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Joint ICTP-IAEA School on Synchrotron Applications in Cultural Heritage and Environmental Sciences and Multidisciplinary Aspects of Imaging Techniques

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X-Ray Absorption Spectroscopy

G. Pepponi
Centre for Materials and Microsystems
Fondazione Bruno Kessler
Trento
ITALY

Strada Costiera 11, 34151 Trieste, Italy - Tel.+39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it

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Giancarlo Pepponi

Foundazione Bruno Kessler
Centre for Materals and Microssystems
Micro-Nano Anallytical Laboratory
Via Sommarive 18, 38123 Povo (Trento) Italy
tel. +39 0461 314491
www.fbk.eu pepponi@fbk.eu

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Florian Meirer - FBK
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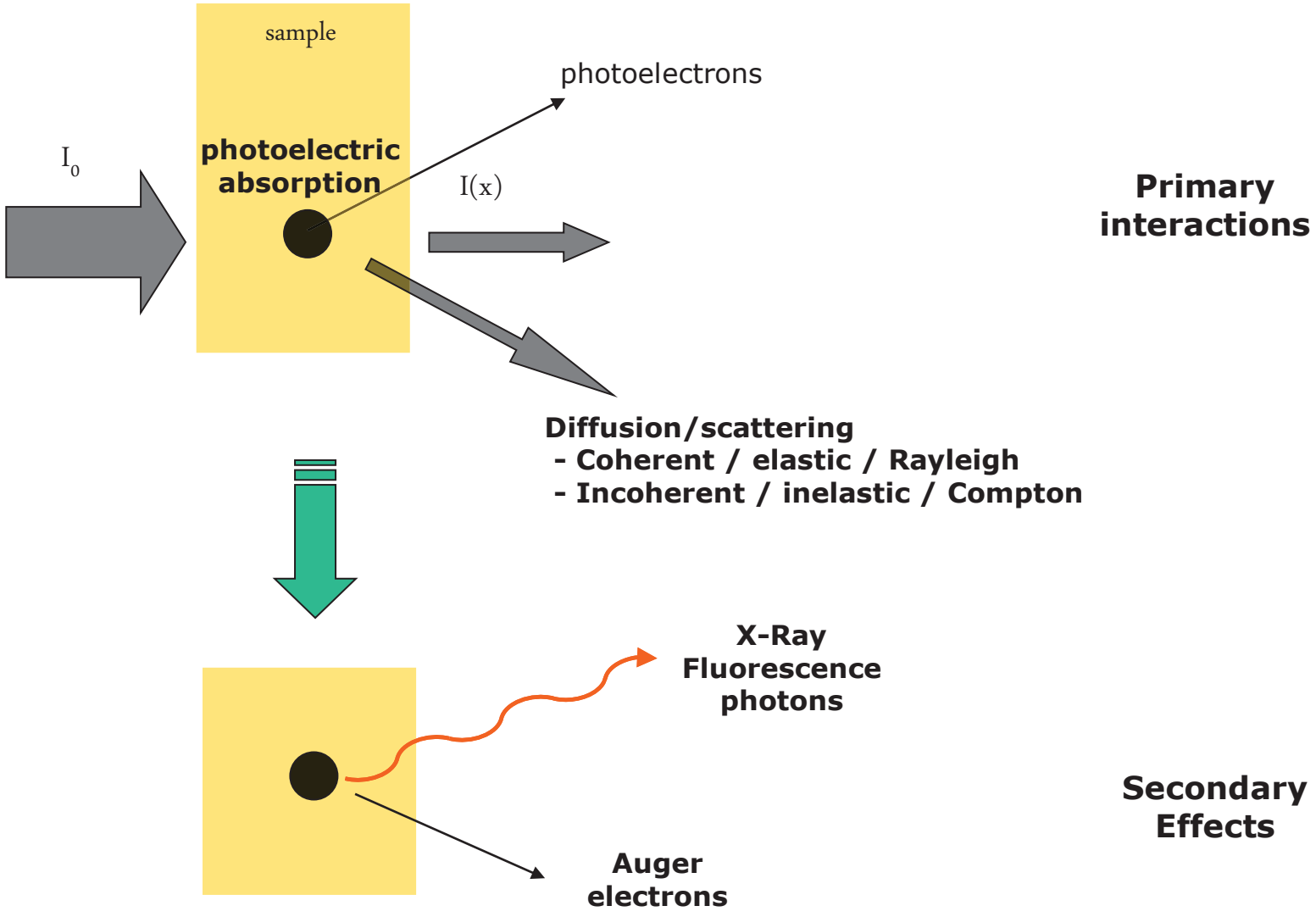
Interaction of X-Rays with matter

