XAFS Spectroscopy

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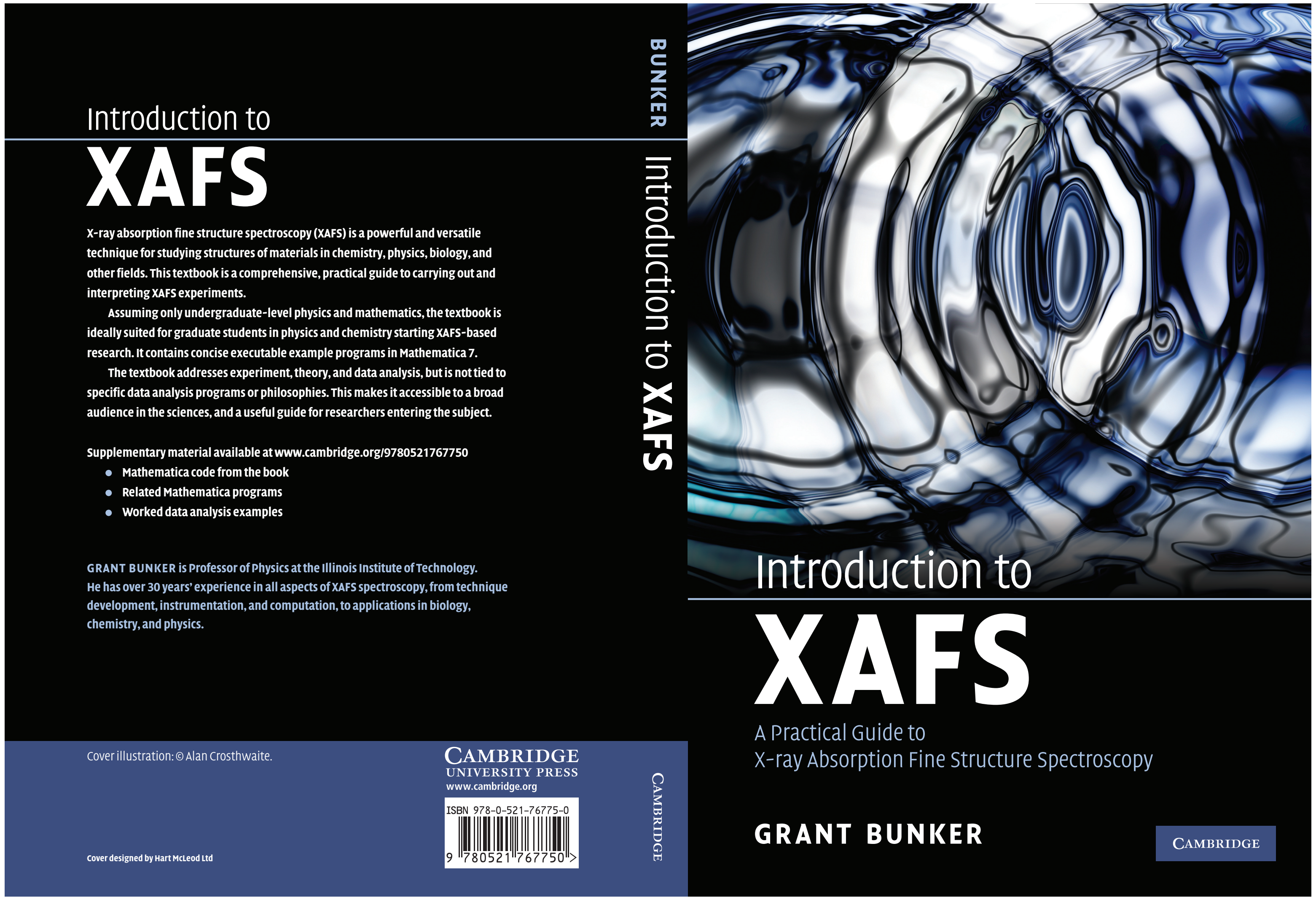
- Brief overview of XAFS and sketch of theory
- Experimental methods and Data Collection
- Overview of Data Analysis
- Conclusion

Acknowledgements

- ~35 years and counting
- Ed Stern, Dale Sayers, Farrel Lytle, John Rehr, Bruce Bunker, Gerd Rosenbaum...
- XAFS community that grew from it
- Students and postdocs

recent book on XAFS fundamentals



google “bunker xafs”
to download free
online tutorials

What is XAFS?

- X-ray Absorption Fine Structure spectroscopy uses the x-ray photoelectric effect and the wave nature of the electron to determine local structures around selected atomic species in materials
- Unlike x-ray diffraction, it does not require long range translational order – it works equally well in amorphous materials, liquids, (poly)crystalline solids, and molecular gases.
- XANES (near-edge structure) can be sensitive to charge transfer, orbital occupancy, and symmetry.

EXAFS experiment

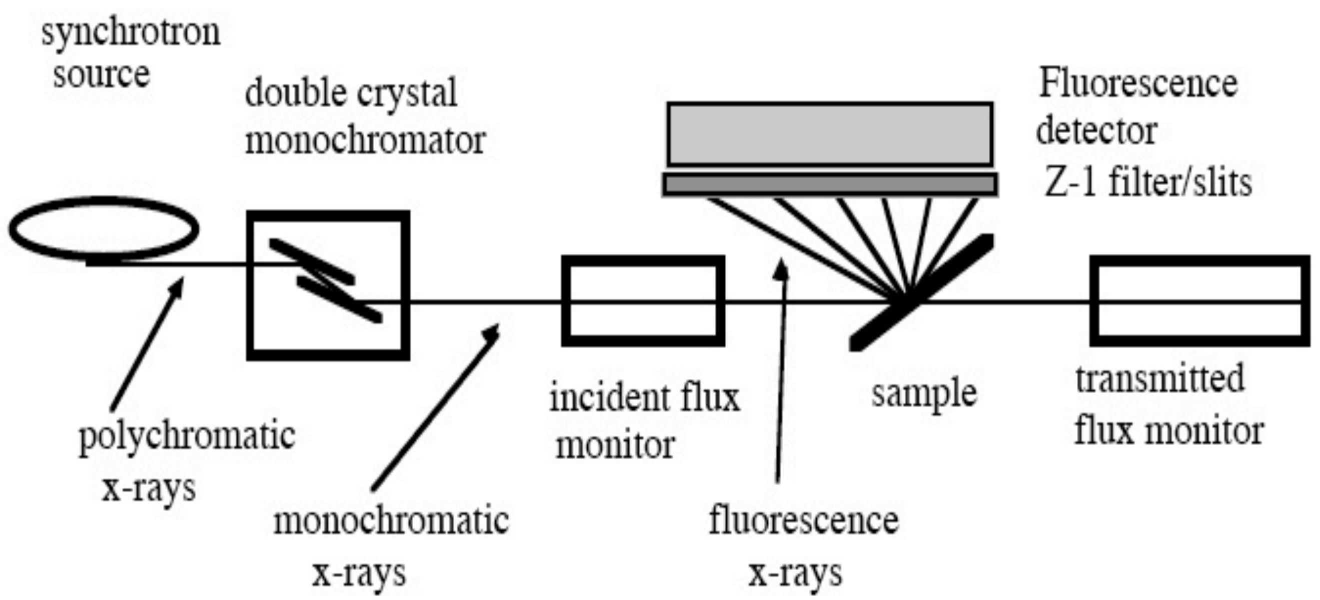


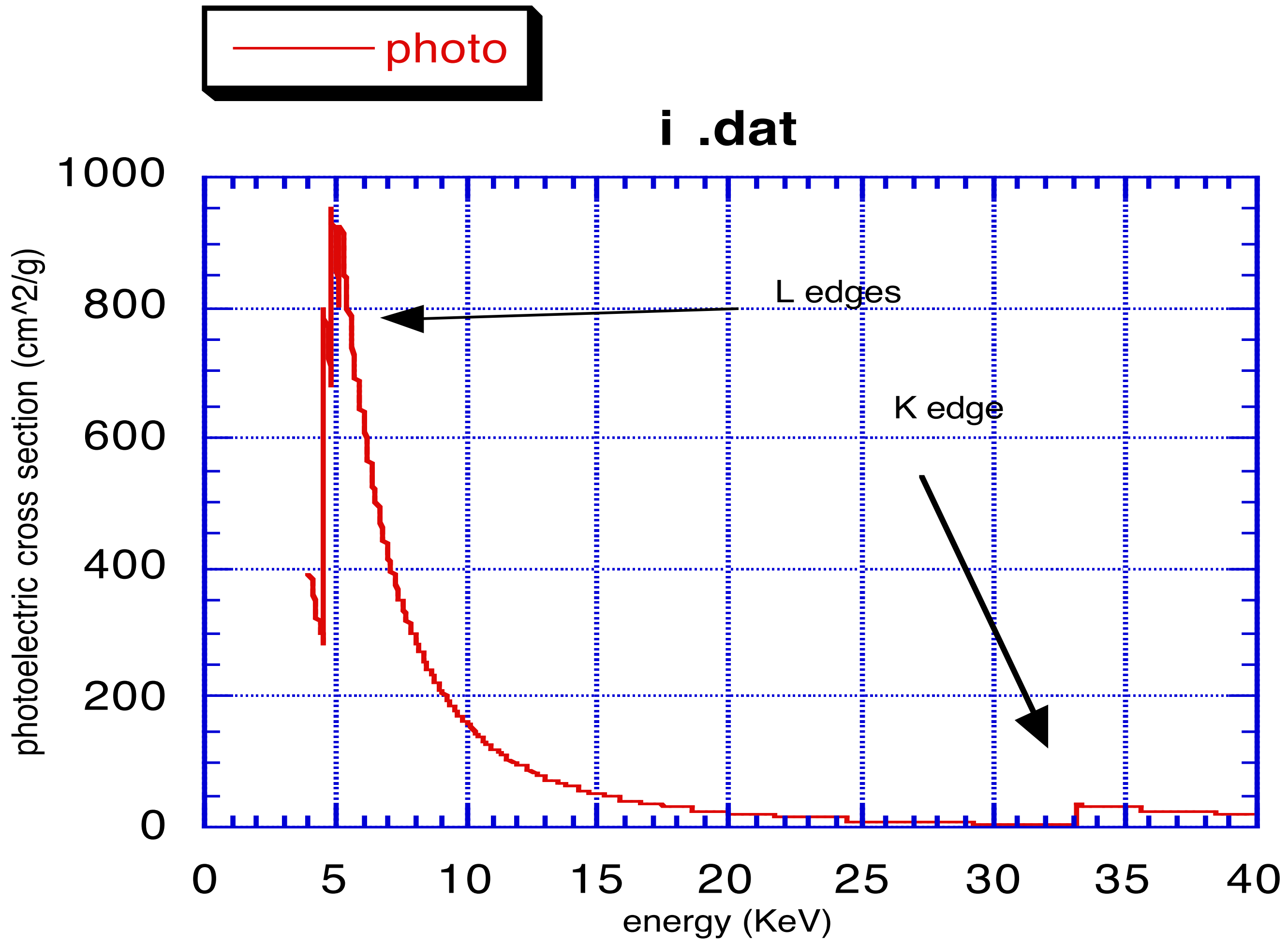
Figure 1 – Schematic XAFS experiment

$$\frac{I}{I_0} = \exp(-\mu(E)x)$$

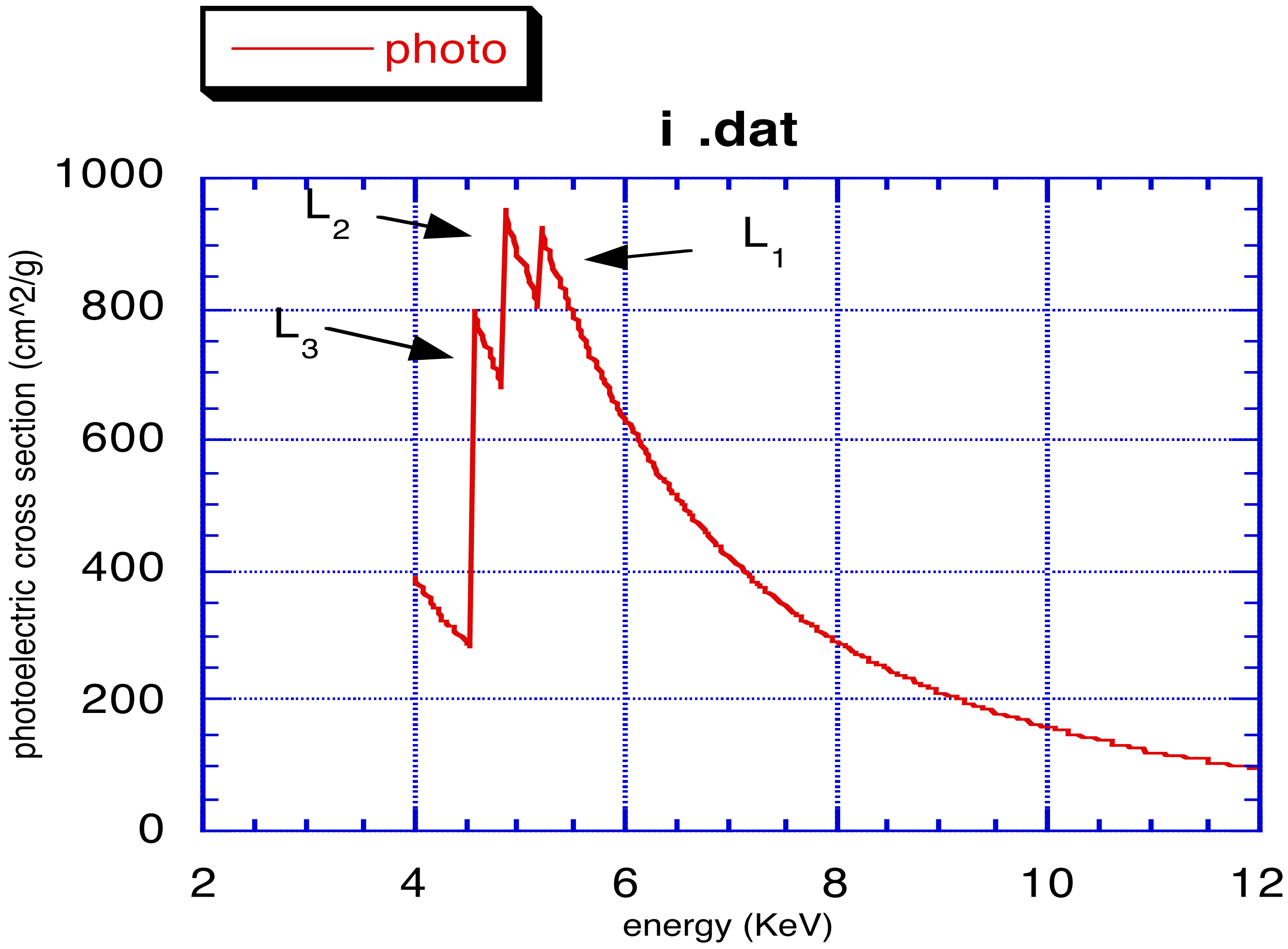
The X-ray absorption coefficient is the central quantity of interest. It is analogous to absorbance in UV-vis spectroscopy, and it is proportional to f''(E).

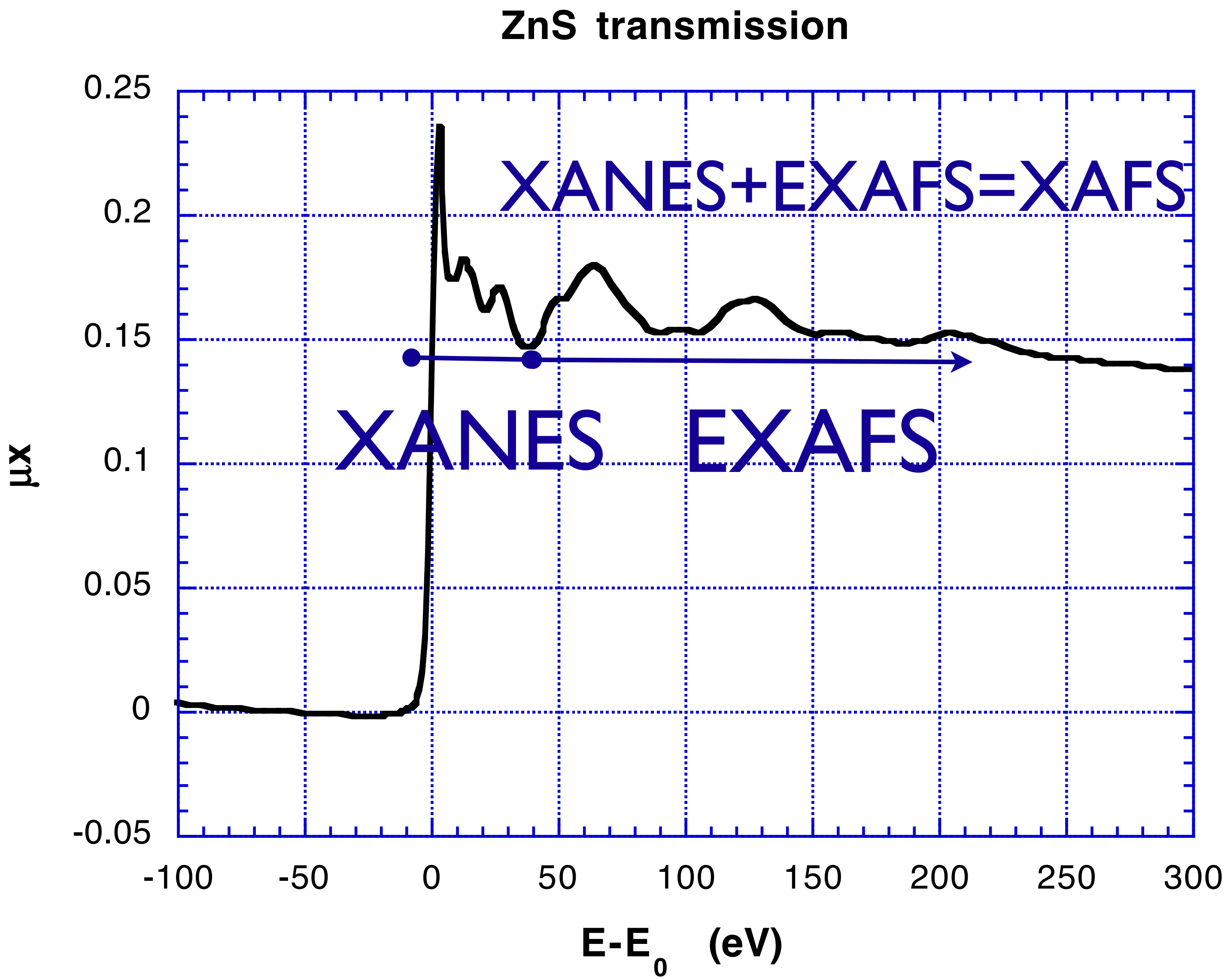
Absorption Edges

example: Iodine

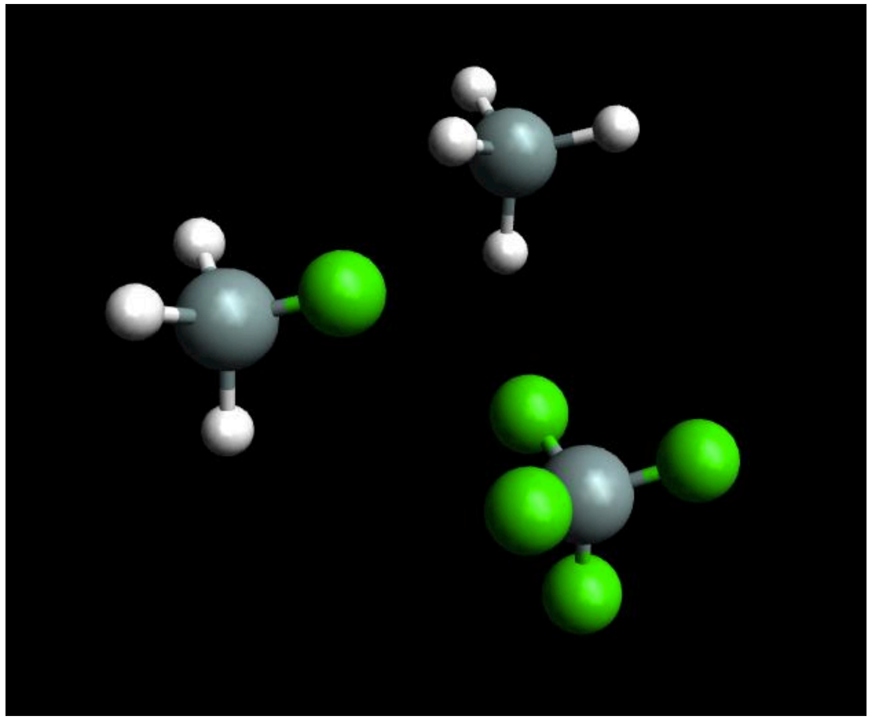


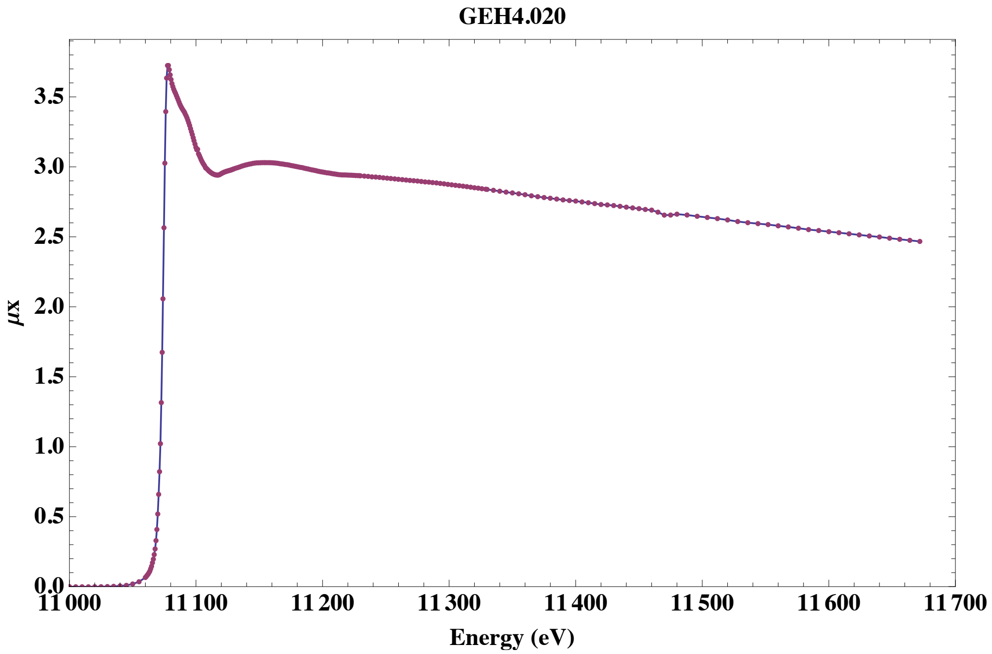
zoom in on L-edges

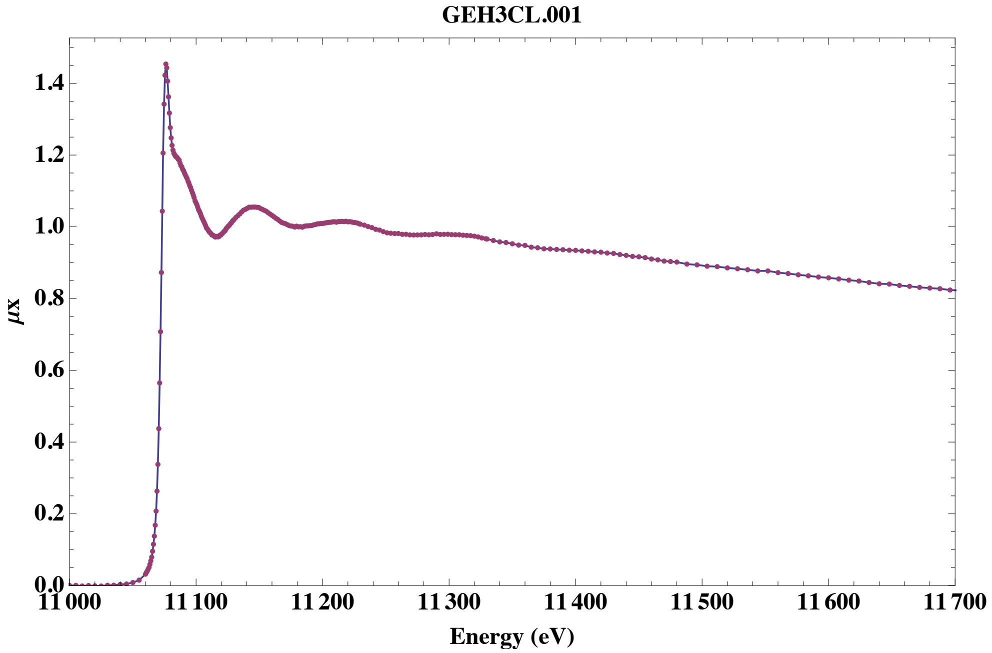


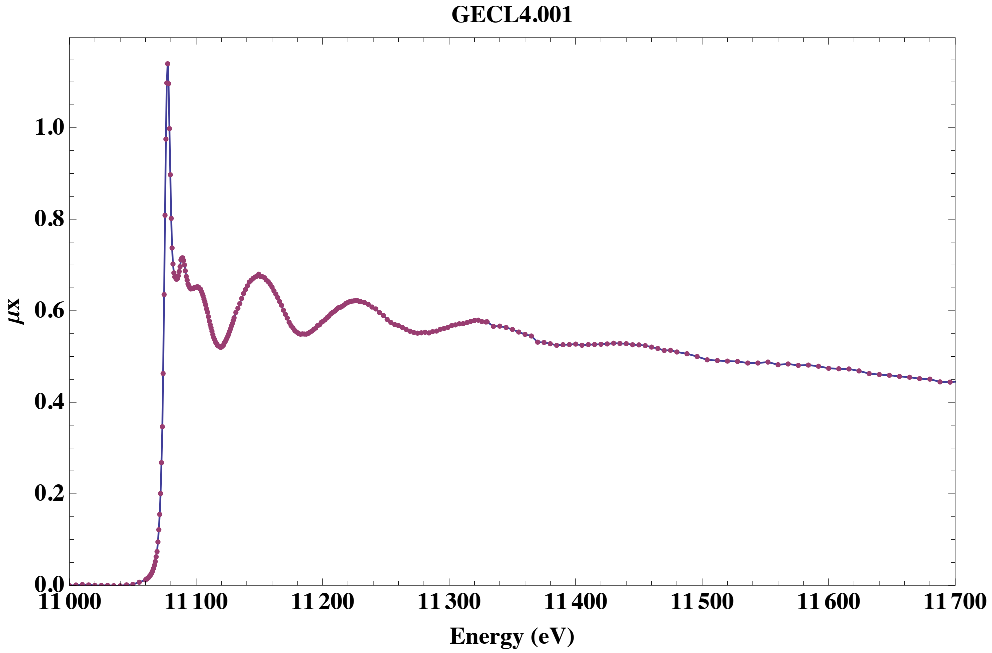

ZnS transmission
XANES+EXAFS=XAFS
XANES
EXAFS
μx
E-E0 (eV)
0.25
0.2
0.15
0.1
0.05
0
-0.05
-100
-50
0
50
100
150
200
250
300

