Lecture 2.  
Practical Aspects of X-ray Absorption  
- Measurement of absorption  
- Energy selection  
- Artifacts (how NOT to measure the right signal)  
- Radiation damage

Detection of x-rays  
X-rays are ionizing radiation – need to collect (and count) ionizations

Transmission measurements  
Beer-Lambert law \( I_t = I_0 10^{-\varepsilon C l} \)  
\( I_t = I_0 e^{-\mu t} \)  
\( I_t = I_0 e^{-\mu_m \rho t} \)  
- \( t \): sample thickness (cm)  
- \( \mu \): absorption coefficient (cm\(^{-1}\))  
- \( \mu_m \): mass absorption coefficient (cm\(^2\)g\(^{-1}\))  
- \( \rho \): Density (g cm\(^{-3}\))

Absorbance  
\[ A = \varepsilon C l = \log \left( \frac{I_0}{I_t} \right) \quad A = \mu t = \ln \left( \frac{I_0}{I_t} \right) \]

X-ray absorption coefficients  
http://csrri.iit.edu/periodic-table.html  
http://physics.nist.gov/PhysRefData/XrayMassCoef/cover.html

http://csrri.iit.edu/periodic-table.html

Periodic Table

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Absorbance is great for concentrated samples, but not for dilute samples.

Transmission is also sensitive to background absorption.

Fluorescence (what goes up must come down)

Fluorescence excitation spectra

Measure fluorescence intensity as excitation energy is scanned.

Fluorescence Detectors
- Energy resolving
- Energy dispersive – Ge or Si(Li)
- Wavelength dispersive
- Exotic
- Non-energy resolving
- Ion chamber
- PIN diode

Energy-dispersive detectors

Solid-state detectors have relatively low maximum count rates

Energy-dispersive detectors typically have high resolution

Wavelength-dispersive detectors

Reasonable solid angle results in low resolution, but unlimited count rate

Non-energy resolving detectors
Z-1 element functions as low-pass filter, but filter fluorescences

Soller slits + Z-1 filter improve fluorescence

Ion chamber
Self-absorption

\[ I_F = I_0 \frac{\Omega}{4\pi} \frac{\mu_X(E)}{\mu_T(E) + \mu_T(E_f)} \left[1 - e^{-\mu_T(E) \mu_T(E_f)}\right] \]

\[ \mu_T = \mu_X + \mu_B \]

Reduces to \( I_F \propto \mu_X \) if \( \mu T \ll 1 \) (thin)

If \( \mu T \gg 1 \) (thick)

\[ I_F \approx \frac{\mu_X(E)}{\mu_T(E) + \mu_T(E_f)} = \frac{\mu_X(E)}{\mu_X(E) + \mu_B(E) + \mu_T(E_f)} \]


Self-absorption continued

\[ \frac{\mu_X(E)}{\mu_X(E) + \mu_B(E) + \mu_T(E_f)} \approx \mu_X(E) \]

Only if \( \mu_X \ll \mu_B \) (dilute)

Fluorescence excitation spectra only give accurate \( \mu_X \) if samples are thin or dilute.

Otherwise, need to correct.


If samples are not either thin or dilute, will have self-absorption

\[ \text{Signal/Noise concerns in XAS} \]

Counting statistics – uncertainty \( \sim (\text{counts})^{\frac{1}{2}} \)

If there is no background, \( S/N = (\text{counts})^{\frac{1}{2}} \)

Typical fluorescence \( 10^4 \text{ sec}^{-1} \) to \( 10^5 \text{ sec}^{-1} \)

Transmission ion-chambers – typical currents \( \geq 10 \text{ nA} \sim 10^{10} \text{ electrons/s} \)

Negligible noise from counting statistics.

Important noise sources: electronic, microphonic, beam problems (below)

Sensitivity
EXAFS amplitude falls of $\approx 1/k^3$
10% effect at $k=2 \text{ Å}^{-1}$; 0.03% at $k=14 \text{ Å}^{-1}$
For EXAFS $S/N=3$ at 14 $\text{ Å}^{-1}$ need
absorption $S/N=3/0.0003=10^4$
Therefore need $10^8$ counts at $k=14 \text{ Å}^{-1}$

Reality
Detected solid angle is 1-5% (i.e., 10^6 sec^{-1})
but – count times of 100 sec/pt are realistic →
total measurement time ~6 hrs (vs. 3 minutes)

However
Effective count rate is often detector-limited:
if scatter:fluorescence is 100:1, $N_{\text{max}} \sim 10^4$
(10^2-fold lower than optimum).

