X-ray absorption spectroscopy

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Outline

X-ray absorption spectroscopy (XAS)

1. EXAFS

2. XANES

3. Applications

Most slides courtesy – Prof. G. N. George,

University of Saskatchewan

Useful Resources
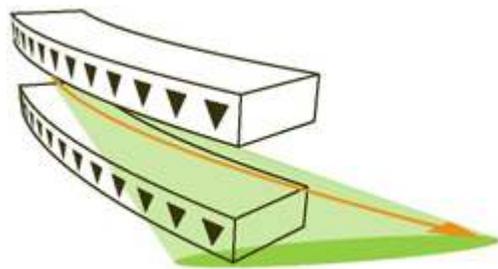
http://www.ixasportal.net/ixas/

http://xafs.org/Tutorials?action=AttachFile&do=get&target=Newville_xas_fundamentals.pdf

Levina *et. al*, 2005, Coord Chem Rev, **249**, pp141-160, sections 1 and 2 only

Bending Magnets and Insertion Devices

- maintain the electron beam orbit
- wide emission cone angle
- low brightness – still valuable though

- insertion device
- electron beam path oscillates in plane of ring
- broad output spectrum (good for spectroscopy as easily tuned)
- incoherent light
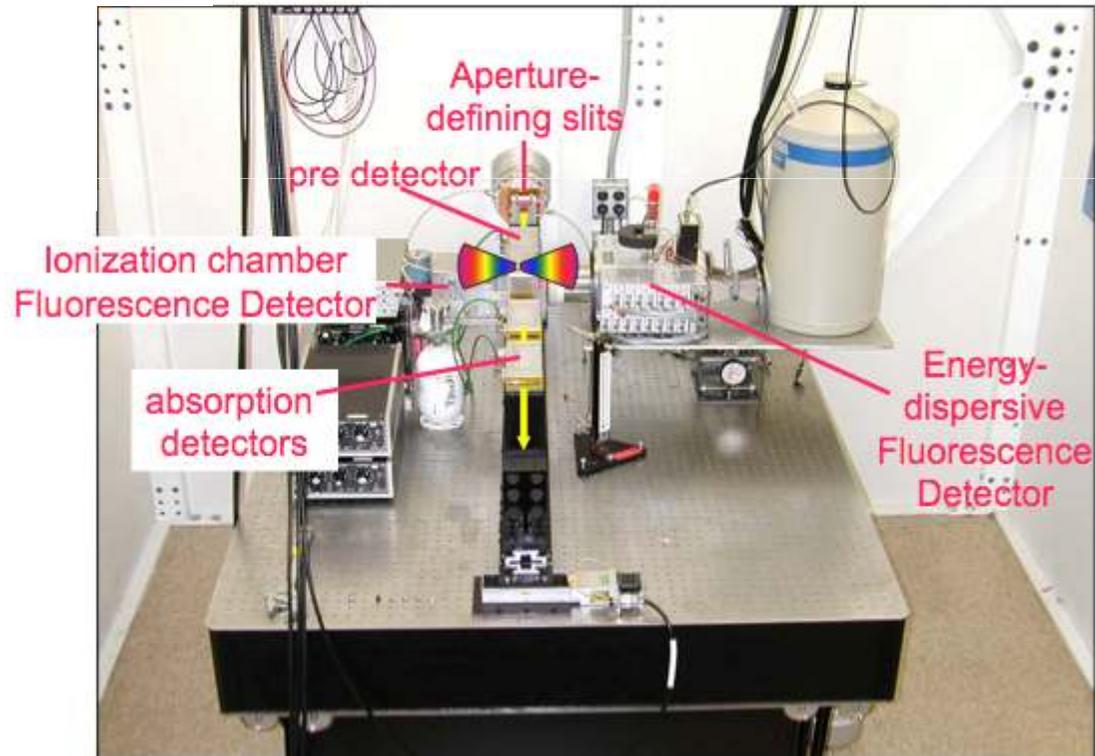- intermediate brightness
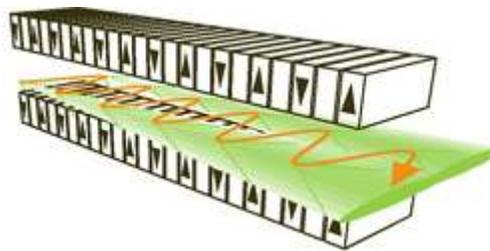
- similar to wiggler but gentler undulations
- wavefronts from consecutive bends constructively interfere
- high brightness in narrow λ band – adjust gap (hence mag. field) for different λ
- difficult to tune (not as good for spectroscopy?)
- narrow cone – coherent!
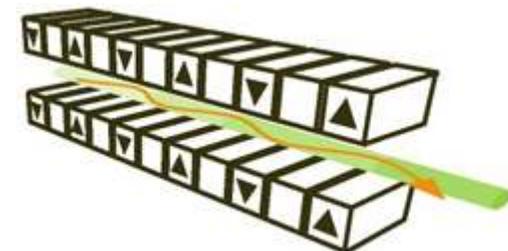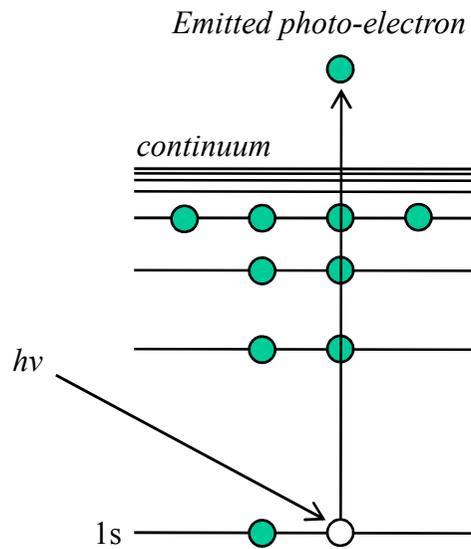
Bending Magnet   Wiggler   Undulator
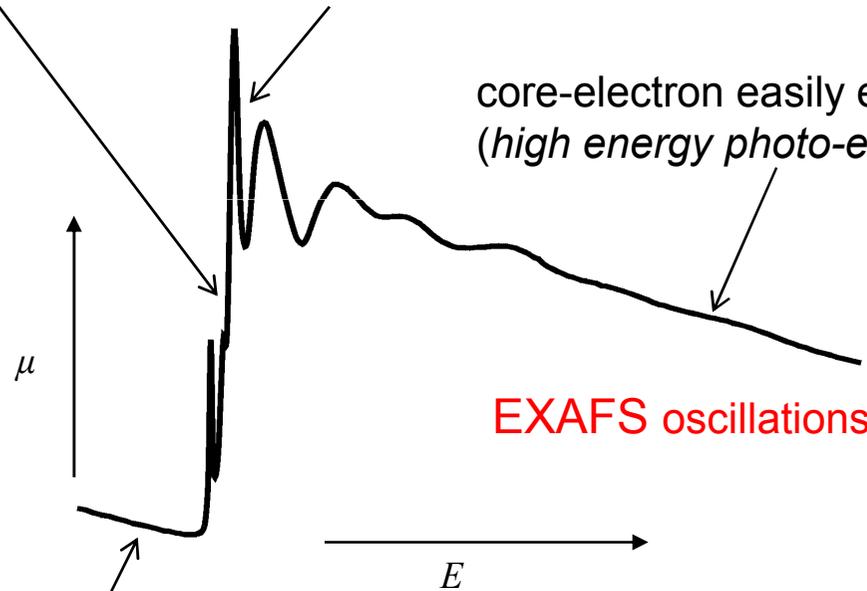
X-ray Absorption Spectroscopy

X-ray Absorption Spectroscopy – Basic Physics

transitions to bound-states
X-ray absorption near-edge structure

Just enough energy to eject core-electron
(*low energy photo-electron results*).

core-electron easily ejected
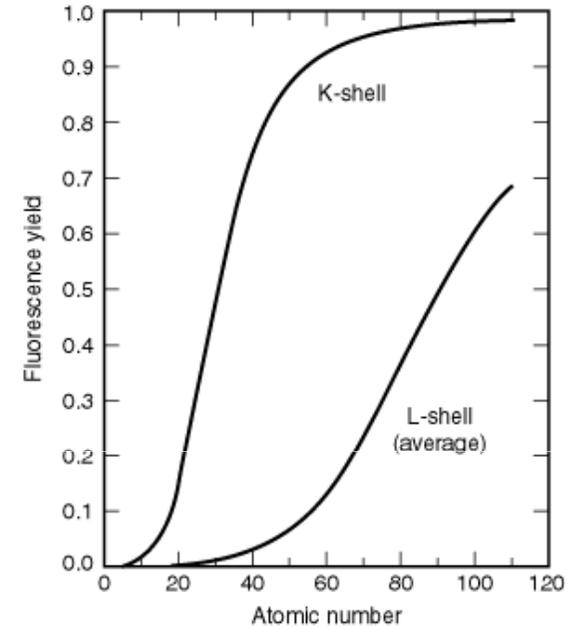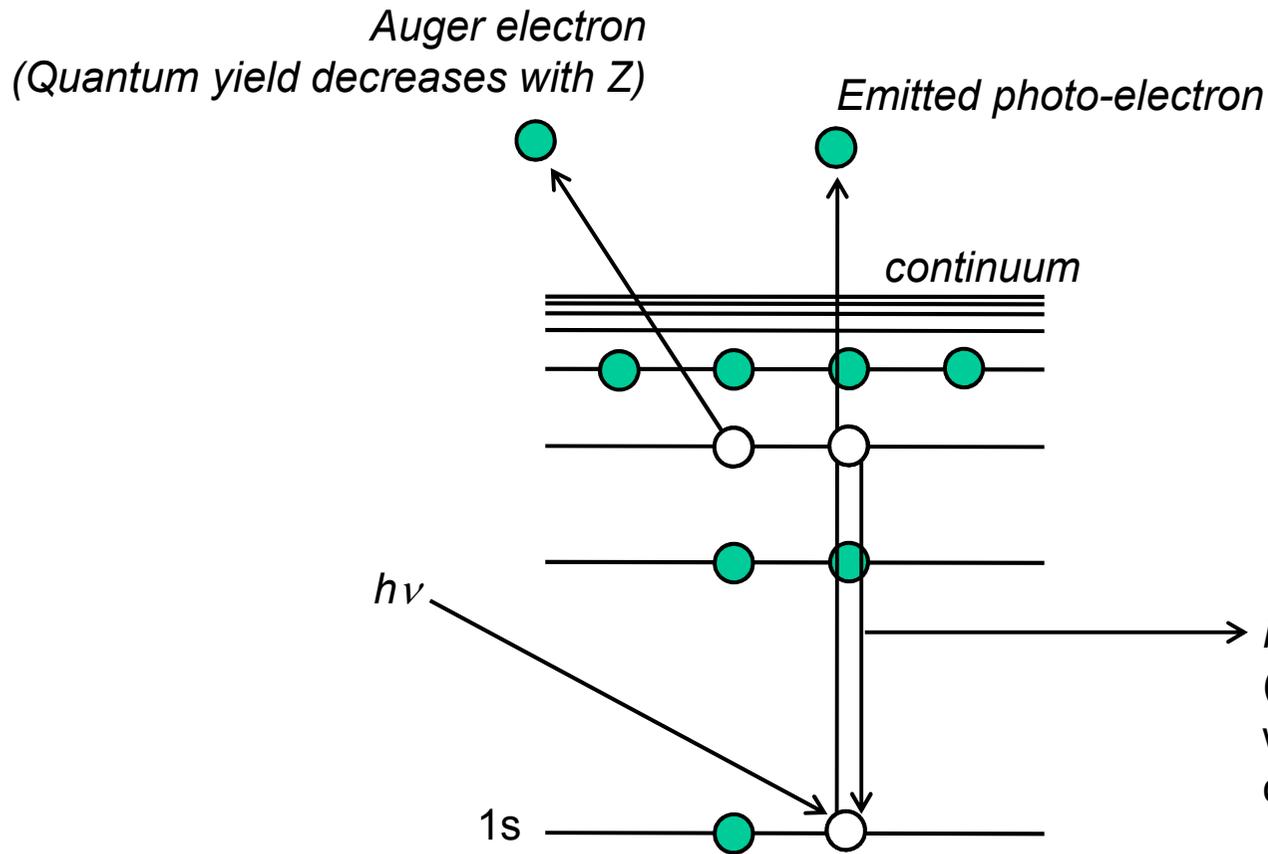(*high energy photo-electron*)

Emitted photo-electron

continuum

hv

1s

μ

EXAFS oscillations

E

Insufficient energy to eject core-electron

(*μ here is the absorption coefficient from Beer's Law, i.e. A = μ c l*)

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X-ray Absorption Spectroscopy – Basic Physics

Auger electron
(Quantum yield decreases with Z)

Emitted photo-electron

continuum

$h\nu$

1s

$h\nu$ *fluorescent photon*
(Quantum yield increases
with Z – energy is also
characteristic for each Z)

NB – fluorescent photons
have lower energy than[7]
incident photons

X-ray absorption spectroscopy is element-specific
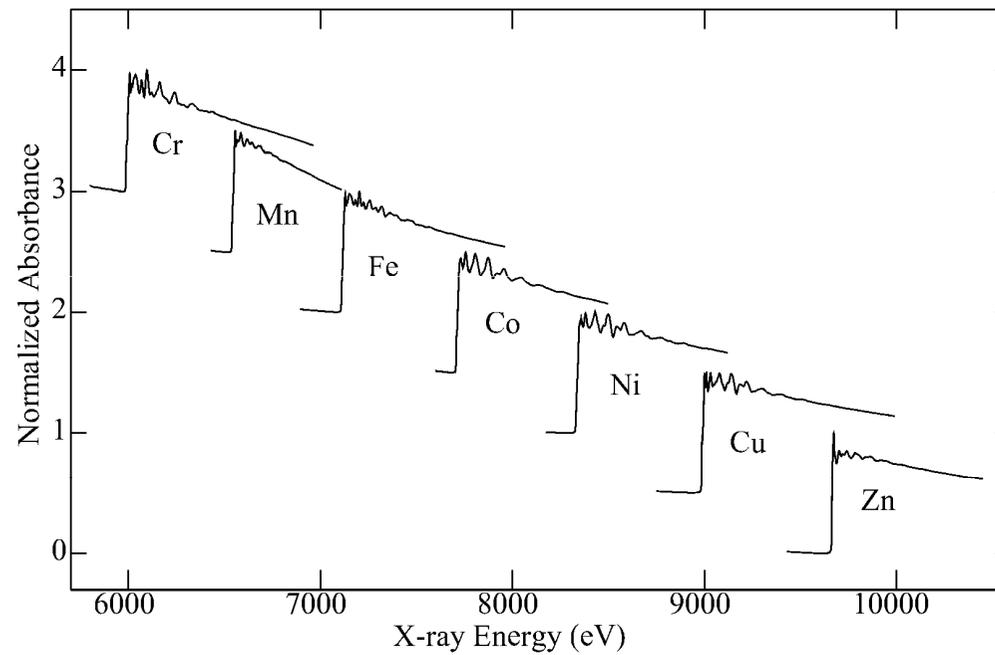
K-edge XAS of some first transition elements.

