A brief overview of X - ray Absorption Spectroscopy (XAS)

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Outline

- The Electromagnetic Spectrum & X - rays
- Interactions between X - rays and Matter
- XANES
- Transmission X - Ray Microscopy
- EXAFS
- The EXAFS Equation
- Summary
- Helpful Resources

The Electromagnetic Spectrum & X - Rays

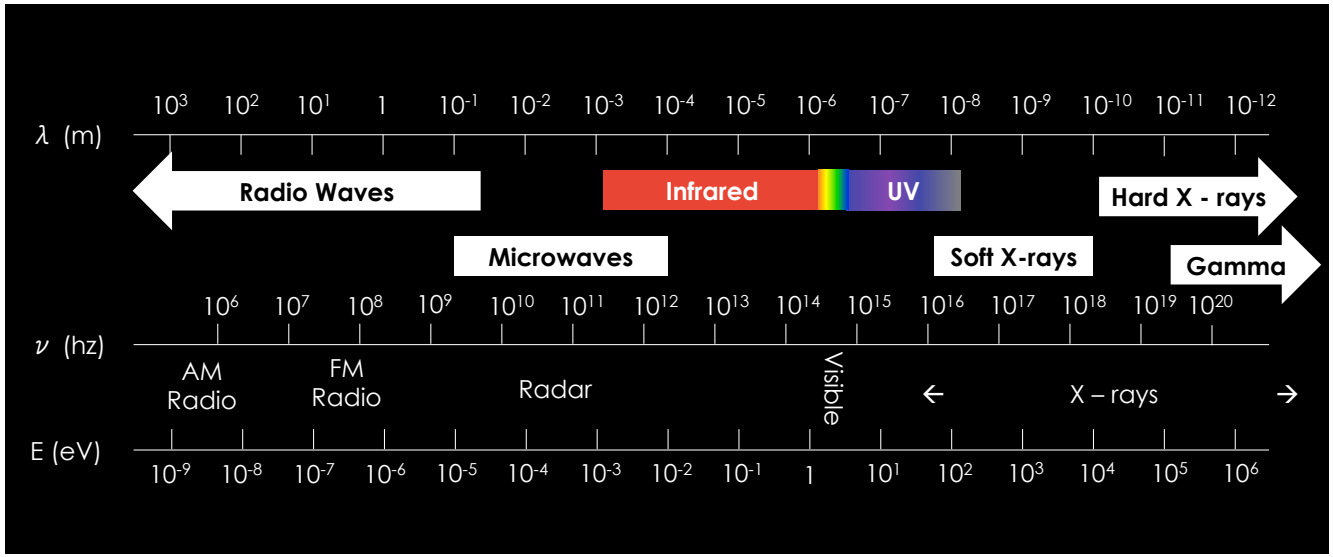


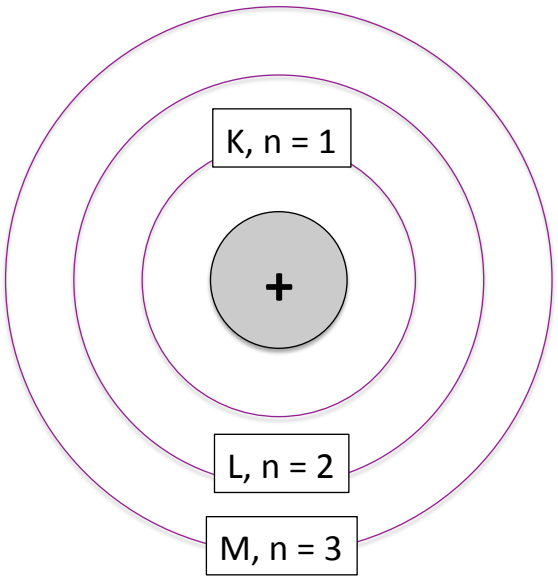
Figure: The Electromagnetic Spectrum

- The electromagnetic spectrum distinguishes light into different regimes based on energy.
- X - rays are high energy forms of light divided into "Soft" and "Hard" regimes.