Molecular gases
GeH4, GeH3Cl, GeCl4
tetrahedral coordination

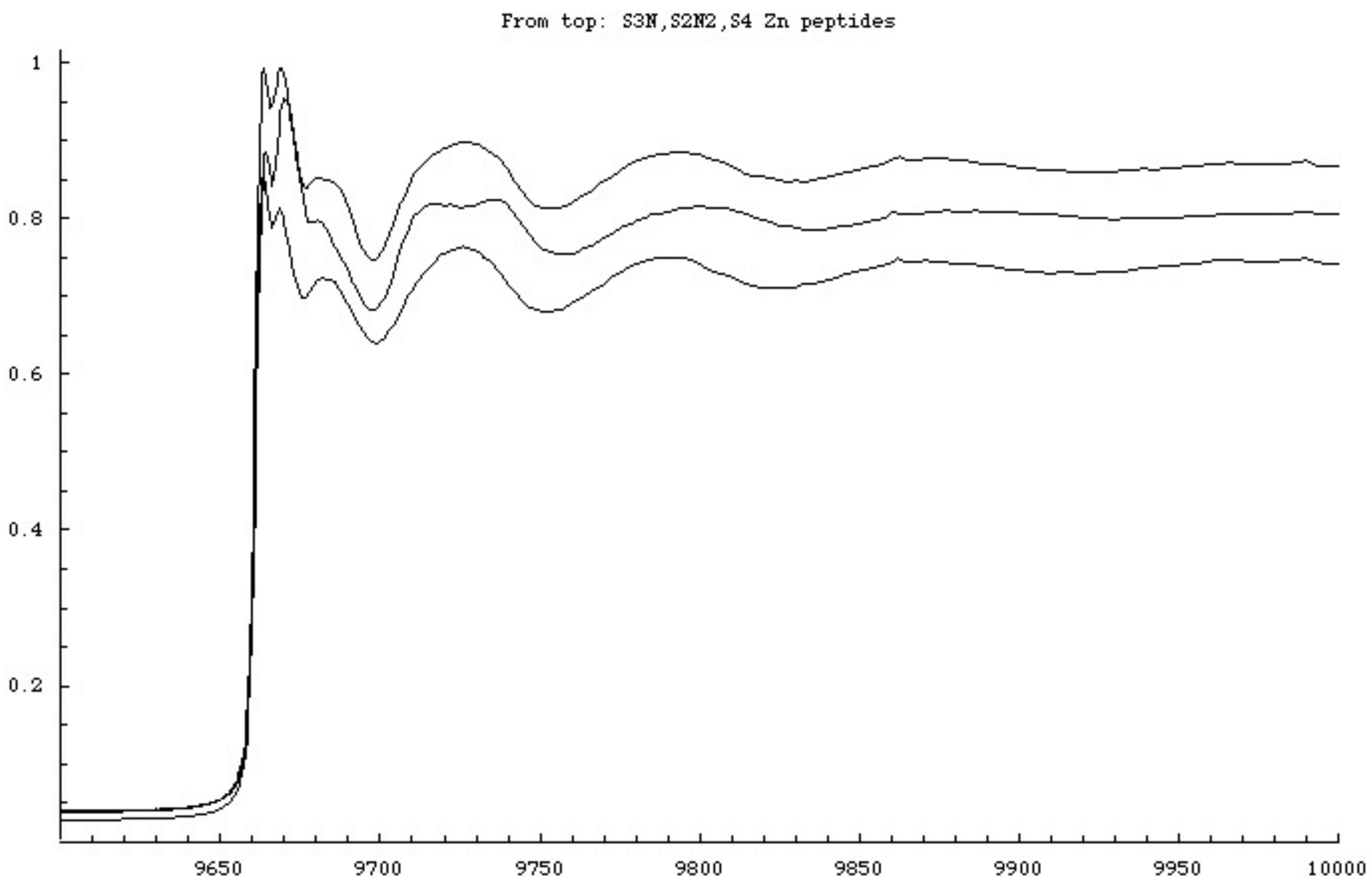






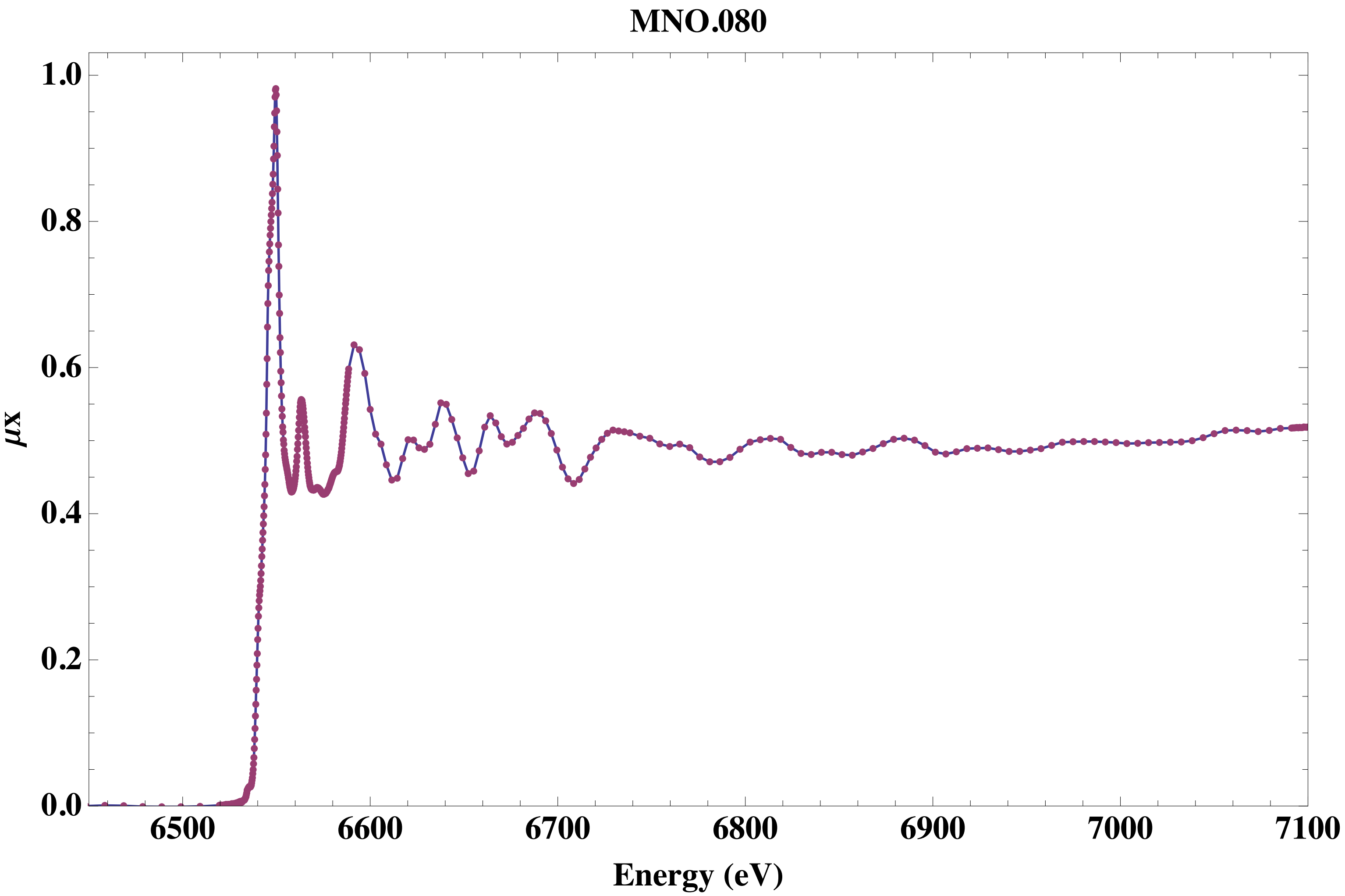


Zn cys/his complexes: XAFS encodes structure



Koch models: spectra courtesy of J. Penner-Hahn

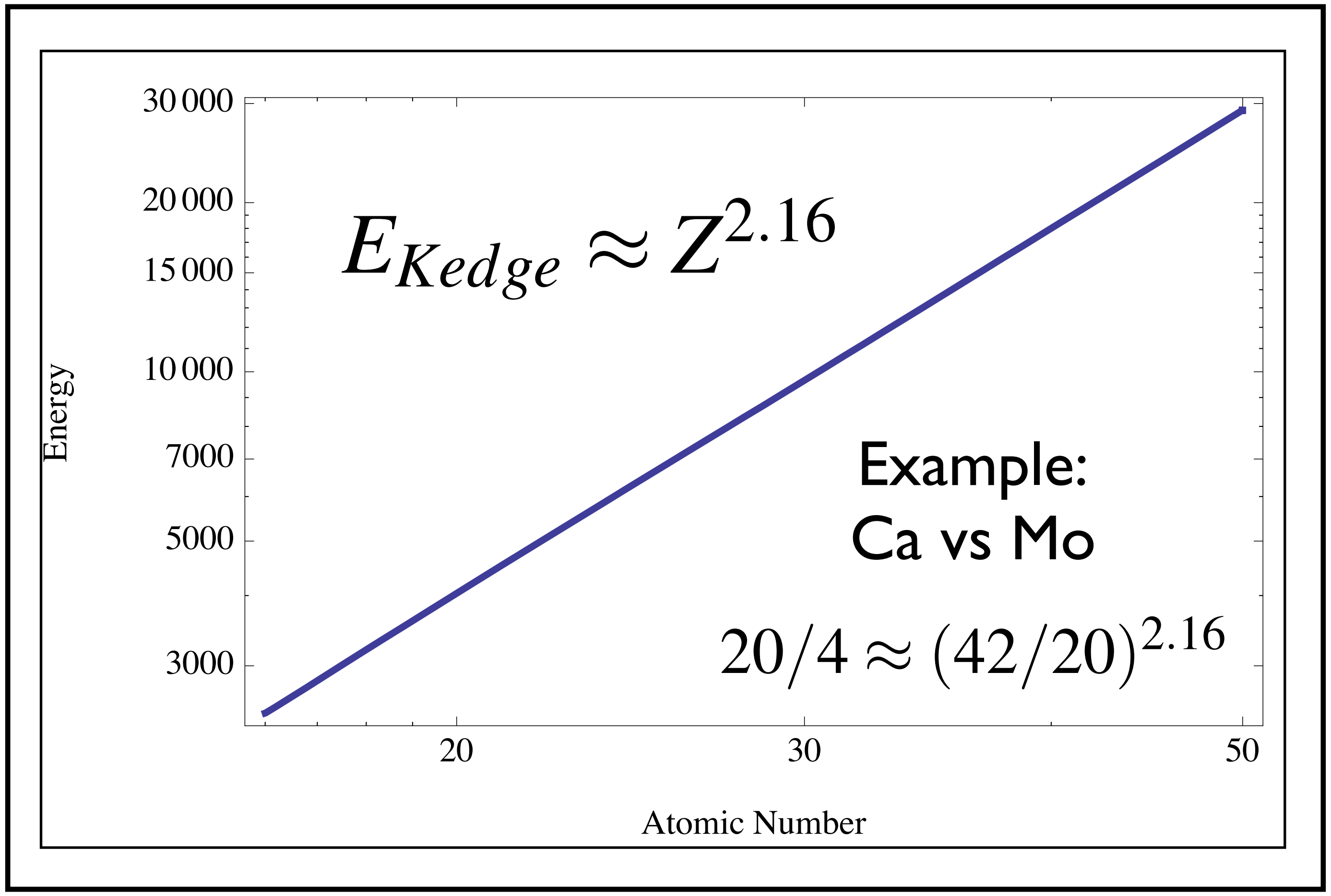
MnO
rock salt
structure
T=80K



XAFS is element selective

By choosing the energy of excitation you can "tune into" different elements in a complex sample.

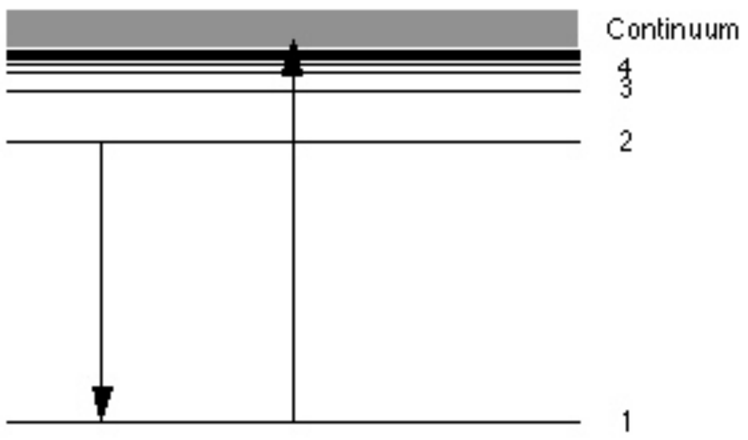
K-edge:
Ca: 4.0 keV
Fe: 7.1 keV
Zn: 9.7 keV
Mo: 20.0 keV



It is usually feasible to work in a convenient energy range by choosing an appropriate edge

X-ray Absorption Process

X-ray photon causes transition from n=1, l=0 (1S) initial state to unfilled p-symmetry (l=1) final state.



Absorption probability depends on dipole matrix element between initial and final quantum states of the electron, which are determined by local structure

$$\left| < \psi_f | \hat{\epsilon} \cdot \vec{r} e^{i\vec{\kappa}\cdot\vec{r}} | \psi_i > \right|^2$$

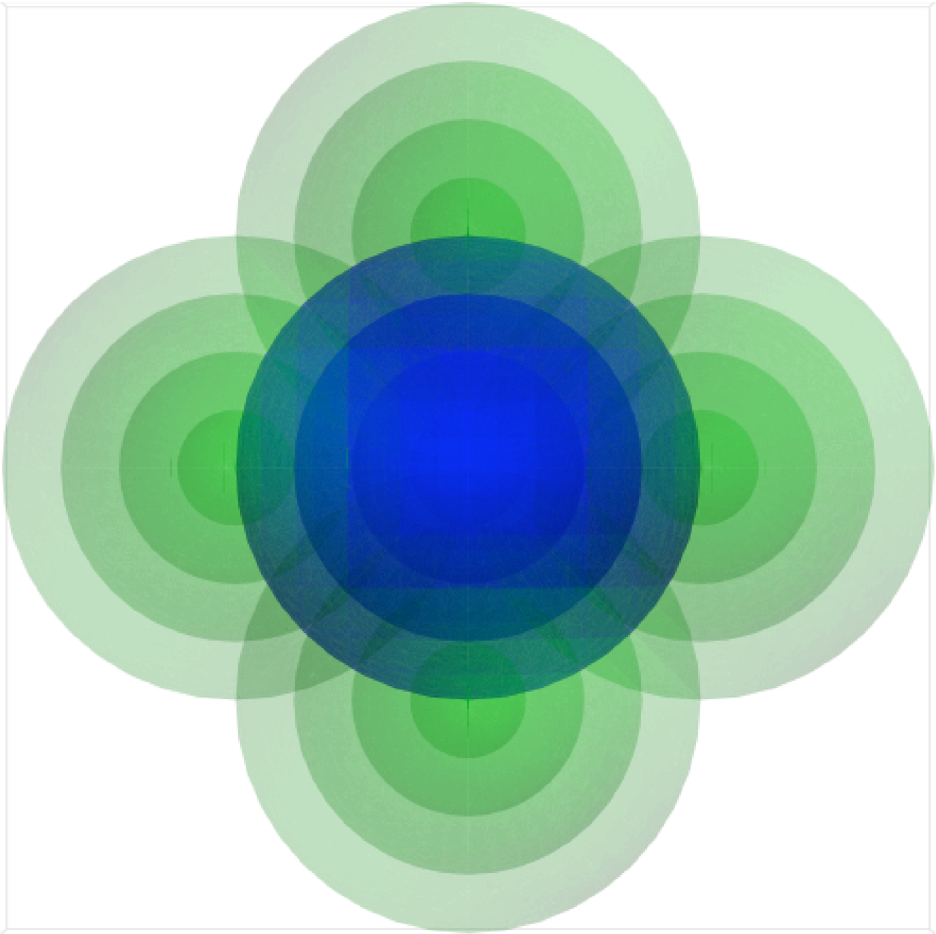
Electron waves

- X-ray photon causes transition from inner level to unfilled final state of appropriate symmetry

- If photon energy exceeds binding energy E_0 , electron has positive kinetic energy and propagates as spherical wave

$$k = \frac{2\pi}{\lambda} = \sqrt{\frac{2m}{\mathrm{h}^2}(E - E_0)}$$

Electron wave emitted by central atom is scattered by neighboring atoms. The outgoing and scattered parts of the final state wavefunction interfere where the initial state is localized.



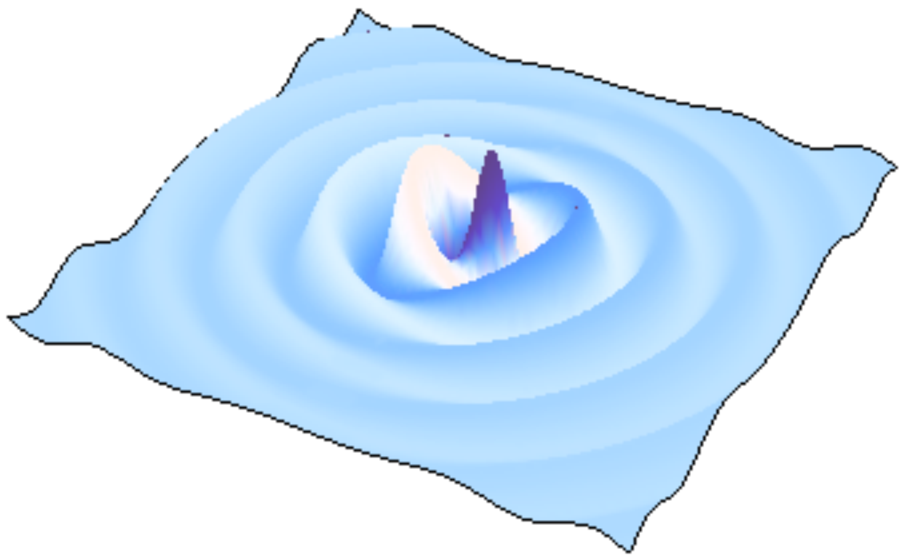
Interference is constructive or destructive depending on the distances and electron wavelength. Scanning the wavelength records an interferogram of distance distribution

Outgoing p-symmetry electron wave no scatterers (animation)

Isolated atom has no final state wavefunction interferences.

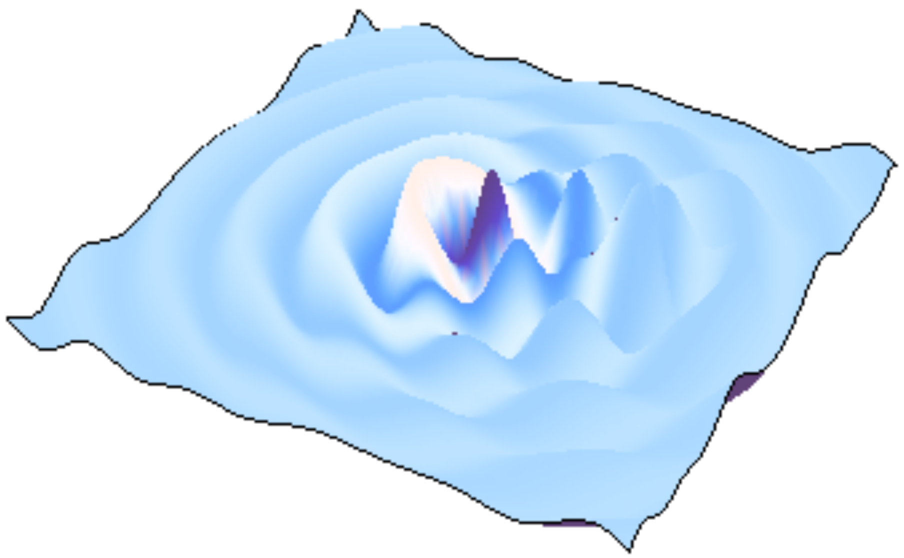
Absorption coefficient varies smoothly with electron wavelength.

This directionality can be useful for polarized XAFS.



Outgoing electron wave, with scatterers (animation)

Scattering from neighboring atoms modifies wavefunction near center of absorber, modulating the energy dependence of the transition matrix element



Time Dependent Perturbation Theory
Fermi's "Golden Rule" (Dirac)

Transition matrix element

$$\mu \propto |\int \psi_f^* \; \hat{\epsilon} \cdot \vec{r} \; e^{i\vec{k}\cdot\vec{r}} \; \psi_i \; d^3r|^2$$

dipole and quadrupole terms

$$\approx |\int \psi_f^* \; (\hat{\epsilon} \cdot \vec{r} \; + i(\hat{\epsilon} \cdot \vec{r})(\vec{k} \cdot \vec{r})) \; \psi_i \; d^3r|^2$$

Matrix element **projects out** the part of the final state that is of right symmetry (e.g p-symmetry for K-edge & dipole selection rules)

S

Selection rules for discrete transitions

		Electric dipole (E1) ("allowed")	Magnetic dipole (M1) ("forbidden")	Electric quadrupole (E2) ("forbidden")
Rigorous rules	1.	$\Delta J = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta J = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta J = 0, \pm 1, \pm 2$ (except $0 \nleftrightarrow 0$, $1/2 \nleftrightarrow 1/2$, $0 \nleftrightarrow 1$)
	2.	$\Delta M = 0, \pm 1$ (except $0 \nleftrightarrow 0$ when $\Delta J = 0$)	$\Delta M = 0, \pm 1$ (except $0 \nleftrightarrow 0$ when $\Delta J = 0$)	$\Delta M = 0, \pm 1, \pm 2$
	3.	Parity change	No parity change	No parity change
With negligible configuration interaction	4.	One electron jumping, with $\Delta l = \pm 1$, Δn arbitrary	No change in electron configuration; i.e., for all electrons, $\Delta l = 0$, $\Delta n = 0$	*No* change in electron configuration; *or* one electron jumping with $\Delta l = 0, \pm 2$, Δn arbitrary
For *LS* coupling only	5.	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
	6.	$\Delta L = 0, \pm 1$ (except $0 \nleftrightarrow 0$)	$\Delta L = 0$ $\Delta J = \pm 1$	$\Delta L = 0, \pm 1, \pm 2$ (except $0 \nleftrightarrow 0$, $0 \nleftrightarrow 1$)

source http://physics.nist.gov/Pubs/AtSpec/node17.html

Final state symmetry

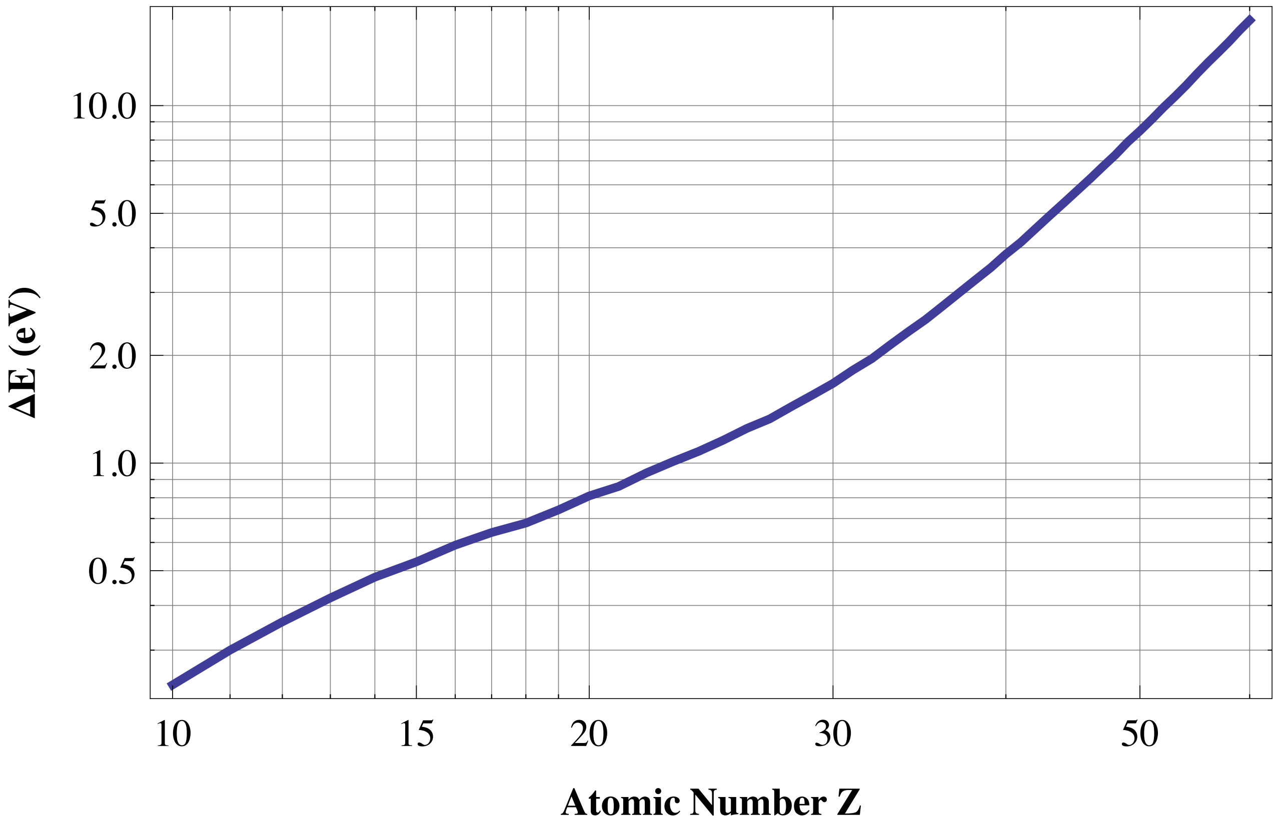
- K-edge: 1s initial state (n=1,l=0,m=0)
- L_1-edge: 2s initial state (n=2,l=0,m=0)
- L_2-edge: 2p (j=1/2) initial state (n=2,l=1)
- L_3-edge: 2p (j=3/2) initial state (n=2,l=1)

- The measured spectrum is a Monte Carlo average of the "snapshot" spectra (~10^{-15} sec) of all the atoms of the selected type that are probed by the x-ray beam

- In general XAFS determines the statistical properties of the distribution of atoms relative to the central absorbers. In the case of single scattering the pair correlation function is probed. Multiple scattering gives information on higher order correlations. This information is encoded in the chi function:

$$\mu(E) = \mu_0(E)(1+\chi(E)); \quad \chi(E) = \frac{\mu(E)-\mu_0(E)}{\mu_0(E)}$$

Core hole broadening



from
gb book

Fig. 2.20. Log-log plot of the K-edge core hole broadening (FWHM) as a function of atomic number Z of the x-ray absorbing atom. The level width over the interval $Z = 16 - 60$ is well represented by $1.0(Z/42) + 2.1(Z/42)^2 - 4.6(Z/42)^3 + 6.0(Z/42)^4$.

EXAFS oscillations

$$\mu(E) = \mu_0(E)(1+\chi(E)); \quad \chi(E) = \frac{\mu(E)-\mu_0(E)}{\mu_0(E)}$$

- Modulations in chi encode information about the local structure
- chi function represents the fractional change in the absorption coefficient that is due to the presence of neighboring atoms

Single Scattering EXAFS Equation

Stern, Sayers, Lytle

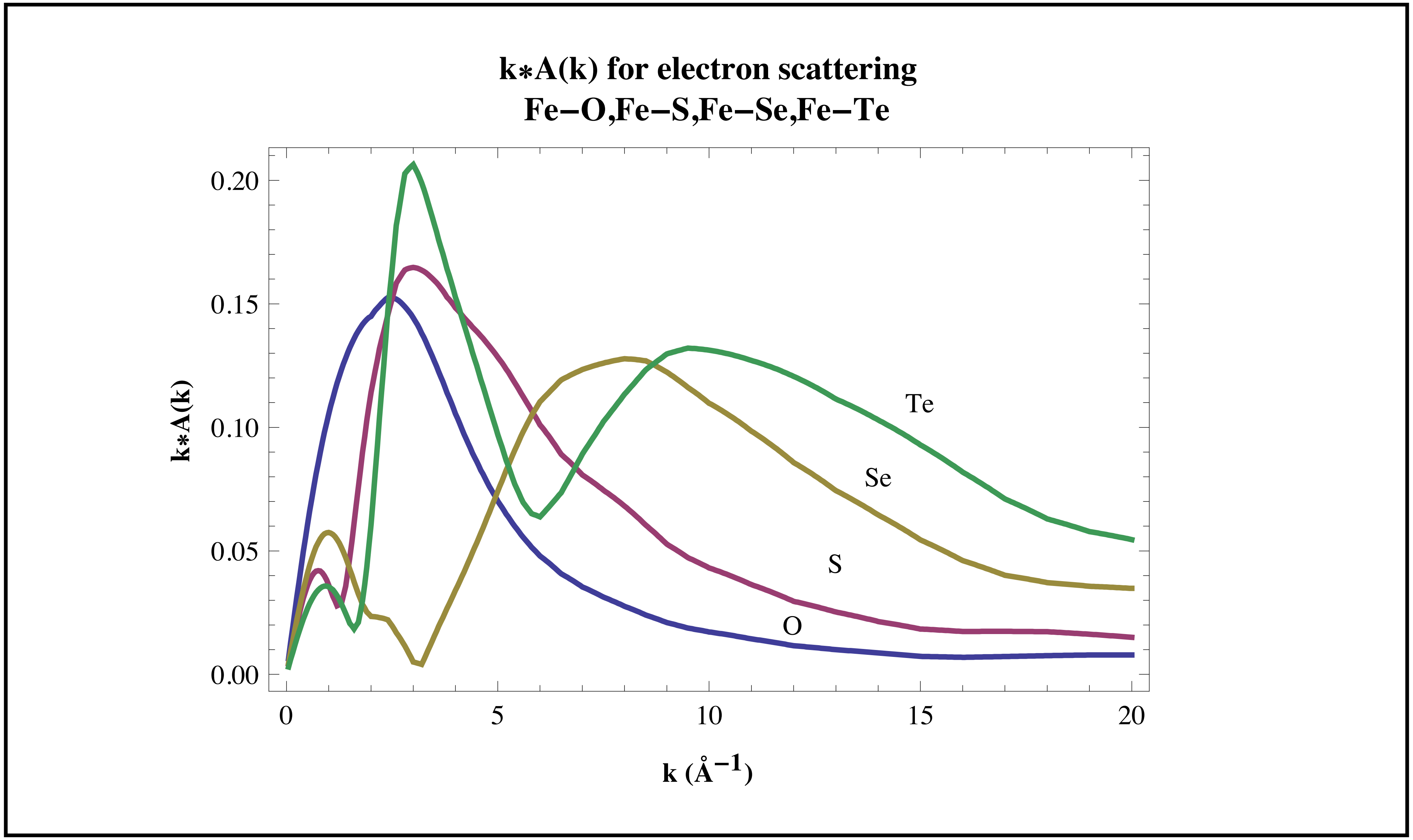
$$\chi(k) = S_0^2 \sum_i \frac{N_j}{kR_j^2} |f_j(k;r)| e^{-2k^2\sigma_j^2} e^{-2R_j/\lambda(k)} \sin(2kR_j + \delta_j(k;r))$$

Experimental data are fit using the EXAFS equation with theoretically calculated (or empirically measured) scattering functions to determine structural parameters.