# X-ray absorption spectroscopy sees all atoms of one element in a sample!

- **Hence the overall XAS signal is the sum of the signals from *every* atom of the particular element in the beam path**

  - **XAS gives the average *local* environment**

- **Contamination can be a big problem – especially where the element of interest is at low concentrations**

- **Occasionally it is possible to determine structural information for two different sites within a sample – but this is rare**

# X-rays have high energy and are penetrative

- **X-rays penetrate further into a given substance with increasing energy**

- **Also XAS does not depend upon long range order in a sample (*cf.* XRD) so XAS can cope with samples in ANY phase – e.g. solids, gases, liquids, mixtures etc.**

- **Heavier elements have higher absorption cross-sections than light elements – so penetration depth (and fluorescence escape depth) must be considered**

Choice of X-ray Absorption Edge

Different core levels may be excited to give rise to K-edge and L-edges
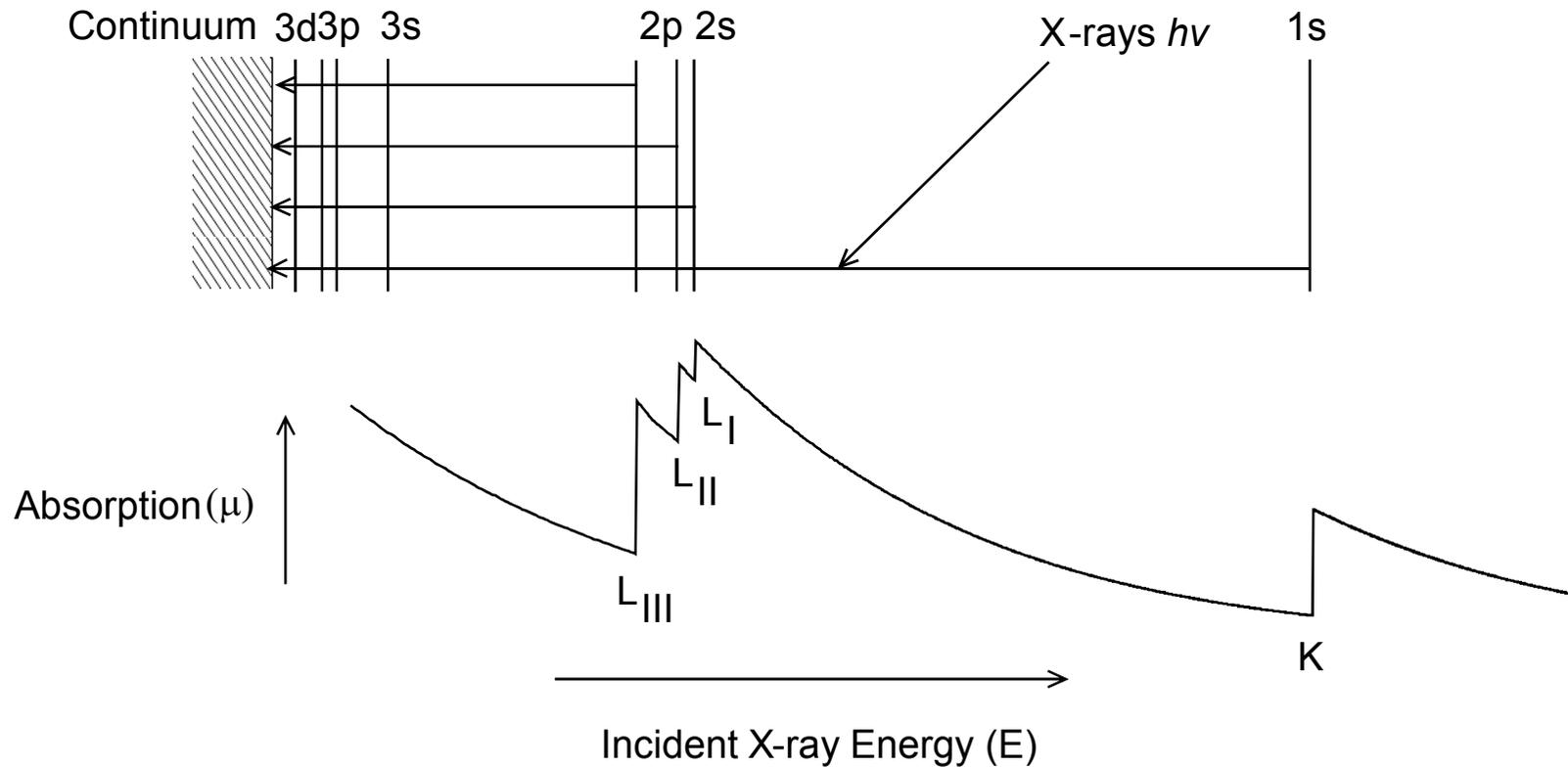
Choice of X-ray Absorption Edge
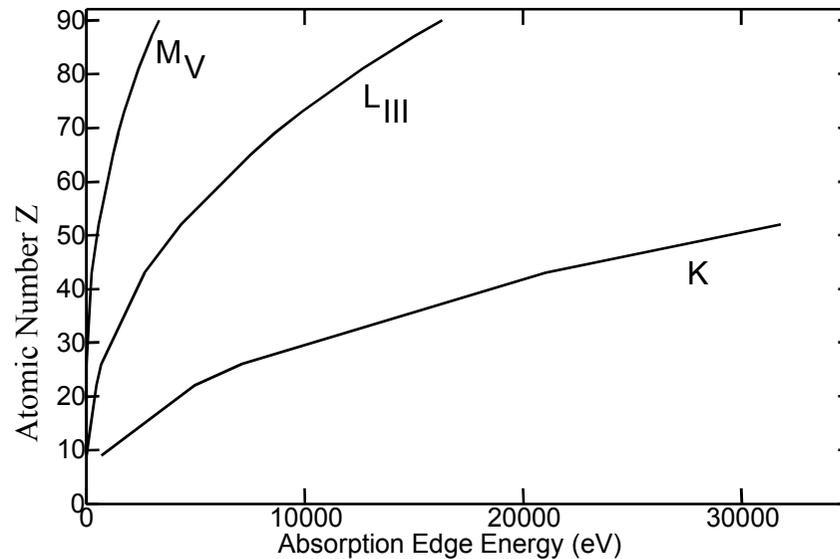
Typical Hard X-ray Experiments:

2.1 keV < E < ~30 keV

- Low energies - require UHV
- High energies - intensity low

EXAFS: K-edges have best edge jump - best signal to noise

L-edges have multiple edges - second edge can truncate EXAFS data

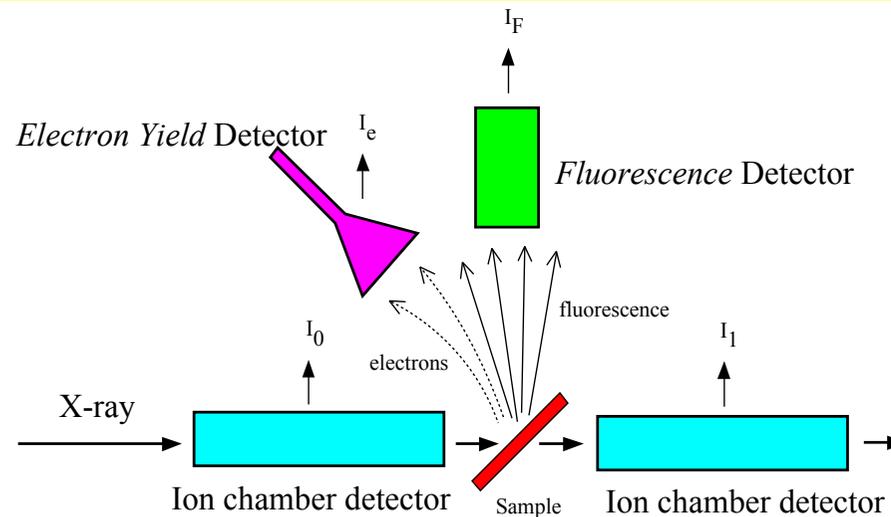For higher atomic numbers (> 50) L-edges are only edge accessible for EXAFS

Edge spectra: Different types of edge have different selection rules, therefore different information

Resolution is better for lower energies

Detection of X-ray Absorption Spectra

1. **by measuring the transmission of X-rays through the sample.**

2. **by measuring the X-ray fluorescence.**

3. **by measuring the electron yield.**

Electron Yield Detector I_e

I_F

Fluorescence Detector

I_0 electrons   fluorescence I_1

X-ray

Ion chamber detector   Sample   Ion chamber detector

Absorbance $\propto log_{10}(I_0 / I_1)$

Absorbance $\propto I_F / I_0$

Absorbance $\propto I_e / I_0$

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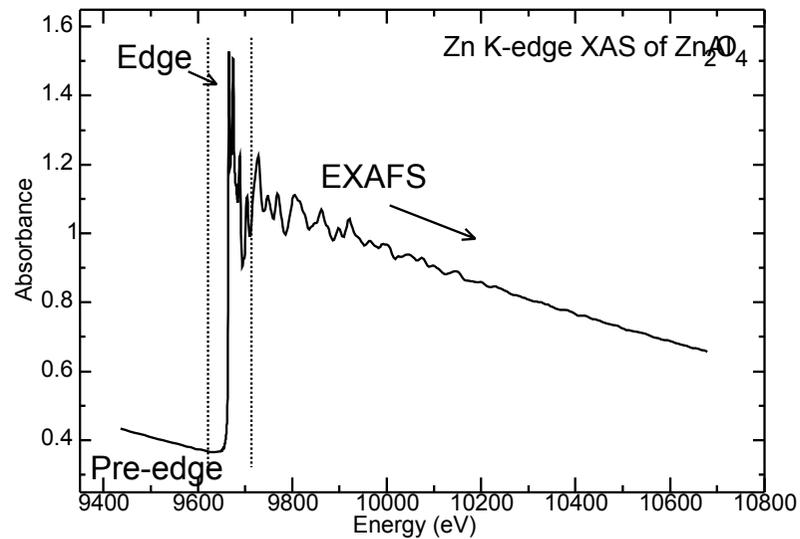# EXAFS – What information can it provide ?

EXAFS spectroscopy provides:

1. Accurate inter-atomic distances to nearby atoms.

2. An estimate of the size (atomic no.) of a nearby atom.

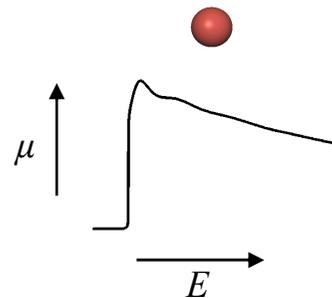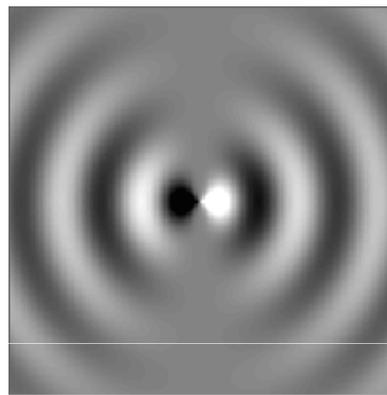3. An estimate of the number of similarly coordinated nearby atoms.

What is EXAFS ?

EXAFS – <u>E</u>xtended <u>X</u>-ray <u>A</u>bsorption <u>F</u>ine Structure
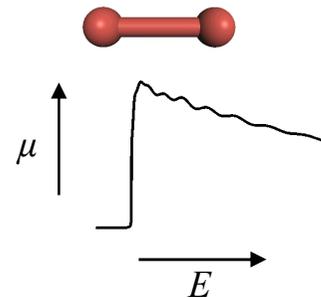
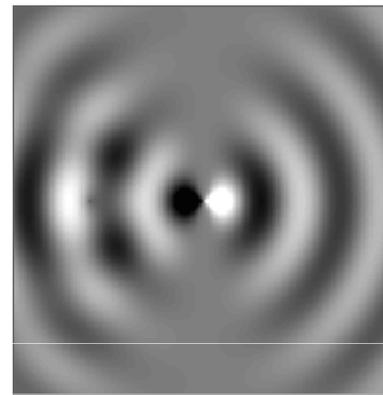The oscillatory X-ray absorption above an edge.

EXAFS – Basic Physics

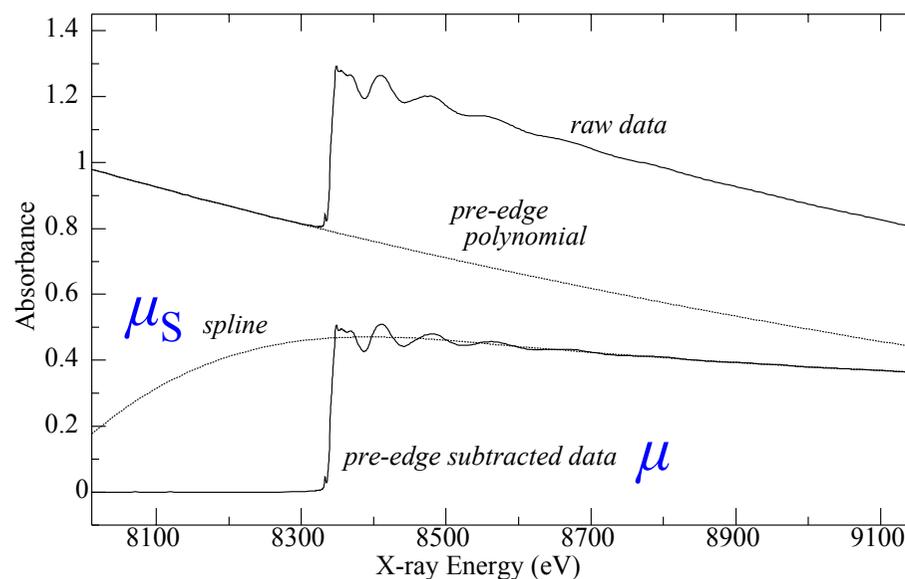*Photo-electron DeBroglie wave.*

Bromine atom

Br$_2$ molecule

Schematics diagrams of final state wave functions.

EXAFS Data reduction
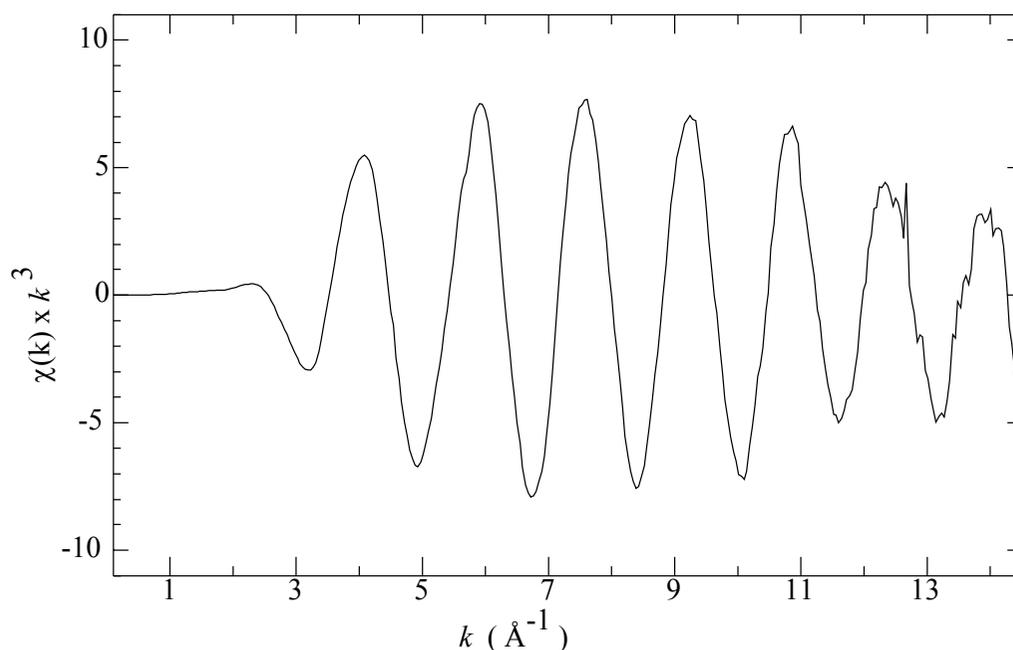
- EXAFS oscillations χ are extracted from the absorbance μ by successive subtraction of a pre-edge polynomial, fitted through the pre-edge region, and then a spline function fitted through the EXAFS region.

