



# X-ray absorption spectroscopy for beginners

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**UMR C.N.R.S. 7223**

# Acknowledgements for the organization



- Co-Chairs

Joaquin García Ruiz,

Professor, Inst. de Ciencia de Materiales de Aragón (Zaragoza)

Hiroyuki Oyanagi,

Chair of the International X-ray Absorption Society

- Organized in Cooperation with

- IUCr 2011 Local Organizing Committee,

- IUCr Commission on XAFS,

- International X-ray Absorption Society

# Aims of this Tutorial



## Promote XAFS among new users

- presenting the technique and its applications
- overview of data analysis software commonly used or under development

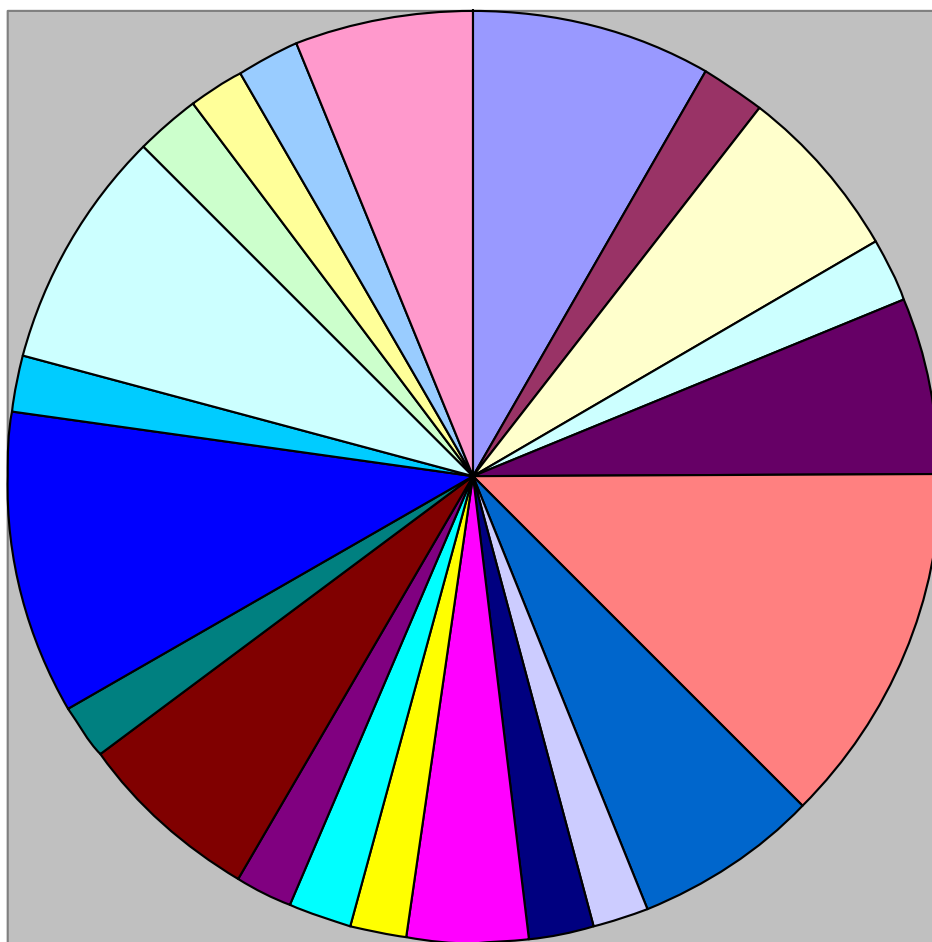
Create a bridge between XAFS and a large IUCr Community

# Other presentations



- XAFS Theory: XANES and EXAFS spectra.  
**Christopher T. Chantler**
- Experimental aspects: synchrotron radiation, beamlines, detectors, measurement modes geometry, sample preparation methods.  
**Hiroyuki Oyanagi**
- Spectroscopy in Physics and Material Science.  
**Joaquin García Ruiz**
- Applications of X-Ray Absorption spectroscopy in Chemistry  
**Marcos Fernandez-García**
- **Britt Hedman**  
Applications of X-Ray Absorption Spectroscopy in Biology
- FEFF and related codes:  
**Anatoly Frenkel**
- FDMNES code  
**Elena Nazarenko**
- EXCURVE code  
**Wolfram Meyer-Klaucke**
- XANES: MXAN code  
**Keisuke Hatada**

# 56 participants registered from 24 Countries



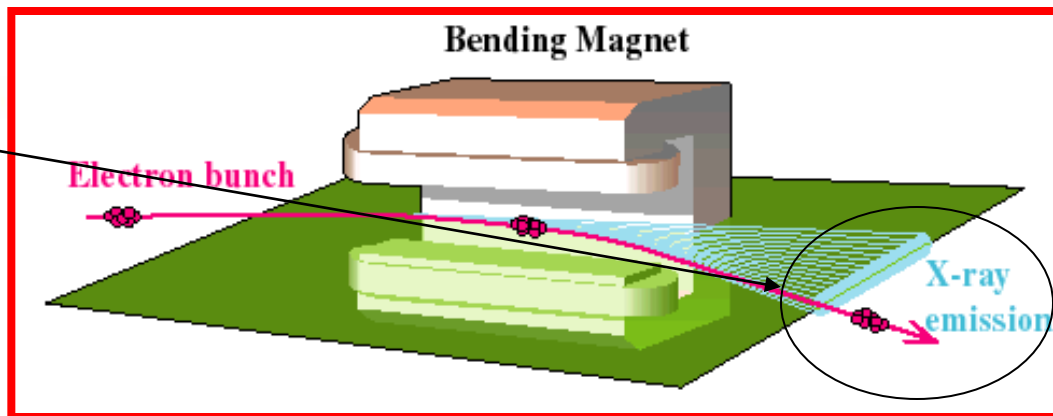
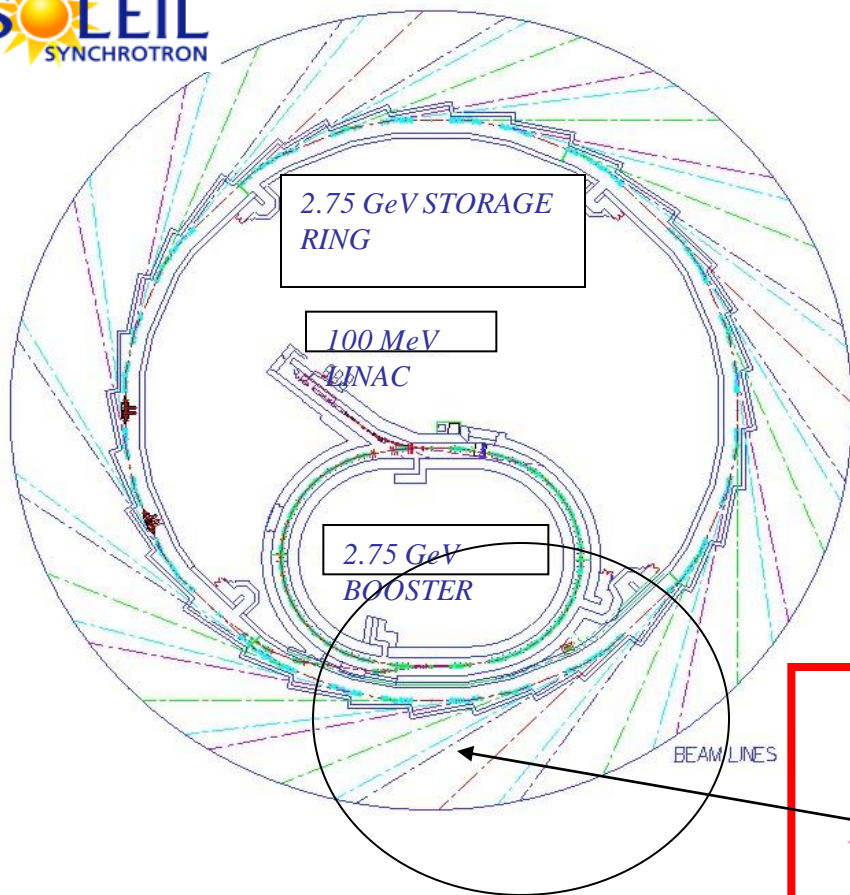
China  
Argentina

# X-ray absorption spectroscopy for beginners



- Experimental aspects
  - synchrotron, specificity of XAS
- Principles of XAS
- Information obtained from XAS
  - accuracy, sensitivity...

