Experimental aspects: synchrotron radiation, beamlines, detectors, measurement modes, geometry, sample preparation methods

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Introduction

X-ray absorption spectroscopy
-brief description
What is spectroscopy?

The study of molecular structure and dynamics through the absorption, emission, and scattering of light.

Astronomers used the “spectroscope”, to observe atomic spectra. Norman Lockyer found helium in the solar spectrum in 1868.
X-ray absorption spectroscopy - schematic presentation

Scatterer atom

photoelectron

\( h \nu \)

vacuum

\( L_1, L_2, L_3 \)

\( 2p \)

\( 2s \)

\( 1s \)

Mathias Laurin

\( K \)

Absorption

Photon energy

Wavelength, Å
Power of Synchrotron radiation


1 week for one spectrum, tube x-ray source + diffractometer

Synchrotron radiation changed quality & Quality of XAS
Fluorescence-XAS probing a dilute system

A. Dilute system
   Biological samples (Metaloproteins)
   Mioglobin (Mb)
   1Fe/17500

B. Thin films/ Surfaces

C. External field dependence (photon, electrical field, magnetic field, pressure)

D. Time resolved measurements

E. Small volume, nanocrystals, solutions

Spin-dependent features

Fluorescence x-ray

- SPIN-STATES
- LOCAL STRUCTURE
- FUNCTION

Local structure and spin states in MbOH

Fe’s 5th bound to Hs, 6th is active site (oxygen bind)

S = 1 / 2

Fe$^{2+}$

\[ \text{eg: } x^2 - y^2 \]

\[ \text{t}_{2g}: \begin{align*}
    x^2 - y^2 \\
    z^2 \\
    yz \\
    xz \\
    xy
\end{align*} \]

LOW SPIN

S = 5 / 2

In HS, Fe is popped out by 0.4A

In LS, Fe in the heme plane

Symmetry breaking

Spin-dependent full multiple scattering

Symmetry breaking to lower ligand field

Synchrotron radiation

Donuts proliferating the world
What are they?
Synchrotron radiation

3rd generation (3G) synchrotron radiation facilities

Started from a “mega” facility
Now proliferating as a “compact” machine

ESRF

ALBA

Apple mother ship
Wavelength and object size

Wavelength

Object

DESY Hamburg
**Synchrotron radiation –relativistic radiation**

Normal radiation (b $\approx 0$) and relativistic radiation (b $\approx 1$)

\[
\beta \approx 0 \quad \frac{dP}{d\Omega} \approx 1 - \sin^2 \theta \\
\beta \approx 1 \quad \frac{dP}{d\Omega} \approx \frac{1}{(1 - \cos \theta)^3}
\]

\[
\Psi \approx \frac{1}{\gamma} = \sqrt{1 - \beta^2}
\]

As electron velocity approaches $c$ (that of light), radiation becomes highly directional, providing a bright white x-ray beam (synchrotron radiation)
**Undulator and wiggler**

\[
K = \frac{eB_{\text{max}} \lambda_0}{2\pi m_o c} = 0.934 B_{\text{max}} [T] \lambda_0 [\text{cm}]
\]

- **B<sub>max</sub>** Maximum flux density, \(l_0\) Period length

**Wiggler** (\(K \gg 1\))

- High magnetic field (\(K \gg 1\))
  - N-pole wiggler radiation enhances brilliance by \(N\)
  - Produces white x-ray but high heat load

**Undulator** (\(K \ll 1\))

- Low magnetic field (\(K \ll 1\))
  - Quasi-monochromatic high brilliance beam
  - Less heat load (high power density)
Undulator

@BESSY
Brilliance

Brilliance

$10^{23}$

Photons/s

/mrad$^2$

/mm$^2$

/0.1% bandwidth

Flux

$10^{12}$

Photons/s

European XFEL
(Hamburg)

LCLS
(Stanford)

FLASH
(Hamburg)

4 keV
(Ca K)

40 keV
(La K)

ERSF
(Grenoble)

PETRA III
(Hamburg)

$10^{23}$
Moore’s law in Synchrotron Radiation

We are here!

Note that exponential growth is due to successive inventions of different devices

10^7 times brighter beam in 30 years

NO EXPONENTIAL IS FOREVER...

