Marianne Liebi– Material Science at Large Scale Facilities

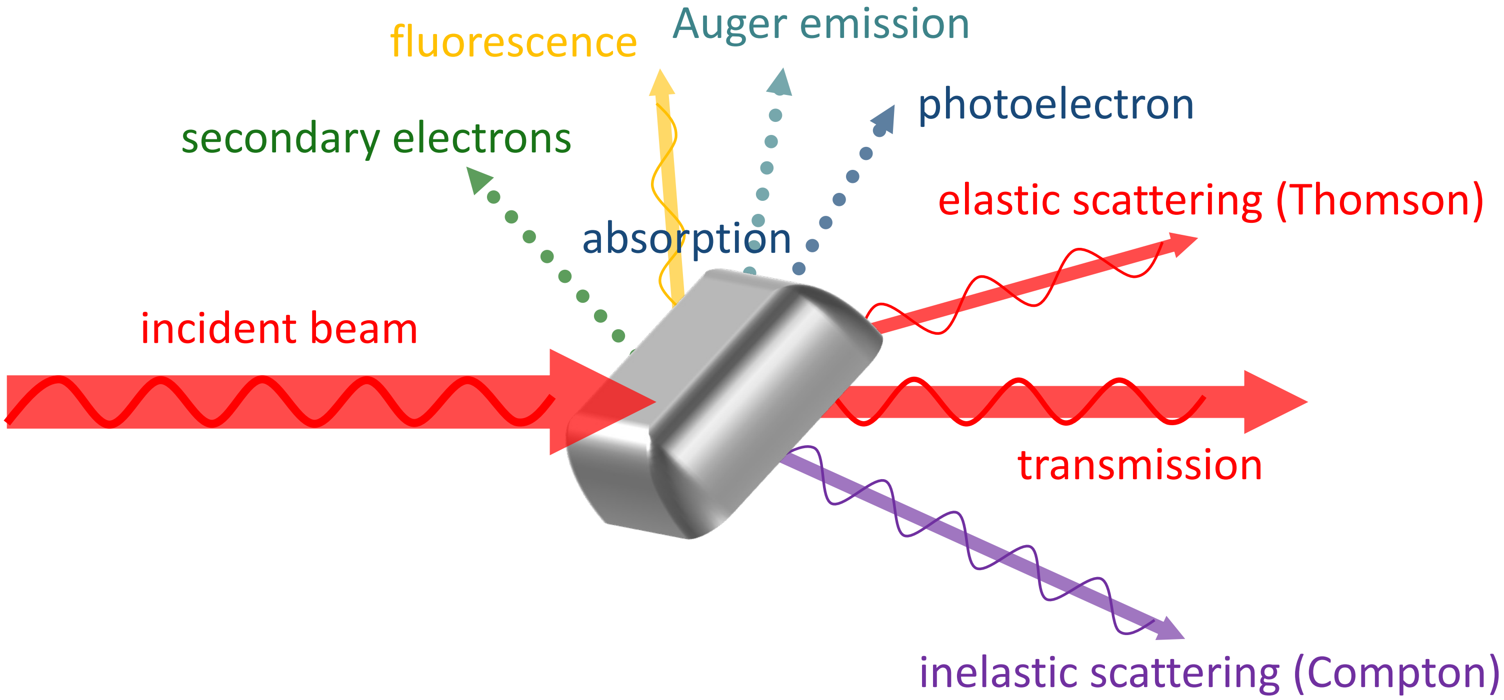
X-ray Absorption Fine Structure(XAFS): XANES/NEXAFS and EXAFS

EPFL Master Course 2024 MSE435

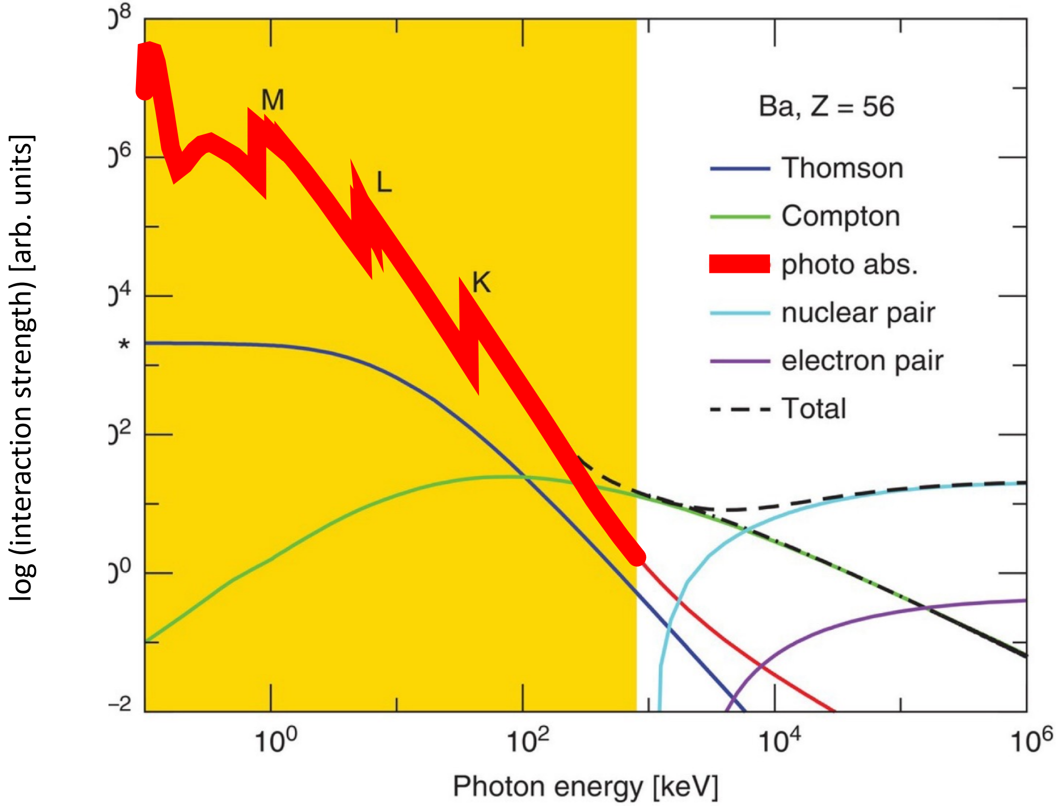
Course program

09.09.24	Introduction, sources, beamlines, detectors	Steven Van Petegem
16.09.24	Holiday	
23.09.24	Excursion to PSI	Steven Van Petegem / Marianne Liebi
30.09.24	Interaction with matter	Steven Van Petegem
07.10.24	Fluorescence	Marianne Liebi
14.10.24	Diffraction I	Steven Van Petegem
21.10.24	Break	
28.10.24	Small angle x-ray scattering	Marianne Liebi
04.11.24	Cancelled	
11.11.24	XANES/EXAFS	Marianne Liebi
18.11.24	Phase contrast / Tomography	Steven Van Petegem
25.11.24	Coherent imaging	Marianne Liebi
02.12.24	Diffraction II / Neutron imaging	Steven Van Petegem
09.12.24	PEEM / Magnetic scattering	Steven Van Petegem
16.12.24	Case study presentations	Steven Van Petegem / Marianne Liebi

Interaction of X-ray with matter



Interaction strengths of x-rays with matter



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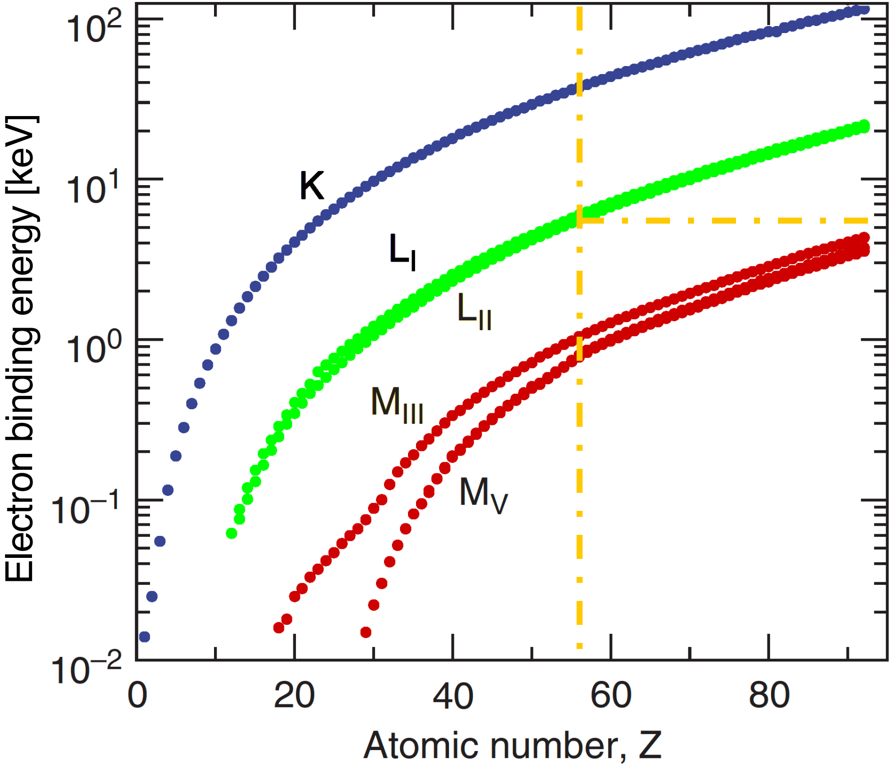
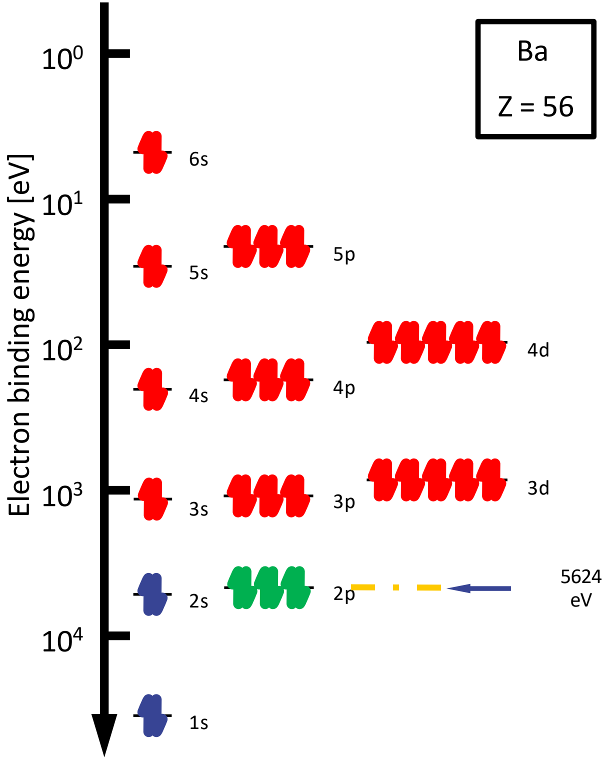
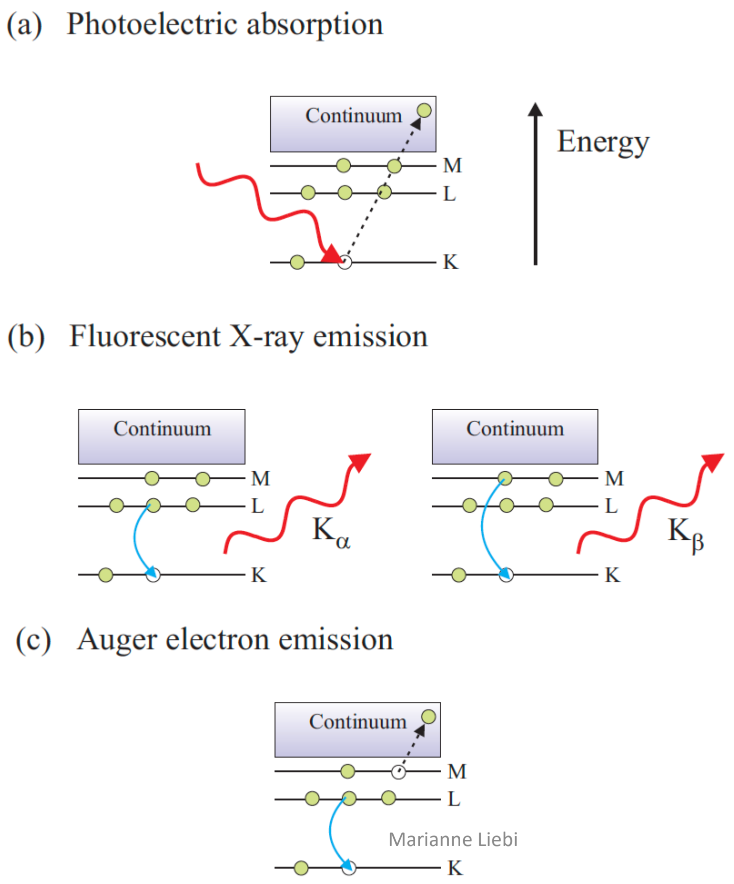
Electron binding energies of the elements





Absorption

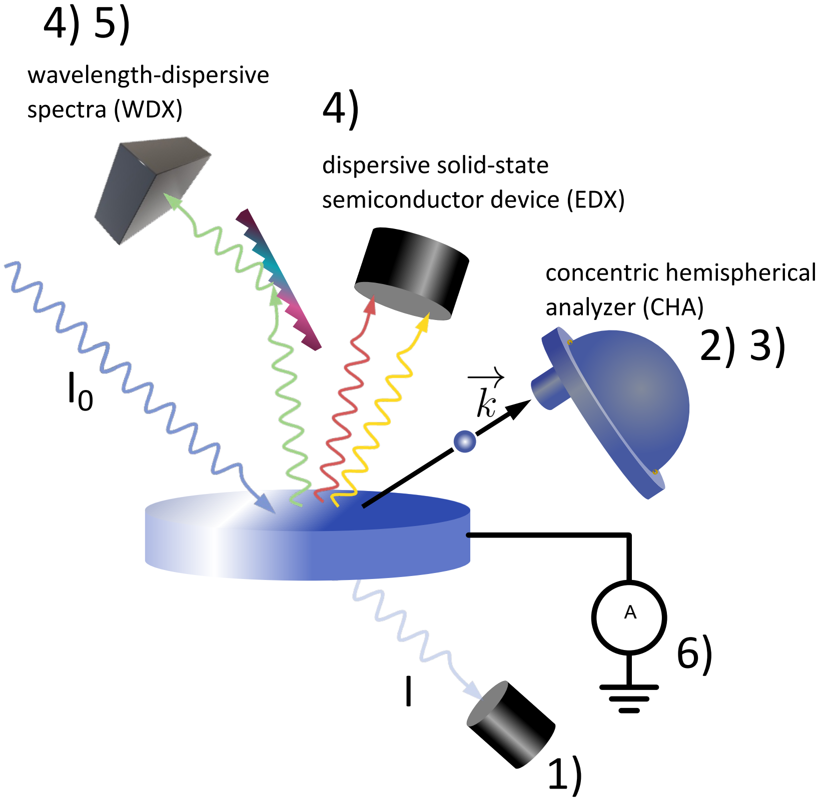


Marianne Liebi

Overview of spectroscopy techniques

Technique	Abbreviation	Scanned $h\nu_{in}$?	Detection methods
X-ray absorption near-edge spectroscopy	**XANES**	✓	1, 2, 4, 6
Photoemission electron microscopy	PEEM Variations of XAS	✓	6
Scanning transmission x-ray microscopy	STXM	✓	1, 3
Extended x-ray absorption fine structure	**EXAFS**	✓	1, 2, 4, 6
X-ray fluorescence	XRF		4
Resonant inelastic x-ray scattering	RIXS	✓	5
Angle-resolved photoelectron spectroscopy	ARPES not covered in this course	(✓)	2
X-ray photoelectron spectroscopy	XPS	(✓)	2, 3

Detection methods



Form of detection

1) **Transmitted x-radiation**
2) **Emitted photoelectrons**
   Also as function of $\vec{k}$
3) Auger electrons
4) **Emitted fluorescence**
5) Inelastically scattered x-radiation

Spectrally resolved

6) **Secondary electrons/total electron yield**

– Not spectrally resolved
– Used as a measure of absorption strength

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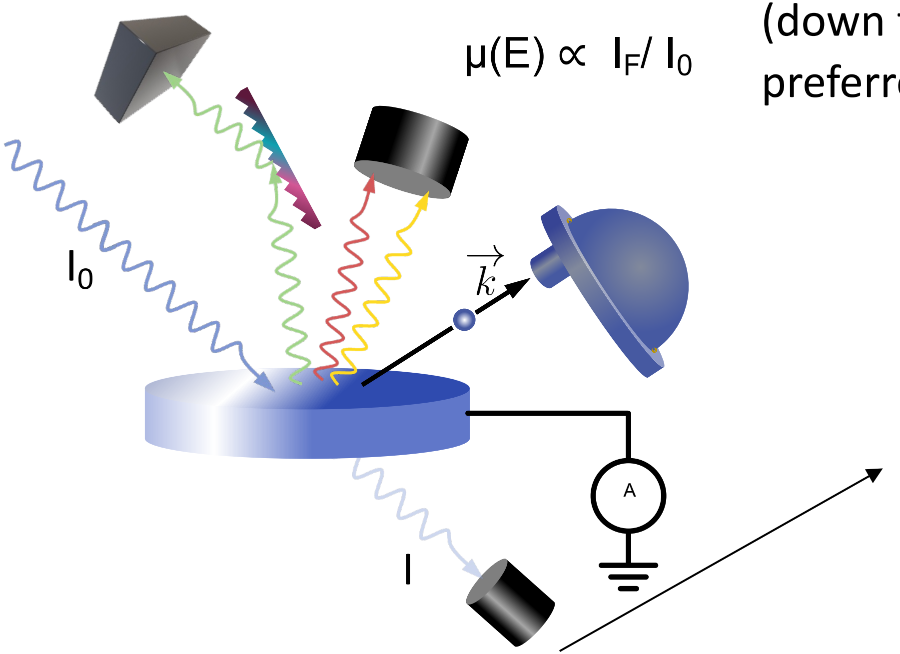
Detection methods



for thick samples or low concentrations (down to ppm level), fluorescence is preferred

$$I = I_0 e^{-\mu(E)t}$$

$$\mu(E)\, t = -\ln(I/I_0)$$

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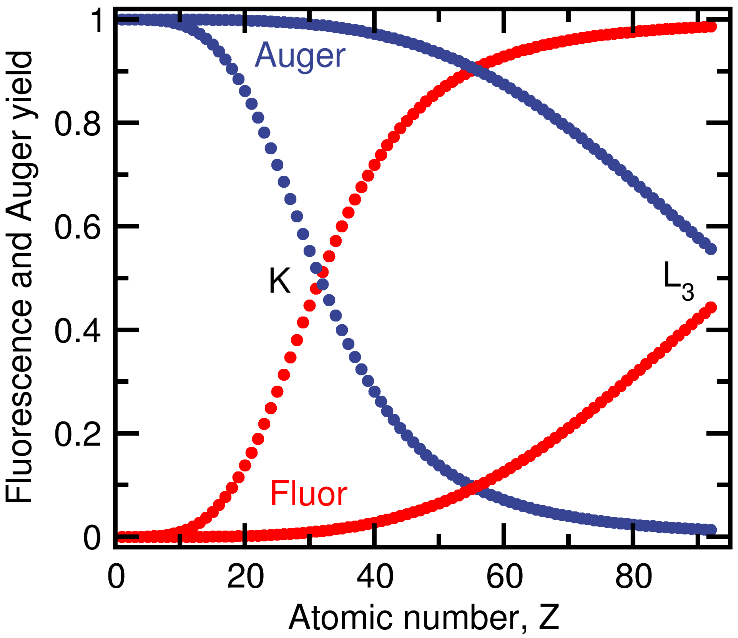
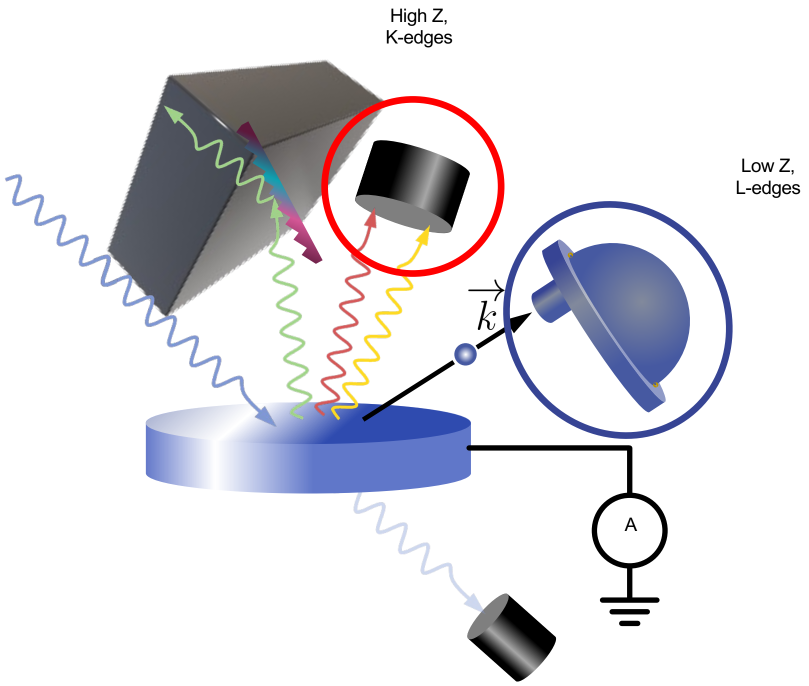
Detection methods





N.B. Detection via Auger-electron yield provides high surface sensitivity!!