- The abscissa is converted from an incident X-ray energy scale to reciprocal Ångströms.
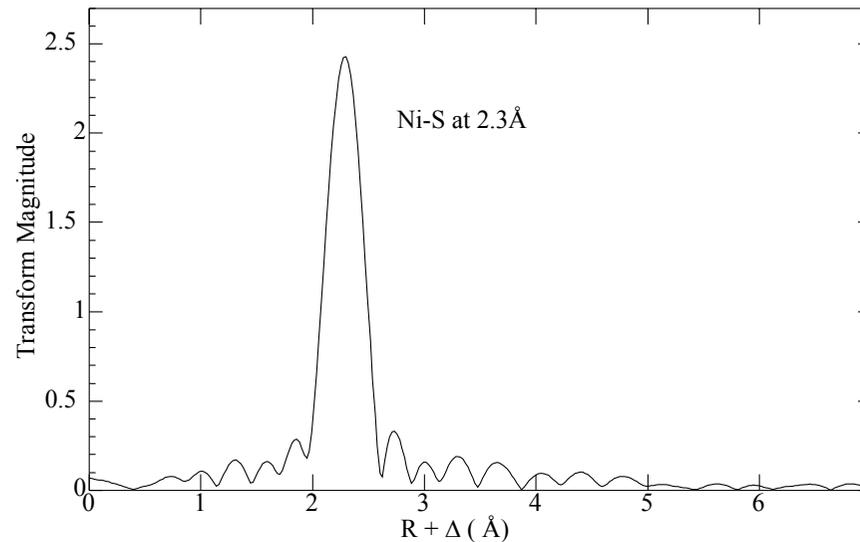
EXAFS Data reduction

$$k = \frac{2\pi}{\lambda_e} = \sqrt{\frac{2m}{\hbar^2}\left(E - E_0\right)}$$

(SI units)

- The EXAFS, χ, which is the oscillatory part of the absorption coefficient, is given by $\chi = (\mu - \mu_S)/\mu_0$ and the EXAFS oscillations are plotted as a function of the wavevector k, and (typically) k^3 weighted.

EXAFS Data reduction

Ni-S at 2.3Å

Y-axis: Transform Magnitude; X-axis: R + Δ (Å)

- **Important for a first look at the data – gives an approximate radial structure.**

- **The EXAFS Fourier transform is calculated from the EXAFS by:** $\rho(R) = \frac{1}{4\pi^{1/2}} \int_{k_{min}}^{k_{max}} \chi(k) k^3 e^{i2kR} dk$

- **Often phase-corrected transforms are calculated:** $\rho(R) = \frac{1}{4\pi^{1/2}} \int_{k_{min}}^{k_{max}} \chi(k) k^3 e^{i2kR + i\phi(k)} dk$
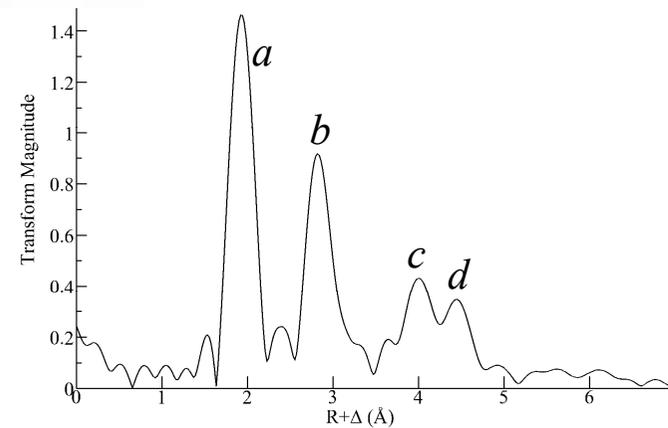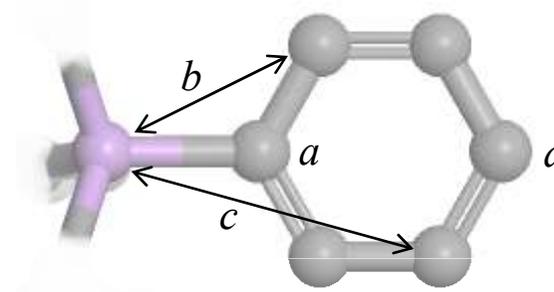
- **The power spectrum (transform magnitude) is calculated from:** $|\rho(R)| = \left\{ \Re[\rho(R)]^2 + \Im[\rho(R)]^2 \right\}^{1/2}$
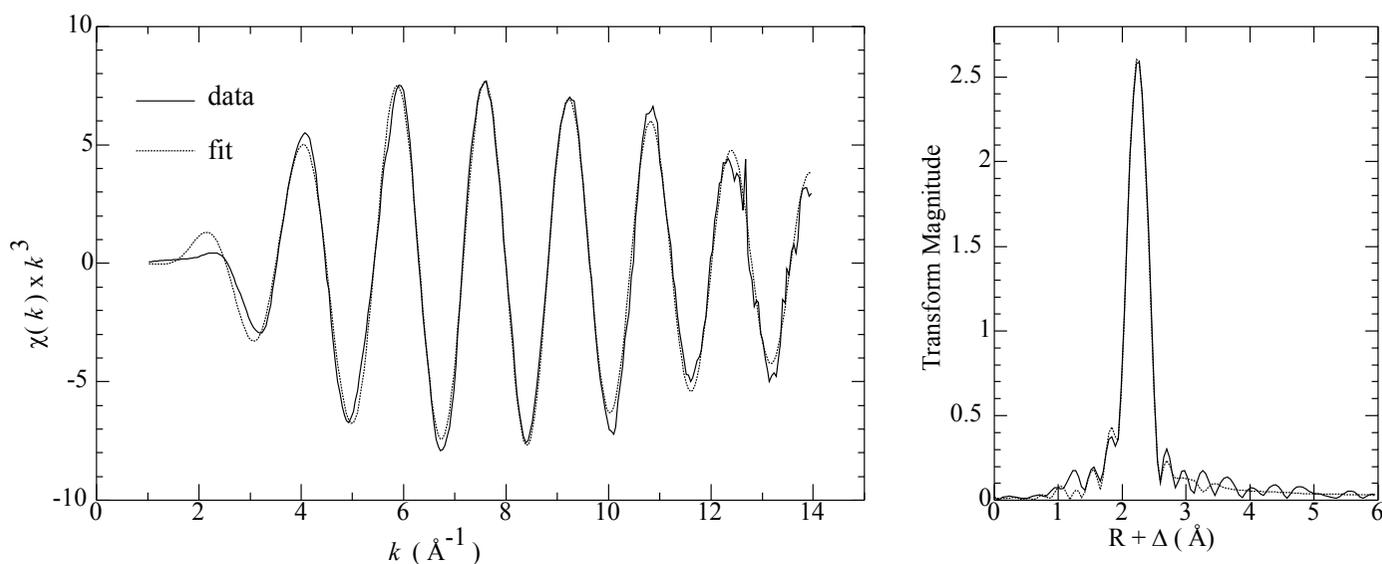
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The EXAFS Fourier transform

The EXAFS Fourier transform of the tetraphenylarsonium cation, phase-corrected for As–C backscattering.

The peaks in the transform correspond to inter-atomic distances.

EXAFS Data reduction

EXAFS Curve Fitting Analysis

**Best fit analysis with 4 Ni-S at 2.292 (3) Å, σ^2 = 0.00270 (12) Å^2**

• A combination of differences in phase and amplitude functions makes determination of scatterer type, coordination number and distance possible.

• EXAFS gives very accurate interatomic distances (typically better than ±0.02 Å).

• EXAFS gives less accurate coordination numbers and Debye-Waller factors (*ca.* ± 25 %).

The EXAFS Equation

$$\chi(k) \simeq \sum_{i=1}^{n} \boxed{\frac{N_i A_i(k, R_i)}{kR_i^2} \exp\left(\frac{-2R_i}{\lambda(k, R_i)}\right) \exp\left(-2\sigma_i^2 k_i^2\right)} \boxed{\sin\left[2kR_i + \phi(k, R_i)\right]}$$

Total amplitude function   *Total phase function*
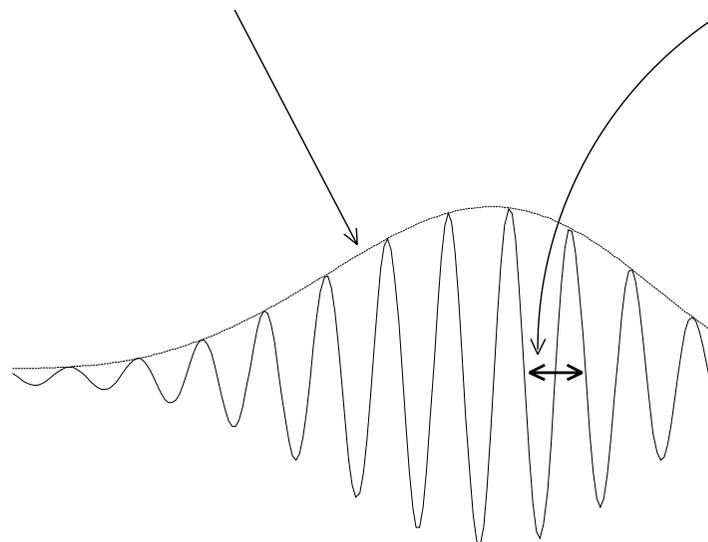
Definitions:

General parameters:		Chemical sensitivity:		Structural parameters:	
$\chi(k)$	The EXAFS function	$\phi(k, R)$	Phase function	N	Coordination number
k	Photoelectron wavevector	$A(k, R)$	Amplitude function	R	Interatomic distance
Σ	Sum over all absorber-backscatterer shells i,	$\lambda(k, R)$	Photoelectron mean free path function	σ^2	Debye-Waller factor

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EXAFS Amplitude Components

$$\chi(k) \simeq \sum_{i=1}^{n} \frac{N_i A_i(k, R_i)}{kR_i^2} \exp\left(\frac{-2R_i}{\lambda(k, R_i)}\right) \exp\left(-2\sigma_i^2 k_i^2\right) \sin\left[2kR_i + \phi(k, R_i)\right]$$

Amplitude

$A(k, R)$

k ($\mathring{A}^{-1}$)

Mean Free Path

$\lambda(k, R)$

k ($\mathring{A}^{-1}$)

Debye-Waller Factor

$\exp\left(-2\sigma^2 k^2\right)$

k ($\mathring{A}^{-1}$)

$\frac{A(k,R)}{kR^2}$

k ($\mathring{A}^{-1}$)

$\exp\left(\frac{-2R}{\lambda(k,R)}\right)$

k ($\mathring{A}^{-1}$)

$k^3 \times \exp\left(-2\sigma^2 k^2\right)$

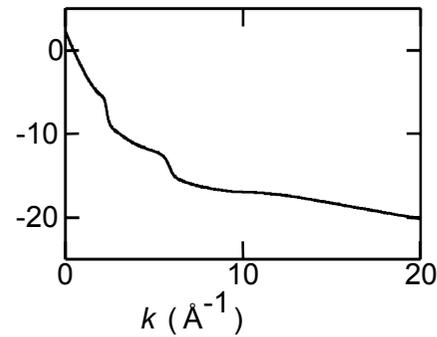k ($\mathring{A}^{-1}$)
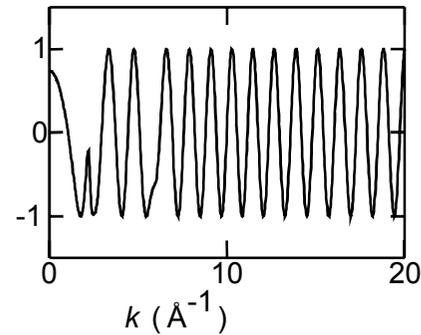
23
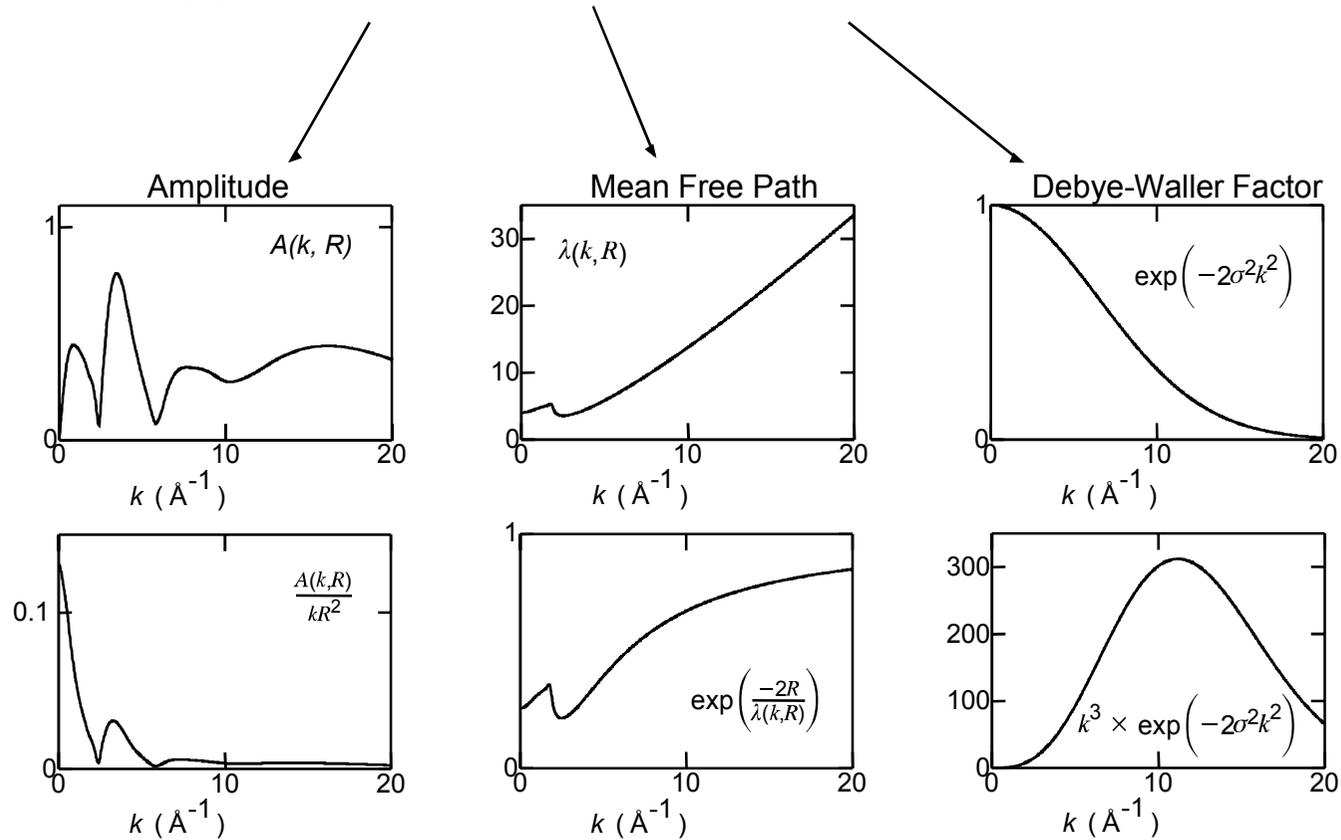
EXAFS Phase function

$$\chi(k) \simeq \sum_{i=1}^{n} \frac{N_i A_i(k, R_i)}{kR_i^2} \exp\left(\frac{-2R_i}{\lambda(k, R_i)}\right) \exp\left(-2\sigma_i^2 k_i^2\right) \sin\left[2kR_i + \phi(k, R_i)\right]$$
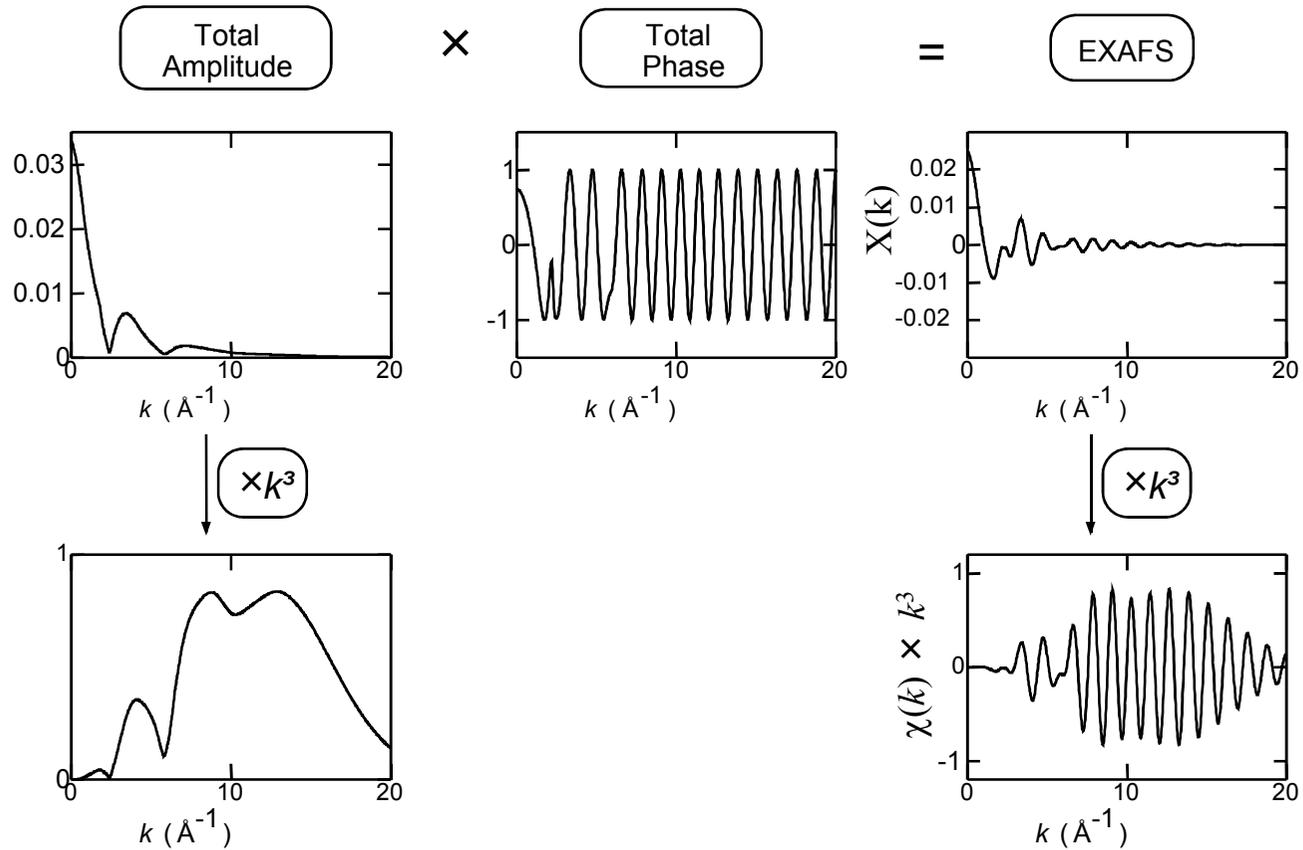
Phase