Photoelectric effect

Electron energy levels

Interaction of X-Rays with matter

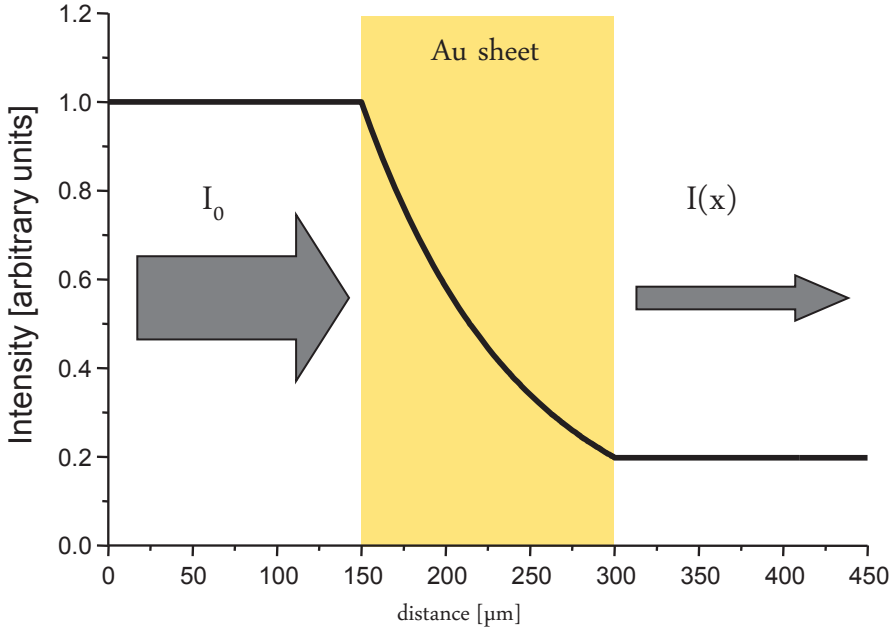


Beer-Lambert´s Law

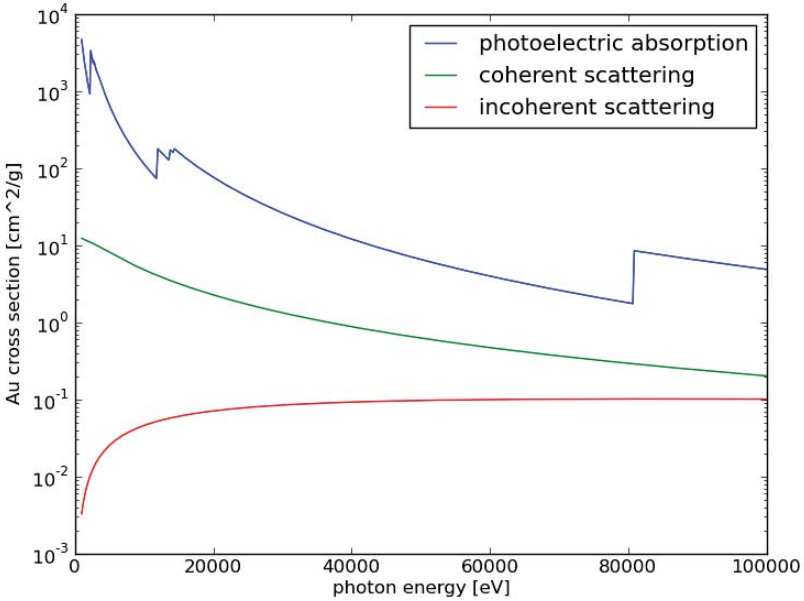
Beer-Lambert´s Law:

$$I(x) = I_0 \exp(-\mu x)$$

$$\mu = \sigma_c + \sigma_i + \tau$$



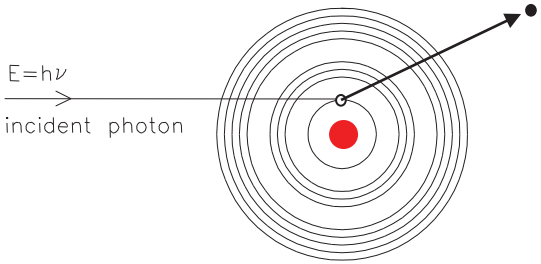
Calculated for E = 17500eV



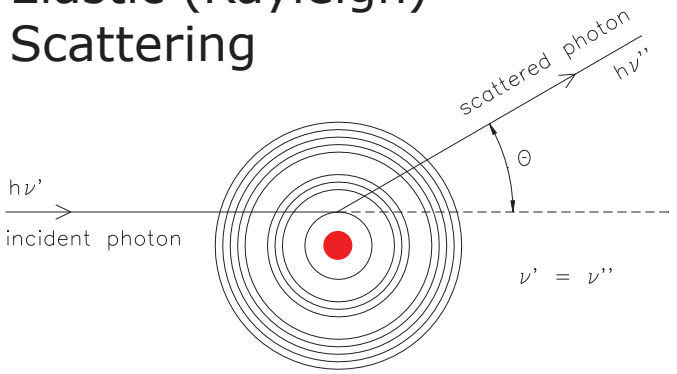
data from:
H. Ebel, R. Svagera, M. F. Ebel, A. Shaltout and J. H. Hubbell, Numerical description of photoelectric absorption coefficients for fundamental parameter programs, X-Ray Spectrometry, 32, 442–451 (2003)