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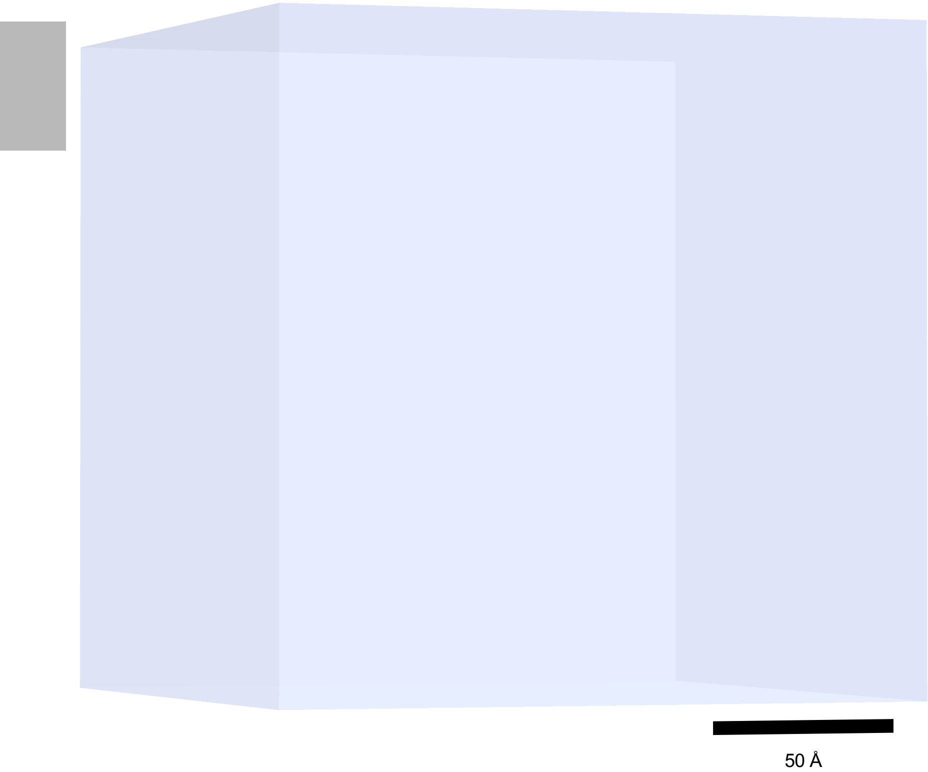
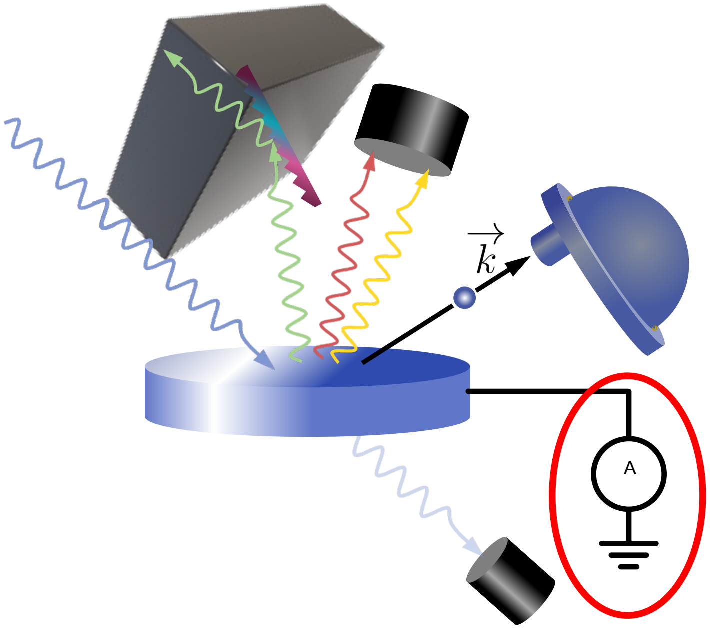
Detection methods





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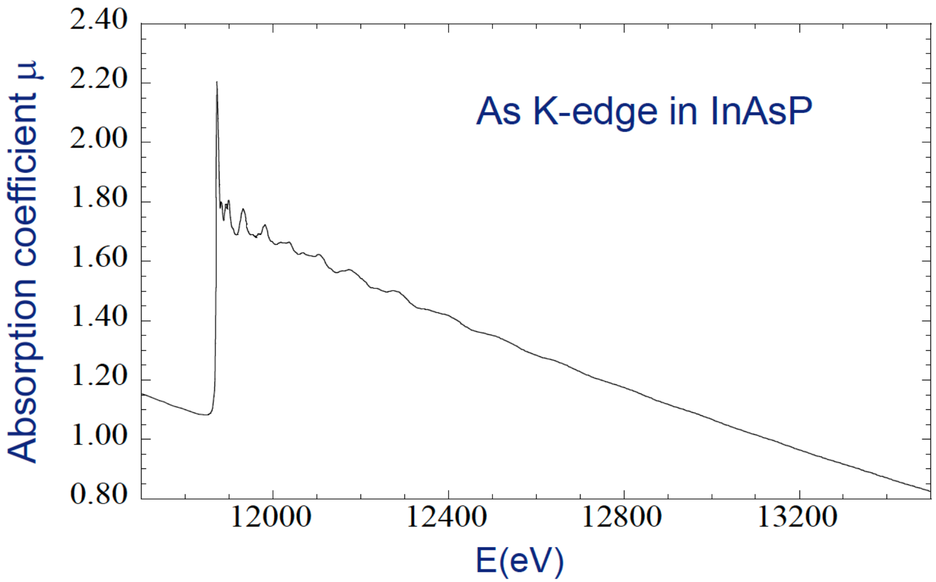
X-ray absorption fine structure XAFS

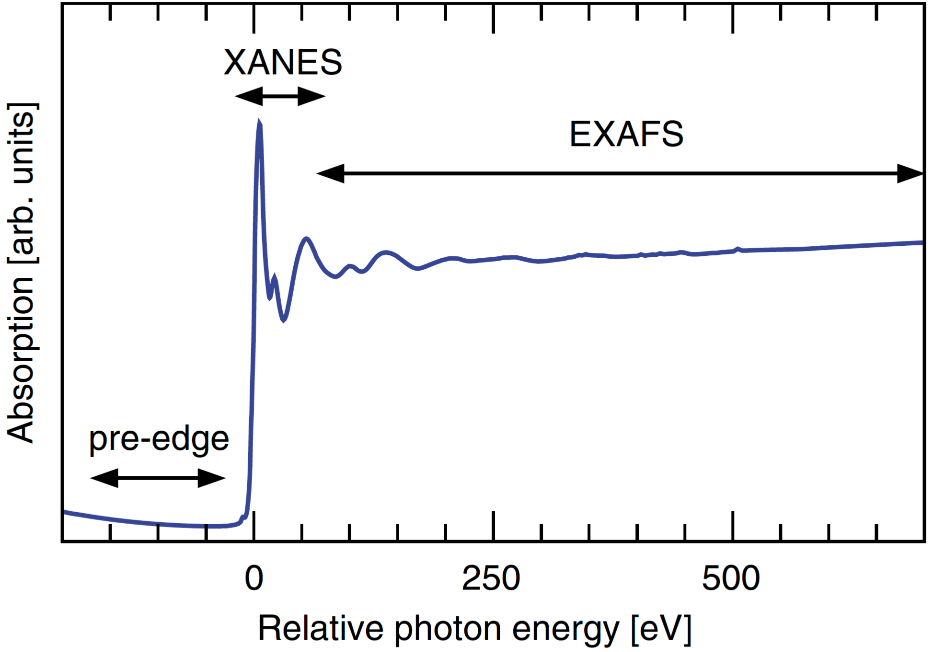
Oscillatory variations of the X-ray absorption as a function of photon energy beyond an absorption edge

Proximity of neighboring atoms strongly modulates the absorption coefficient

Determine the chemical state and local atomic structure for one selected element (element specific)



XAFS – XANES and EXAFS



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XANES

X-ray absorption near-edge spectroscopy (alternatively, NEXAFS)

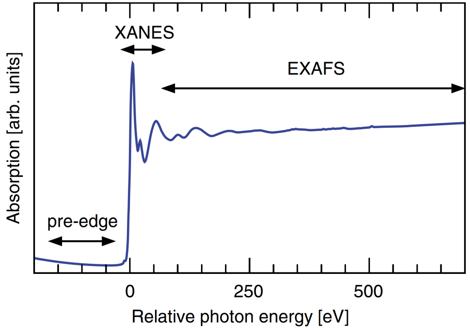
Pre-edge to ca. 50 eV above edge

EXAFS

Extended x-ray absorption spectroscopy

ca. 50 – 1000 eV above edge

XAFS – XANES and EXAFS



XANES

X-ray absorption near-edge spectroscopy (alternatively, NEXAFS)

Pre-edge to ca. 50 eV above edge

transitions to unfilled bound states, nearly bound states, continuum: low energy photoelectrons

EXAFS

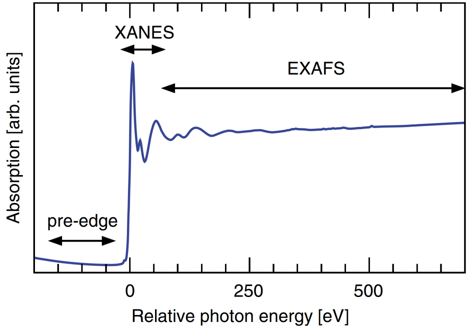
Extended x-ray absorption spectroscopy

ca. 50 – 1000 eV above edge

transitions to continuum: high energy photoelectrons

local structure (bond distance, number, type of neighbors, static and thermal relative displacements)

XAFS – XANES and EXAFS



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local site symmetry, charge state, valence, oxidation state, orbital hybridization

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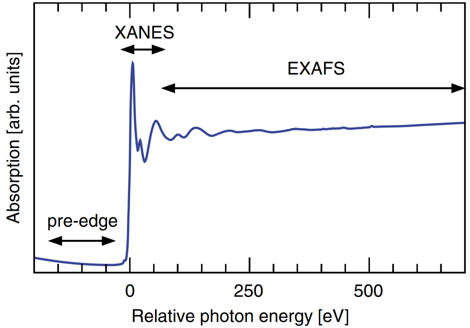

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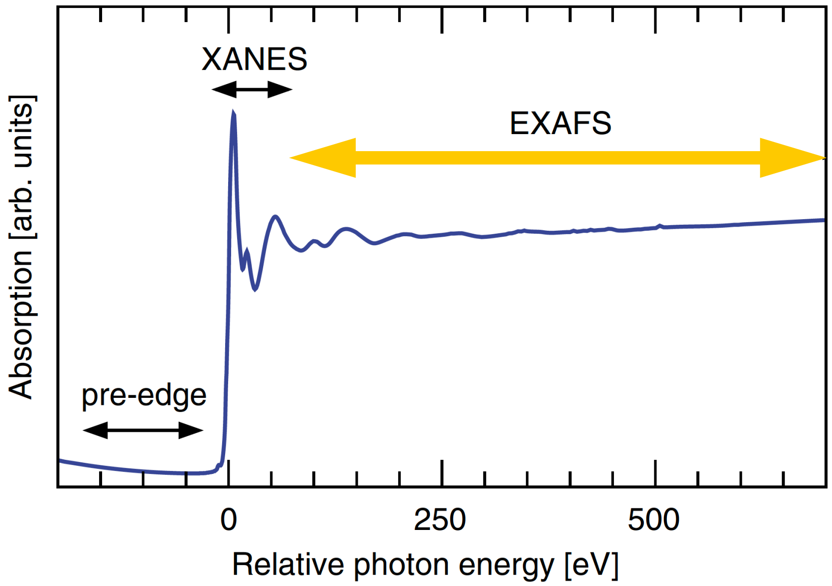
approximations can be used to interpret EXAFS, that are not valid for XANES –> different analysis

EXAFS



ca. 50 – 1000 eV above absorption edge

Probes immediate neighbourhood around absorbing atom

Single-scattering dominates

Oscillations due to interference of backscattered electron with outgoing photoelectron

Sensitivity down to ca. 50 ppm

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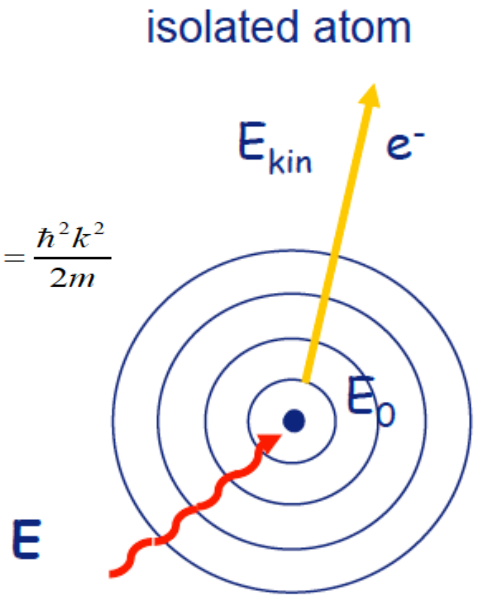
EXAFS

$$E_{kin} = E - E_0 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

$\lambda = 2\pi/k$



The absorption coefficient μ

→probability of photon absorption

→probability of electron presence at origin (is there an available state for the photo-electron?)

→”amount of wave” of the ejected photoelectron at origin

kinetic Energy of the ejected photoelectron changes if the Energy E is scanned

illustrations from S.Pascarelli, Hercules lecture

Origin of the oscillations in EXAFS

$$E_{kin} = E - E_0 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

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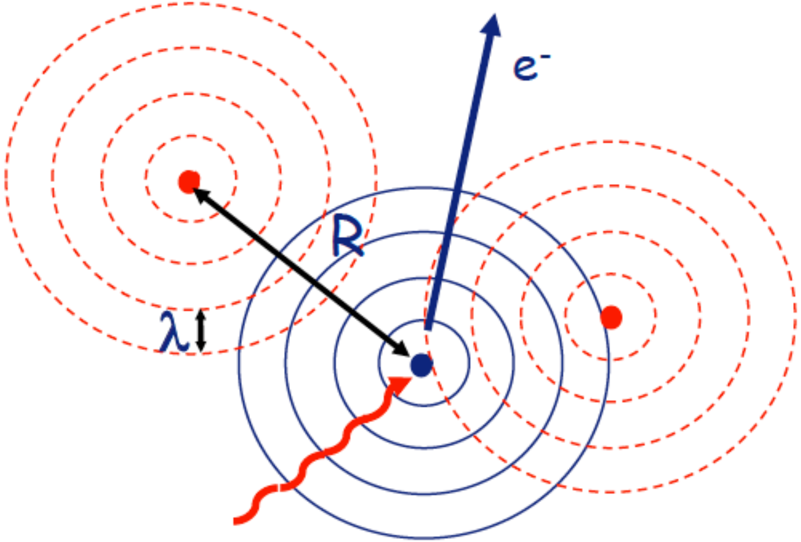


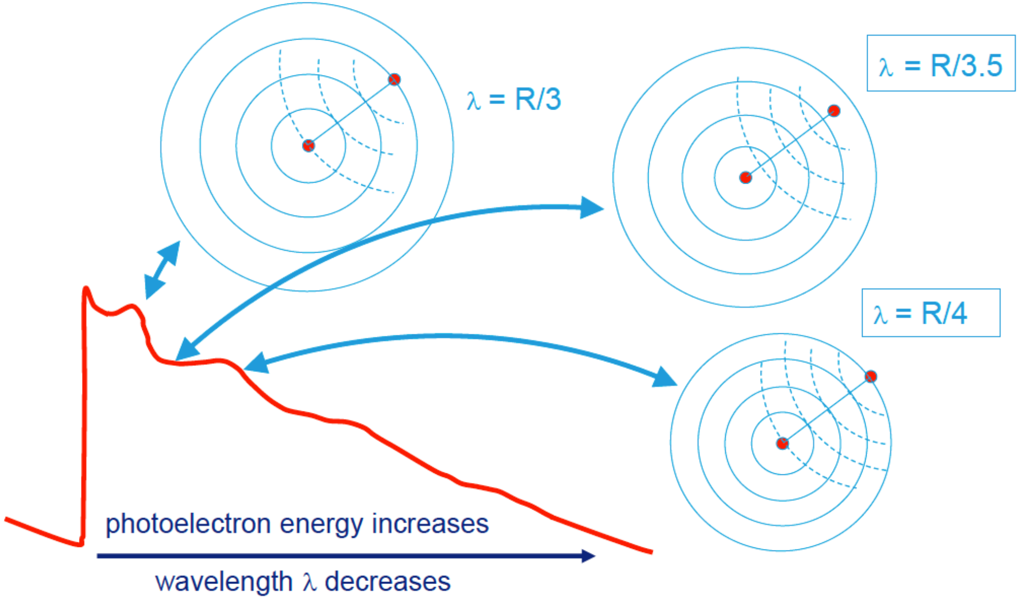
Oscillations due to interference of backscattered electron with outgoing photoelectron

The outgoing and backscattered parts of the wave interfere either constructively or destructively, depending on the ratio between λ and R