The k-dependence of scattering amplitudes and phases helps distinguish types of backscatterers

This equation is a bit too simple {large disorder, multiple scattering [focussing effect]}, but it can be generalized.

k-dependence of scattering amplitudes helps identify scatterers



XAFS spectroscopy provides:

- Precise local structural information (distances, numbers of atoms, types, disorder) in crystalline or noncrystalline systems e.g. metalloprotein active sites, liquids, amorphous materials
- All atoms of selected type are visible - there are no spectroscopically silent atoms for XAFS
- Information on charge state, orbital occupancy may be available by studying XANES depending on system and edge
- ***in situ* experiments, under conditions similar to natural state, as well as crystals.**
- XAFS probes effects of arbitrary experimental conditions on sample (high pressure, low temperature, pH, redox state, pump-probe, T-jump, p-jump…)
- Oriented samples provide more angular information

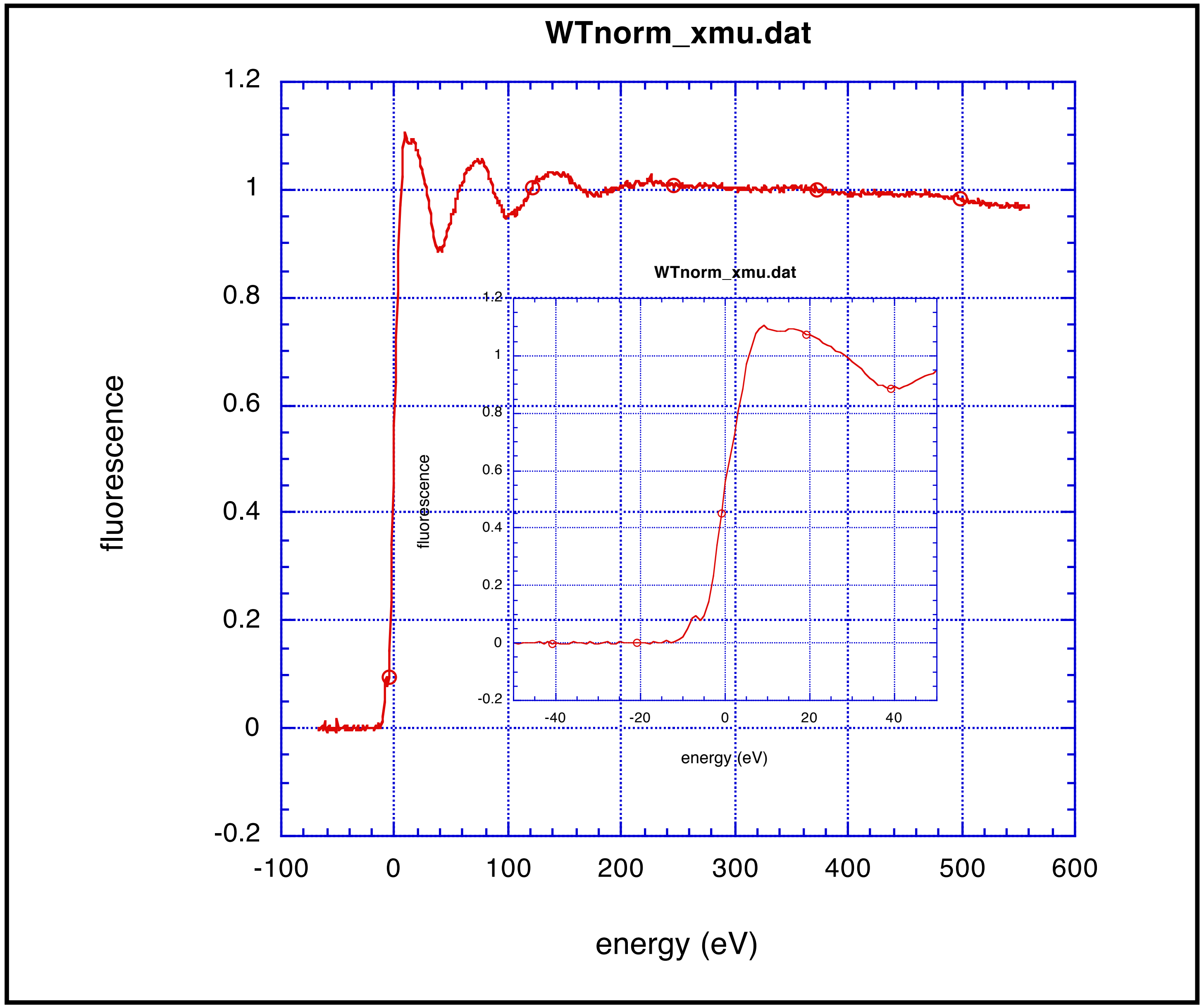
Complementary Structure Probes

- X-ray and Neutron diffraction
  - powerful and fast (x-ray), need good crystals, no solutions
  - Pair Distribution Function (PDF)
- X-ray scattering
  - SAXS gives only low resolution information
  - wide angle can be informative
- 2-D and higher dimensional NMR
  - Atomic resolution structures in solution, no large molecules, slow

Related techniques

- XMCD: X-ray Magnetic Circular Dichroism uses circularly polarized x-rays to probe magnetic structure
- IXS: Inelastic X-ray Scattering analyzes the fluorescence radiation at high resolution, providing a 2-D excitation map. Provides a great deal of information in the near-edge region
- X-ray Raman: essentially allows one to obtain XAFS-like information using high energy x-rays
- DAFS: hybrid diffraction/XAFS gives sensitivity to inequivalent sites in crystals and multilayers
- XPS, ARPEFS, fluorescence holography...

