Introduction to Near Edge X-ray Absorption Fine Structure of Molecules
Maddalena Pedio
TASC-INFM Trieste

NEXAFS exploiting anisotropies
mainly within 10-20 eV above the edge

• NEXAFS Basic Principles

• Instrumentation for low Z element XAS

• Examples: Anisotropy in Solids 6H SiC Di-atomic Molecules Complex molecules
X-Ray Absorption Spectroscopy (XAS)
Absorption Coefficient and Cross Section

The central physical quantity is the absorption coefficient

\[ \mu = \frac{4\pi k}{\lambda} \]

\[ \tilde{n} = n - ik \]

\[ \tilde{\varepsilon}_r = \varepsilon_1 + i\varepsilon_2 \]

\[ \varepsilon_1 = n^2 - k^2 \]

\[ \varepsilon_2 = 2nk \]

The cross section \( \sigma \) is related to the transition probability of an interaction process. It is typically calculated by perturbation theory.

\[ \sigma \] is a measurable quantity and has the dimensions of an AREA. Its units are the BARN: 1 barn = \( 10^{-24} \text{ cm}^2 \)

\[ \mu = \sigma N \]
In X-Ray Absorption Spectroscopy (XAS)
Fine structure induced by surroundings
Cu Metal

Fig. VII.1. K-shell X-ray absorption coefficient $\mu$ of Cu versus X-ray photon energy. Insert: qualitative overview of the absorption coefficient $\mu(h\omega)$ for a wide range of photon energies covering two L edges and one K edge [VII.5]
(1-R)^2 loss of intensity due to the 2 interfaces, exponential derives from the integration of the linear relation
\[ \frac{dI}{dx} = -\mu I(x) \]
R given by the Fresnel relations, i.e. a combination of incidence angle, complex dielectric constants of the two media at the interfaces and light (s or p) incidence conditions.
In experimental observation processes related with an optical transition - optical absorption, reflectivity and photoemission - the electronic properties and the structure show up simultaneously as the two faces of the same coin.

VB Photoemission on H/GaAs(110): the comparison between a photoemission spectrum due to valence emission and the theoretical calculation allowed to single out electronic properties and structure (A).

A: 1 ML of hydrogen chemisorbed on both Ga and As atoms in the ideal configuration along the dangling bonds directions;
B: hydrogens bonded to both anion and cation sites in on-top geometry
X-Ray Absorption Spectroscopy (XAS)

Detection Modes: Direct Methods

Transmission mode

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

Reflection mode

Reflectivity > 50%
Penetration depth < 20 Å
\[ \theta < \theta_c \]
\[ \sin \theta_c = (2\delta)^{1/2} \]
\[ (1 - \delta) \]
Real part of the refractive index
X-Ray Absorption with Strong NEXAFS Features and Weak EXAFS Oscillations

Three Parts in a X-ray Absorption Spectrum depending on the kinetic energy of the photoelectron

\[ \lambda = \frac{h}{p} \]

\[ k = \sqrt{\frac{1}{\hbar^2} 2m(h\nu - E_0)} \]

(N)EXAFS
The main properties of NEXAFS technique are:

• Involves core level so NEXAFS is *element specific* because the x-ray absorption edges of different elements have different energies.
• NEXAFS is also very *sensitive to the bonding environment* of the absorbing atom. The NEXAFS spectrum exhibits considerable fine structure above each elemental absorption edge.
• Another great asset of NEXAFS spectroscopy is its *polarization dependence*. Linearly polarized x-rays are best suited for covalent systems like low-Z molecules, macromolecules and polymers, which possess directional bonds.
In the common interpretation frameworks the process is described in terms of transition probability between eigenstates of the unperturbed Hamiltonian and the total x-ray absorption cross section (that is proportional to the SPECTRUM) The calculation of the transition probability is treated with the following approximations:

- Dipole approximation, used to treat the radiation field in its interaction with matter
- One-electron approximation

\[ \sigma(\omega) = 4\pi^2\alpha \sum_{f,i} \left| \langle \psi_f | \vec{p} \cdot \vec{D} | \psi_i \rangle \right|^2 \delta(\hbar \omega - E_f - E_i) \]

