Tutorial on XAFS analysis

Danilo OLIVEIRA DE SOUZA

danilo.oliveiradesouza@elettra.eu

Material almost integrally taken from Carlo Meneghini (Università Roma 3): EXAFS tutorial at Synchrotron Radiation school of Duino 2011
Characteristics of a XAS spectrum

- **Pre-edge**
- **Edge**
- **XANES**
- **EXAFS**

![Graph showing XANES and EXAFS regions](image)
In an XAS experiment the $\alpha = x\mu(E) = \ln \frac{I_0}{I_1}$ is collected, but only the oscillating part contains the information of the local structure such as:

- Coordination number
- Bond lengths
- Bond lengths distribution
\[ \chi(k) = \sum_j N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2 \sigma_j^2} \frac{kR_j^2}{\sin[2kR_j + \delta_j(k)]} \]
From experiment to results

Data collection

Preliminary data treatment

Extraction of XAFS structural signal: $\chi(k)$

Structural refinement

Check the results

END

Structural model(s)

revision

revision

revision
From experiment to results

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END

Structural model(s)

revision
Some considerations:
1) Proposal submission + proposal evaluation + beamtime scheduling = 6 to 12 months
2) Difficult to have new beamtime in case of proposal failure

- Check the proposal submission deadlines
- Discuss your experiment with local contacts

Choose properly the experimental set-up & sample preparation

Check data quality constantly during the experiment

Optimize your beamtime

Measure reference samples

Choose properly data collection strategy
Data collection

Choose properly the experimental set-up & sample preparation

- For massive concentrated samples: **TRANSMISSION**

  Jump \( 0.5 \leq \Delta \mu t \leq 1.5 \)

  Total absorption \( \mu t \leq 2 \).

\[
\mu(E)t = \alpha = \ln \frac{I_0}{I_1}
\]

⚠️ inhomogeneities, holes, not parallel surfaces, etc...
Data collection

Choose properly the experimental set-up & sample preparation

- For thin concentrated or thin diluted samples, thick samples: FLUORESCENCE

\[ \mu(E)t = \alpha \propto \frac{I_F}{I_1} \]

Self absorption, detector linearity, Bragg reflections
Data collection

Choose properly the data collection strategy

- Acquisition time per point
- Single scan or repeated scans
- $\Delta E$ constant or $\Delta k$ constant step

\[ K = \sqrt{0.2625(E - E_0)} \]
Data collection

Measure reference sample

![Diagram showing data collection setup with energy levels and normalized absorption graph.]

- Energy (eV) scale on the x-axis from 6530 to 6580
- Normalized Absorption on the y-axis from 0.0 to 1.5
- Various energy levels labeled as 0, 2+, 3+, 4+
Data collection

- Evaluate signal/noise ratio

\[ S/N > 10^4 \]

\[ S/N \sim J/\sigma \]
Data collection

Check data quality constantly during the experiment

Glitches

Discontinuities

edge shift
From experiment to results

Data collection

Preliminary data treatment

Extraction of XAFS structural signal: $\chi(k)$

Structural refinement

Check the results

END

Structural model(s)
Preliminary data treatment

Choose the best spectra and useful data regions

Optimize your time and do it during the experiment

Deglitch → Average

Align
Preliminary data treatment

Choose the best spectra and useful data regions

- do not use the blue one!
- do not use data beyond 13000 eV!
Preliminary data treatment

Deglitch
Preliminary data treatment
Preliminary data treatment

![Graphs showing data analysis and comparison]

- Preliminary data treatment
- Average

The graphs illustrate the normalized intensity as a function of energy (E, eV) with data from various sources labeled as Cr836A_008.txt, Cr836A_007.txt, Cr836A_006.txt, Cr836A_005.txt, Cr836A_004.txt, and Cr836A_003.txt. The graphs show trends and patterns that are being analyzed.
From experiment to results

Data collection

Preliminary data treatment

Extraction of XAFS structural signal: $\chi(k)$

Structural refinement

Check the results

END

Structural model(s)
Extraction of the XAFS structural signal: $\chi(k)$

1. $\alpha(E)$
2. pre-edge line + post-edge line
3. Normalized data
4. $\mu_o$ calculation
5. structural signal $\chi(k)$
6. Fourier Transform
7. Fourier Filtering
8. revise preliminary treatment

$$\chi(k) = \frac{\mu - \mu_o}{\mu_o}$$

Structural refinement
Extraction of the XAFS structural signal: $\chi(k)$

$\alpha(E') \rightarrow$ pre-edge line + post-edge line $\rightarrow$ Normalized data
Extraction of the XAFS structural signal: $\chi(k)$
Extraction of the XAFS structural signal: $\chi(k)$

1) Define $E_0$

$E_0$ will allow to set the starting point of $\chi(k)$.