λ changes when the energy of the incoming X-rays is scanned

illustrations from S.Pascarelli, Hercules lecture

Origin of the oscillations in EXAFS



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EXAFS signal

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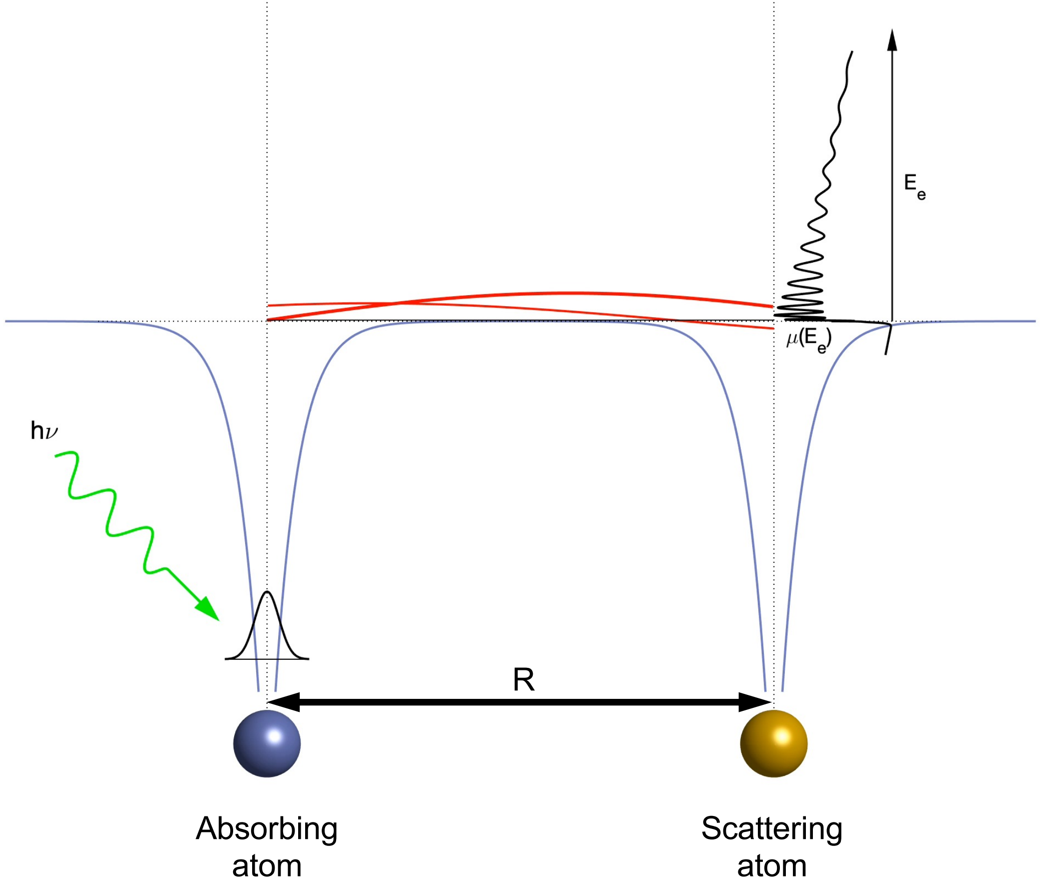

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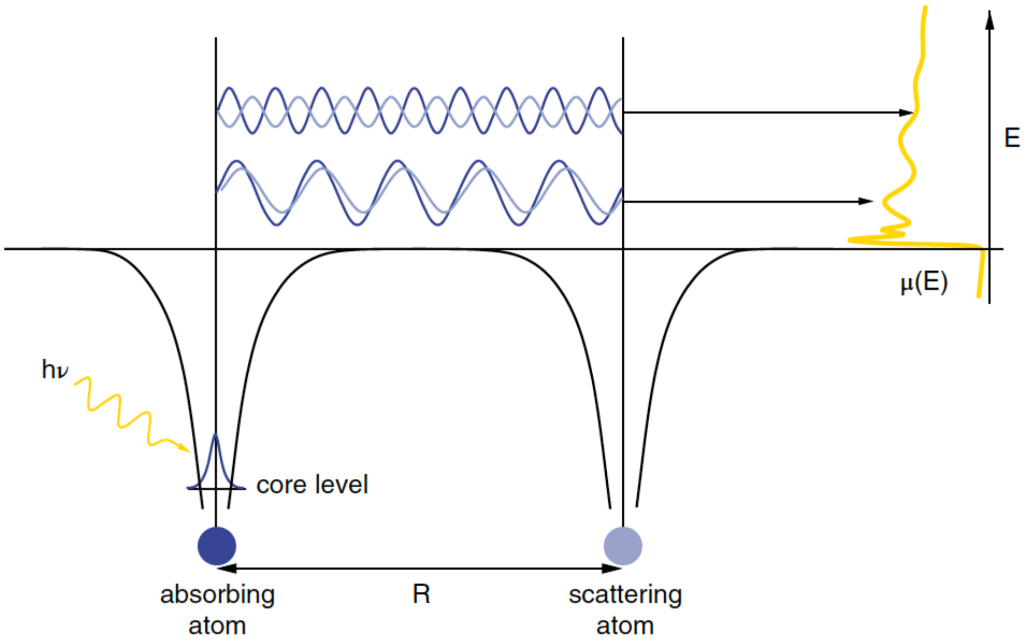

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The EXAFS signal – rules of thumbs

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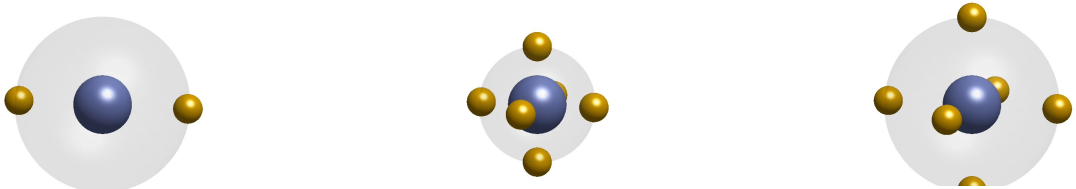
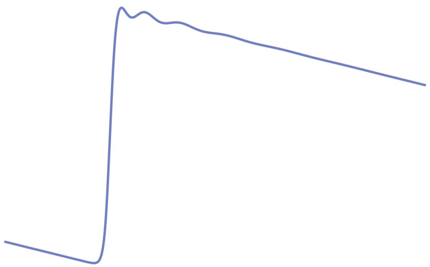


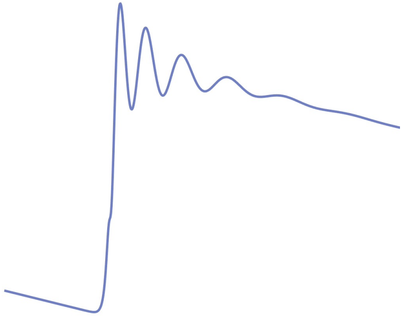
frequency → distance from neig

amplitude → number and type

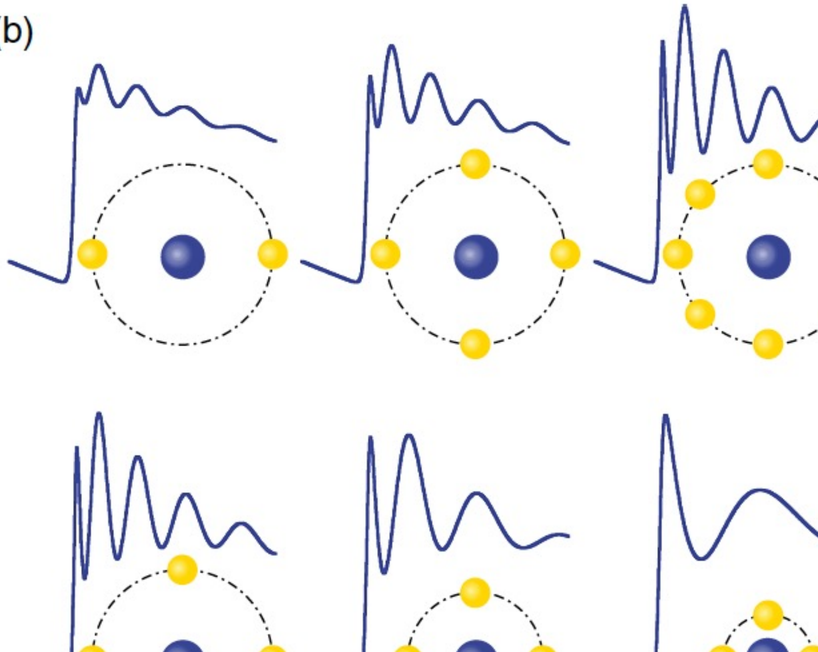
(b)



Number of scatterers



Absorber-scatterer distan



The EXAFS signal – rules of thumbs

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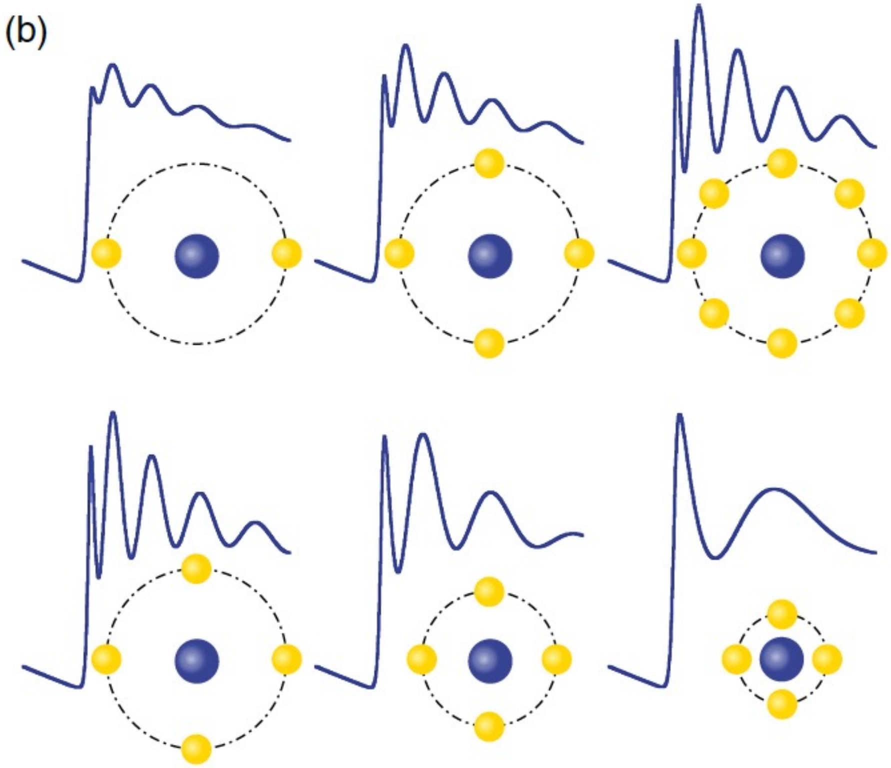


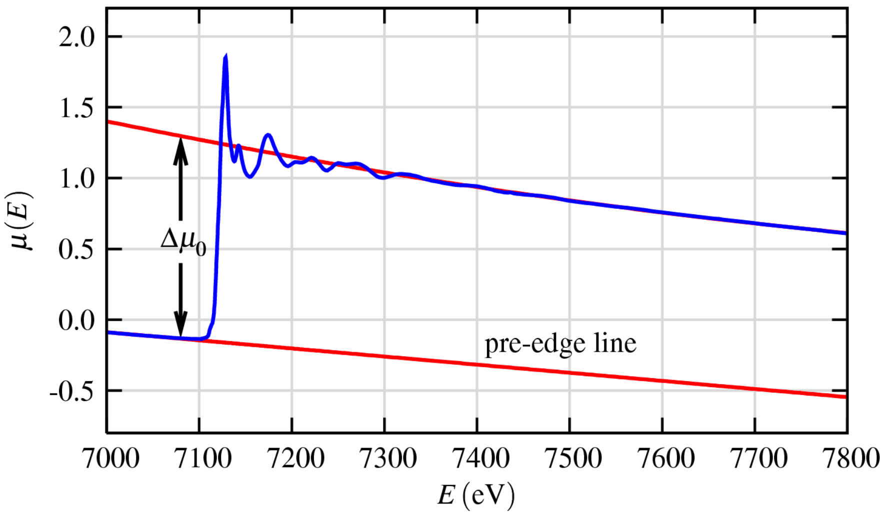
amplitude → number and type of neighbors

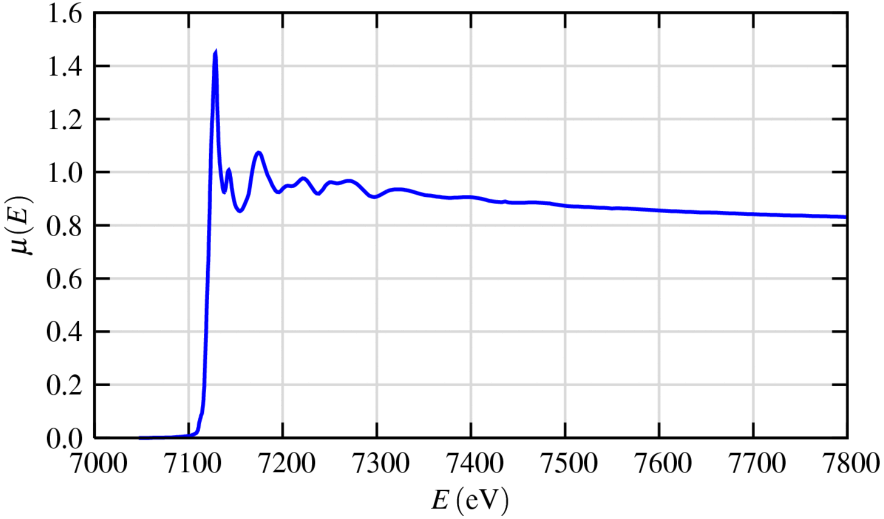
frequency → distance from neighbors

XAFS – data reduction steps

1. Convert measured intensities to μ(E), possibly correcting systematic measurement errors such as self-absorption effects and detector dead-time.

2. Subtract a smooth pre-edge function from μ(E) to get rid of any instrumental background and absorption from other edges.

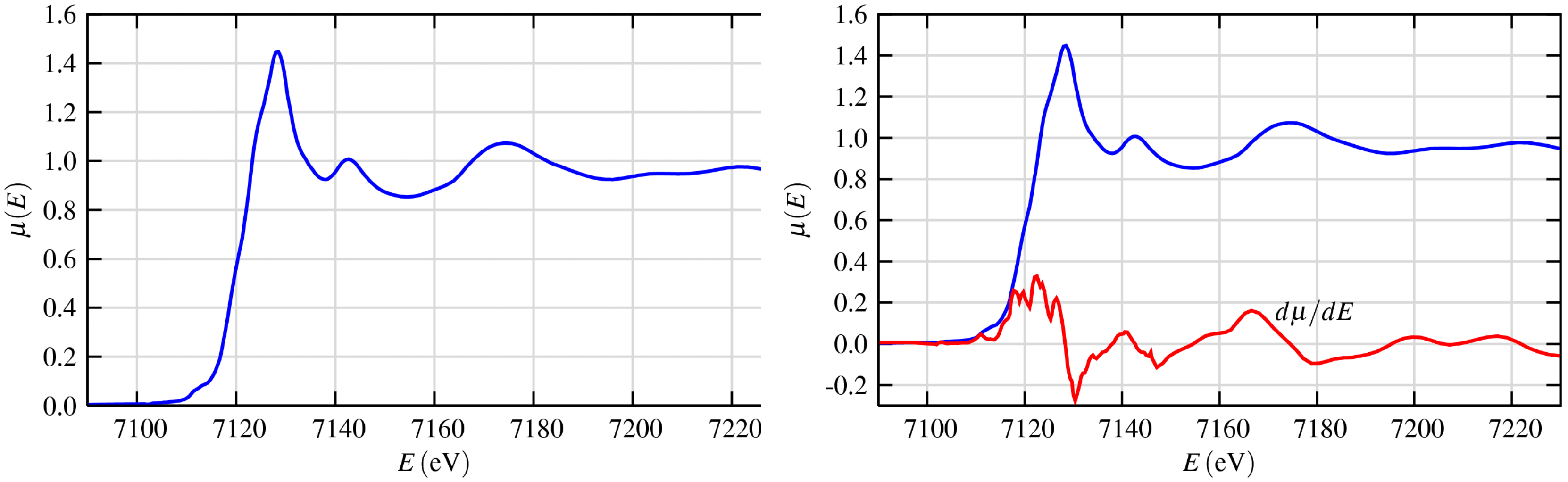




XAFS – data reduction steps → XANES

3. Identify the threshold energy E0, typically as the energy of the maximum derivative of μ(E).

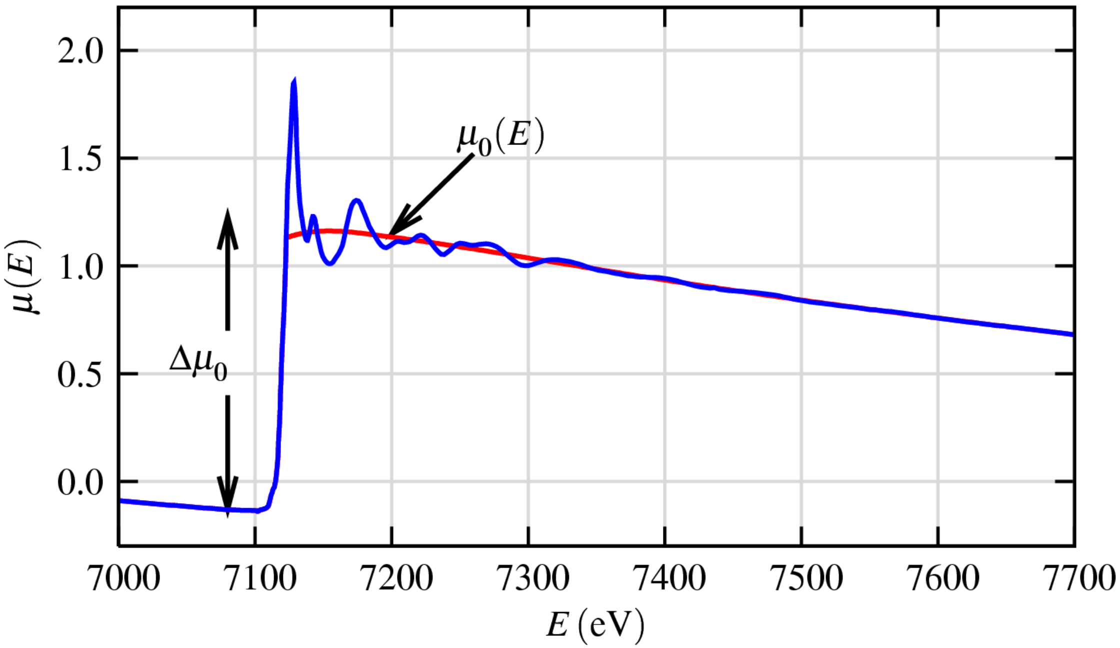
4. Normalize μ(E) to go from 0 to 1, so that it represents the absorption of 1 x-ray. The normalized spectra are useful for XANES analysis.