# XAS experiments require a synchrotron radiation facility



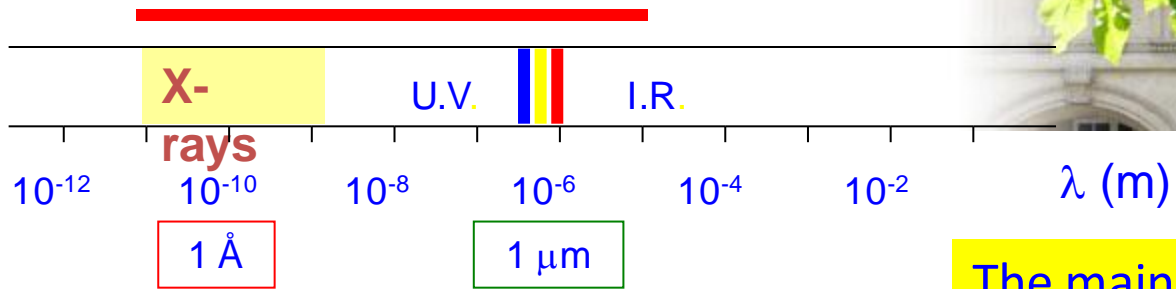
# The World of Synchrotron Radiation

Click an area or button for further listings of synchrotrons around the world.



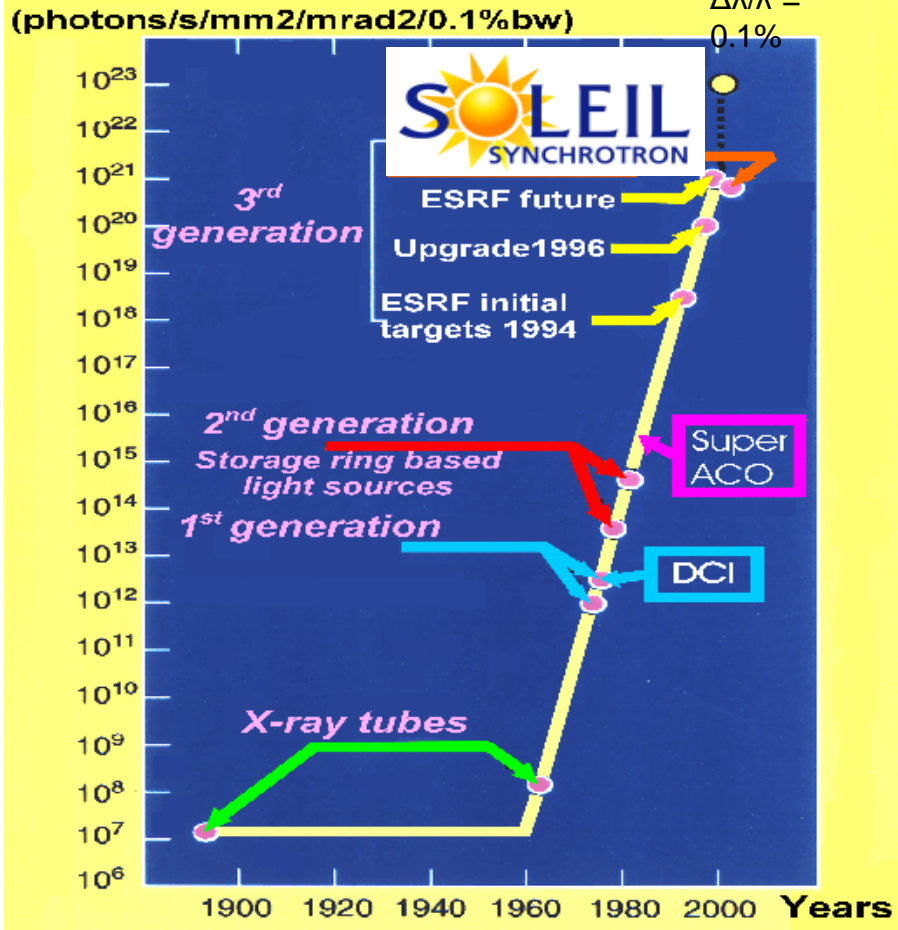
XAFS developments are linked to the SR facilities which are all over the world





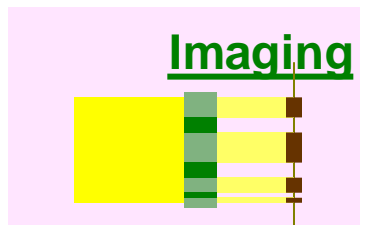
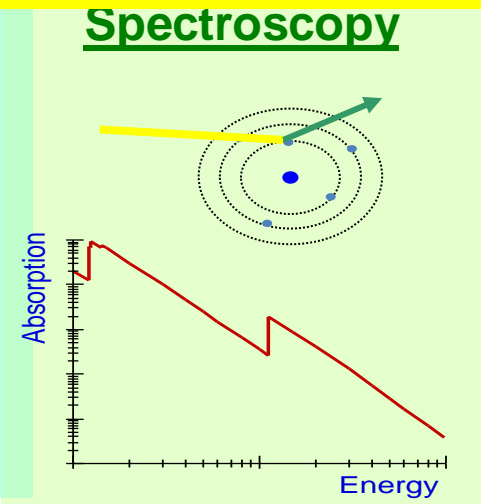
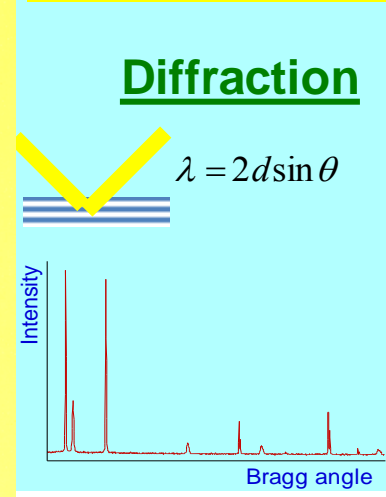
$$E[\text{keV}] = \frac{12.4}{\lambda[\text{\AA}]}$$

### Brilliance

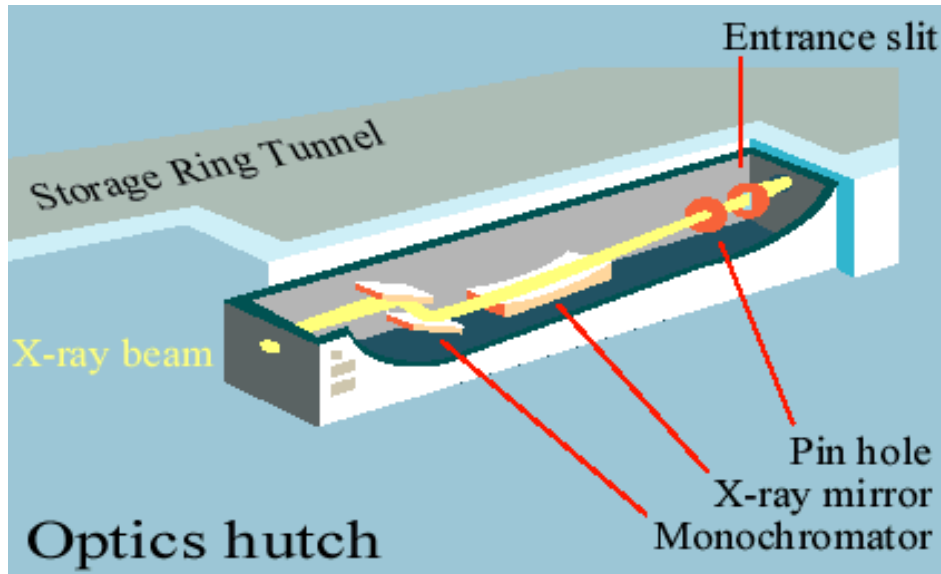


The main advantages of the synchrotron source :

