X-ray Absorption Near Edge Structure (XANES), also known as Near edge X-ray Absorption Fine Structure (NEXAFS), is loosely defined as the analysis of the spectra obtained in X-ray absorption spectroscopy experiments. It is an element-specific and local bonding-sensitive spectroscopic analysis that determines the partial density of the empty states of a molecule.

**Introduction**

X-rays are ionizing electromagnetic radiation that have sufficient energy to excite a core electron of an atom to an empty below the ionization threshold called an excitonic state, or to the continuum which is above the ionization threshold. Different core electrons have distinct binding energies; consequently, if one plots the X-ray absorbance of a specific element as a function of energy\(^1\), the resulting spectrum will appear similar to Figure \((\PageIndex{1})\).

![Figure \((\PageIndex{1})\): Transitions that contribute to XAS edges. (CC BY-SA 3.0; Atenderholt via Wikipedia)](image-url)

**Theory of XANES**

**Core hole**

As stated above, a core hole is the space a core electron occupied before it absorbs an X-ray photon and ejected from its core shell. Core holes are extremely energetic (electronegative) which leads to their unstable nature. The average life span of a core hole is close to 1 femtosecond. A core hole is created through processes in which either a core electron absorbs an X-ray photon (X-ray absorption) or absorbs part of the an X-ray photon's kinetic energy (X-ray Raman...
scattering). The successor process is the decay of a core hole which can take place either through Auger electron ejection of X-ray Fluorescence.

Absorption edge

As the energy of X-ray radiation is scanning through the binding energy regime of a core shell, a sudden increase of absorption appears, and such phenomenon corresponds to absorption of the X-ray photon by a specific type of core electrons (eg. 1s electrons of Cu). This gives rise to a so-called absorption edge in the XAS spectrum due to its vertical appearance. The name of the absorption edges are given according to the principle quantum number, n, of the excited electrons (Table \(\PageIndex{1}\)).

<table>
<thead>
<tr>
<th>Absorption Edges</th>
<th>Principal Quantum Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>K edge</td>
<td>1s</td>
</tr>
<tr>
<td>L edge</td>
<td>2s 2p</td>
</tr>
<tr>
<td>M edge</td>
<td>3s 3p 3d</td>
</tr>
<tr>
<td>N edge</td>
<td>4s 4p 4d 4f</td>
</tr>
</tbody>
</table>

Energies of absorption edges in X-ray absorption spectra reveal the identity of the corresponding absorbing elements. However, more useful information can be obtained by a closer examination of a giving absorption edge (Figure \(\PageIndex{1}\)).

Illustrated by Figure \(\PageIndex{2}\), the absorption edge is often much more complex than simply an abrupt increase in absorption illustrated in figure 1. There are weak transitions below the absorption edge, namely pre-edge structures, as well as significant absorption features in the immediate neighborhood of the absorption edge and well above the edge. The structure found in the immediate neighborhood of the absorption edge, conventionally within 50 eV of the absorption edge, is referred to as X-ray Absorption Near Edge Structure (XANES). Beyond XANES, the oscillatory structure cause by the interference between the outgoing and the back-scattered photoelectron waves is referred to as
Extended X-ray absorption Fine Structure (EXAFS), which can extend to 1000 eV or more above the absorption edges.  

**Dipole selection rules**

XANES directly probes the angular momentum of the unoccupied electronic states: these states can be bound states (excitonic) or unbound states (continuum), discrete or broad, atomic or molecular. The dipole selection rule for transition determination is: \(\Delta l = \pm 1\), \(\Delta j = \pm 1\), \(\Delta s = 0\). Commonly observed ALLOWED transitions are tabulated in Table \(\PageIndex{2}\).

<table>
<thead>
<tr>
<th>Initial state</th>
<th>Final state</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>p</td>
</tr>
<tr>
<td>p</td>
<td>s, d</td>
</tr>
<tr>
<td>d</td>
<td>p, f</td>
</tr>
<tr>
<td>f</td>
<td>d, g</td>
</tr>
</tbody>
</table>

**White Line**

In certain XANES spectra, the rising absorption edge might lead to a sharp intense peak referred as “white line”. The reason is that in the past, X-ray absorption spectra were recorded using photographic plates, and the strong absorption of certain wavelength leads to an unexposed band on the photographic plates which after develops in negative, appear as a white vertical stripe, hence the term “white line”.