These assumptions correspond to the calculation of the cross section for the radiation-matter interaction at the first order of perturbation i.e. in the context of the linear response theory, valid for the spectroscopies
X-Ray Absorption Spectroscopy (XAS)

Single-Particle Energy Level Scheme

- Site selectivity
- Orbital Selectivity via Dipole selection rules
  \[ \ell \rightarrow (\ell \pm 1) \]

The photon energy is swept while crossing a core level threshold

The XAS profile is expected to mimic the unoccupied DOS projected onto the excited atomic site via the dipole selection rules
The fine structure of XAS edges can be interpreted as the Dipole transition from the localized core level of the element of interest into unoccupied electronic states

The one-electron cross section may be further decomposed into the product of an energy dependent matrix element overlap factor $P(E)$ and a projected density of states $N(E)$ with appropriate symmetry

$$\sigma(E) \sim P(E) \, N(E)$$
NEXAFS interpretation frameworks: two different approach have been developed:

**Electron Transitions (molecules LCAO)**

**Solids: Band structure calculations**
- A periodic potential is assumed
- Final states are Bloch electronic States
- Information of the different contributions to the LDOS relative to that initial state core level of that element

The initial state is the core level and the final are the unoccupied Bloch states $n, k$.

\[
\sigma(\omega) \propto 4\pi^2 \alpha \sum_{k,n} \left| \langle \psi_f | \vec{e} \cdot \vec{r} | \psi_i \rangle \right|^2 \delta(\hbar \omega - E_{k,n} - E_{\text{core}})
\]
NEXAFS interpretation frameworks: two different approach have been developed:

**Multiple Scattering calculations**
- Final states are scattering states
- The potential is calculated for a cluster of atoms (up to about 10 Å from the central atom) in real space with Green’s Function Formalism

Information on the local geometrical arrangement of the excited atom, even though further details can be obtained by using self consistent calculations

\[
\sigma(\omega) \propto \int \left\langle \psi_f \left| \mathbf{p} \cdot \hat{D} \text{Im} G^+(E_f) \hat{p} \cdot D \psi_i \right\rangle = \sigma_{\text{atom}} + \sigma_{\text{scatter}}
\]

(cfr. M. Benfatto contribution)
The interpretation in real space is in terms of scattering events of the photoemitted electron that interacts with the surrounding atoms, the number of scattering processes depending on the energy above the edge while in the electronic states band space we speak of transitions from a filled core electronic state to an empty electronic state (or molecular states) following the dipole selection rules. In any case the dipole transitions dominate the process of photoabsorption, an electron from a core level having angular momentum $l$ is excited into the $l+1$ finale states. If the spectrum is taken at a K edge the dipole selection rule leads to a outgoing p wave (or in terms of electronic states the local density of states of p character)
A unifying scheme of NEXAFS interpretation based on the multiple scattering theory is possible.

Natoli and Benfatto demonstrated it analytically by using the Green function formalism and the KKR band calculation method.

Roughly speaking the multiple scattering in the real space cluster model can be interpreted as the exact formulation of the X-ray absorption fine structure problem with infinitely many scattering events included.

Both the calculation frameworks are valid in the context of the approximation that the single electron processes dominate following the dipole selection rules.
Low-Z element XAS

• The study of C, N and O is fundamental for many topics of fundamental and technologic interest, such as catalysis and chemisorption processes => SOFT X-RAYS
• Control of the detection depth

• hundreds meV => High photon energy Resolution
  Once a core hole has been created it will decay. The dominant decay mechanisms are fluorescence emission or Auger electron emission. Because of the Heisemberg uncertainty relationship a short core-hole lifetime (rapid x-ray emission and/or Auger decay) is associated with a large uncertainty in energy. The lifetime broadening leads to Lotentzian lineshapes

  \[ 0.5 \text{ FWHM} = \Gamma_L = \frac{h}{\tau} = 6.58 \times 10^{-16}/\tau \text{ eV} \]

• Light Z elements (O, C, N 1s) XAS required very high photon flux. For K edge cross section, the absorption coefficient depends on Z as \( Z^4 \).
Carbon configurations

- **Carbon**
  - Covalent C-C bonds within 'molecule'
  - Variable sp hybridisation