Interactions of X - rays with Matter

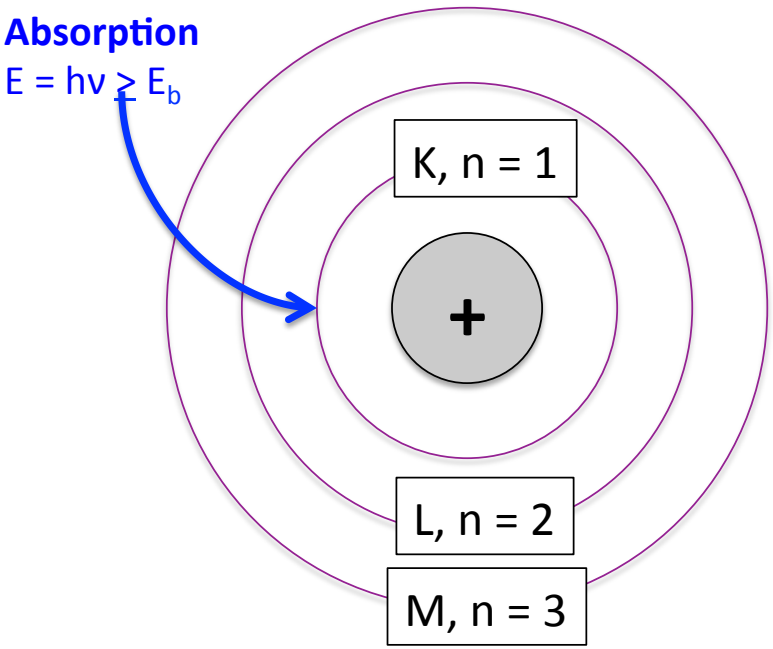
The atom

An atom has a positively charged nucleus surrounded by negatively charged electrons located in orbitals around the nucleus. Each electron has a characteristic set of quantum numbers which defines its position, orbital shape, direction and spin state.

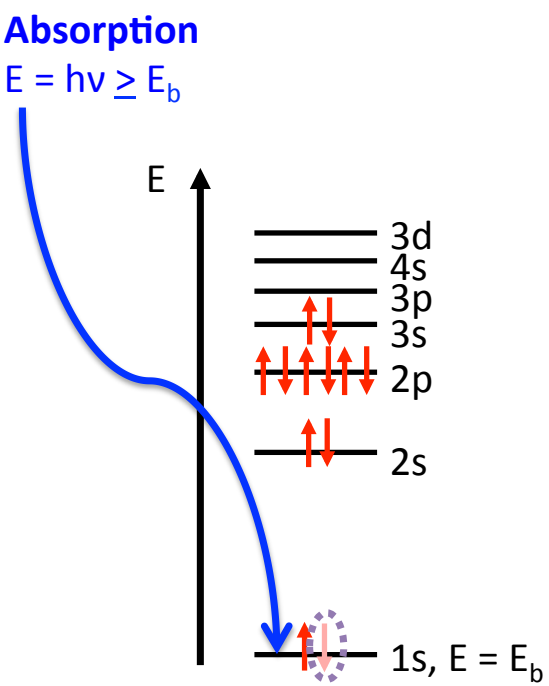


- The principal quantum number, n defines the energy level of the electron.
- Energy levels may also be defined by K, L, M... instead of n = 1, 2, 3...