- extended wavelength range,
- continuous tunability
- brightness



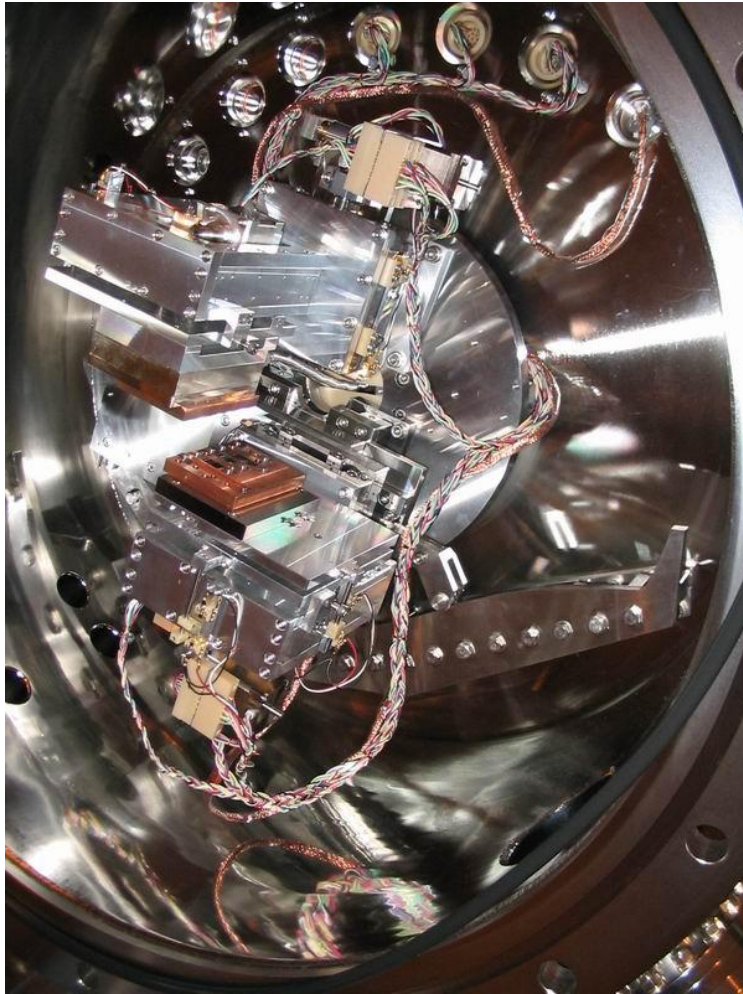
# Optics hutch



Example of optics hutch at ESRF

- Optics hutch
- Experimental hutch: sample experimental environment, detectors etc.

## Optics hutch



Ex. double crystal  
monochromator (Synchrotron Soleil)

The energy is selected by a monochromator

$$2d_n \sin \theta_b = n\lambda$$

Crystals used for X-ray monochromators

Si(111), Si(220),  
Si(311), Ge(111)

# Definitions



## General definitions for the spectroscopy

- X-ray Absorption Spectroscopy (**XAS**) is a technique for measuring the linear absorption coefficient  $\mu(E)$
- X-ray Absorption Fine Structure (**XAFS**)

## Terms used to define spectral regions

- **XANES** (X-ray Absorption Near Edge Spectroscopy) or **NEXAFS** (Near-Edge X-ray Absorption Fine Structure)
- Extended X-ray Absorption Fine Structure (**EXAFS**)

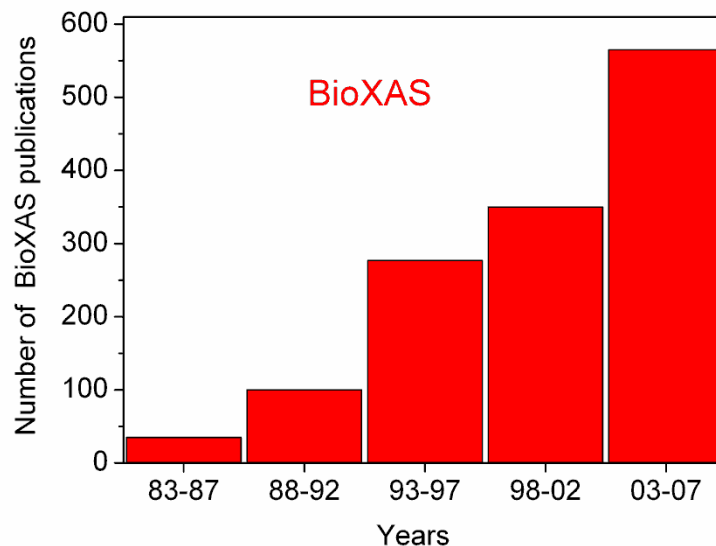
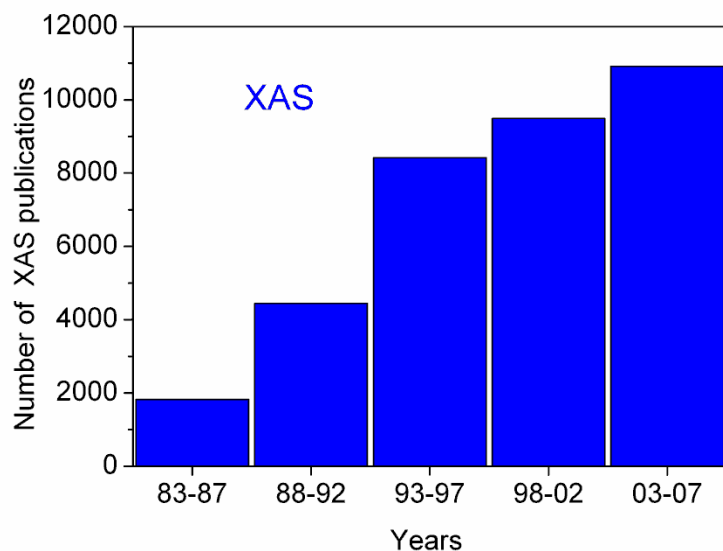
**Contribution of IUCr XAFS Committee to IUCr Online Dictionary.  
The working group on the XAFS Nomenclature and Advisory  
Committee suggested definitions for XAFS related terms  
In cooperation with IXAS and other organisations**

<http://www.iucr.org/resources/commissions/xafs/xafs-related-definitions-for-the-iucr-dictionary>

# X-ray absorption spectroscopy



**Application to physics, earth science, chemistry and biology (see presentations of Profs. Joaquin García Ruiz, Fernandez-García and Britt Hedman)**



The impact of the biological x-ray absorption spectroscopy (BioXAS) has increased as indicated by the number and ranking of publications

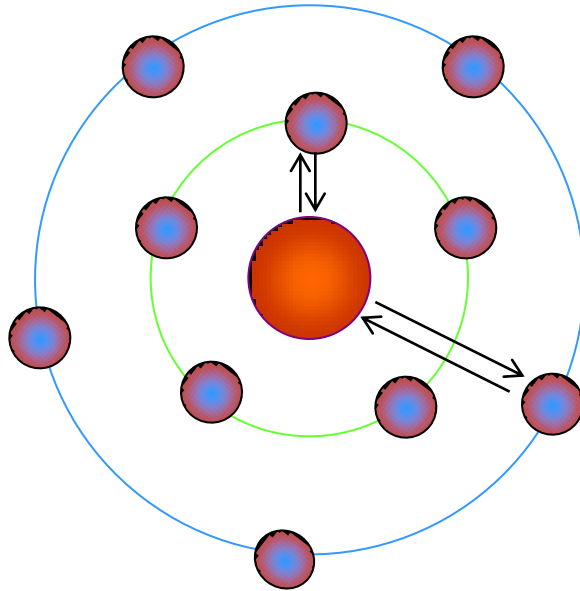
Ascone et al. (2009). Journal of Synchrotron Radiation 16, 413-42.

# XAFS

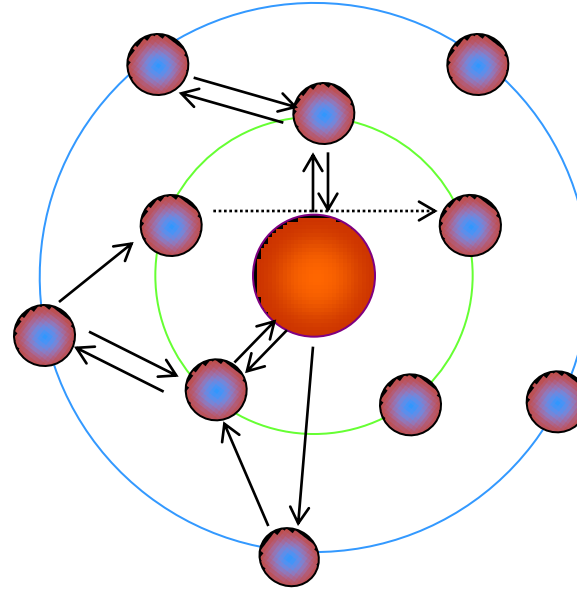


XAFS is commonly divided into the 'near edge' region (XANES or NEXAFS) and the 'extended' region (EXAFS)

XAFS can be interpreted as due to scattering of the photo-electron ejected from the absorbing atom by the photo-electric effect.