0. C$_{60}$

1. Nanotubes

2. Graphite

3. Diamond

Hybridisation Types:
- sp$^2$
- Pure sp$^3$
C K-edge
Optics absorption

Grasshopper Transmission

Jumbo Transmission

Figure III-B-1

(a) Original beam splitter mirror-surface roughness 186 Å (1975)
(b) New beam splitter mirror-surface roughness 38.9 Å (1976)

Grasshopper Transmission

November 11, 1977

C Ti O

March 2, 1978

Transmission Function

Beryl (10T0)

Al K edge Si K edge

Al in Beryl EXAFS

Transmission Function

InSb(III)

Pt(MX)

MII

MIII

ML

In(LIII)

Transmission Function

Ge(III)

Pt(MX)

MII

MIII

ML

Pt(LIII)
X-Ray Absorption Spectroscopy (XAS)

Lay-out of XAS Experiment at a Synchrotron Radiation Source
BEAR Optics Layout @ ELETTRA
Detection mode is related to the detection depth of XAS measurements
X-Ray Absorption Spectroscopy (XAS)

Detection Modes: Indirect Methods

Fluorescence

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Photon emission

Electron Yield (Total vs. Partial)

Auger emission

Indirect Methods

By-products of the core hole de-excitation process are collected. The thus-measured signal is expected to mimic the behavior of

\[ \mu = \mu(\hbar \omega) \]
X-Ray Absorption Spectroscopy (XAS)
How Partial Spectral Components May Contribute to the Measurement
X-Ray Absorption Spectroscopy (XAS)
Electron Yield Detection Modes

Collimator
Metal Grid
Channeltron Electron Multiplier (CEM)
Evaporator

Cylindrical Mirror Analyzer (CMA)
Sample Needle Doser
Phosphor Screen

Retarding Grid
Accelerating Grid
Drift Tube
Channel-Plate Electron Multiplier
X-Ray Absorption Spectroscopy (XAS)

Electron Yield Detection Mode

High Current Channel Electron Multiplier

Collector Anode ($V_2$)

Battery Box

Voltage Divider 10:1

Power Supply ($V_1$)

Picoammeter

Voltage to Frequency Converter

To Scaler

Sample or Metal Grid
X-Ray Absorption Spectroscopy (XAS)

Electron IMFP vs. Photon MFP Surface vs. Bulk Sensitivity

Electron Escape Depth: L ~ 50 Å

Energy, E

Valence level, Eᵥ

X-ray fluorescence

Core level, Eₖ

Auger electron
AY and TY C K-edge NEXAFS of a 3C SiC ordered film (>500 Å) obtained by C\textsubscript{60} decomposition on Si(100) grown ex situ and exposed to air before measurements.

The two spectra have been taken simultaneously.

The thickness of detection in the Auger Yield mode is about 10 Å, while for Total Yield is higher 1 order of magnitude.

The difference in the two detection mode is due mainly to oxygen contamination and trace of nitrogen.
Anisotropy in solids

Silicon Carbide structures in different polytypes

Fig. 4. The tetragonal bonding of a carbon atom with the four nearest silicon neighbours. The distances \( a \) and \( C-Si \) are approximately 3.08\AA{} and 1.89\AA{} respectively.

3C  2H  4H  6H

Fig. 5. The stacking sequence of double layers of the three most common SiC polytypes.

6H-SiC structure
C K-edge NEXAFS of 3C SiC 8000 Å ordered film taken at normal incidence in total yield detection mode and 6H SiC monocrystal taken at nearly normal (75°) and grazing incidence (15°) in fluorescence yield mode.
Surface NEXAFS: Atomic adsorbates

O/Ni(110) strong anisotropy

O 2p empty states are superimposed in the [001] azimuth $\Rightarrow$ increasing of cross section (label 3 atoms)
**Surface NEXAFS: Atomic adsorbates**

**Multiple Scattering**

**Missing Row Model**

**Saw-tooth Model**

**Unreconstructed Surface**

Among the MS paths that lead to the enhancement of the intensity in the NEXAFS, are those scattering events that involve the central atom the nearest neighbor atoms and also neighboring adsorbate atoms (Oxygens labeled 3 in the [001] azimuth).

