4.8: Introduction to X-ray Absorption Spectroscopy (XAS)

> ✏️ **Definitions**
>
> - **XAS: X-Ray Absorption Spectroscopy:** Generic term for various techniques involving absorption of x-rays
> - **XAFS: X-Ray Absorption Fine Structure:** Alternate generic term for following two techniques
>   - **XANES: X-Ray Absorption Near Edge Structure:** Structure in x-ray absorption spectrum just before and after edge and its analysis – a spectroscopic technique
>   - **EXAFS: Extended X-Ray Absorption Fine Structure:** Structure in x-ray absorption spectrum after edge and its analysis – a structural technique

The X-ray absorption spectra show a steep rise at the core-level binding energy of X-ray-absorbing atoms and attenuates gradually with the X-ray energy. The XAS spectra are usually divided in two energy regions:

1. the X-ray Absorption Near Edge Structure (XANES)
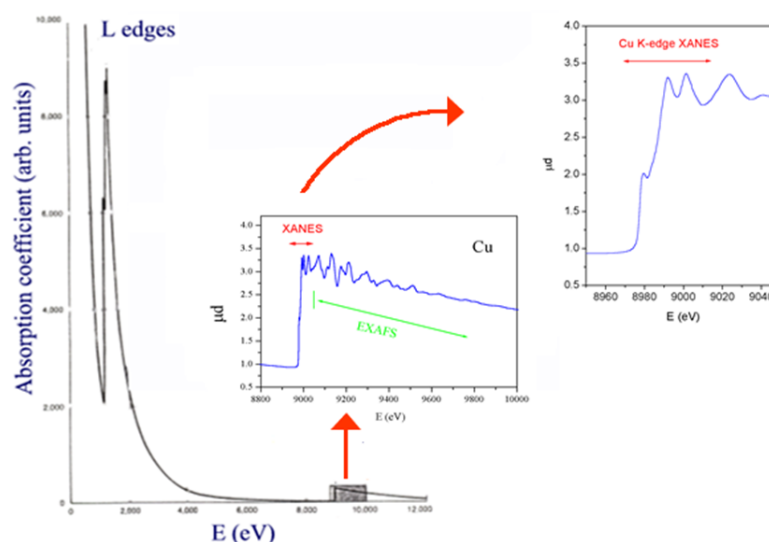2. the extended X-ray absorption fine structure (EXAFS)

Figure 4.8.1: X-ray absorption coefficient of copper in the region of L and K edges. The box area is expanded in the inset to show EXAFS and XANES signal.

Spectroscopy (XANES)

Analysis of the edge region (XANES) provides information (i.e., position of the edge and the assignment of peaks near or on the edge) about oxidation state, covalency (e..g, increasing ligand character of metal d orbitals), molecular symmetry of the site, including coordination numbers.

- Oxidation State
- Covalency
- Site Symmetry
- Coordination Number

Structure (EXAFS)

The EXAFS provides direct, local structural information about the atomic neighborhood of the element being probed (usually a metal). The information content consists of numbers of ligands (coordination number), the identity of the ligand atoms, and precise radial distances. It can be particularly informative when there are other metals in the atomic neighborhood of the metal being probed (as in clusters).
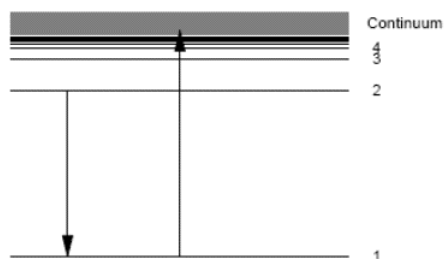
- Radial Distances
- Coordination Numbers
- Types of Ligands

Band Edge Transitions

Absorption edge energies are characteristic of the absorbing element. XAFS allows you to tune into different types of atoms by selecting the energy:

$$E_{n,l} = -hcR_\infty \frac{Z_{eff}^2}{n^2}$$

R is the Rydberg constant for this element; **Z is the atomic number**, i.e. the number of protons in the atomic nucleus of this element. X-ray absorption probability can be calculated using standard quantum theory. As in optical spectroscopy discussed earlier, the absorption coefficient is proportional to the square of the transition matrix element, here shown in dipole approximation.

$$\mu \propto |\langle f | \vec{\varepsilon} \cdot \vec{r} | i \rangle|^2$$

with the **dipole approximation selection rule** $\Delta l = \pm 1$.

Absorption edges

The K-edge is a sudden increase in x-ray absorption occurring when the energy of the X-rays is just above the binding energy of the innermost electron shell of the atoms interacting with the photons. The term is based on X-ray notation, where the innermost electron shell is known as the K-shell. Physically, this sudden increase in attenuation is caused by the photoelectric absorption of the photons. For this interaction to occur, the photons must have more energy than the binding energy of the K-shell electrons (K-edge). A photon having an energy just above the binding energy of the electron is therefore more likely to be absorbed than a photon having an energy just below this binding energy or significantly above it.

- $K: 1s \leftarrow p$
- $L_3: 2p_{3/2} \leftarrow s, d$
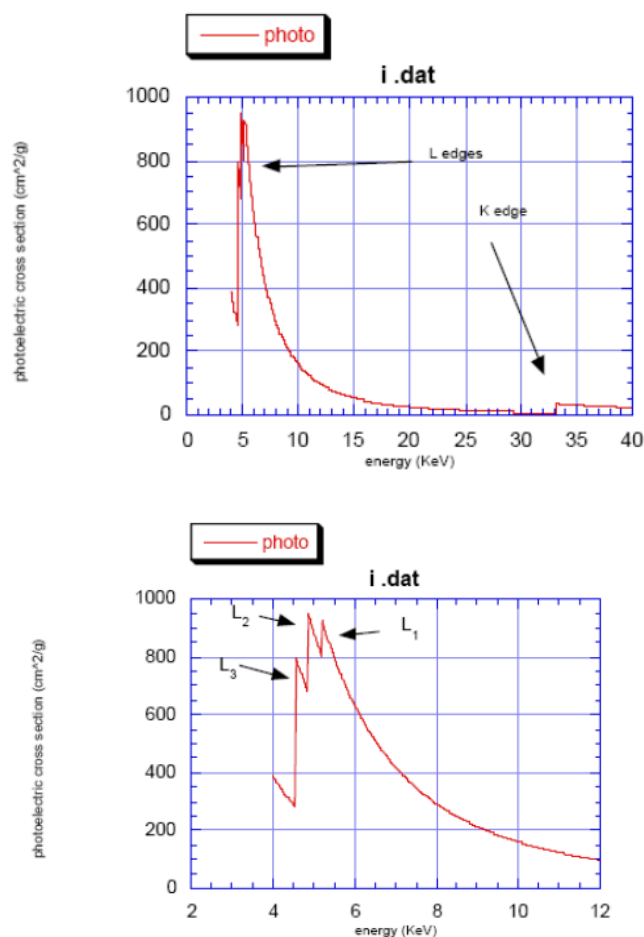- $L_2: 2p_{1/2} \leftarrow s, d$
- $L_1: 2s \leftarrow p$

Figure 4.8.4: A schematic representation of x-ray absorption spectroscopic measurements in fluorescence and electron detection mode.