Mainly single scattering contributions



Multiple scattering contributions

# Cross section



**Cross-section is a measure of the probability of interaction between the incident photons with the material via photoabsorption or scattering processes.**

$$\sigma/(uA) = [\mu/\rho]$$

X-ray mass absorption coefficient

$\sigma$  is the cross-section in barns/atom (1 barn =  $10^{-24}$  cm<sup>2</sup>),

$u$  is the atomic mass unit

$A$  is the relative atomic mass of the target element (i.e. in amu; the mass relative to 12 for carbon 12).

# X-ray absorption spectroscopy



K	1s
---	----

L <sub>1</sub>	2s
L <sub>2</sub>	2p <sub>1/2</sub>
L <sub>3</sub>	2p <sub>3/2</sub>

M <sub>1</sub>	3s
M <sub>2</sub>	3p <sub>1/2</sub>
M <sub>3</sub>	3p <sub>3/2</sub>
M <sub>4</sub>	3d <sub>3/2</sub>
M <sub>5</sub>	3d <sub>5/2</sub>

Fermi Golden Rule for XAS  $\mu(\omega)$

$$\mu(\omega) \sim \sum_f |\langle \psi_f | d | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

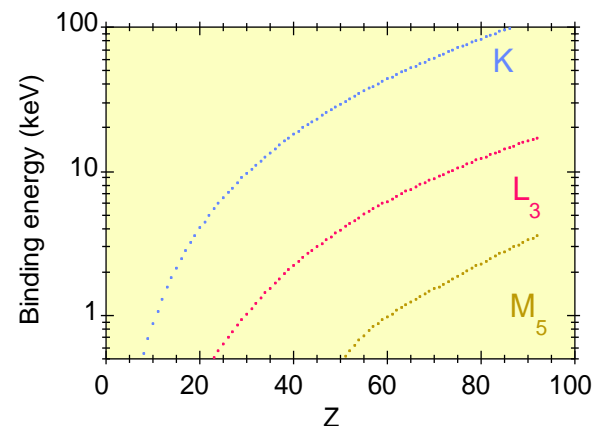
Atomic-like electric dipole transitions  
(change of angular momentum  $\Delta l \pm 1$ )

s  $\rightarrow$  p

2p  $\rightarrow$  3d

2p  $\rightarrow$  4s

**Absorbing atoms are selected performing the experiment at energy range including binding energy**



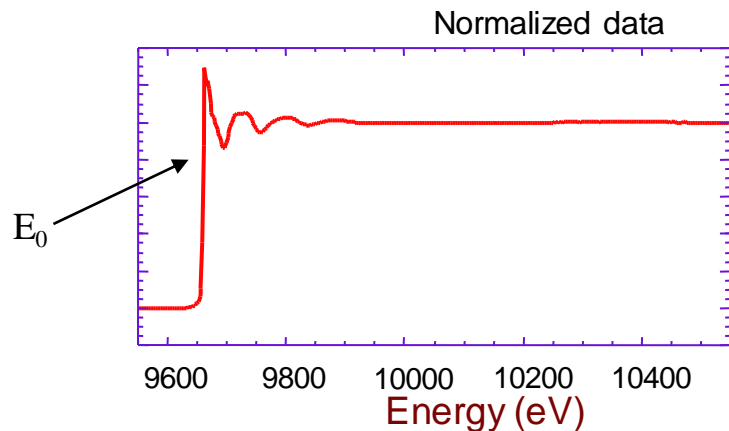


# Absorption edge



Definition: an absorption edge is the energy at which there is a sharp rise (discontinuity) in the (linear) absorption coefficient of X-rays by an element, which occurs when the energy of the photon corresponds to the energy of a shell of the atom ( $K$ ,  $L_I$ ,  $L_{II}$ ,  $L_{III}$ , etc. corresponding to the creation of electron holes in the  $1s$ ,  $2s$ ,  $2p^{1/2}$ ,  $2p^{3/2}$  etc. atomic subshells).

The **absorption threshold** is associated with this transition and is characterized by the corresponding energy ( $E_0$ ).



# Absorption threshold and $E_0$

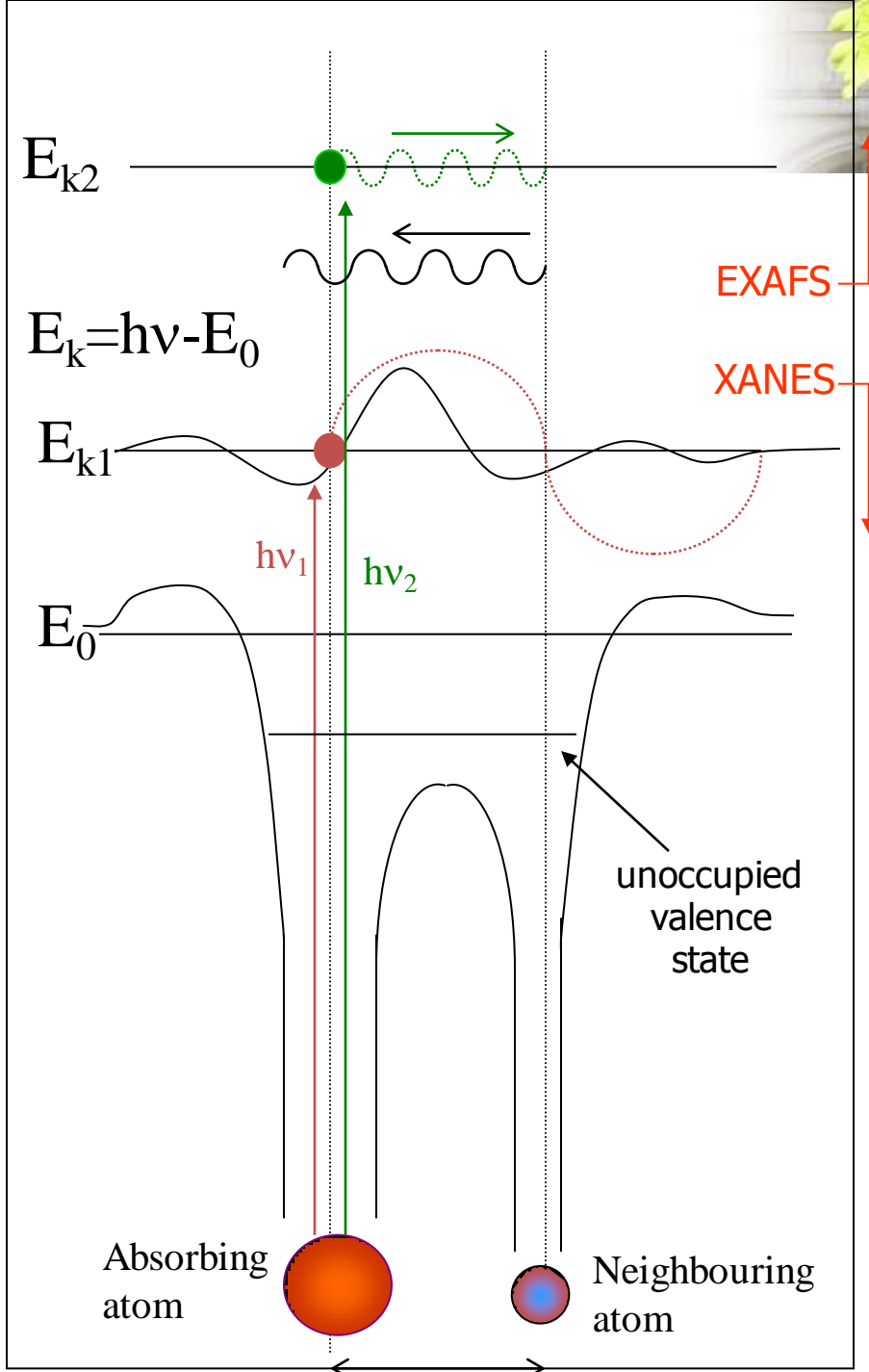


- Theoretically, the **absorption threshold** is defined as the energy at which the open continuum channel for photo-electric absorption becomes available, producing a continuum photo-electron. This has an exact value from theory, subject to convergence issues.
- Experimentally, the **absorption threshold** is defined as the inflection point in the first derivative of the experimental XANES spectrum.
- Computationally, an **absorption threshold** is defined for EXAFS fitting (and occasionally XANES fitting) as  $E_0$  which is considered either as an arbitrary fitting coefficient or the starting point of  $k$

Other definitions are used in literature :