$\phi(k, R_i)$

k (Å^{-1})

Total Phase Term

$\sin\left[2kR_i + \phi(k, R_i)\right]$
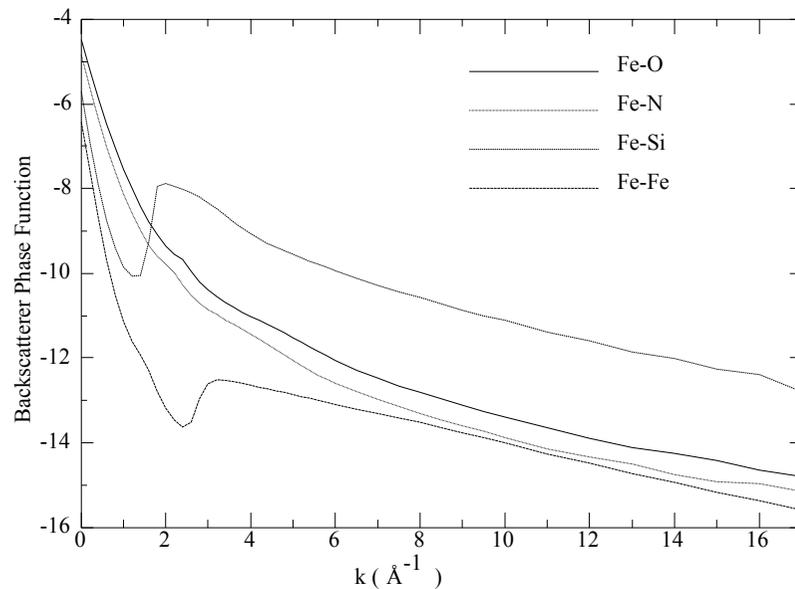
k (Å^{-1})

Total EXAFS

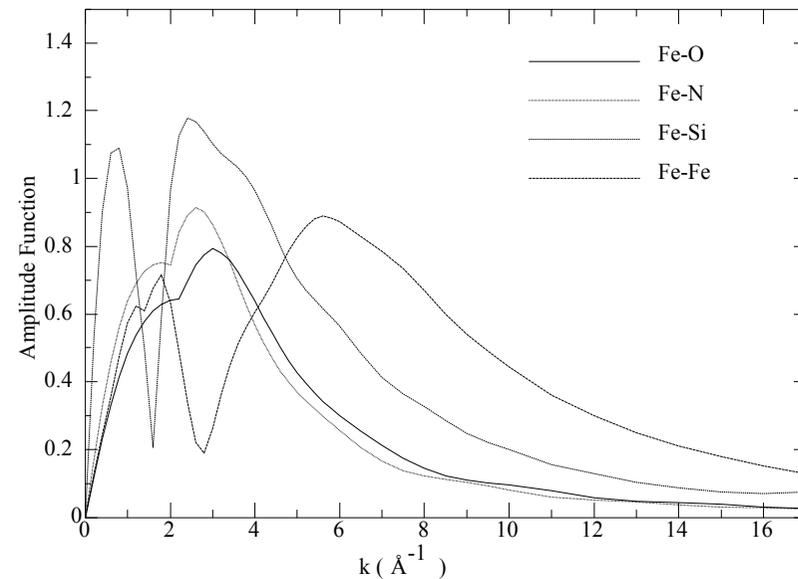# Chemical Sensitivity from Phase and Amplitude Functions

Backscatterers of different Z (*e.g.* O, Si, Fe) can be easily distinguished

Backscatterers of similar Z (*e.g.* N and O) cannot

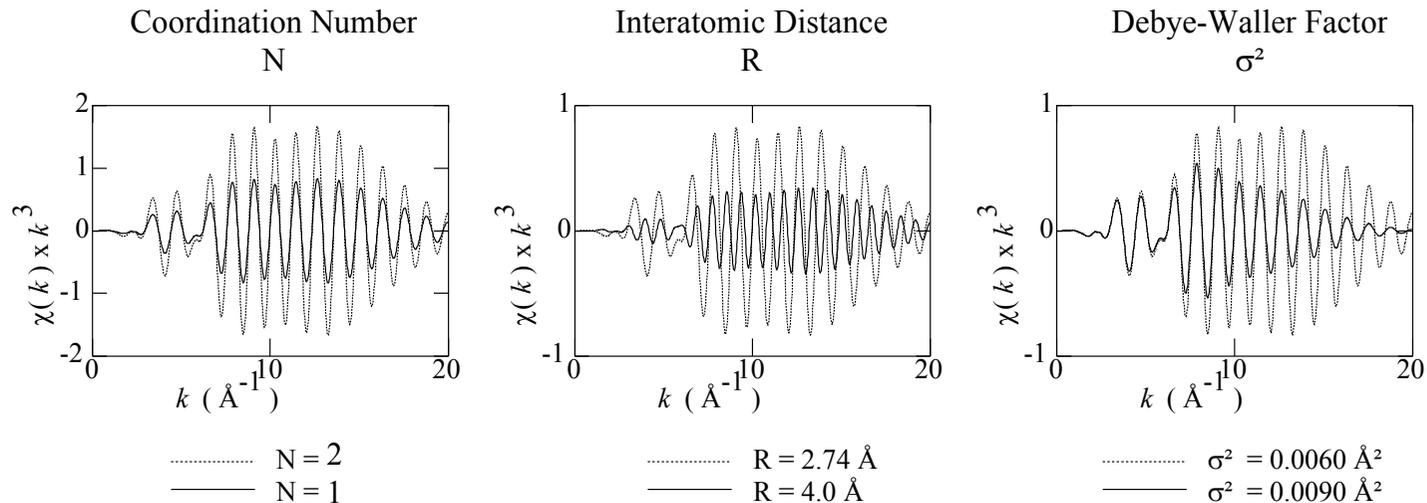*Backscatterer Phase Function, Fe K-edge EXAFS*　　　　*Amplitude Function, Fe K-edge EXAFS*

The structure in the phase and amplitude functions is due to the interaction of the photoelectron with the electron clouds of both the absorber and backscatterer atoms, and hence is element-specific.

Structural Parameters in EXAFS

Coordination Number
N

Interatomic Distance
R

Debye-Waller Factor
σ^2

N = 2
N = 1

R = 2.74 Å
R = 4.0 Å

σ^2 = 0.0060 Å²
σ^2 = 0.0090 Å²

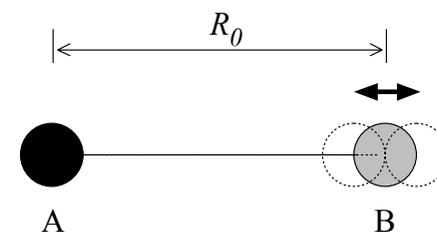*N* acts as a scaling factor for the EXAFS.

R contributes to both the phase and amplitude of the EXAFS (larger R means higher frequency and smaller amplitude).

σ^2 acts to damp out the amplitude at higher k (larger *σ^2* gives greater damping).

The Debye-Waller Factor

• The Debye-Waller factor σ^2 is the mean-square displacement from the mean separation R_0 of the backscatterer B relative to absorber A in the direction of the A-B vector.

• The Debye-Waller factor can be expressed as the sum of a vibrational contribution and a static contribution. The magnitudes of the two components can be deduced by means of temperature-dependent EXAFS measurements.

• The static contribution is due to a structural distribution of mean interatomic distances, and can be expressed as the mean square distribution σ^2_{stat}.

• The vibrational contribution is temperature dependent. For diatomic harmonic systems, σ^2_{vib} can be approximately given by the equation shown, and can be used as a qualitative measure of bond strength for closely related systems.

• Reduced thermal vibrations at **low temperatures** give rise to increased EXAFS amplitudes, and therefore to improved signal to noise and greater availability of structural information.
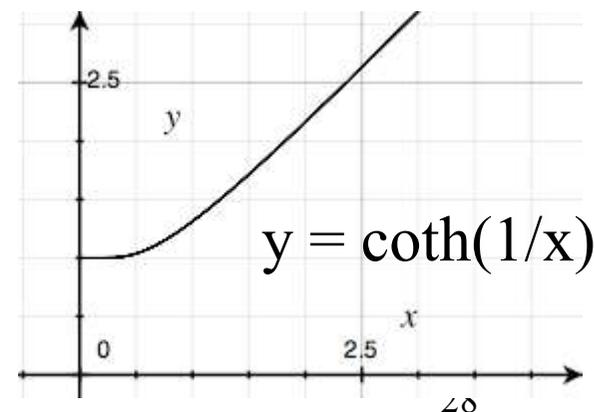
μ - reduced mass

T - temperature

v - vibrational frequency

k_B - Boltzmann's constant

$$\sigma^2_{tot} = \sigma^2_{stat} + \sigma^2_{vib}$$

$$\sigma^2_{stat} \approx \sum \frac{(R_j - R_0)^2}{N}$$

$$\sigma^2_{vib} = \frac{h}{8\pi^2 \mu v} \coth \frac{hv}{2kT}$$

$$y = \coth(1/x)$$

What EXAFS Curve Fitting can and cannot do.

R − *Interatomic distance*
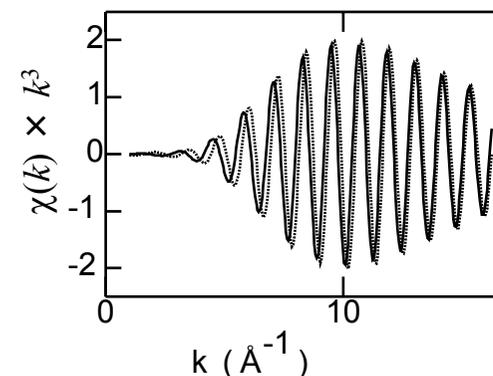
  Accuracy − $\pm$ 0.02 Å, *i.e.* well-defined

N − *Coordination number*

  Accuracy − $\pm$ 25 %, *i.e.* less well-defined

σ^2 − *Debye-Waller factor*

  Typical range: $0.0015 \leq \sigma^2 \leq 0.0080$ Å^2

ΔE_0 − *refinable energy offset for k = 0 threshold*

Effect of ΔE_0=10 eV.

Correlations:
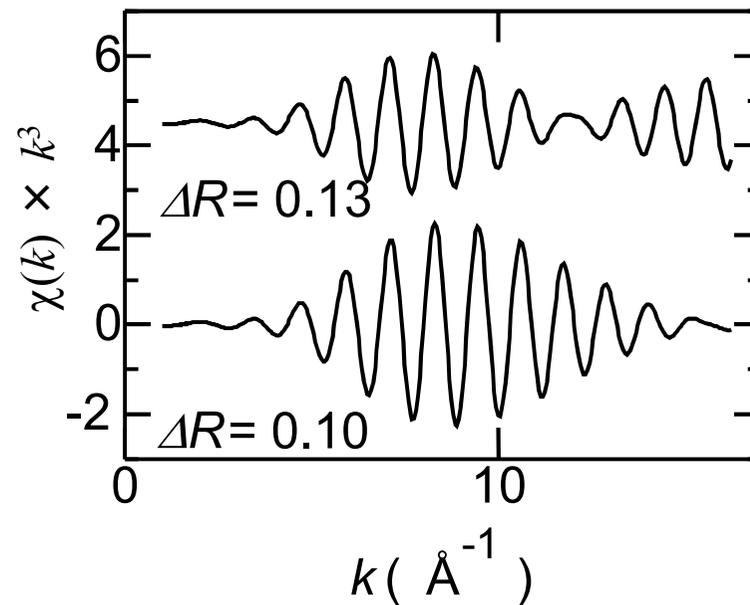 N correlates strongly with σ^2, R correlates with E_0.

Resolution: two shells, same backscatterer type.
  $\Delta R \approx \pi / 2k$

Distinguishing different backscatterer types.
  elements with similar atomic number cannot be distinguished (*e.g.* P and S, Si and Al).

EXAFS Resolution

two shells, same backscatterer type, $\Delta R \approx \pi / 2k = 0.103$ Å

Detection of X-ray Absorption Spectroscopy

Detection method	Concentration range	Comments
Transmittance	High concentration (typically > 2 wt. %)	Easiest detection method; least prone to distortions
Fluorescence (non-dispersive)	Medium to low concentrations (> 5 mM)	Thickness effects occur for too high a concentration
Fluorescence (energy dispersive)	Low concentrations (> 1 ppm, 0.1 mM)	Detector linearity and countrates can be a problem
Electron yield	High to medium concentrations Low Z absorbers	"Surface sensitive" (typically probes 20-100Å)

X-ray absorption spectroscopy – experimental setup.
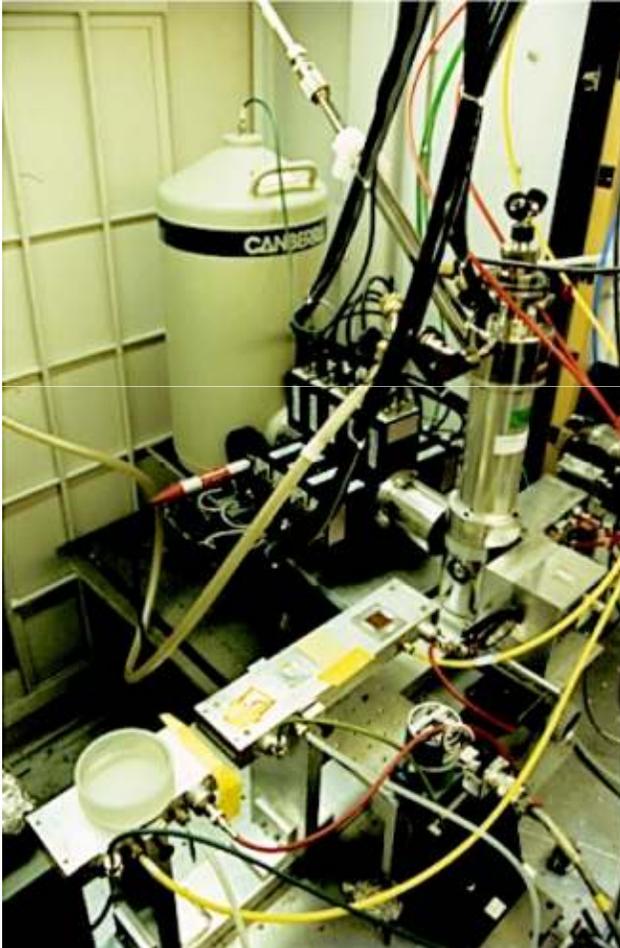
Setup includes a liquid He cryostat and 30 element Ge detector array.