What is required to have $10^8$ fluorescent photons
Incident flux $\approx 2 \cdot 10^{13}$ sec^{-1} in 10^{-8} m^2
Fluorescence yield $\approx 0.5$ → need
absorbance of 10^{-5} to give $10^8$ fluorescent
photons in 1 second
Absorbance = 3·10^4 barns/atom
$= 3 \cdot 10^{-16} \cdot N$
Need $N \approx 3 \cdot 10^{10}$
50 fmole, 50 μM if sample is (100 μm)^3

Bragg’s Law
$n\lambda = 2d \sin \theta$; $E = \frac{hc}{\lambda}$
$E = \frac{nhc}{2d \sin \theta}$

Double-crystal monochromator

Energy resolution
$n\lambda = 2d \sin \theta$

Angular divergence gives spread in energy. Vertical
slits decrease $\Delta \theta$, and thus $\Delta E$.

For many 3rd generation sources, angular divergence of beam is
small compared to intrinsic width of reflection

• Solids
  – If absorbance of element of interest $>$ background
    absorbance use transmission
  – If absorbance of element of interest $<<$ background
    absorbance use fluorescence
  – Samples need to be optically thin – often requires
dilution
• Solutions
  – If concentrated, treat like a solid
  – If dilute (negligible edge jump) use fluorescence
  – Typical limits
    • $- 100 \mu M \text{ Zn in 50 } \mu L \text{ aqueous solution (5 nmole)}$
    • $-1.0 \text{ mM } \text{ V in 10 } \mu L \text{ aqueous solution (10 nmole)}$
    • $10 \mu M \text{ Mo in 200 } \mu L \text{ aqueous solution (2 nmole)}$
Energy calibration

\[ n\lambda = 2d \sin \theta \]

Want to know \( E \) to \( \sim 0.1 \text{ eV} \) \((1 \text{ part in } 10^5)\)

Accurate absolute energy determination is hard. Typically, settle for precise relative energy.

For absolute calibration, see:


Internal energy calibration

\[
A_{\text{sample}} = \ln\left(\frac{I_0}{I_1}\right) \quad \quad A_{\text{foil}} = \ln\left(\frac{I_1}{I_2}\right)
\]

Harmonic contamination

\[ n\lambda = 2d \sin \theta \]

\[
I_0 = I_0 + \beta I_{0,2E}
\]

\[
I_1 = e^{-\mu l}I_0 + \beta I_{0,2E}
\]

\[
A = \ln\left(\frac{I_0}{I_1}\right) = \ln\left(\frac{I_0 + \beta I_{0,2E}}{e^{-\mu l}I_0 + \beta I_{0,2E}}\right)
\]

Experimental consequence of harmonic contamination

pinholes and self-absorption cause similar effect – amplitudes are too small

Harmonic rejection mirror

“Detuning” monochromator

\[ \Delta \theta \]

\[ n=1 \quad n=2 \quad 50\% \text{ detuned} \]
Dependence of XANES on Oxidation State

Normalized Absorption vs. Energy (eV)

II/II
II/III
III/III
III/IV

Radiation damage

Mn(III) shows significant radiation damage
Room temperature, 30 minute scans

Increasing time

Low temperature (4K) reduces but does not eliminate radiation damage

Low temperature can’t be used if thermochromic

Flowing fluid samples can prevent radiation damage
Mn
(salpn}(acac) in Acetone + 15% H2O

Flow rate = 0.05 - 6.4 μL/s
Residence time in beam = 2 s - 16 ms

Flow system can be used for time resolved measurements

Kirkpatrick-Baez focusing optics
~ 1 μm spot size

Zone plate
~ 30 nm spot size

Requirements (for reasonable sample volumes):
• Rapid scanning
• Small sample (i.e., small beam)
Polarized XAS

- X-ray beam
- Crystal or other oriented sample
- Sample positioner
- Fluorescence Detector

Polarized XAFS of Mo/Fe/S clusters

Fourier Transform Magnitude

R vs. (Å)