Not only the local symmetry but also the adsorbate configuration are responsible for the pronounced azimuthal dependence.

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**Fig. 12.** — a) Comparison between experimental and calculated NEXAFS spectra at normal incidence in the azimuth (100) for Ni(110)(2 x 1)-O. Calculations are presented for the unreconstructed surface (UR) and two reconstruction models, the sawtooth (ST) and missing-row (MR) model. b) Multiple-scattering (MS) calculations for the missing-row reconstruction displaying the effect of including more shells. The topmost curve represents a single-scattering (SS) calculation using 5 shells.
NEXAFS of di-atomic molecules
Surface NEXAFS: Exploiting the X-Ray Polarization

FIG. 1. $K$-shell excitation spectra of molecular nitrogen. (a) IEELS $K$-shell excitation spectrum for $N_2$ gas (Ref. 6). Peak $A$ corresponds to a $1s$ to $\pi^*$ transition ($\pi^*$ resonance), peak $B$ to a $1s$ to $\sigma^*$ transition ($\sigma^*$ resonance). The weaker structures between peaks $A$ and $B$ are Rydberg and/or multielectron excitations. The $N$ $1s$ binding energy relative to the vacuum level is denoted as “XPS.” (b) NEXAFS spectrum of $N_2$ chemisorbed at 90 K on a Ni(110) surface (Ref. 7). The pronounced dependence of the $\pi^*$ and $\sigma^*$ resonance intensities on x-ray incidence is caused by the vertical orientation of $N_2$ on the surface. The Rydberg and/or multielectron resonances are quenched. The $N$ $1s$ binding energy relative to the Fermi level of the screened (lowest binding energy) photoemission peak (Ref. 7) is indicated as “XPS.”
NEXAFS intensity for a diatomic molecule adsorbed on a substrate. Variation of light incidence angle is used to determine alignment of adsorbate bonds: $\cos^2\alpha$ law for the $\pi$ and $\sigma$ excited empty molecular orbital.
Simulations of the NEXAFS spectra by the MXAN code (M. Benfatto and S. della Longa)
The new version of MXAN calculates correctly the polarization dependence \((\cos^2\theta \text{ law})\) for the \(\pi\) and \(\sigma\) excited empty molecular orbital of the NO molecule and their energy separation as a function of the NO distance:
\[
\begin{align*}
R=1.2 \text{ Å} & \quad \Delta E(\pi-\sigma)=14.5 \text{ eV}, \\
R=1.3 \text{ Å} & \quad \Delta E(\pi-\sigma)=10.2 \text{ eV}
\end{align*}
\]
Our simulations correctly reproduce the NO molecule in gas phase spectra.
Effect in the N K-edge induced by the variation of N-O distance

NO single molecule NEXAFS N K-edge for an angle between the E vector and the molecular axis of 0, 60 and 90 degrees.
Empirically (the so called rule of thumb) the kind of bond results related to the energy position of the $\sigma^*$ resonance, for example in molecules containing C-C bonds,
Oxygen interaction with Alkali Metal Thin Films

- $\text{O}_2$-Alkali Metals interaction:
  - Model system: NOT TOO SIMPLE
- NEXAFS
  -> Local Density of States + Structural Information
- High Resolution Photoemission
  -> Chemical Surrounding
- Systems
  $\text{O}_2$/Cs, $\text{O}_2$/K
  $\text{O}_2$+K on Si(100) oxidation enhanced $10^5 - 10^6$
  $\text{O}_2$+Cs on InP(110) oxidation enhanced $10^9$
O$_2$-Alkali metal interaction

> **Interest for the O$_2$/alkali metal (Cs, K) systems**

  • Oxygen Interaction with simple metals
  • technological interest.

> **Alkali-oxides as reference samples**:

  • Model systems to study O$_2^{-}$ anion molecular localized state evolution

> **NEXAFS**

  --> Local Joint Density of States + Structural Information

  • MS calculation in real space to get structural details and SCF understand the charge transfer mechanism.