Protein sample showing image of beam (X-ray induced color centers).

Why use Low Temperatures?

● *Low temperatures help to prevent radiation damage to the sample.*

Low temperature sample holder containing an aqueous solution of a metalloprotein (immersed in a bath of liquid nitrogen) after a four hour exposure to the Xray beam at a temperature of 10K. The image of the Xray beam can be clearly seen on the sample, the coloration being due to hydrated electrons trapped in the ice matrix.
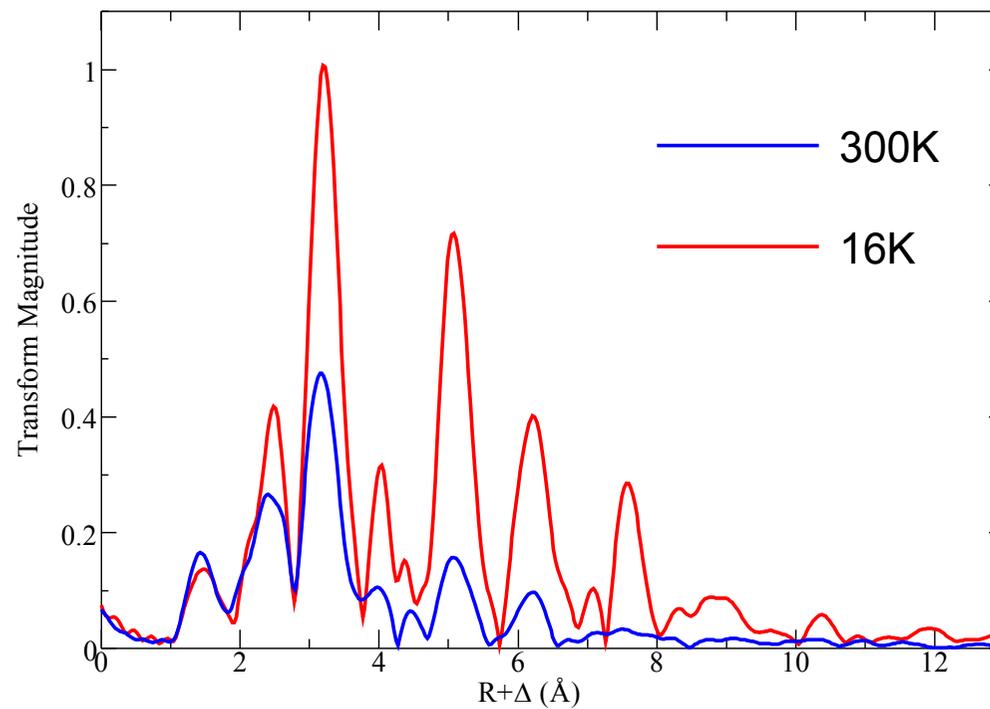
The color vanishes after *ca.* 10 min. at 77K.

Why use Low Temperatures?

- **The EXAFS is more intense due to freezing out of atomic vibrations.**

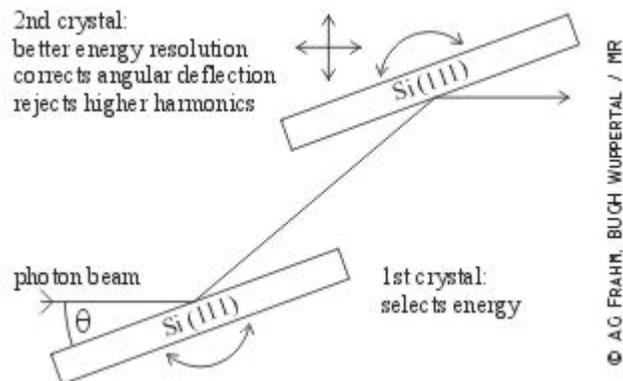*e.g.* **Fourier transform of Sr Kedge EXAFS of $SrCo_{0.8}Fe_{0.2}O_{2.5}$**

Monochromators

• For XAS experiments we need to be able to scan through a range of energies (really choose a bunch of single energies, very close to each other)

• this is commonly achieved using diffraction off two crystals – a "double crystal monochromator"
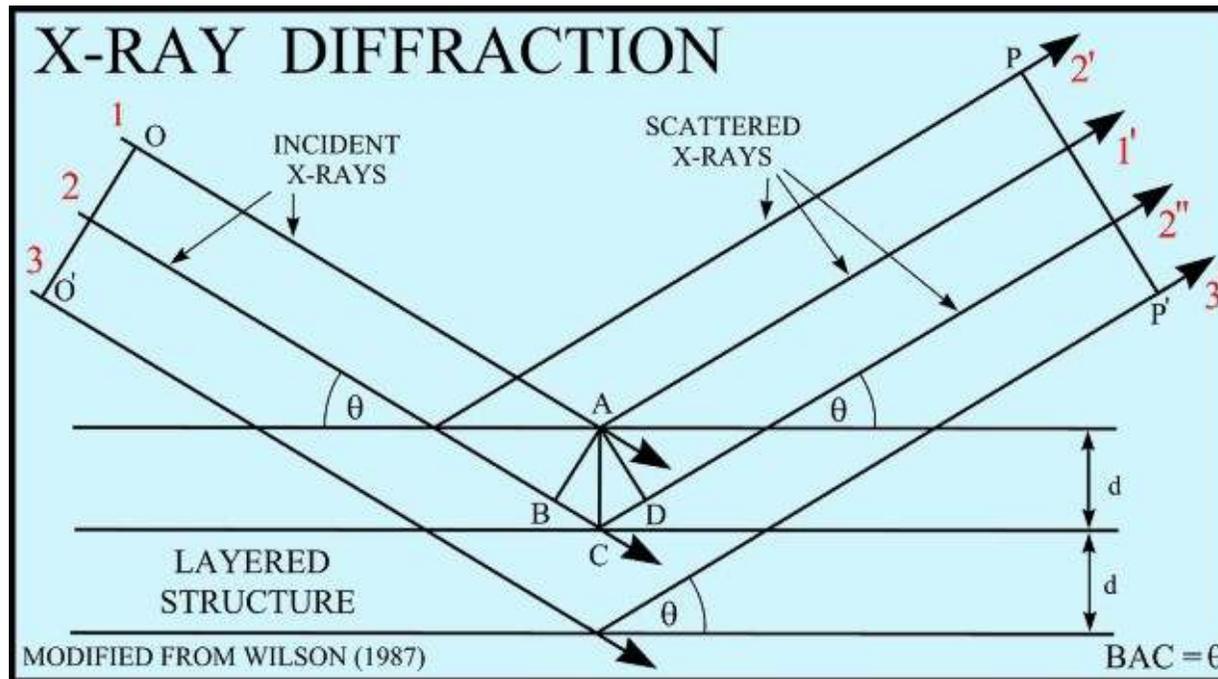
$$n\lambda = 2d \,.\, \sin\theta$$

• d is spacing between crystal planes, λ is wavelength, n is an integer

• "white" light in – a narrow band of wavelengths out

• harmonics and glitches will appear

2nd crystal:
better energy resolution
corrects angular deflection
rejects higher harmonics
Si(111)

photon beam
θ
Si (111)

1st crystal:
selects energy

© AG FRAHM, BUGH WUPPERTAL / MR

Diffraction Monochromators

$$n\lambda = 2d \cdot \sin\theta$$

• *d* is spacing between crystal planes, λ is wavelength, n is an integer

• "white" light in – a narrow band of wavelengths out

X-RAY DIFFRACTION

INCIDENT X-RAYS

SCATTERED X-RAYS

LAYERED STRUCTURE

MODIFIED FROM WILSON (1987)

BAC = θ

Choice of monochromator crystals

- Monochromator crystal material must have excellent stability to X-rays, thermal loading; high reflectivity, *etc.*

  Silicon is most widely used material

- Choose different cuts based on:
  - Working energy range:

Crystal cut	d (Å)	E_{min} (eV)	E_{max} (eV)
Si(111)	3.1356	1977	~18500
Si(220)	1.9201	3228	~29000
Si(400)	1.3577	4556	~42000

  - Energy resolution Si(111) < Si(220) < Si(400)

    Note that vertical slits before monochromator also control resolution
  - Flux: Si(111) > Si(220) > Si(400)
  - Crystal glitches

Choice of monochromator crystals

Energy Calibration

Absolute energy determination is very difficult. XAS is normally done in a relative energy sense against an arbitrary agreed standard.

Sample   *Standard foil*

X-rays

I_0 I_1 I_2
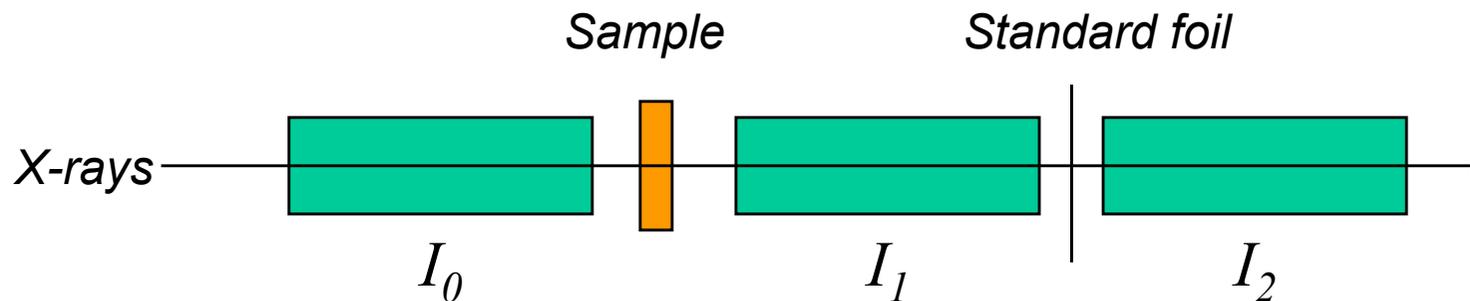
Typically calibrate on lowest energy inflection of elemental foil of correct thickness.

Data modeling or "curve fitting"

Fitting the EXAFS and the "goodness of fit" parameter

• first we need to guess at what backscatterers are present and calculate phase and amplitude functions for these

• then we make an initial guess at the parameters in the EXAFS eqn i.e. for each scattering path, N, R, σ^2, ΔE_0 (same for all paths) and calculate

$$R_{\text{EXAFS}} = \sqrt{\int [\chi_{\text{expt}}(k) - \chi_{\text{calc}}(k)]^2 \, \mathrm{d}k \Big/ \int \chi_{\text{expt}}(k)^2 \, \mathrm{d}k}$$

• Because the experimental data is actually numeric (i.e. pointwise) and because it is common to k^3-weight the data, this reduces to

$$R_{\text{EXAFS}} = \sqrt{\sum k^6 (\chi_{\text{expt}} - \chi_{\text{calc}})^2 \Big/ \sum k^6 (\chi_{\text{expt}})^2}$$

• we (i.e. the computer program) then makes small adjustments to some or all of the parameters and determines if R_{EXAFS} has decreased or not, if yes then keep going, if not then make opposite adjustments

• continue until the change in R_{EXAFS} is smaller than some arbitrary amount

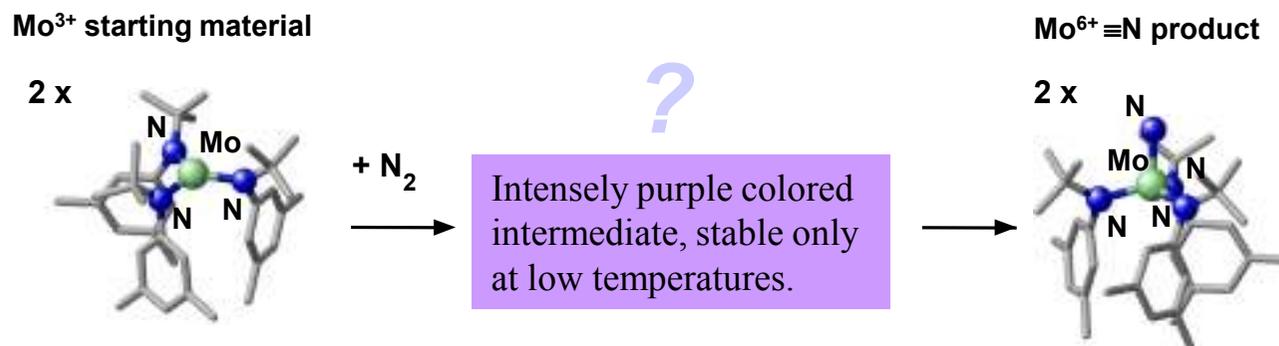• i.e. this is an iterative minimisation!

Comparing models

• This is fine for chemical species whose compositions we are sure about and will provide N, R, etc

• However, in many cases we may not necessarily know the number and identity of all ligands

• In these cases a number of potential theoretical model species can be fitted to the experimental data and their similarity to the reality of the actual sample assessed by comparison of R_{EXAFS} (the smaller the better).

• In this way EXAFS can provide more than just N, R etc – it can also identify ligands that are present

• Caution is needed however – increasing the number of parameters will reduce R_{EXAFS} without necessarily improving the fit.

The amount of data vs. the number of fitted parameters – "determination"

• The actual number of data points is limited in EXAFS – this means that we can only fit a parameter set of a certain size

• For the structural information we derive from the fitting process to be statistically significant (i.e. trustworthy) the number of *independent* experimental data points (N_i) must be greater than the number of fitted variables (p) in the model

• For EXAFS $N_i = 2(\Delta R . \Delta k)/\pi$

• If $N_i > p$ then the fit is *overdetermined* (this is good)

• so if $\Delta R = 3$ and $\Delta k = 12$ then we can determine ~ 23 independent parameters – must do $S_0 2$ and ΔE_0 which leaves 21, so we can just get away with N, R and σ^2 for six distinct ligands in a six coordinate complex but NO multiple scattering

• (the estimate of N_i is a BIG guess so best to have very overdetermined models)

A solution N≡N cleavage reaction.

- Laplaza and Cummins have reported a remarkable N≡N cleavage reaction that proceeds via the formation of an N_2-containing intermediate which is stable at low temperatures.
- We determined the core structure using EXAFS spectroscopy.

Mo^{3+} starting material

2 x

+ N$_2$

?

Intensely purple colored intermediate, stable only at low temperatures.

Mo^{6+}≡N product

2 x

Laplaza, C.E.; Cummins, C.C. 1995, Science, *268,* 861-863.

