TUNTWIN's Workshop

Session A: Basics in Synchrotron Techniques for Environmental and Food from Basics to Application

Funded by the Horizon 2020 Framework Programme of the European Union under the GA N° 952306

Session: Spectroscopy techniques

X-ray absorption & X-ray emission spectroscopies

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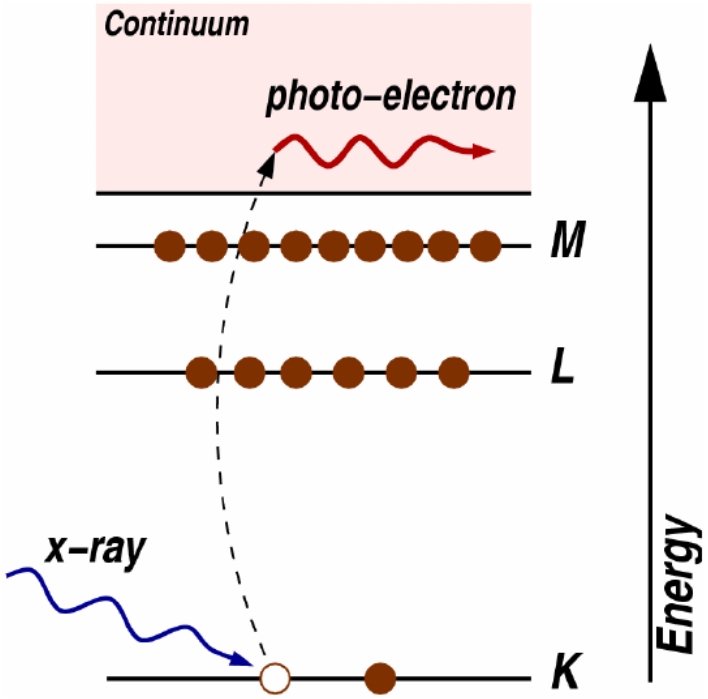
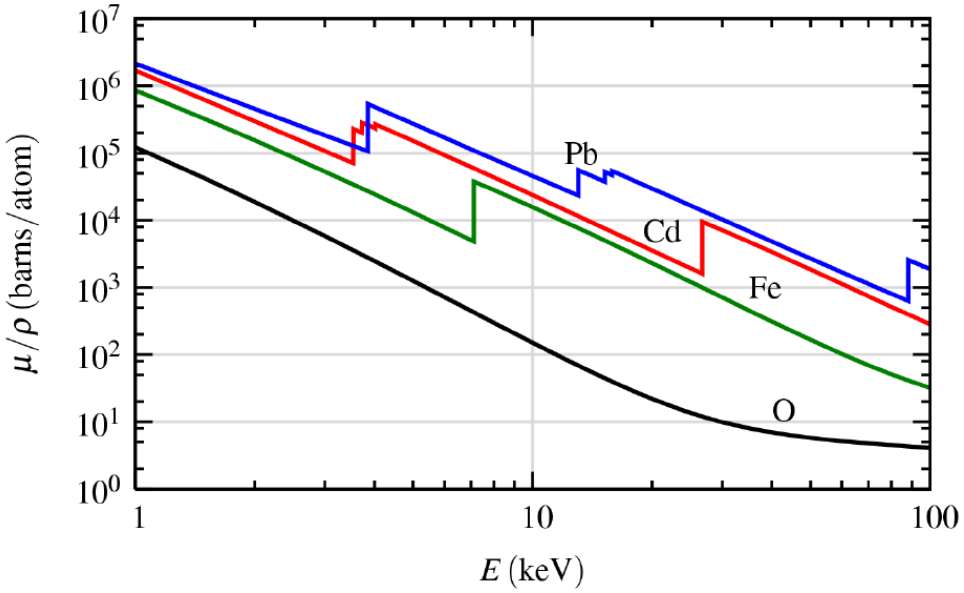
X-ray absorption spectroscopy (XAS)

An X-ray is absorbed at the atom and then an electron is promoted (creating a hole) to an unoccupied level. Thus, the photon energy is transferred to an electron, if the energy is large enough, the electron is ejected from the atom (photoelectric effect). The excess of energy from the X-ray is given to the ejected photo-electron.



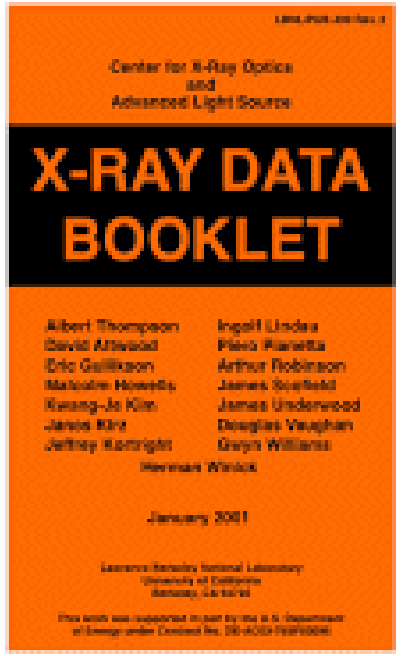
X-ray absorption cross section



M. Newville, Fundamentals of XAFS, Rev. Miner. and Geochem. **78** (2014), 33-74

X-ray absorption spectroscopy (XAS)

- **Element-specific**
- **Shell-specific**



https://xdb.lbl.gov

Table 1-1. *Electron binding energies, in electron volts*

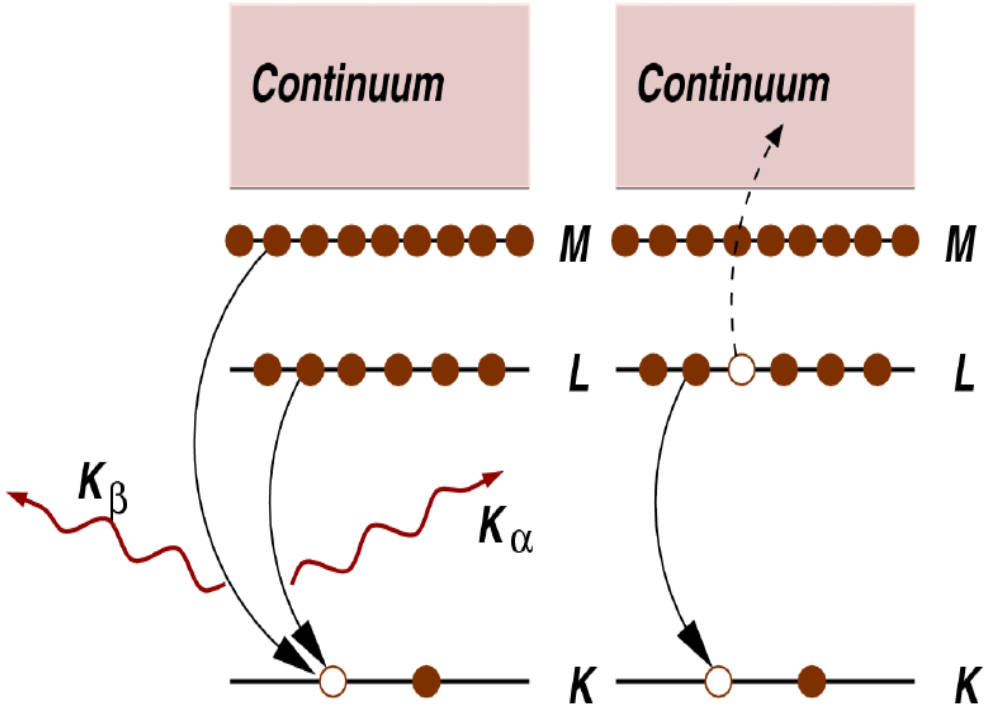
Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$
23 V	5465	626.7†	519.8†	512.1†
24 Cr	5989	696.0†	583.8†	574.1†
25 Mn	6539	769.1†	649.9†	638.7†
26 Fe	7112	844.6†	719.9†	706.8†
27 Co	7709	925.1†	793.2†	778.1†
28 Ni	8333	1008.6†	870.0†	852.7†
29 Cu	8979	1096.7†	952.3†	932.7
30 Zn	9659	1196.2*	1044.9*	1021.8*
31 Ga	10367	1299.0*b	1143.2†	1116.4†
32 Ge	11103	1414.6*b	1248.1*b	1217.0*b
33 As	11867	1527.0*b	1359.1*b	1323.6*b
34 Se	12658	1652.0*b	1474.3*b	1433.9*b
35 Br	13474	1782*	1596*	1550*
36 Kr	14326	1921	1730.9*	1678.4*

A. C. Thompson et al., X-ray data booklet, Lawrence Berkeley National Laboratory, University of California (2009)

X-ray absorption spectroscopy (XAS)

After an x-ray absorption, the decay of the excited state: x-ray fluorescence (left) and the Auger effect (right). In both cases, the probability of emission (x-ray or electron) is directly proportional to the absorption probability.

X-ray fluorescence: a higher energy electron, core-level electron, fills the deeper core hole, ejecting an x-ray of well-defined energy

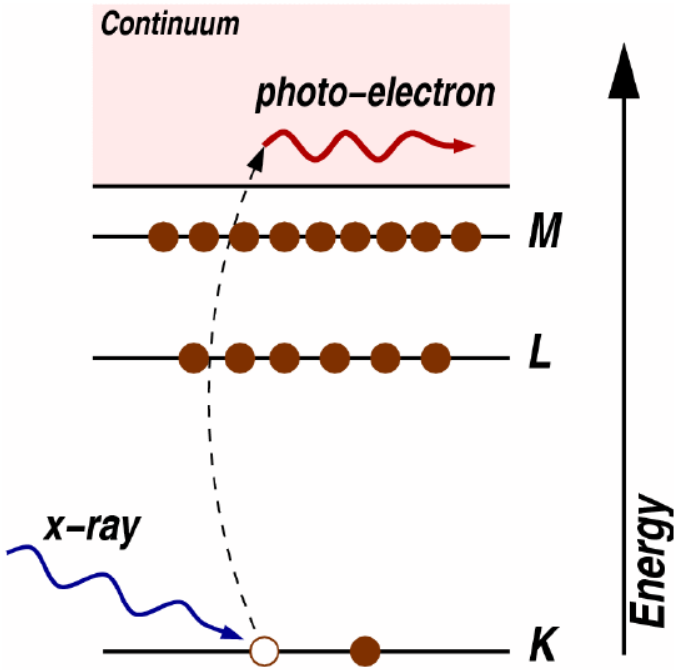


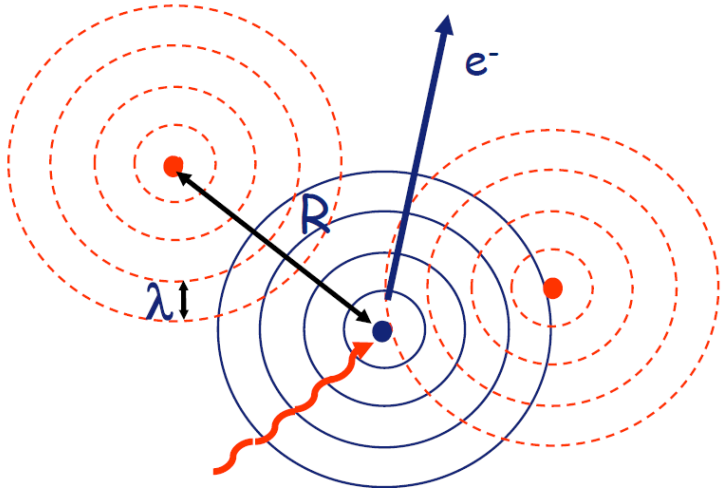
Auger Effect:

an electron drops from a higher electron level and a second electron is emitted into the continuum

M. Newville, Fundamentals of XAFS, Rev. Miner. and Geochem. **78** (2014), 33-74

X-ray absorption spectroscopy (XAS)





The photoelectron will interact with the unoccupied states of the absorber (the atom absorbing the X-ray photon) and, when reaching the continuum (X-ray energy larger than the binding energy, i.e., the excess is converted into kinetic energy), with the neighbouring atoms surrounding around the absorbing atom providing information about the chemical state of the absorbing atom and the local structure around it.

M. Newville, Fundamentals of XAFS, Rev. Miner. and Geochem. **78** (2014), 33-74

X-ray absorption spectroscopy (XAS)