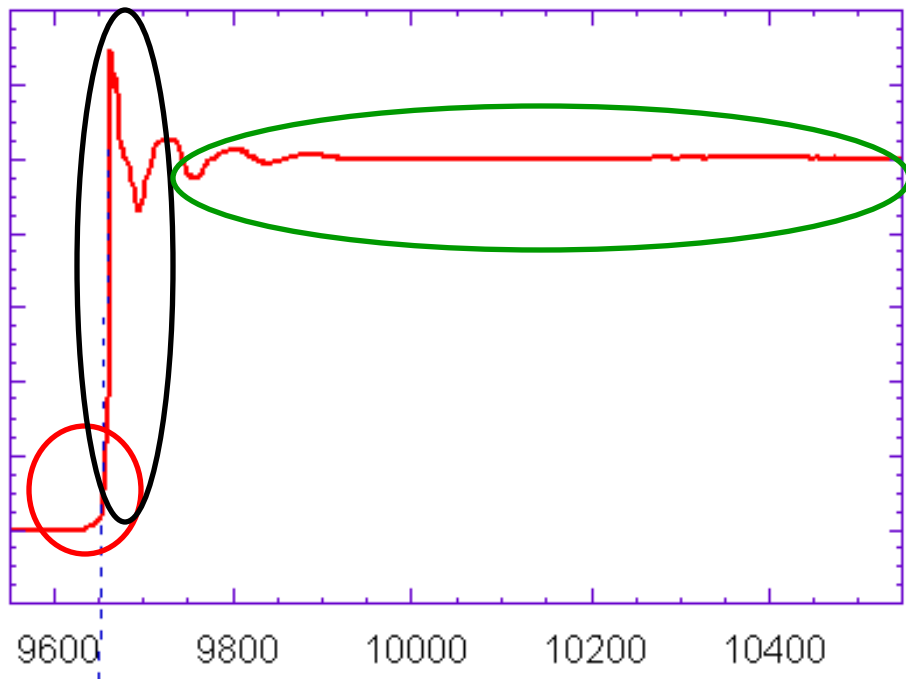
<http://www.iucr.org/resources/commissions/xafs/xafs-related-definitions-for-the-iucr-dictionary>

ENERGY



XAFS:  
a tool for local  
investigations

# Information obtained by XAS



## XANES and EXAFS:

Types of Ligands

Distances

Coordination Number

## PRE-EDGE

Covalency

electronic structure

## XANES

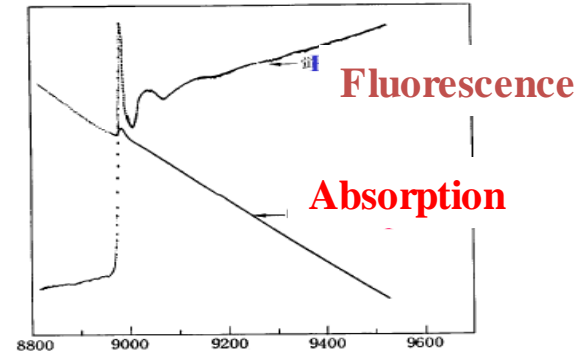
Oxidation State

Site Symmetry

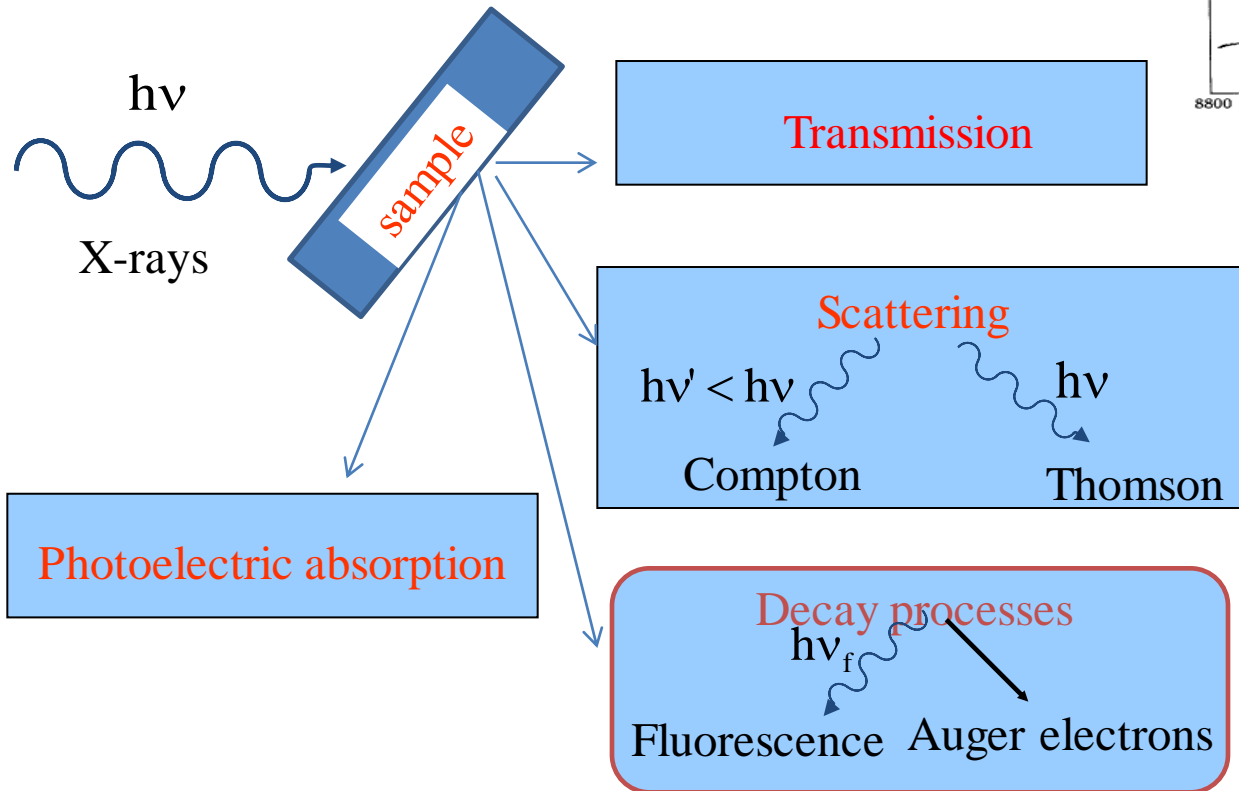
# X-rays/sample Interactions



Spectra recorded for low-concentration of the absorber element



The absorption coefficient



# Mass attenuation coefficient



The **mass attenuation coefficient** in  $\text{cm}^2/\text{g}$  can be written as a sum of separated mass absorption coefficients

$$[\mu/\rho]_{\text{TOT}} = [\mu/\rho]_{\text{PE}} + [\mu/\rho]_{\text{coh}} + [\mu/\rho]_{\text{incoh}}$$

coherent scattering contributions

incoherent scattering contributions

It is recommended that  $[\mu/\rho]_{\text{TOT}}$  be used to distinguish this from the mass absorption coefficient  $[\mu/\rho]_{\text{PE}}$  (q.v.) as they are both commonly presented as  $[\mu/\rho]$ .

