

X-ray Absorption Spectroscopy in the Physical and Biological Sciences

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Historically Black Colleges and Universities Workshop
23 July, 2008

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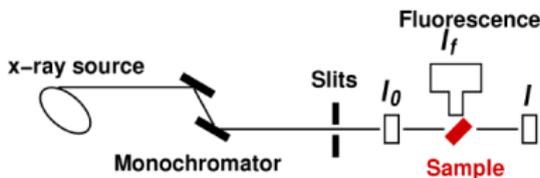
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The XAS Experiment

An **X-ray Absorption Spectroscopy** experiment measures the probability as a function of energy that a material will absorb a photon in a given energy range.

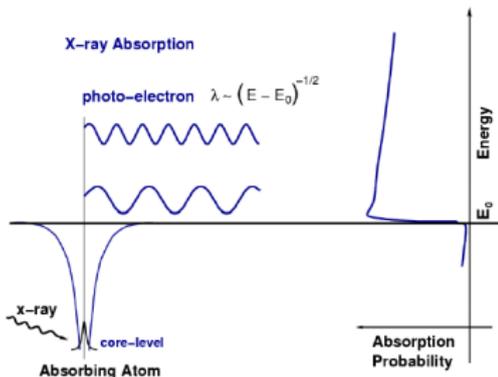
In its simplest form, an XAS beamline looks like this:



The monochromator uses Bragg diffraction to select the desired energy. The energy is scanned by changing the angle of the mono and the x-ray beam is directed from the mono to the sample.

A simple picture of X-ray absorption

An atom absorbs an x-ray of energy E , destroying a core electron with energy E_0 and emitting a photo-electron with kinetic energy $(E - E_0)$. The core state is eventually filled, ejecting a fluorescent x-ray or an Auger electron.



An empty final state is required.

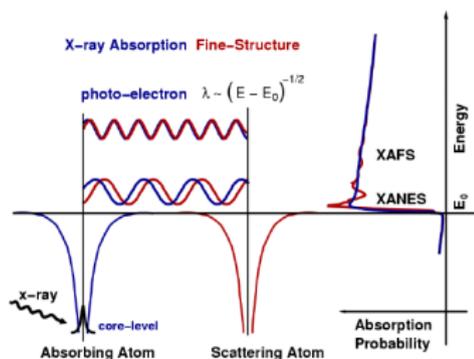
No available state,
no absorption!

Once the x-ray energy is large enough to promote a core electron to the continuum, there is a sharp increase in absorption.

For an isolated atom, $\mu(E)$ has a sharp step at the core-level binding energy and is a smooth function of energy above the edge.

X-ray absorption in condensed matter

The ejected photo-electron can scatter from neighboring atoms. R has some relationship to λ and there is a phase shift associated with the scattering event. Thus the outgoing and scattered waves interfere.

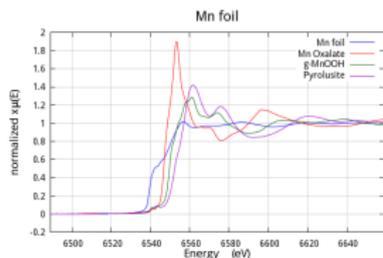


The scattering of the photo-electron wave function interferes with itself.

$\mu(E)$ depends on the density of states with energy $(E - E_0)$ at the absorbing atom.

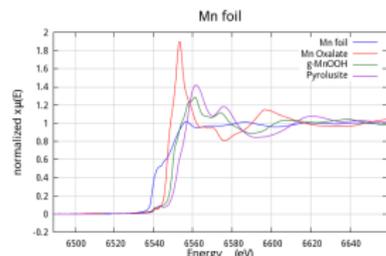
This interference **at the absorbing atom** will vary with energy, causing the oscillations in $\mu(E)$.