Purple intermediate – Mo K-edge EXAFS

Starting compound

Purple Intermediate

Product
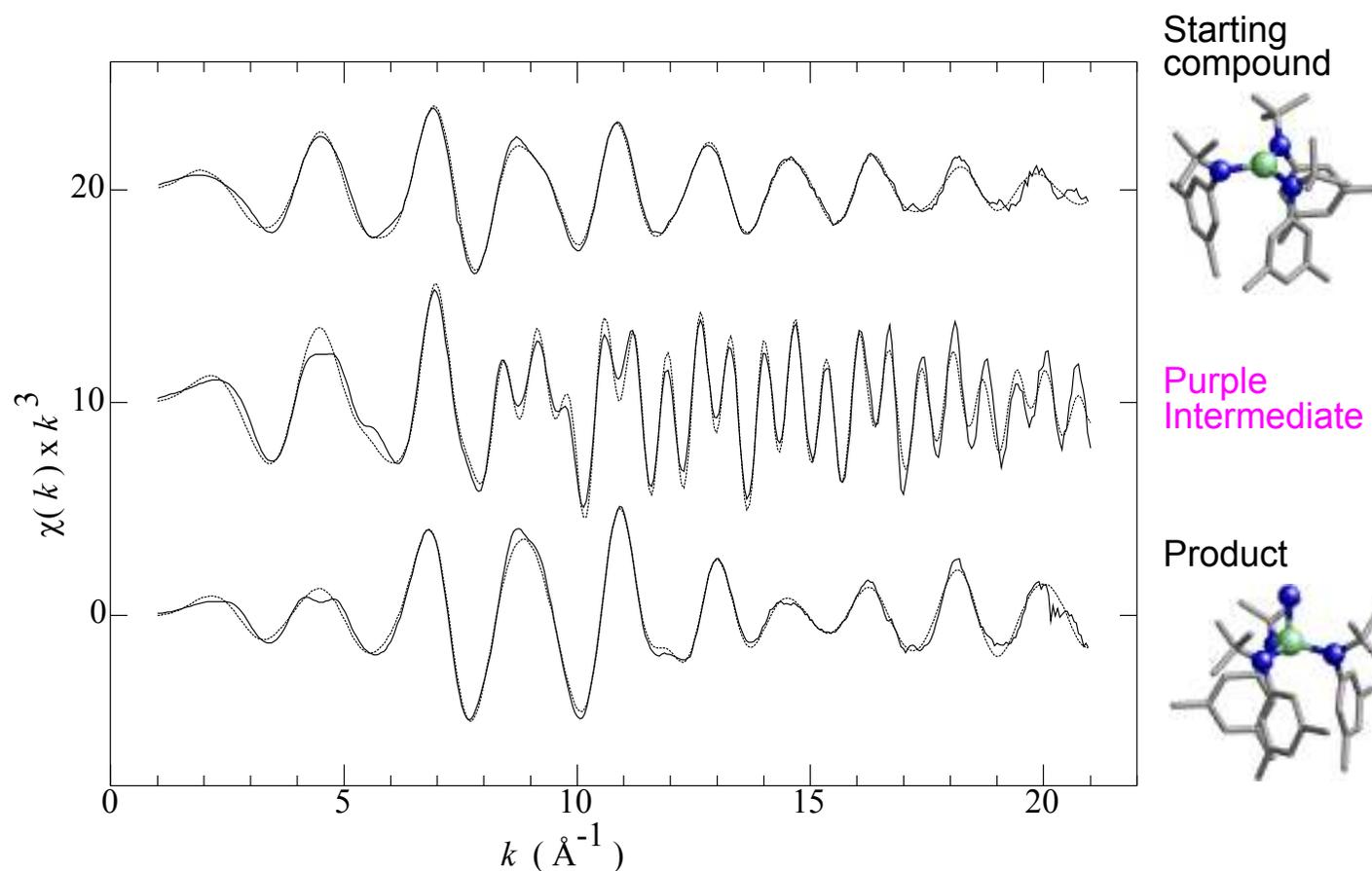
Solid lines experimental data, broken lines best fit (see below).

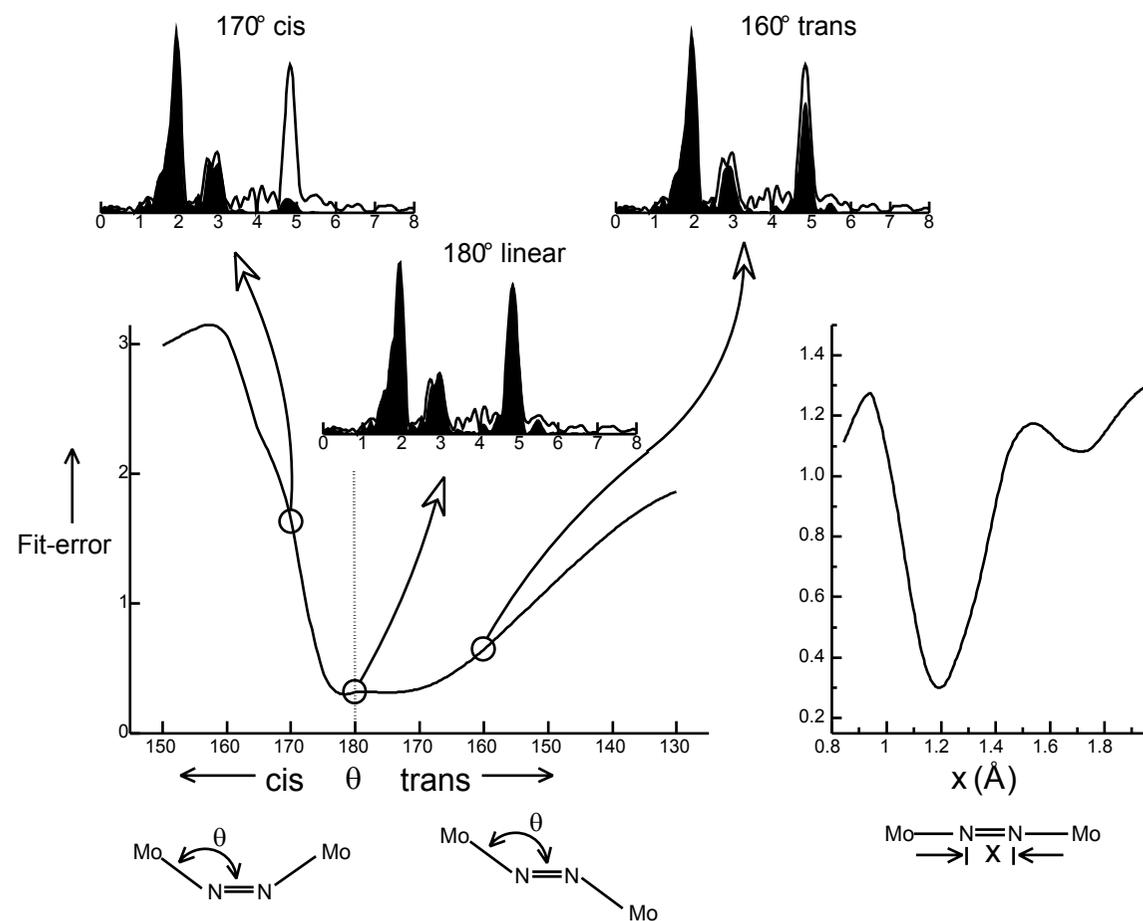# Purple intermediate – Mo K-edge EXAFS Fourier transforms
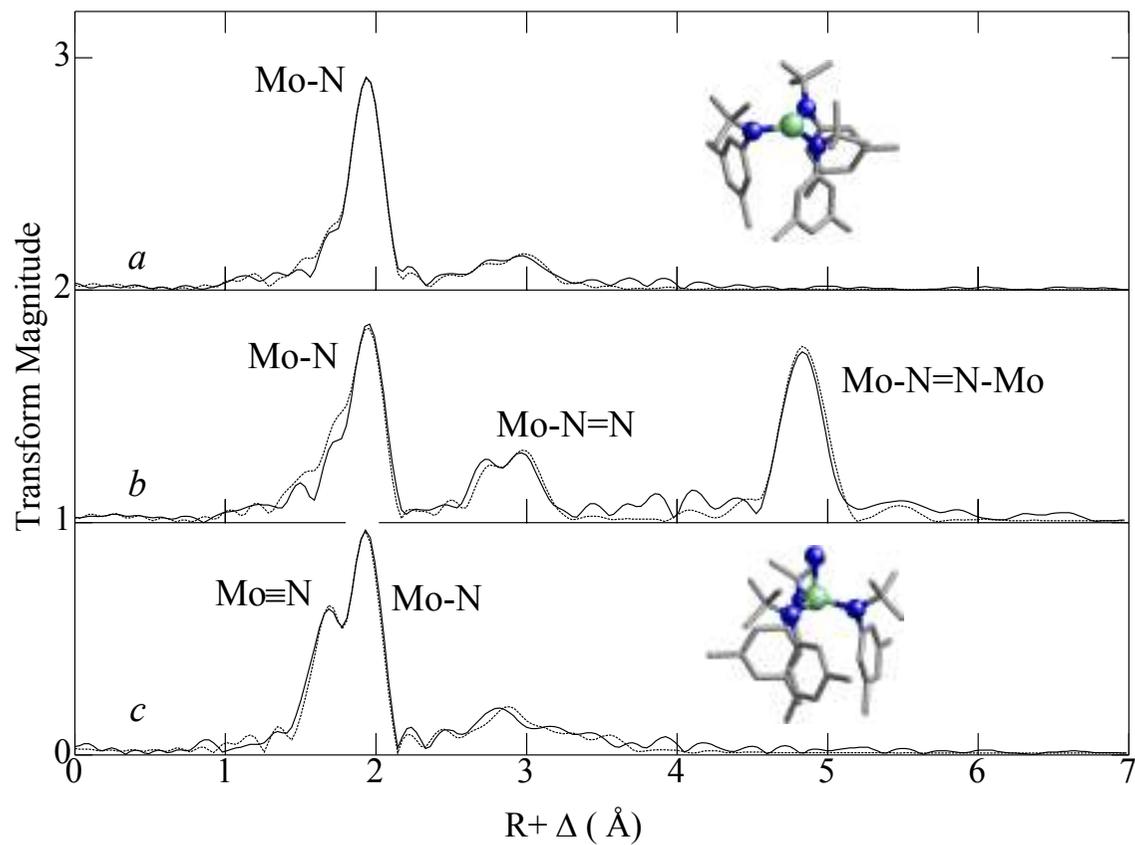
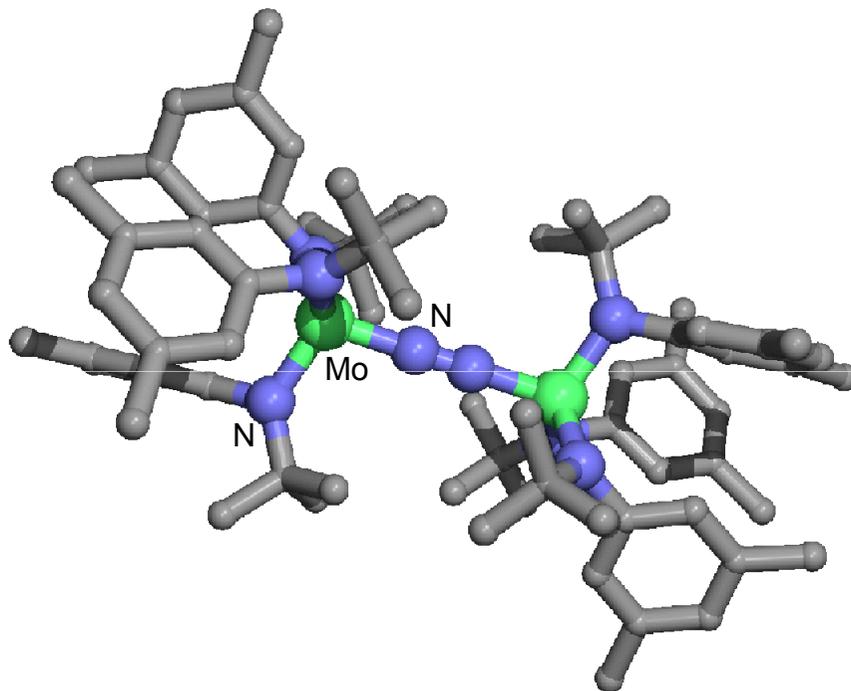# Mo K-edge EXAFS Multiple scattering contributions
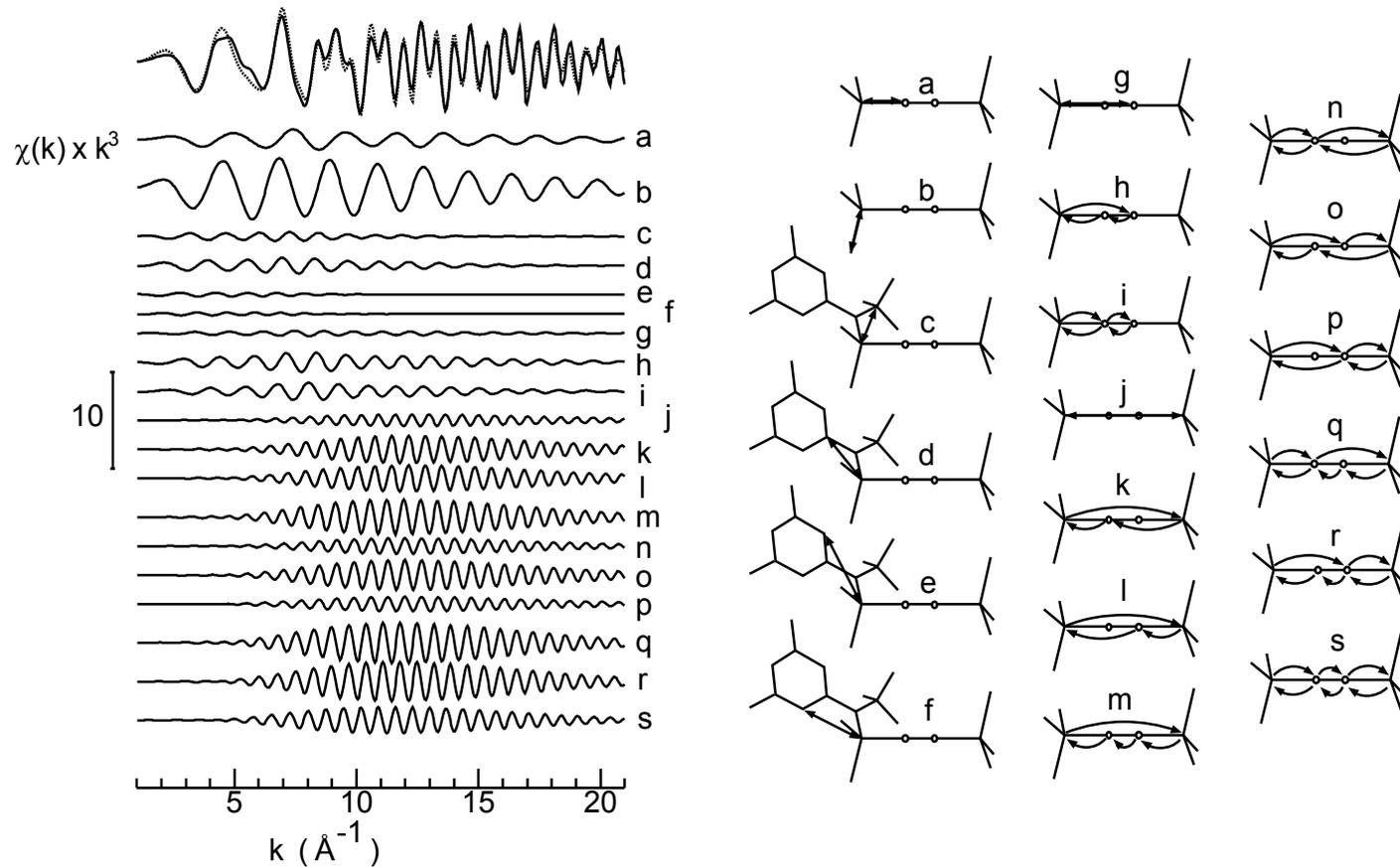
Multiple scattering makes the EXAFS of the Mo–N=N–Mo compound sensitive to geometry.

Mo–N=N–Mo EXAFS Geometry sensitivity
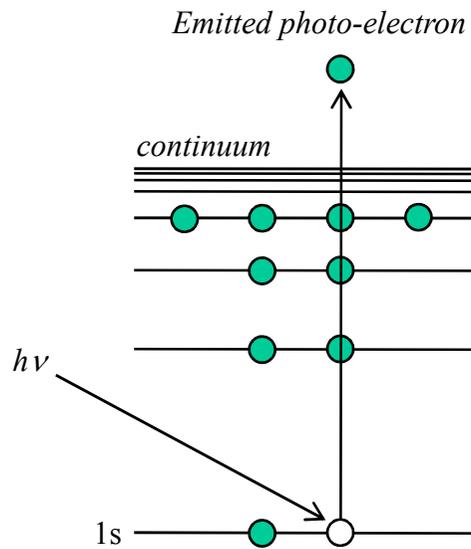
Postulated structure of purple intermediate.