Gordon E. Moore
Beamline

Monochromators and mirrors

Omitted topics

VUV beamline
Soft x-ray beamline
+ XAS measurement – fundamental setup

**SINGLE BEAM**

**SR beamline**

**Source**

**Monochromatized beam** (with higher harmonics)

**Sample**

**F detector**

**Detector for transmission**
Storage ring and beam transport (beamline)
X-ray Absorption Spectroscopy

- how to measure

**XANES, EXAFS, ...**

Most fundamental technique is a transmission mode

### Transmission

Ionization chamber

\[ m_t(E) = \ln \left( \frac{i_0}{i} \right) \]

You measure attenuated beam intensity, that “exponentially” decreases

### Fluorescence

Energy resolving detector

\[ m_t(E) = \frac{F}{i_0} \]

You measure emitted beam intensity, which “linearly” proportional to conc.
Example
- Crystalline and glassy GeO$_2$

Okuno et al.

![Graph showing absorption spectra for GeO$_2$ in different phases at 80K and 300K.](chart)

Si (311) monochromator, 10B@PF
Fourier Transform - example

FT magnitude function for crystalline and glass GeO₂ Okuno et al.

Crystal structure (hexagonal)

Acta Cryst. 17, 842 (1964)

Glass structure

Short range order is close to the hexagonal crystal
Disorder in arrangement of GeO₄ units (connectivity)
X-ray absorption – atom and shell specific phenomena
Monochromator

Double crystal monochromator

Source

Incident beam

Slit

First crystal

Second crystal

$2d \sin q = n \lambda, \ d = 3.13551 \text{ for Si}(111)$

$E \text{ (keV)} = \frac{12.39852}{l} = \frac{1.9771}{\sin q}$

<table>
<thead>
<tr>
<th>Spacing ($d$-value)</th>
<th>Crystal plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3578 Å</td>
<td>Si (400)</td>
</tr>
<tr>
<td>3.1356 Å</td>
<td>Si(111)</td>
</tr>
<tr>
<td>1.6376 Å</td>
<td>Si(311)</td>
</tr>
<tr>
<td>1.0452 Å</td>
<td>Si(511)</td>
</tr>
</tbody>
</table>
Monochromator – energy range

\[ E \ (\text{keV}) = \frac{12.39852}{M} \]

Si(111) 1st harmonic 5-15 keV
Si(111) 3rd harmonic 15-30 keV

Geometrical limitation

\[ K_y = 0.3 \ (22 \ \text{mm}) \]

3 degree

Si 111 refl.

Undulator limitation

\[ K_y = 2.3 \ (9.6 \ \text{mm}) \]

21.5 degree

Goto @Spring-8
Example of XANES – why resolution?

Si (311) monochromator  Okuno et al.

Short range in glass sample is close to that of hexagonal crystal
**Energy resolution**

Energy resolution  \[ \frac{D_E}{E} = \sqrt{(dq_g)^2 + (dq_w)^2 \cot q_B} \]

Geometrical resolution: \( dq_g \)

Darwin width: \( dq_B \)

\[ dq_W = \frac{2e^3 |F|}{pmc^2 V \sin 2q_B} = 8 \text{ sec. (4x10}^{-5} \text{ rad) (Si(111), 9keV)} \]

Energy resolution is given as a convolution of geometrical resolution and Darwin width

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**Guidelines**

a. Bragg-angle-dependent energy resolution degrades with the increase of energy

b. Darwin width is smaller for high index planes, i.e. better resolution
Evidence for high energy resolution -bromine gas K-edge

How to evaluate the energy resolution
Br gas By K-edge (13.5 keV)

★Darwin width and angle-dependent term
★Abberation caused by a focusing mirror placed in front of monochromator degrades energy resolution T. Matsushita@SSRL
Monochromator - mechanism

Rotating a double crystal results in beam height change
How to correct the beam height variation

Fixed beam height or Correction by stage

Constant beam-height double crystal monochromator

Monochromator - outlook

BL13MPW@PF, KEK
Beamline optics -strategy

Wiggler@2G
Emittance ≈ 30 nmrad

Strategy: 1:1 mirror focusing or 3:1 sagittal focusing

2 Crystal Monochromator

Top view

Source
4m rad
Collimating Mirror
Be window
Beam shutter
M1
c1 c2
M2
Downstream Shutters
F1=44m
F2=35m
Focus

1mm (H)
0.3 mm (V)

Side view

0.5 mrad
M1
35
2
10
35
79
Distance from source point (m)
Optics of BL10XU (U032V) beamline@Spring-8

5-30 keV energy range
1\textsuperscript{st} & 3\textsuperscript{rd} radiation (tunable)
T.P. 12kW  (465W)
P.D.  (76W/mm\textsuperscript{2})

Ray tracing results

Emittance: 3 nmrad
Strategy: unfocused

Distance from source (mm)

1mm (H)
0.3 mm (V)