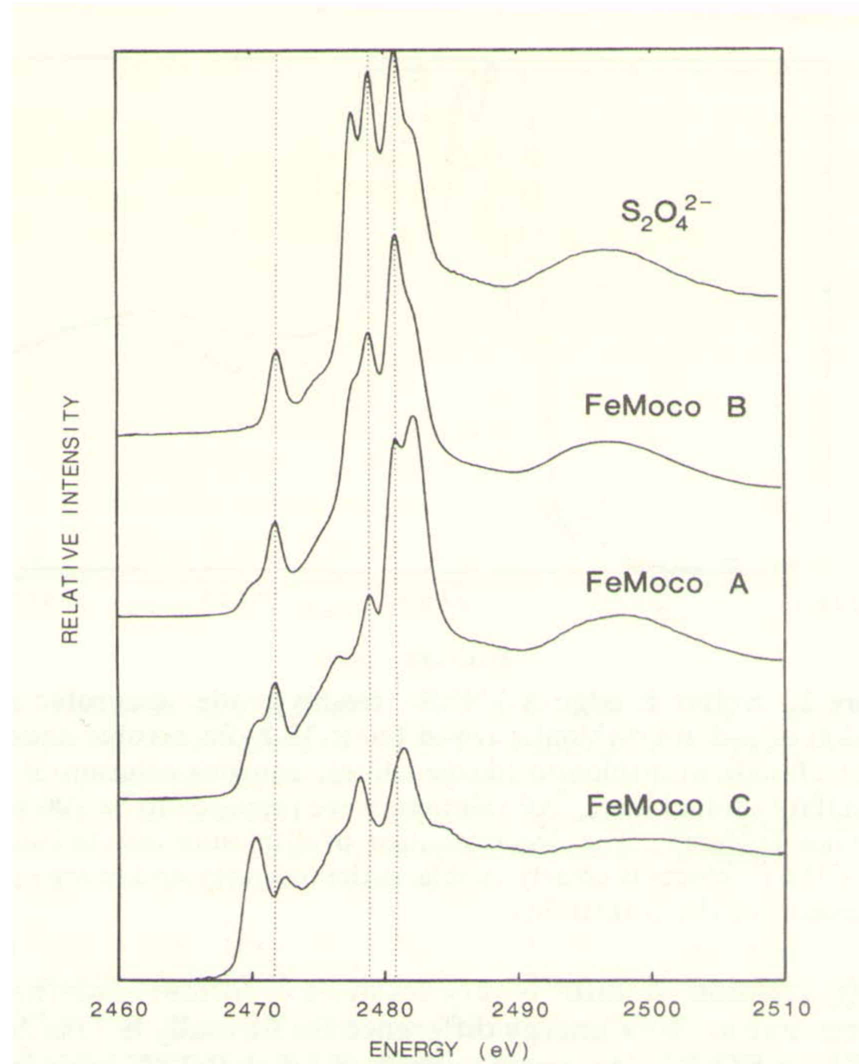
S K data of blood cells of tunicates (V accumulating sea squirts at ultra-low pH) (*P Frank, RMK Carlson, KO Hodgson*)

Soft XAS – Early Biology – Metalloenzymes – Nitrogenase

$N_2 + 8H^+ + 8e^- + 16MgATP \rightarrow 2NH_3 + H_2 + 16MgADP + 16P_i$

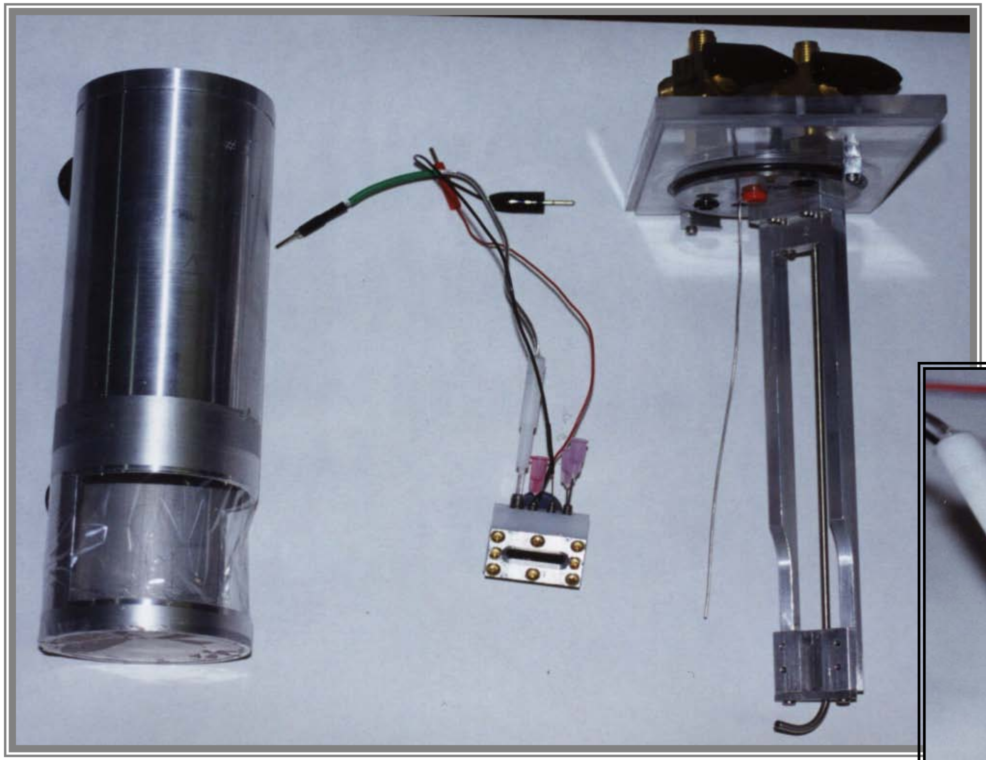


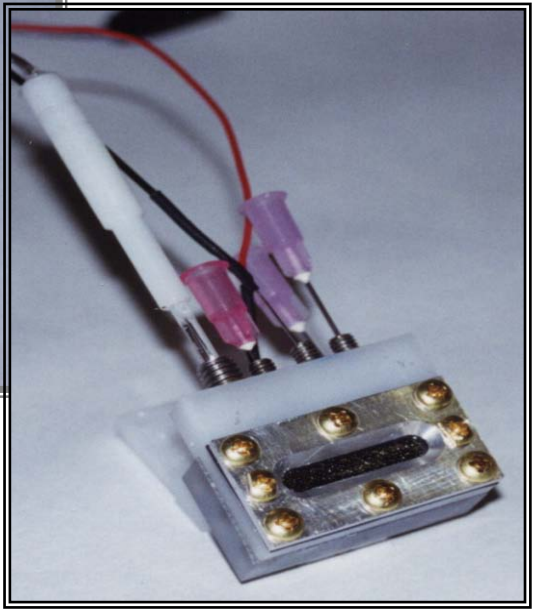
- Iron-molybdenum-sulfur cofactor from the MoFe protein of *A. vinelandii* nitrogenase at the S-K edge
- In addition to providing electronic structure determination, the experiments revealed the contamination and aided in removal of dithionite and by-products from the biochemical preparation