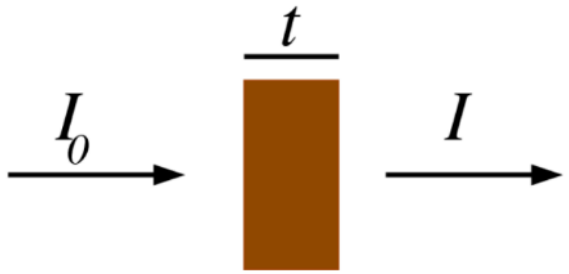
Beer-Lambert law

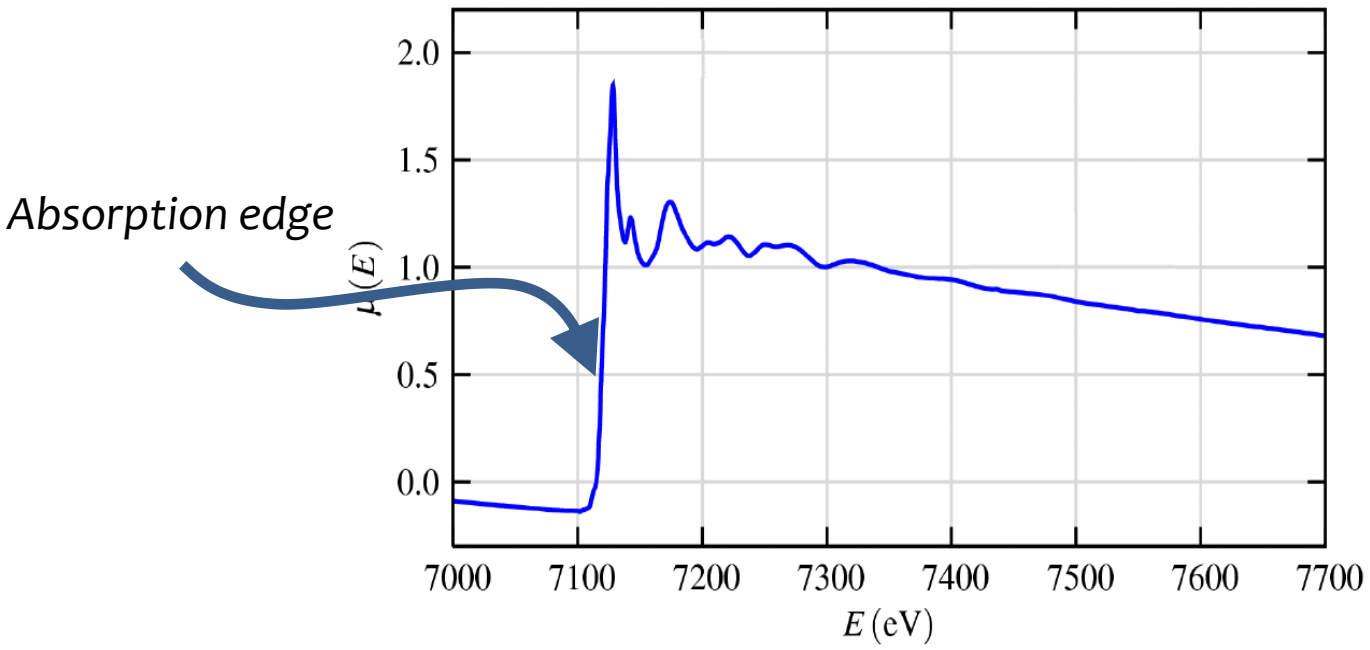
$$I = I_0 e^{-\mu t}$$

t: thickness of the material

μ: X-ray absorption coefficient

$$\mu \approx \frac{\rho Z^4}{A E^3}$$





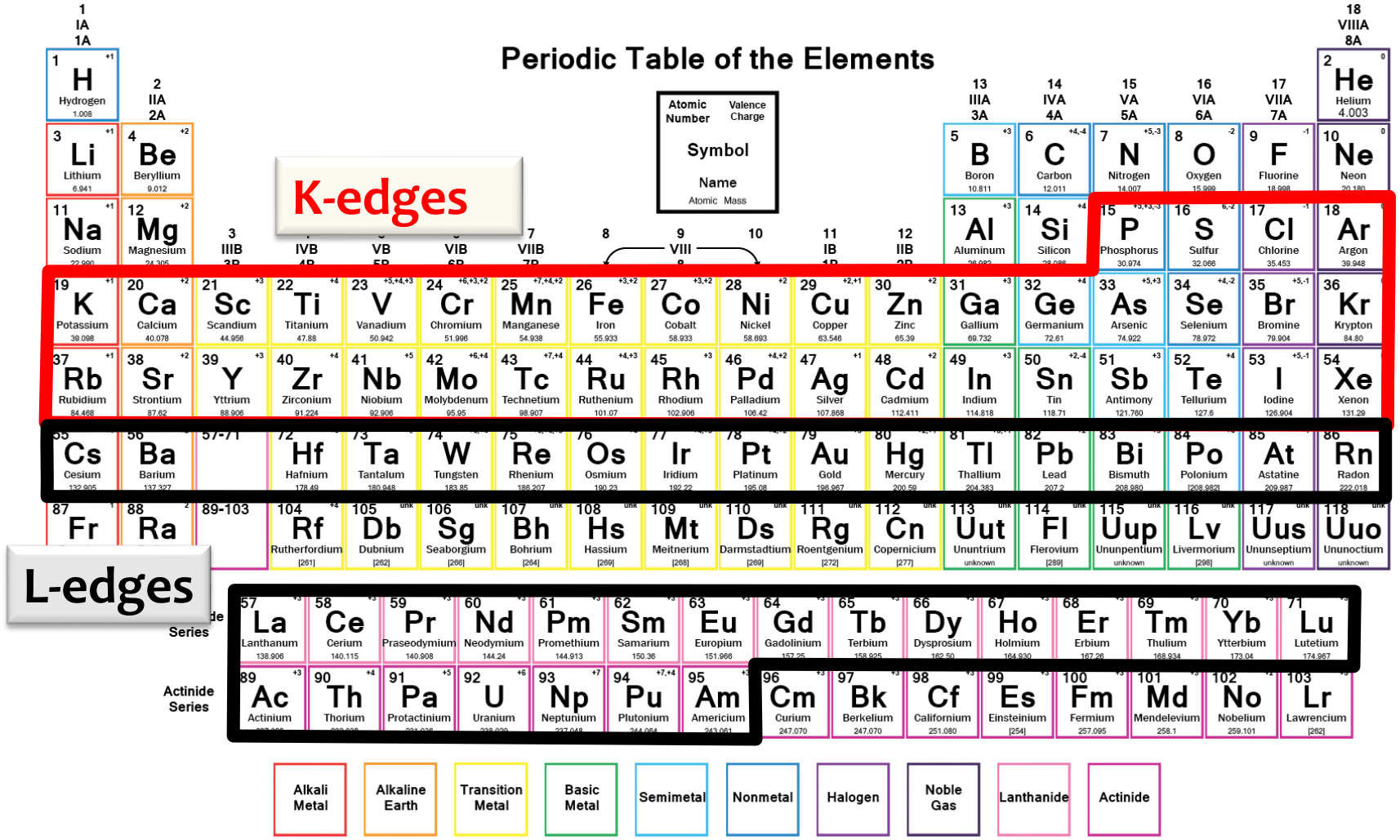
At the ***absorption edge***, the X-ray photon will have enough energy to promote the transition to the unoccupied state.

(e.g., in K-edge XAS to go from 1s → np)

M. Newville, Fundamentals of XAFS, Rev. Miner. and Geochem. **78** (2014), 33-74

X-ray absorption spectroscopy (XAS) – hard X-ray region

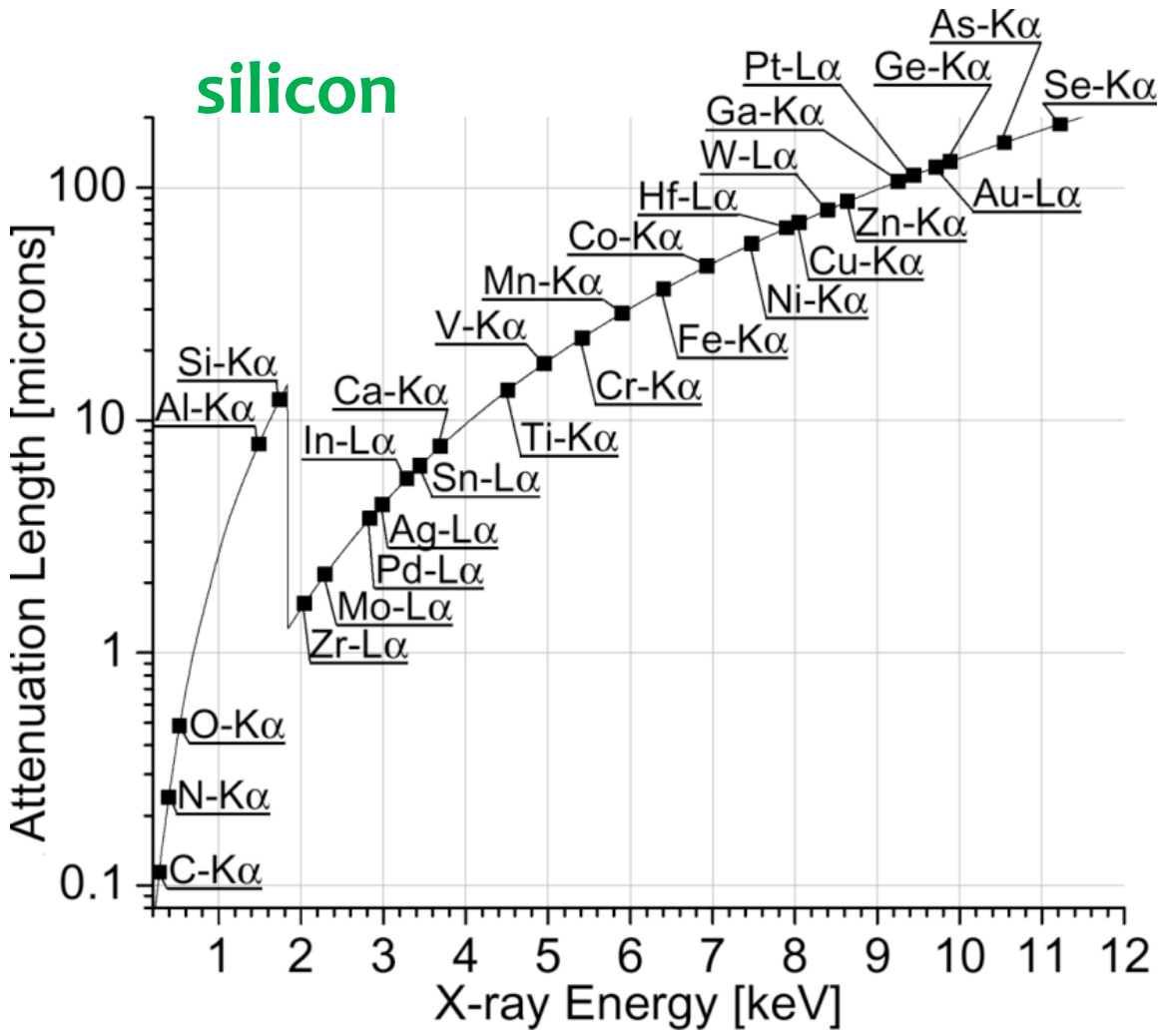
Si(111)
Si(311)



X-ray absorption spectroscopy (XAS) – hard X-ray region

Attenuation length

The depth into the material measured along the surface normal where the intensity of x-rays falls to 1/e of its value at the surface.

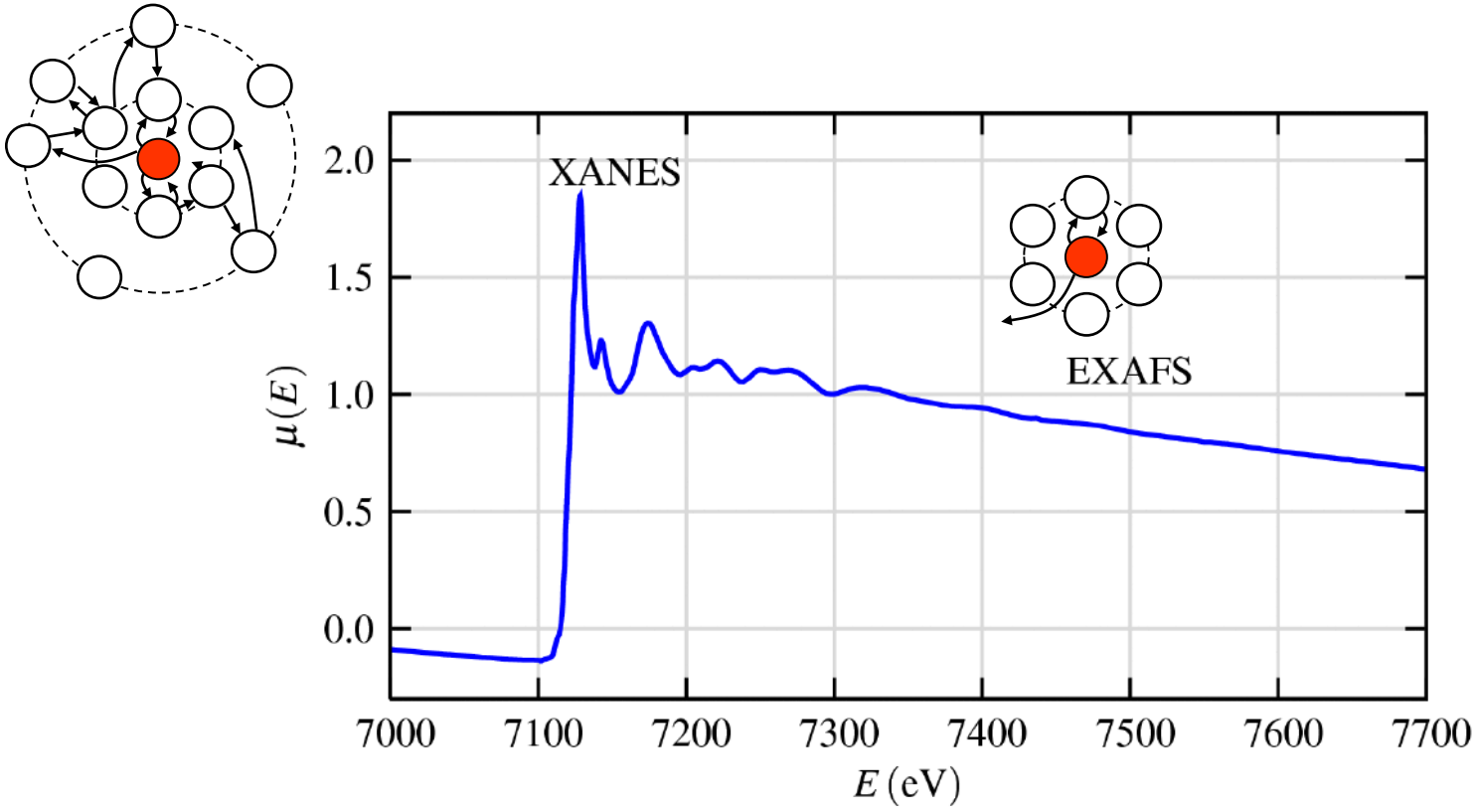


X-ray absorption spectroscopy (XAS)

The photo-electron will scatter with the surrounding atoms and depending on its kinetic energy, single or multiple scattering processes will occur. Accordingly, the XAS spectrum is divided in two regions which provide complementary chemical information:

XANES: X-ray absorption near-edge structure (multiple scattering)

EXAFS: Extended X-ray absorption fine structure (single scattering)

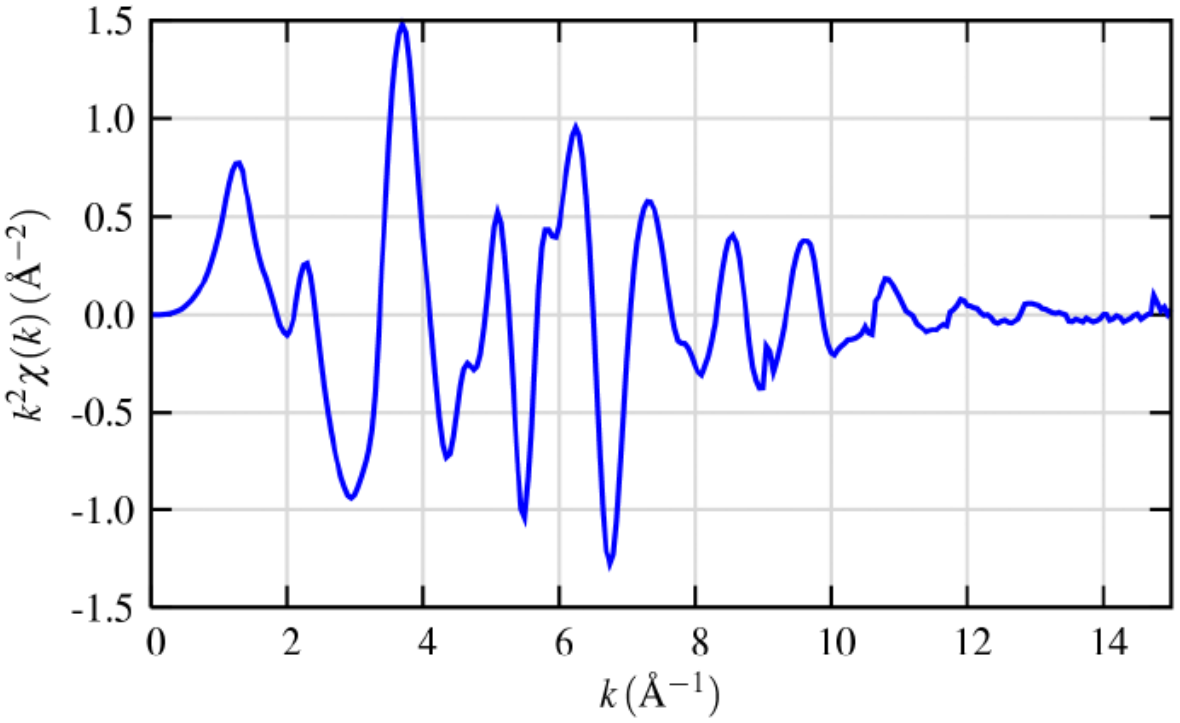


M. Newville, Fundamentals of XAFS, Rev. Miner. and Geochem. **78** (2014), 33-74

X-ray absorption spectroscopy (XAS)

EXAFS: sensitive to the local structure around the absorbing atom

Extracting the oscillatory behaviour of the X-ray absorption coefficient we can study the interference effects of the different scattering events in the material.

