X-ray absorption spectroscopy

Literature recommendations


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### Nice and handy abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Structure</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near Edge X-ray Absorption Fine Structure</td>
</tr>
</tbody>
</table>
### Historical development

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
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<tbody>
<tr>
<td>1895</td>
<td>Discovery of X-rays (Röntgen)</td>
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<tr>
<td>1920</td>
<td>Discovery of EXAFS Phenomenon</td>
</tr>
<tr>
<td>1970</td>
<td>Synchrotrons become available as synchrotron source</td>
</tr>
<tr>
<td>1971</td>
<td>Theoretical description by Sayers, Stern, Lytle</td>
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<tr>
<td>80's</td>
<td>Application in catalysis</td>
</tr>
<tr>
<td>90's</td>
<td>First <em>in situ</em> studies and combination with other techniques</td>
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<tr>
<td>2004</td>
<td>First hard X-ray beam at an EXAFS beamline in CH at the SLS</td>
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</table>
Outline of the Technique

Advantages / Applications
- Wide range of applications
- Structural information (EXAFS)
- Electronic information (XANES)
- Capable of in-situ application

Disadvantages
- Synchrotron needed
- Careful planning of experiments necessary
- Data interpretation sometimes difficult
Synchrotron needed
Comparison: XPS, XRD, XAS

- Yields electronic information
- Surface sensitive
- In-situ application difficult
- Needs UHV

- Yields structural information
- Bulk technique
- In-situ applications realizable
- Needs long range order to work

- Yields electronic and structural information
- In-situ application easy to realize
- Needs a synchrotron
- Data interpretation difficult
Absorption through matter

\[
I = I_0 \cdot e^{-\mu d}
\]

Lambert Beer’s Law: \( I = I_0 \cdot e^{-\mu d} \)
Reminder: Photoemission, Fluorescence, Auger Emission

Continuum
photo-electron

Energy (eV)
L3
L2
L1

Au Foil

Energy
K
M
L

Kα

Kβ

Continuum
Absorption as function of energy of the x-ray
Shape is structure dependent
Creation of a photo-electron

\[ E_{\text{kin}} = h\nu - E_{\text{Binding}} \]

Photo-electron has kinetic energy
Photo-electron has kinetic energy
XANES

\[ P \left| \langle \Psi_i | T | \Psi_f \rangle \right|^2 \delta_{E_f - E_i - \hbar \nu} \]

Initial state \quad Final state

Transition operator

Fermi's Golden Rule

scattering atom

absorbing atom

scattered photo-electron

outgoing photo-electron

Continuum

photo-electron

M

L

x-ray

K

Energy
XAFS Theory: Substance with neighbor atoms present

\[ \psi_{\text{final}} = \psi_{\text{outgoing}} + \psi_{\text{back scattering}} \]

Outgoing wave === backscattering === interference pattern
Constructive / destructive interference
EXAFS is the wiggling part of the absorption
Tuning the energy
Double crystal monochromator

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

BM26 (DUBBLE), ESRF Grenoble
Lambert Beer’s law
\[ dl = -\mu(E)I\,dx \]
\[ I = I_0 \exp(-\mu(E)x) \]
Sample environment
Absorption of X-rays is limiting factor

Find a good window material
- Size of window
- Thickness
- Inertness
- Temperature resistance
- Pressure
- Safety

Transmission through 25 μm and 1 mm
In situ EXAFS cells for gas-solid reactions

- Reaction gas mixture flows around a pellet
- Reaction gas flows through a catalyst pellet
- Small Glass Reactor with very thin windows (0.01mm)

Large dead volume
Good for stationary conditions

Critical d/l (smaller effectivity of the catalyst)

Small dead volume
Optimal d/l
Good for structural changes
Structure-activity relations
**XANES**

\[ P \propto \left| \langle \Psi_i | T | \Psi_f \rangle \right|^2 \delta_{E_f - E_i - \hbar \nu} \]

- Initial state
- Final state
- Transition operator

**Dipole transition:**

- K edge: \( 1s \rightarrow p \)
- L edge: \( 2s \rightarrow p \)
  - \( 2p \rightarrow s, d \)

**However**

**Quadrupole transition:**

- \( \Delta l = \pm 2 \)
- K edge: \( s \rightarrow d \)
  - p \rightarrow f

*Quad. Trans.* probability is about \( 10^{-3} \) smaller, but d-DOS >> p-DOS

*Visible in the K pre-edges!!*
What determines the shape of XANES spectra?