Simple example: Fx Fe-S protein from Plant PhotoSystem I



Structure of Fe-S cluster in Fx from Photosystem I

XAFS fits for 4 Fe- 4 S cluster

```
Fe-S  N= 4.00 R=2.27(2) SS= 0.007(1)
Fe-Fe N= 3.00 R=2.68(2) SS= 0.007(1)
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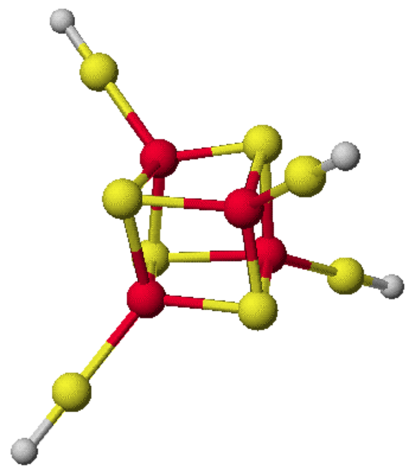


The figure shows a molecular model based on XAFS that is consistent with the determined distances. These require a distortion of the cubane-like box. Bunker and Carmeli, 2002

Protein solution only - no crystals!

Single Scattering EXAFS equation

Stern, Sayers, Lytle...

The most basic form of the EXAFS equation is:

$$\chi(k) = \left\langle S_0^2 \sum_i \frac{3\cos^2(\theta_i)}{kr_i^2} |f_i(k;r)| e^{-2r_i/\lambda(k)} \sin(2kr_i + \delta_i(k;r)) \right\rangle$$

where r_i is the distance to the $i_{\rm th}$ neighbor; $< ... >$ represents an average over all sites in the sample; λ is the electron mean free path, and S_0^2 is a loss factor; f_i and δ_i are the scattering amplitude and phase shift of atom i; θ_i is the angle between the electric polarization vector of the x-ray beam $\hat{\epsilon}$ and the vector $\hat{r}_i$ from the center atom to neighboring atom i. The r-dependence of f and δ is weak.

note: angle dependence is more complicated for L edges

EXAFS equation (isotropic average)

Averaging over angle and grouping atoms of the same atomic number and similar distances into "shells" we obtain:

$$\chi(k) = S_0^2 \sum_i \frac{N_j}{kR_j^2} |f_j(k;r)| e^{-2k^2\sigma_j^2} e^{-2R_j/\lambda(k)} \sin(2kR_j + \delta_j(k;r)),$$

where N_j,R_j,σ_j^2 are the coordination number, average distance, and mean square variation in distance to atoms in shell j. These are the leading terms in the "cumulant expansion". If $k\sigma$ is not $<< 1$, higher order terms should be considered.

EXAFS is basically a sum of damped sine waves
=> Fourier Transform, beat analysis

EXAFS DWFs are comparable to, but distinct from, diffraction DWFS.
There are both static and thermal contributions to sigma^2

Multiple Scattering Expansion

Multiple scattering is accounted for by summing over MS paths Γ, each of which can be written in the form [ref: Rehr, Rev. Mod. Phys., 2000]

$$\chi_\Gamma(p) = S_0^2 \,\mathrm{Im}\left(\frac{e^{i(\rho_1+\rho_2+\cdots+\rho_N+2\delta_l)}}{\rho_1\rho_2\cdots\rho_N} e^{-2p^2\sigma_\Gamma^2} \times \mathrm{Tr} M_l F^N \cdots F^2 F^1\right)$$

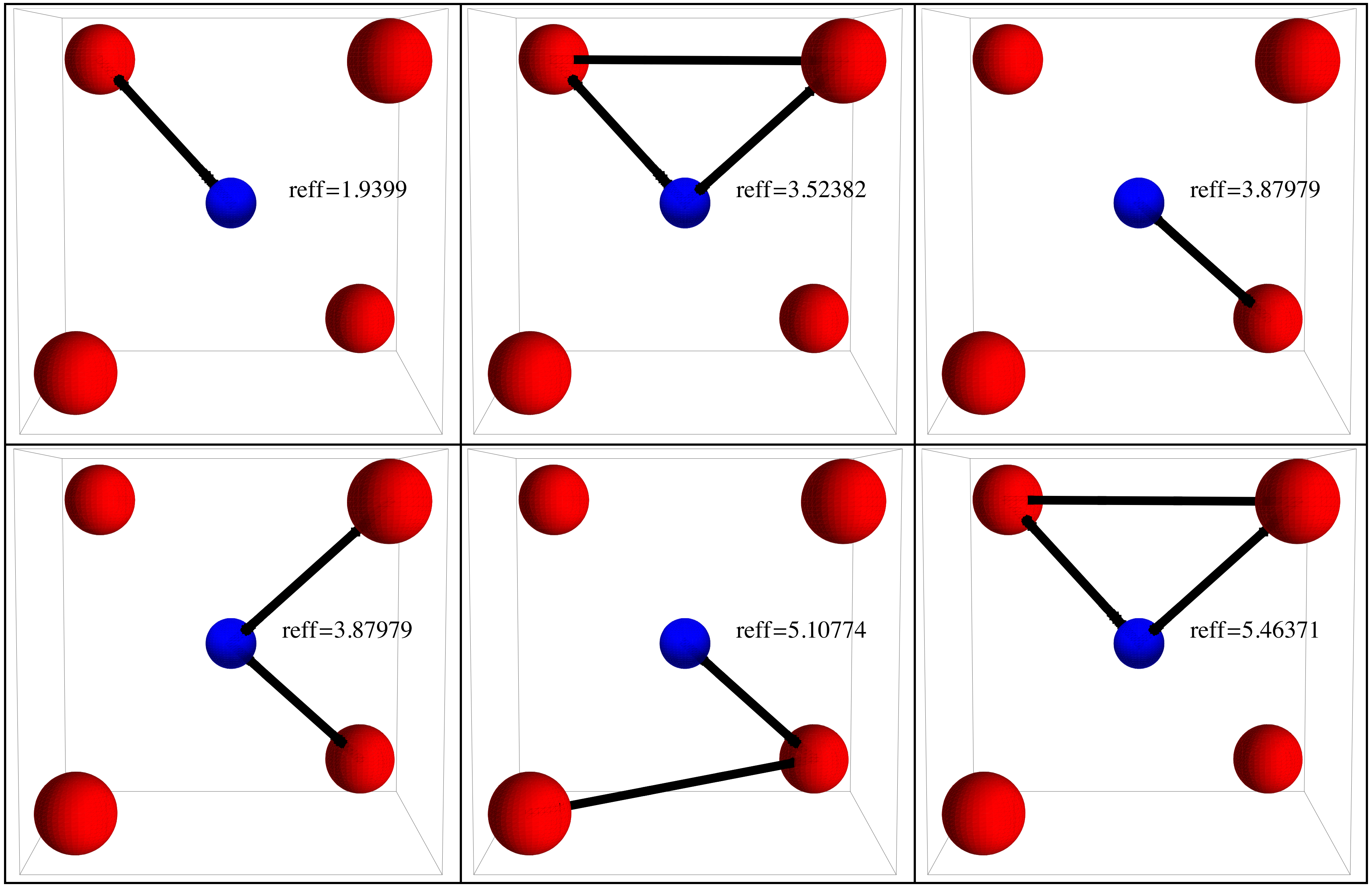
where p is the complex photoelectron momentum, ρ_j are p times the path lengths of the $i_{\rm ith}$ leg of the MS path Γ; the F matrices describe the scattering from each atom in the path; M is a termination matrix.

This can be expressed similarly to SS form

$$\chi_\Gamma(p) = S_0^2 \,\mathrm{Im}\left(\frac{f_{\rm eff}}{kR^2} e^{2ikR+2i\delta_l} e^{-2p^2\sigma_\Gamma^2}\right)$$

whence "Feff"

Leading MS paths tetrahedral MnO_4

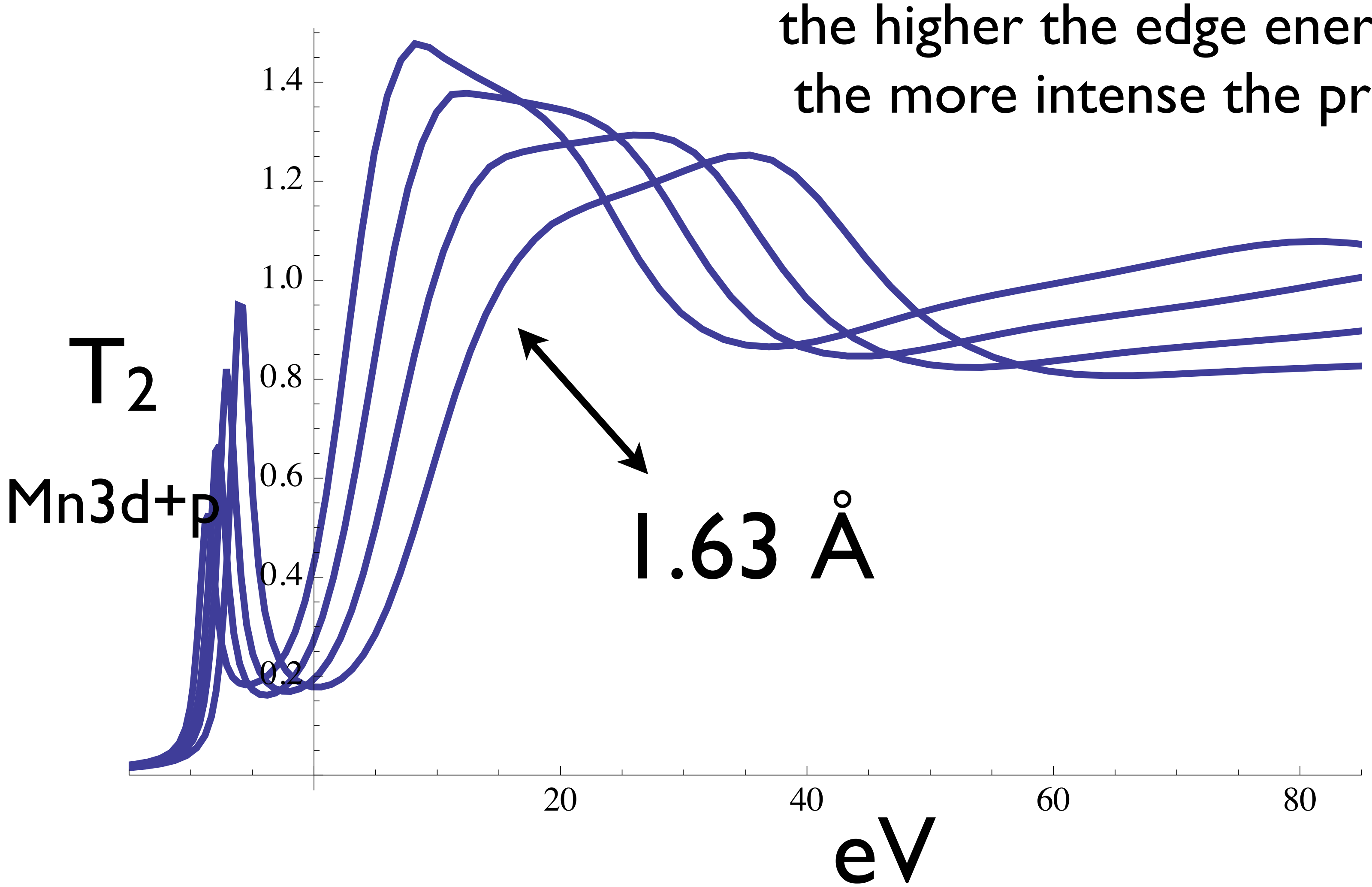


theory

MnO_4 tetrahedral cluster

r=1.63,1.73,1.84,1.94Å feff8.2 SCF/FMS

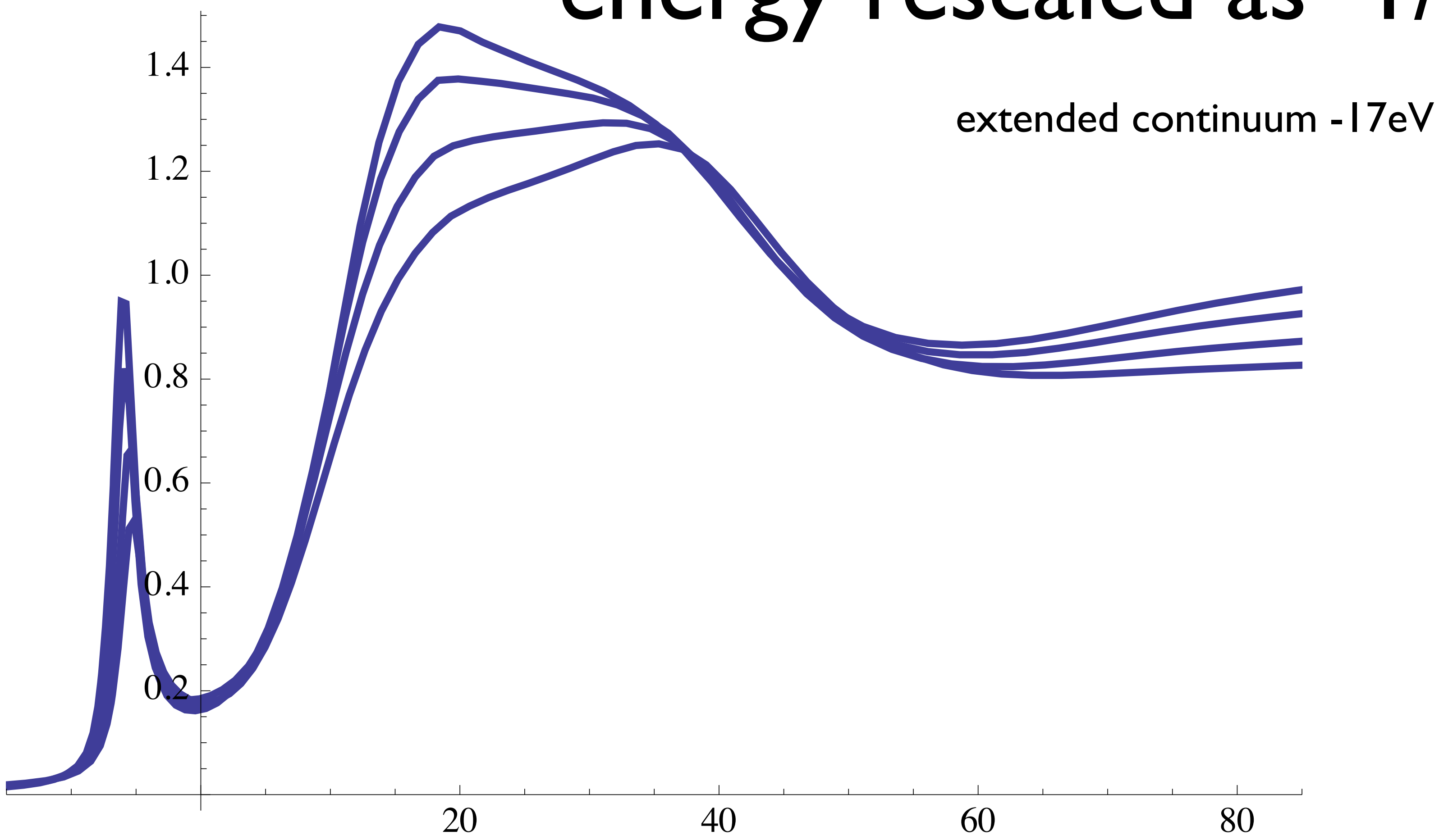
the shorter the distance,
the higher the edge energy and
the more intense the pre-edge



MnO_4 tetrahedral cluster

r=1.63,1.73,1.84,1.94Å feff8.2 SCF/FMS

energy rescaled as 1/r^2



edge shifts Mn oxides

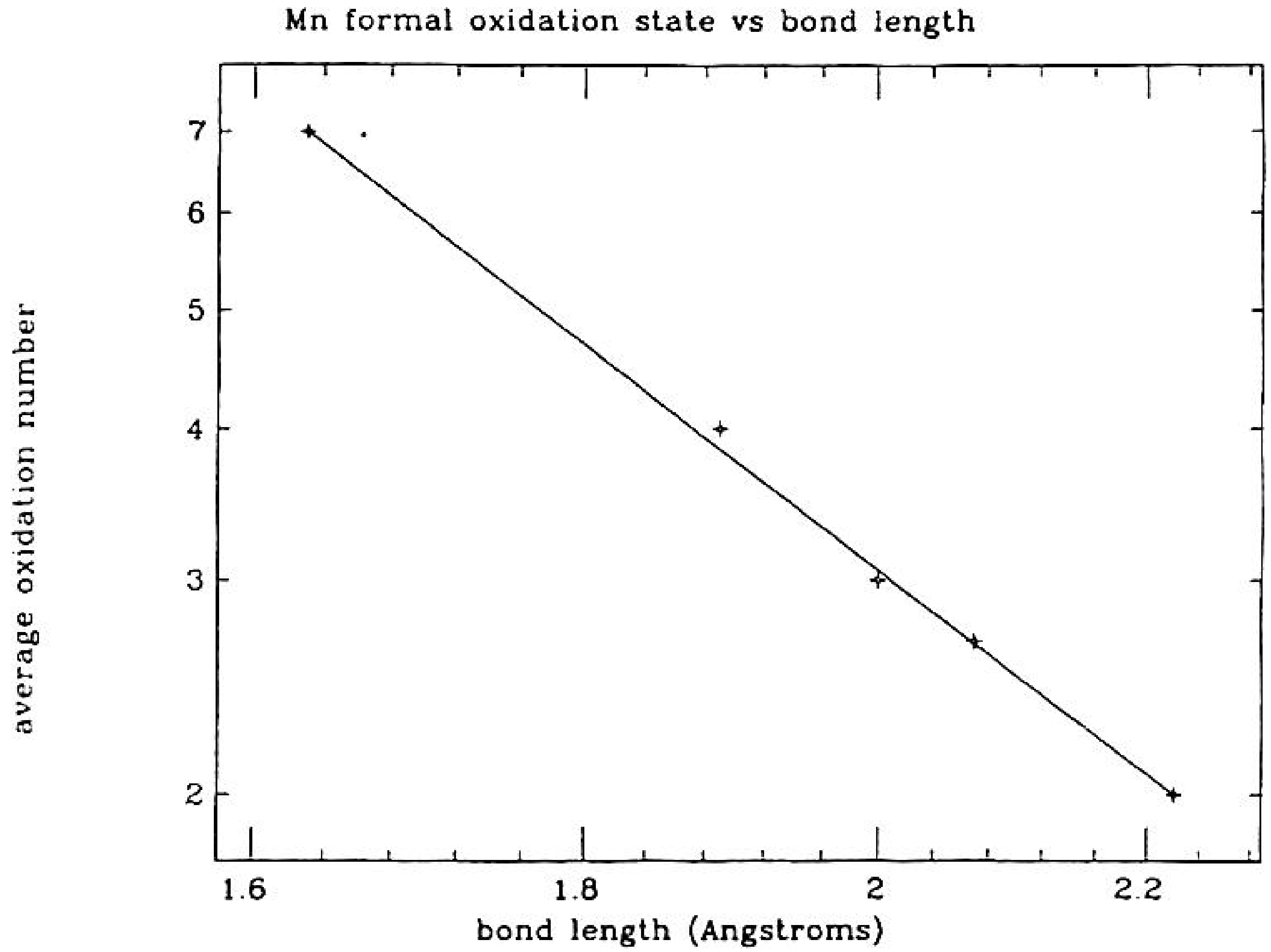
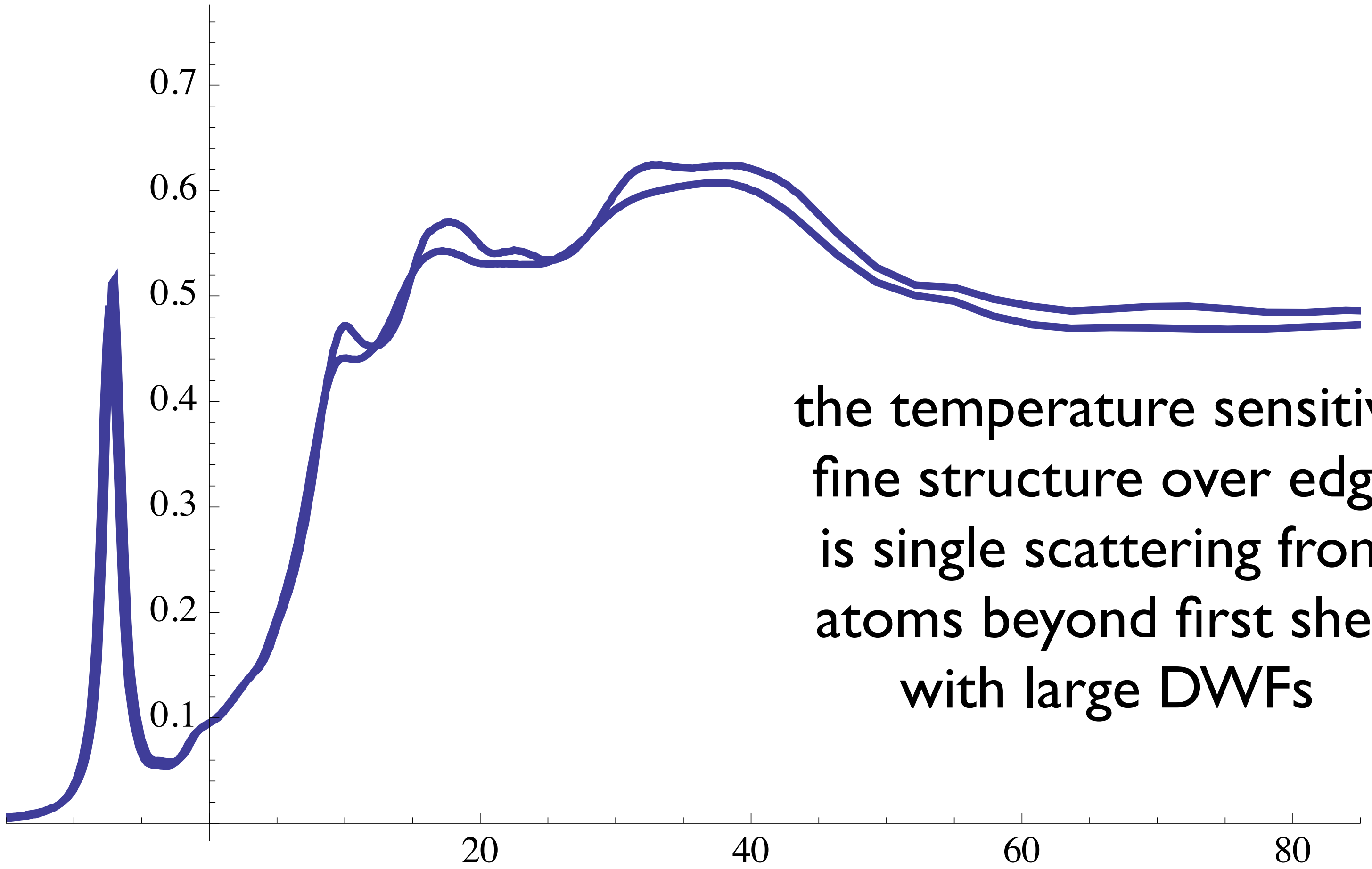


Fig. 5.2. Log-Log plot of formal oxidation state in Mn oxides vs average bond length. Image from gb84[52].

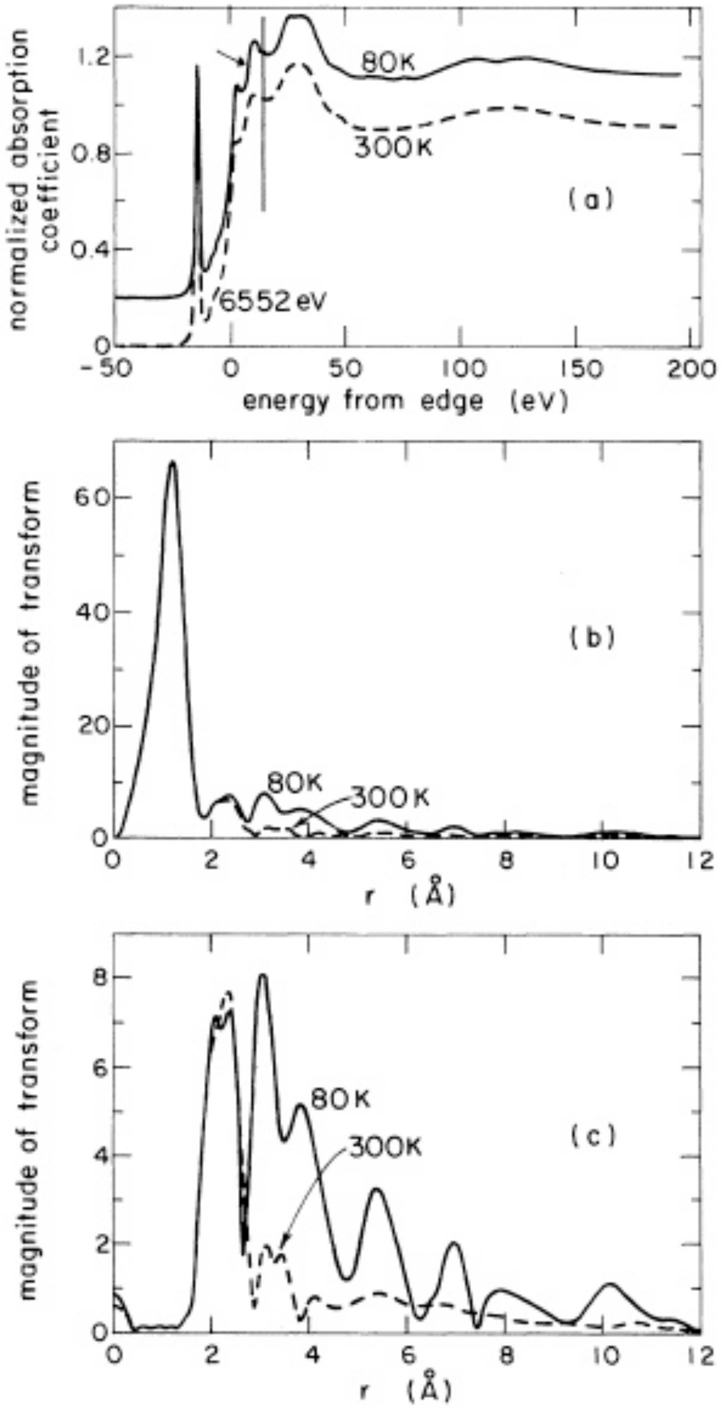
expt.

Solid $KMnO_4$ at 80K and 300K experimental data*



the temperature sensitive fine structure over edge is single scattering from atoms beyond first shell with large DWFs

* G Bunker thesis 1984



XANES landscape is from SS+MS
among nearest neighbor tetrahedron
SS from distant atoms adds
temp dependent fine structure

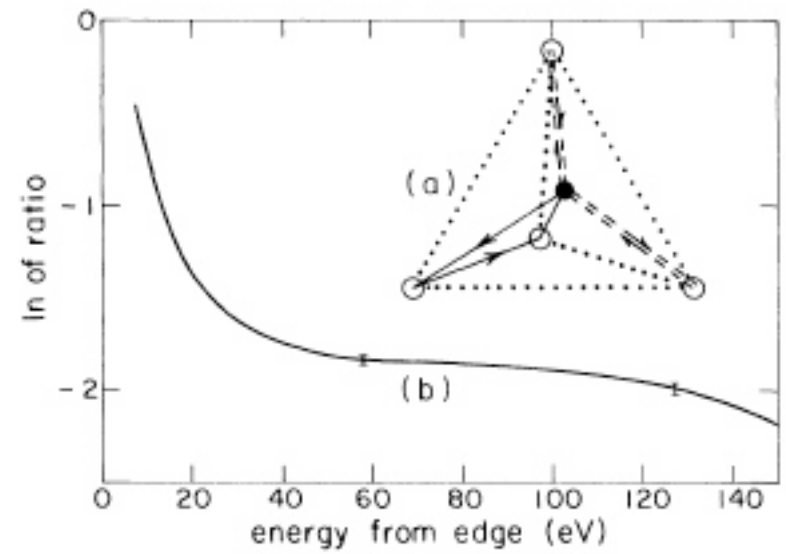
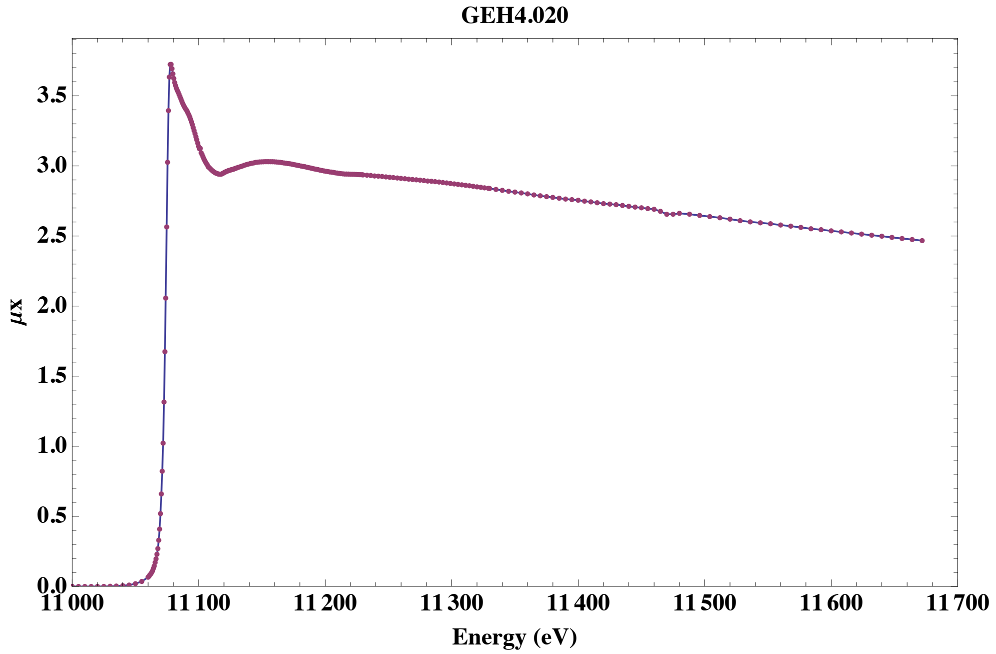
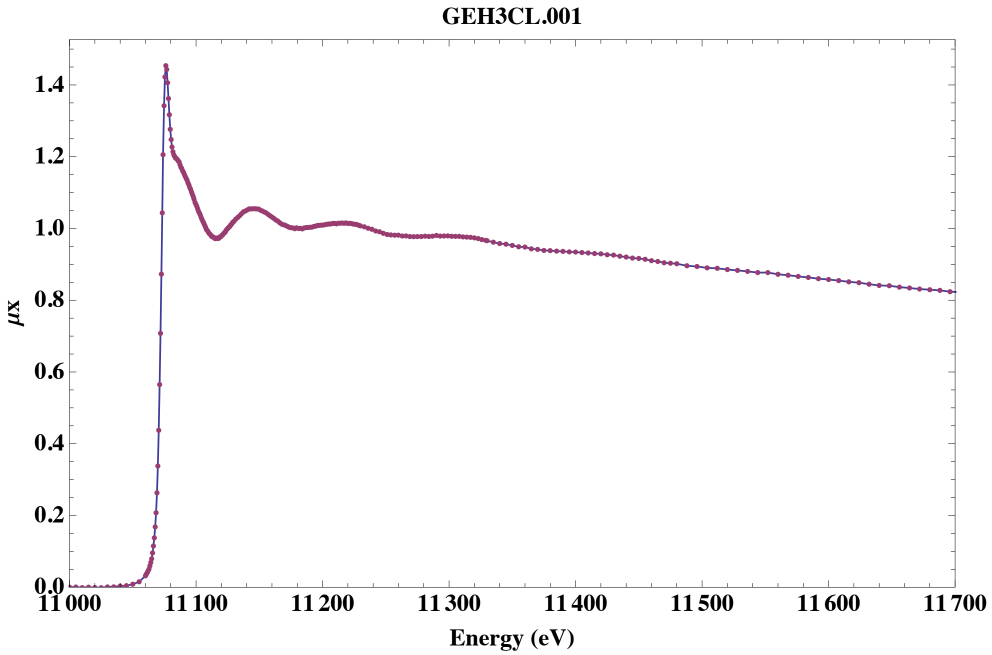


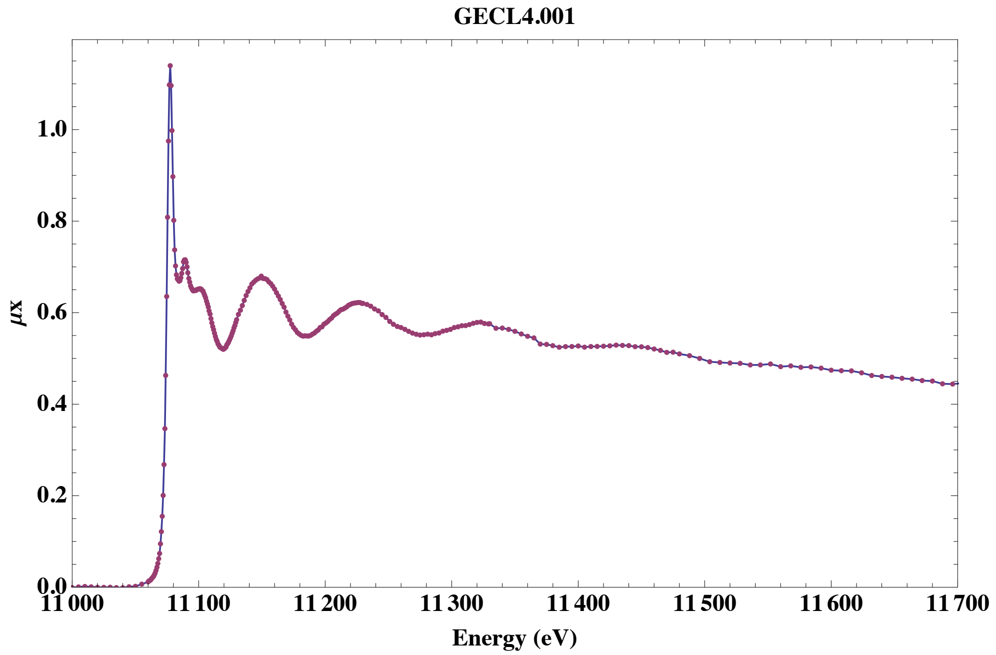
FIG. 2. (a) The two multiple-scattering paths that contribute to the second peak in the Fourier transform of $KMnO_4$, denoted by solid and dashed lines. The black dot is Mn, and the open dots are O atoms. (b) The logarithm of the ratio of the *k* dependence of the amplitudes of the first (SS) peak to the second (MS) peak of Fig. 1(b), plotted vs energy from the edge.

Bunker and Stern
PRL **52,** 22 (1984)

Molecular gases GeH4, GeH3Cl, GeCl4 tetrahedral coordination







Multiple scattering in the x-ray-absorption near-edge structure of tetrahedral Ge gases

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National Biostructures Participating Research Team, Institute for Structural and Functional Studies, University City Science Center, Suite 320, 3401 Market Street, Philadelphia, Pennsylvania 19104

R. A. Forman and J. J. Ritter
National Institute of Standards and Technology, Gaithersburg, Maryland 20899
(Received 27 May 1988)

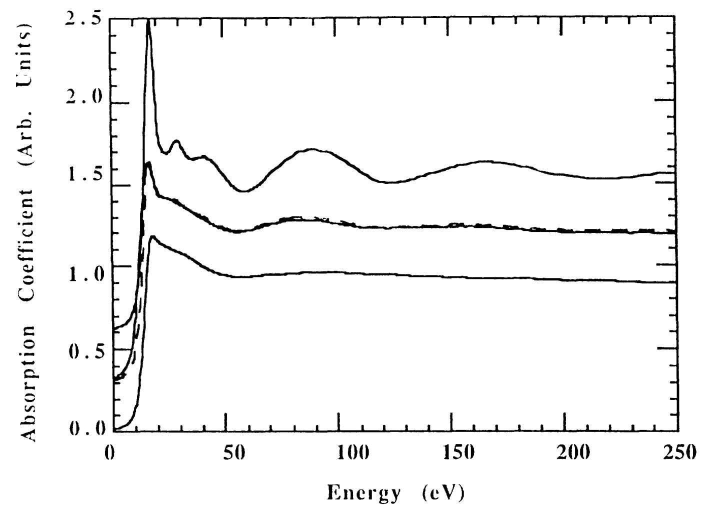
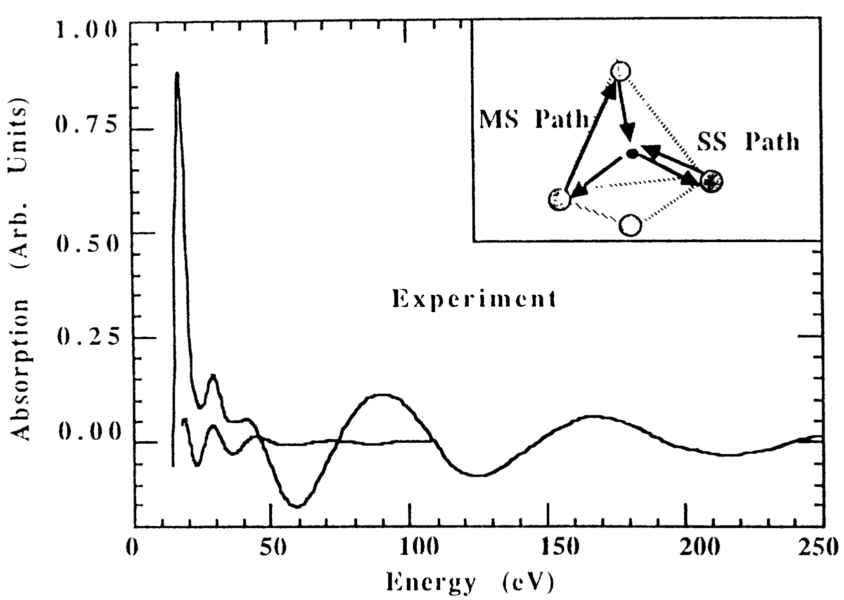


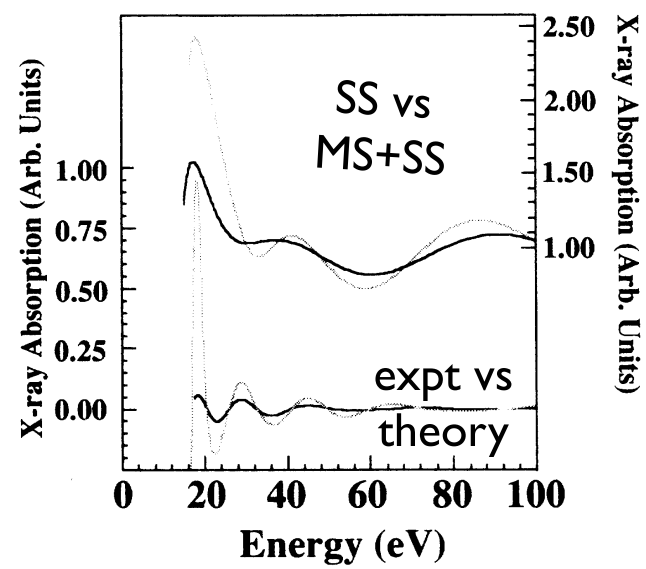
FIG. 1. Measured x-ray absorption spectra of, from top to bottom, $GeCl_4$, GeH_3Cl, and GeH_4. Data have been normalized and have had a linear pre-edge background removed. The dashed curve is an approximation of GeH_3Cl made by a linear superposition of $GeCl_4$ and GeH_4 as described in the text. Deviation between the solid and dashed lines for GeH_3Cl is due to multiple scattering.

GeCl4 vs GeH3Cl vs GeH4

SS is additive; MS is not

MS ~ [GeCl4]-3[GeH4]-4[GeH3Cl]





Same features in ZnS4 proteins!

Data Collection

- experimental requirements
- sources