Interactions – microscopic view

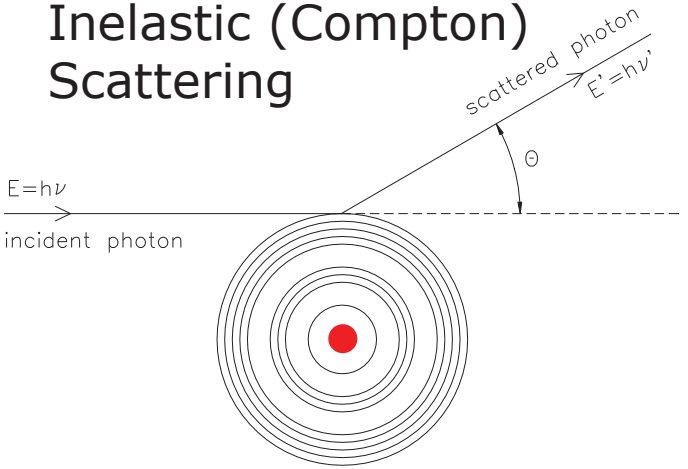
Photoelectric absorption



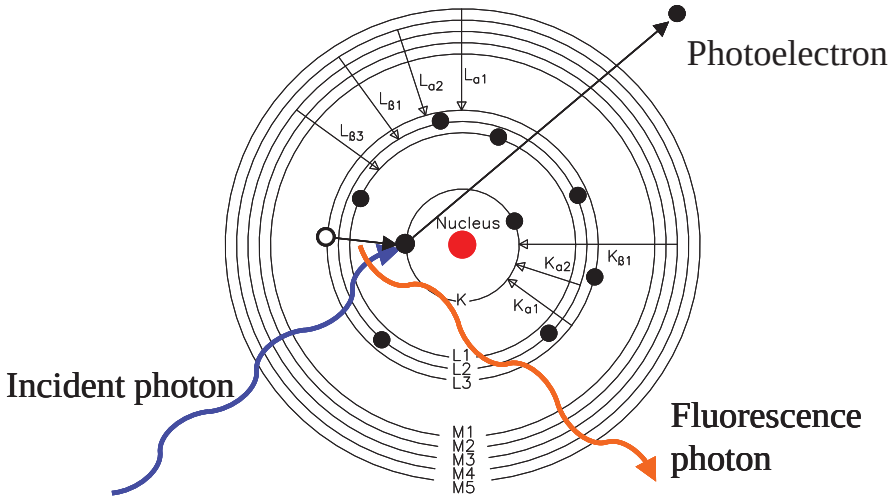
Elastic (Rayleigh) Scattering

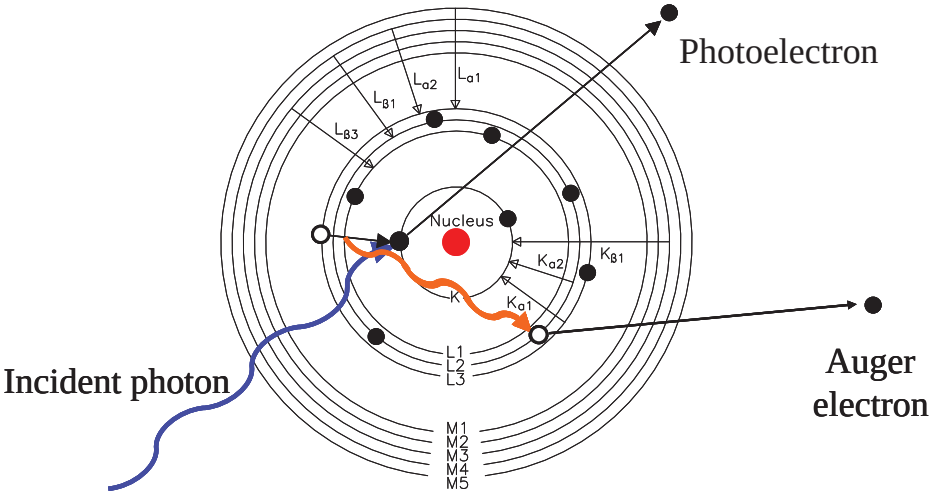


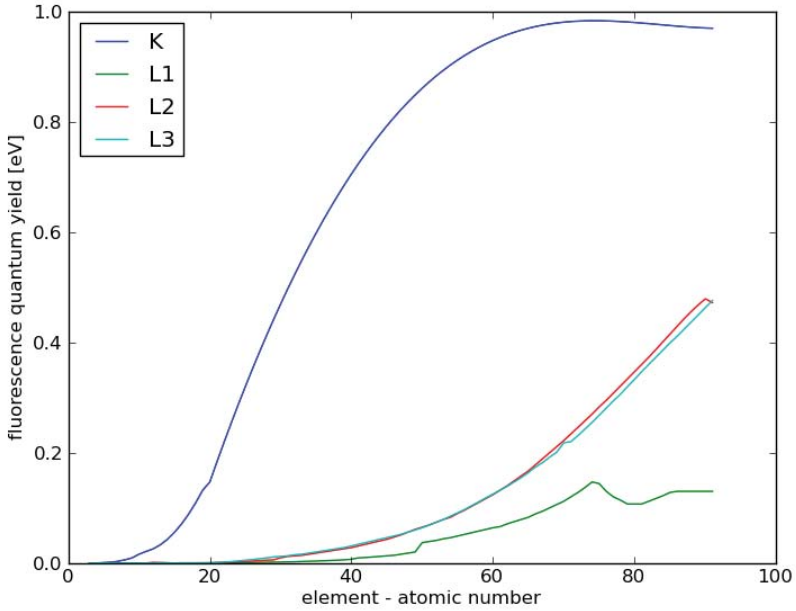
Inelastic (Compton) Scattering



Secondary effects – Fluorescence vs Auger

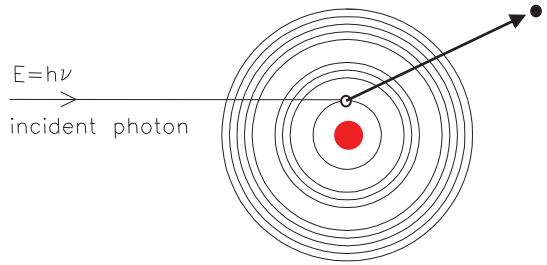






data from:
M. O. Krause,
J. Phys. Chem. Ref. Data 8 (1979) 307

Photoelectric effect – energy levels

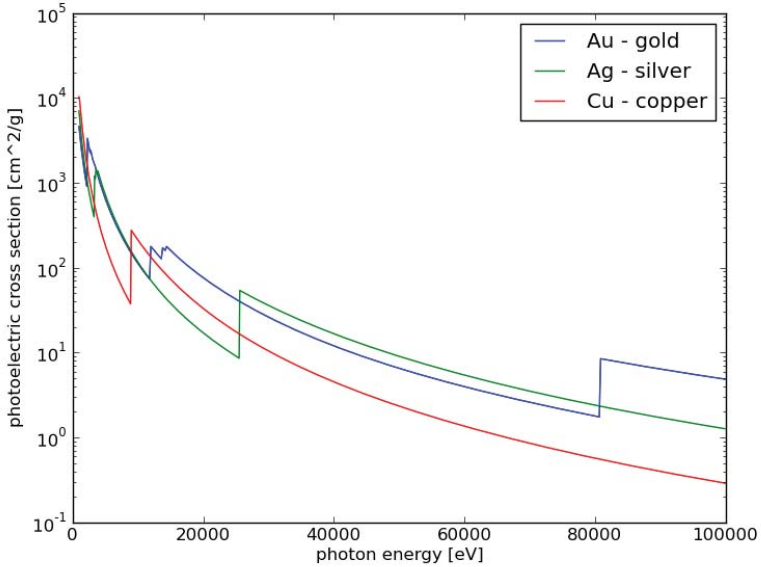


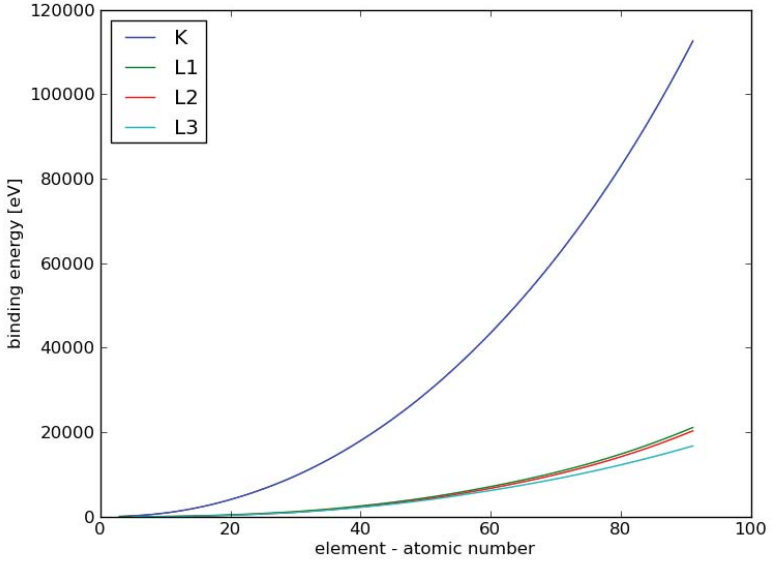
Absorption edges
Electron energy levels
Shells

shell	n	l	j	spin sign	max number of electrons
K	1	0	0.5	1	2
L1	2	0	0.5	1	2
L2	2	1	0.5	-1	2
L3	2	1	1.5	1	4
M1	3	0	0.5	1	2
M2	3	1	0.5	-1	2
M3	3	1	1.5	1	4
M4	3	2	1.5	-1	4
M5	3	2	2.5	1	6