XAFS – data reduction steps → EXAFS

5. Remove a smooth post-edge background function to approximate μ0(E).

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



Newville, M. (2014). Fundamentals of XAFS. *78*, 33–74

EXAFS

EXAFS is best understood in terms of the wave behavior of the photo-electron created in the absorption process. Because of this, it is common to convert the x-ray energy to k, the wave number of the photo-electron, which has dimensions of 1/distance and is defined as

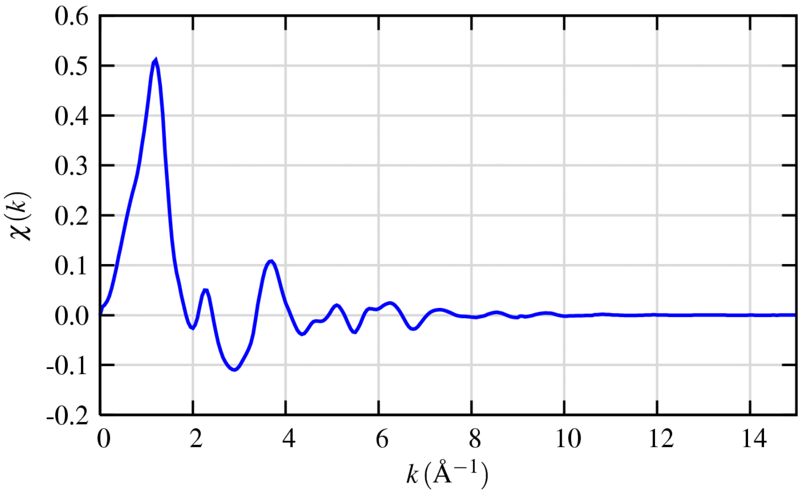
$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

Newville, M. (2014). Fundamentals of XAFS. *78*, 33–74

XAFS data reduction steps → EXAFS

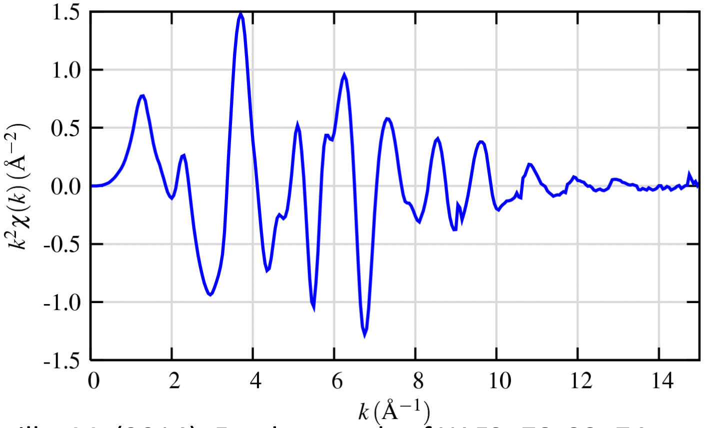
6. Isolate the XAFS χ(k), where $k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$

k-weight the XAFS



isolated EXAFS *χ(k)* for FeO
oscillatory, decays quickly with *k*

k-weighted EXAFS $k^2\chi(k)$ for FeO



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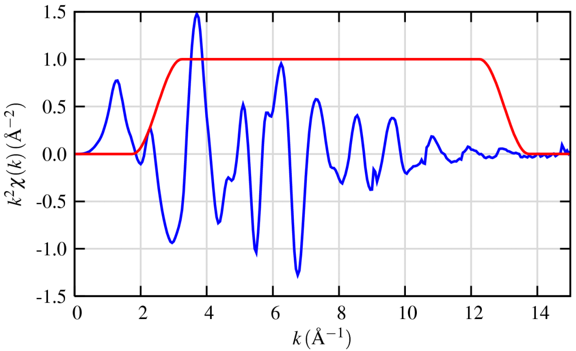
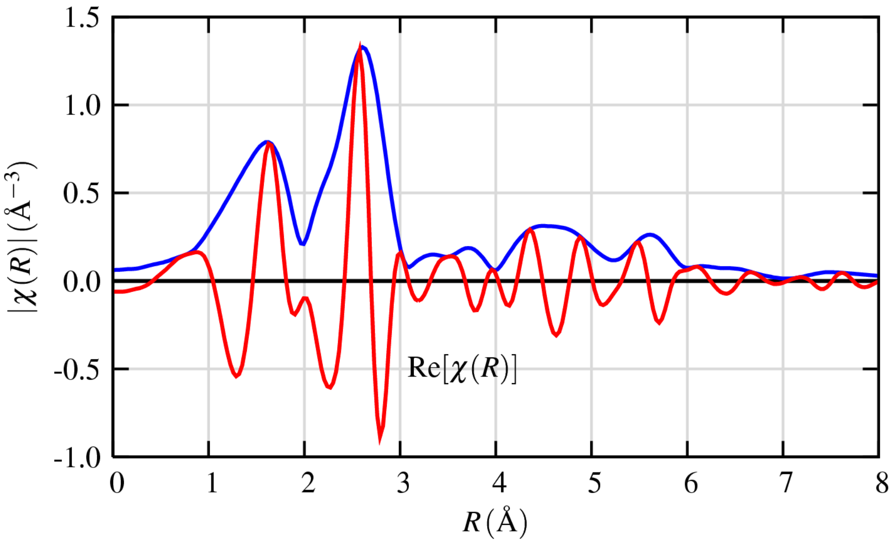
8. Fourier Transform to χ(R)



Window function before doing a Fourier transform

Fourier transformed EXAFS, a complex function



magnitute |χ(R)|

real part Re [χ(R)]

EXAFS equation

Can be dervied by a formal descripton of X-rax absorption as a transition probability between two quantum states

initial state
an X-ray
a core electron
no photo-electron

→

final state
no X-ray
core hole
a photo-electron

core electron tightly bound, not altered by neighboring atoms

photo-electron "sees" the nighboring atoms

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

"bare atom absoprtion", only depends on the absorbing atom

fine structure $\chi(E) \propto \langle i|H|\Delta f\rangle$

for derivation see: Newville, M. (2014). Fundamentals of XAFS. *78*, 33–74

EXAFS equation

Mean-square displacement of distance (disorder in neighbor distance)

Number of neighboring atoms

Amplitude

Phase shift

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

EXAFS fine structure function

distance to neighboring atom (± 0.03 Å)

f(k) and *δ(k)* are scattering properties of the neighbouring atoms to the excited atom
→ EXAFS is sensitive to the atomic species of the neighboring atom

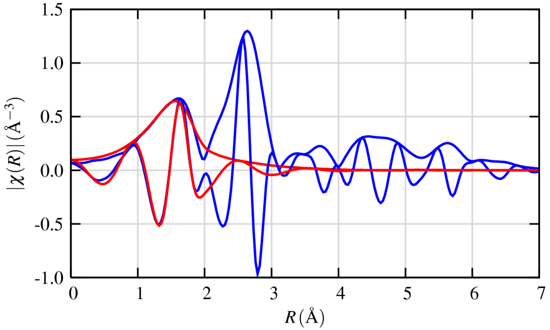
EXAFS data fitting

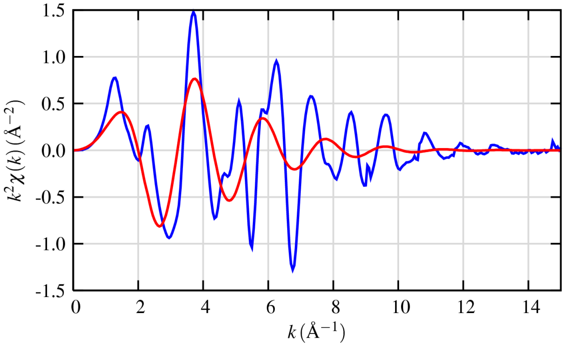
calculation of the theoretical scattering factors *f(k)* and *δ(k)*

refine structural parameters *R, N* and σ^2 by fitting the data,

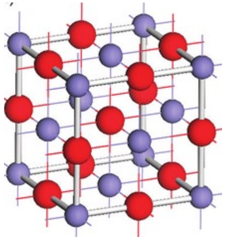
either fit χ(k) or the Fourier transformed, which has the advantage of fitting one shell at a time

first shell fit

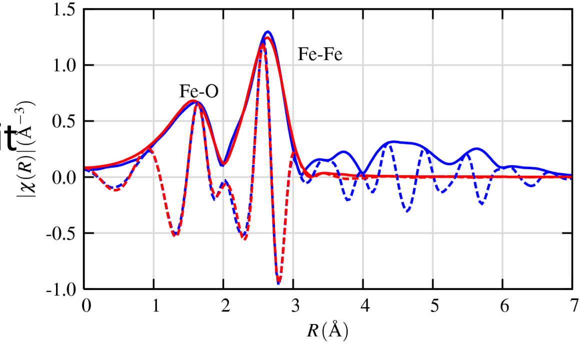


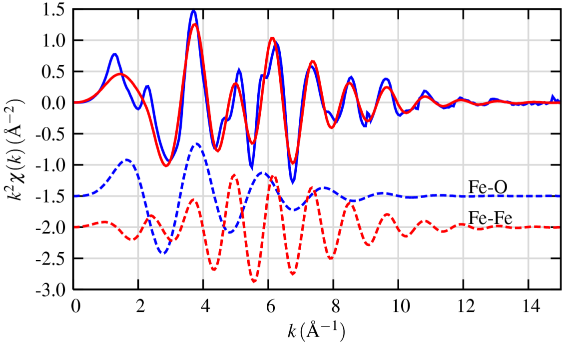


FeO



second shell fit





EXAFS equation

Can be dervied by a formal descripton of X-rax absorption as a transition between two quantum states

initial state		final state
an X-ray	$\longrightarrow$	no X-ray
a core electron		core hole
no photo-electron		a photo-electron

approximation of neglecting multple scattering is valid in the EXAFS regime, but **not for the XANES part**, the EXAFS equation breaks down: interpretation of XANES is complicted as there is not a simple analytical (or even physical) description of XANES

But the edge position and shape is sensitve to fromal valence state, ligand type and coordination enviornment → fingerprint

Newville, M. (2014). Fundamentals of XAFS. *78*, 33–74

XANES

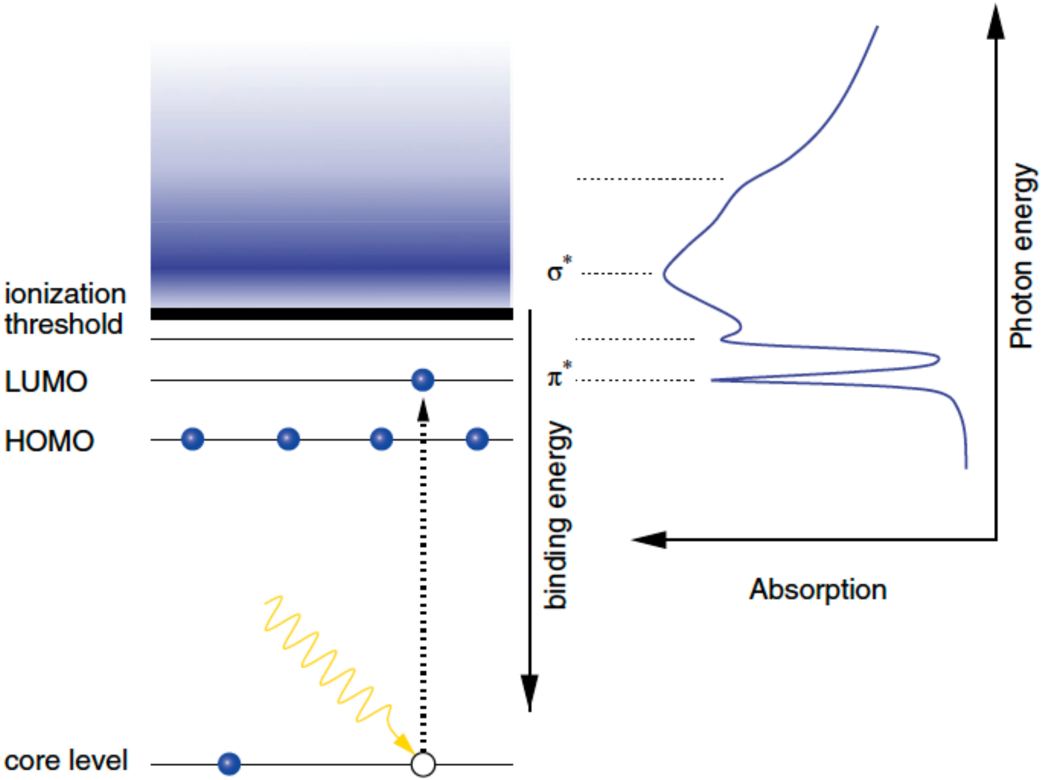
- XANES is a much larger signal than EXAFS
  - XANES can be done at lower concentrations, and less-than-perfect sample conditions.
- XANES is harder to fully interpret than EXAFS
  - The exact physical and chemical interpretation of all spectral features is still difficult to do accurately, precisely, and reliably.
- XANES is easier to crudely interpret than EXAFS
  - For many systems, the XANES analysis based on linear combinations of known spectra from "model compounds" is sufficient: compositional fraction of these components
  - often Principle Component Analysis and Factor Analysis are used

- key factors influencing XANES: ligands/charge, symmetry, bond length

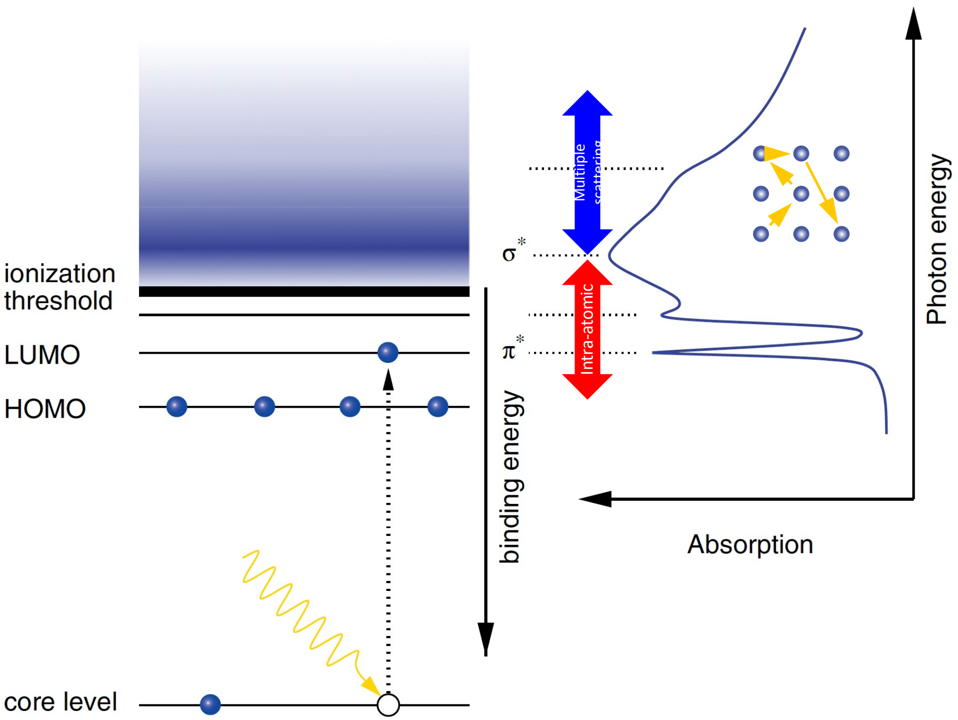
XANES

lowest unoccupied molecular orbital

highest occupied molecular orbital



Transitions in XANES



Core electron promoted to unoccupied excited state (both bound and unbound)

- "White lines": unoccupied bound states
- LUMO
  - e.g. π^*, σ^*
- Partially empty valence electron shell
  - e.g. 5d shell of noble metals

- Probes large local region around absorbing atom
- Multiple elastic-scattering events
  - ⇒ difficult to model

XANES

allowed transitions determined by the symmetry of the local environment

initial and final states must have opposite symmetries

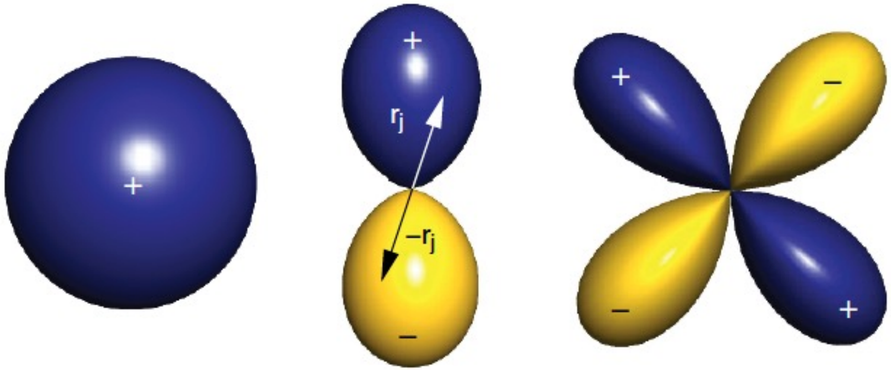
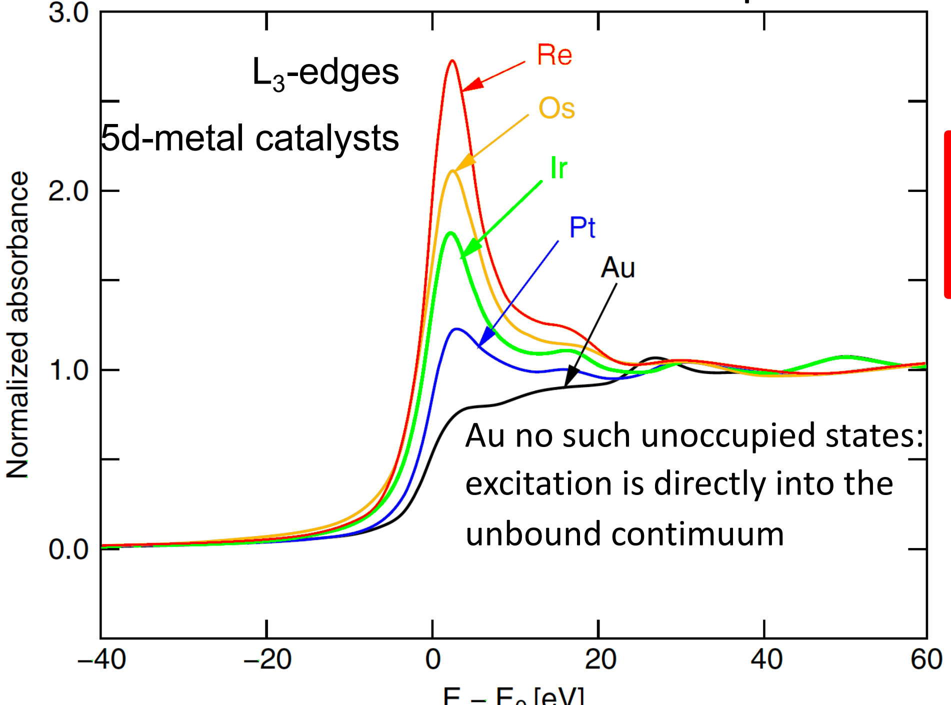


Figure 7.12 Parity and symmetry. The parity of an atomic electron orbital is either positive or negative, depending on how it is transformed when moving all the elements *j* of the orbital's amplitude wavefunction from r_j to $-r_j$. So, for example, *p* orbitals are antisymmetric with negative parity, while *d* orbitals are symmetric and have positive parity.