- Core structure determined from EXAFS.
- Remainder of molecule from computational chemistry.
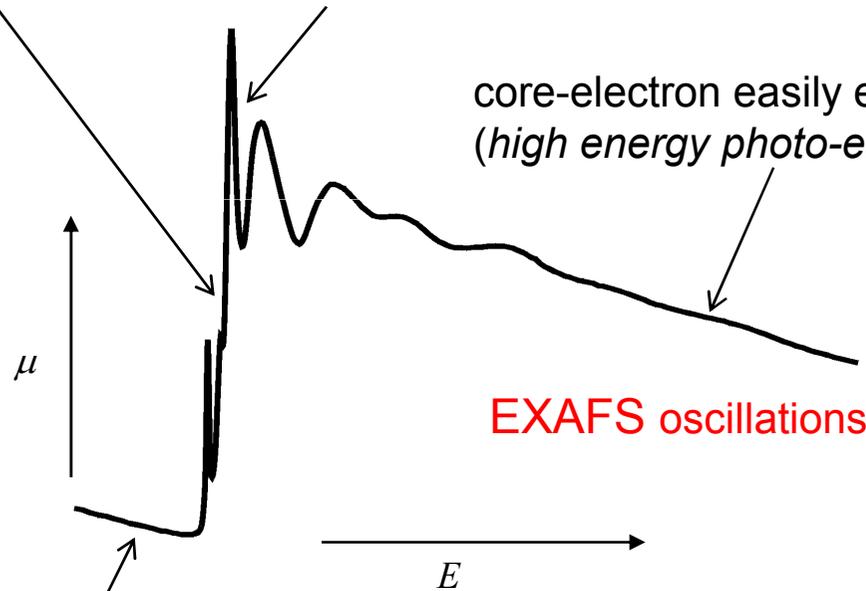
X-ray absorption near-edge structure (XANES)

X-ray Absorption Spectroscopy – Basic Physics

transitions to bound-states
X-ray absorption near-edge structure

Just enough energy to eject core-electron
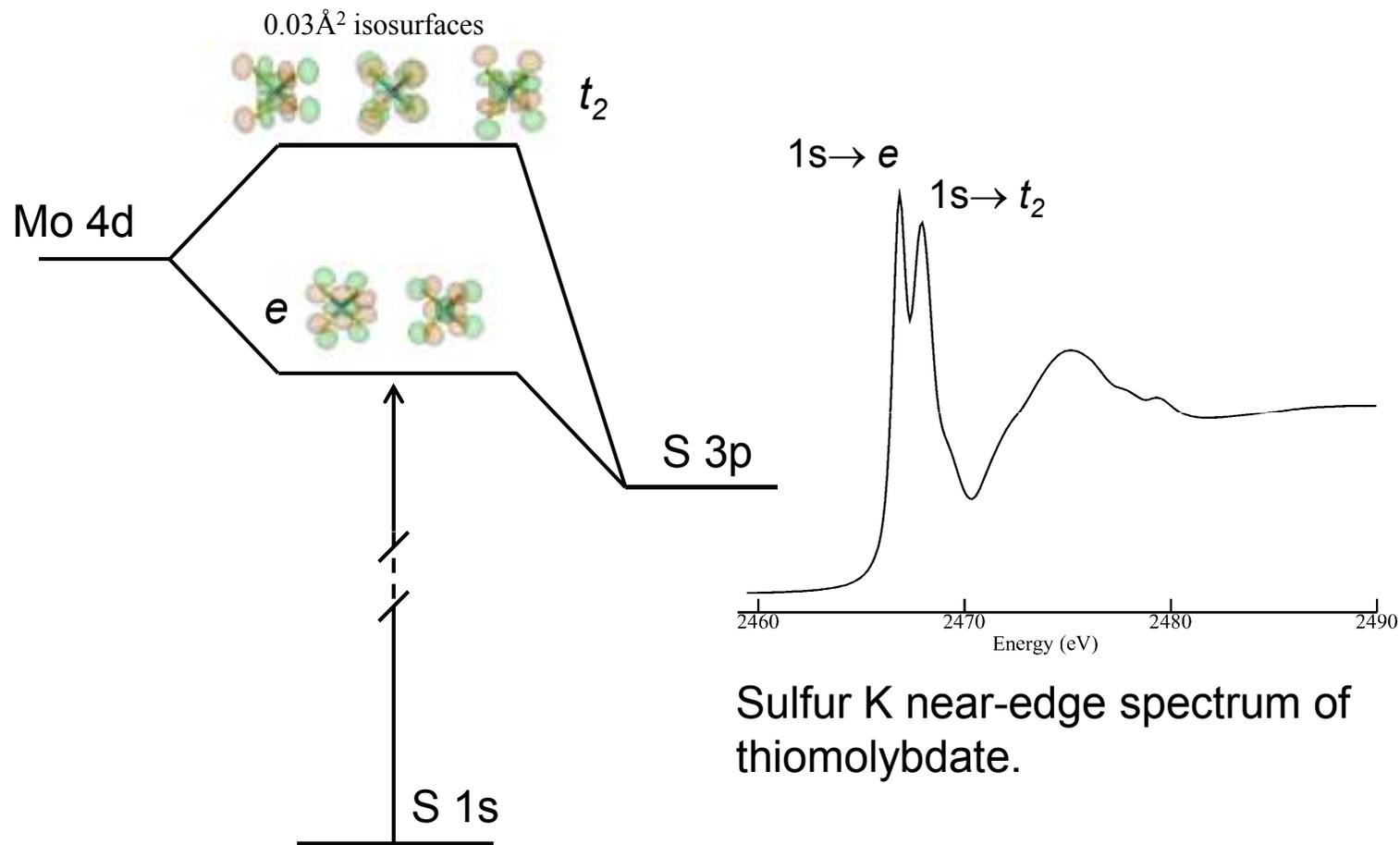(*low energy photo-electron results*).

Emitted photo-electron

continuum

core-electron easily ejected
(*high energy photo-electron)*
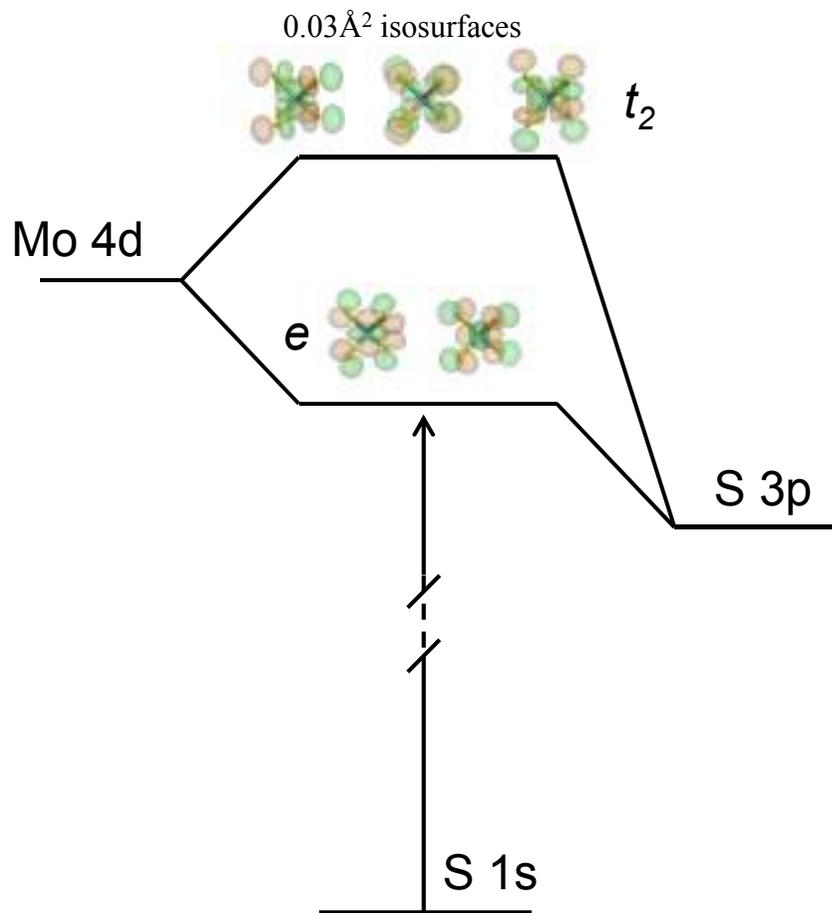
$h\nu$

1s

μ

EXAFS oscillations

E

Insufficient energy to eject core-electron

(μ *here is the absorption coefficient from Beer's Law, i.e. A = μ c l*)

# X-ray absorption near-edge spectra – MoS_4^{2-}

Sulfur K near-edge spectrum of thiomolybdate.

X-ray absorption near-edge spectra

0.03Å^2 isosurfaces

t_2

Mo 4d

e

S 3p

S 1s

- as the oxidation state of the absorbing atom increases the energy position of the absorption edge increases
- this is due to the fact that the frontier orbitals are more shielded from the nucleus than the 1s
- the energy of both orbitals decreases but 1s goes further
- hence XANES is sensitive to oxidation state of the absorbing atom
- also, the excited electron probes the valence orbitals so the XANES is very sensitive to coordination environment

X-ray absorption near-edge spectra

• Near-edge spectra are sensitive to electronic structure.

• They can be used to "fingerprint" the chemical species present.

• Complex mixtures can be analyzed by fitting to a linear combination of model spectra.
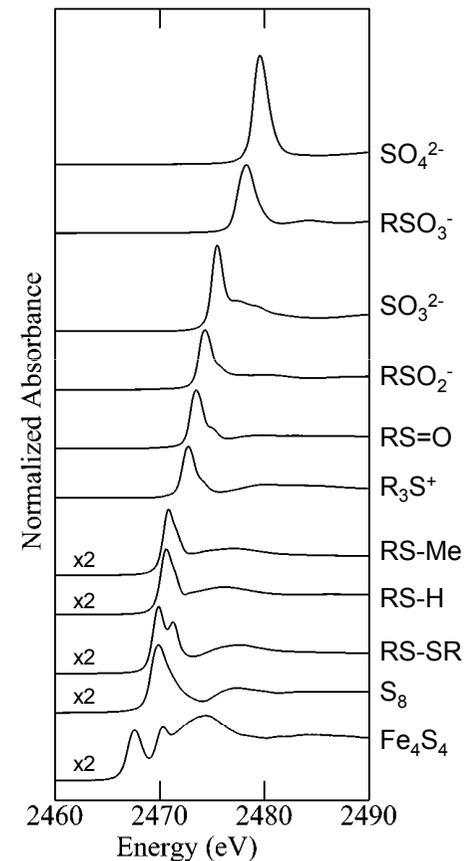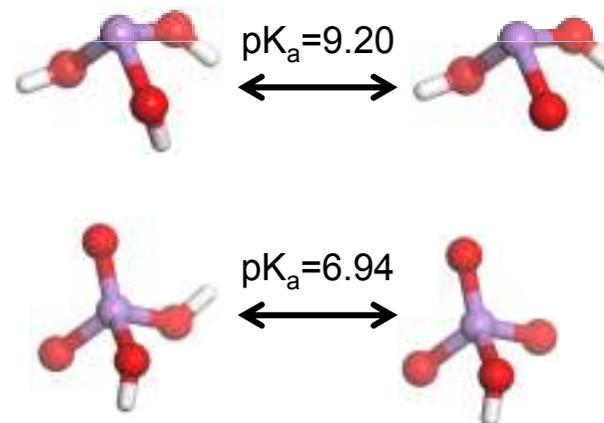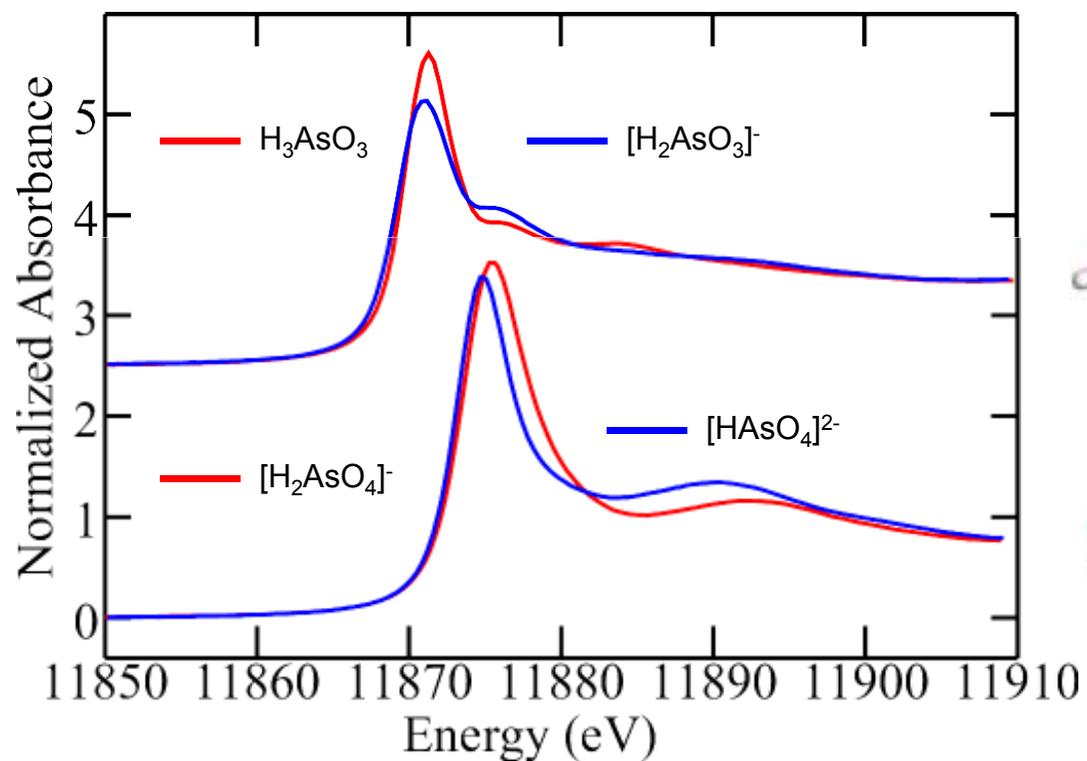
XANES monitoring of photodamage

• Successive scans on a Cu compound indicate that exposure to the x-ray beam is modifying the sample!