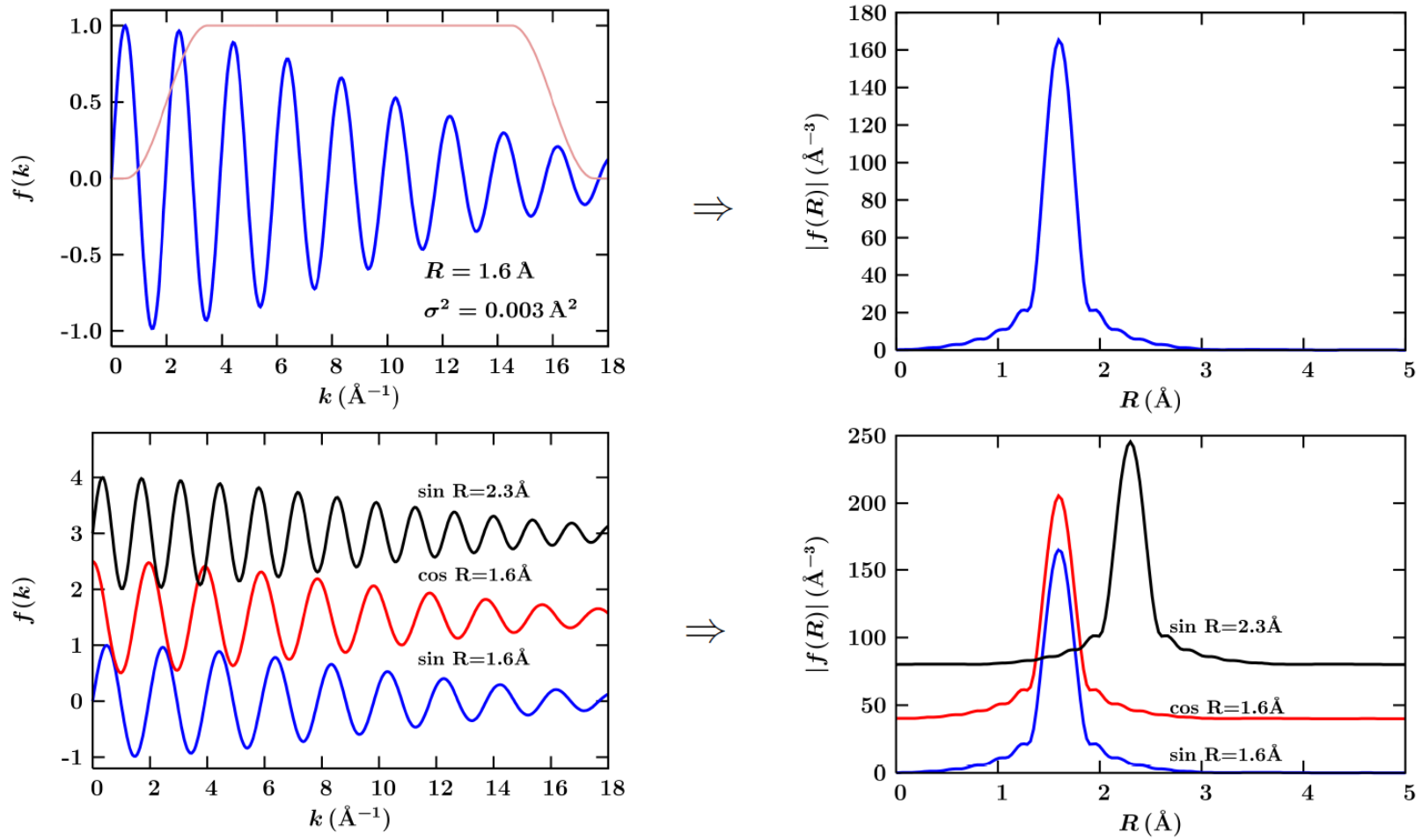


Wave number: $k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$

M. Newville, Fundamentals of XAFS, Rev. Miner. and Geochem. **78** (2014), 33-74

X-ray absorption spectroscopy (XAS)

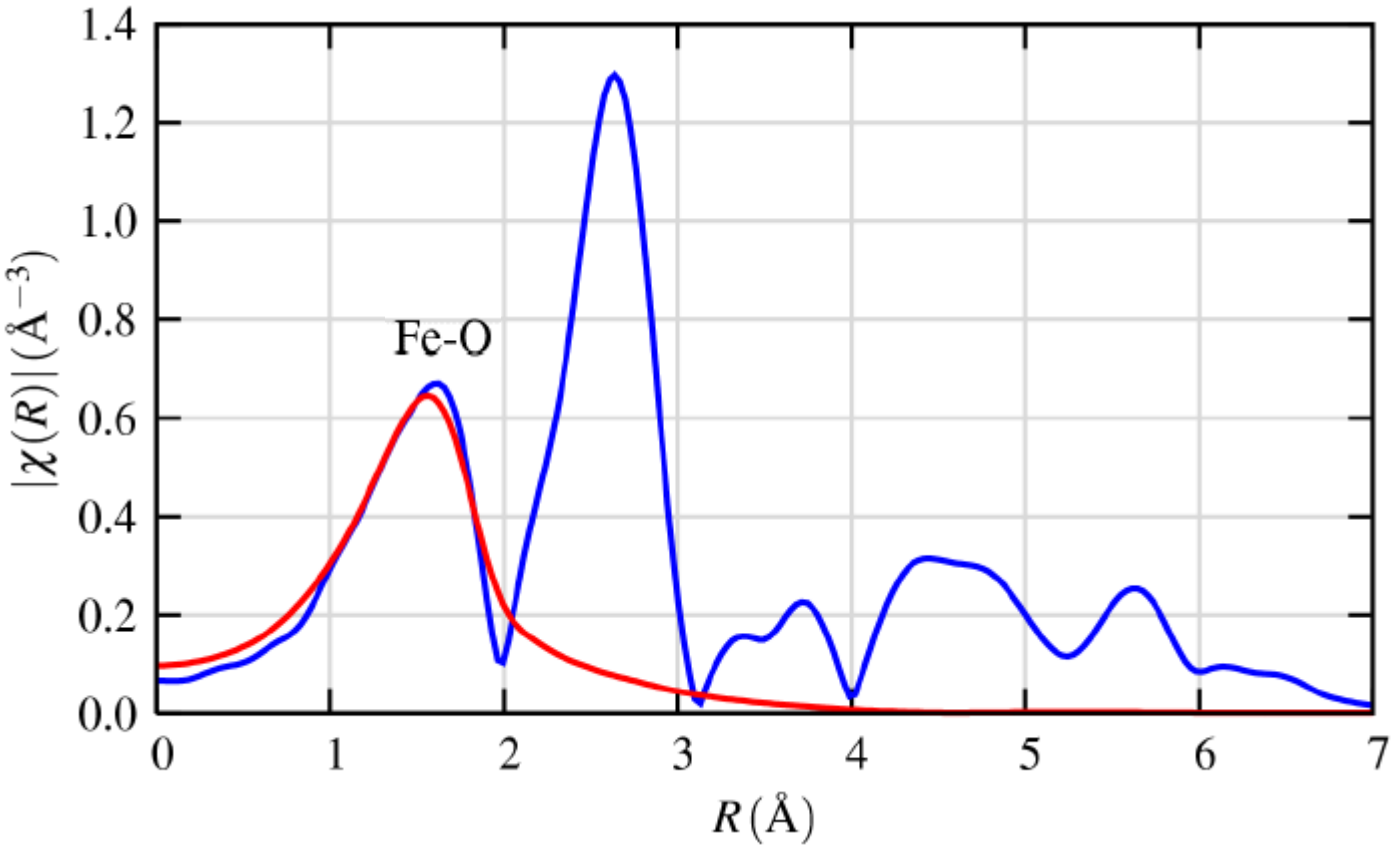
Fourier Transform
of a sine wave



M. Newville, Data Processing with ifeffit, athena, & artemis (2007)

X-ray absorption spectroscopy (XAS)

Fourier transform of the EXAFS signal to obtain a pseudo-radial distribution function in the real space.

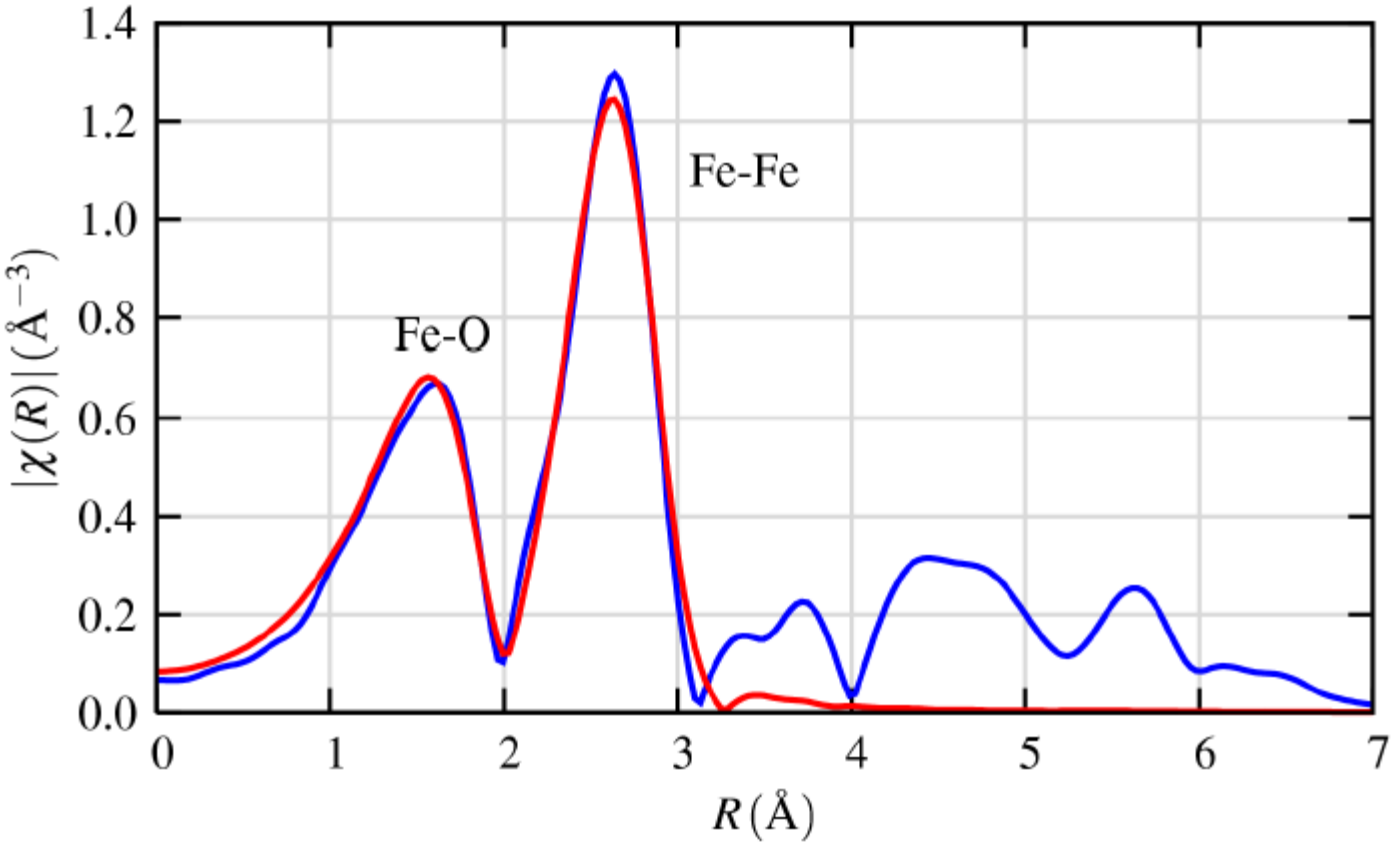


M. Newville, Fundamentals of XAFS, Rev. Miner. and Geochem. **78** (2014), 33-74

X-ray absorption spectroscopy (XAS)

EXAFS equation:

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



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EXAFS equation:

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

where $f(k)$ and $\delta(k)$ are *photo-electron scattering properties* of the neighboring atom. If we know these properties, we can determine:

R distance to neighboring atom.

N coordination number of neighboring atom.

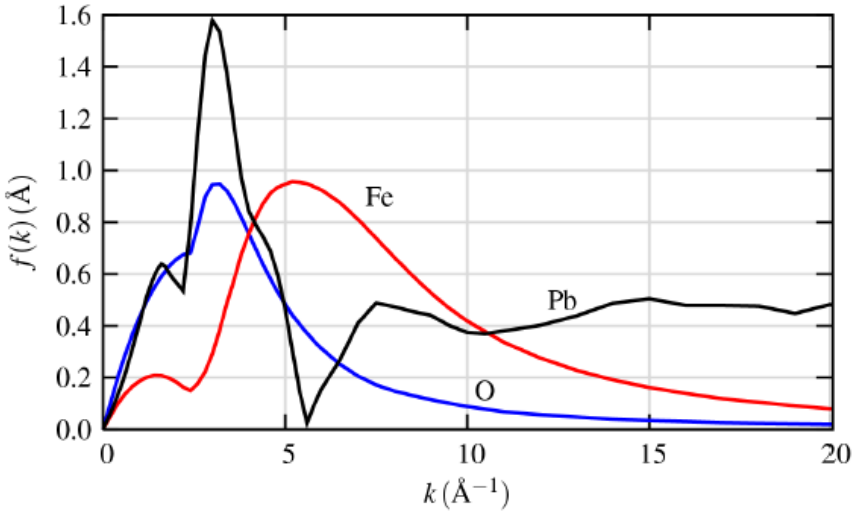
σ^2 mean-square disorder of neighbor distance.

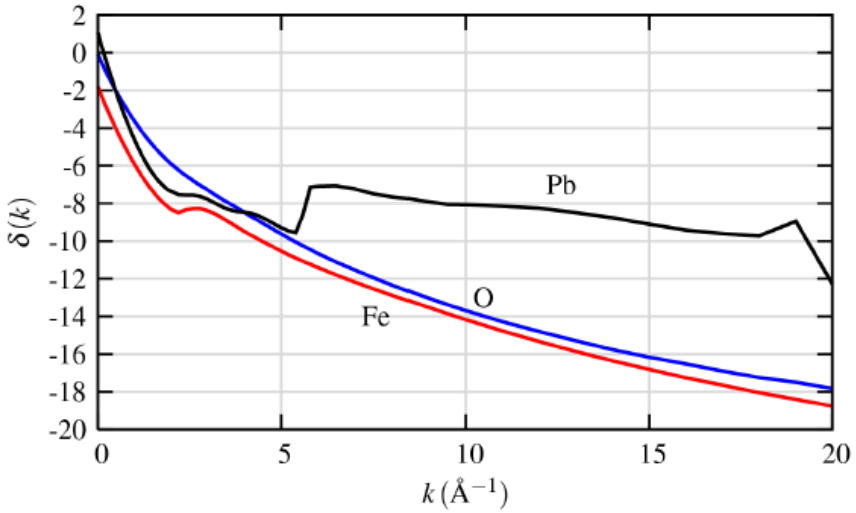
Plus: $f(k)$ and $\delta(k)$ depend on atomic number Z of the scattering atom, so we can also determine the species of the neighboring atom.

M. Newville, Fundamentals of XAFS, Rev. Miner. and Geochem. **78** (2014), 33-74

X-ray absorption spectroscopy (XAS)

Photo-electron scattering amplitudes and phases





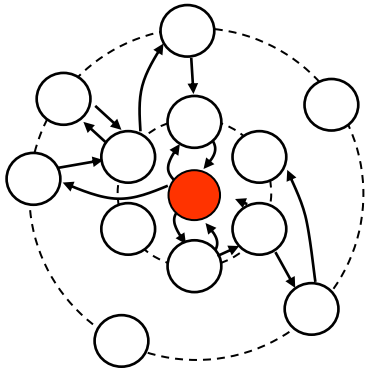
f (k) peaks at higher k as Z increases. For heavy elements, there is a minimum in *f (k)*.

The phase shift δ(k) also shows strong Z dependence, and has sharp jumps for heavy elements.