# Beer-Lambert law

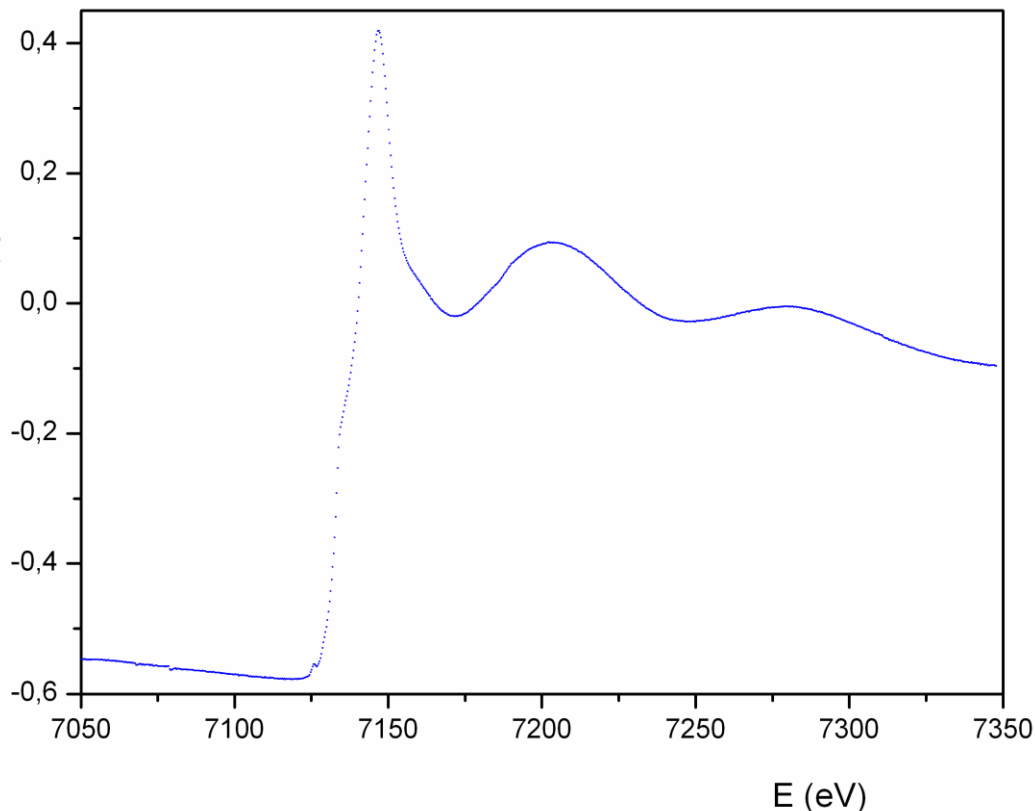


XAS is a technique for measuring the linear absorption coefficient  $\mu(E)$

$$I(t) = I_0 e^{-\left[ \frac{\mu}{\rho} \right] \rho t}$$

X-ray mass absorption coefficient

$$\frac{\mu}{\rho} = \sum_i w_i \left( \frac{\mu}{\rho} \right)_i$$



# Fluorescence signal



$$I = I_0 \left[ 1 - e^{-[\mu_t(E) + \mu_t(E_F)]d} \right] \varepsilon \frac{\Omega}{4\pi} \frac{\mu_A(E)}{\mu_t(E) + \mu_t(E_F)}$$

$\varepsilon$  fluorescence yield

For low concentration of absorber atoms and high thickness of the sample

$$[\mu_t(E) + \mu_t(E_F)]d \gg 1 \Rightarrow I \approx I_0 \varepsilon \frac{\Omega}{4\pi} \frac{\mu_A}{2\mu_t}$$



# Experimental aspects



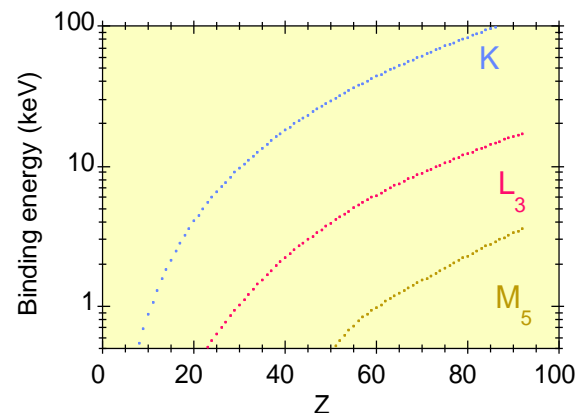
Sample environment/preparation depends on

- Energy domain:  
vacuum or atmospheric pressure

- Sample state

- Gel
- crystal
- Solution
- Solid/powder

- Sample properties (chemical composition)