Z	shell	energy_eV	jump	level_width_eV
79	K	80724.9	4.874	52.1
79	L1	14352.8	1.15567	9.8
79	L2	13733.6	1.4	5.53
79	L3	11918.7	2.55	5.54
79	M1	3424.9	1.04	15.0
79	M2	3147.8	1.058	9.5
79	M3	2743.0	1.15776	8.5
79	M4	2291.1	1.07	2.18
79	M5	2205.7	1.092	2.18

www.txrf.org/xraydata





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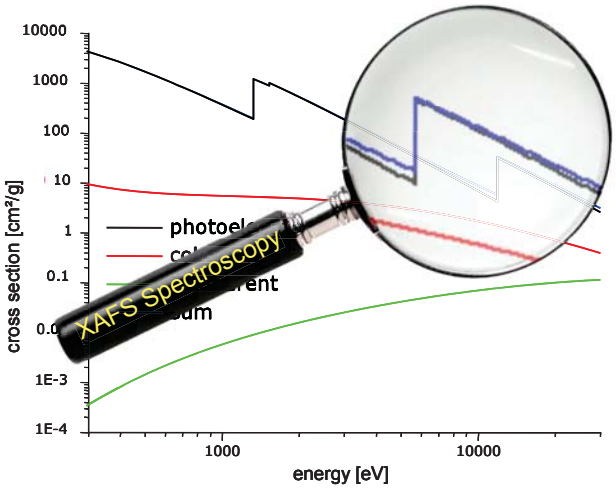
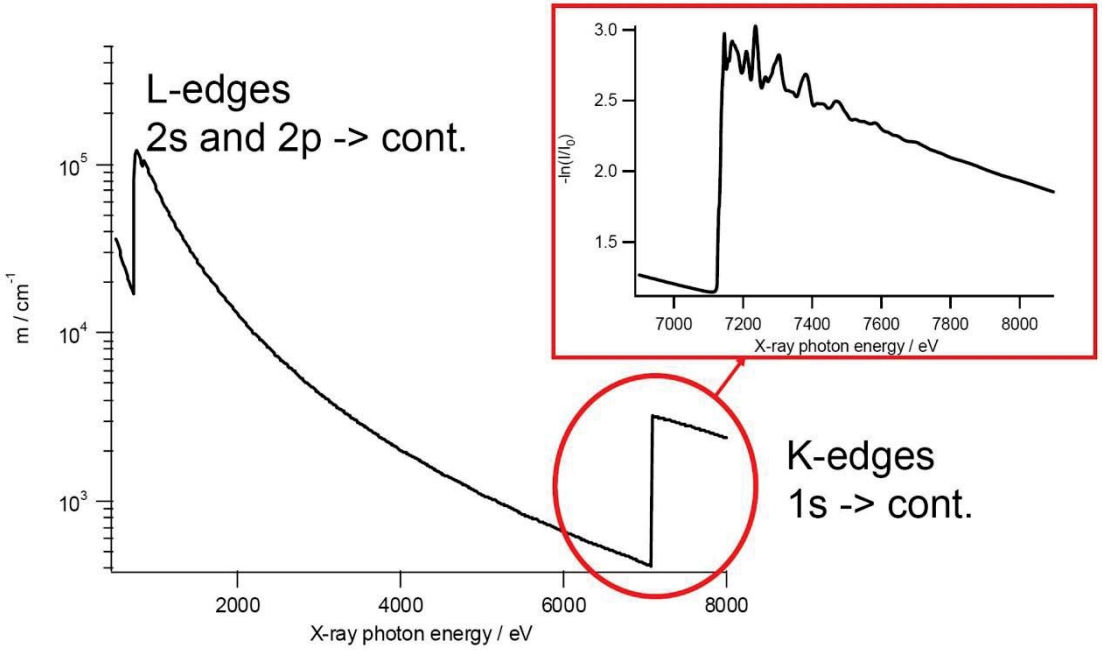
The fine Structure