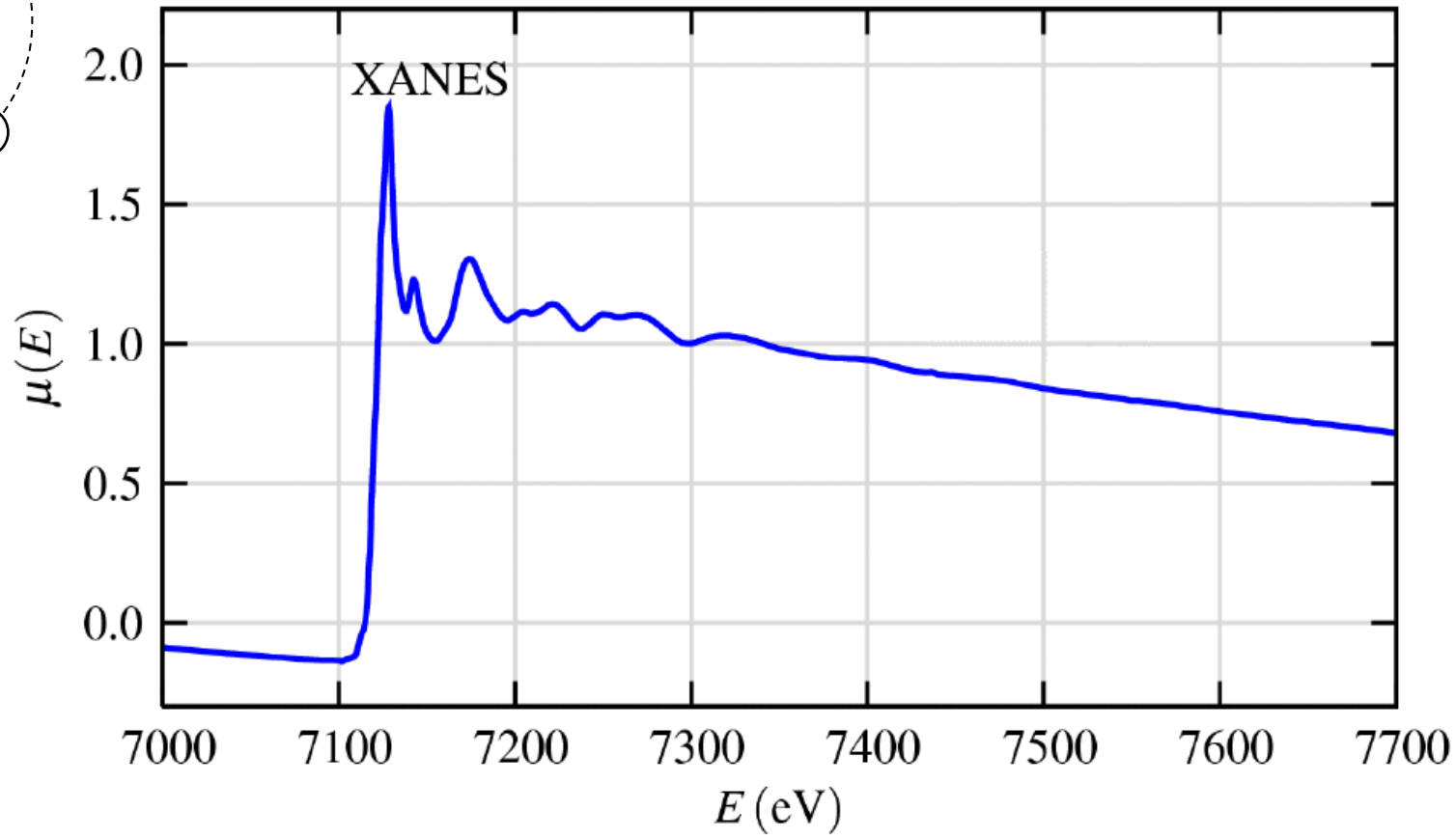
Z can usually be determined to ±5.
Fe and O can be distinguished
N and O cannot be distinguished!!!

M. Newville, Data Processing with ifeffit, athena, & artemis (2007)

X-ray absorption spectroscopy (XAS)



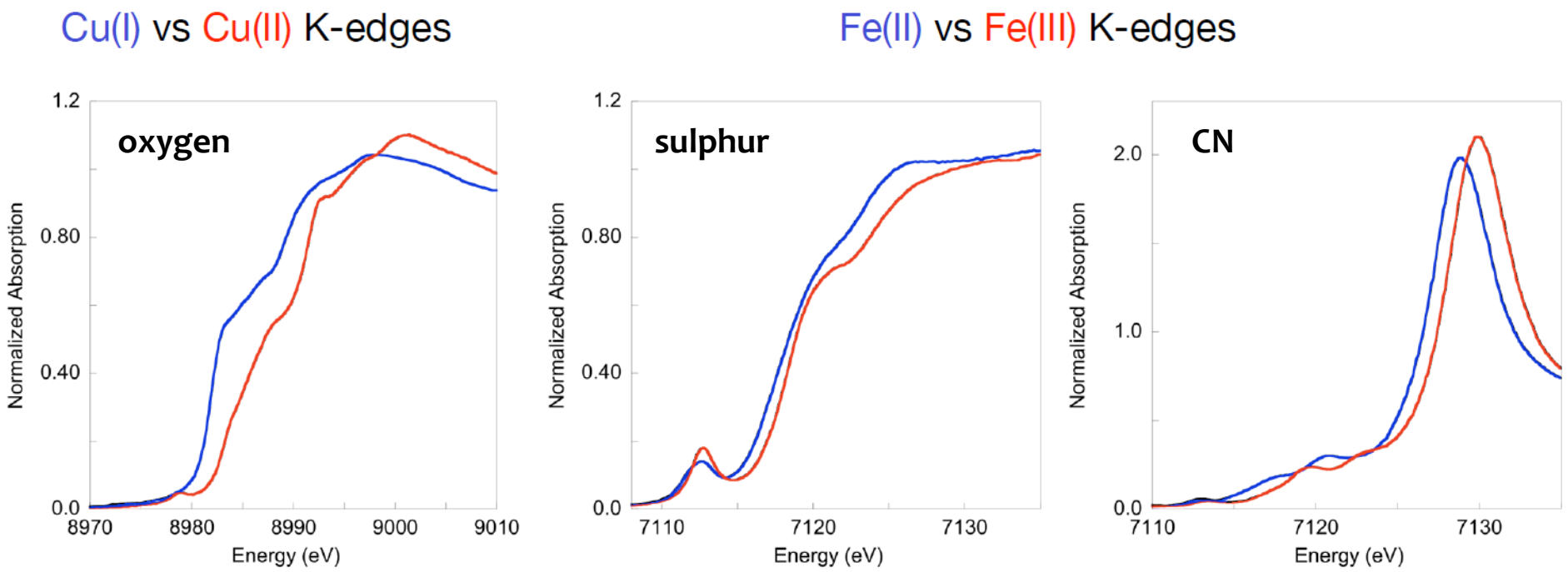
XANES: Sensitive to the oxidation state and stereochemical details of the local environment around the absorbing atom.



M. Newville, Fundamentals of XAFS, Rev. Miner. and Geochem. **78** (2014), 33-74

X-ray absorption spectroscopy (XAS)

Metal K-edge XAS: oxidation state

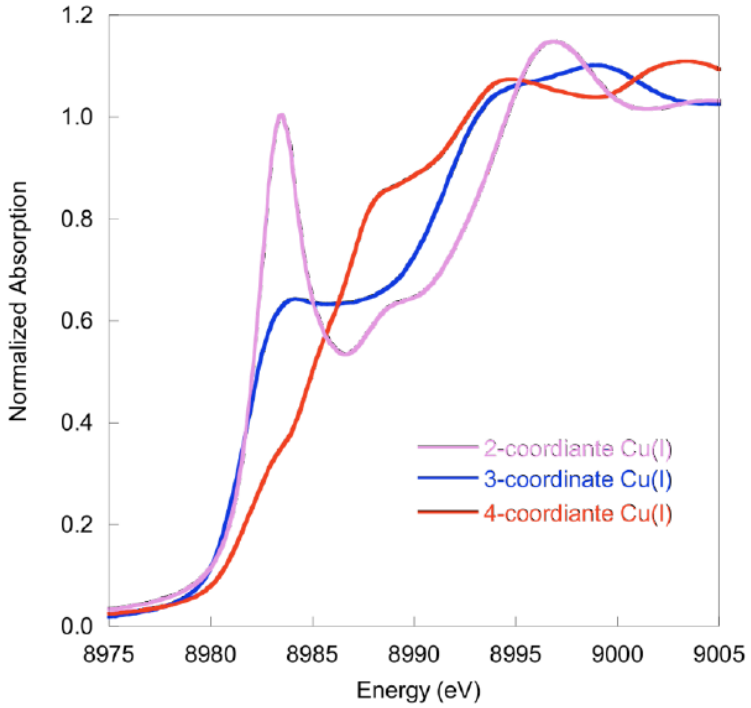


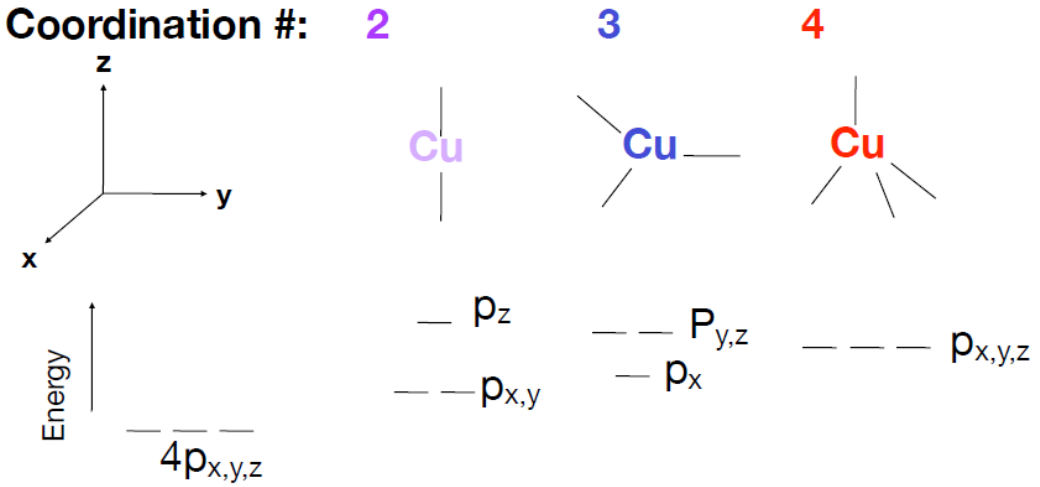
However, need to compare oxidation state trends within similar ligand environments

S. DeBeer, Introduction to X-ray Spectroscopy: mainly XAS and a bit of XES... (2012)

X-ray absorption spectroscopy (XAS)

Metal K-edge XAS: coordination number



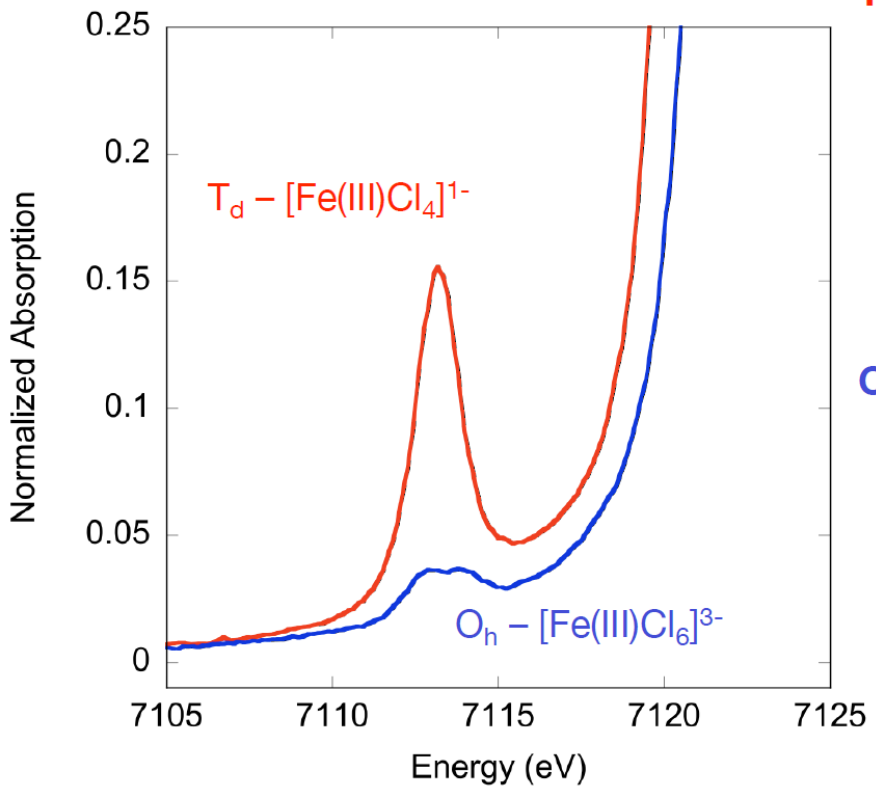


The rising edges of Cu(I) complexes can be easily understood in terms of a simple ligand field (LF) model.

L.S. Kau et al., J. Am. Chem. Soc., 1987, 109, 6433

X-ray absorption spectroscopy (XAS)

Symmetry-Based 3d-4p Mixing



T_d – $[Fe(III)Cl_4]^{1-}$

4p orbitals transform as t_2

3dxy, xz, yz orbitals transform as t_2

allows 3p-4d mixing and intense pre-edge

O_h – $[Fe(III)Cl_6]^{3-}$

4p orbitals transform as t_{1u}

d-orbitals transform as t_{2g} and e_g

No 3d-4p mixing, quadrupole Only

In general, the larger the distortion of the site, the greater the 3d-4p mixing.

S. DeBeer, Introduction to X-ray Spectroscopy: mainly XAS and a bit of XES... (2012)

X-ray absorption spectroscopy (XAS)

Data interpretation:

- Finger print analysis (comparison with reference materials).
- Principal component analysis, PCA.
- Linear combination fitting, LCF (appropriate library of reference spectra required).
- Ab-initio calculations:
    - Multiple scattering formalism (Muffin-tin or full-potential)
    - Density functional theory, DFT (bound states).

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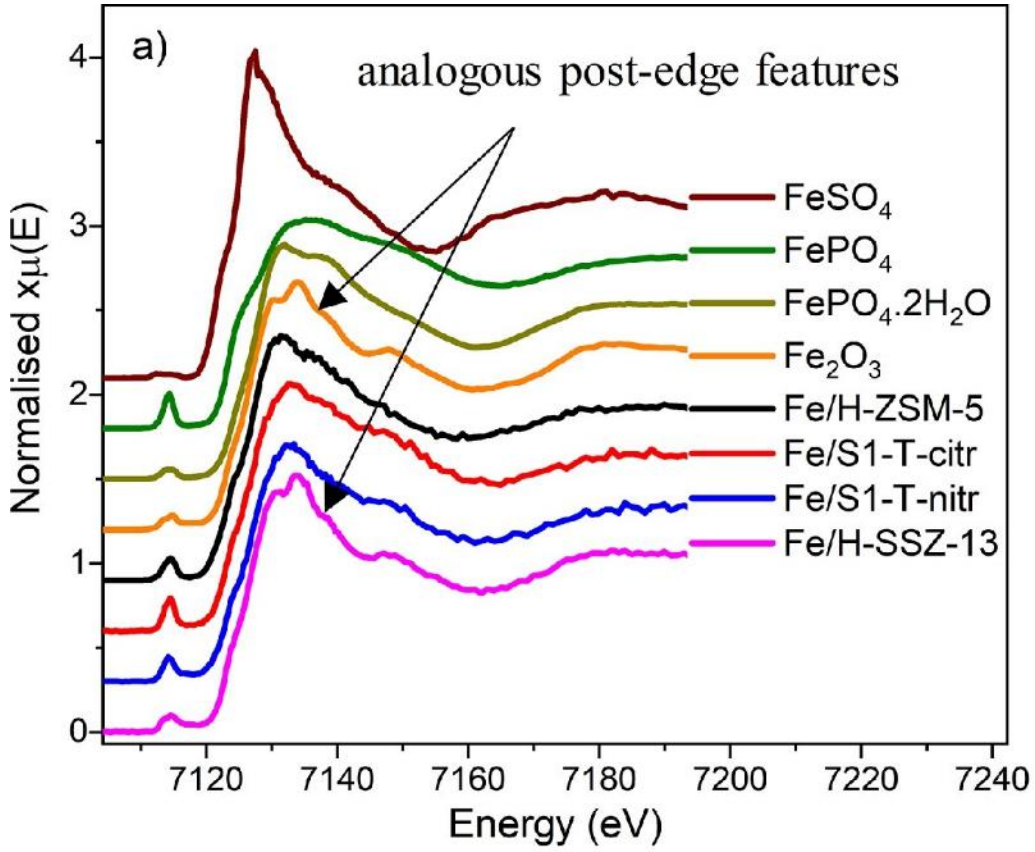
Warning!!!

How many standards are necessary?
Which standards are required?
Which standards are unphysical?
Is the final fit reasonable?

- Use all the a-priori knowledge on the sample
- Check carefully the results

X-ray absorption spectroscopy (XAS)

Data interpretation: Finger print analysis (comparison with reference materials).