• In-built monitoring

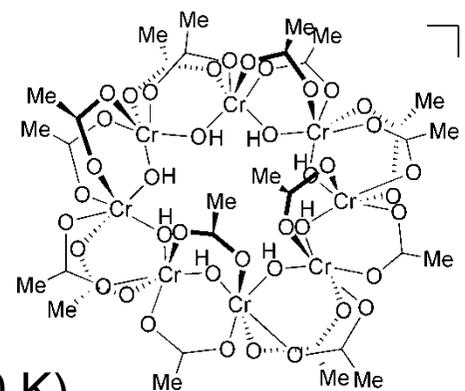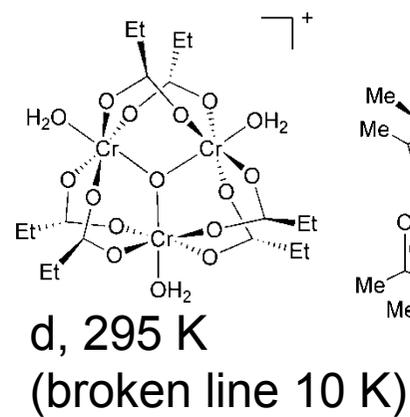• In this case the reduction in the edge energy with time indicates photoreduction
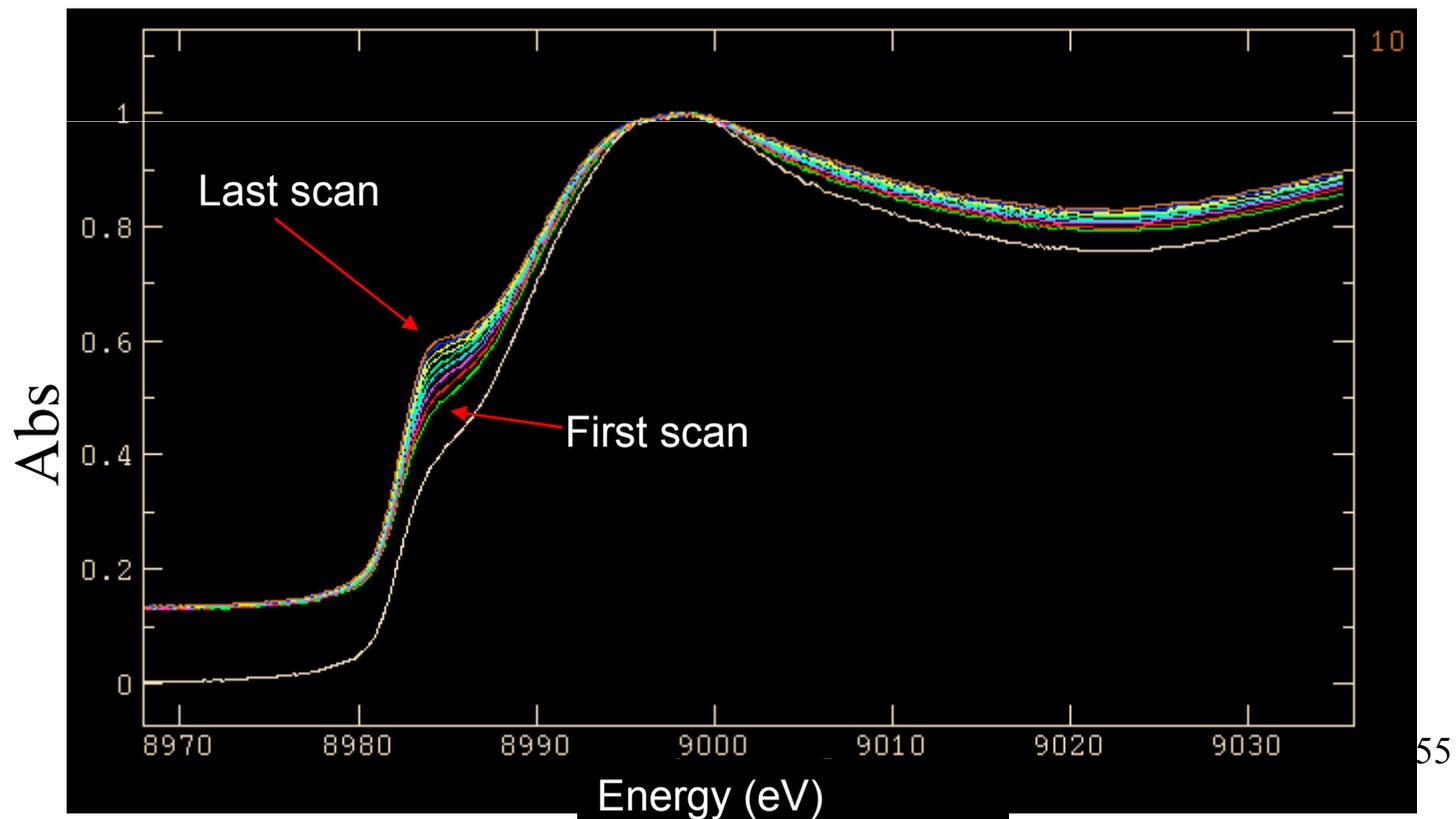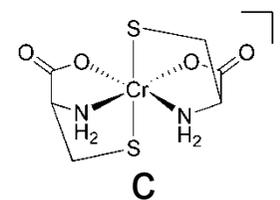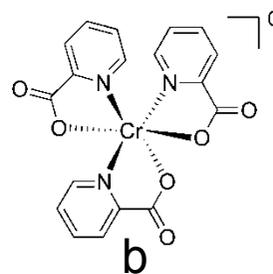
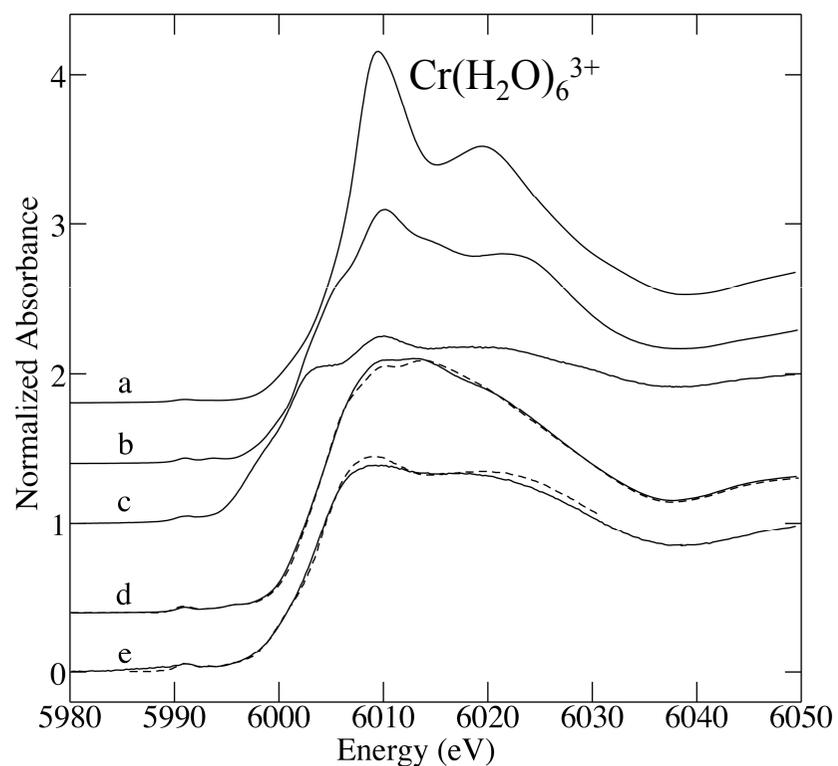# XANES sensitivity to chemical form

- Could accurately determine pH for sample containing arsenate or arsenite

XANES sensitivity continued

Levina A, Harris HH and Lay PA, *J. Am. Chem. Soc*, 2007, **129**, 1065-1075
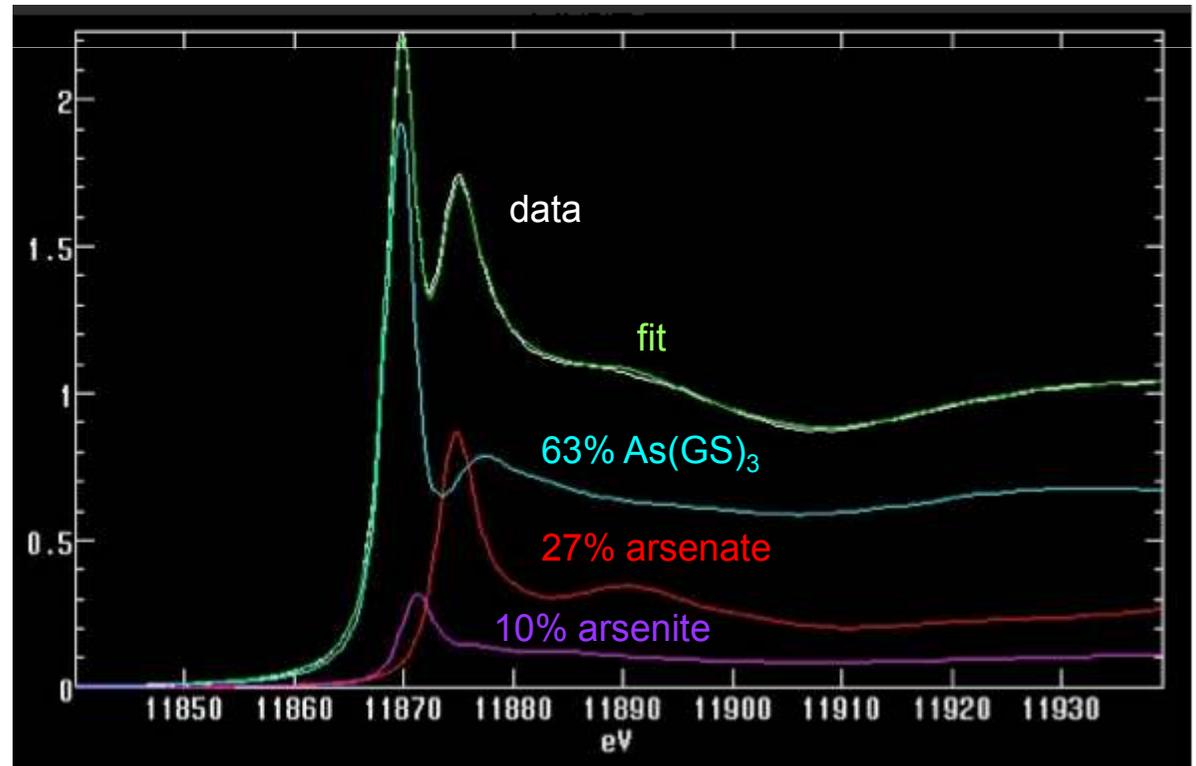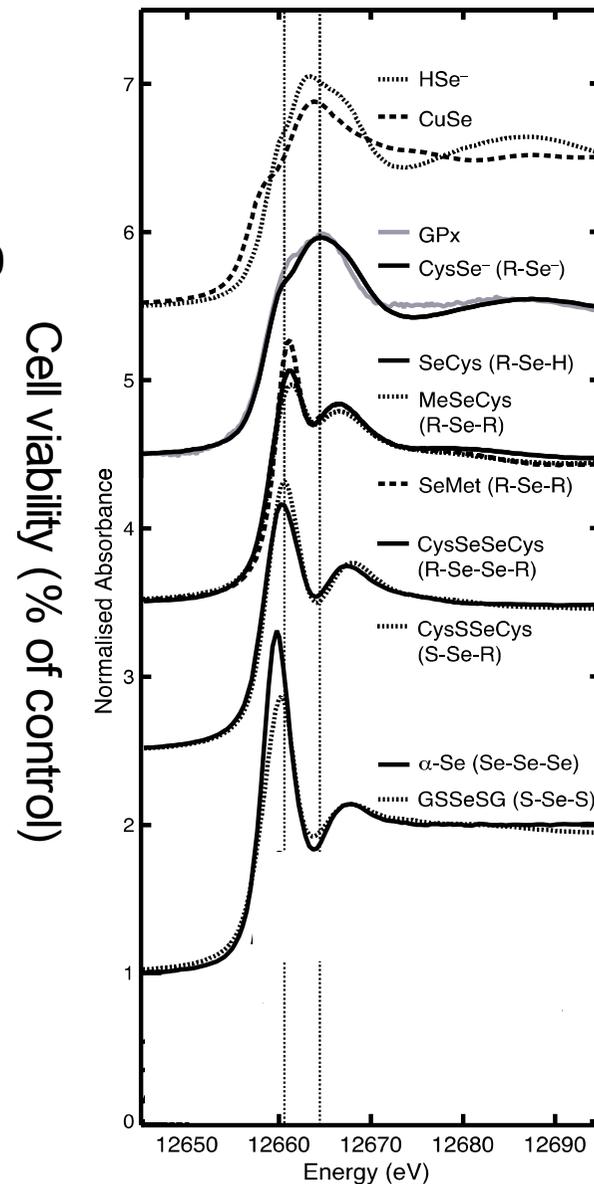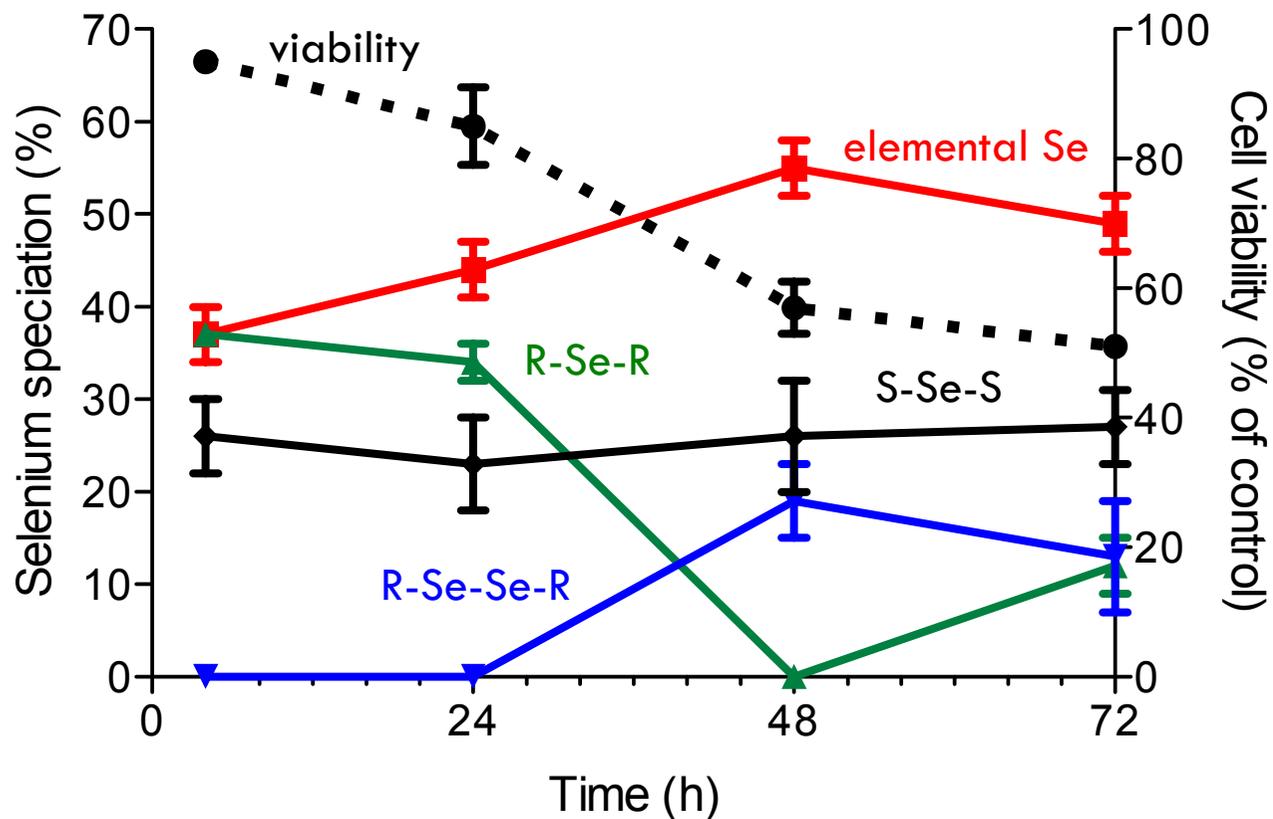
XANES analysis of mixtures

Percentage compositions of mixtures of compounds of one element can be determined by fitting a linear combination of model compound XANES to the XANES of the mixture

• Need good model compound spectra – i.e. good energy calibration and no distortion

• need spectra for all components!

• error of ~ ± 5% -depending on spectral noise

Selenite metabolism – A549 human lung cancer

5 µM selenite treatment (i.e. ca. 72 h IC_{50})

viability

elemental Se

R-Se-R

S-Se-S

R-Se-Se-R

Selenium speciation (%)

Time (h)

Cell viability (% of control)

HSe⁻

CuSe

GPx

CysSe⁻ (R-Se⁻)

SeCys (R-Se-H)

MeSeCys (R-Se-R)

SeMet (R-Se-R)

CysSeSeCys (R-Se-Se-R)

CysSSeCys (S-Se-R)

α-Se (Se-Se-Se)

GSSeSG (S-Se-S)

Normalised Absorbance

Energy (eV)

Weekley, C. M. et al. (2011). *J. Am. Chem. Soc., 133*, 18272–9

Selenite metabolism – A549 human lung cancer

5 µM selenite treatment – 24 h

treatment (μM)	scatterer	coordination number (N)	interatomic distance (R, Å)	Debye-Waller factor (σ^2, Å^2)	$-\Delta E_0$ (eV)	fit error
5	S	1.3	2.195(5)	0.0023(3)	9(1)	0.30
	Se	0.7	2.370(4)	0.0017(1)		

Weekley, C. M. et al. (2011). *J. Am. Chem. Soc., 133*, 18272–9