Interactions at the atomic level

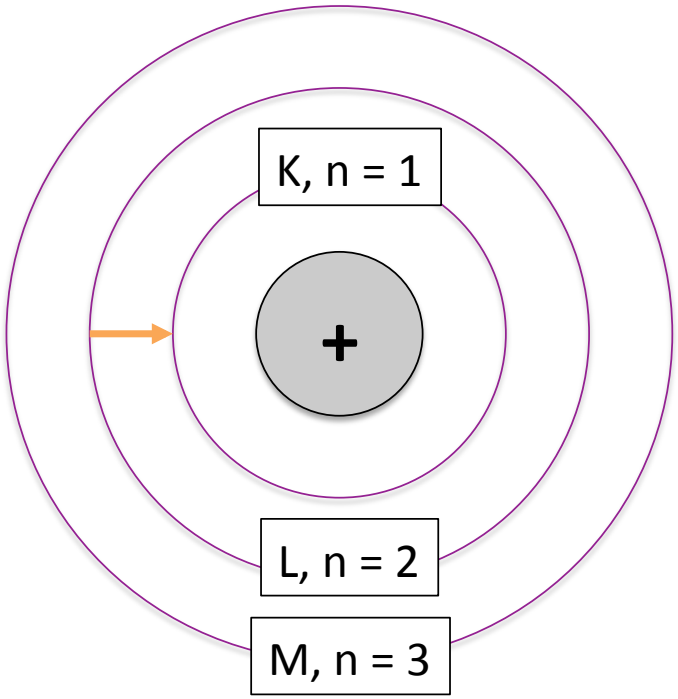


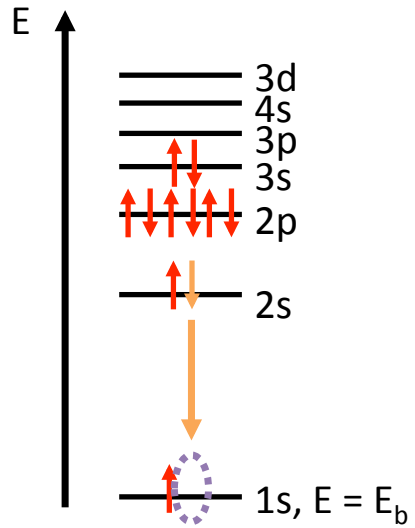
(A) Atom absorbs the x – ray, of energy greater than binding energy for the core electron (E_b).



(B) Energy is sufficient to remove an electron from the core and leave a hole.

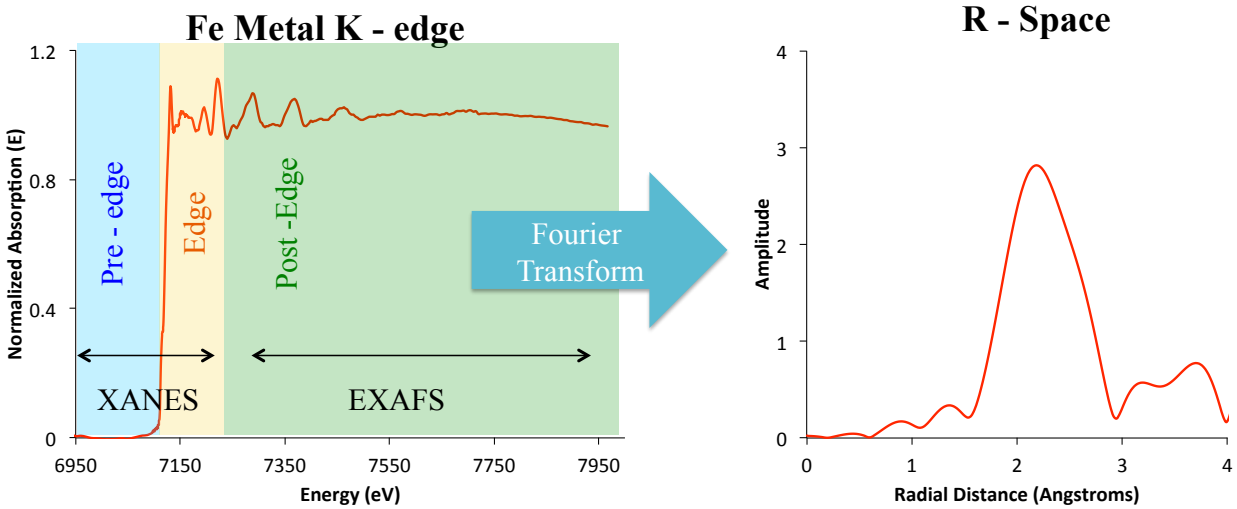
Interactions at the atomic level





Fluorescence: An electron from a higher shell (L, M, ...) fills the hole and emits light.