X-ray absorption fine structure XAFS

"white line": bound excited state features here:

bound but unoccupied 5d states, below the ionization threshold



Au no such unoccupied states: excitation is directly into the unbound contimuum

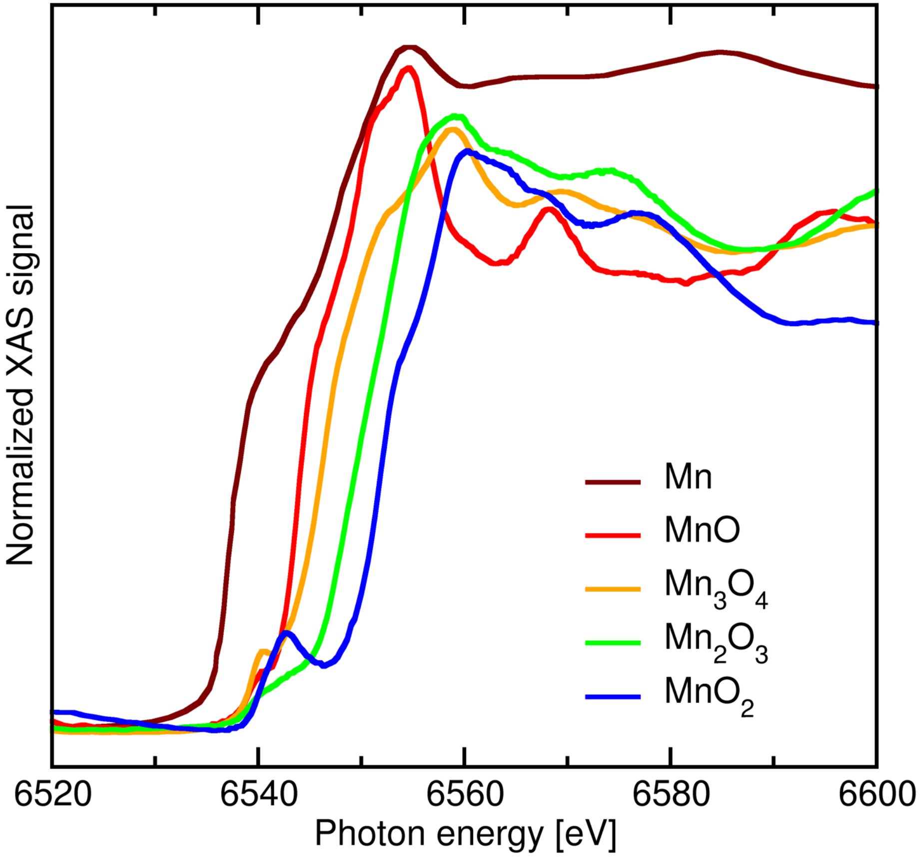
G. Meitzner *et al.*, J. Phys. Chem., **96**, pp. 4960–4964 (1992)

75 Re	76 Os	77 Ir	78 Pt	79 Au
186.207	190.23	192.217	195.085	196.967
[Xe]$4f^{14}5d^5 6s^2$	[Xe]$4f^{14}5d^6 6s^2$	[Xe]$4f^{14}5d^7 6s^2$	[Xe]$4f^{14}5d^9 6s^1$	[Xe]$4f^{14}5d^{10} 6s^1$
5	4	3	1	0

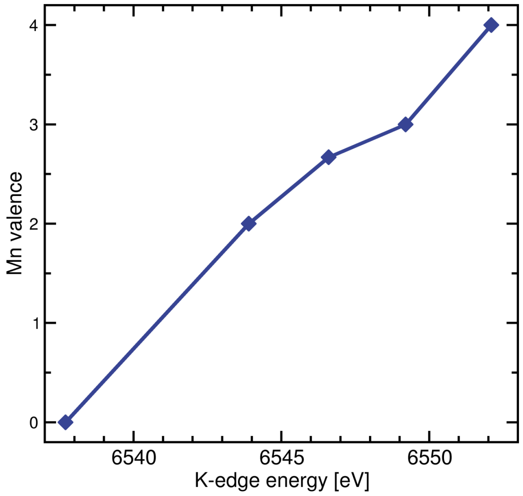
d-band filling

Philip Willmott: Synchrotron and X-ray Free Electron Laser

XANES: Oxidation state



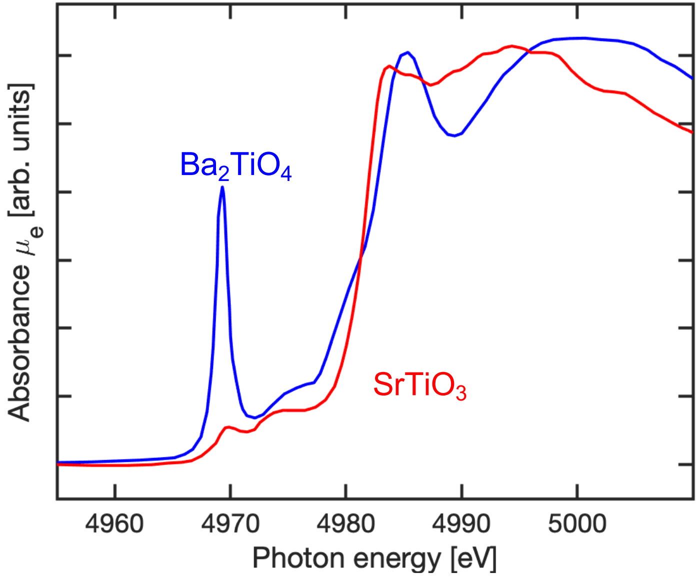
Contains information about the oxidation state:
shift in edge energy

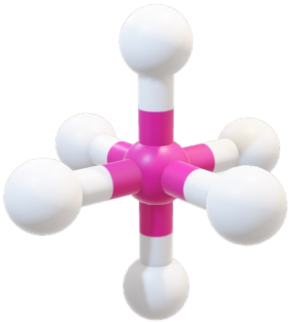


XANES: coordination chemistry/bond geometry

Contains information about coordination chemistry/bond geometry

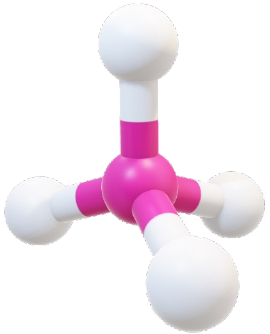
XANES on Ti K-Edge





TiO_6 octahedra in $SrTiO_3$

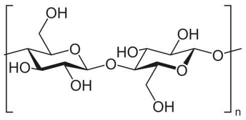
- t_{2g}: LUMO with octahedral inversion symmetry
- Cannot be accessed by dipole from 1s core state
- Very weak signal via quadrupole (2-electron) perturbation

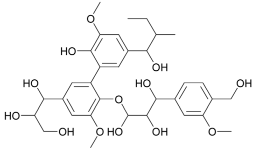


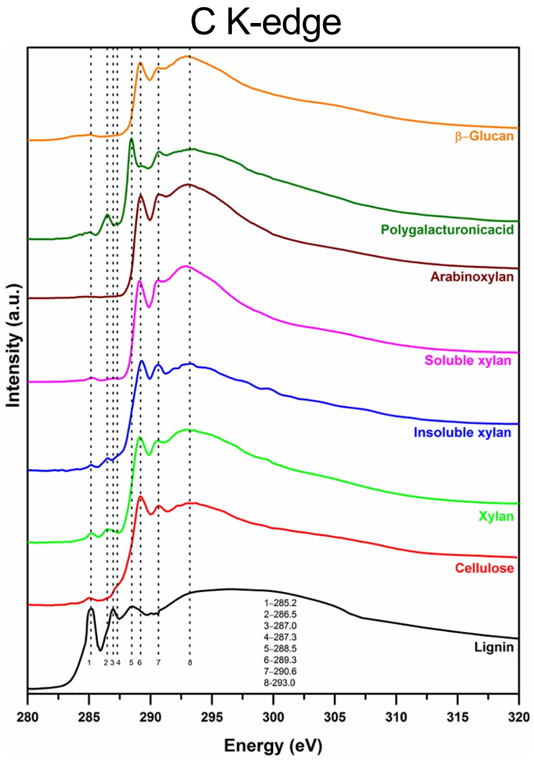
TiO_4 tetrahedra in Ba_2TiO_4

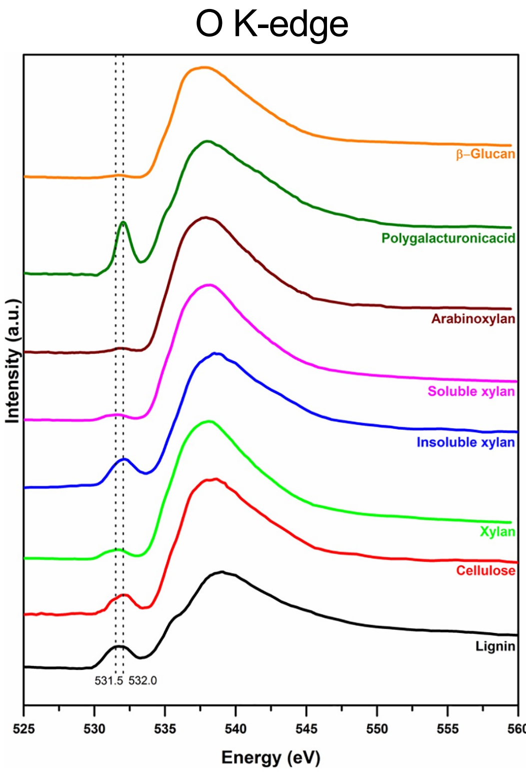
- $3d^3 4p$ mixed LUMO states
- p-character of these MOs can be accessed from 1s core state via direct dipole perturbation ($\Delta l = 1$)

XANES of Bio-Polymers









Karunakaran C, et al. (2015) Introduction of Soft X-Ray Spectromicroscopy as an Advanced Technique for Plant Biopolymers Research.

PLOS ONE 10(3): e0122959. https://doi.org/10.1371/journal.pone.0122959

XANES interpretation

XANES can be described qualitatively (and nearly quantitatively) in terms of

- coordination chemistry regular, distorted octahedral, tetrahedral, . . .
- molecular orbitals p-d orbital hybridization, crystal-field theory, . . .
- band-structure, the density of available electronic states
- multiple-scattering, multiple bounces of the photoelectron

These chemical and physical interpretations are all related, of course:

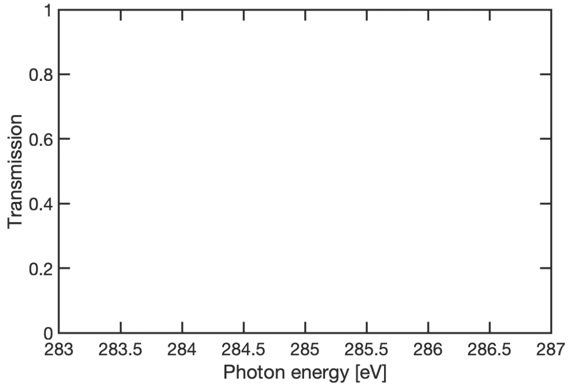
What electronic states can the photoelectron fill?

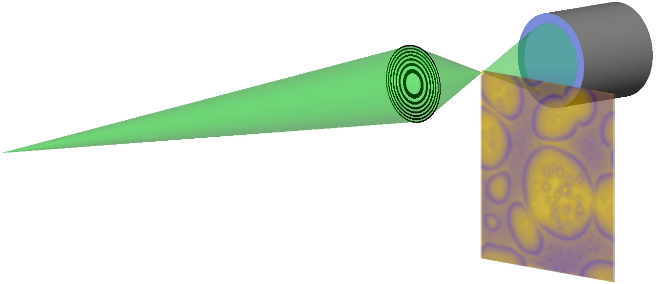
XANES calculations are becoming reasonably accurate and simple. These can help explain what bonding orbitals and/or structural characteristics give rise to certain spectral features.

Quantitative XANES analysis using first-principles calculations are still rare, but becoming possible...

S.Pascarelli, Hercules lecture

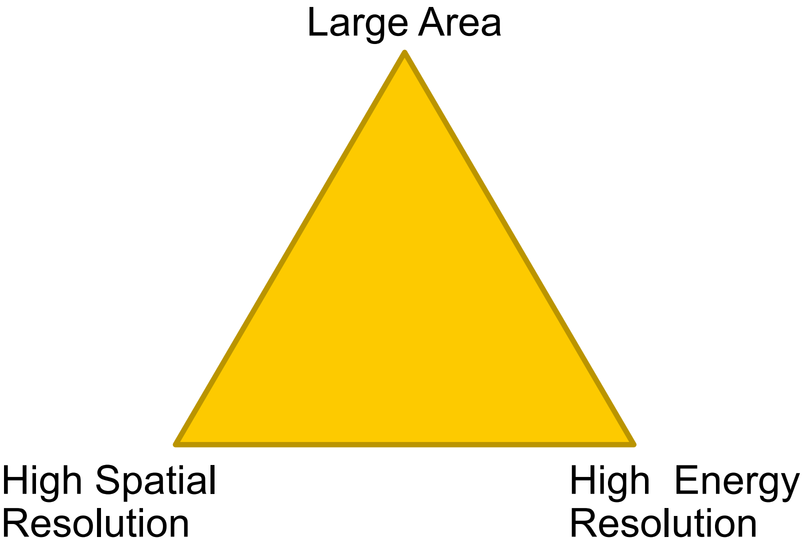
STXM: scanning transmission X-ray microscopy





STXM: scanning transmission X-ray microscopy

- full energy scan at highest resolution for large areas take a long time
- additional problem: radiation damage (multiple exposure, high flux density)
- Combination of two approaches:
  - Energy stacking
    - full Energy range over edge e.g. from 280-350 eV (Carbon edge) with a resolution of >0.1 eV
    - Gives full energy spectra containing information of the chemical compounds present
    - Slow
    - Small Areas or Large stepsize
  - Scan at resonance energies
    - Only predetermine energies
    - Fast
    - Allows high spatial resolution over extended areas

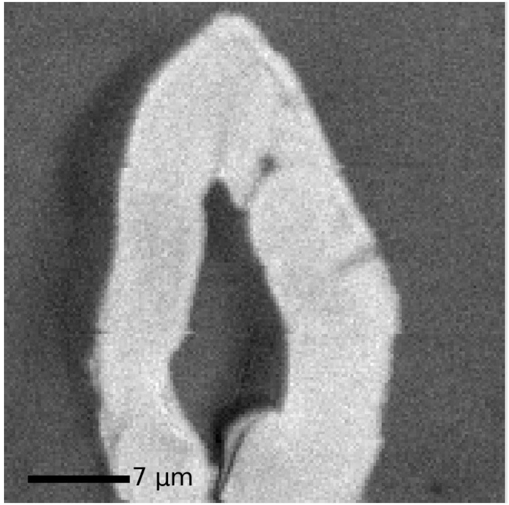


STXM: high spatial resolution vs. high energy reolution

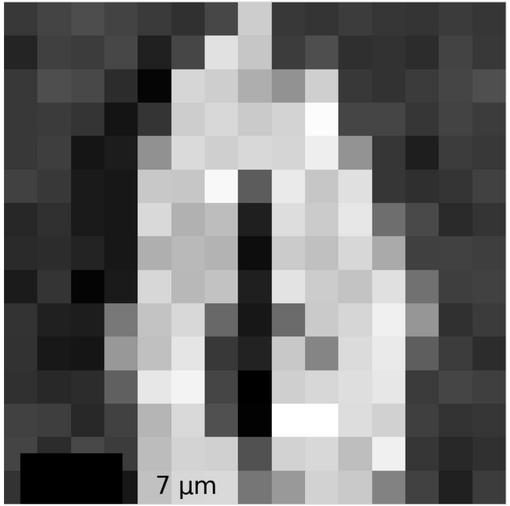
cellulose fibre

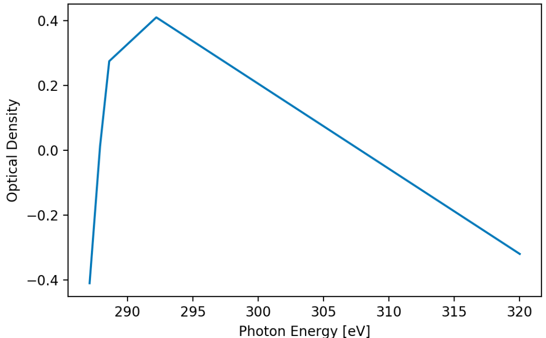
- Trade off between high spatial resolution and high energy resolution

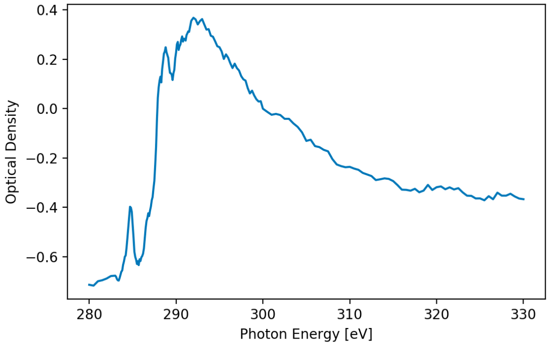
High spatial resolution scan at 287.1 eV



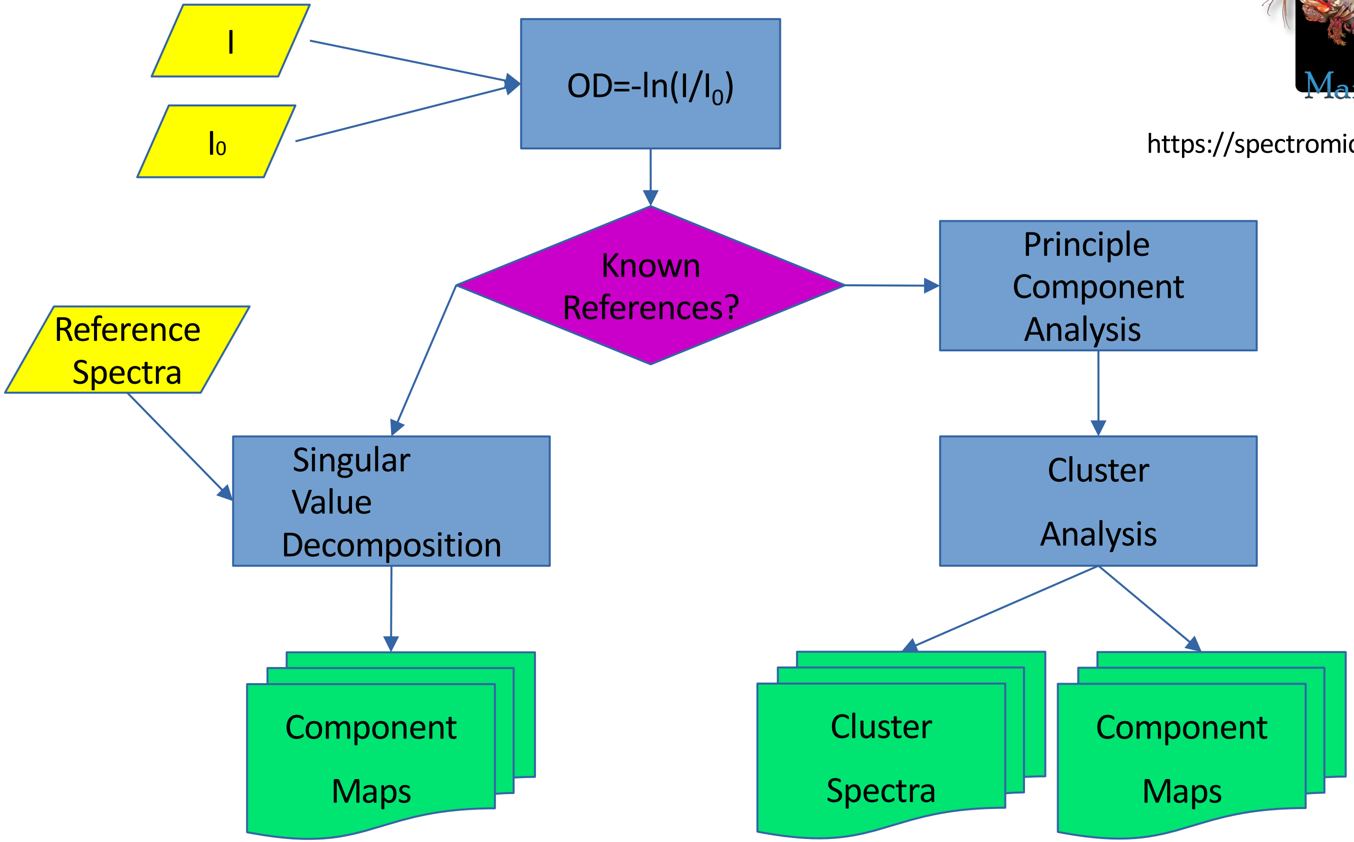
Low spatial resolution scan at 287.1 eV







XANES Data analysis: SVD and PCA

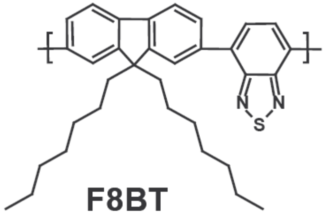


https://spectromicroscopy.com/

Ben Watts, Pollux, PSI

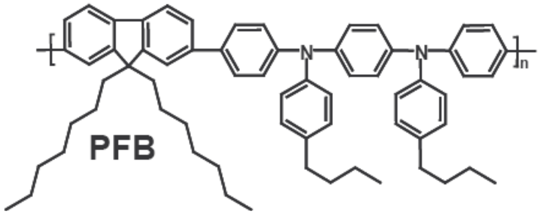
Model Conjugated Polymers

Electron Acceptor

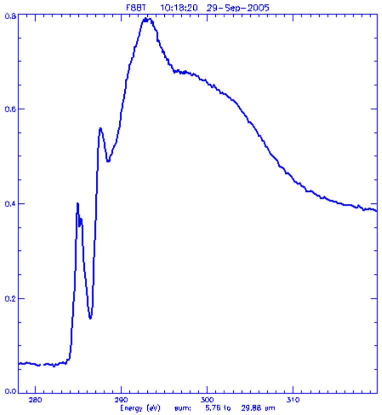


Poly(9,9’-dioctylfluorine-co-benzo-thiadiazole)