- optics

XAFS experimental requirements

- suitable sample (depends on measurement mode)
- intense broad-band or scannable source
- monochromatic (~ 1 eV bandwidth), scannable beam, energy suitable for elements of interest
- suitable detectors (depends on measurement mode)
- special equipment (cryostats, goniometers..)

Advances: X-ray Sources

- Third generation sources
  - APS, ESRF, SPRing8, ALS…
- Insertion devices
  - undulators and wigglers
- Beamlines
  - High flux, high stability beamlines
  - **Full beam (>10^{13} photons/sec) into < 20 micron by 100 micron spot**
  - **Bend magnet fluxes into micron sized spots**
  - High-energy capability - highly penetrating x-rays

Synchrotron Radiation

- What is "Synchrotron Radiation"?
  - Source of broad spectrum light from infrared through x-ray wavelengths
  - Unique properties
  - Available through dedicated national user facilities
  - World-class facility in our backyard: APS

Properties of Synchrotron Radiation

- Broad energy (wavelength) spectrum extends from infra-red into x-ray region. Best x-ray source available at present for demanding applications.
- Tunable (selectable) energy (wavelength)
- Very high intensity compared to conventional sources
- Highly collimated beams (in one or two directions)
- Linear, circular polarization, elliptical
- Brilliance: high flux, small angular divergence, small source size

Advanced Photon Source

Synchrotron Radiation Facilities

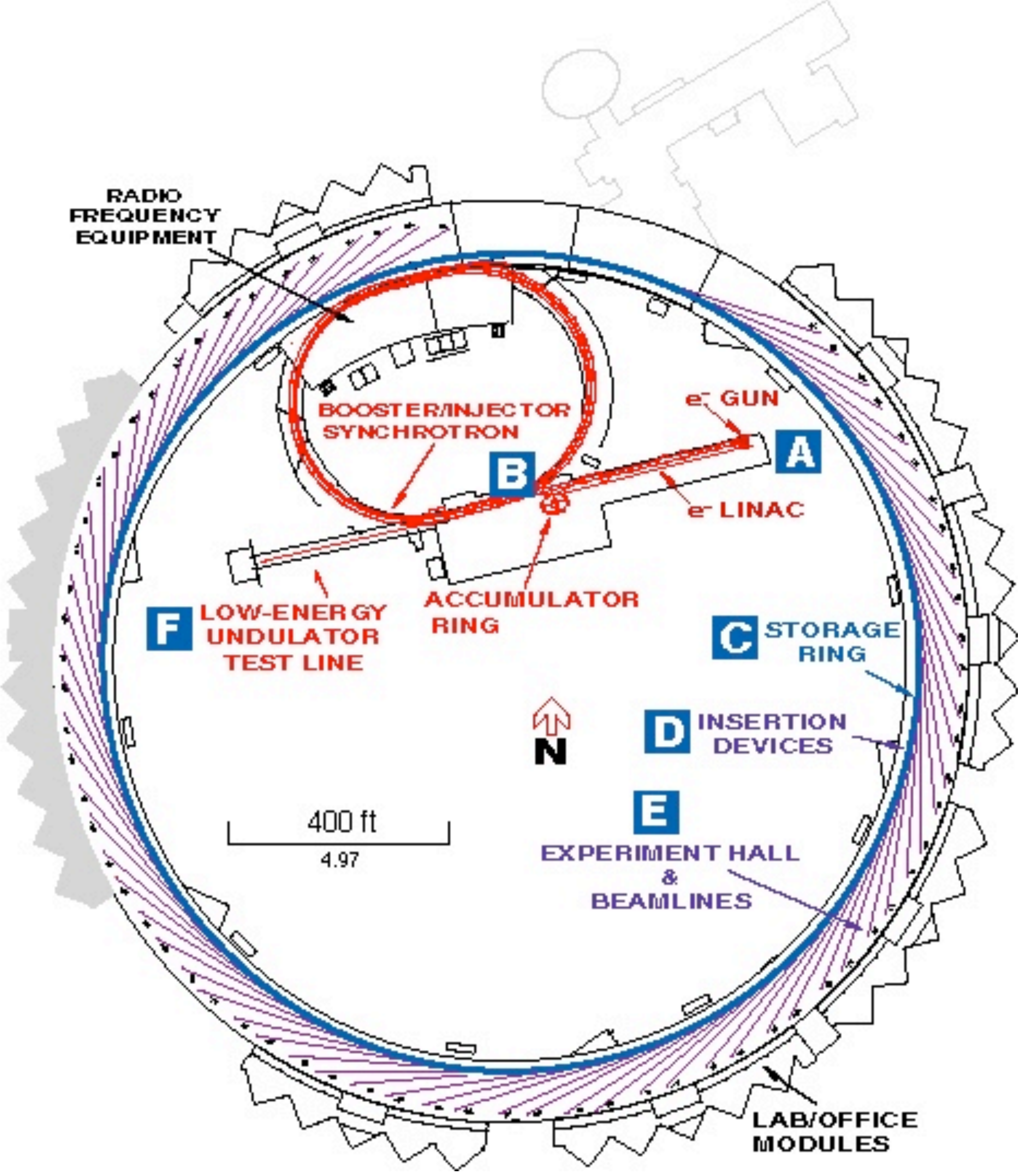
- Uses technologies developed by particle physicists and complementary technologies to produce x-ray beams for studies of materials, stuff, and whatnot.

- Major difference between HEP and SyncRad rings: facilities are designed to **enhance** Synchrotron Radiation, not minimize it. Use electrons/positrons, not protons as at Tevatron, CERN's Large Hadron Collider. Low mass -> copious radiation.

- Extensive applications in biology, chemistry, physics, engineering, materials science, environmental science, archaeology… sorry, no metaphysics.

- They are complex multi-user facilities in which 50-100 diverse experiments may be going on simultaneously with different groups. Great for cross-disciplinary pollenization.

inside the APS



Inside the ring

The electrons circulate at speeds extremely close to the speedof light within an evacuated beam pipe.

Dipole bend magnets, and quadrupole, sextupole, and octupole magnets bend and focus the electron beam, to maintain the proper electron beam dynamics as the beam continuously recirculates.

Electron beam energy is replenished by "surfing" through RF cavities. Sometimes smaller "damping rings" with bends of sharp radius are used to damp out the momentum spread of the beam.

The electron beam stays in the machine producing x-rays for many hours before it is replenished. "Top-off mode" also may be used to preserve stable beam intensity. The x-ray photons produced are conveyed to beamlines for experiments.

Sources

- Bend Magnets
- Insertion Devices
  - Wigglers
  - Undulators
    - Planar
    - Helical
    - Fixed magnet
    - electromagnetic

Insertion Devices

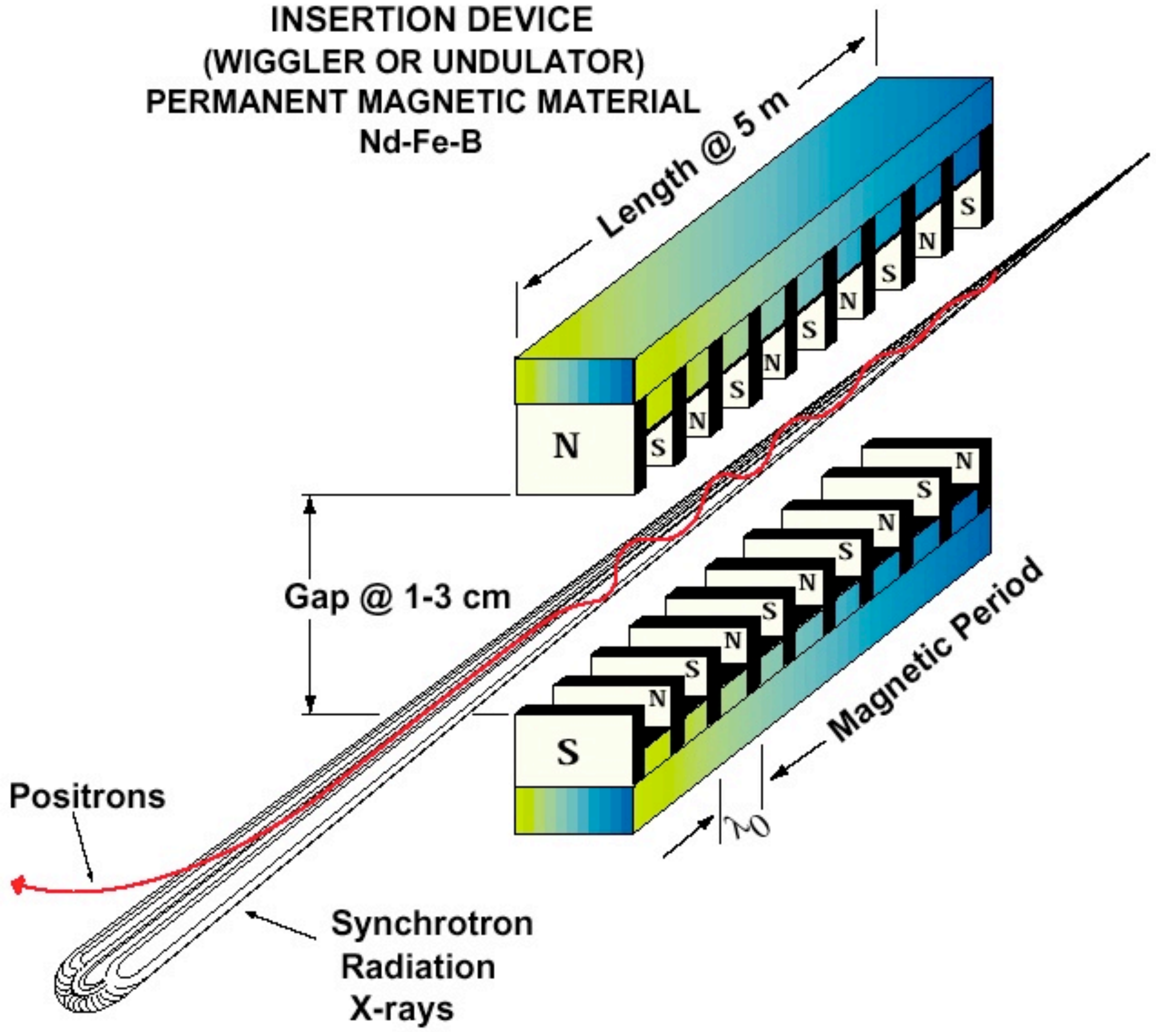
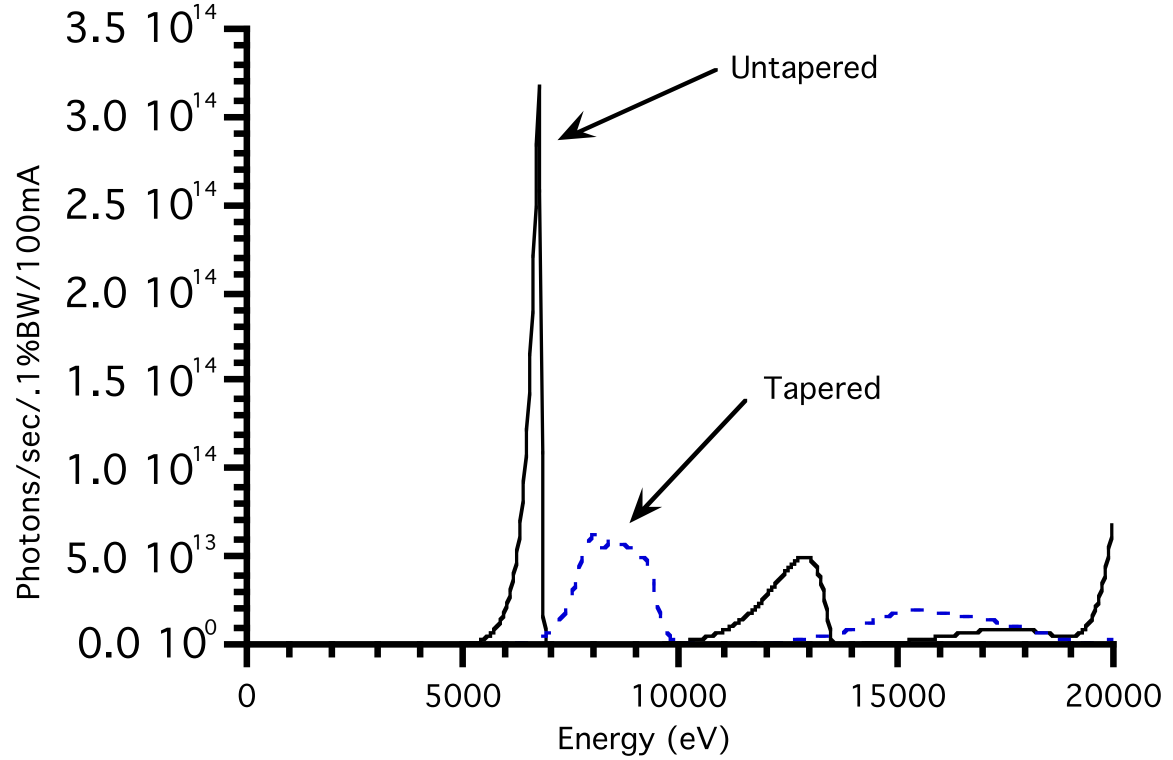


figure courtesy of APS

Spectrum APS Undulator A



The x-ray frequency of the fundamental is given approximately by $2\,\gamma^2\ \Omega_w\,/(1+K^2/2 + \gamma^2\,\theta_0^2)$. Here $K=\gamma\delta_w$, where $\delta_w=\lambda_0/2\pi\rho_0$, λ_0 is the undulator period, and ρ_0 is the bend radius corresponding to the peak magnetic field.

Spectral Brilliance of Synchrotron Radiation Sources

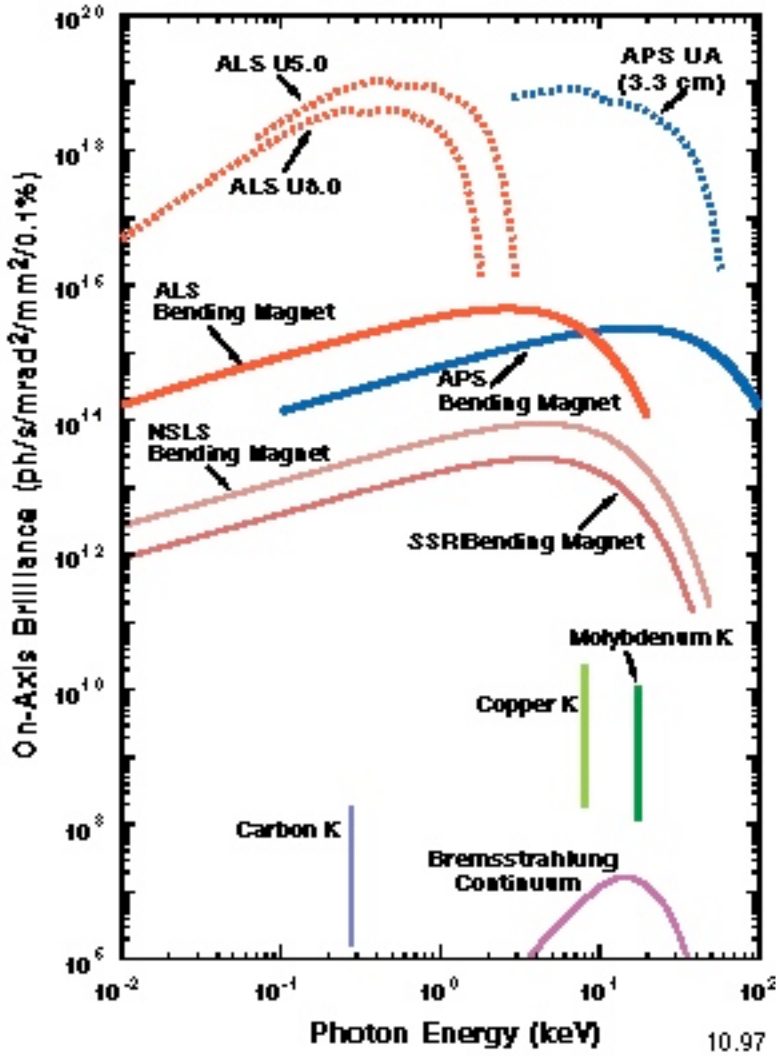
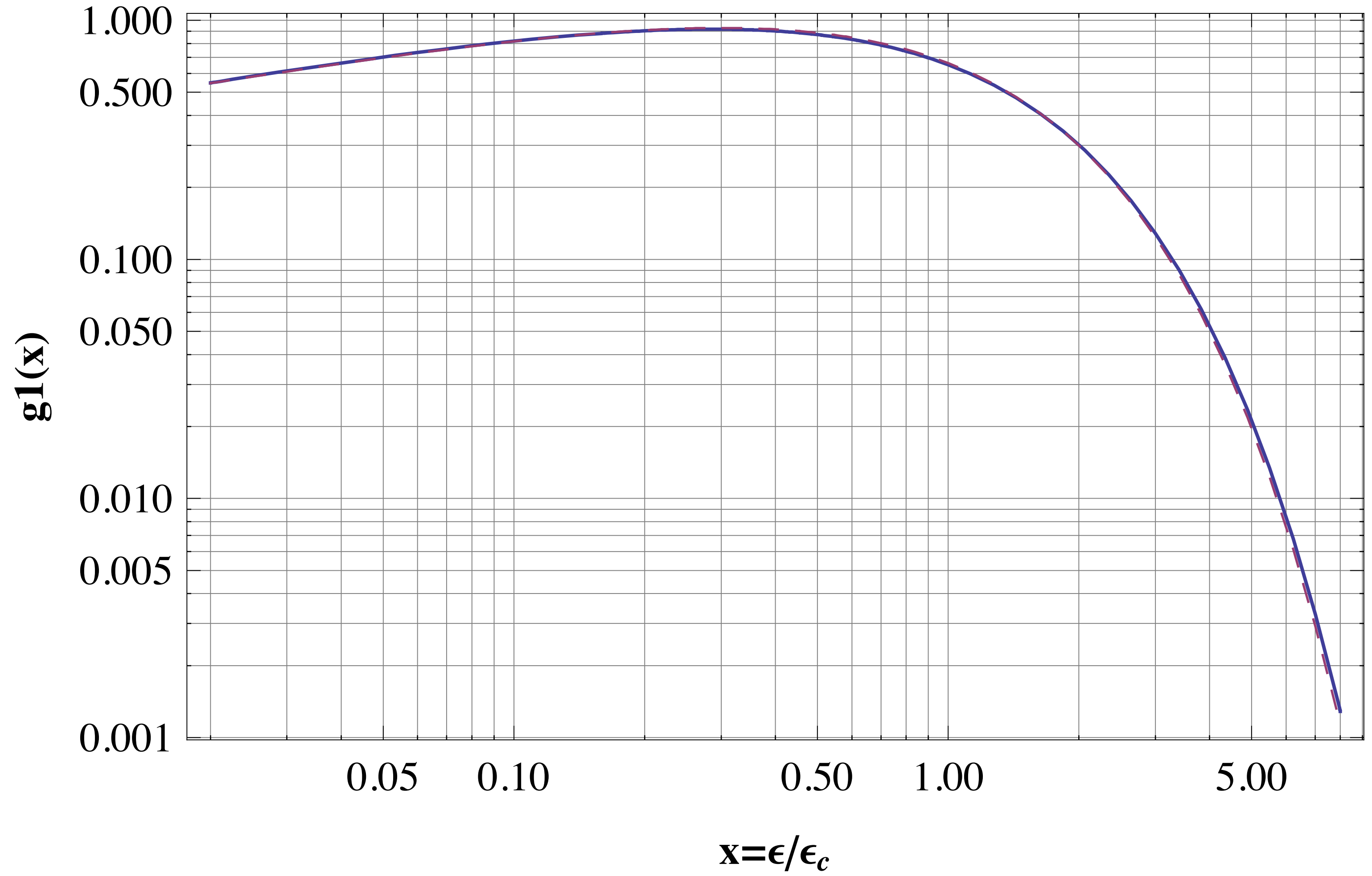


figure courtesy of APS

universal curve



critical energy ~19.5 keV for APS bend magnet

for wiggler, scale by number of periods

g1(x)~ 1.8 x^.3 exp(-x)

flux calculation
bend magnets/wigglers

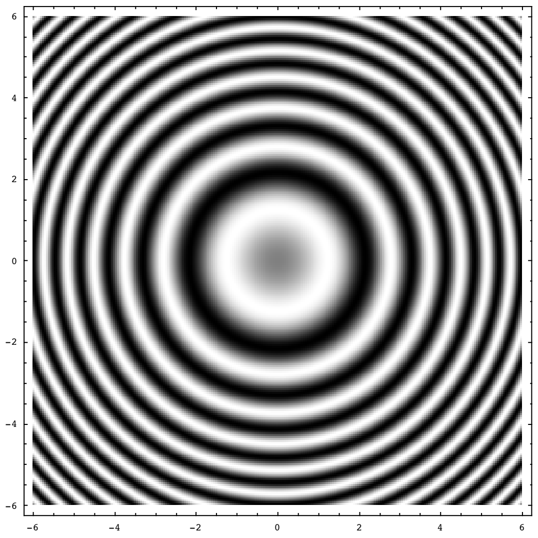
The critical energy is $\epsilon_c = \gamma^3(3hc)/(4\pi\rho)$ where $\gamma = E/mc^2$, E is the electron beam energy, ρ is the bend radius of the electron path, m is the electron mass, c is the speed of light, h is Planck's constant ($hc \approx 1.24 \cdot 10^{-9}$ KeV meter). The bend radius ρ (meters) is related to the magnetic field strength (Tesla) and the beam energy (GeV) by $\rho \approx 3.336E/B$.

For example, consider a 7 GeV beam energy, 100 milliamps of beam current, with a 0.6 Tesla bend magnet field, and we collect 2 cm horizontal width of the beam at 20 meters (1 mrad), and all of the beam in the vertical direction. The bend radius is then $3.336 \cdot 7/0.6 \approx 39$ meters; with $\gamma \approx 7000$ MeV/.511 MeV $\approx 1.37 \cdot 10^4$, we have a critical energy of $(1.37 \cdot 10^4)^3(3 \cdot 1.24 \cdot 10^{-9})/(4\pi \cdot 39) \approx 19.5$ KeV. Then the flux at 10 KeV in a 10^{-3} bandwidth (e.g. 10 eV @ 10 KeV) can be calculated as $1(\mathrm{mrad}) \cdot 100(\mathrm{mA}) \cdot 1.256 \cdot 10^7 \cdot 1.37 \cdot 10^4 \cdot 1.8 \cdot (10/19.5)^{0.3} \mathrm{e}^{-10/19.5} \approx 1.5 \cdot 10^{13}$ photons/sec. In a 1 eV bandwidth ($10^{-4}\Delta\epsilon/\epsilon$) it would be $1.5 \cdot 10^{12}$ photons/sec.

BioCAT ID line

Advanced: Microfocus beams

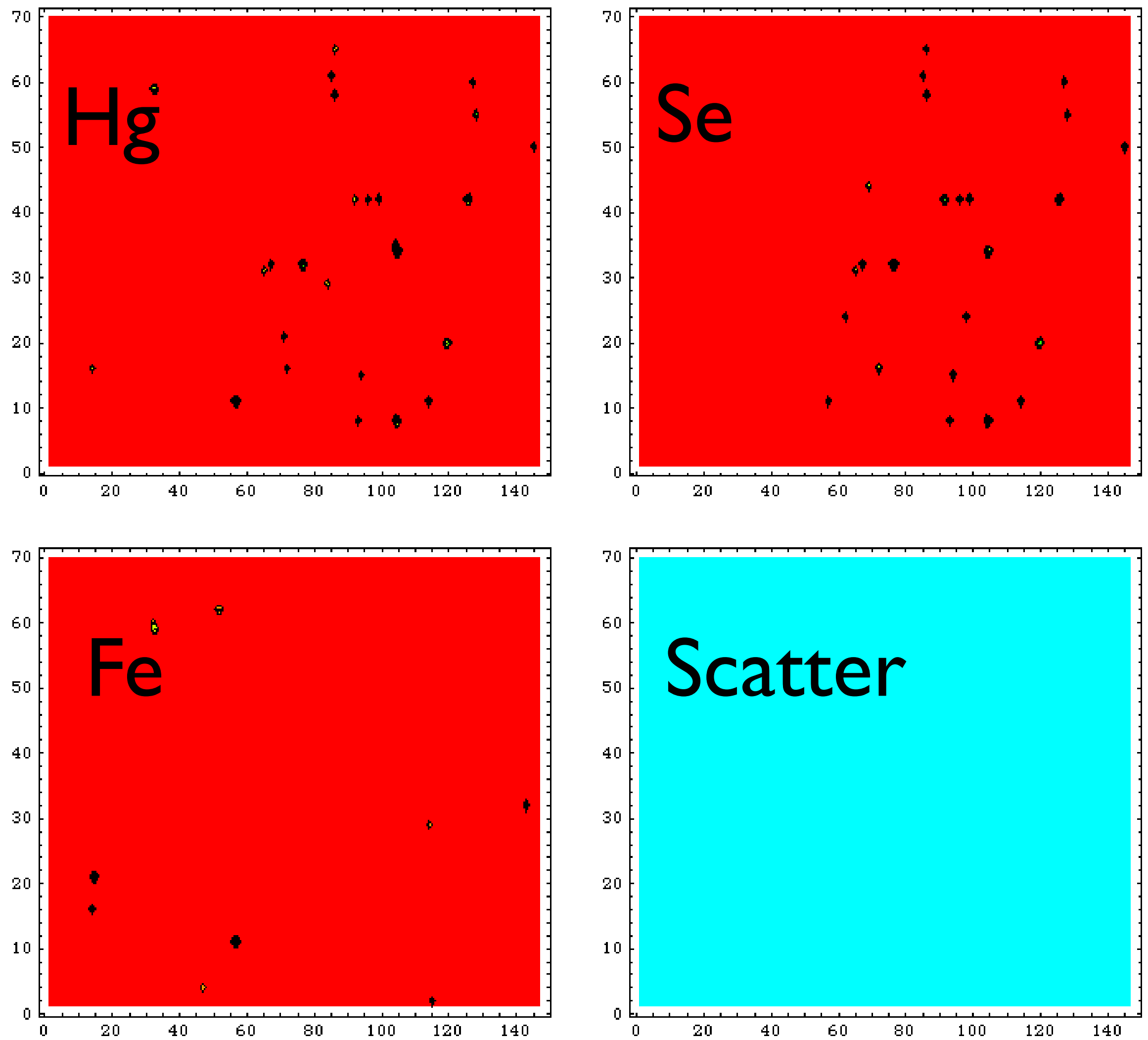
X-ray Kirkpatrick Baez (KB)
mirror pairs and
X-ray Fresnel zone plates
in combination with undulators
can provide micron-scale
to sub-micron beams
with fluxes comparable to
bend magnet beamlines



Advantages of small beam sizes

- Can study small ordered domains and small crystals
- Makes x-ray analyzers practical