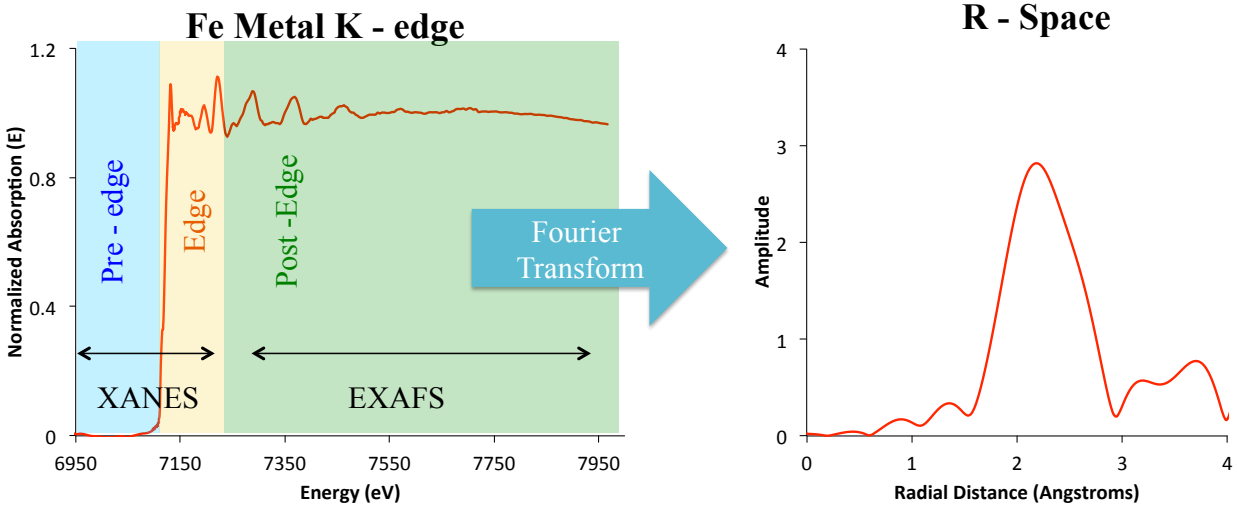
XAS: X - ray Absorption Spectroscopy



- The pre - edge region occurs at $h\nu \leq E_b$. This region is often featureless with little absorption occurring. In some cases there are pre - edge peaks, resulting from d $\rightarrow$ p transitions.

S. Calvin, *XAFS for Everyone*, (CRC Press, 2013)
Figure adapted from C. A. Cama, L. Holtzman, Y. Zhang, E. S. Takeuchi, K. J. Takeuchi, A. C. Marschilok, *ECS Transactions* **77**, 35–45 (2017)

XAS: X - ray Absorption Spectroscopy



- The edge region is identified as the steep rise in absorption when $h\nu = E_b$ and the electron is ejected.
- The post - edge region $h\nu > E_b$. exhibits oscillations due to constructive interference with the ejected electron.