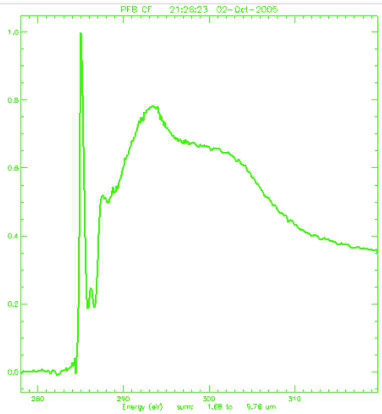
Electron Donor



Poly(9,9’-dioctylfluorine-co-bis-N,N’-(4,butylphenyl)-bis-N,N’-phenyl-1,4-phenylene-diamine)



- Absorption step due to photoemission
- Resonance peaks due to core to anti-bonding transitions



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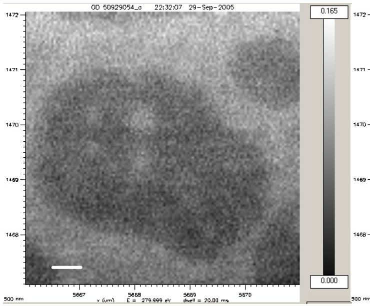
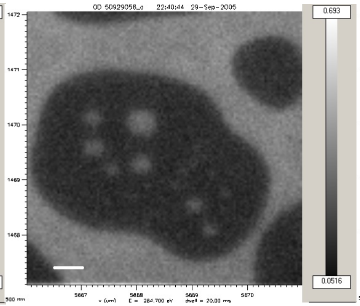
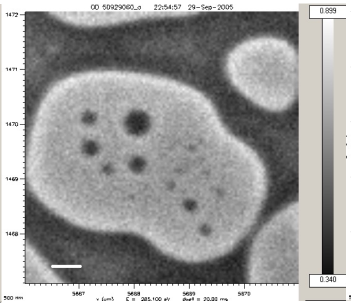
STXM Contrast and Composition Mapping



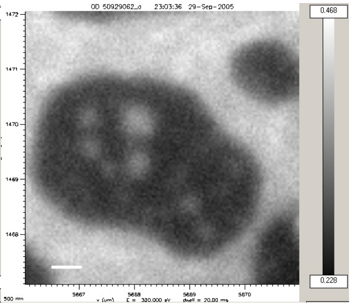
280 eV



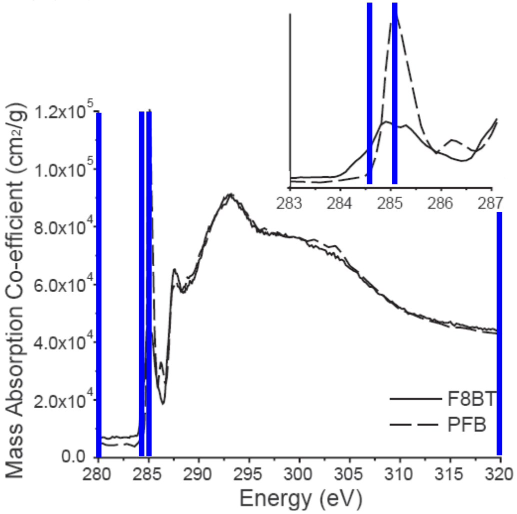
284.7 eV



285.1 eV



320 eV



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Singular Value Decomposition

Reference Spectra

Quantity

Measurements in one pixel position

$$\begin{bmatrix} f(E_0) & f(E_1) & f(E_2) & f(E_4) \\ g(E_0) & g(E_1) & g(E_2) & g(E_3) \end{bmatrix} \times \begin{bmatrix} X_0 \\ X_1 \end{bmatrix} = \begin{bmatrix} M(E_0) \\ M(E_1) \\ M(E_2) \\ M(E_3) \end{bmatrix}$$

- Solve for X!
- Need at least as many energy measurements as there are material components to solve for.
- Oversampling helps to reject noise.

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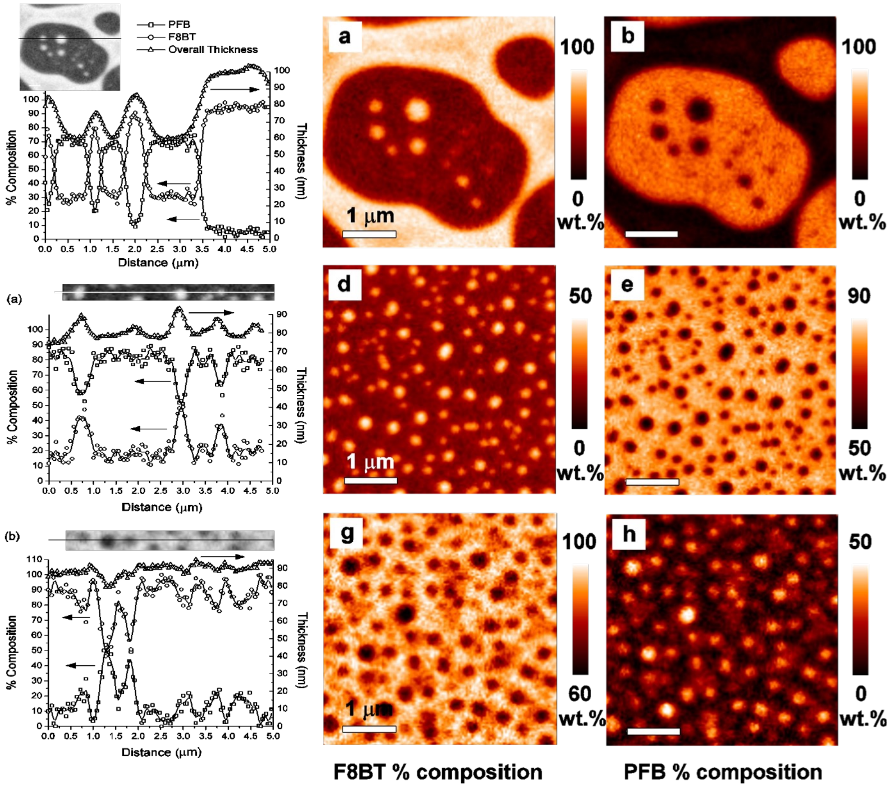
Composition maps from SVD

segregated domains are not as pure as it was expected

1:1

5:1

1:5

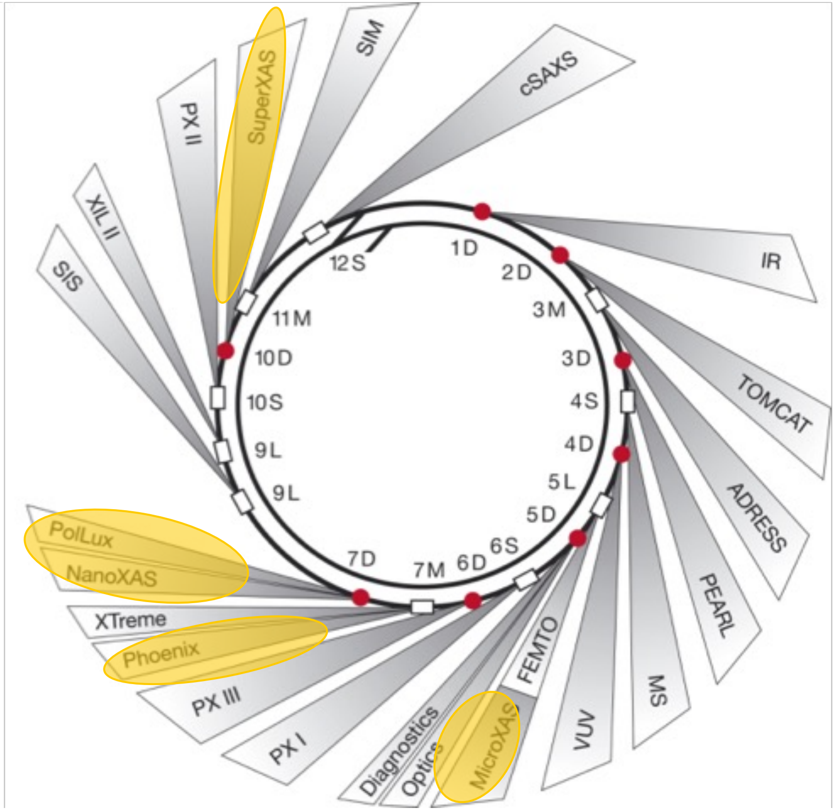


PFB-rich Domains	F8BT-rich Domains
70% PFB 30% F8BT	5% PFB 95% F8BT
90% PFB 10% F8BT	~50%
~50%	~100% F8BT

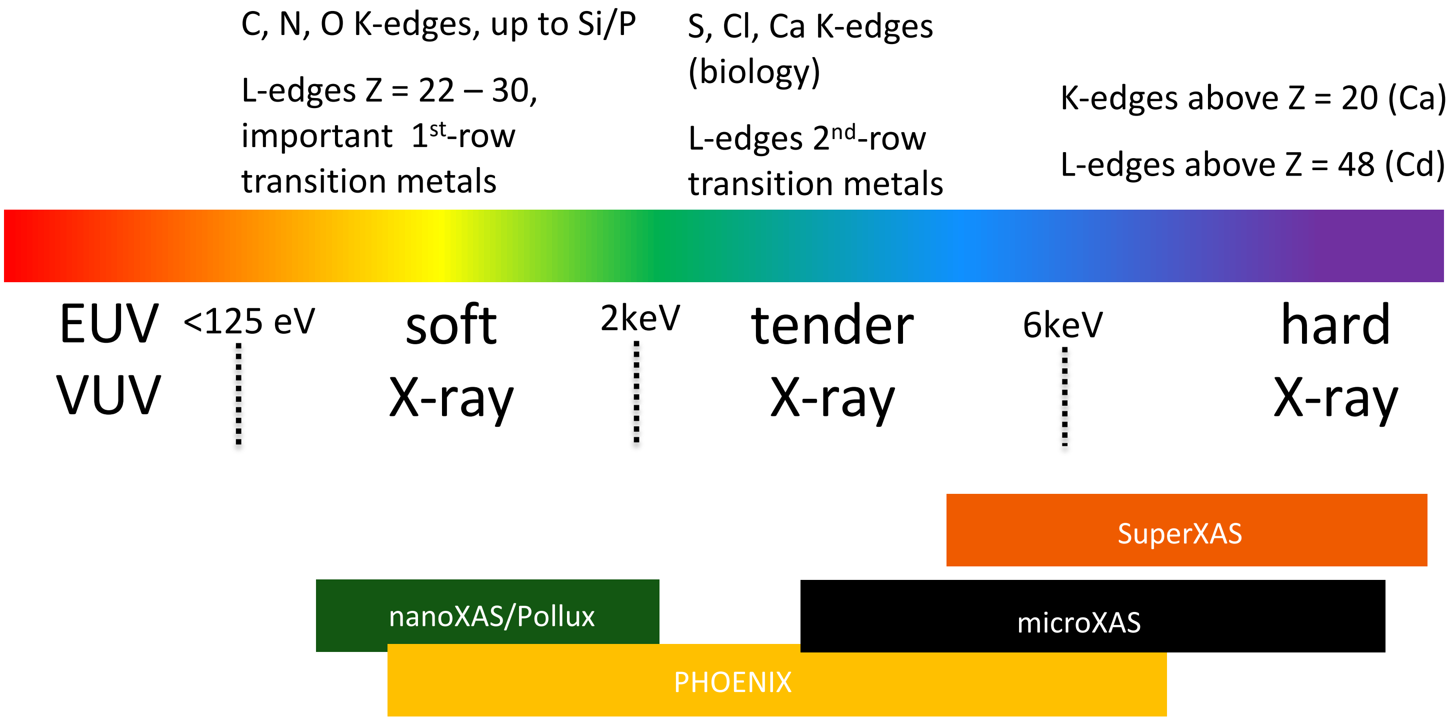
Ben Watts, Pollux, PSI

C.R. McNeill, B. Watts, L. Thomsen, H. Ade, N.C. Greenham and P.C. Dastoor, *Macromolecules* **2007,** *40,* 3263-3270.