Data Processing and Atomic Structure

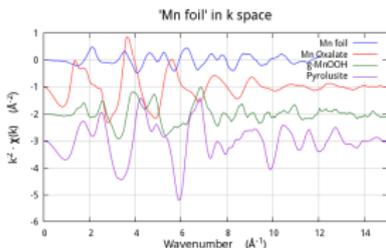


- The absorption data show clear differences for Mn species of different valence. As the valence increases (Mn^0 , Mn^{2+} , Mn^{3+} , Mn^{4+}), the edge position shifts to higher energy.

Data Processing and Atomic Structure

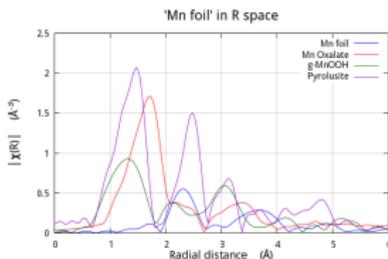
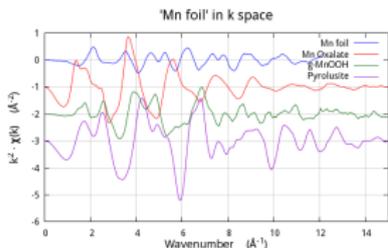
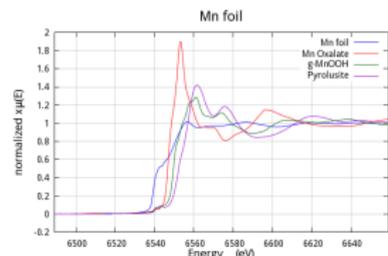


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- The oscillatory portion of the spectrum can be isolated and ...

Data Processing and Atomic Structure



- The absorption data show clear differences for Mn species of different valence. As the valence increases (Mn^0 , Mn^{2+} , Mn^{3+} , Mn^{4+}), the edge position shifts to higher energy.
- The oscillatory portion of the spectrum can be isolated and ...
- ... Fourier transformed. This FT function can be interpreted to yield a partial pair distribution functions of atoms about the absorber. The Mn-O distances are different for the Mn^{2+} , Mn^{3+} , and Mn^{4+} and clearly different from the Mn-Mn distance in Mn metal.

Information in the XAS Measurement

XAS is used to measure:

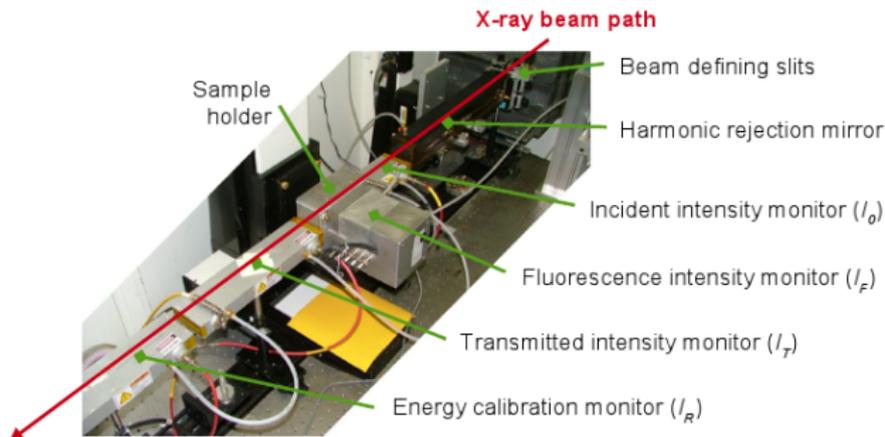
- The valence state of the absorbing atom independently of the chemistry of the rest of the sample
- The local configuration of atoms around the absorbing atom

XAS and Other Techniques

XAS is **complementary** to other synchrotron and laboratory measurements techniques, such as diffraction, NMR, electron microscopy, and many others.

Standard Hutch Instrumentation

Virtually every beamline provides a basic complement of detectors, optics, and sample positioners.