Hedman, Frank et al., *JACS* **110**, 3798 (1988)

Soft XAS – Nitrogenase and in-situ Electrochemistry

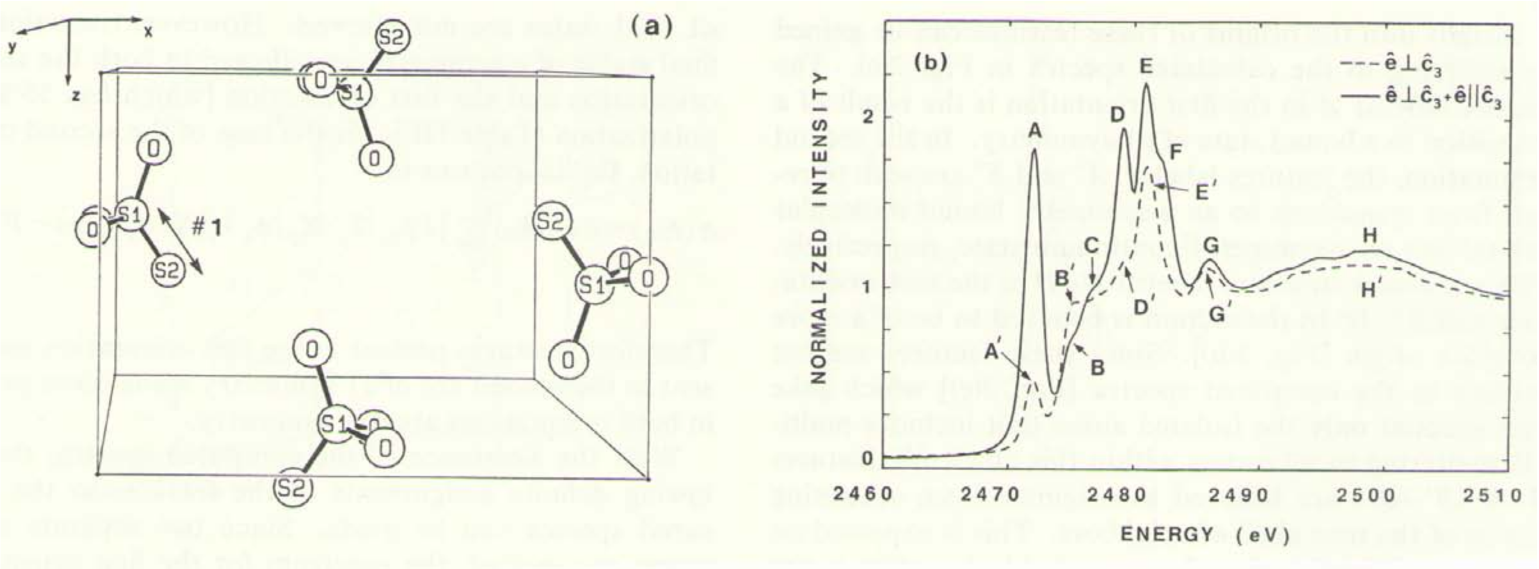




... under *in-situ* electrochemical control

(P Frank, SF Gheller, WE Newton, F Schulz, B Hedman, KO Hodgson)

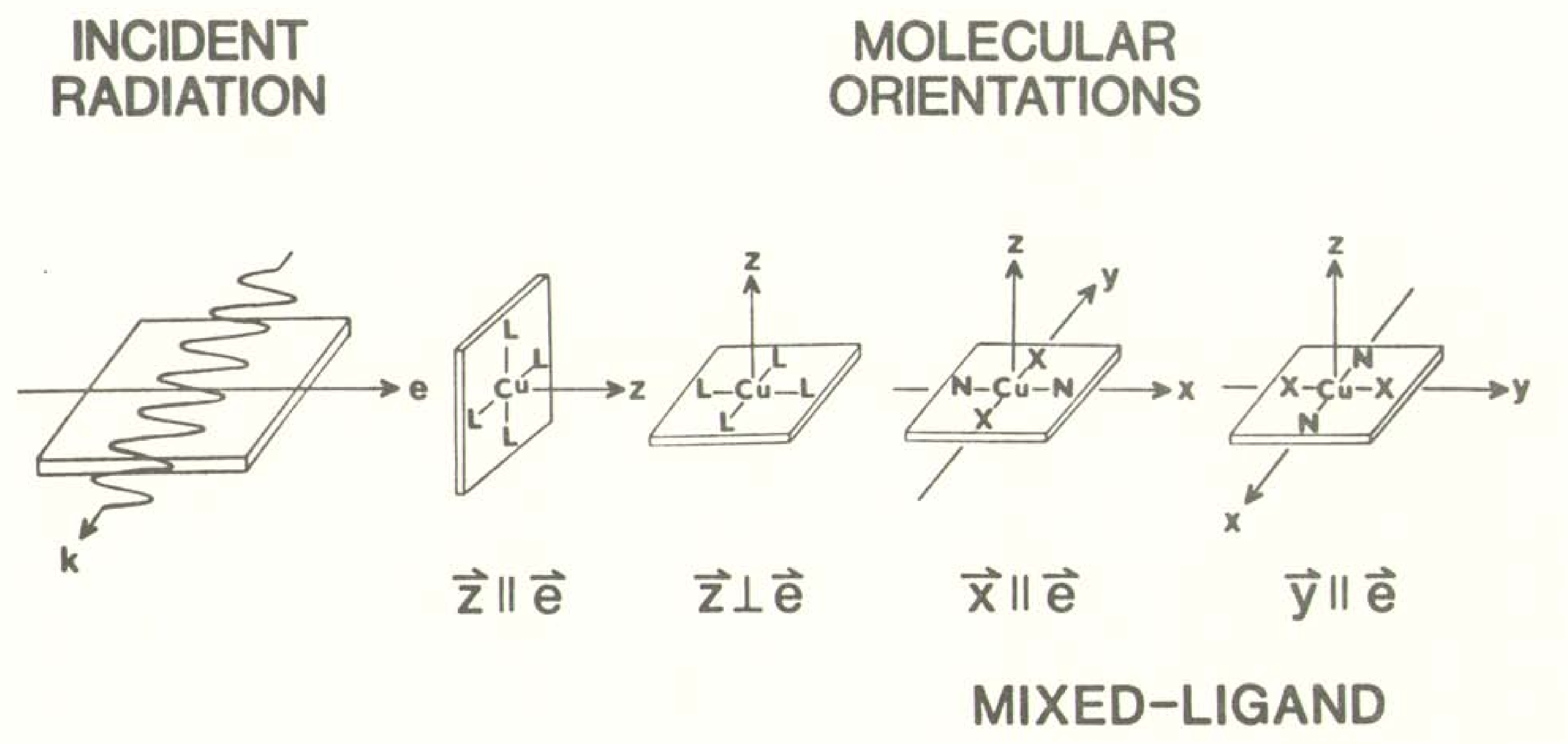
Soft XAS – Early Fundamentals



Polarized single crystal studies to understand electronic structure

(*TA Tyson, AL Roe, P Frank, B Hedman, KO Hodgson*)