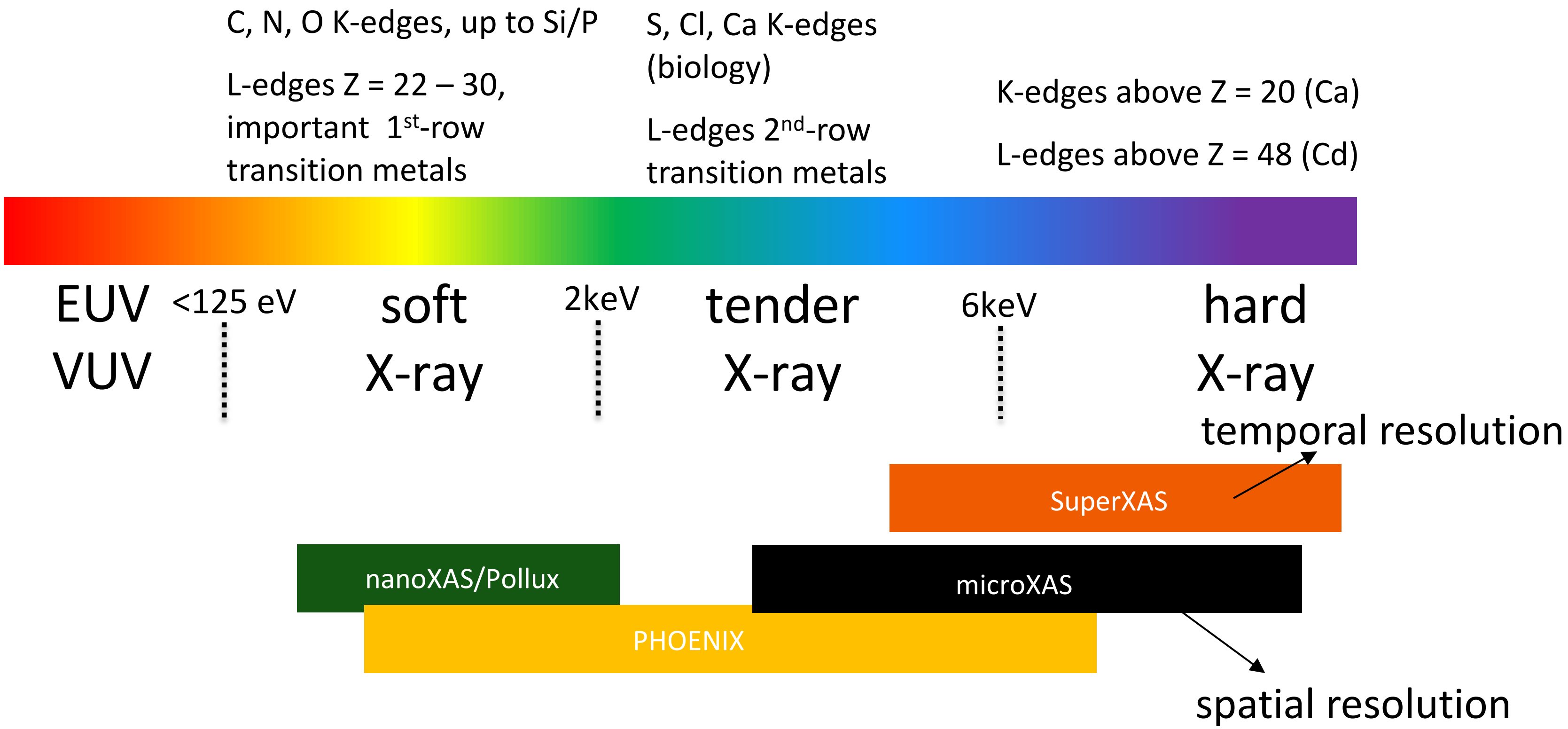
XANES/EXAFS @PSI



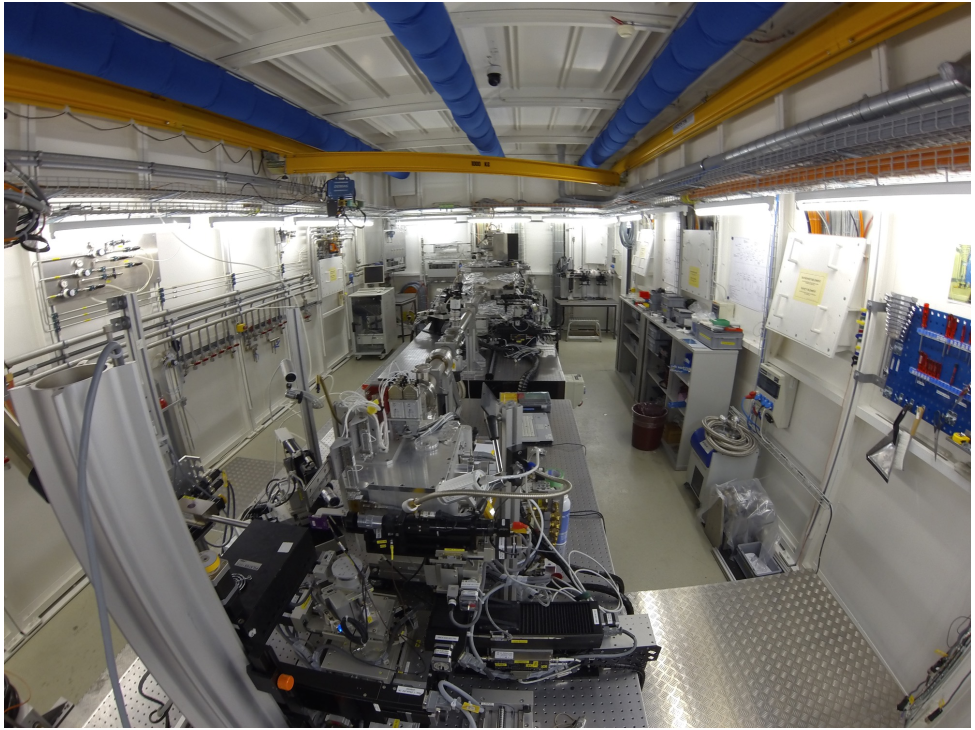
XANES/EXAFS@PSI



XANES/EXAFS@PSI



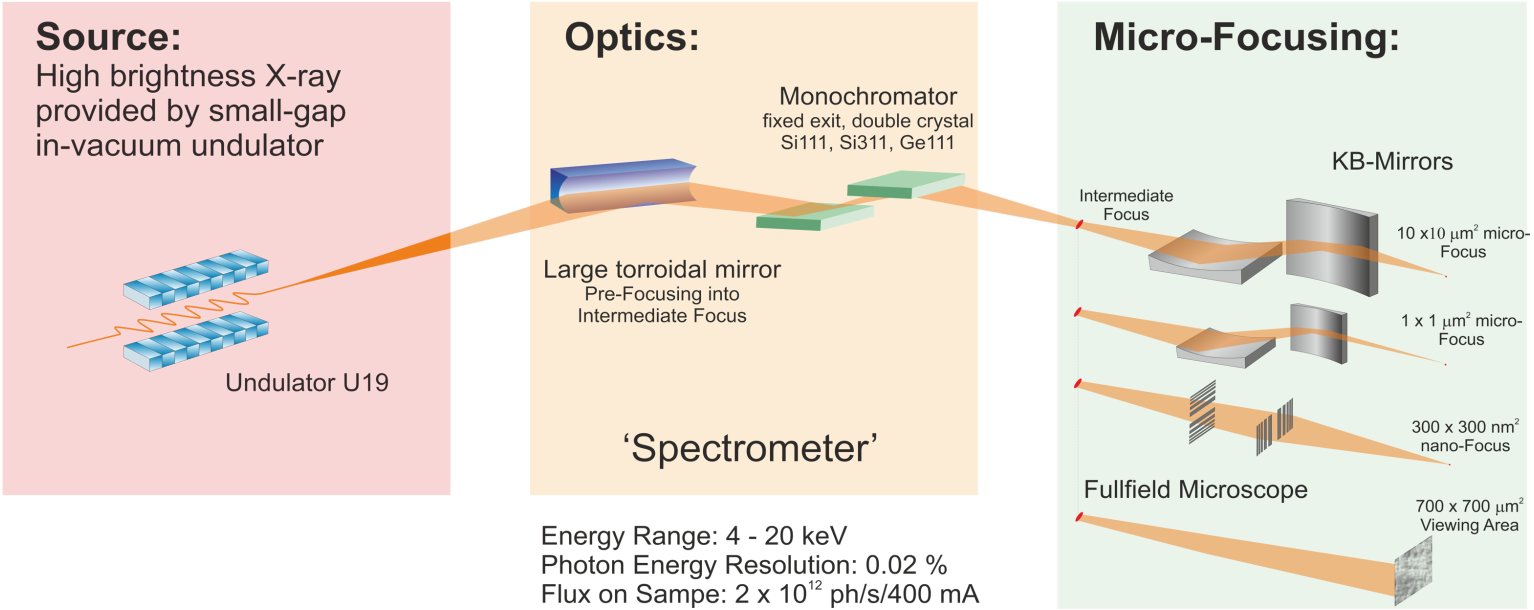
MicroXAS



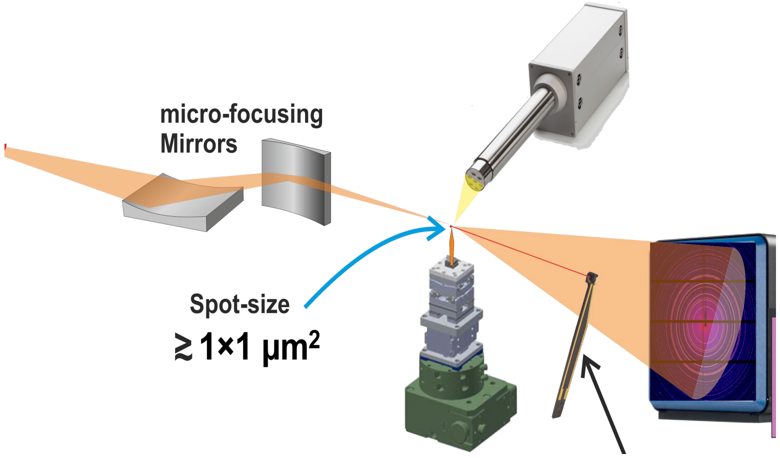
EPFL PAUL SCHERRER INSTITUT PSI

MicroXAS

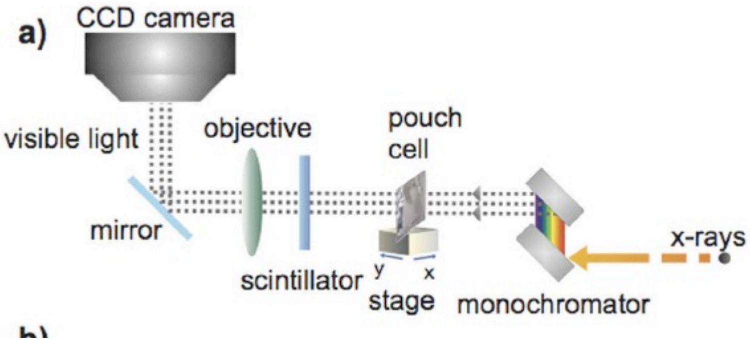
The Beamline



MicroXAS



scanning imaging with small spot: multi-mode

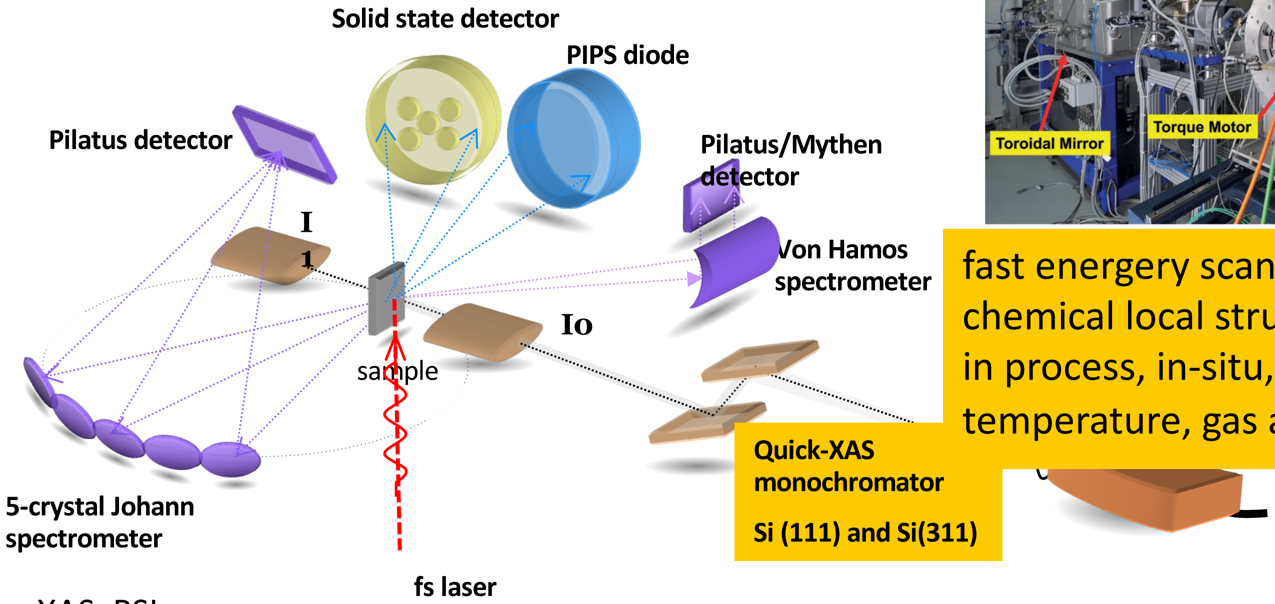


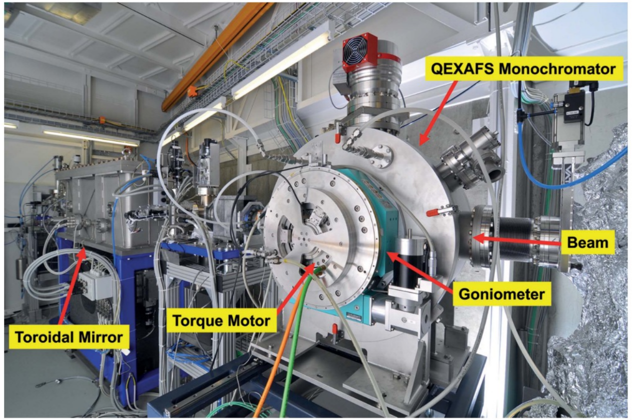
full-field imaging: XANES only needs absorption

SuperXAS: Hard X-ray spectroscopy

SuperXAS

Energy range: 4.5-35 keV
Flux : up to 1x10^{12} ph/s (@ 12 keV)
Beam size: from 100 x 100 μm^2 to 5000 x 500 μm^2





fast energery scan! (full spectra in s)
chemical local structure transformed in process, in-situ, in-operando temperature, gas atmosphere, etc.

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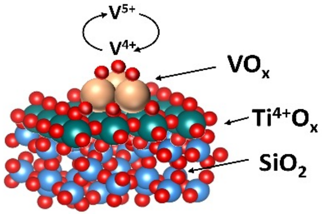
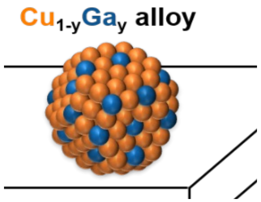
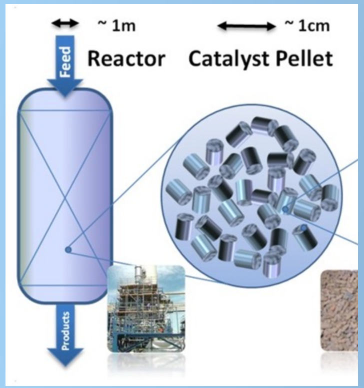
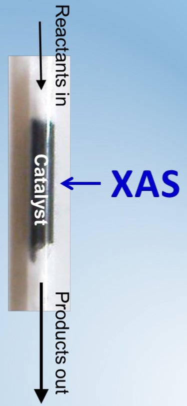
Catalytic Materials

nanoparticles, supported oxides, interfaces…









catalysis: complex materials with several elements: which part of the material is working and in which oxidation state

Supported Pt-FeO$_x$ Catalysts for Preferential CO Oxidation (PROX) for H_2 Purification

Hydrogen stream: oxidation of CO without oxidation of H_2

~ 0.5% O_2

~0.5% CO in H_2

(industrial H_2)

$2CO + O_2 = 2CO_2$

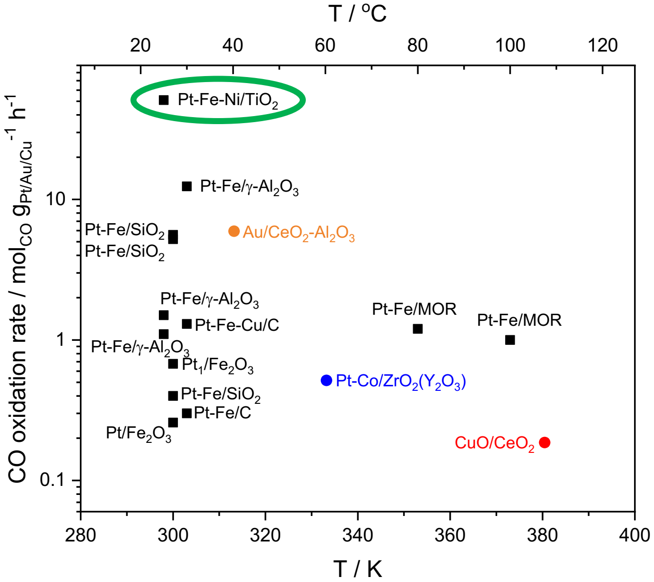
$2H_2 + O_2 \neq 2H_2O$

$H_2 + CO_2 \neq CO + H_2O$

$CO + 3H_2 \neq CH_4 + H_2O$

$CO_2 + 4H_2 \neq CH_4 + 2H_2O$

pure H_2, <100 ppm CO



why are some much more active? what is the active site

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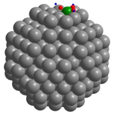
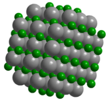
Active Sites in Pt-FeO$_x$ System Proposed in the Literature

Atomically-dispersed $Fe^{+3}(OH)_x$ / Pt



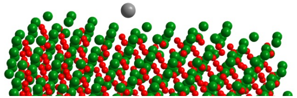
Cao L. et al, *Nature*, **2019**, *565*

Pt-Fe^0 alloy



Yin J. et al, *Catal. Let.*, **2008**, *325*

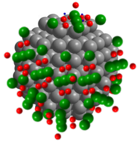
Atomically-dispersed Pt / $Fe^{+3}{}_2O_3$



Fu Q. et al, *Science*, **2010**, *328*

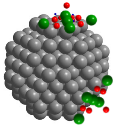
?

Core-shell Pt@FeO$_x$



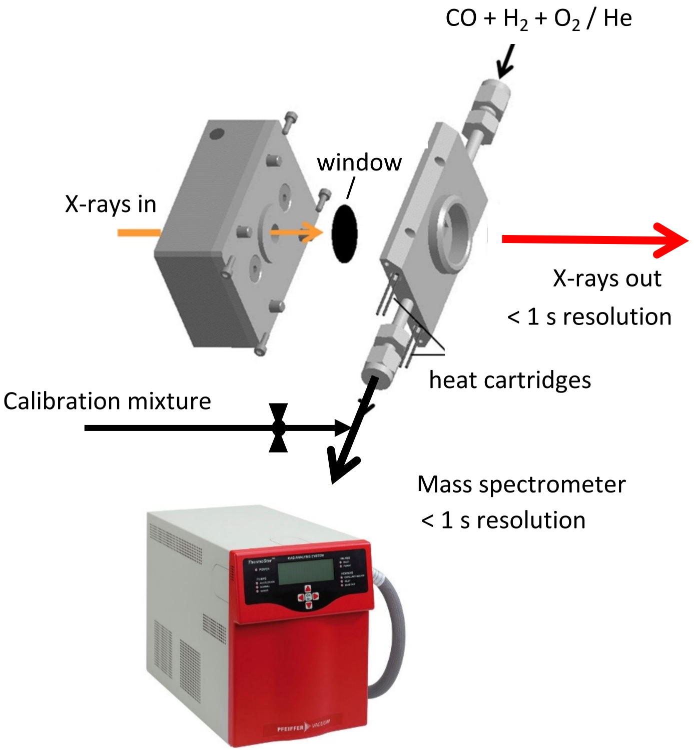
Da Silva T.L. et al, *Mater. Res. Expr.*, **2018**, *6*

$Fe^{+2}O$ islands on Pt

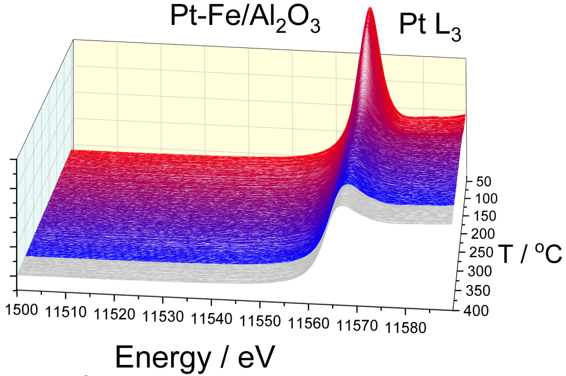


Kudernatsch W. et al, *ACS Nano*, **2015**, *9*

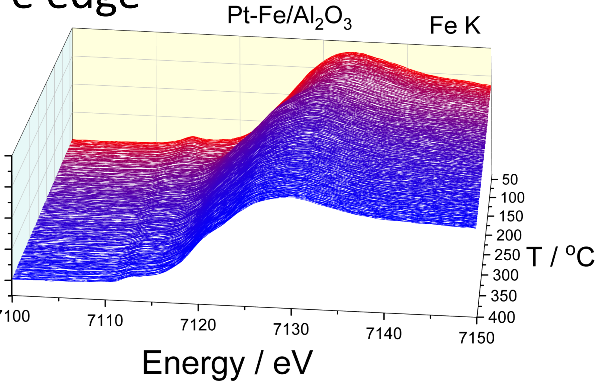
Operando XAS Study of Pt-FeO_x catalysts



Pt edge



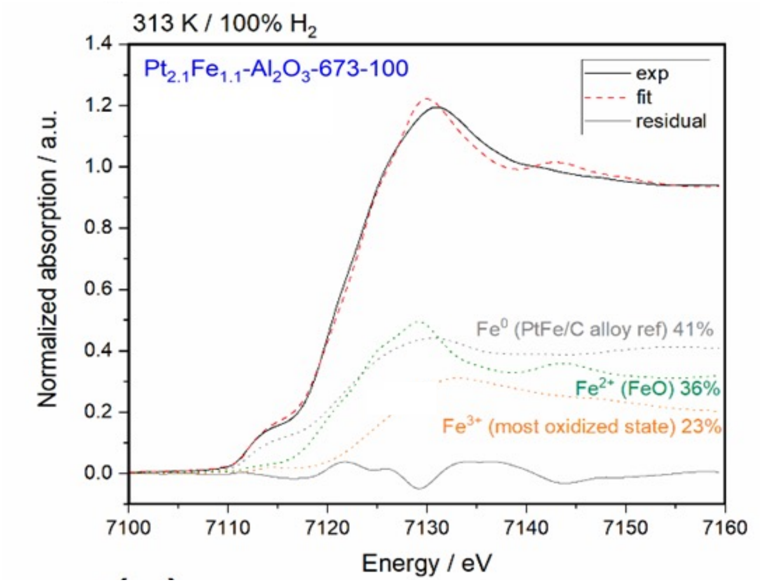
Fe edge



Olga Savonova, SuperXAS, PSI

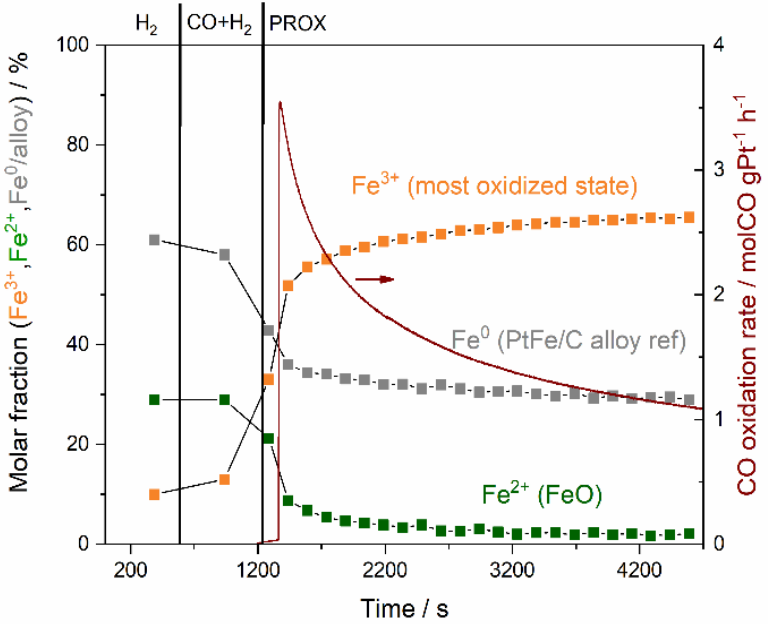
Supported Pt-FeO_x Catalysts: Operando XAS

Operando Fe K-edge XAS



fit: linear combination of components

Fe speciation - PROX activity correlation (mass spectrometer)