It is generally taken at the maximum of the 1st derivative of the absorption.

2) Calculate $\mu_0$

$\mu_0$ is the bare atom atomic background.

It is calculated empirically as a smooth curve across the data.

Different XAFS data analysis softwares apply different (equivalent) approaches.

3) Subtract $\mu_0$ from $\mu$
Extraction of the XAFS structural signal: $\chi(k)$

structural signal $\chi(k)$ \[\rightarrow\] Fourier transform
Extraction of the XAFS structural signal: $\chi(k)$

- FT shows more intuitively the main structural features in the real space: the FT modulus represent a pseudo-radial distribution function (RDF)
- $|FT|$ peaks represent interatomic correlation
- Peak position are not the true correlation distances due to the phase shift effect
Minor effects are given by type of windows (Hanning, Kaiser-Bessel, Sine) and apodization
Extraction of the XAFS structural signal: $\chi(k)$
Extraction of the XAFS structural signal: $\chi(k)$

Fourier transform

Fourier filtering

Fourier filtering allows isolating contributions of selected regions of the FT

Background contribution
From experiment to results

Data collection

Preliminary data treatment

Extraction of XAFS structural signal: $\chi(k)$

Structural refinement

Check the results

END

Structural model(s)
Structural refinement

Theoretical $\chi(k)$

$\chi(k) = \sum_j N_j S_0^2 f_j(k) e^{-2R_j/\chi(k)} e^{-2k^2\sigma_j^2} \frac{1}{kR_j^2} \sin[2kR_j + \delta_j(k)]$

Experimental $\chi(k)$

Require data analysis programs
Structural refinement

Choose a model

Define the relevant structural contributions

Refine the structural parameters: N, R, $\sigma^2$

add new contributions?

Change the model?

Revise your data extraction

END

Exp. $\chi(k)$
FeO has a rock-salt structure.

To model the FeO EXAFS, we calculate the scattering amplitude $f(k)$ and phase-shift $\delta(k)$, based on a guess of the structure, with Fe-O distance $R = 2.14$ Å (a regular octahedral coordination). We will use these functions to refine the values $R$, $N$, $\sigma^2$, and $E_0$ so our model EXAFS function matches our data.

Fit results
$N = 5.8 \pm 1.8$
$R = 2.10 \pm 0.02$ Å
$E_0 = -3.1 \pm 2.5$ eV
$\sigma^2 = 0.015 \pm 0.005$ Å$^2$.

$|\chi(R)|$ for FeO (blue), and a 1st shell fit (red).
Modeling the first shell of FeO - 2

1\textsuperscript{st} shell fit in k space

The 1\textsuperscript{st} shell fit to FeO in k space. There is clearly another component in the XAFS.

1\textsuperscript{st} shell fit in R space

|\chi(R)| and Re[\chi(R)] for FeO (blue), and a 1\textsuperscript{st} shell fit (red).
Modeling the second shell of FeO - 1

To add the second shell Fe to the model, we use calculation for $f(k)$ and $\delta(k)$ based on a guess of the Fe-Fe distance, and refine the values $R, N, \sigma^2$.

Such a fit gives a result like this:

$|\chi(R)|$ data for FeO (blue), and fit of 1$^{st}$ and 2$^{nd}$ shells (red).

The results are fairly consistent with the known values for crystalline FeO:

6 O at 2.13Å, 12 Fe at 3.02Å.

Fit results (uncertainties in parentheses):

<table>
<thead>
<tr>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\Delta E_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O</td>
<td>6.0(1.0)</td>
<td>2.10(.02)</td>
<td>0.015(.003)</td>
<td>-2.1(0.8)</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>11.7(1.3)</td>
<td>3.05(.02)</td>
<td>0.014(.002)</td>
<td>-2.1(0.8)</td>
</tr>
</tbody>
</table>
Modeling the second shell of FeO - 2

Other views of the data and two-shell fit:

The Fe-Fe EXAFS extends to higher-k than the Fe-O EXAFS.
Even in this simple system, there is some overlap of shells in R-space.
The agreement in Re[\chi(R)] look especially good – this is how the fits are done.
The modeling can get more complicated than this.