Polarized Single Crystal XAS – Orientation Effects



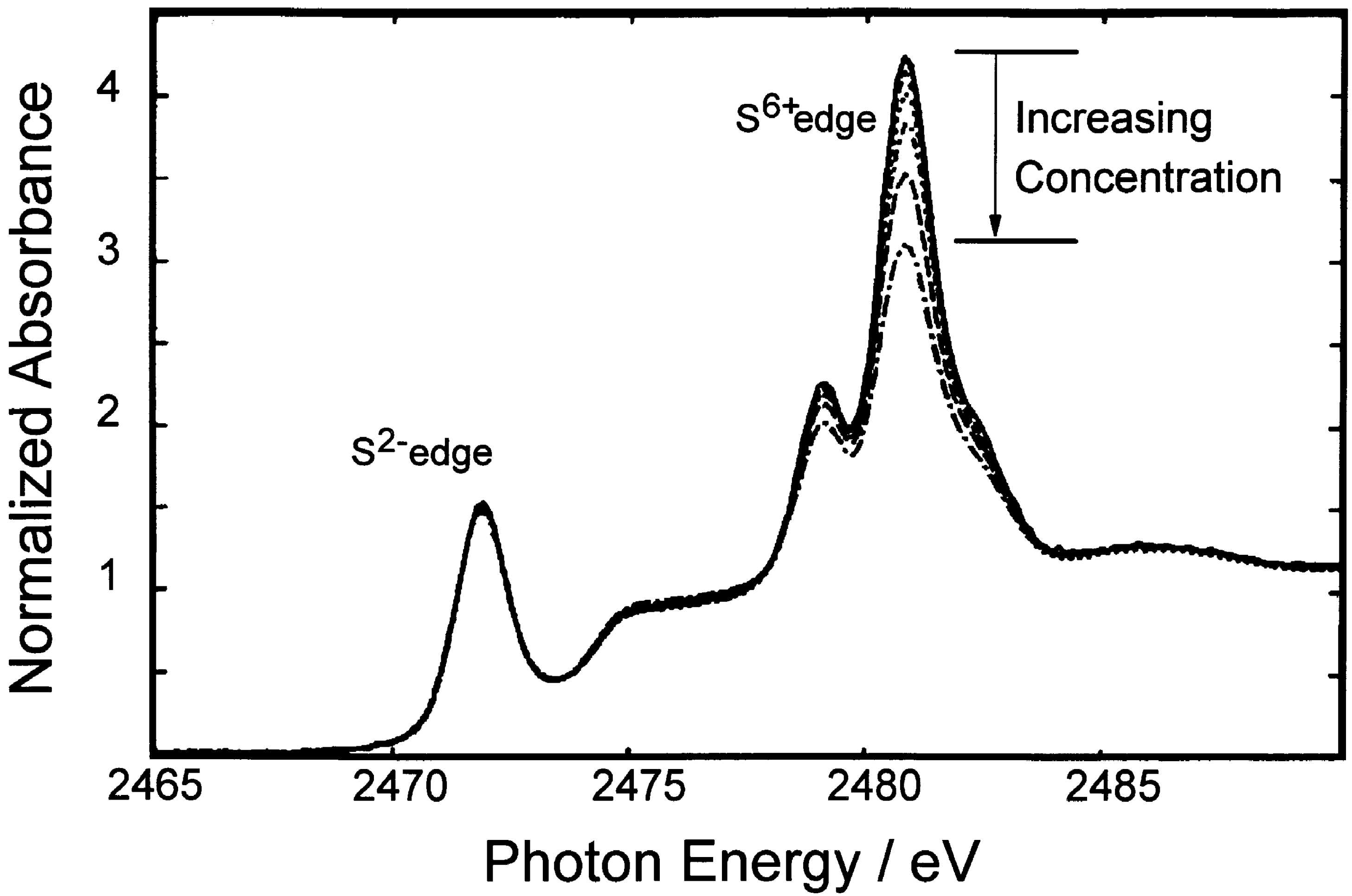
Polarized measurements can provide unique and/or enhanced electronic and structural information compared to isotropic measurements