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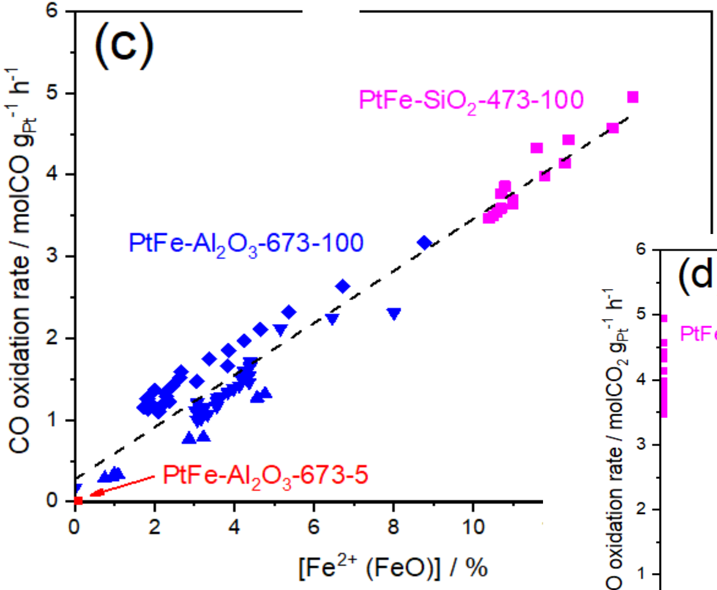
Supported Pt-FeO_x Catalysts: Activity vs. Fe species

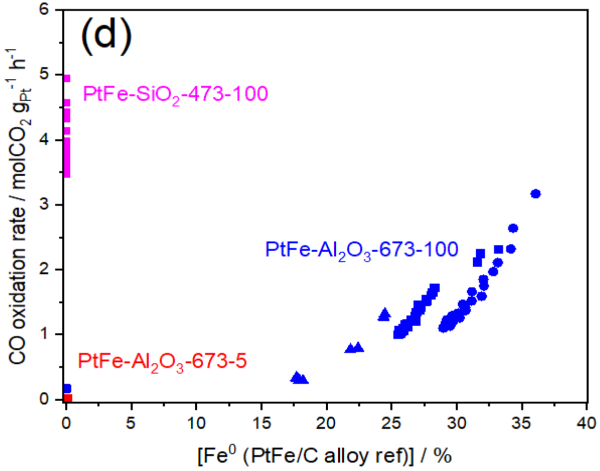
different catalysts with differetn support

→ clear correlation with Fe^{2+}, negative correlation with Fe^{3+}

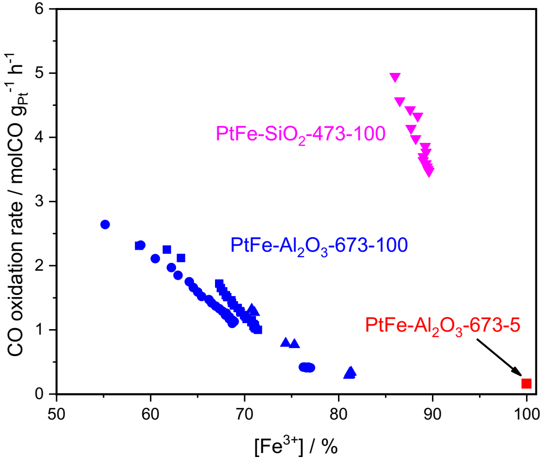
Fe^{2+} ☑



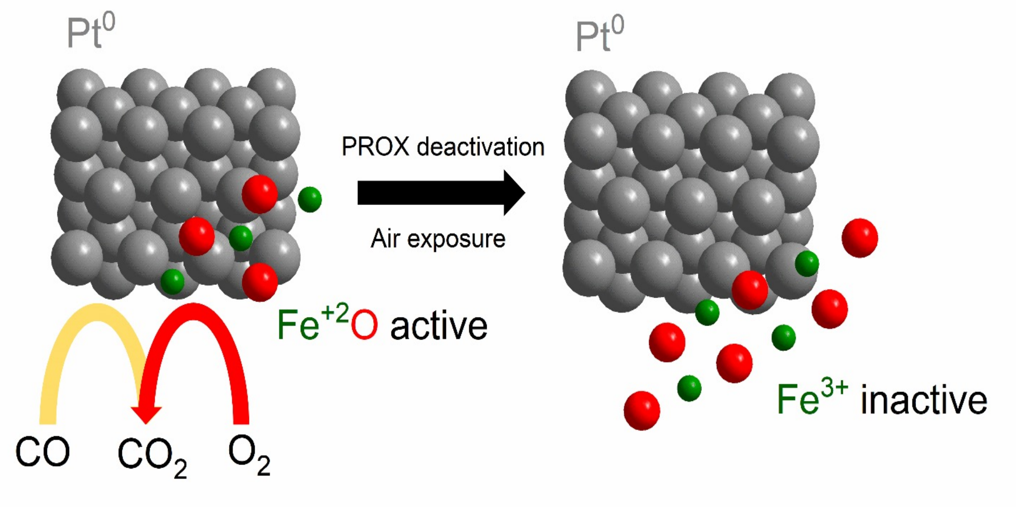
Fe^{0} ☒



Fe^{3+} ☒

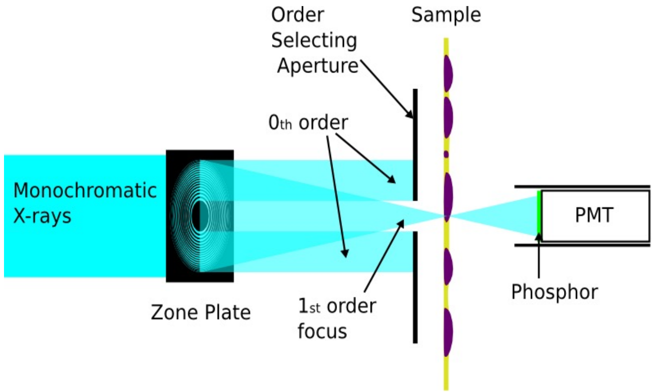


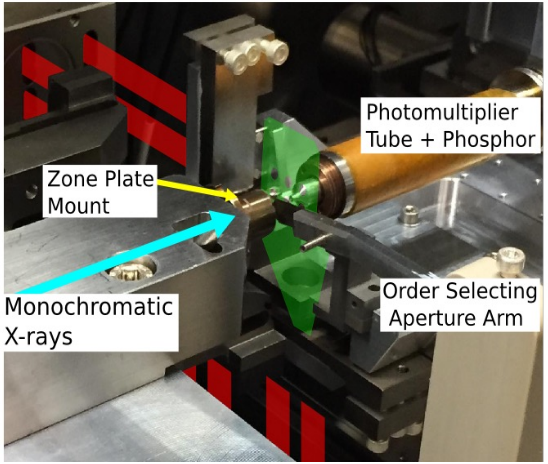
Supported Pt-FeO$_x$ Catalysts: Active site and its deactivation



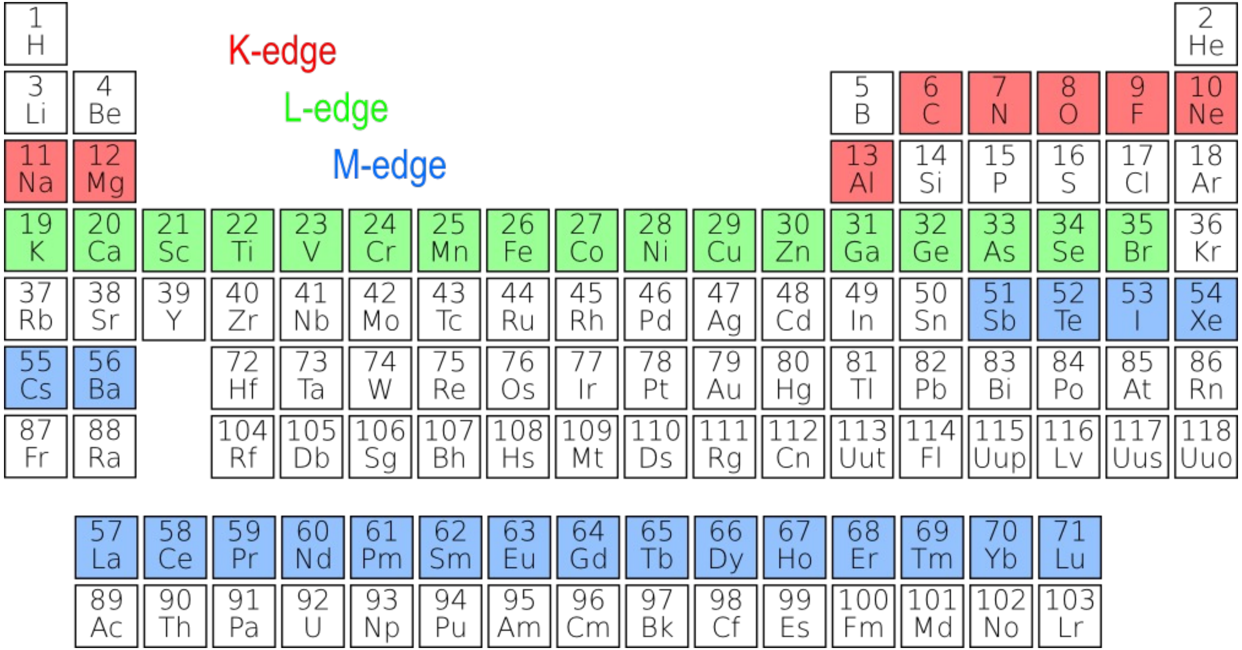
I. Sadykov et al. Angew. Chem., 2023,135, e2022140

Pollux

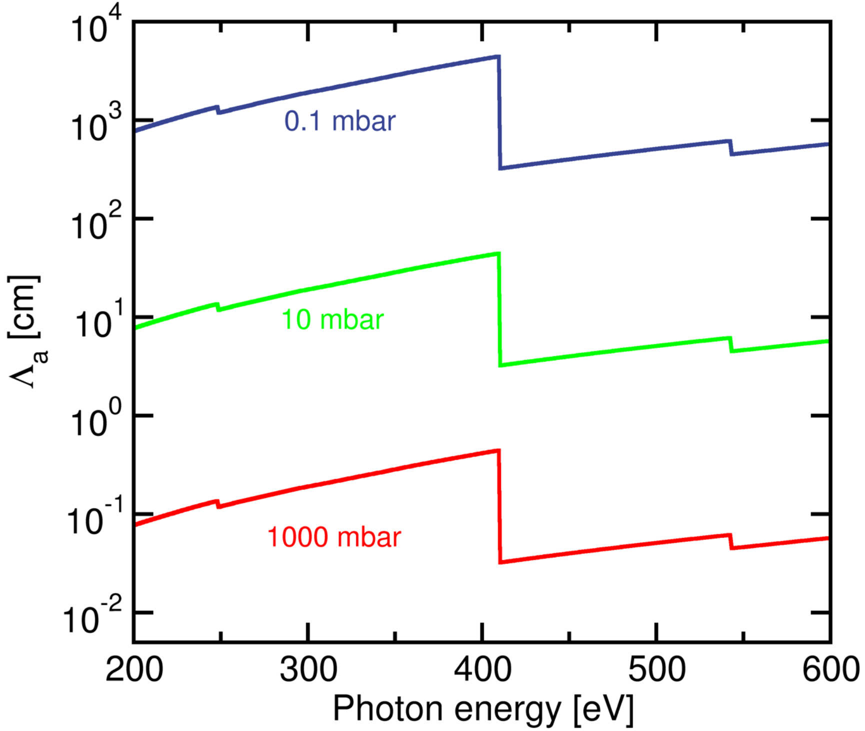

Order Selecting Aperture
Sample
0th order
Monochromatic X-rays
PMT
Zone Plate
1st order focus
Phosphor


Photomultiplier Tube + Phosphor
Zone Plate Mount
Order Selecting Aperture Arm
Monochromatic X-rays

Accessible Elemental X-ray Absorption Edges at Pollux

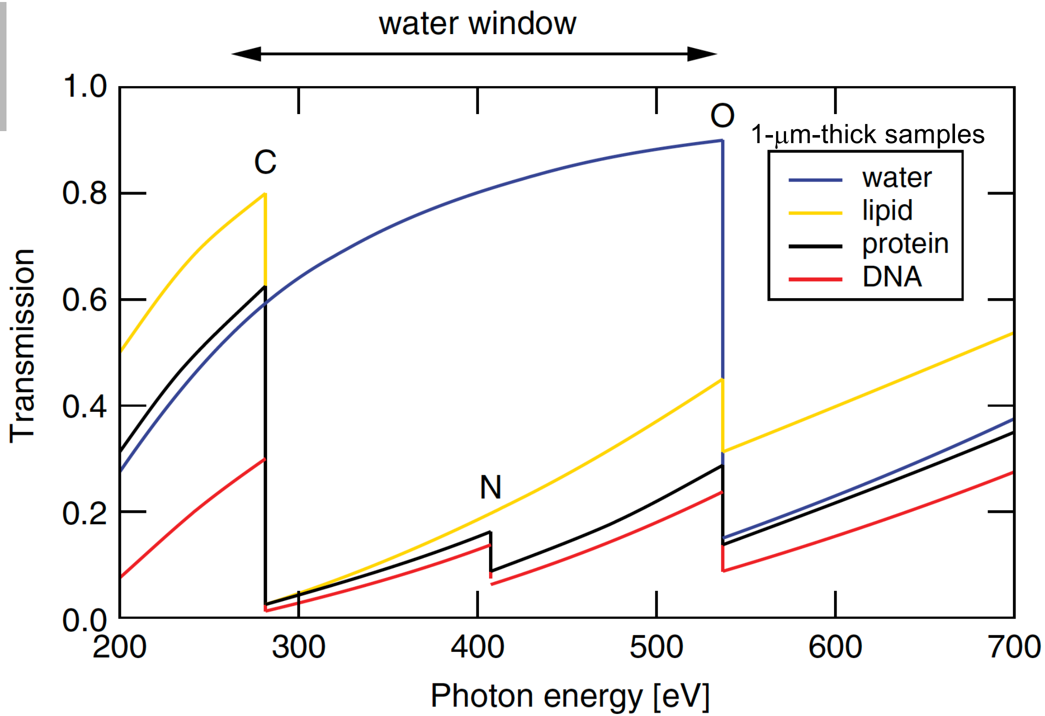


STXM



- Synchrotron-only technique
  - Scan photon energy
- Strict vacuum requirements between source and sample/detector
  - Transmission for 1-mm air = 6% above N-edge @ 410 eV
  - Typically requires 0.1 mbar or better
- Long-term accumulation of carbon contamination on optics (cryo worse!)
  - Compromises "real" sample C-XANES
  - Incident radiation "cracks" CO_2 on surface
  - Remove using low-pressure O_2 leak
- FZP
  - Focal length $\propto h\nu$: requires axial scanning
  - OSA

The water window



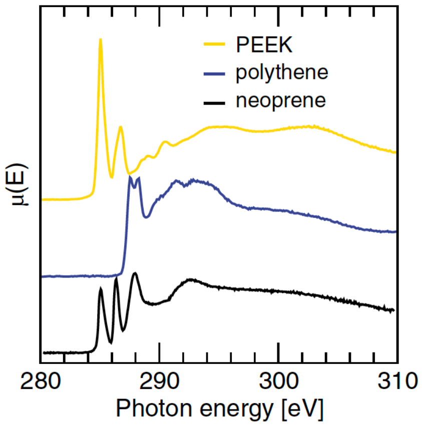
Water transparent below oxygen K-edge down to ca. 200 eV

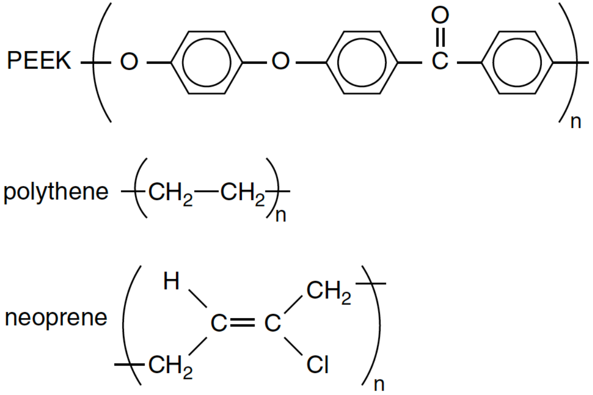
At lower photon energies, transmission drops due to $L_a \propto (hn)^3$

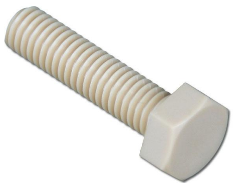
Organic compounds containing C, N, O have high absorption contrast

L-edges of other biologically relevant elements accessible, especially K, Ca

The water window: polymers

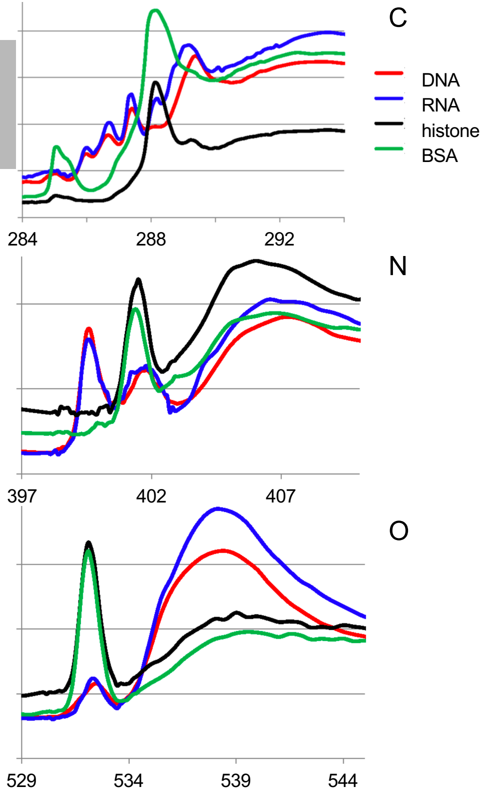


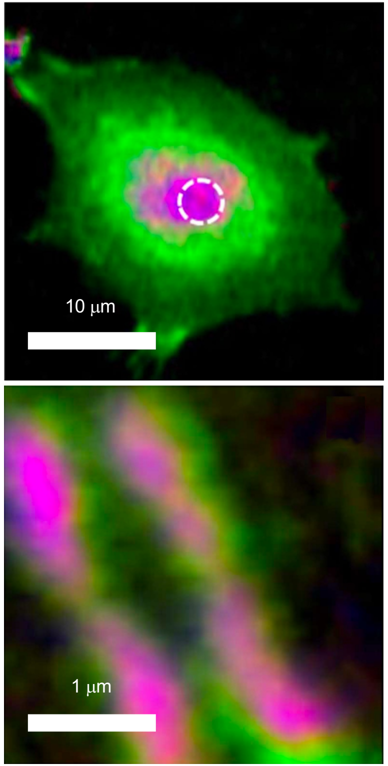




Reference spectra: O. Dhez *et al.*, "Calibrated NEXAFS spectra of some common polymers" J. Electron Spectrosc. Rel. Phenom., **128**, 85–96 (2003) and linked spectra

The water window: cells/biological samples





In-vivo or cryo-experiments possible

DNA, RNA, histone, protein

Easily distinguishable (c.f. hard x-ray phase-contrast methods)

cell: DNA, proteins other than histone, and histone are displayed as red, green, and blue, respectively

chromosome: DNA, RNA, and histone are displayed as red, green,and blue, respectively.

Adapted from: K. Shinohara *et al.*, Cells **8** 164 (2019) https://doi.org/10.3390/cells8020164