**X-ray absorption Measurements**

**X-ray fluorescence**

As a core electron absorbs an X-ray photon and is ejected from its core shell, the absence of the electron left in the core shell leads to a core hole state. Core hole states are highly excited and can relax in mainly two ways: Auger electron emission or X-ray fluorescence. For higher-energy excitation (e.g., for the K edges of elements with atomic numbers greater than 40), X-ray fluorescence is the primary relaxation process. The scheme of an X-ray fluorescence is illustrated in Figure \(\PageIndex{3}\).
The intensity of X-ray fluorescence is described by Equation \ref{(1)}.

\[
A = \left( \frac{I_F}{I_1} \right)
\]

Transmittance of X-ray flux

As X-ray was transmitted through a sample, it becomes attenuated. The intensity ratio of the incoming X-ray and the outgoing X-ray is proportional to the exponential of the absorption coefficient times the thickness. The spectrum will show a sudden decrease in transmittance as the beam of scanning X-ray meets the absorption edge. The obtained transmittance spectra are usually converted to absorption spectra afterward. X-ray Absorption is described by Equation \ref{(2)}.

\[
A = \ln \left( \frac{I_0}{I_1} \right)
\]

This method is limited to moderately concentrated samples (e.g. greater than 500 ppm). In cases of certain samples or solvents, the incoming X-ray photons could be nearly completely absorbed, and leaves the detector little signal to detect. For example, dichloromethane (CH$_2$Cl$_2$) is nearly opaque to low energy X-rays, and this will cause complication in data interpretation if dichloromethane is largely present in the sample or used as the solvent.

Interpretation of XANES
Oxidation state sensitivity

As the oxidation-state of the absorption site increases, the absorption edge energy increases correspondingly. This observation can be explained using an electrostatic model: atoms with a higher oxidation state require more energetic X-ray to excite its core electron because the nucleus is less-shielded and carries a higher effective charge.

However, an alternative interpretation of edge energies is more suitable. This interpretation treats the edge features as continuum resonances. A continuum resonance refers to a short lived the excitation process in which a core electron is excited into a higher energy state that is usually above the continuum. An example is the potential well created by the absorbing and scattering (between nearest neighboring) atoms. As the absorber–scatterer distance gets shorter, the energy of the continuum state increases as $1/R^2$. Since higher oxidation-states implies shorter bond lengths in molecules, the edge energies increases as the oxidation-states increases.

As stated above, XANES is oxidation sensitive. Moreover, multiple scattering is particularly important in the XANES region. In principle, one can argue that it is possible to determine the three-dimensional structure of the absorbing atom to its environment from analysis of the XANES features. Experimentally, this has been proven true. The XANES region is quite sensitive to small structural variations. For instance, two sites with identical EXAFS spectra can nevertheless have distinct XANES spectra. Such sensitivity is intuitively, at least in part, due to the fact that geometrical differences between sites alter the multiple scattering pathways, and thus the detailed structure in the immediate vicinity of the absorption edge.

Bound state transitions

Weak pre-edge structures usually result from bound state transitions. The pre-edge structures prior to K edges of first row transition metals arise from 1s to 3d transition. These pre-edge structures are observed for every first row transition metal as long as its 3d orbital is not fully occupied. Although the 1s to 3d transition is forbidden by dipole selection rules, it is nevertheless observed due to 3d to 4p orbital mixing and as well as direct quadrupolar coupling.

As the 3d to 4f mixing improves, the 1s to 3d transition increases, which means that such a trend can be utilized as tool to probe the molecular geometric properties of the absorption sites. As the 1s to 3d transition increases, the geometry of the absorption site distorts away from a centrosymmetric geometry.

Example \ref{PageIndex{1}}

Examining the X-ray absorption spectrum of a first row transition metal closely, one would notice that the "L edge" contains three edges namely L$_1$, L$_2$ and L$_3$ edge in a energy decreasing order. L$_3$ edge intensity is twice as much as of the L$_2$ and L$_3$ intensity. Rationalize this observation.

Solution

The so called L$_1$ edge corresponds to the excitation of a 2s electron which requires more energy than a 2p electron. The 2p electron excitation is split into two edges namely L$_2$ and L$_3$, as a 2p electron gets excited, an open shell 2p$^5$ electronic configuration forms, consequently, spin–orbit coupling of such a system occurs. A 2p5 excited states
corresponds to two terms, $^{2}P_{1/2}$ which has higher energy and give rise to the L$_2$ edge, and $^{2}P_{3/2}$ which has lower energy and give rise to the L$_3$ edge. Due to degeneracy, the L$_3$ edge has twice the edge jump of the L$_2$ and L$_1$ edges.

References

1. PENNER-HAHN, J. E. X-ray Absorption Spectroscopy. University of Michigan, Ann Arbor, MI, USA