Types of Experiments

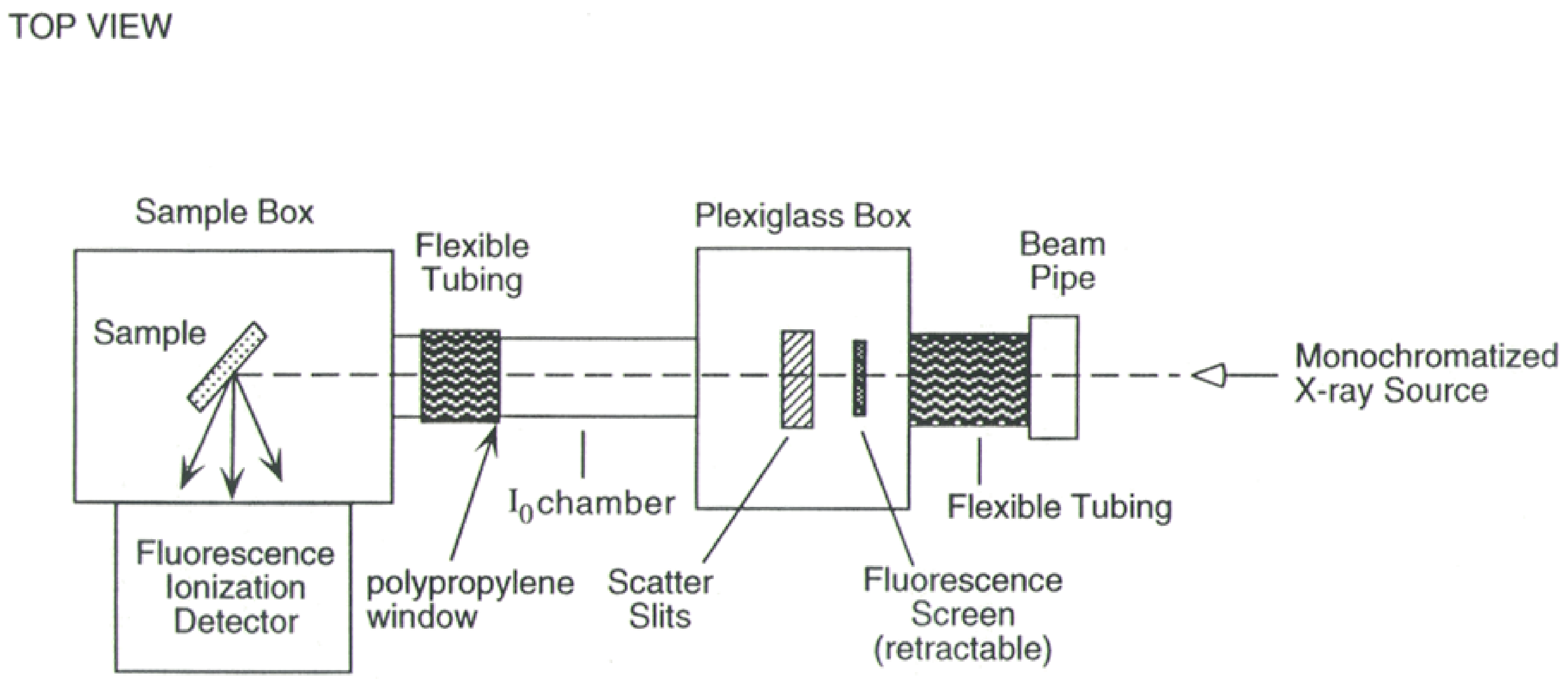
SSRL

- Gas cell experiments using He as carrier gas
- Solids – typically fine dust on tape with S-free adhesive and polymer
- Solutions – teflon cells with thin polymer window – fits with detector chamber
- Anaerobic gas-cooled cell for proteins – double jacketed – somewhat complicated to use (typically +4 °C temperature; can reach ca. –50 °C)
- Electrochemical cell for solutions – voltammetry and coulometry to poise samples and to reach states not possible to produce chemically (FeMoco, Fd, models) – *in situ* measurements
- Optical spectroscopy to monitor sample status *in-situ*
- Alignment devices for pre-oriented single crystals for polarized measurements
- Grazing incidence XAS measurements for signal increase and polarized studies of surfaces

Self-absorption Effects – Concentration Series of $S_2O_3^{2-}$ (aq)