    - **Medium resolution → high throughput for dilute samples (multilayer and bent laue analyzers)**
    - **High resolution → x-ray fluorescence analysis - distinguish atoms in different chemical states (Cramer, Bergmann)**
    - X-ray raman: low energy edges at high energy
- **Small volume stopped flow → better signal averaging**
- Photoexcitation - laser beam intersects x-ray beam

Hg/Se/Fe/scatter maps of
cormorant liver 20 micron sections

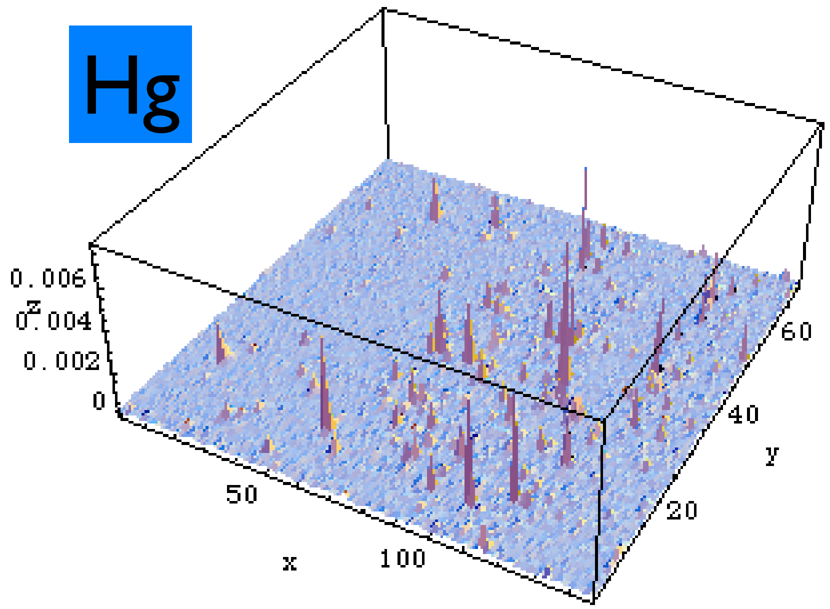


Hg and Se show up in the same hot spots

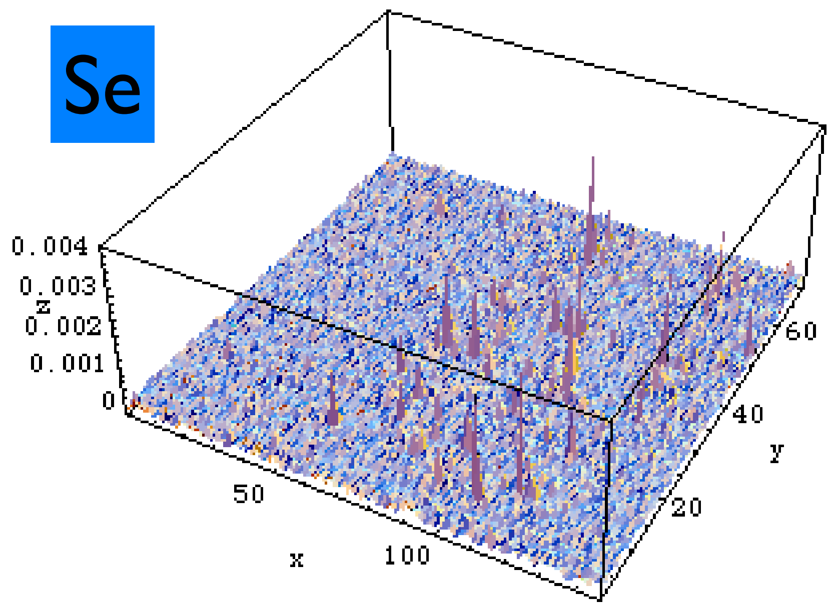
(Bunker, Karanfil, Bischoff, Barrea)

Hg and Se are highly localized in hot spots

Hg

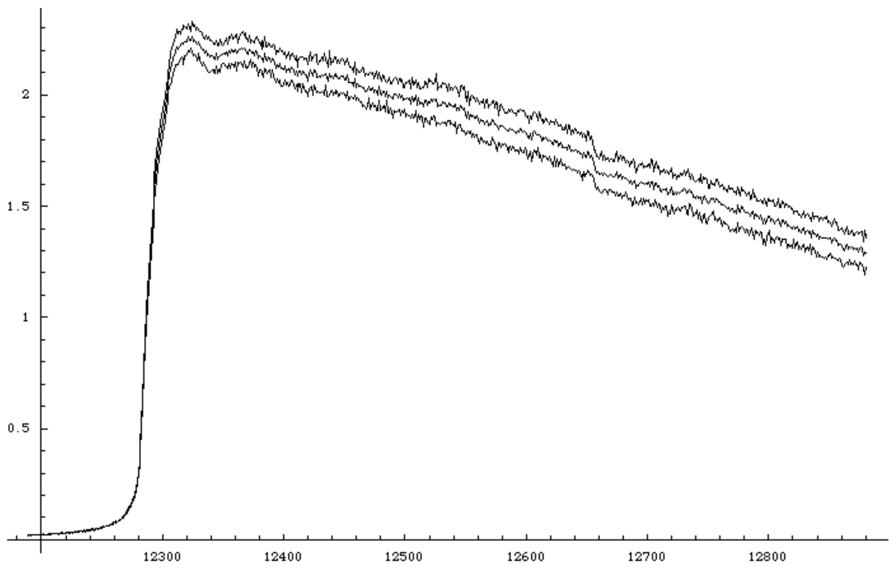


Se

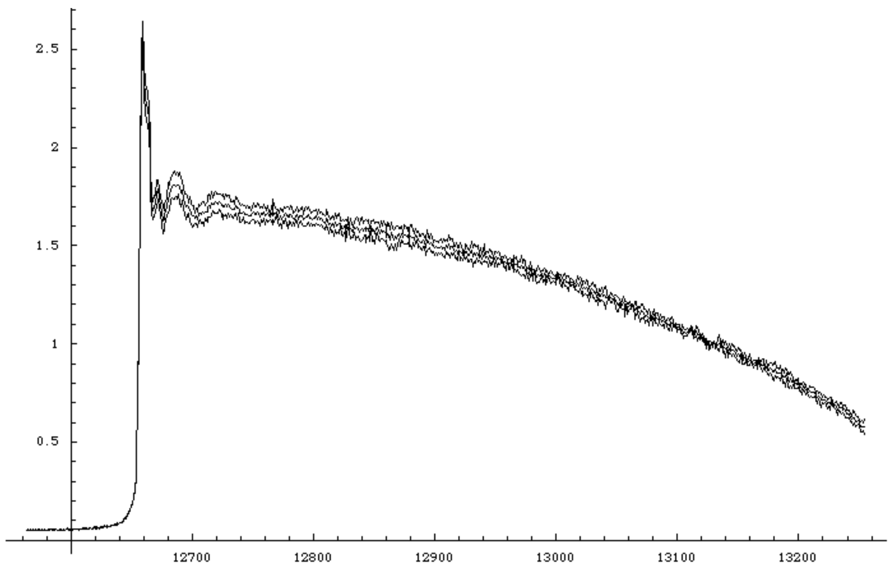


Initial XAFS spectra on hot spot

Hg



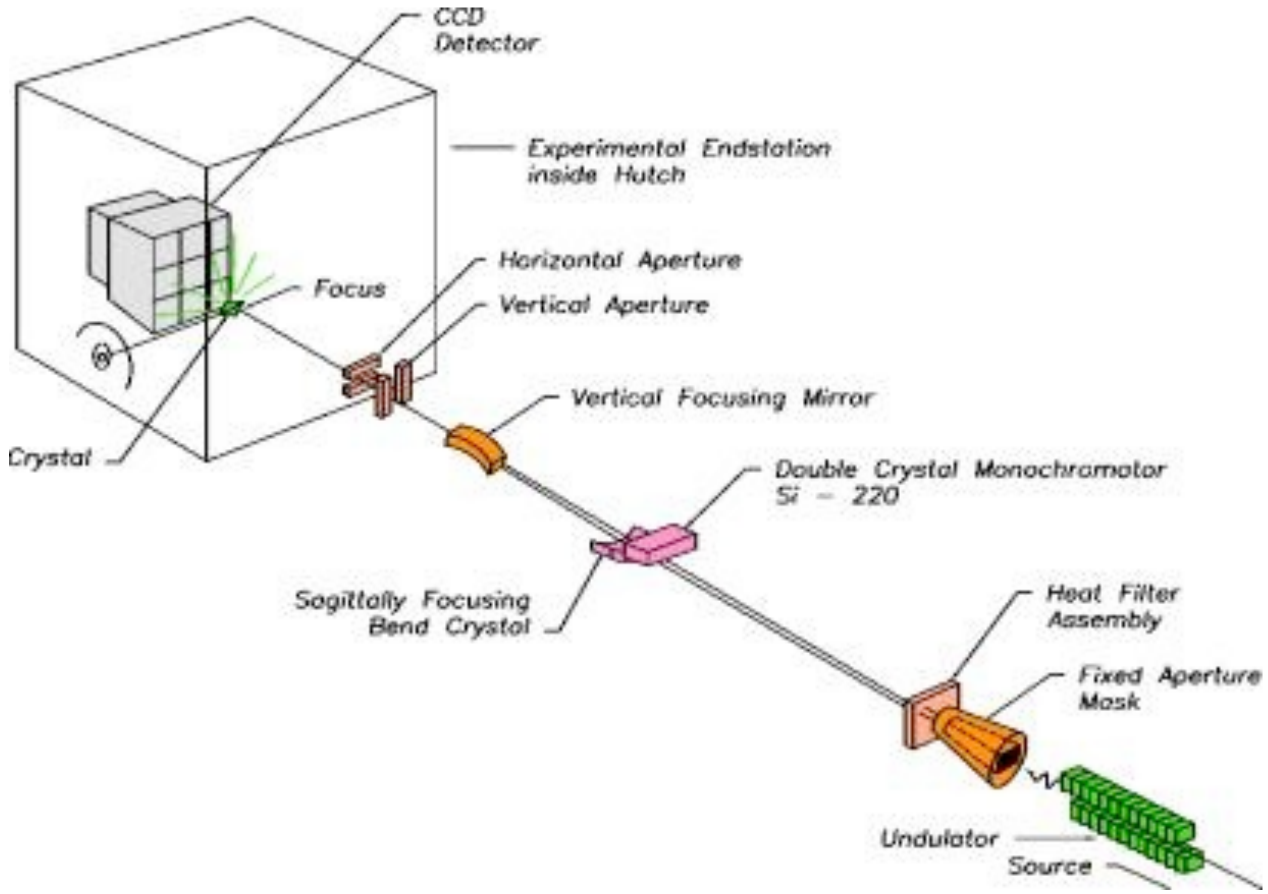
Se



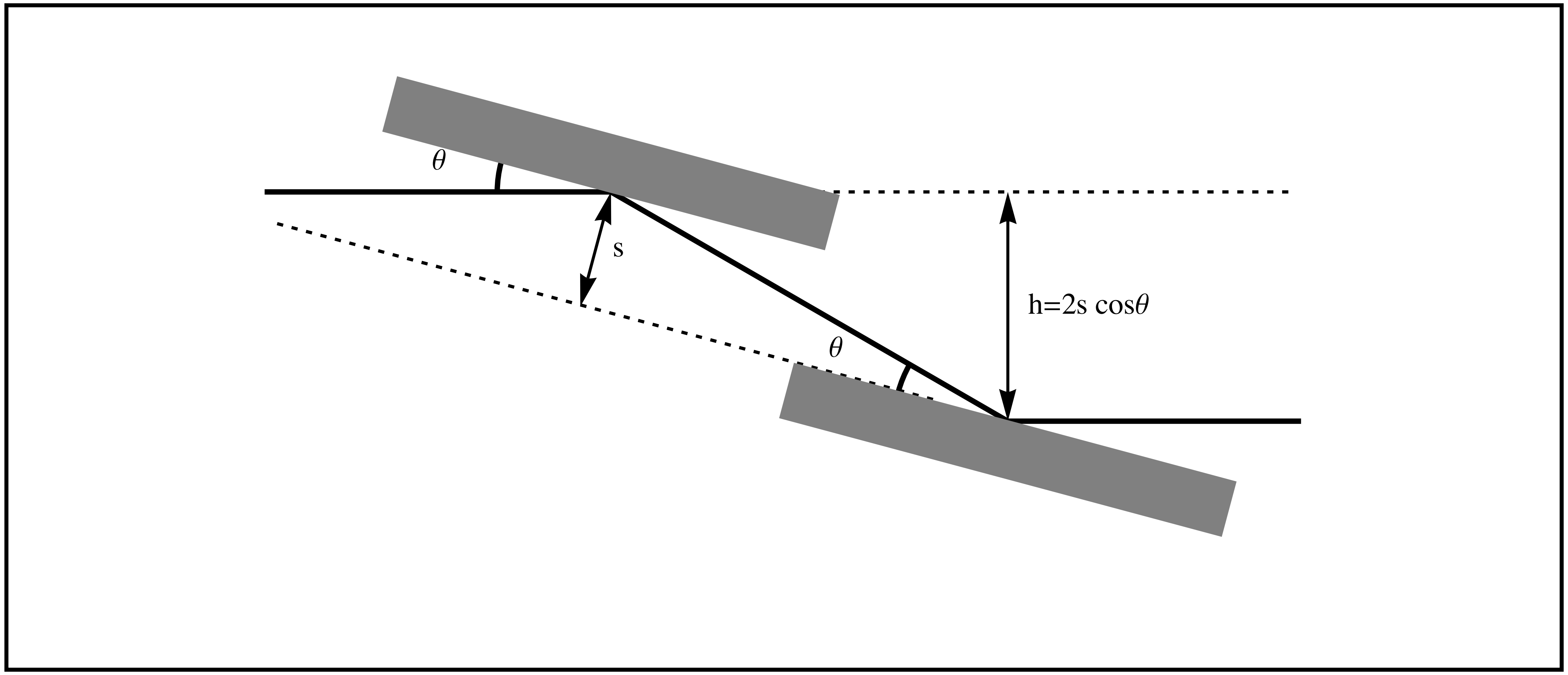
source | (mirror) | monochromator | (mirror) | slits | detectors

Collimating mirror is sometimes used to match source to acceptance of mono

mirror following mono is often used for harmonic rejection or focussing



graphic courtesy of SER-CAT


θ
s
θ
h=2s cosθ

Experimental modes

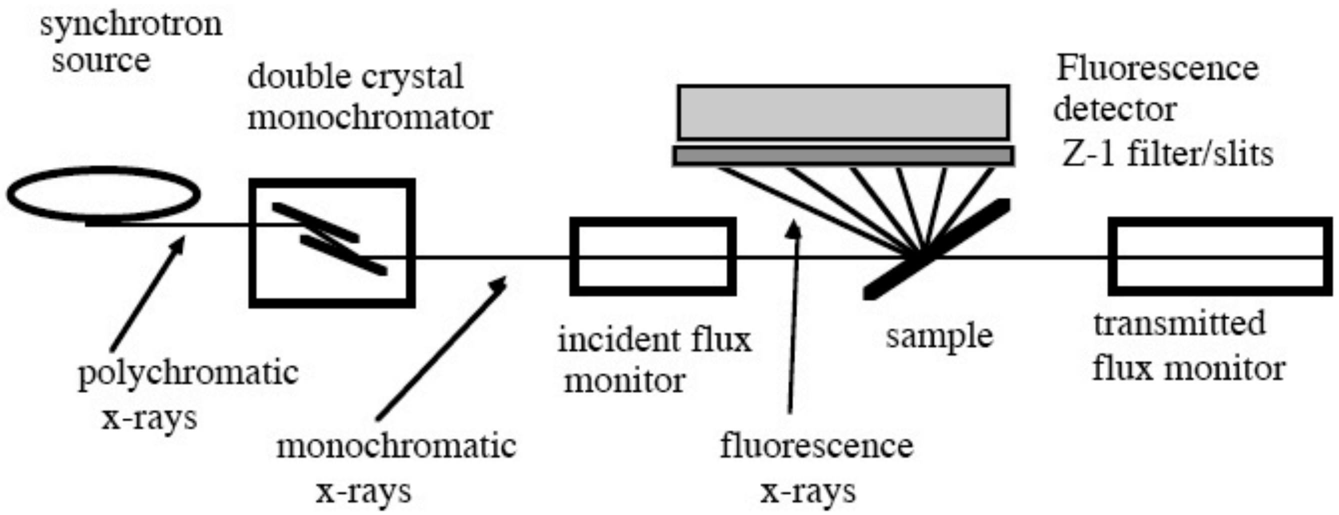


Figure 1 – Schematic XAFS experiment

Detection

- Transmission mode
- Fluorescence mode
- Electron yield
- Inelastic X-ray Scattering

Geometry

- Oriented e.g. single crystal
- Magic Angle Spinning
- Total External Reflection
- Grazing (glancing) incidence

Which mode to use?

- concentrated, not too thick: => use transmission
  want edge step ~1.0 (>0.1, <2.0)
- concentrated, thick: => use electron yield, total external reflection fluorescence, or apply fluorescence corrections numerically
- dilute samples: (< .1 absorption length edge step) use fluorescence detection
- microbeams can used to measure small grains which may be concentrated even if sample is dilute on average (still must worry about particle size effects though)

Checklist: "HALO" Mnemonic

- **H**armonics - get rid of them using mirrors, detuning, or other means, especially for thick transmission samples.
- **A**lignment - the beam should only see homogeneous sample and windows between the I_0 and I (or I_f) detectors
- **L**inearity - ionization chambers must be plateaued. Other detectors may need deadtime corrections
- **O**ffsets - dark currents must be measured and subtracted to compensate for drifts

more hints

- during the experiment check the apparatus (linearity etc) yourself; don't assume everything is OK
- in fluorescence run a blank sample without the element of interest in it
- calculate how much signal and background to expect before the experiment; calculate "effective counts"
- be aware of and avoid sample self-absorption, particle size, and thickness effects (http://gbxafs.iit.edu/training/XAFS_sample_prep.pdf)
- bring enough experimenters that you can use the beam time effectively 24/7

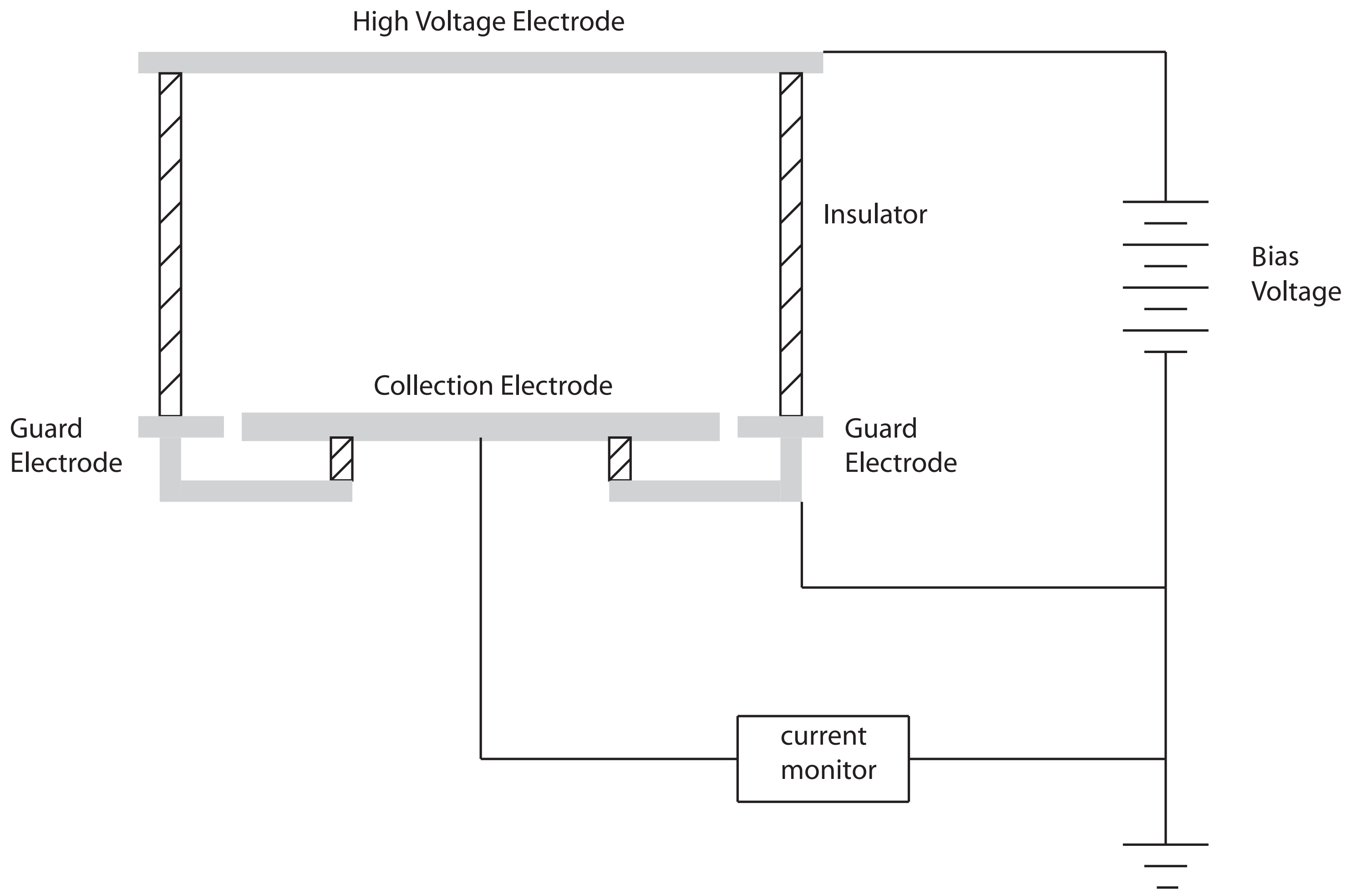
Advances: Detectors

- Faster solid state detectors & electronics - well suited for microfocussing expts
- Fluorescence ion chambers/soller slits work better in point focus geometry at 3rd generation sources
- Scintillator/PMT gives faster time response, larger area, lower cost than fluorescence ion chamber
- X-ray Analyzers

Standard EXAFS Detectors

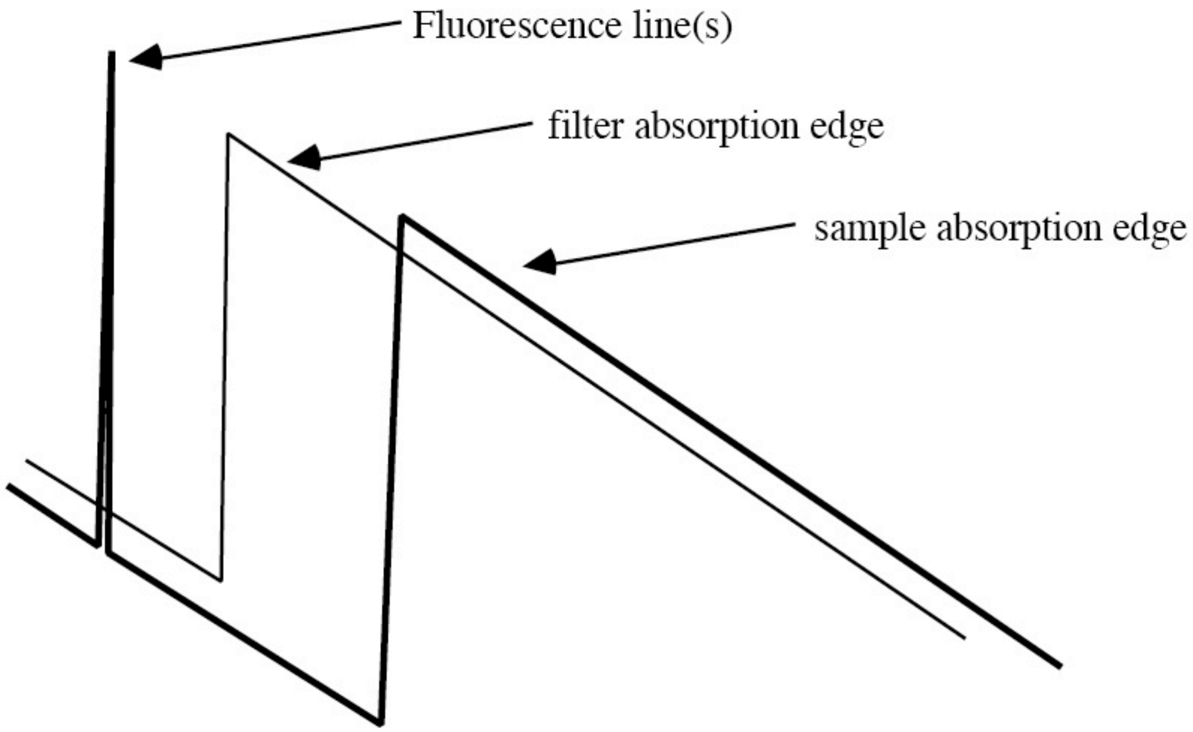
- Integrating (non-energy resolving)
  - Ionization chambers
  - Fluorescence ionization chambers (Stern/Heald)
  - PIN diodes/PIPS detectors
- Pulse counting (energy resolving)
  - Solid State (Ge/Si) detectors
  - Silicon Drift Detectors (SDD)
  - Scintillator/Photomultiplier (PMT)
  - Proportional Counters (PC)
  - Avalanche Photodiodes (APD)

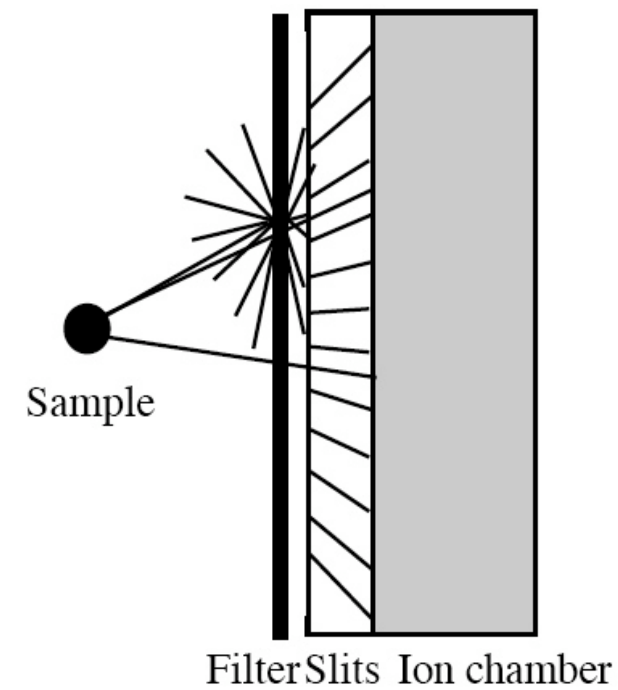
transmission
ionization chambers



Fluorescence ion chamber

Stern/Heald/Elam + Lytle

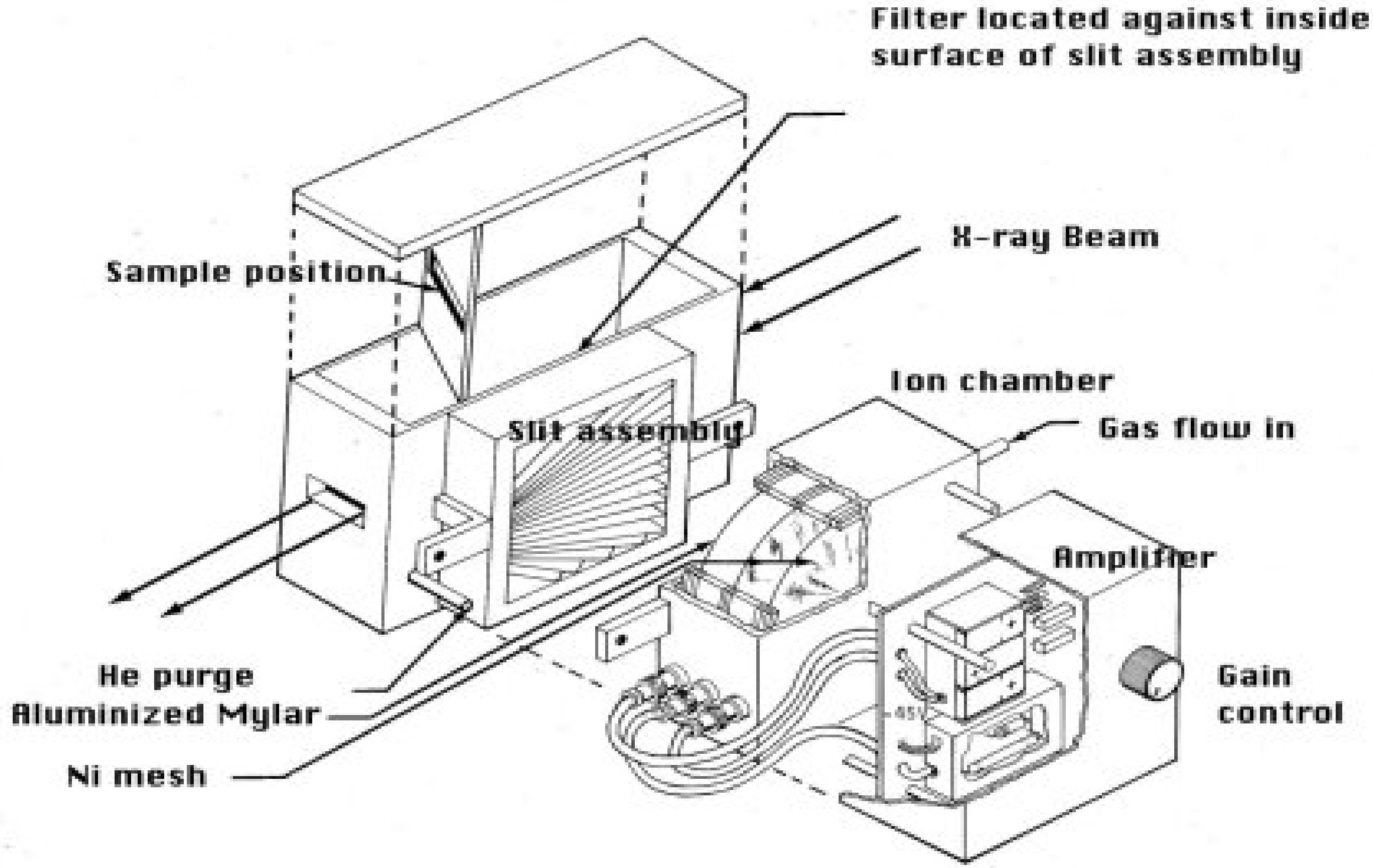




Often used with filter and soller slits to keep scattered background out of detector

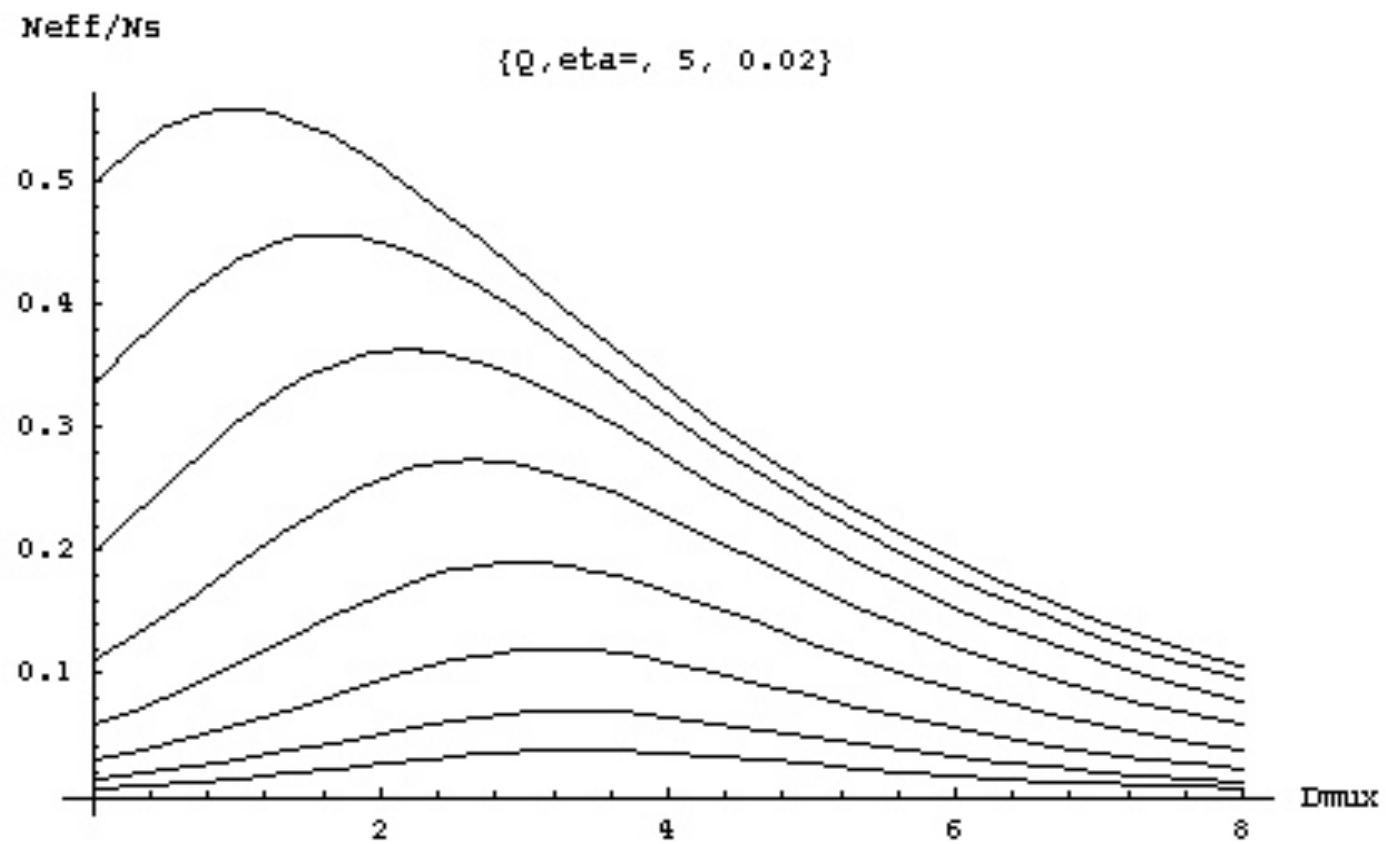
"Lytle Detector"

www.exafsco.com



Stern/Heald Detector cont'd

Limitations to common slit systems seriously degrade performance at high dilution



Even with optimized filters, efficiency drops to a few percent for large (>100) background to signal ratios

for more info see: http://gbxafs.iit.edu/training/tutorials.html
or book "Introduction to XAFS" Cambridge University Press, 2010

Multielement Germanium Detector

13 element
Canberra

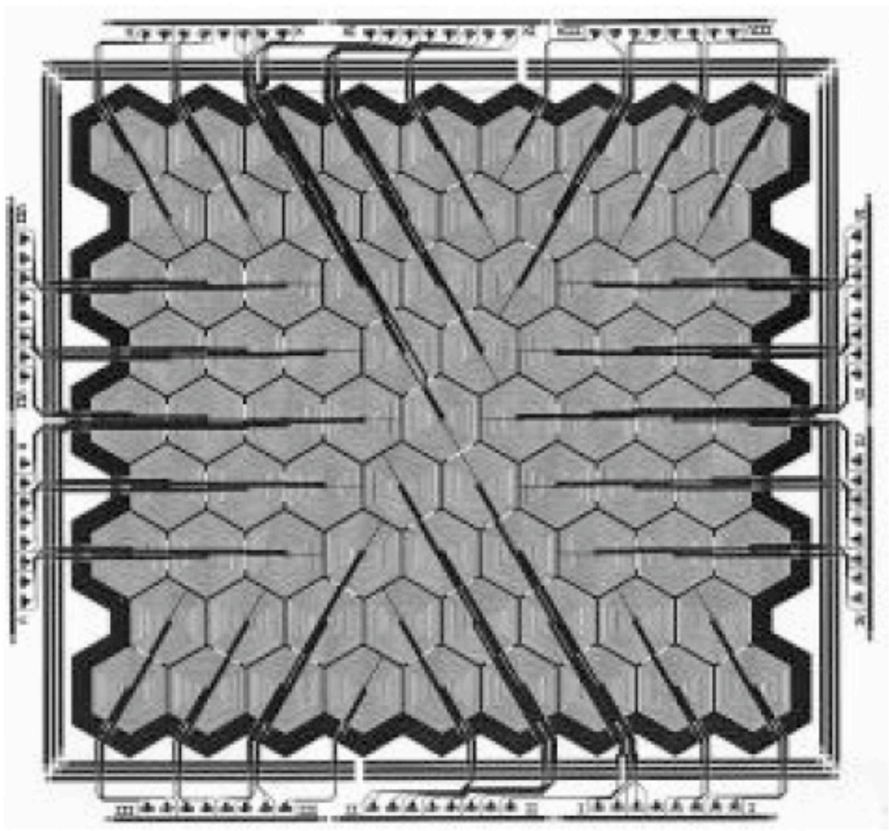
detector->
preamp->
shaping amp->
multichannel analyzer
or SCA & scaler

Maximum count rates of several hundred KHz total (signal +background)/channel.

Can use together with
Z-1 filters and Soller slits

SDD Arrays

higher count rates are under active development



77 element prototype
silicon drift detector
C. Fiorini et al

Total active area
6.7 cm^2

X-ray Analyzers

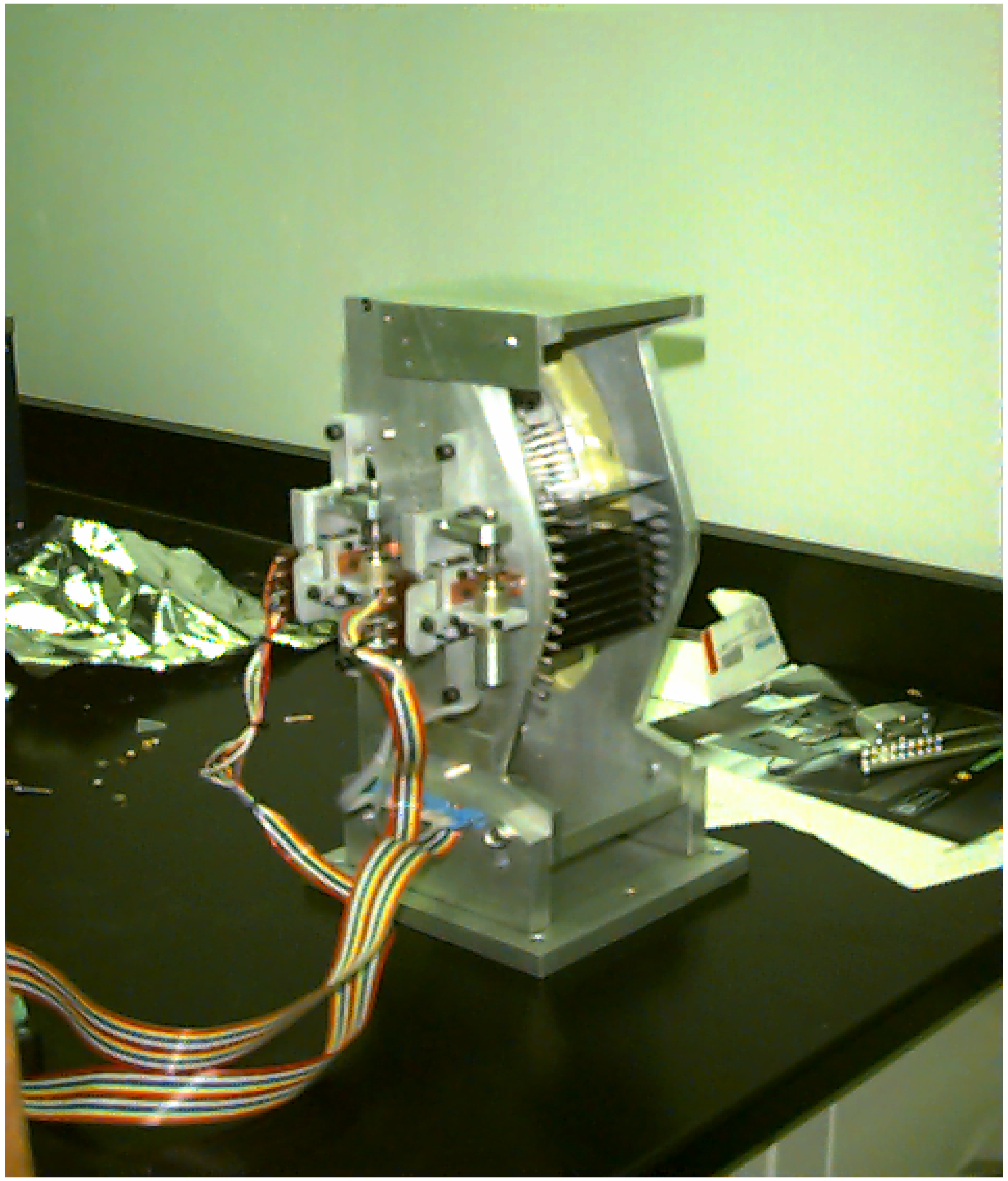
- Conventional solid state detectors can be easily saturated at high flux beamlines
- They spend most of their time counting background photons you throw out anyway
- **Multilayer, bent crystal Laue, and other analyzers eliminate background *before* it gets to detector**
- graphite log-spiral analyzer (Pease), Bragg log spiral analyzer (Attenkofer et al) are also good approaches
- Effectively no count rate limits, and good collection efficiency, or better resolution
- effectively no count rate limits from pulsed nature of source (which normally is a concern)

Multilayer Array Analyzer Detector

This device uses arrays of synthetic multilayer structures to diffract the signal and eliminate scattered background. It makes possible some experiments that are otherwise intractable