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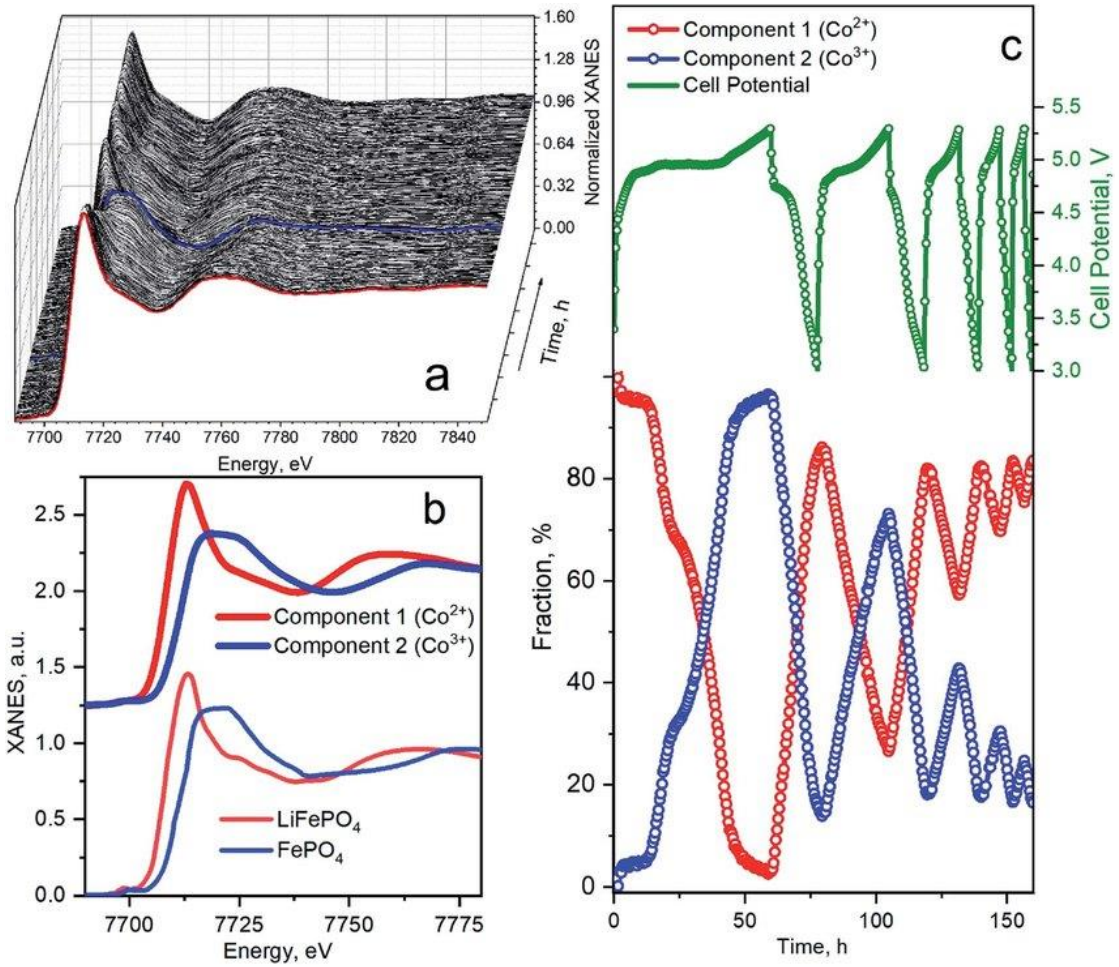

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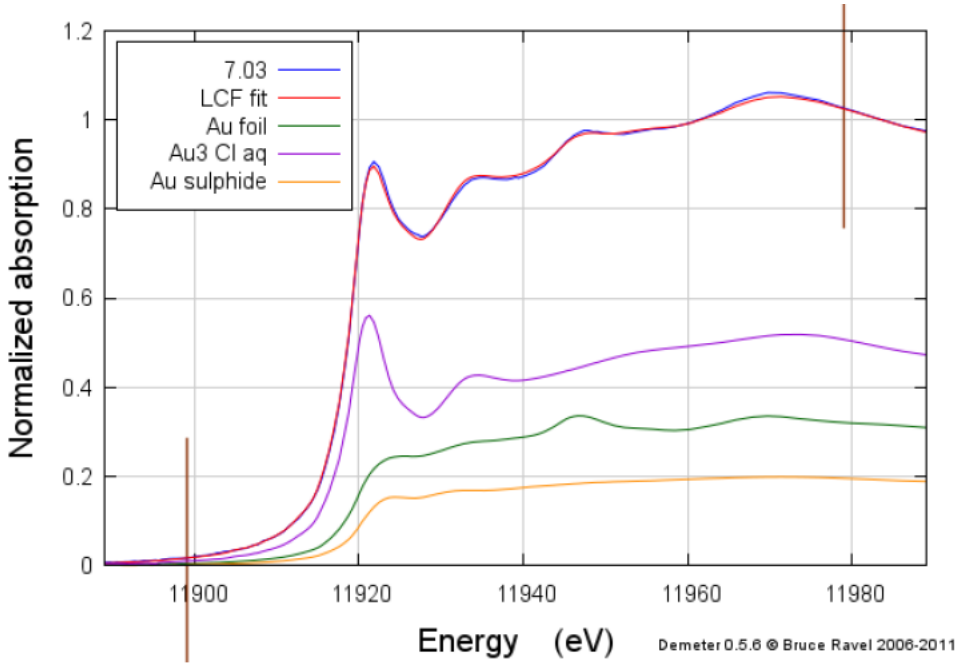
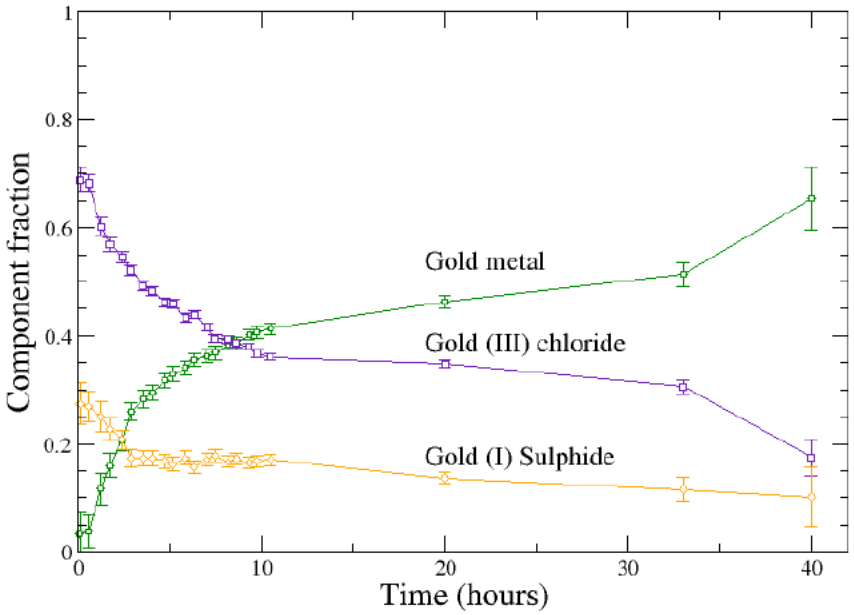




Au chloride fluids rise from the deep earth, wash over cyanobacteria colonies, and reduce to metallic gold.

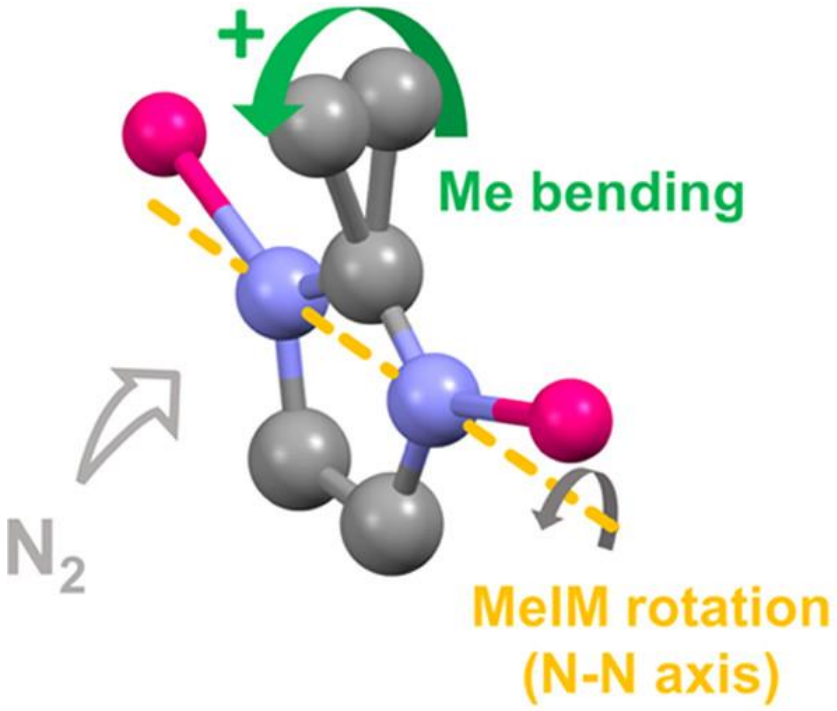
M. Lengke et al., Environ. Sci. Technol. ***40****(20) p. 6304-6309. (2006) DOI: 10.1021/es061040r*

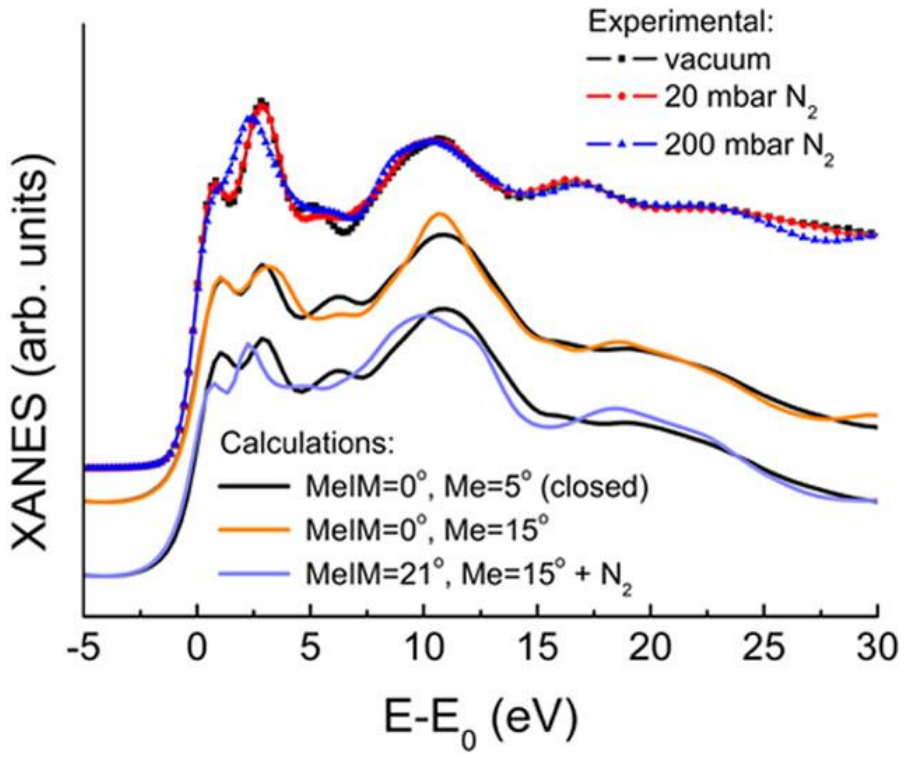
X-ray absorption spectroscopy (XAS)

Data interpretation:

- Ab-initio calculations: * Multiple scattering formalism (Muffin-tin or full-potential)

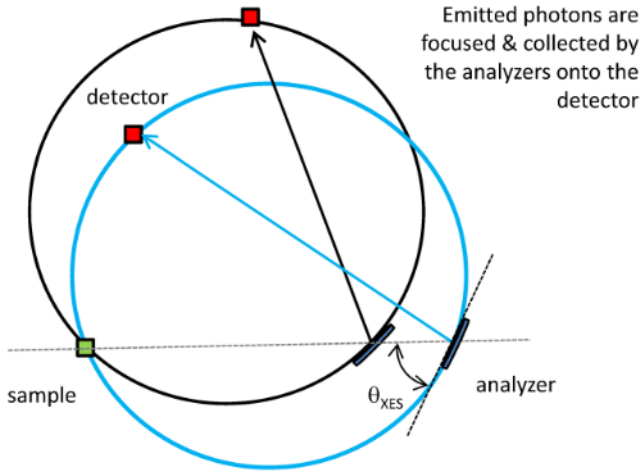
  * Density functional theory, DFT (bound states).



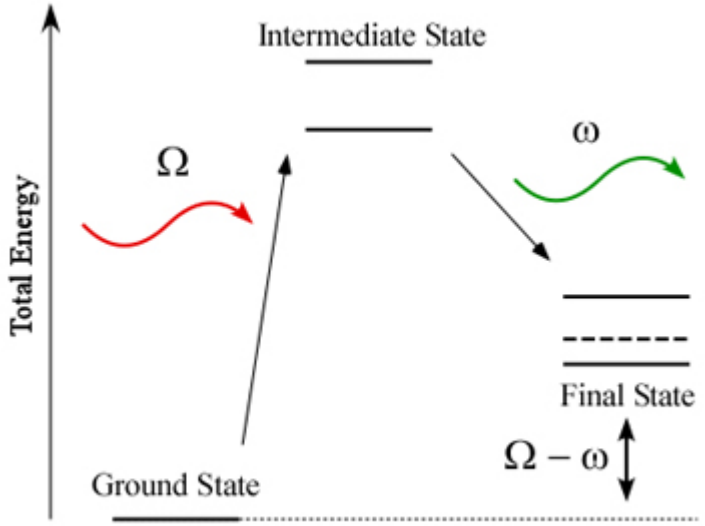


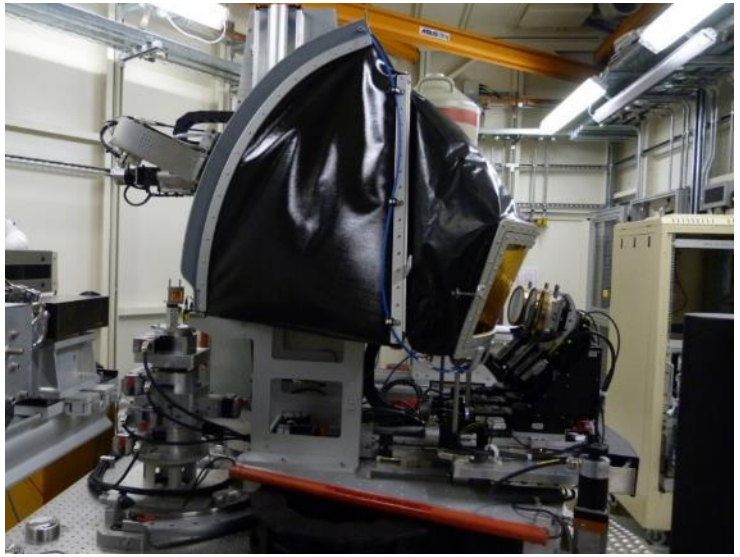
X-ray emission spectroscopy (XES)

- **Photon-in – photon-out techniques**:
  - HERFD-XAS
  - XES
  - resonant XES
  - non resonant Raman (XRS)



- Vertical Rowland circle geometry (<1 eV resolution)