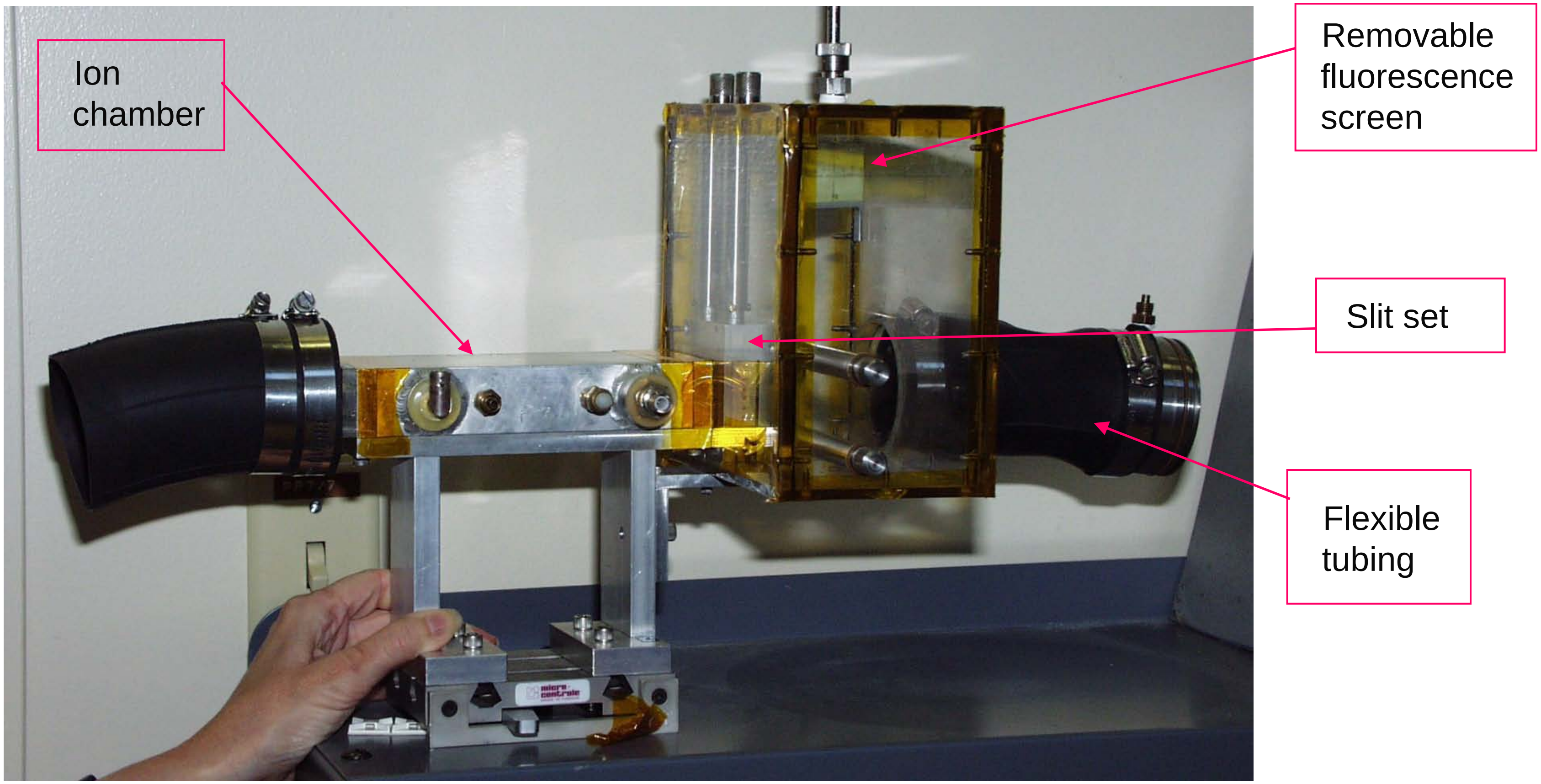


Soft X-ray Experimental Setup



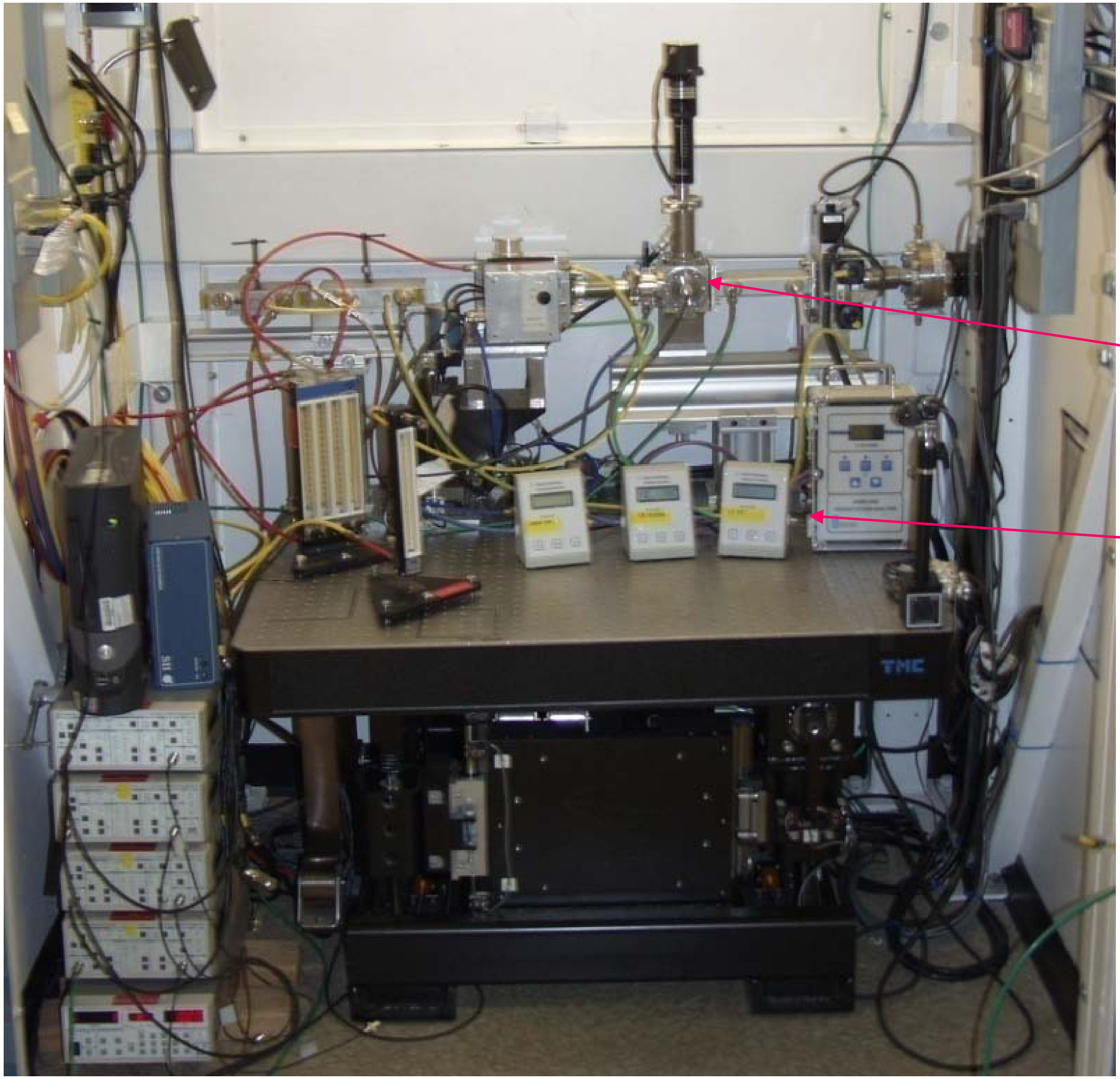
Schematic view of the experimental setup for S K-edge work on SSRL BL6-2

S K-edge Experimental Setup – in the Hutch – Many Expts



Separate He gas flows in front and rear sections; only one window in the path…

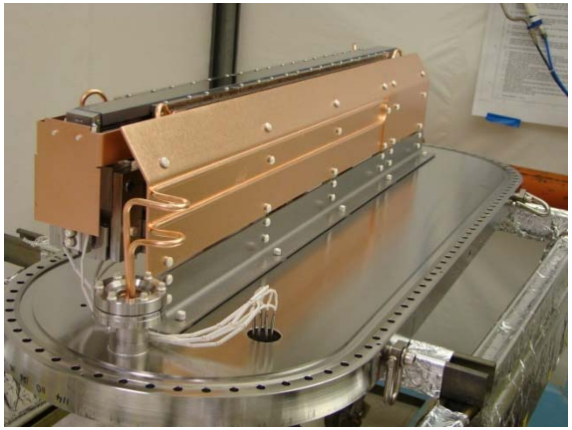
S K-edge Experimental Setup – in the Hutch – Today – BL4-3



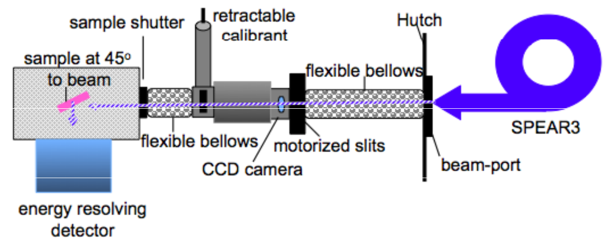
"Internal" calibration

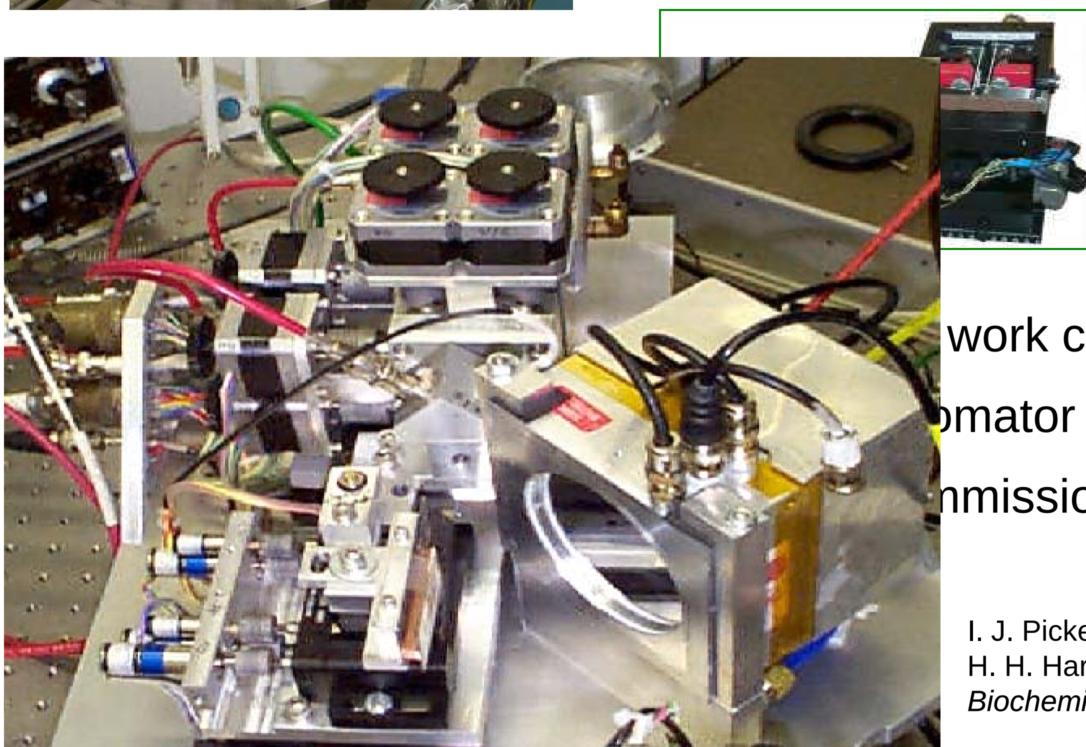
Oxygen analyzers and flow meters

BL14-3 for Focused Soft X-ray XAS incl. Imaging



- BL14-3 new focused station; two sets of Si(111) crystals; in-vacuum up to Be window in hutch
- 2-5 keV (P K edge)
- K-B based μ-XAS imaging facility + “standard” XAS