Advanced versions of these analyzers are under development (Dr. Zhang Ke)

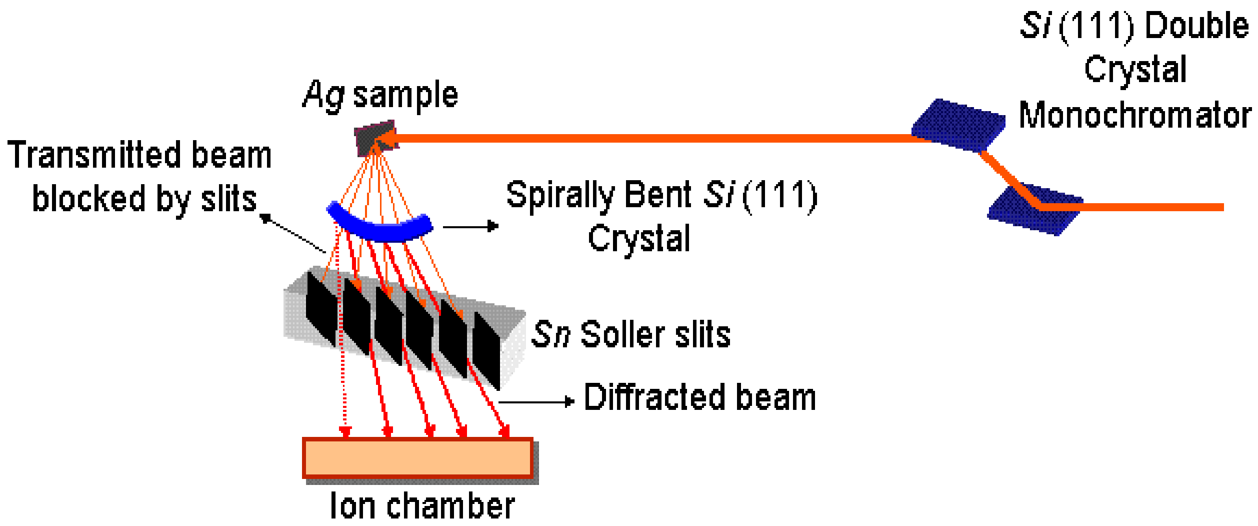
www.hdtechinc.com



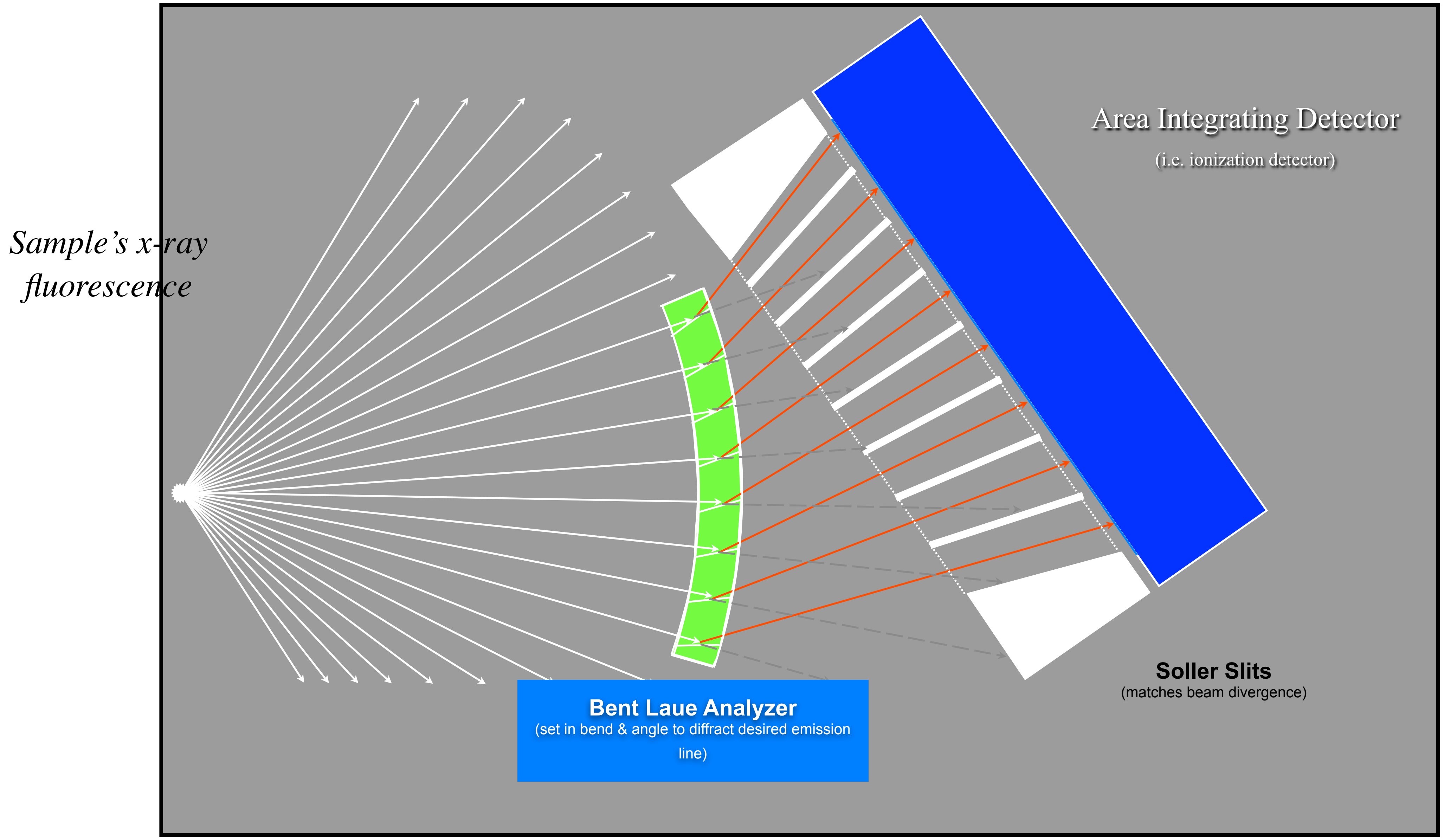
Bent Crystal Laue Analyzers

Extremely bent silicon crystals have very high efficiency and wide angular acceptance

Logarithmic spiral bent crystal

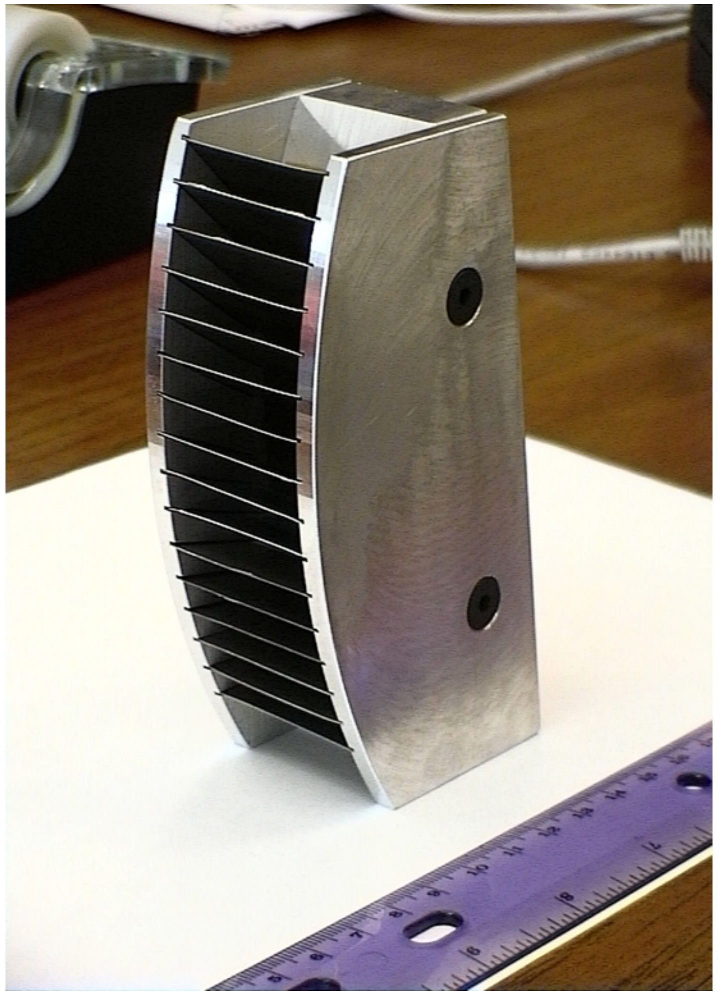


Bent Crystal Laue Analyzer



note: these require < 100 micron beam in diffraction plane for good efficiency

Bent Crystal Laue Analyzer



www.quercustech.com

Data Analysis

- Modern codes for calculating theoretical XAFS spectra are accurate enough to use to fit experimental data directly. "FEFF9" (J.J. Rehr et al) is a leading program for calculating spectra. Others are included in GNXAFS and EXCURV.
- FEFF does not analyze the data for you, however. Analysis programs of various kinds (e.g. Artemis/Athena,...) use FEFF-calculated spectra or other data to fit the experimental spectra by perturbing from a guess structure. Parameterizing the fitting process can be quite involved.
- Another approach (Dimakis & Bunker) uses FEFF as a subroutine and combines it with other info (e.g. DFT calculations) to estimate DWFS. Computationally intensive (but computers are cheap).

Data Reduction

- Apply instrumental Corrections (e.g. detector dead-time)
- Normalize data to unit edge step (compensates for sample concentration/thickness)
- Convert from E -> k space (makes oscillations more uniform spatial frequency, for BKG and Fourier transform)
- Subtract background using cubic splines or other methods
- Weight data with k^n, $1 <= n <= 3$; (compensates for amplitude decay)
- Fourier transform to distinguish shells at different distances
- Fourier Filter to isolate shells (optional)

Example: Raw XAFS data

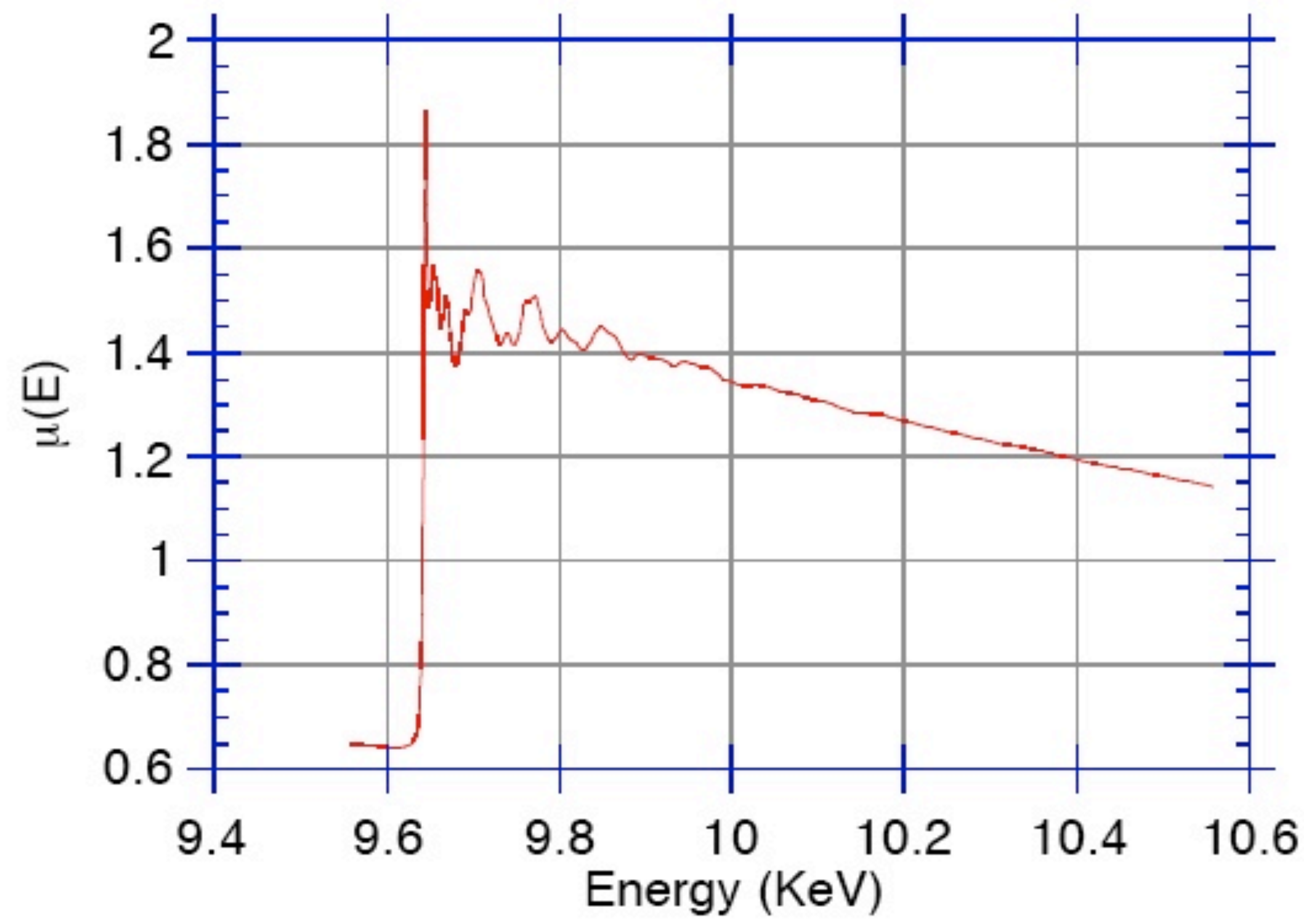
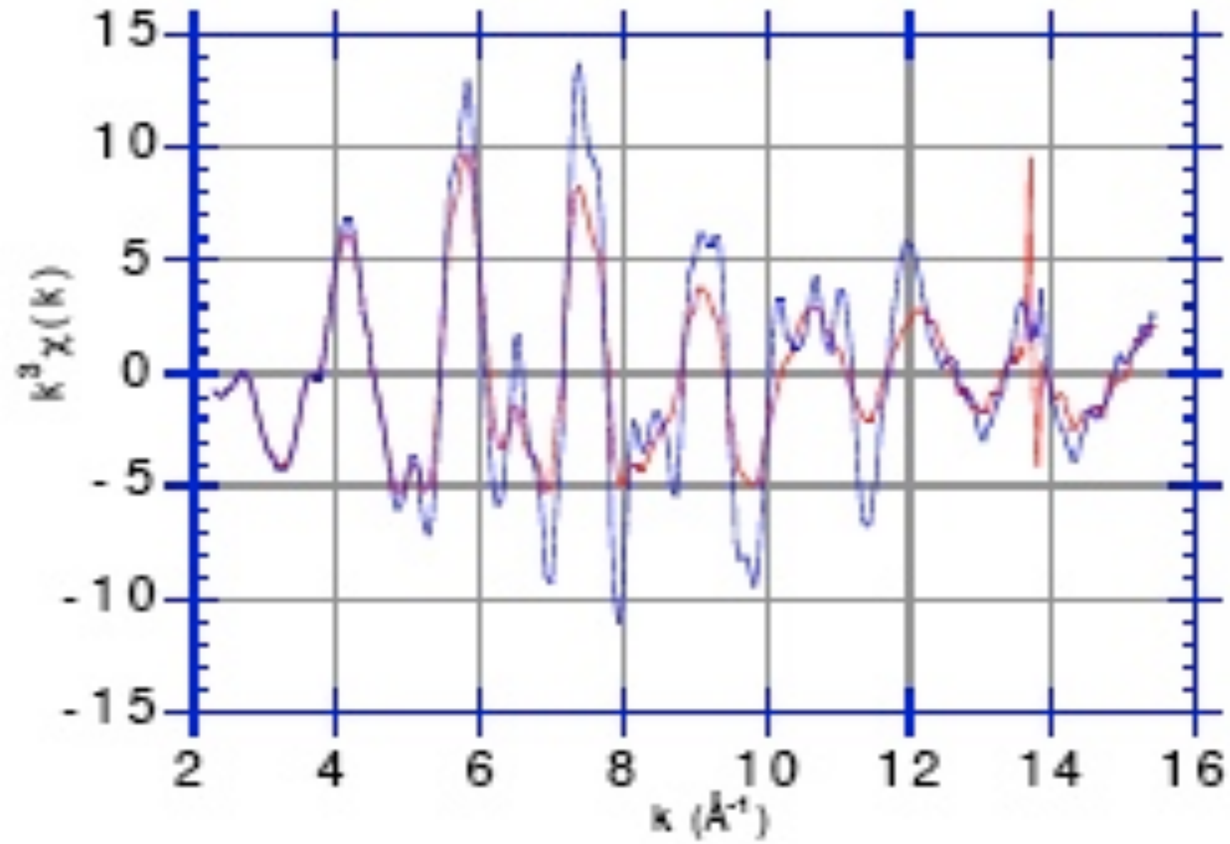


Figure 2 – Transmission XAFS spectrum of ZnS

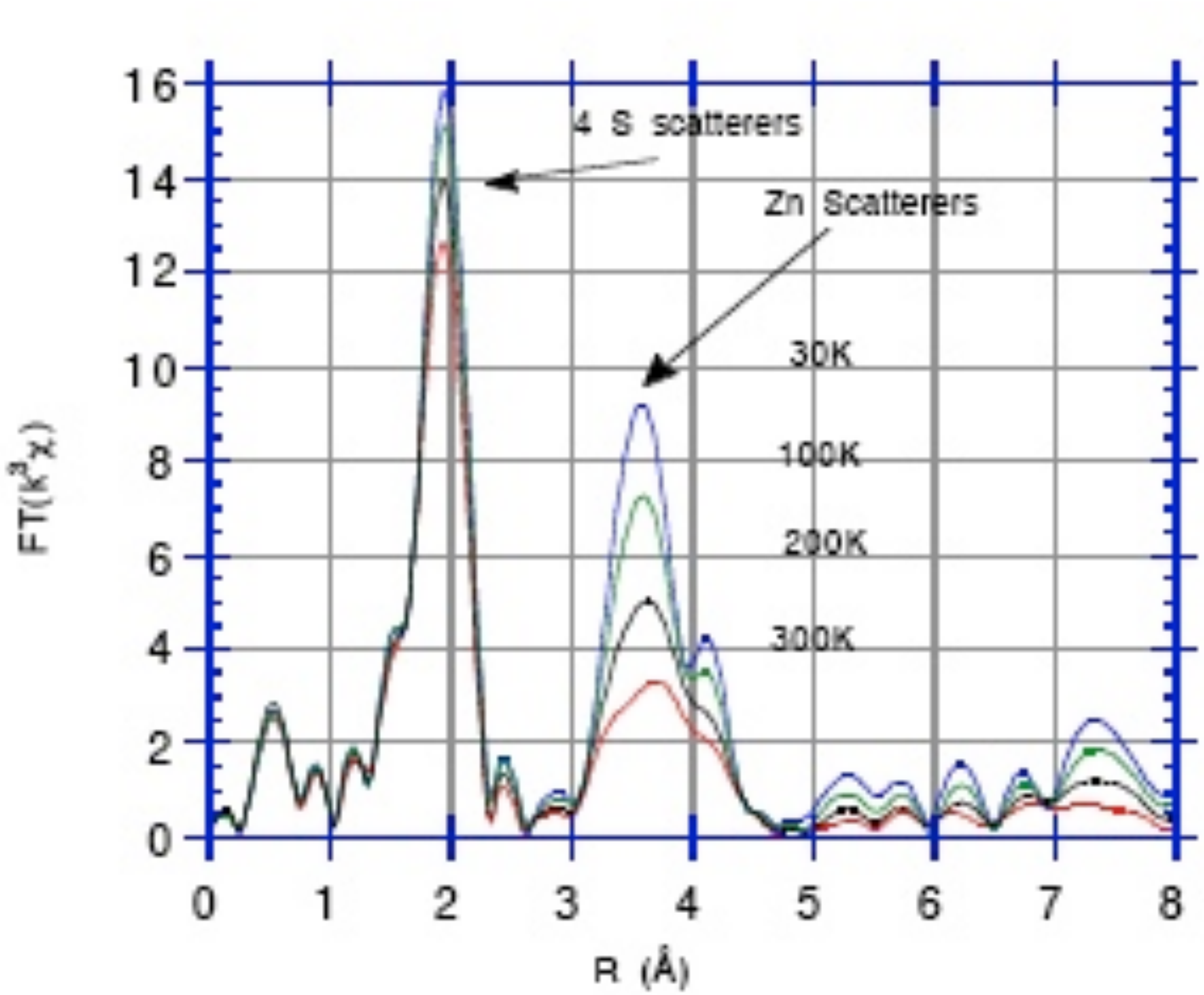
-> normalize, convert to k space, subtract spline background

K^3 weighted EXAFS



$k^3\chi$, 300K vs 30K

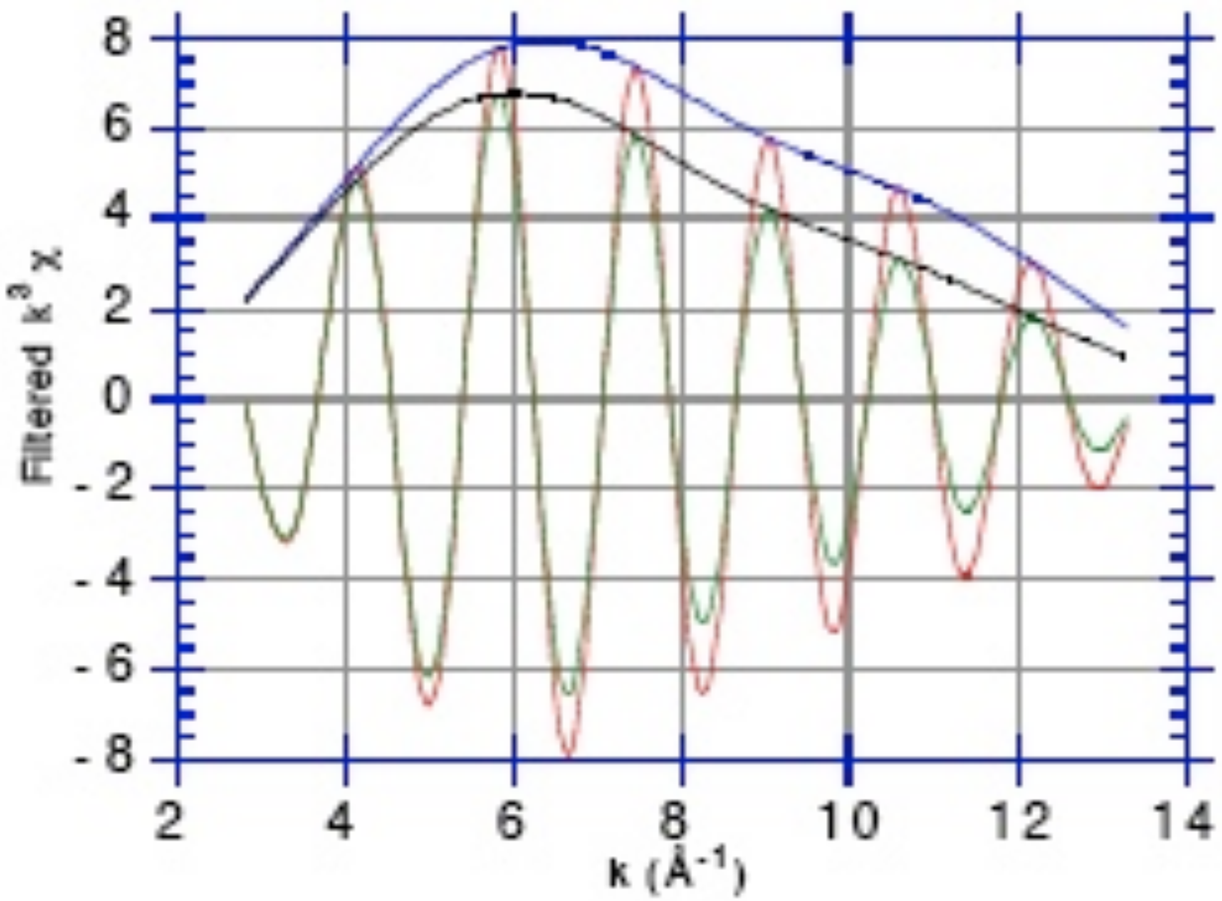
Fourier Transforms



Fourier transforms

Average EXAFS signal decreases at higher temperatures because of increased thermal DWFs

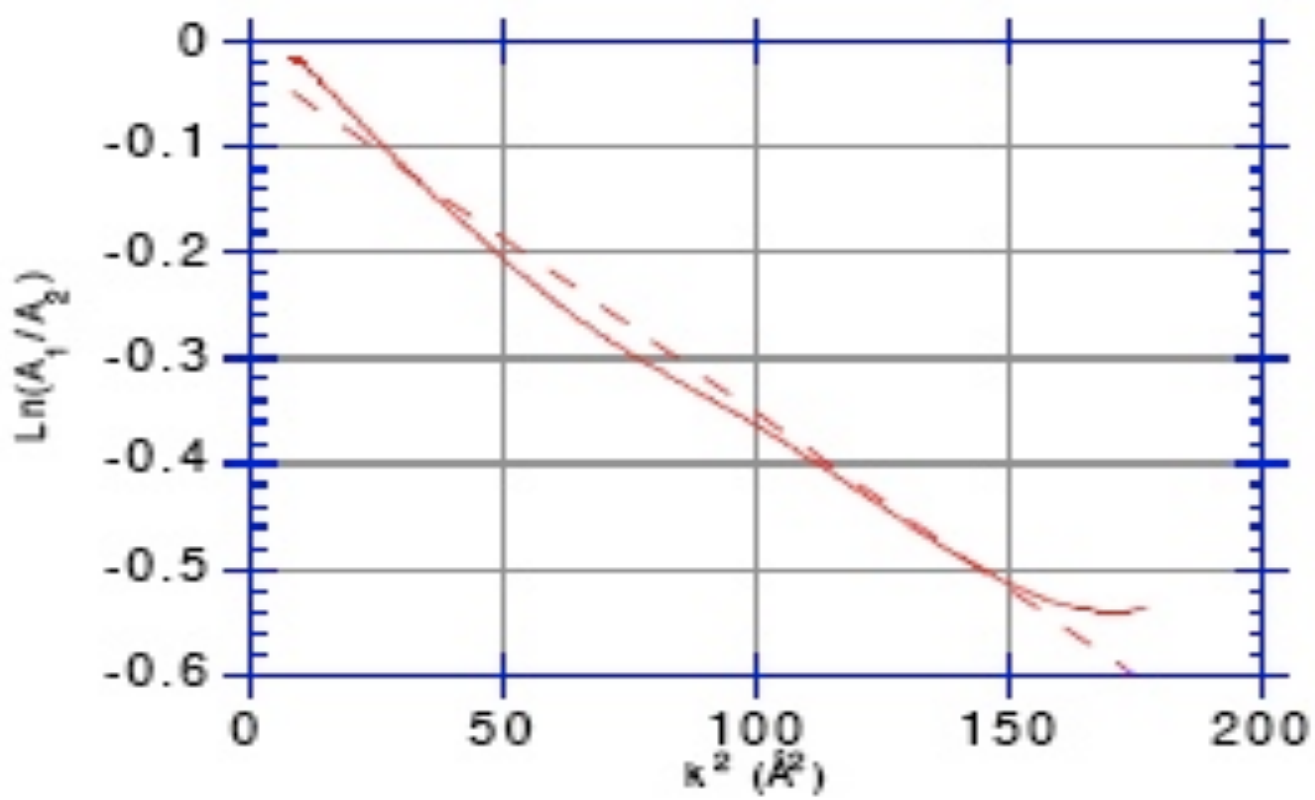
Fourier Filtered First Shell



Filtered $k^3\chi$

determine single shell's amplitude and phase from real and imaginary parts of inverse FT

Log-Ratio Amplitude



$\ln(A_{300}/A_{30})$

Slope gives difference in sigma^2, intercept gives ln[CN ratio] vs reference spectrum. Can also find E0 and cumulants C3, C4.

Data Modeling

- Fit data in k-space, r-space, or E-space using single or multiple scattering theory, and theoretical calculations (e.g. FEFFX, GNXAS, EXCURV)
- Fitting is done by describing an approximate hypothetical structure in terms of a limited number of parameters, which are adjusted to give an acceptable fit.
- Good open-source software is available e.g. feff6 (Rehr), ifeffit/Artemis/Athena (Ravel/Newville), SixPack (Webb) GNXAS (Di Cicco/Filliponi), RoundMidnight(Michalowicz), EXAFSPAK (George)...
- FEFF9 must be licensed, but it's at reasonable cost.
- Other programs e.g. Mathematica 8 can be useful.

Single Scattering fitting

- If SS is a good approximation, and shells are well isolated, you can fit shell by shell
- Complications still occur because of large disorder, accidental cancellations, and high correlation between fitting parameters
- Multishell fits in SS approximation

Multiple scattering fitting

- MS often cannot be neglected (e.g. focussing effect)
- MS fitting introduces a host of complications but also potential advantages
  - SS contains no information about bond angles
  - MS does contain bond angle information (3-body and higher correlations)
- Parameter explosion -> how to handle DWFs?
  - Dangers of garbage-in, garbage-out
- (more on this later in the talk)

Theory

- Improved Theory and Practical Implementations
  - Fast sophisticated electron multiple scattering codes
  - Still limitations in near-edge (XANES) region
  - Solves the forward problem (structure->spectrum), but not the inverse problem (spectrum -> structure),
  - More work on better fitting direct methods is needed
  - Sophisticated quantum chemistry codes have been made easier to use; they can be leveraged to combine DFT and XAFS
  - correlate electronic and vibrational structure

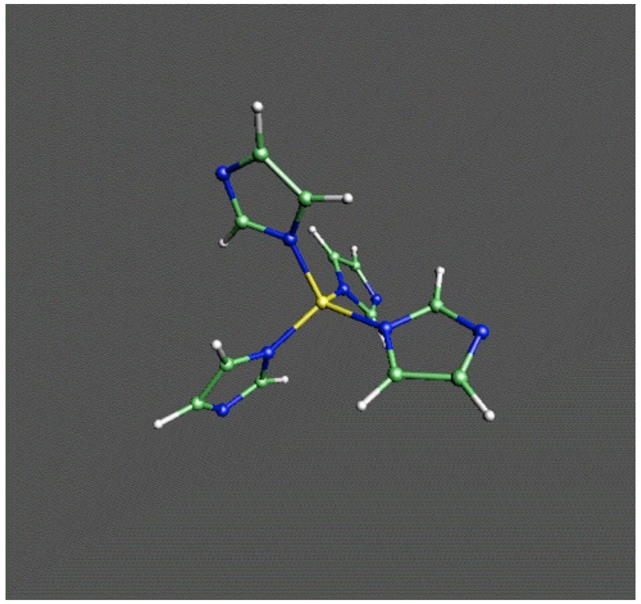
Computing Multiple Scattering with FEFF8

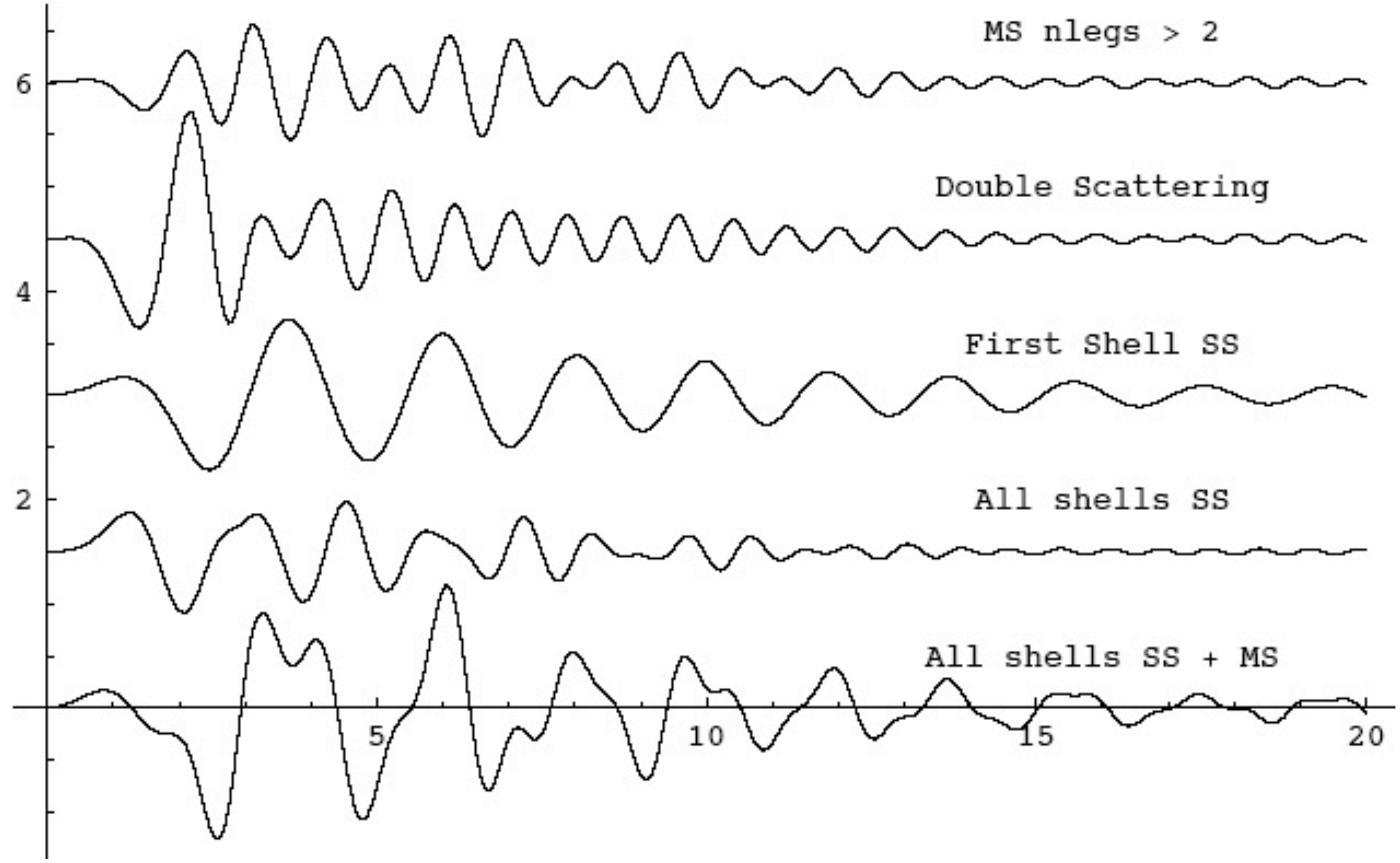
- {Rewrite golden rule squared matrix element in terms of real-space Green's function and scattering operators; expand GF in terms of multiple scattering from distinct atoms}
- initial atomic potentials generated by integration of Dirac equation (relativistic analog of Schrödinger); modified atomic potentials generated by overlapping (optional self-consistent field; use for XANES)
- complex exchange correlation potential computed -> mean free path
- scattering from atomic potentials described through k-dependent partial wave phase shifts for different angular momentum l
- radial wave function vs E obtained by integration to calculate mu zero
- unimportant scattering paths are filtered out (except FMS)
- Feffs for each path calculated (e.g. Rehr Albers formalism)
- final spectrum generated by summing finite number of paths, or, over restricted energy range, FMS (use for XANES)
- **-> All of this is accomplished in a few seconds**

FEFFx: see papers of Rehr, Ankudinov, Zabinsky et al

see also DLXANES, GNXAS, and EXCURV programs