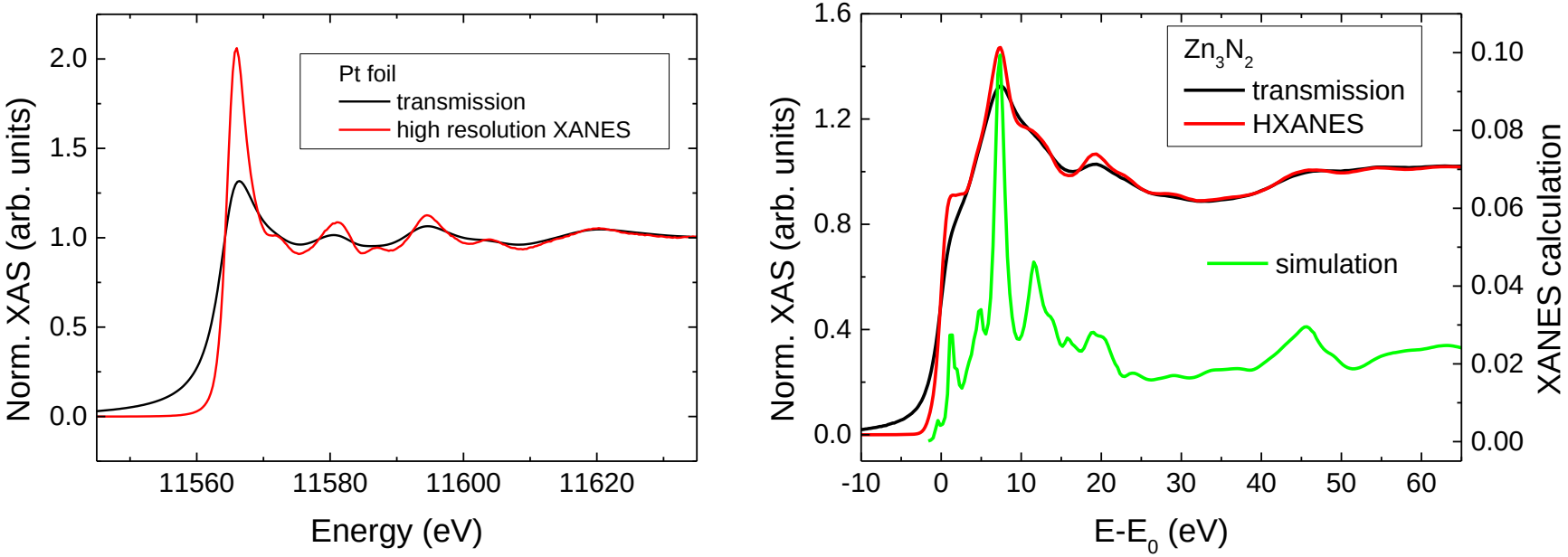




http://www.pieter-glatzel.de/XASXES.html
https://www.diamond.ac.uk/Instruments/Spectroscopy/I20/XAS_XES_Branchline/Techniques-and-Resources/XES.html

X-ray emission spectroscopy (XES)

High energy fluorescence detected XANES (HERFD-XANES): Overcoming the core-hole lifetime energy broadening

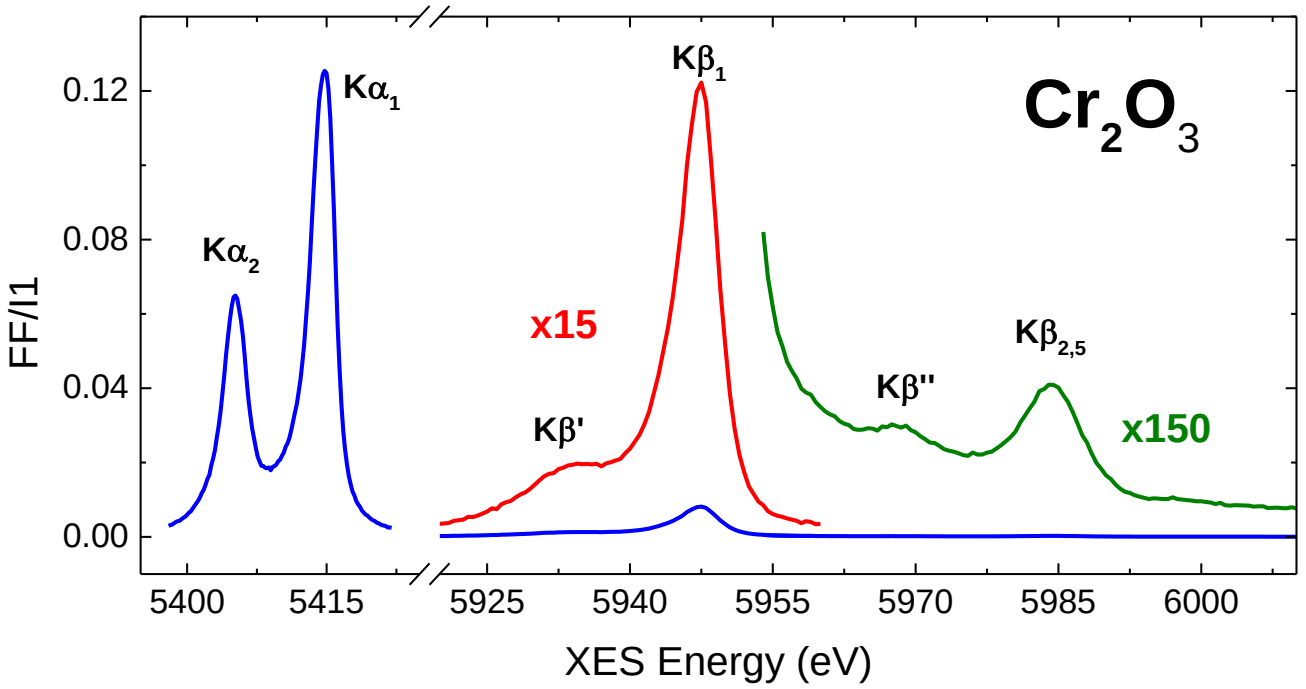


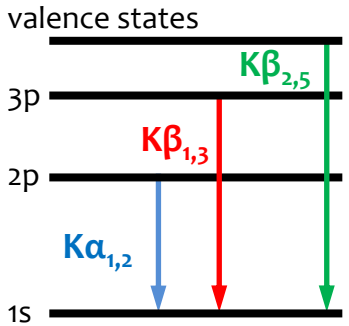
core-hole lifetime is the time that the atom remains in the excited state until the core created by the X-ray gets filled again. For heavier atoms (larger *Z*) is much smaller than for lighter atoms. Considering Heisenberg's Uncertainty Principle ($\Delta E \cdot \Delta t \geq \hbar/2$), then, in terms of energy, heavier atoms will have larger energy broadening of the XAS features.

Courtesy of I20-scanning beamline at Diamond Light Source

X-ray emission spectroscopy (XES)

Monitoring different decay channels provides different information about the absorbing atom.

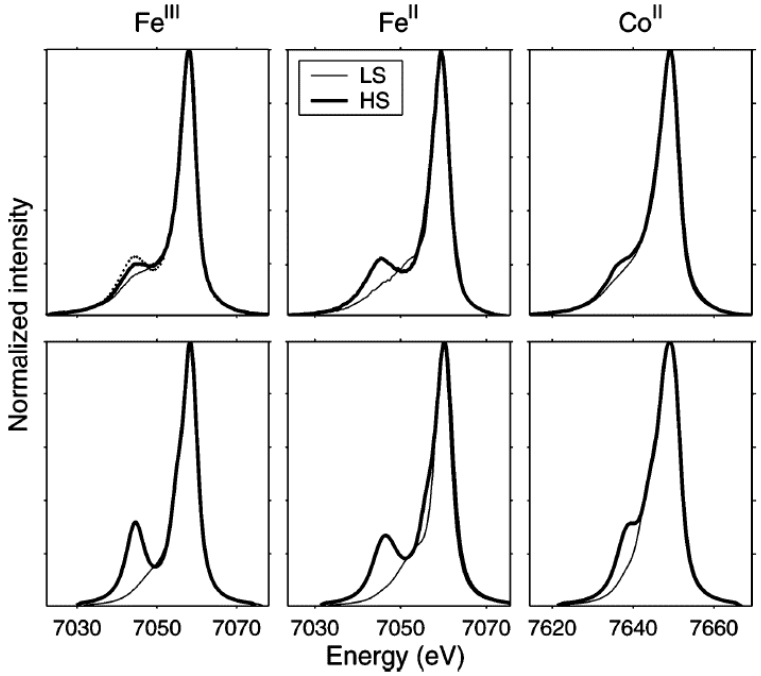




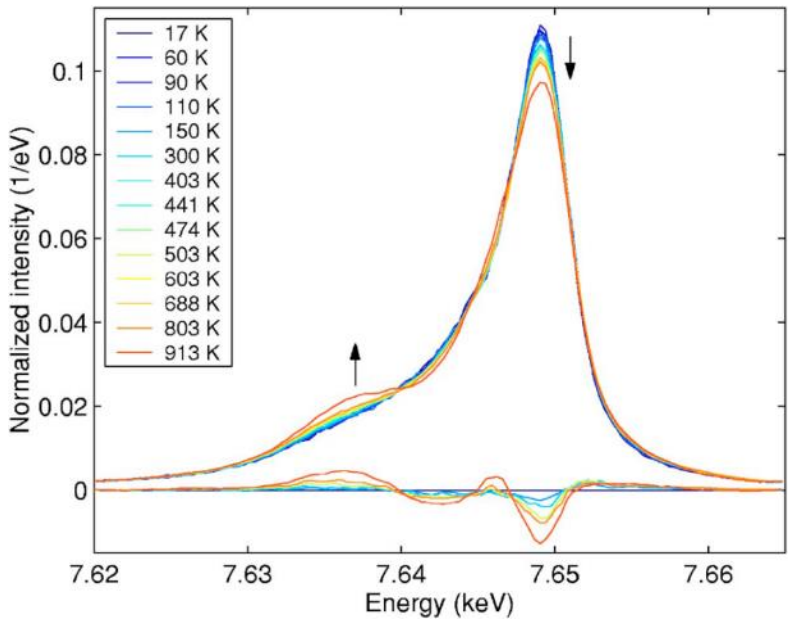
Courtesy of I20-scanning beamline at Diamond Light Source

X-ray emission spectroscopy (XES)

The splitting between $K\beta_{1,3}$ and Kβ' is mainly due to the 3p–3d exchange interaction and thus reflects the spin density located on the transition metal ion



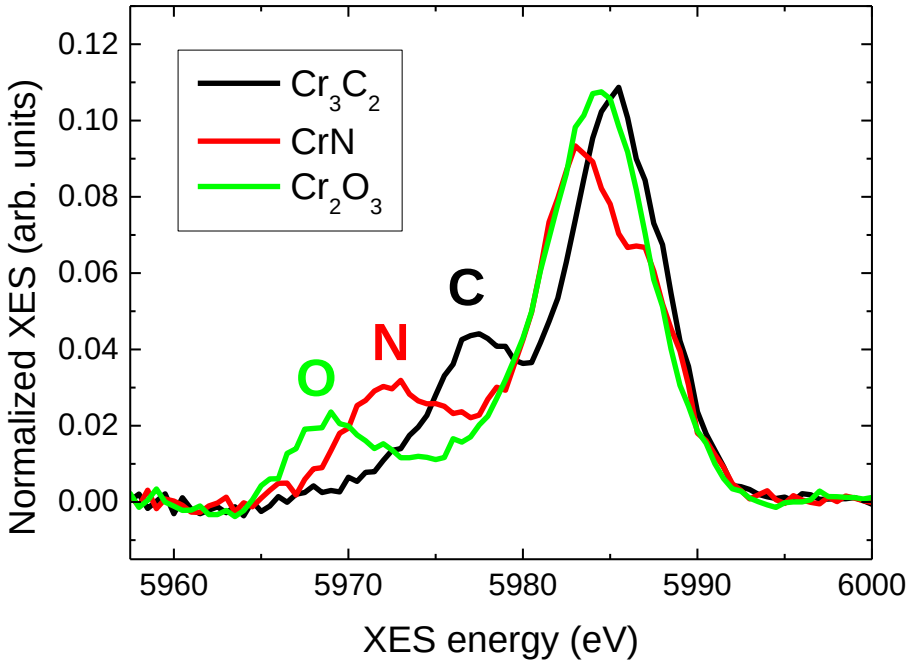
$LaCoO_3$



G. Vanko *et al.*, J. phys. Chem. B **110** (2006) 11647
G. Vanko *et al.*, Phys. Rev. B **73 (2006)** 024424

X-ray emission spectroscopy (XES)

The **valence-to-core X-ray emission** lines are sensitive to the local environment of 3d transition-metal elements

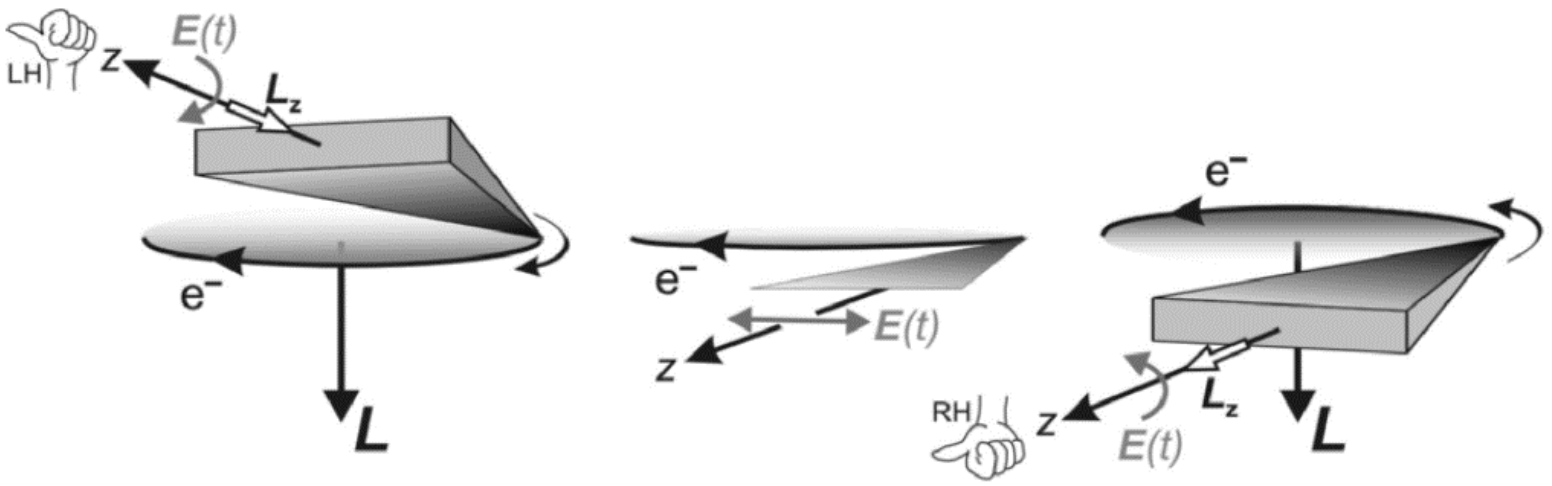


In contrast to EXAFS, valence-to-core XES is able to discriminate between ligands with similar atomic number such as O, N, C, etc. in the first coordination sphere of the metal atom with homogenous ligating atoms.

Courtesy of I20-scanning beamline at Diamond Light Source

X-ray spectroscopy & polarization

Bending magnets

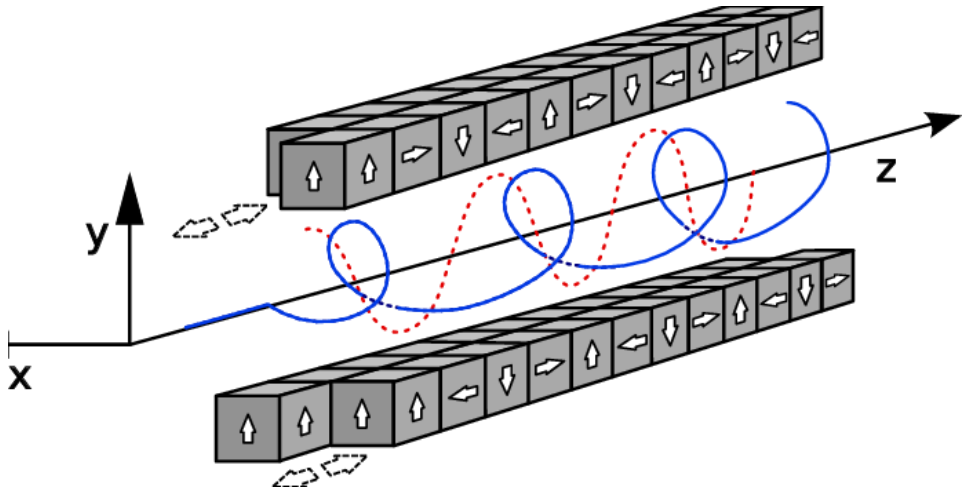


In a similar way, the X-ray polarization depend on the view angle. Thus, the X-ray polarization will depend on "our" position respect to the electron orbit in the storage ring.