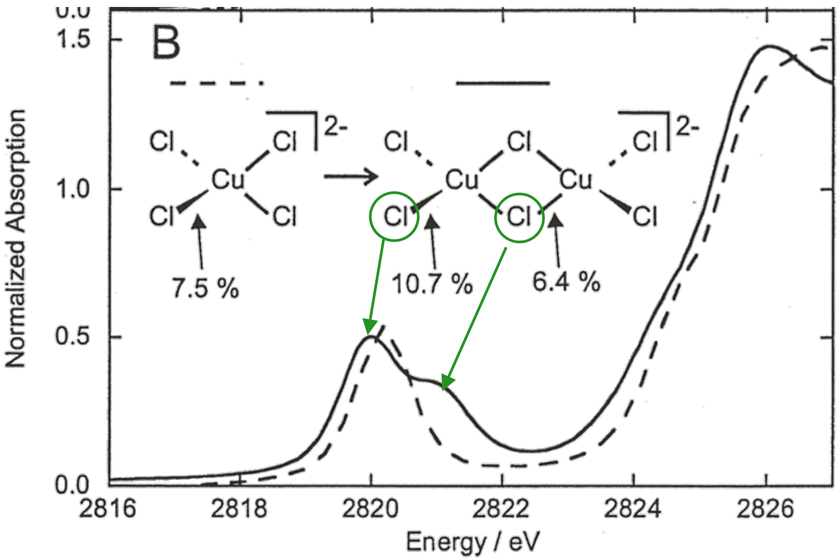
work complete (front-end, mirror)

omator still in the works

nmissioned in the Fall 2010

I. J. Pickering, E. Y. Sneeden, R. C. Prince, E. Block, H. H. Harris, G. Hirsch and G. N. George, *Biochemistry* **48**, 6846 (2009)

Ligand K Pre-edge Energy Position - Terminal vs Bridging

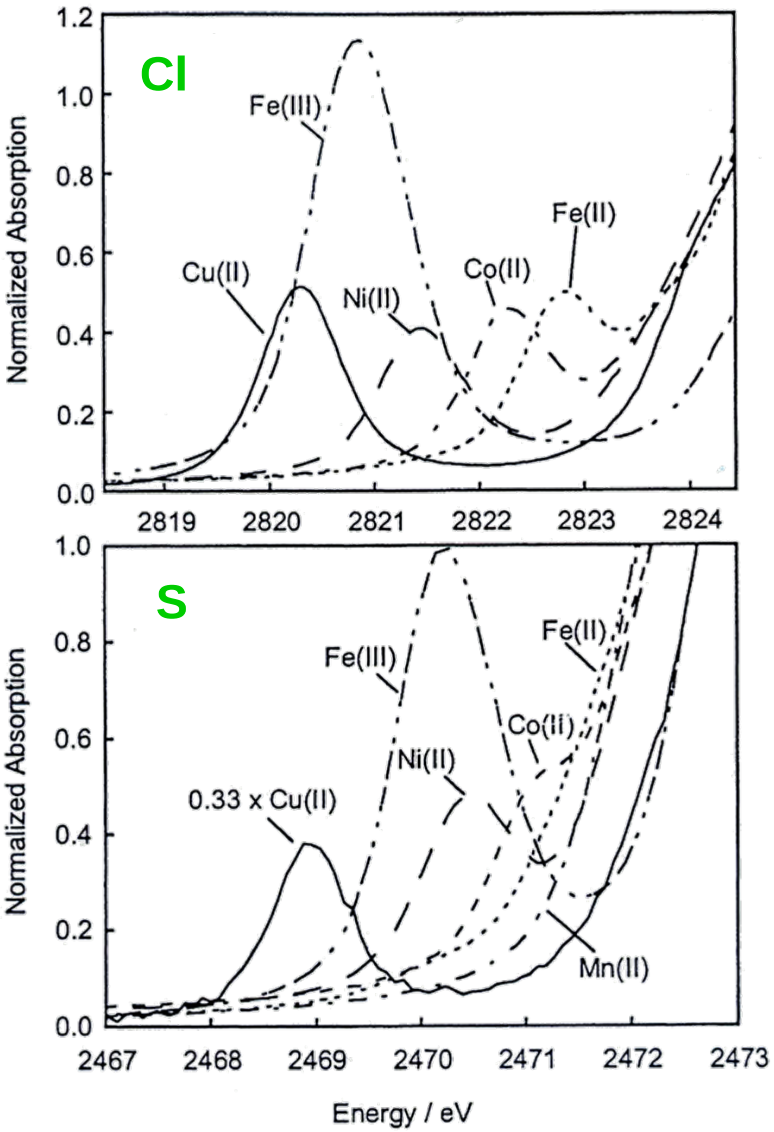


- Bridging complex displays two resolved features, representing the two different types of ligands
- *Delocalization* of ligand *electron density* to *two* metals due to bonding (Z_{eff}) ⇨ shift to deeper binding energy ⇨ "bridging" pre-edge transition moves to higher energy
- Terminal ligand has reduced total donation ⇨ effective negative charge increases ⇨ shifts to lower energy

- Method allows for separation of different types of the same ligand element

S.E. Shadle, B. Hedman, K.O. Hodgson, E.I. Solomon, *Inorg. Chem*. **33**, 4235 (1994)

Ligand K Pre-edge Energy Position – Vary the Metal



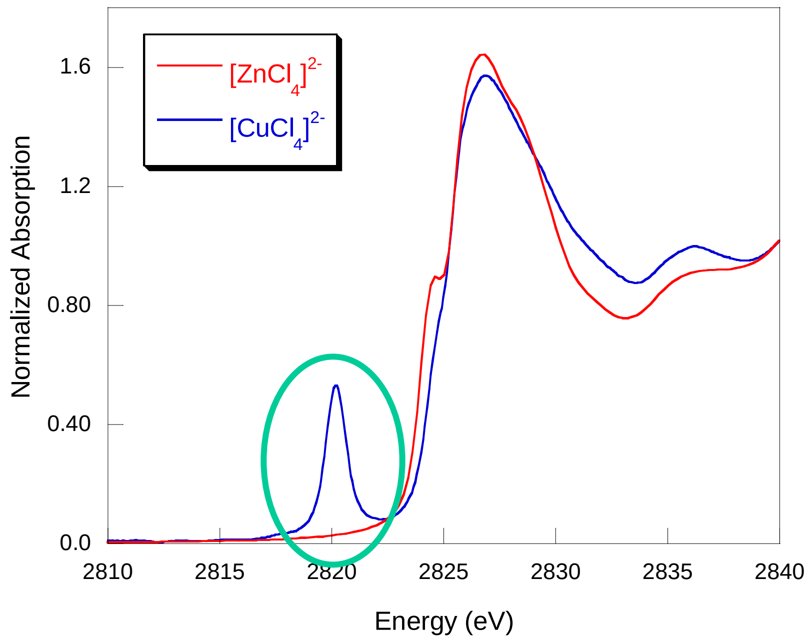
- Similarity in rising 1s->4p edge energy ⇨ Cl 1s energy and thus effective charge *not* cause for large pre-edge energy shifts
- Excited-state ligand field splittings ~2 eV, varying few tenths of eV over the series – also *not* cause for large change
- Main effect derives from change in effective charge of ***metal*** ion, which increases:

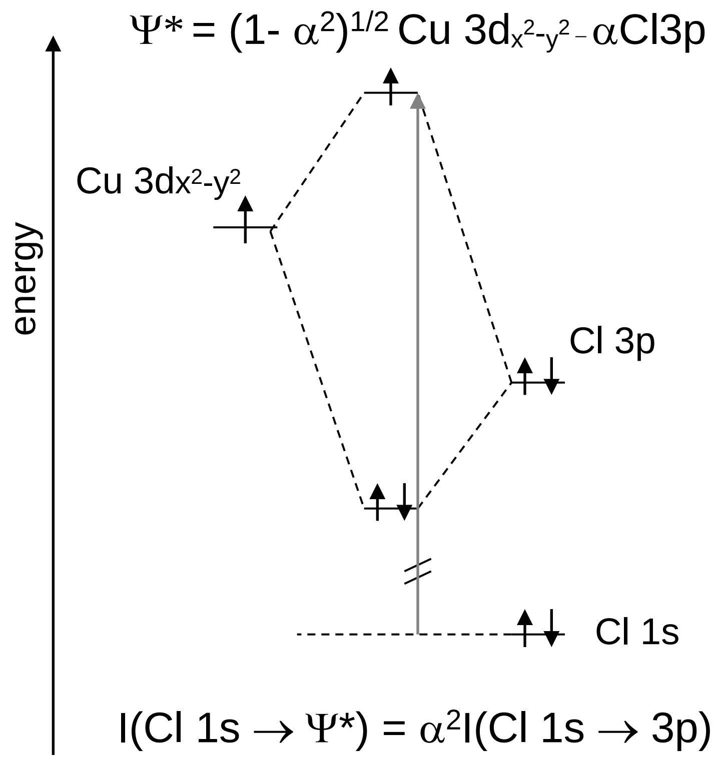
  $Fe^{II} < Co^{II} < Ni^{II} < Cu^{II}$

  impacting d manifold level and thus energy needed for transition to occur
- Fe^{II} to Fe^{III} change mainly reflects impact by oxidation state change

S.E. Shadle, B. Hedman, K.O. Hodgson, E.I. Solomon, *JACS* **117**, 2259 (1995);
K. Rose Williams, B. Hedman, K.O. Hodgson, E.I. Solomon, *Inorg. Chim. Acta* **263**, 315 (1997)

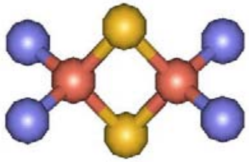
Ligand K-edges as a Probe of Metal-Ligand Covalency



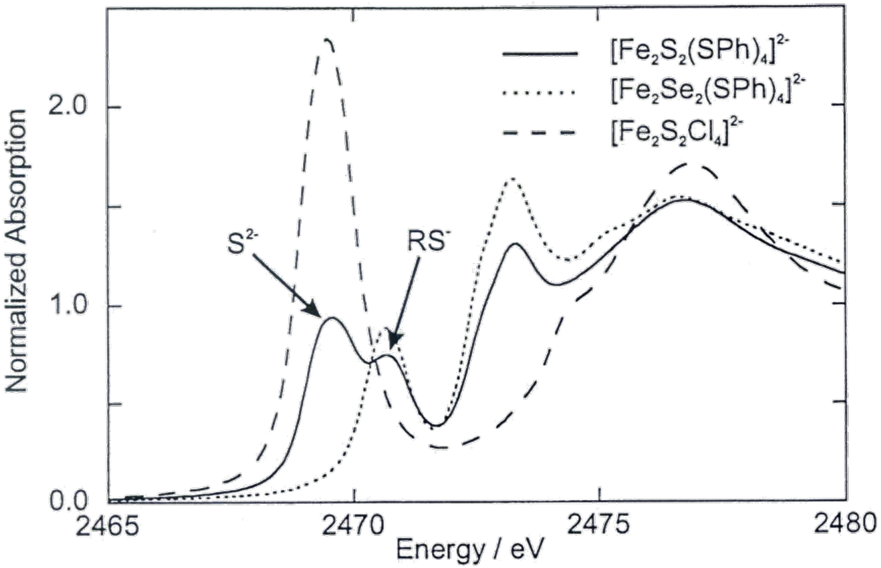


Provides a direct experimental measure of ligand 3p character in the HOMO and thus covalency of the interaction between metal & ligand

Ligand K Pre-edge – $Fe^{III}{}_2S_2(SR)_4$ Cluster Models



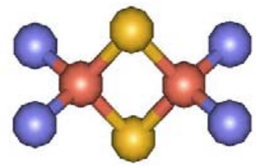
- Selective substitution of S allows direct identification of sulfide vs. thiolate transitions
- By relating intensity of each peak/ transition to that of sites for which covalency is known ⇨ measure of covalency per type of sulfur ligand (and for the Fe-S site)
- Can therefore use the S ligand as reporter ligand for the metal
- Covalency of thiolate-Fe related to that of pre-edge of plastocyanin, and sulfide-Fe to that of $KFeS_2$ / $CsFeS_2$
- Thiolate insensitive to bridge change; sulfide somewhat sensitive to terminal ligand type