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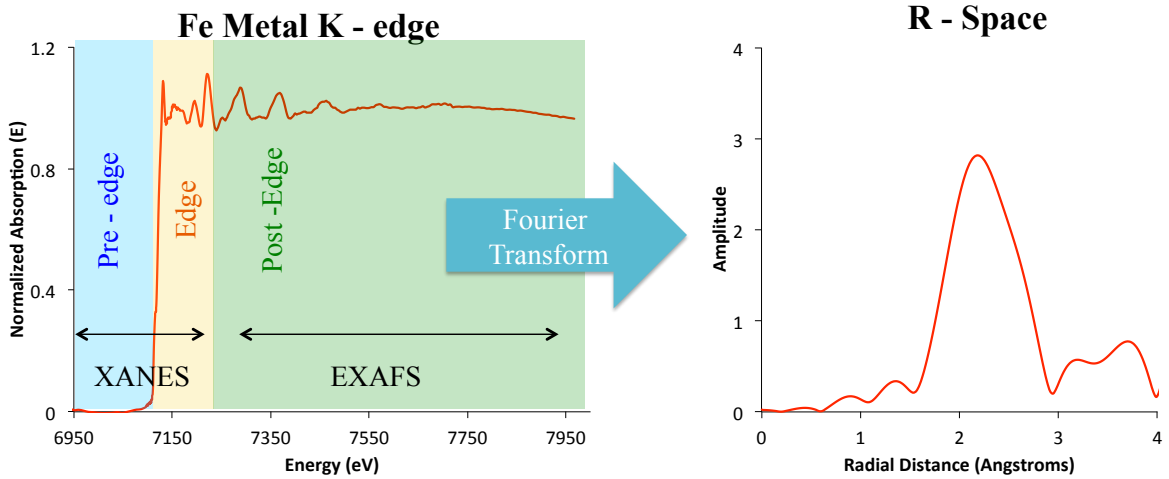
XANES: **X**-Ray **A**bsorption **N**ear **E**dge **S**pectroscopy



- The XANES region is composed of the pre - edge and edge regions.
- The edge energy can indicate the oxidation state of the absorber.
- Pre-edge peaks can indicate geometry of the absorbing atom.

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XANES Analysis Methods

XANES analysis requires the measurement of standards with similar geometry and varying oxidation state.

Types of analysis methods:

Fingerprinting Analysis: Qualitative comparison of XANES spectra of standards to unknowns.

Calibration Plot

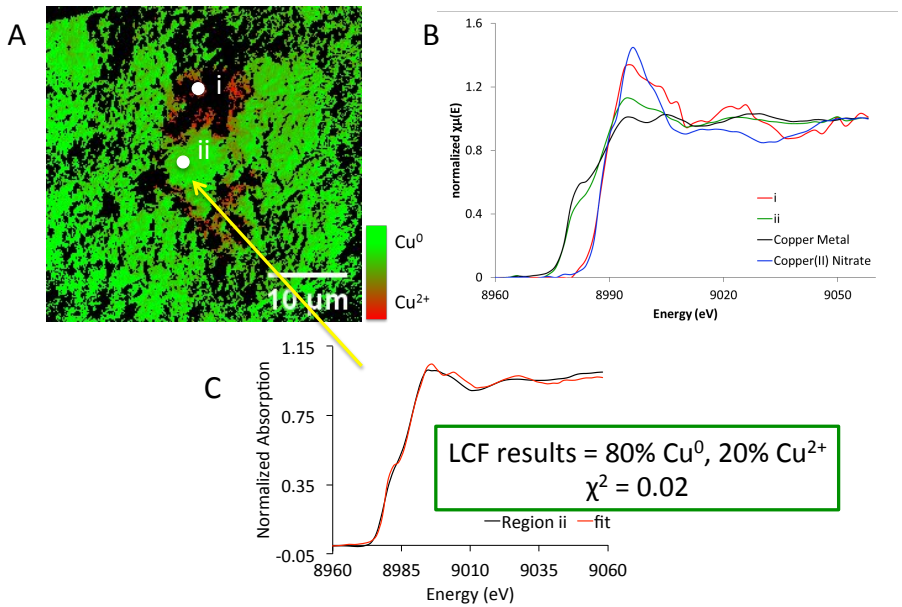
- Calculate the linear equation for the plot of edge energy vs. oxidation state.
- Use the linear equation to calculate the oxidation state of an unknown sample.

Linear Combination Fitting: The spectrum of an unknown sample is the weighted sum of the spectra of standards.