J. Stöhr and H.C. Siegmann, Magnetism: From Fundamentals to Nanoscale Dynamics (Springer , 2006)

X-ray spectroscopy & polarization

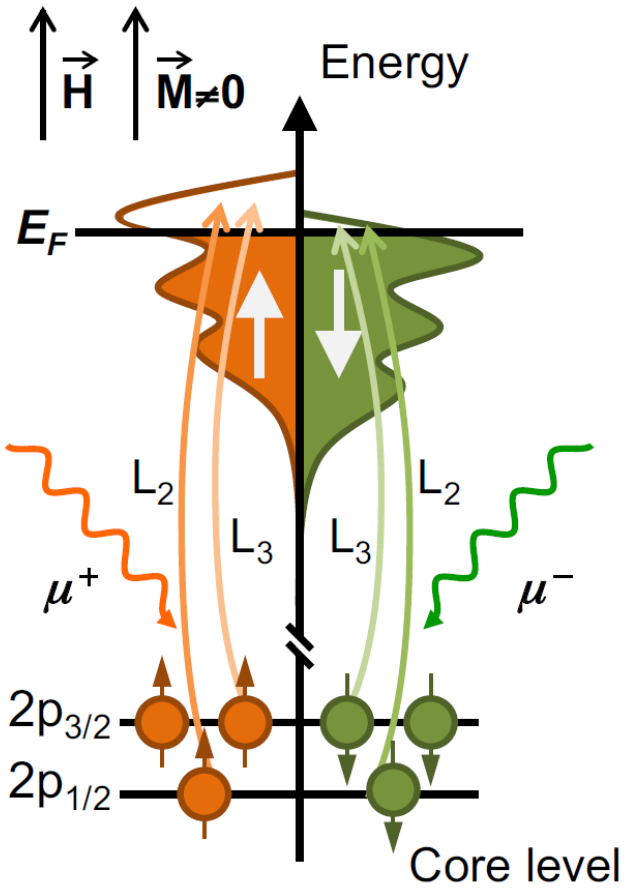
Helical undulator: permanent magnets



The electrons are forced to follow an helical trajectory
(exploiting also the interference effect of the SR light generated)

J. Clarke, Undulator magnet designs, Lecture 4 at Cockcroft Institute (2014)

X-ray magnetic circular dichroism (XMCD)



Circularly polarized light

RIGHT (RCP): $\nu = +1 \longrightarrow \Delta m_l = +1$

LEFT (LCP): $\nu = -1 \longrightarrow \Delta m_l = -1$

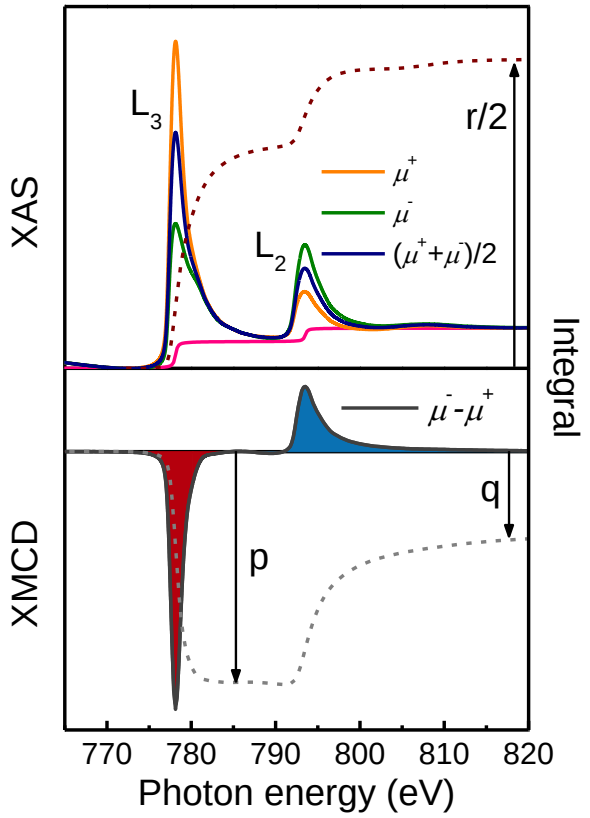
Probing the 3d spin polarized unoccupied valence band.

G. van der Laan, A.I. Figueroa, Coordination Chemistry Reviews 277–278 (2014) 95–129

X-ray magnetic circular dichroism (XMCD)

Magnetic sensitivity

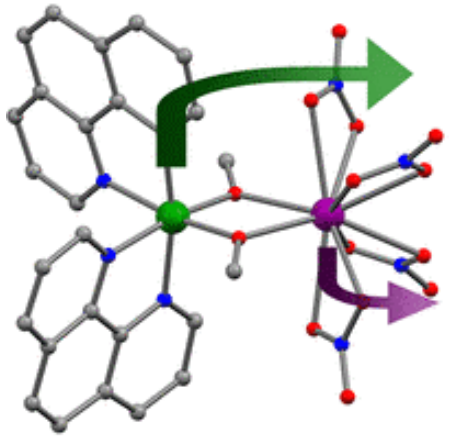
- Spin-dependent absorption of circularly polarised photon
- Maximum when magnetization parallel to X-ray propagation

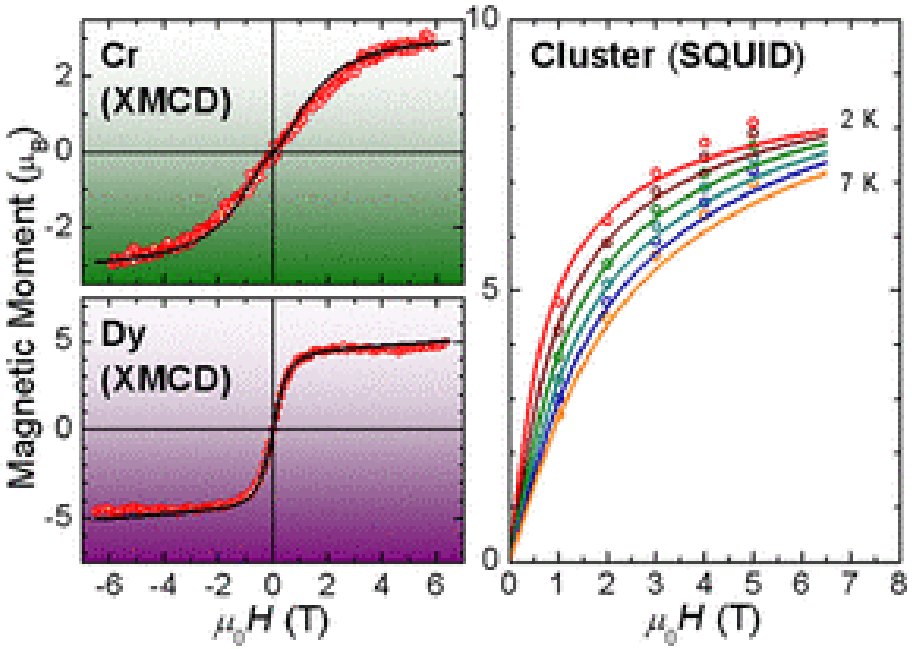


SUM RULES

$$m_L = -\frac{4}{3}\frac{q}{r} n_h$$

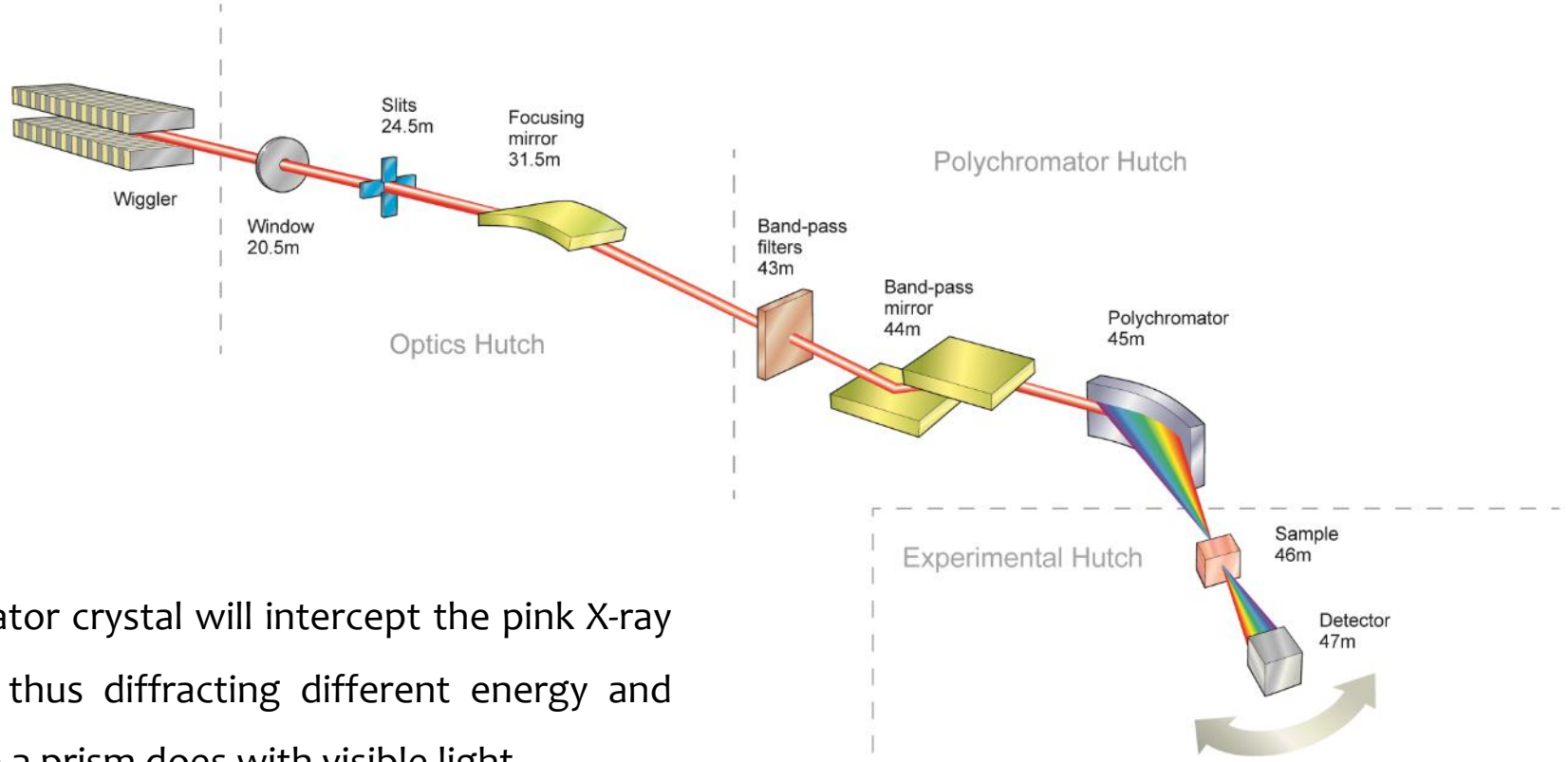
$$m_{S_{\text{eff}}} = -\frac{6p - 4q}{r} n_h$$





G. van der Laan, A.I. Figueroa, Coordination Chemistry Reviews 277–278 (2014) 95–129

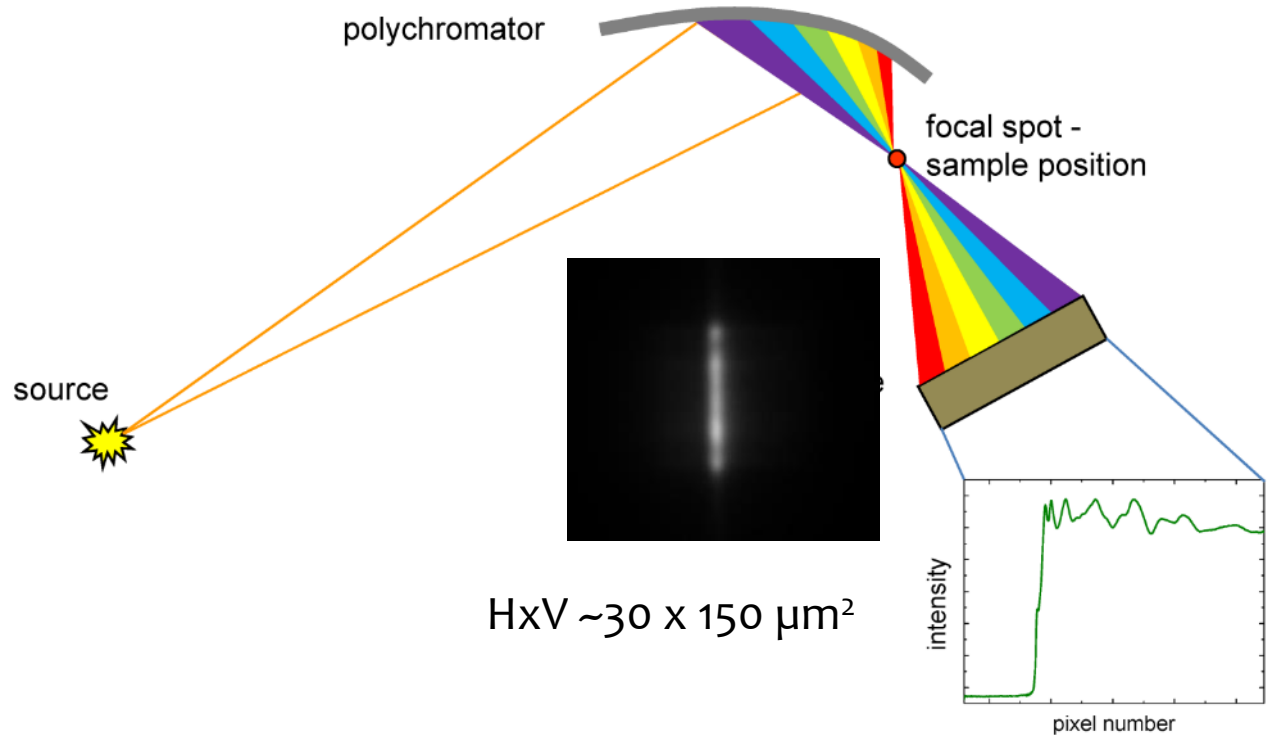
Energy dispersive XAS



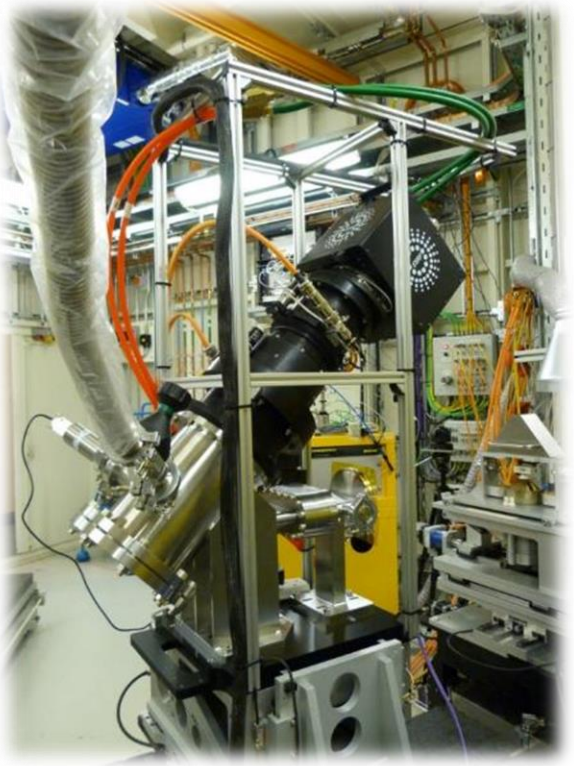
Each point of the polychromator crystal will intercept the pink X-ray beam at a particular angle, thus diffracting different energy and dispersing the X-ray beam like a prism does with visible light.