# Experimental hutch (SAMBA, Soleil)

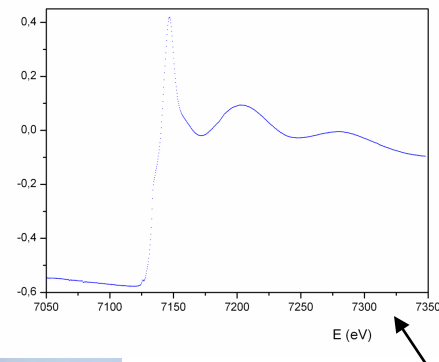


## Setup for transmission measurements

$$I(t) = I_0 e^{-\left[\frac{\mu}{\rho}\right] \rho t}$$

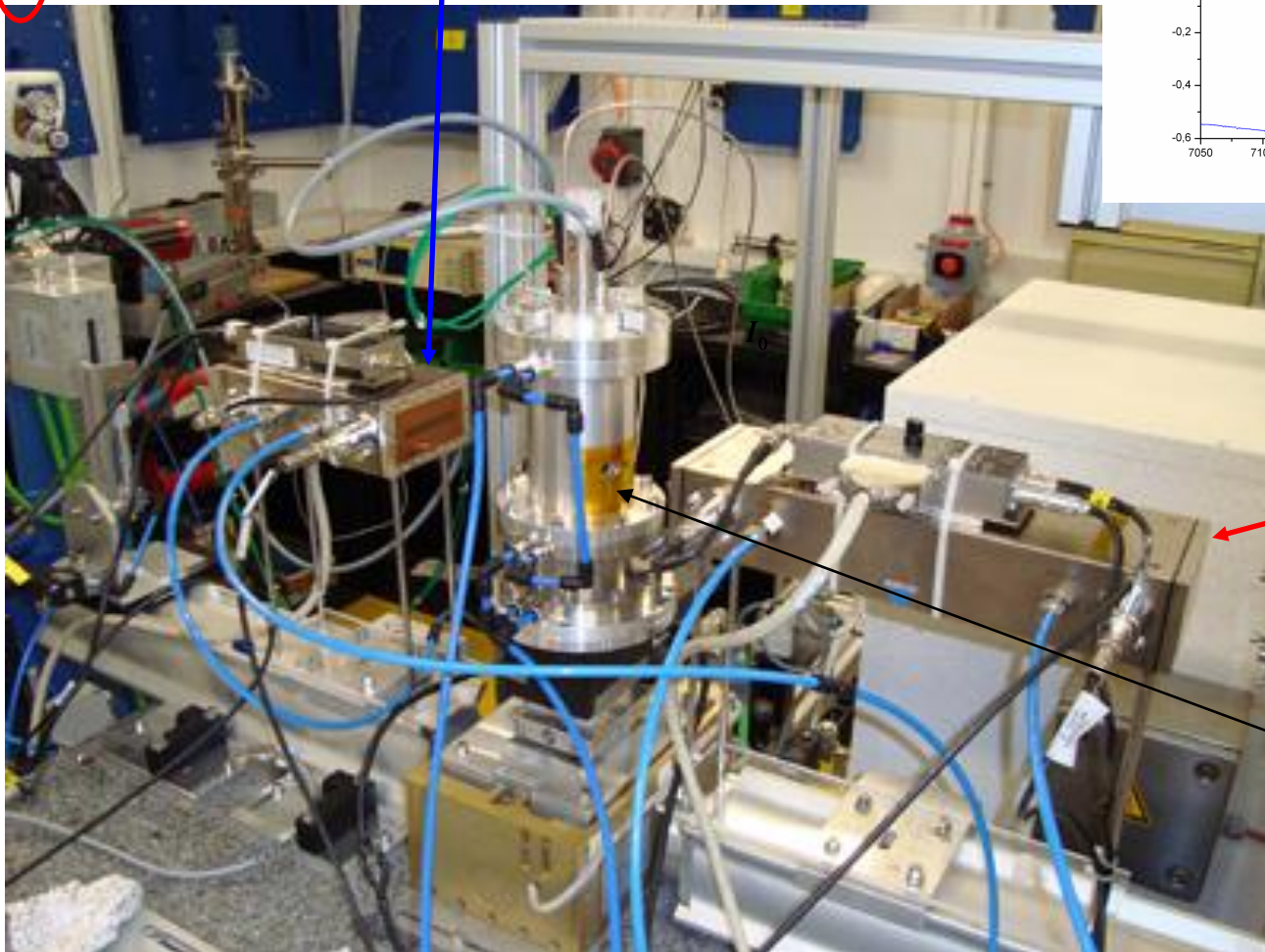
Ionization chamber

to measure  $I$



$I$  and  $I_0$  are measured for each energy value

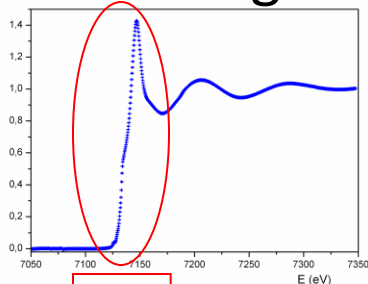
Ionization chamber to measure  $I_0$



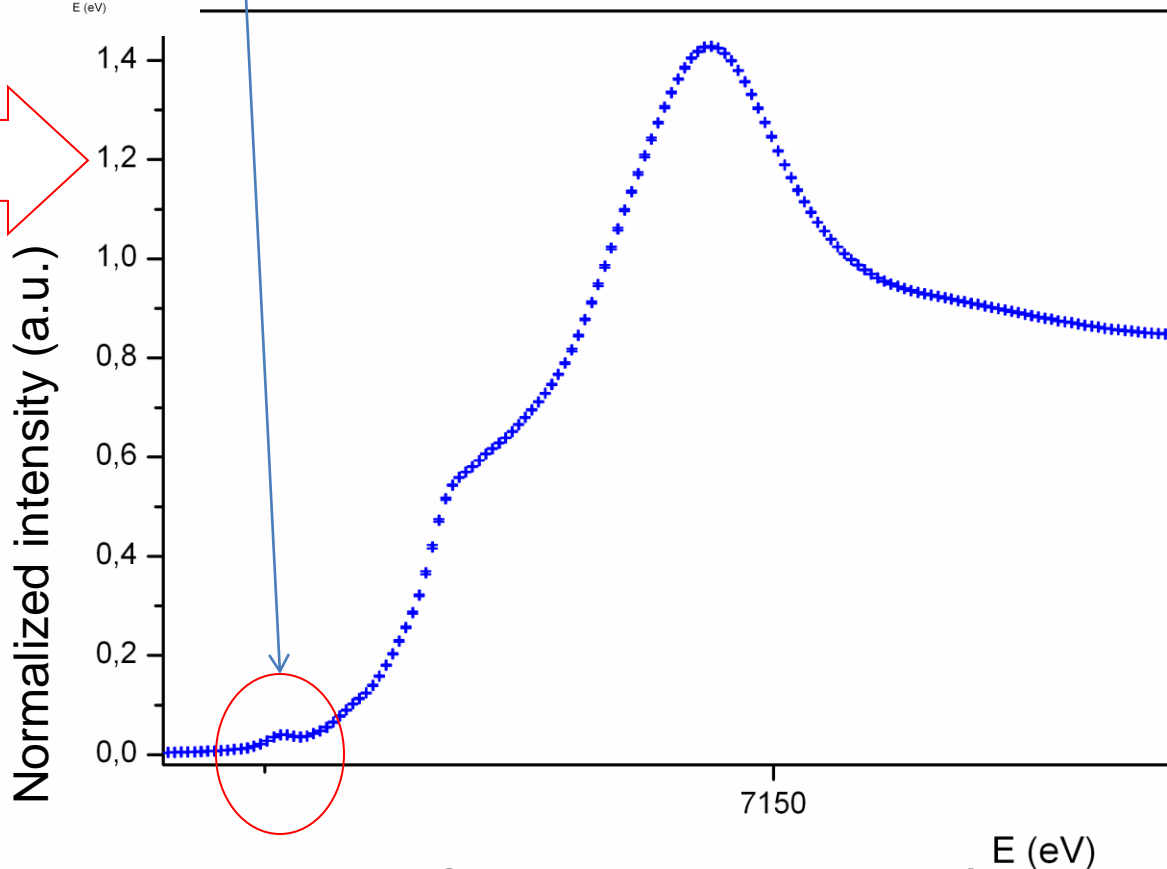
Sample environment



## Pre-edge structure



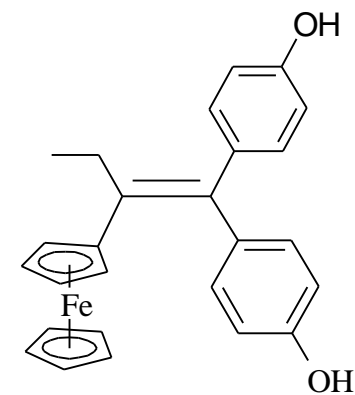
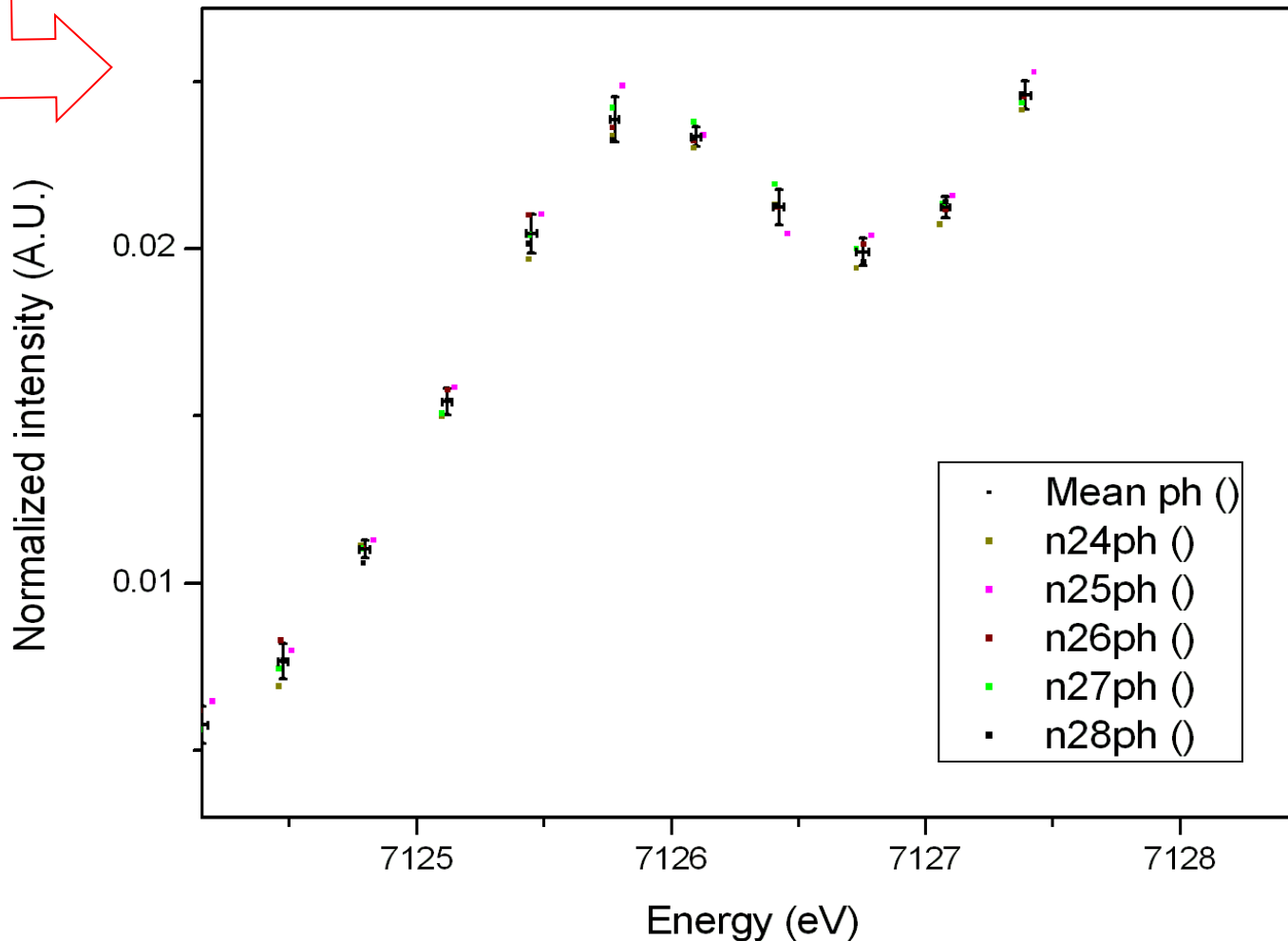
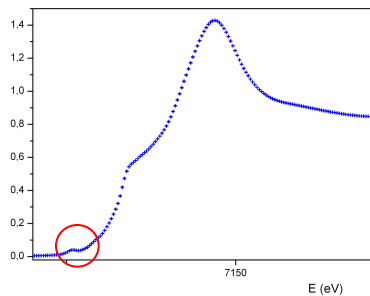
## Average of intensity and E for five spectra



I. Ascone, D. Hamels, P. Pigeon, M. Salome, Y Joly, T. Prangé, A. Vessières, S. Top, G. Jaouen. (2011) unpublished data

## Precision of data set: average of intensity and E for five spectra and standard deviations

Spectra recorded at ESRF: 0.1 sec/pt, Energy step=0.3 eV  
Average standard deviation (E) = 0,02038 eV