S. Calvin, *XAFS for Everyone*, (CRC Press, 2013)

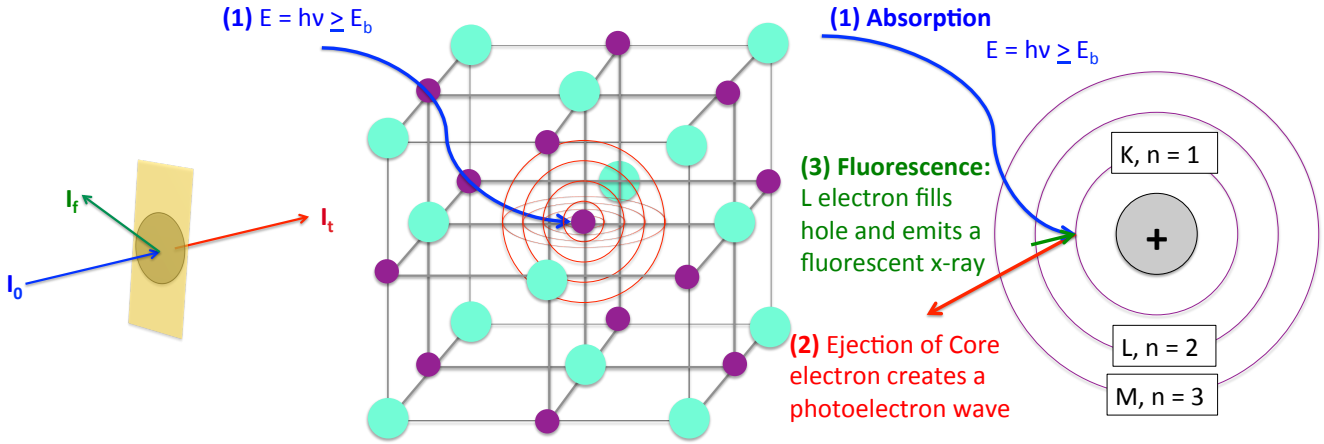
Linear Combination Fitting, LCF

LCF calculates the percentage of each standard required to reproduce the measured spectrum. Below is a Transmission X-ray Microscopy (TXM) image which maps the electrode surface. Each pixel corresponds to a spectrum. The color of the pixel is the result of the LCF.



C. A. Cama, C. J. Pelliccione, A. B. Brady, J. Li, E. A. Stach, J. Wang, J. Wang, E. S. Takeuchi, K. J. Takeuchi, A. C. Marschilok, *Physical Chemistry Chemical Physics* **18**, 16930–16940 (2016)

EXAFS: **E**xtended **X**-ray **A**bsorption **F**ine **S**tructure



During absorption, a photoelectron is ejected and has wavelike property ($\lambda = \frac{h}{m\nu}$). It is called a photoelectron wave. The wave scatters to neighboring atoms, undergoing constructive and deconstructive interferences resulting in oscillations in the post - edge of the absorption spectrum. The interference pattern is characteristic of the geometry around the absorbing atom.

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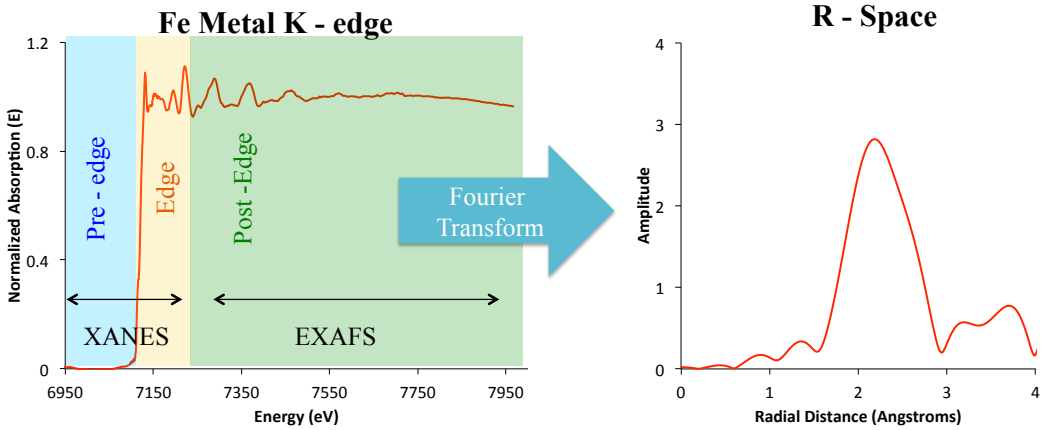
EXAFS Analysis



- The Fourier transform of the absorption spectrum calculates the R-space, which describes the radial distribution of neighboring atoms in the first shell, second shell and on.
- The EXAFS Equation is used to fit this space and provide details regarding bond length, occupancy, and disorder.