> **Results**:

  • Comparison Codeposited K-O system and KO$_2$ simulation
  • SCF: effect of the charge transfer amount on the localized anion states.
Alkali superoxides

NEXAFS
O k-edge

\[ \text{O}_2 / \text{Cs} \]

codeposited Cs+O

CsO₂ \( a = 4.44 \, \text{Å} \)
\( c = 7.20 \, \text{Å} \)

KO₂ \( a = 4.03 \, \text{Å} \)
\( c = 6.69 \, \text{Å} \)
The diagram represents the molecular orbital structure of $\text{O}_2^-$ with the following orbitals and bonds:

- $2p$ orbitals
- $2s$ orbitals
- $3\sigma_u$
- $3\sigma_g$
- $1\pi_u$
- $1\pi_g$
- $2\sigma_u$
- $2\sigma_g$

The table summarizes the bond lengths and energy differences:

<table>
<thead>
<tr>
<th>$R_{O-O}$ Å</th>
<th>$E(\sigma) - E(\pi)$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.28</td>
<td>8.7</td>
</tr>
<tr>
<td>1.34</td>
<td>7.4</td>
</tr>
<tr>
<td>1.40</td>
<td>6.1</td>
</tr>
</tbody>
</table>

The bond length $R_{O-O} = 1.40$ Å and $E(\sigma) - E(\pi) = 6.1$ eV correspond to transitions at 1.34 Å and 1.28 Å, respectively.
NEXAFS Oxygen K-edge

Yield (arb. units)

Photon Energy (eV)

ΔE = 0.7 eV

codeposited Cs + O

ΔE < 0.1 eV

codeposited K + O

ΔE = 0.7 eV
a) The SCF calculations for the model structure Cs$^+$$O_2^-$ with O-O distances of 1.40 and 1.45 Å compared with the experimental data (dotted line).
b) SCF simulations (solid line) for the Cs$^{+0.5}$$O_2^{-0.5}$ with an O-O distance of 1.40 Å.

The energy separation between the low $\pi$ resonance and the prominent peak at about 538 eV that is due to the $\sigma$ resonance of the $O_2^-$ anion, changes both for the O-O distance and for the amount of the charge transferred from Cs to $O_2^-$.
The growth of KO$_2$ compound for codeposition of K+O$_2$ is confirmed.

$R_{O-O}$ [Å]

KO$_2$ 1.34
CsO$_2$ 1.40

Even though the superoxide system has a complete (100%) ionic character the π resonance (transition involving the π empty state) show a fine structure due to scattering path among the O$_2^-$ anions.
Complex molecules

The Search Light Effect

Polarization dependent NEXAFS spectra of benzene chemisorbed on Ag(110), illustrating the capability of the technique to determine molecular orientations following the maximum of the p orbital intensity as a function of the incidence angle of light.
Fig. 14. – NEXAFS spectra for CO$_3$ on Ag {110} taken at $a$) the oxygen K-edge and $b$) the carbon K-edge with the polarization vector of the incident radiation aligned in the $\langle 110 \rangle$ azimuth at polar angles of $\theta = 20^\circ$ and $\theta = 90^\circ$. 
Surface NEXAFS: Exploiting the X-Ray Polarization
Surface NEXAFS: Exploiting the X-Ray Polarization

Fig. 15. – \( \pi \) and \( \sigma \) resonance intensities for \( \text{CO}_2 \) on \( \text{Ag}\{110\} \) measured at the oxygen \( K \)-edge as a function of the polar angle \( \theta \). The calculated curves are given for three different tilt angles \( \alpha \) between the surface normal and the \( C^\parallel \) axis of the carbonate: —— \( \alpha = 0 \), \( \cdots \cdots \alpha = 10^\circ \), --- \( \alpha = 15^\circ \).
Basic Building Blocks of Polymers

Examples for carbon atoms in multi-atom molecules with different bonding configurations, often found in polymers. The spectra exhibit chemical shifts within each group similar to XPS spectra but more importantly considerably different fine structure for carbon in different molecular groups. This clearly illustrates the power of NEXAFS to distinguish chemical bonds and local bonding. In many ways it is superior to XPS, which does not provide local structural information.
ANNEALING TEMPERATURE DEPENDENCE OF \textit{C}_6\textit{O} ON SILICON SURFACES: BOND EVOLUTION AND FRAGMENTATION AS DETECTED BY NEXAFS