**Measurements should be accurate**

# Data analysis: normalization

Linear absorption coefficient measured or calculated

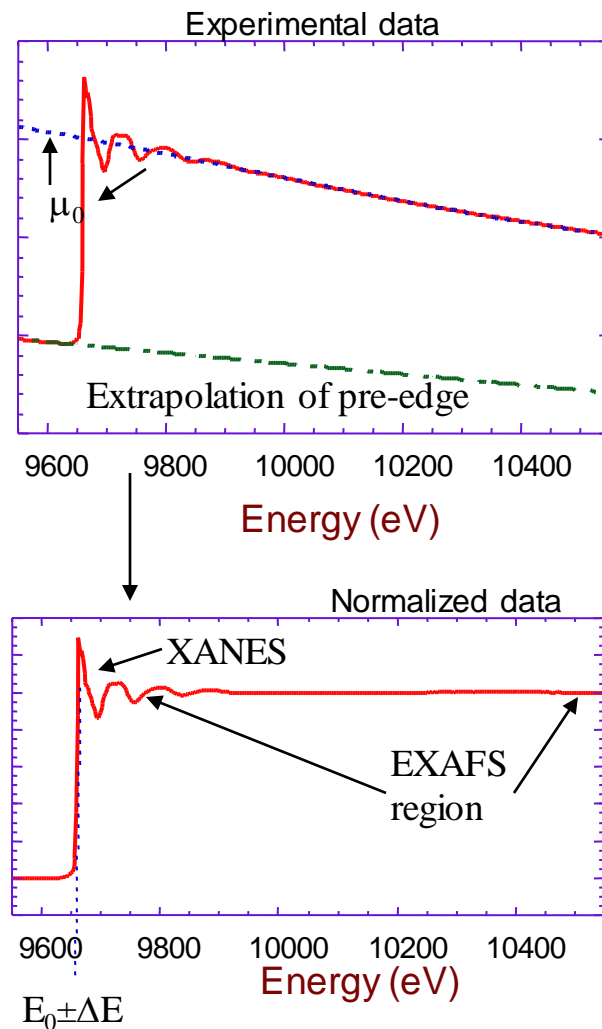
$$\mu(E) = \mu_0(E)[1 + \chi(E)]$$

smooth background as calculated in the absence of scattering or fit (e.g. a spline fit)

$$\chi(E) = \frac{[\mu(E) - \mu_0(E)]}{\mu_0(E)}$$

Other definitions are used in literature :

<http://www.iucr.org/resources/commissions/xafs/xafs-related-definitions-for-the-iucr-dictionary>





# EXAFS signal

EXAFS signal may be expressed as function of the energy or of the photoelectron wavenumber

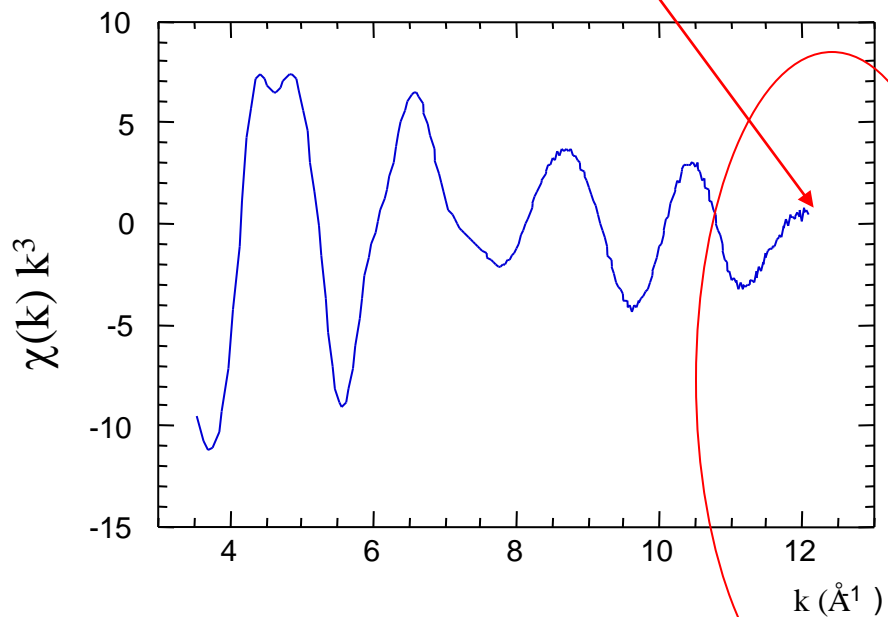
$$\chi(E) \quad \text{or} \quad \chi(k)$$

$$k = \frac{2\pi}{\lambda} = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}}$$

photoelectron wavenumber

electron mass

For accurate measurements  $k_{\max}$  should be increased



Number of degree of freedom ( $\nu$ ):

$$\nu = N_{\text{ind}} - N_{\text{par}}, \quad N_{\text{ind}} = \frac{2\Delta k \Delta r}{\pi}$$

Number of independent data points

# EXAFS signal fitting



$$\chi(k) = \sum_j \chi_j(k)$$

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

$F_j(k)$  Photo-electron scattering factors

$S_0^2$  Amplitude reduction factor accounting for relaxation of the absorbing atom

$e^{-2R_j/\lambda_k}$   $\lambda$  = mean free path

$e^{-2k^2 \sigma_j^2}$   $\sigma_j^2$  = mean-square disorder in R

# Simulation of EXAFS and XANES



Different theoretical approaches and/or formula used by different programmes

(see presentations of Prof. Frenkel, Dr. Nazarenko, Dr. Mayer-Klaucke, Dr. K. Hatada)

**FEFF and related codes:** Spherically symmetric potentials (Muffin-tin (MT) approximation). Simulation of XANES spectra and fitting of EXAFS region. (developed in US)

**EXCURVE :** Potentials and corresponding phase shifts are calculated for each constituent atom of the examined material sample from a superposition of neutral atomic solutions or potential files produced by *ab initio* codes are used. Simulation of XANES spectra and fitting of EXAFS region. (developed in UK)

**MXAN:** Full multiple scattering calculations with MT approximation and **FPMS** (Non MT approximation). Structural and electronic properties are **fitted in XANES** region (developed in Italy)

**FDMNES:** Finite Difference Method (FDM) to solve the Schrödinger equation (non MT approximation) and MT approximation. **Pre-edge** and XANES spectra are simulated (developed in France)

**Fit-it:** Use **FEFF** and **FDMNES** to **fit XANES** (developed in Russian Federation)



# Accuracy



Accuracy of XAS measurements depend on the data quality (e.g. it is recommended to optimise S/N ratio,  $k_{\max}$  and harmonics rejection, to chose appropriate detectors, etc. )

## EXAFS

- Distances  $\pm 0.02 \text{ \AA}$  This value could increase or decrease depending on quality data or other factors (e.g. errors in  $E_0$  of order 10 eV or more which can result in bond length errors of order 0.02  $\text{\AA}$  or more )
- Coordination number  $\pm 20\text{-}25\%$
- Scattering Atom DZ  $\pm 1$  (Z=6-17)  
DZ  $\pm 3$  (Z=20-35)

## XANES

- Be carefull to the calibration of the E scale
- Measure error bar for accurate comparison of XANES spectra

# Suggestions for XAS experiments



- Select the XAS set-up (detectors, monochromators, sample environment etc.) adapted to the sample properties and objectives for the project
- Combine XAS with other techniques (RX, other spectroscopies etc.)
- For EXAFS :
  - Limit the number of fitting parameters
  - High signal to noise ratio
  - large K range

Thank you for your attention

# References and links



## References

**Metal Sites in Biology:** R. H. Holm, P. Kennepohl, and E. I. Solomon. Chemical Reviews (1996) 96 :2239

**Experimental aspects: a)** I. Ascone, W. Meyer-Klaucke and L. Murphy J. Synchr. Rad. (2003) 10, 16-22

**b)** N. A. Rae, C. T. Chantler, Z. Barnea, M. D. de Jonge, C. Q. Tran, J. R. Hester, Phys. Rev. A 81 (2010) 022904

**Covalency of Ligand-Metal Bonds:** E. I. Solomon, B. Hedman, K.O. Hodgson, A. Dey, and R. Szilagy. Coord. Chem. Rev. (2005) 249, 97

**“Spectroscopically silent” metals :** Penner-Hahn, J. E. Coord. Chem. Rev. (2005) 249, 161-177.

**BioXAS/metalloproteomics:** I. Ascone and R. Strange. J. Synchr. Rad. (2009) 16, 413-42.

**Book:** Bunker, G. (2010). In Introduction to XAFS: A practical guide to X-ray Absorption Fine Structure Spectroscopy, Cambridge University Press.

- links to XAFS websites

- <http://www.iucr.org/iucr/commissions/xafs>

- <http://www.xafs.org/>

- <http://www.ixasportal.net/ixas/>