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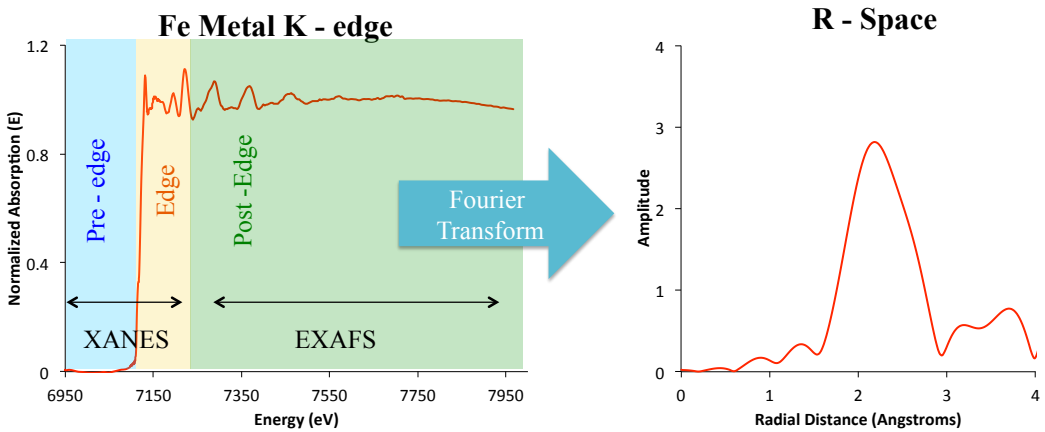
EXAFS Analysis



- The first shell describes the atoms closest to the absorbing atom. For example, if Fe^{3+} exists in an octahedral arrangement with oxygen atoms located at the octahedron's vertices, then the first shell will describe the Fe - O bond length and coordination.
- The second shell describes the atoms that are not immediately bound to the absorbing atom.

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The EXAFS Equation

$$\chi(k) = \sum_j \frac{S_0^2 N_j f_j(k) e^{\frac{-2R_j}{\lambda(k)}} e^{-2k^2\sigma_j^2}}{kR_j^2} sin[2kR_j + \delta_j(k)]$$

Fitting Parameters

- $\mathbf{S_0}^2\mathbf{N}_j$, The product of the Amplitude Reduction factor and the degeneracy for path j, respectively will provide information regarding coordination around the absorbing atom.
- ${\sigma_j}^2$ is the deviation in the absorber to scattering distance for path j.
- $\mathbf{R}_j$ is the absorber to scatterer distance
- $\lambda\mathbf{(k)}$ defines the photoelectron path
- $\mathbf{f}_j$, $\delta_j\mathbf{(k)}$ are parameters defined by the scattering atom.

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Let's Review

- In x - ray absorption, an atom absorbs an x-ray and ejects an electron, creating a photoelectron wave. The energy at which the atom absorbs the energy is indicative of the atom's state. This detail is provided in the XANES portion of the absorption spectrum.
- The photoelectron wave undergoes scattering processes with neighboring atoms, providing detail regarding the number and type of neighboring atoms in the EXAFS region.
- XANES analysis techniques can provide information regarding the oxidation state and geometry around an atom.
- EXAFS fitting can provide further detail on the local structure around an absorbing atom including bond lengths, occupancy, and degree of disorder.

Helpful Resources and References

Here are some helpful resources regarding XAS:

- http://xafs.org/Tutorials
- *XAFS for Everyone* by Scott Calvin
- *Introduction to XAFS: A Practical Guide to X - Ray Absorption Fine Structure Spectroscopy* by Grant Bunker