- Pre-edge
- Edge-energy
- Shape over the edge

Pre-edge
- intensity
- energy

BUT......

...... there is not always a pre-edge

K edge (1s $\to$ 4p) of VO$_x$ compounds

Normalized absorption ($\mu$X)

X-ray energy (eV)
In order of increasing distortion from octahedral:

- VO$_2$
- V$_6$O$_{13}$
- V$_2$O$_5$
- NH$_4$VO$_3$

Increasing pre-edge:

- VOSO$_4$
- Distorted Octahedral
- VOSO$_4$·3H$_2$O
- Distorted Square Pyramidal
- NH$_4$VO$_3$
- Tetrahedral
Isolation of the pre edge

by edge subtraction

Arctangent / polynomial
Pre-edges intensity & energy varies (K edge)

**Pure octahedral case**
Centro-symmetry: no p-d mixing allowed: only quadrupole transition
→ very low intensity

**Distortion from octahedral**
P-d mixing allowed: dipole transition in pre-edge + quadrupolar trans.
→ increasingly large intensity

**Pure tetrahedral** => largest pre-edge

*Intensity pre-edge indicative of geometry*
(Pre-)edge Energy and Valence

*Edge position is measure of oxidation state*

\[ E_{\text{kin}} = h\nu - E_0 \]

\[ E_f \]

\[ E_{\text{pre}} \]

\[ E_{\text{edge}} \]

\[ \nu > E_o \]
Shape of the whiteline
For L edges > 3 keV and all K edges

“Whiteline is first intense peak(s) in spectrum”

VOSO$_4$ Distorted Octahedral
VO$_2$ Distorted Octahedral
V$_6$O$_{13}$ Distorted Octahedral
V$_2$O$_5$ Distorted Square Pyramidal
NH$_4$VO$_3$ Tetrahedral
Shape of the whiteline: L-edges

Whiteline reflects holes in d-band

Very small whiteline

Totally different
In situ
Au$^{3+}$ reduction in He/H$_2$

HAuCl$_4$ on Al$_2$O$_3$

Isobestic points

70 °C : Au$^{3+}$
200 °C : Au$^0$

Reference spectra
Shape of the whiteline: **L-edges**

**Pure metals:**

- Mo 0.5
- Tc 0.6
- Ru 0.7
- Rh 0.8
- Pd 0.9
- Ag 1.0

*Whiteline reflects holes in d-band*

**Alloying:**

*Whiteline reflects charge transfer*

Ideal d-band filling
Abstract (I)

Pre-edge  | Edge  | Shape over the edge
---|---|---
- Valence  | - Valence  | - Geometry
- Geometry  |  | - D-band filling ($L_{III}$-edge)
  |  | - (Non- / Anti-bonding) DOS states
  |  | (- Adsorbates)

For many (many!) compounds structures and spectra are available in literature

**Note**

Variations in XANES may be very subtle and hardly visible in the data: 
*take (negative) second derivative*
L edges
Whiteline intensity reflects number of holes in the \( d \) band (valence)

K edges
(Pre) edge position reflects valence

Shape of XANES indicative of geometry
Typical XANES Experiment

• Catalyst samples, measured in desired conditions
  \emph{temperature, pressure, aggregation state}

• Reference samples that likely resemble the state of the catalyst
  - Various oxidation states
  - Various coordinations

• Identification of trends, similarities in reference samples

• Comparison of trends, similarities to ‘unknowns’

• Application of theory to obtain ultimate information (expert option).