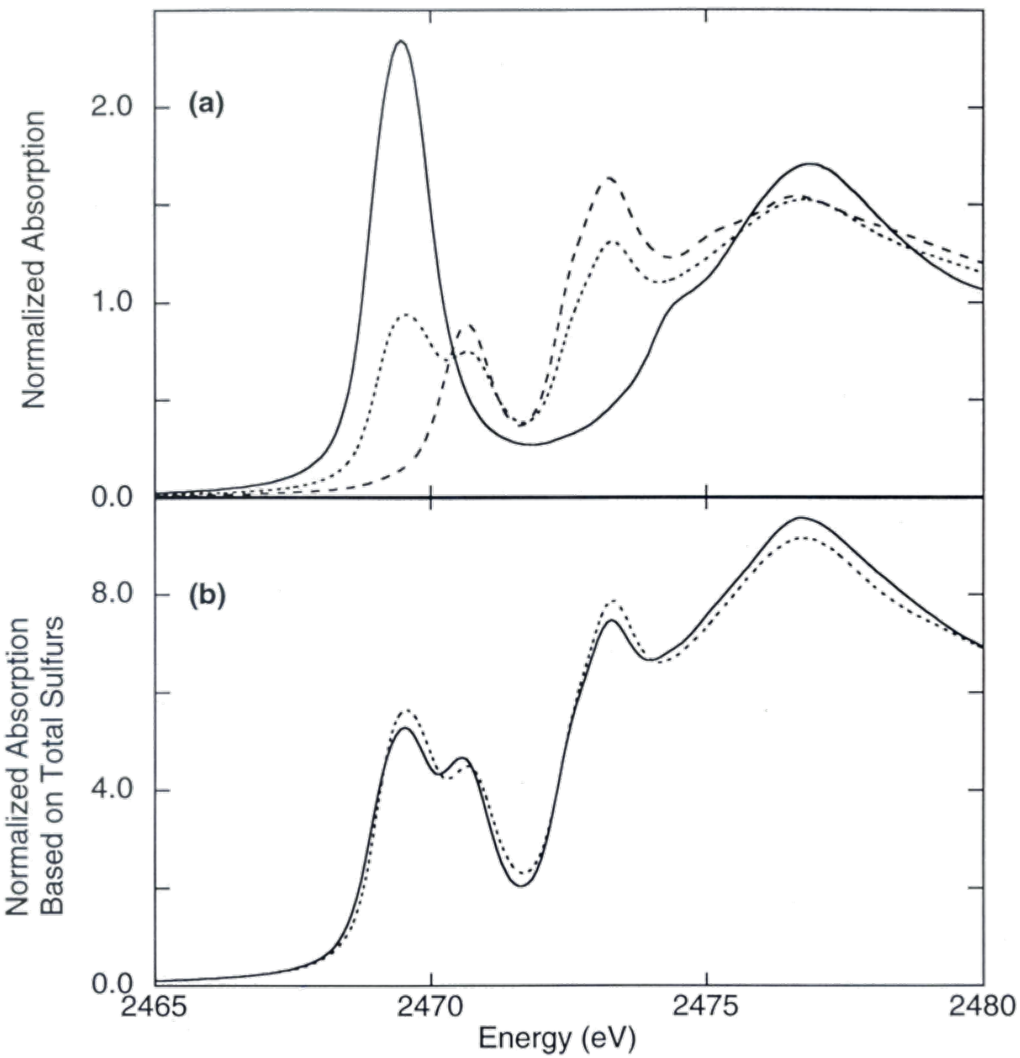


	Sulfide Cov 1S/Fe (%)	Thiolate Cov 1S/Fe (%)
$Fe_2S_2(SPh)_4$	72±5	30±3
$Fe_2Se_2(SPh)_4$		31±2
$Fe_2S_2Cl_4$	65±5	

- Covalency much higher for sulfide than for thiolate

Ligand K Pre-edge – $Fe^{III}{}_2S_2(SR)_4$ Cluster Models





- Summation of the two separate spectra:

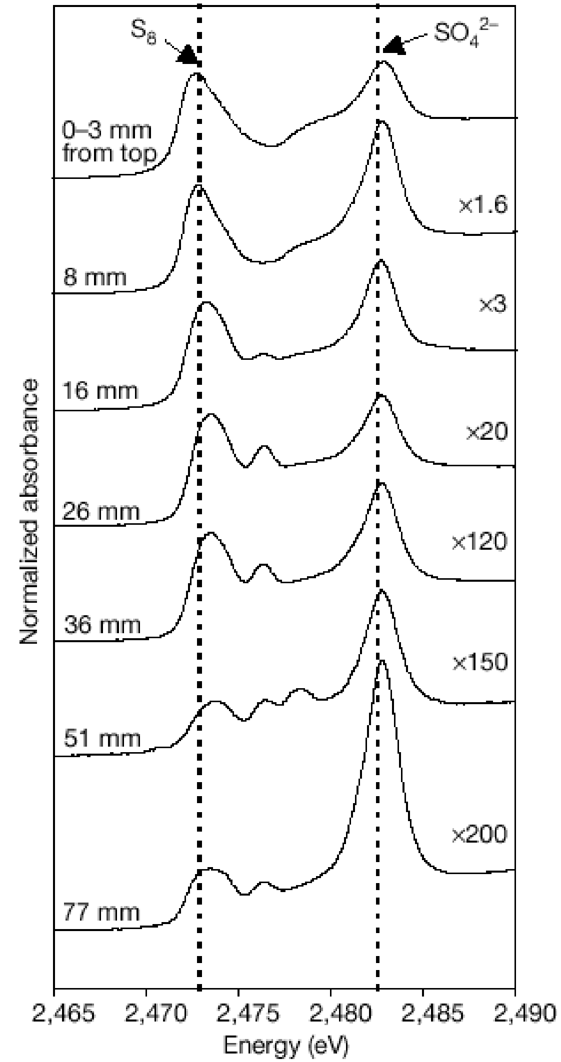
  $[Fe_2Se_2(SPh)_4 + 2*Fe_2S_2Cl_4]/2$

  results in spectrum that is closely similar to that of $Fe_2S_2(SPh)_4$

- Confirms the “insensitivity” and the validity of the approach

K. Rose, S.E. Shadle, T. Glaser, S. de Vries, A. Cherepanov, G.W. Canters, B. Hedman, K.O. Hodgson, E.I. Solomon, *JACS* **121**, 2353 (1999)

Using Sulfur X-ray Spectroscopy to Save the 17th-Century Swedish Warship Vasa



- Methodology & instrumentation that had been developed enabled this study to be initiated and opened up the path for other such projects

M Sandström, F Jalilehvand, P Frank, *et al*., *Nature* **415**, 893 (2002)

Experimental Considerations?

- Shorter energy range to measure ->

  enables lower absorber concentration as signal is strong compared to EXAFS (at high *k*...)

  allows for quick measurements

  not as affected by radiation damage (and provides an internal monitor)

- Requires

  stable and reproducible monochromator

  high energy resolution of optics (e.g. pre-collimating mirror; high-energy resolution monochromator crystal cut)

  good detectors

Experimental Considerations – and Why Edges?

- Radiation damage (and provides an internal monitor)
- Can be used to monitor quick changes - as a function of time - but can also apply to "slower" SR experiments
- Used as fingerprinting for unknown structure by comparing against spectra of known structures
- Edge structure -> knowledge of electronic structure / coordination -> CN can be locked or constrained in EXAFS fits
- Provide the basis for theoretical calculations / simulations of edge structure that enhance the understanding of the electronic structure

Approaches to Interpreting XAS Edges

I. Qualitatively

- use edges as a “fingerprint” of the electronic structure
- compare to known model complexes

II. Molecular Orbital-Based Approach

- obtain a more quantitative description
- understand energy and intensity distributions using ligand field theory
- couple to density functional calculations
- use a TD-DFT approach (ORCA, StoBe)
- works well for bound state transitions (i.e. pre-edge and to some extent the rising edge)

III. Ab Initio Multiple Scattering-Based Approach

- required to simulate rising edge
- FEFF, MXAN (talk later today)
- difficult to relate back to an MO-based picture

IV. Band Structure Approach

- density of states

Summary

- “Soft” energy experiments under non-vacuum conditions are providing a wealth of scientific information, in biology, environmental science, chemistry and materials science
- They require specific considerations as for beam line setup, sample preparation, detector and data analysis, but can be used for a wide range of sample types and with different approaches
- Ligand soft x-ray absorption spectroscopy provides unique information on active site electronic structure and covalency; Ligands can be used as *“reporters”* of the electronic structure and covalency of a metal cluster site
- Theoretical calculations in combination with the experimental data can provide detailed electronic information

Acknowledgements and Thanks

SSRL operations and research in materials science and chemistry is funded by the Department of Energy, Office of Basic Energy Sciences

Additional support for the SSRL Structural Biology Program is provided by

Office of Science
Department of Energy

Office of Biological and Environmental Research

National Center For Research Resources

National Institute of General Medical Sciences
NATIONAL INSTITUTES OF HEALTH