\textit{C}_6\textit{O} Interaction with ordered surfaces leads to different bond as detected by e- spectroscopies

\textit{C60 on Silicon surfaces}

NEXAFS results on Si(100) and Si(111)

Fragmentation
C\textsubscript{60}

- Buckyball diameter \( \approx 7.1 \) Å
- Single bond length \( \approx 1.45 \) Å
- Double bond length \( \approx 1.40 \) Å
- All C sites are equivalent

Truncated icoesahedron “Magic” Cluster

Large molecule acts as e- acceptor + super “alkene”
Interaction with ordered surfaces
Different bond as detected by e-spectroscopies

Examples

**Ionic bond**  \( \text{C}_6\text{O}/\text{Au}(110) \)

**Covalent bond**  \( \text{C}_6\text{O}/\text{Pt}(111) \)

**C\text{60 Fragmentation}**  \( \text{SiC production} \)

C_{60}/Si(111) and Si(100)

Temperature dependence of the electronic structure of C60 films adsorbed on Si (001) 2x1 and Si (111) 7x7 surfaces

STM
PES
HREELS
NEXAFS

Strong Interaction - Covalent bond

NEXAFS


C$_{60}$/Si(111) and Si(100)

Covalent bond

Thermal Fragmentation
SiC by thermal decomposition of C\textsubscript{60} precursors

- covalent bond (no charge transfer)
- number of covalent bonds increases with increasing temperature
- T > 1050 K C\textsubscript{60} disruption and SiC formation

$C_{60}/\text{Si}(111)$

Dependence on the E direction polarization

ALOISA Beamline Molecular states detectable in GI
Dependence on the polarization of E vector

STM model:
Si atoms moves toward C atoms

Pascual et al.
Surf. Sci
C$_{60}$/Al XAS

FIG. 1. Schematic of the expected angular dependence of the x-ray absorption cross section for C$_{60}$ adsorbed on a surface. We have assumed that the direction of maximum amplitude for the $p$ component of the core-excited $\pi^*$ wave function is radial, consistent with a tight-binding picture [22] of the ground state. The angular dependence of the cross section is then given by $\cos^2 \phi$, where $\phi$ is the angle between the electric field vector of the linearly polarized synchrotron radiation and the normal to the molecular surface at the excited atom. Grazing incidence corresponds here to $75^\circ$ from the crystal surface normal for the Poynting vector. Since the LUMO has predominantly $\pi^*$ character, it is clear that, in the geometry shown above, there will be a higher cross section for the core hole to be located on the sides (top and bottom) of the molecule in normal (grazing) incidence.

FIG. 2. XAS spectra for the samples and incidence angles indicated. The photon energies marked with arrows for solid C$_{60}$ and 1 ML C$_{60}$/Al(110) spectrum for grazing incidence (GI) and normal incidence (NI) are those used during RPES measurements. The spectrum for solid C$_{60}$ is independent of the x-ray incidence angle.

Two detection mode

C K-edge Auger Yield

C_{60}/Si(100)

Photon Energy (eV)

Multilayer

BEAR beamline  E in plane
Difference curve
C<sub>60</sub> fragmentation

C 1s Photoemission Spectra

Auger Yield C K edge
C<sub>60</sub>/Si(100)

Molecular states visible at 1040 K in Auger mode:
Surface sensitive
Initial absorption configurations according to STM (300 K)

(a) $S_5$

(b) DB

Optimized absorption configuration according to first-principle DFC (for $T=800$ K)

Stable absorption configuration proposed on the basis of our XPS data (above 800 K, optimized C-Si bonds)

STM performed on both Si(100) and Si(111) during $C_{60}$ fragmentation revealed that all the cages break

STM image of an isolated $C_{60}$ molecule on Si(111) after annealing at 800 K
$C_{60}$ fragmentation starts at a temperature of about 1020 K.

By changing the probing depth of NEXAFS, the residual molecular states of the fragmented $C_{60}$ cage are localized on the topmost surface layer,

**Molecular states at the more external site with respect to the C-Si interface.**

The feature intensities of the electric field direction for the $C_{60}$/Si(111) system suggest that the molecular fragment have $\pi$ character and are directed almost orthogonal to the surface.