Example: Multiple Scattering within Histidine Imidazole Ring

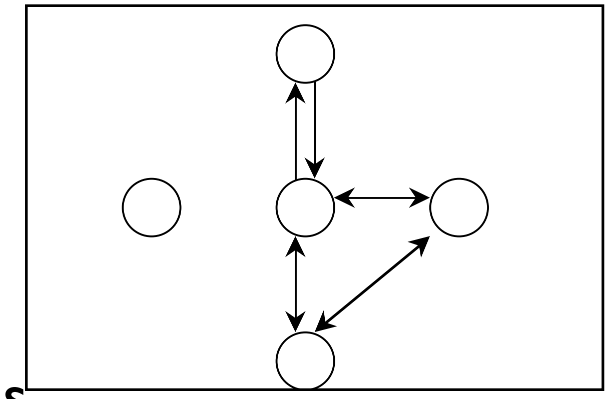




Information content of XAFS spectra is limited

- Estimate from Nyquist criterion
- Can completely describe band limited function by finite set of fourier coefficients
- **N degrees of freedom = $2\, \Delta k\, \Delta r / \pi$**
  - **$2 * 10 * 3/\pi \sim 20$ for solution spectra**

Parameter explosion in MS fitting



- Multiple scattering expansion
- May be tens or hundreds of important paths
- Each path has degeneracy, pathlength, debye waller factor, …
- Geometry allows you to interrelate the pathlengths within certain limits
- Group fitting (Hodgson & Co)
- Determining all the MS Debye Waller parameters by fitting is a hopeless task
- What can you do?

Dealing with Parameter Explosion

- **Use *a priori* information;** extend k-space range
- Simultaneous fitting to multiple spectra e.g. different temperatures
- Suppress DWFs by measuring samples cryogenically -> zero point motion and static DWFs
- minimize use of ad-hoc assumptions!
- Calculate DWFs on physical grounds (Dimakis & Bunker, Poiarkova & Rehr) using density functional theory or faster methods
- If you can orient your sample, do it - you can double or triple information for low symmetry sites with polarized XAFS; better yet, do joint refinement with XRD

Path by path fitting

- reduce the number of variables by expressing the large number of "numerical path parameters" (e.g. path length, DWFs) for each path in terms of smaller set of global fitting variables
- this is the most tedious and tricky part of multishell fitting of MS data
- there is a danger of making ad hoc assumptions that are incorrect
- GIGO: Garbage In -> Garbage Out

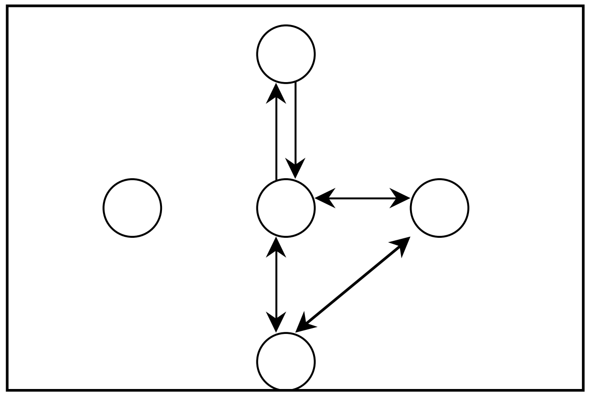
Parameters needed to describe structure

- Neglecting inter-ligand MS, how many parameters needed to define structure for metal protein site?
  - rho, alpha, beta for 4 ligands -> 12 parameters
  - rho, alpha, beta for 6 ligands -> 18 parameters
  - Need more parameters to describe disorder
  - Neglects multiple scattering between ligands
  - Indeterminate or nearly so for 3D structure

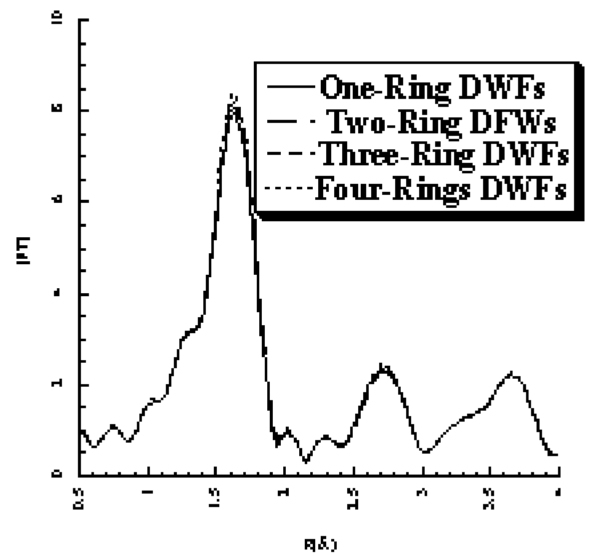
Polarized XAFS helps

- Second rank tensor – 3 by 3 matrix - 9 components, each a function of energy
- Diagonalize to 3 independent functions
- Isotropic average in solution (and cubic symmetry) to one independent function – the usual XAFS
- Low symmetry structures – can get up to 3 times the information (~60 parameters) from polarized XAFS
- Can use crystals that are not perfect enough for atomic resolution diffraction
- In principle could solve for 3D active site structure in crystal
- Joint refinement: crystallography and XAFS

Ab initio XAFS: scattering + vibrations



By combining sophisticated electron multiple scattering codes with density functional based quantum calculations of molecular vibrations, one can accurately calculate spectra with no fudge factors



Zn tetraimidazole

automatic fitting: DE+ DWFs from DFT

THE JOURNAL OF CHEMICAL PHYSICS 128, 115104 (2008)

Zinc cysteine active sites of metalloproteins: A density functional theory and x-ray absorption fine structure study

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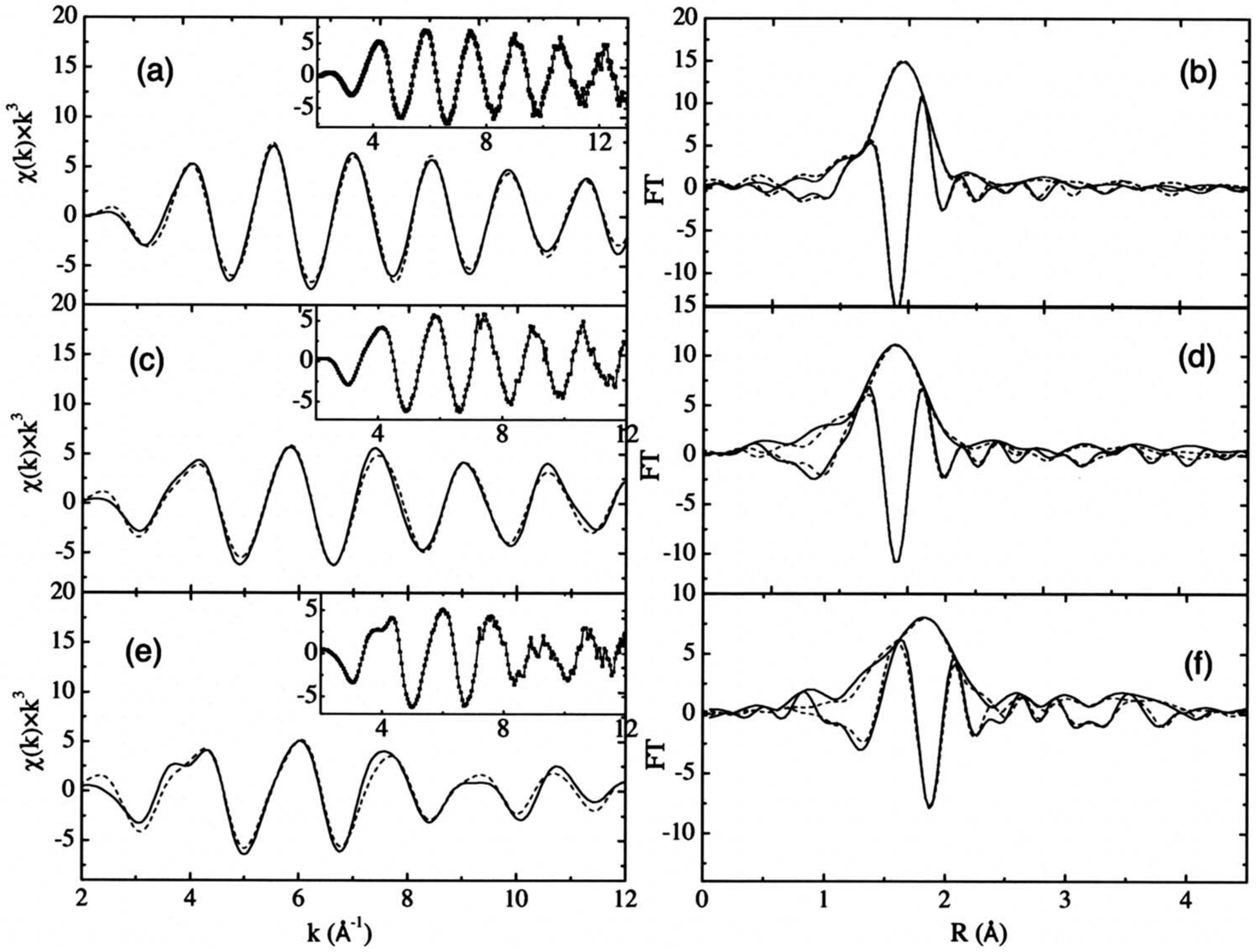
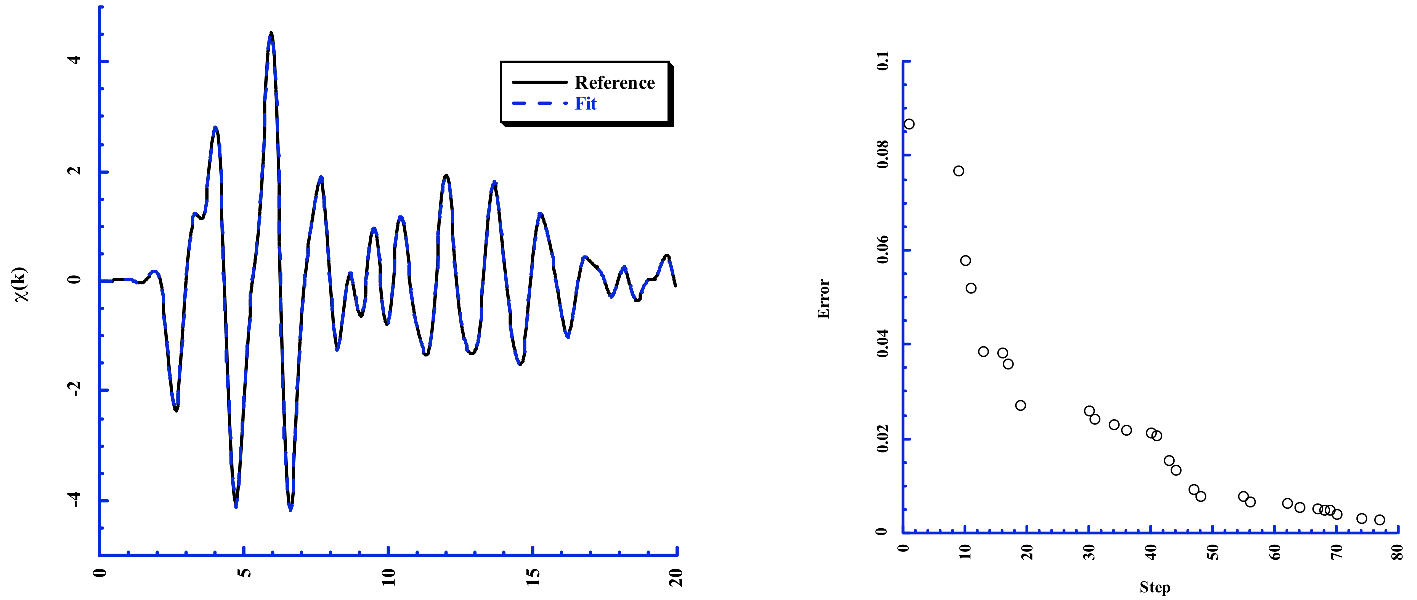


FIG. 4. Least squares fit of hypothetical $Zn(His)_{4-n}(Cys)_n$, $n=4$ [(a) and (b)], $n=3$ [(c) and (d)] and $n=2$ [(e) and (f)] structures with respect to filtered experimental XAFS spectra. Original $\chi(k)$ XAFS spectra can be seen at the inserts. (b), (d), and (f) are Fourier transforms (magnitude and imaginary part) of (a), (c), and (e) filtered $\chi(k)$ spectra. Fit is over filtered k-range with $\Delta k=2-12.5$ Å^{-1} for $ZnCys_4$, $\Delta k=2-12$ Å^{-1} for the mixed ligation complexes due to noise at high k range; $\Delta R=0.5-4.5$ Å for all cases to include MS. SS and MS σ^2s were kept fixed during the fitting procedure to the values obtained by the DE algorithm, whereas ΔE_0, S_0^2, and ΔR were allowed to vary. In all cases the $\Delta R^{\mathrm{error}} < 0.01$ Å.

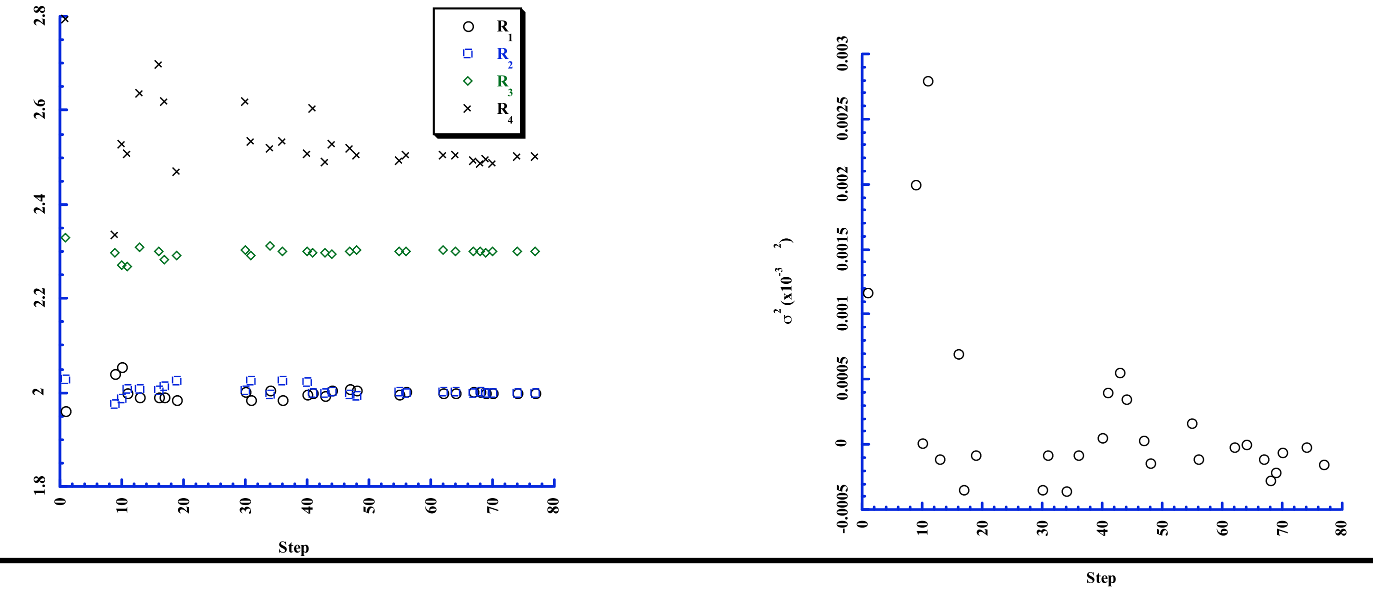
His(3), Cys(1) Zn site:

Automated fitting using a genetic algorithm, + FEFF7 + ab initio DWFs.

(Dimakis & Bunker, Biophys. Lett. 2006)

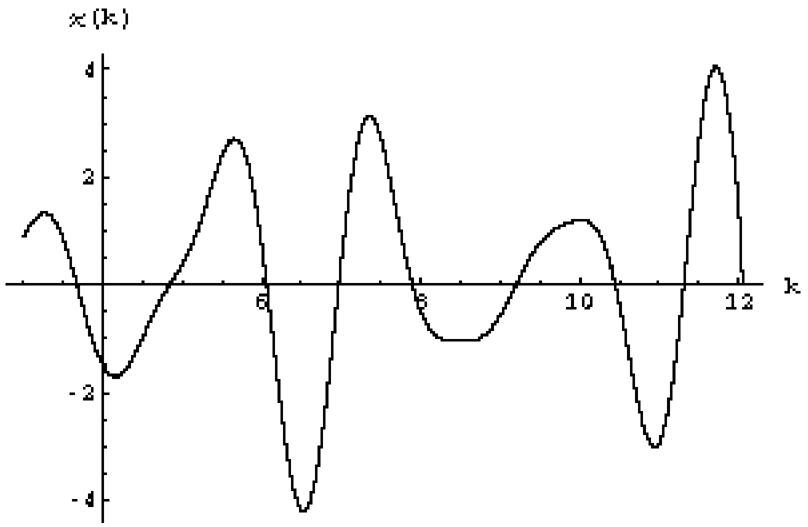


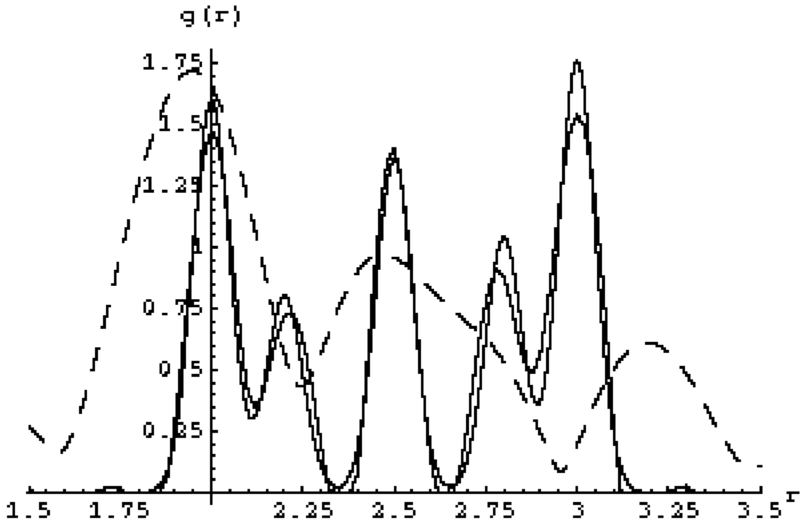
These tests show robust convergence on best fit



Direct Methods

Direct methods for determining radial distribution functions from EXAFS using Projected Landweber-Friedman Regularization





Khelashvili & Bunker 2001

Chemical Speciation

- Mobility and toxicity of metals in the environment strongly depends on their chemical state, which can be probed in situ with XAFS
- Under appropriate conditions, total absorption coefficient is linear combination of constituent spectra
- Use singular value decomposition, principal components analysis, and linear programming (Tannazi) methods to determine species
- These provide direct methods for determining speciation
- Nonlinearities from particle size effects can cause significant errors in speciation (Tannazi & Bunker)

Conclusion

- XAFS is a powerful tool for studying the local structure in both disordered and ordered materials.
- Recent advances have made the technique more powerful and flexible. Much more can be and is being done to build upon and exploit recent advances in theory, experiment, and data analysis.
- for more info, see "Introduction to X-ray Absorption Fine Structure Spectroscopy", G. Bunker, Cambridge University Press (2010) and references therein