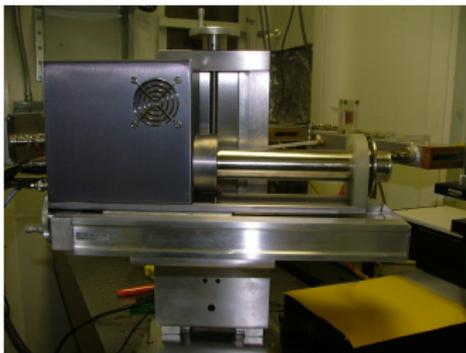


Transmission EXAFS: $\mu \cdot t = \ln(I_0/I_T)$ (Beer's law)

Fluorescence EXAFS: $\mu \propto I_F/I_0$

Specialized Sample Environments

The fluorescence detector can be replaced with an energy discriminating detector which electronically isolates the desired signal.



This is particularly useful for sample with many components or with very low concentrations of the target element.

The sample holder can be replaced with:

- electrochemistry cell
- peristaltic fluid flow apparatus
- furnace
- cryostat
- magnet
- ... and so on ...

XAS Looks at Matter in All Forms

So ... why do an XAS experiment?

- XAS can be measured and interpreted with no assumption of symmetry or periodicity
- XAS is non-destructive
- X-rays penetrate deeply into the sample containment

XAS is used by researchers in a surprisingly broad array of scientific disciplines, such as:

- Catalysis and energy sciences
- Environmental sciences
- Materials science
- Organic and inorganic chemistry
- Life sciences
- and many others

XAS Beamlines at NSLS

We have a comprehensive XAS program at NSLS – some highlights:

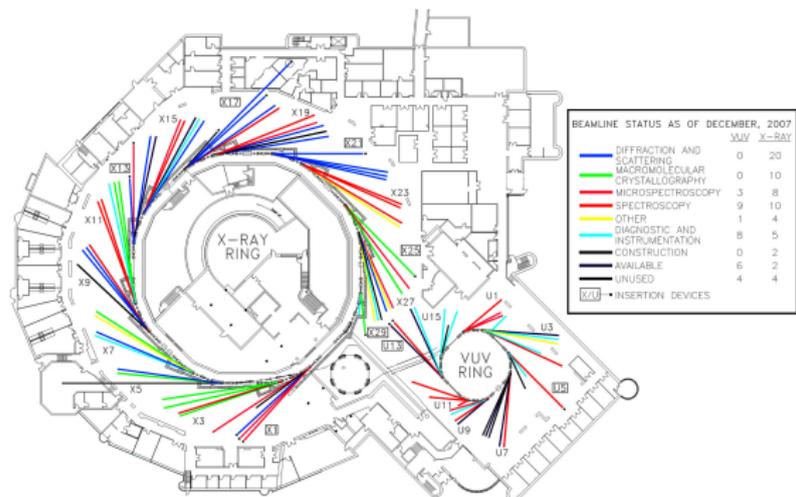
X3b Biological applications

X18b Time resolved XAS

X23a2 NIST + Industrial applications

X15b and X19a “Tender” x-rays, including S, P, and Cl.

U7a and U4a Soft x-rays, first row elements, transition metal L edges



The beamlines marked in **red** do XAS or a related inner shell spectroscopy.

Internet Resources

The screenshot shows the homepage of xafs.org. The main heading is "XAFS, EXAFS, and XANES". Below this, there is a paragraph explaining XAFS as a spectroscopic technique used to probe the physical and chemical structure of matter. A sidebar on the left contains navigation links such as "Tutorials", "Software", and "Equipment". At the bottom, there are links for "About XAFS.ORG" and "The International X-ray Absorption Society".

<http://xafs.org> offers a growing volume of educational resources.

This talk has been posted on the [Tutorials](#) page.

NSLS is developing web-based synchrotron education resources, starting with XAS!

The screenshot shows a mailing list archive for IFEFFIT from June 2008. The title is "June 2008 Archives by thread". It lists messages sorted by subject, author, and date. The archive includes several threads with multiple replies, such as "Linear combination analysis" and "Ti K-edge reference spectra". The interface includes standard email client navigation buttons at the bottom.

The **IFEFFIT mailing list** focuses on the analysis software package I co-authored. It is a **great** place to ask questions about any aspect of XAS measurement, theory, or interpretation.