J. Sutter *et al.*, *Nucl. Instr. and Meth. A*, **621**, p. 627-636 (2010)
https://www.diamond.ac.uk/Instruments/Spectroscopy/Techniques/EDE.html

Energy dispersive XAS



HxV ~30 x 150 µm²

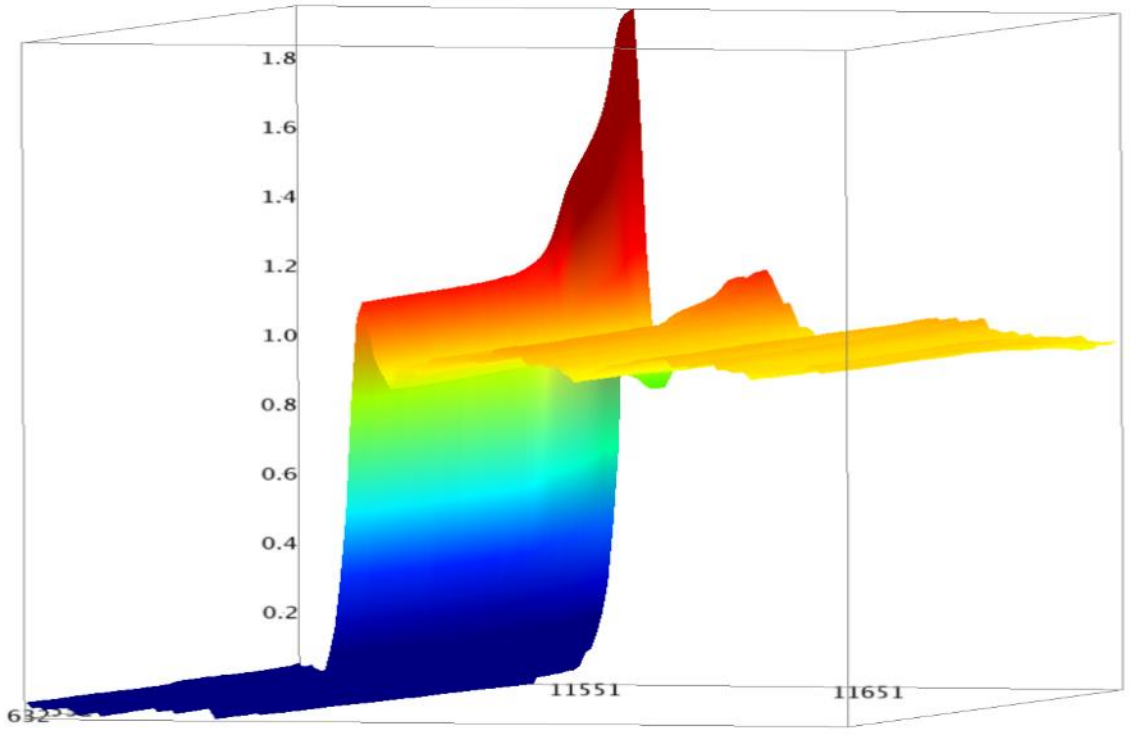


- Phosphor screen → lenses → CCD sensor
- 2048 x 2048 (14µm pixels)
- Phosphor P43, Gd_2O_2S:Tb

Provides a single shoot XAS spectrum (**~ms**) which allows monitoring chemical reactions.

https://www.diamond.ac.uk/Instruments/Spectroscopy/Techniques/EDE.html

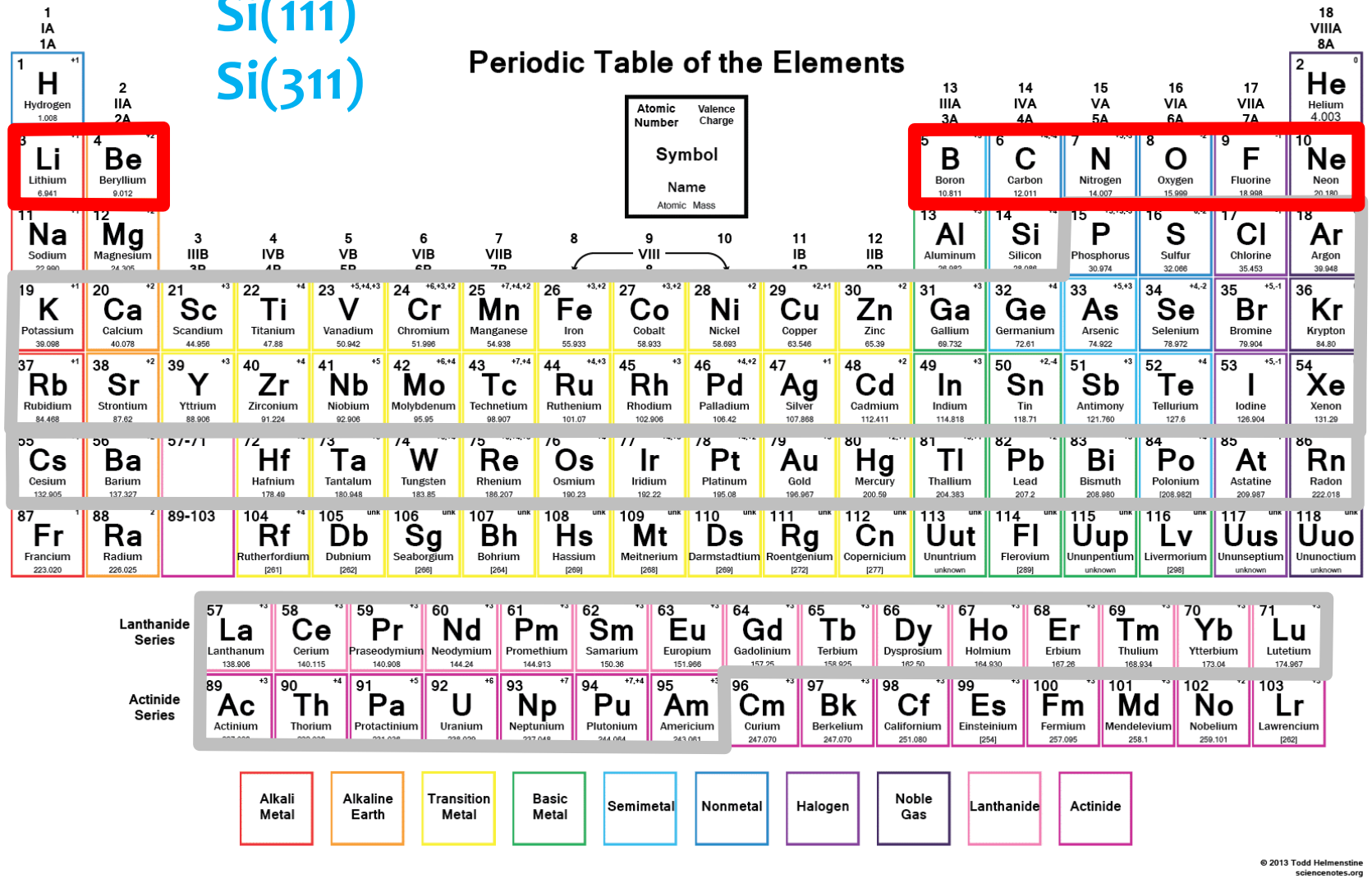
Energy dispersive XAS



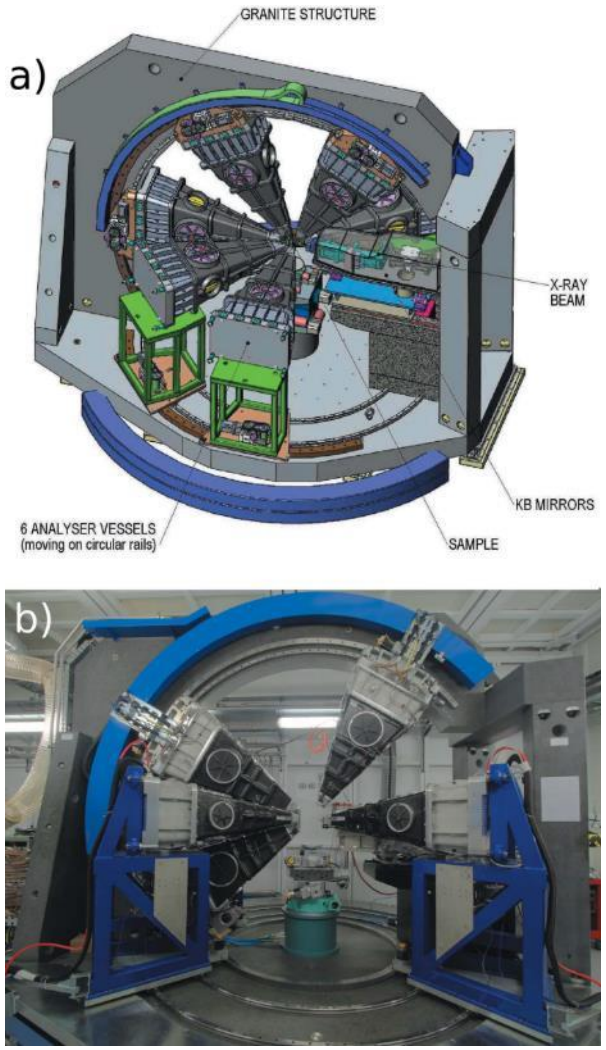
10 minute reaction followed with 1s time resolution

Courtesy of Dr. Tristan Youngs (ISIS, STFC) & I20-EDE beamline (Diamond Light Source)

X-ray Raman scattering: Soft XAS using Hard X-rays

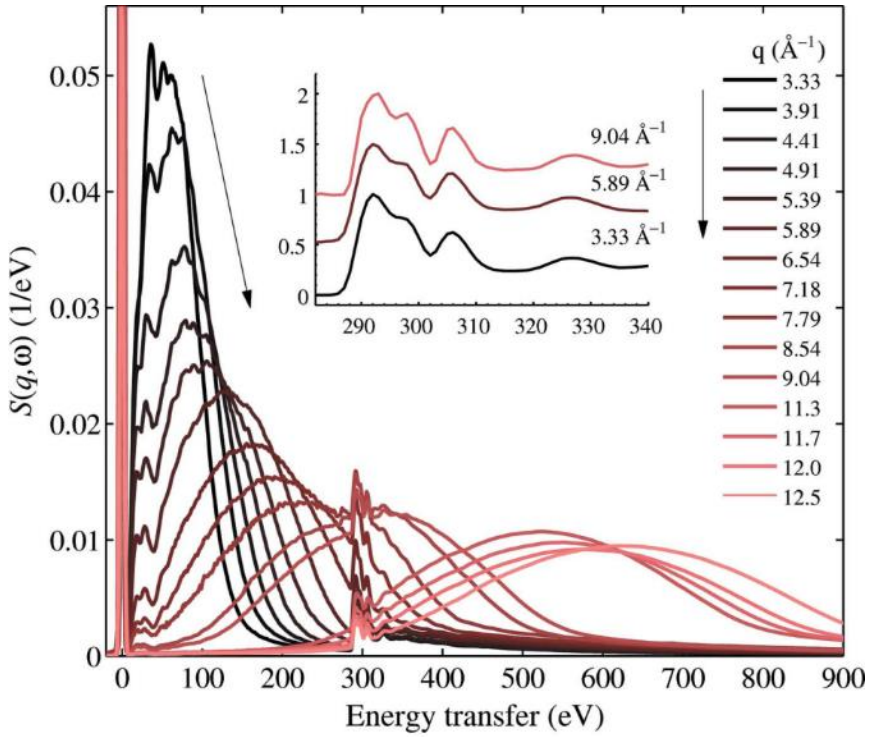


X-ray Raman scattering (XRS): Soft XAS using Hard X-rays



Soft X-ray spectroscopy performed with hard X-ray photons!!!

Exploring the chemical state of lighter atoms with highly penetrating hard X-rays



R. Verbeni et al. J. Synchrotron Rad. 16, 469 (2009) 469

X-ray Raman scattering (XRS): Soft XAS using Hard X-rays

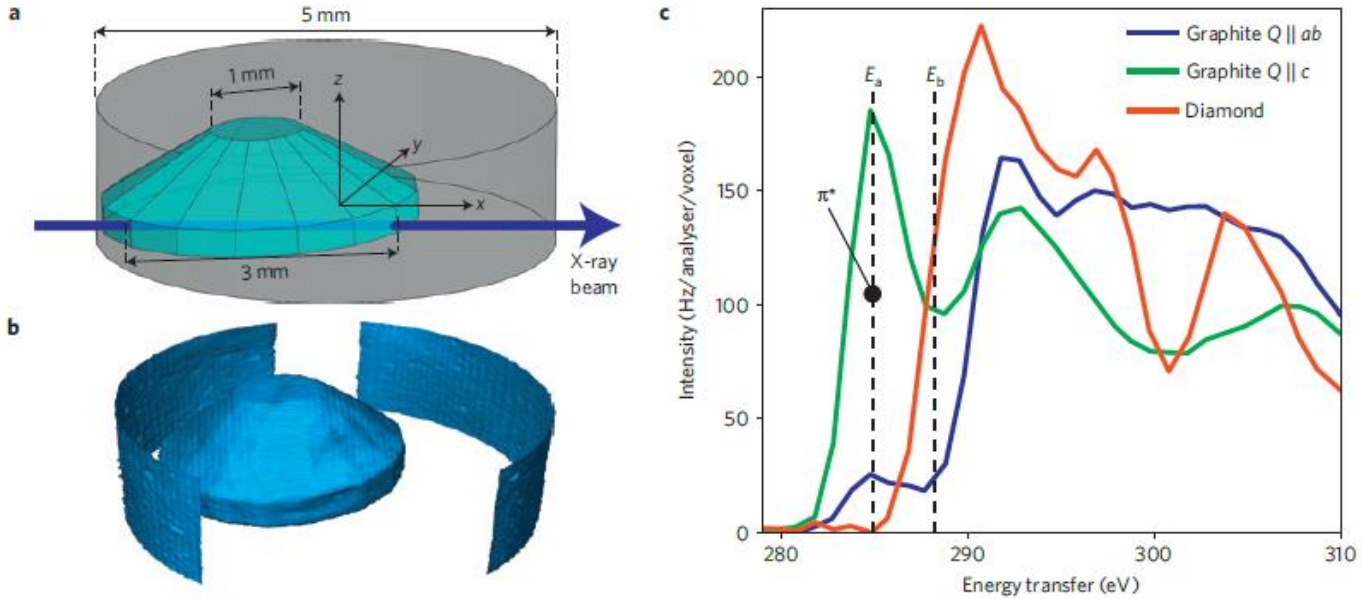
nature materials

LETTERS

PUBLISHED ONLINE: 29 MAY 2011 | DOI: 10.1038/NMAT3031

Direct tomography with chemical-bond contrast

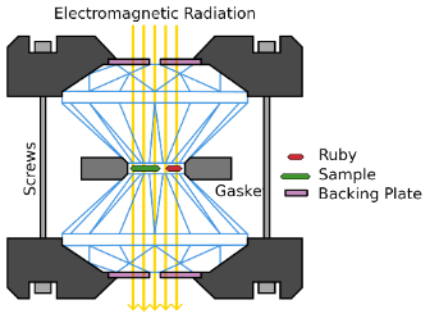
Simo Huotari[1,2]*, Tuomas Pylkkänen[1,2], Roberto Verbeni[1], Giulio Monaco[1] and Keijo Hämäläinen[2]

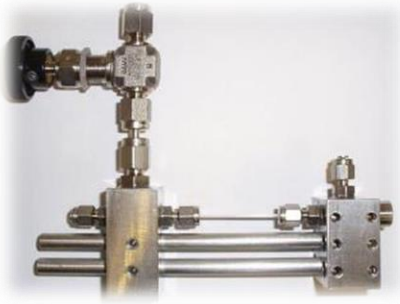


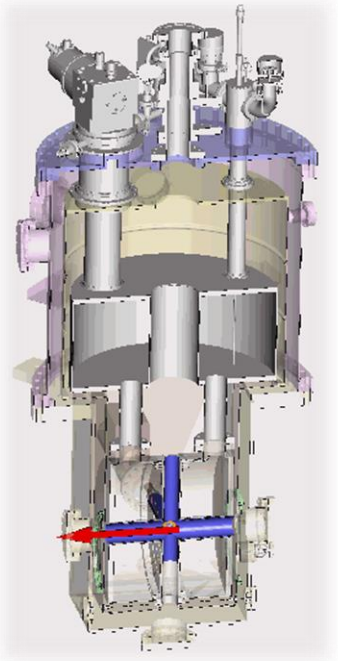
Huotari *et al.* Nature Materials Letters 10 (2011) 489

XAS and XES sample environment

- Liquid N_2 and liquid He cryostats
- Liquid N_2 cryojet for capillary experiments
- IR furnace for X-ray fluorescence measurements
- Gas capillary cell for static measurements
- In-situ gas plug-flow reactor
- Gas portable system (gas mass flow controllers and switching valves)
- Liquid cells for RT and cryostat
- Stopped flow cell for liquid-liquid reactions
- Diamond anvil cells for applying high pressure
- High magnetic fields







X-ray absorption spectroscopy (XAS)

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X-ray absorption spectroscopy (XAS)

TUNTWIN's Workshop

شكرا

Merci!

Thank you!

¡Gracias!

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Email: roberto.boada@uab.cat

Commission européenne

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TUNTWIN