Phenomenological Overview

Near Edge Fine Structure



The X-ray Absorption Fine Structure (XAFS) of an iron foil



Different phenomena for:

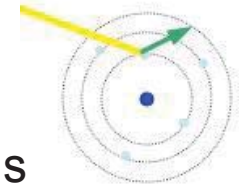
- 'free' atoms
- molecules
- condensed systems

Near Edge Fine Structure – origin - atoms

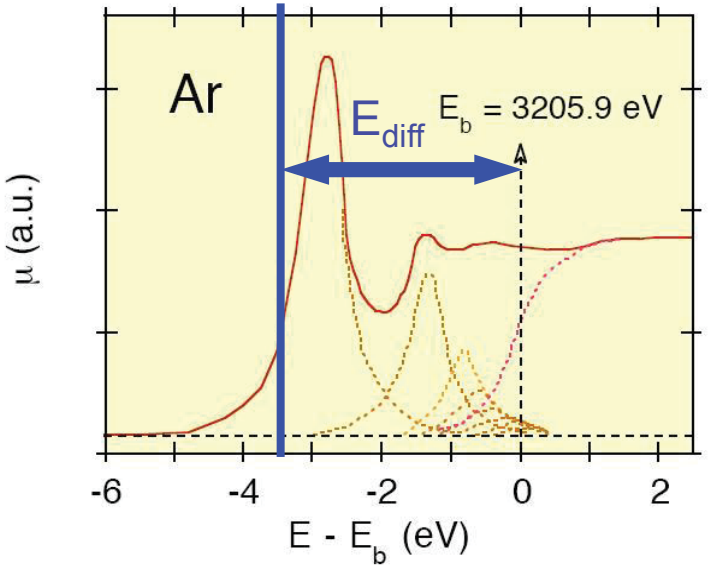
$E_{ph} < E_b$

Core electron

unoccupied levels



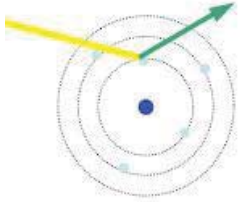
⇨ Edge fine structure



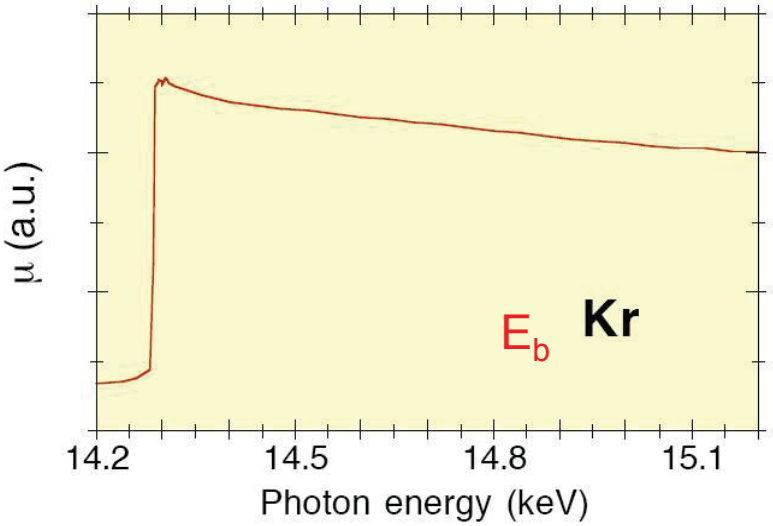
$E_{ph} > E_b$

Core electron

continuum

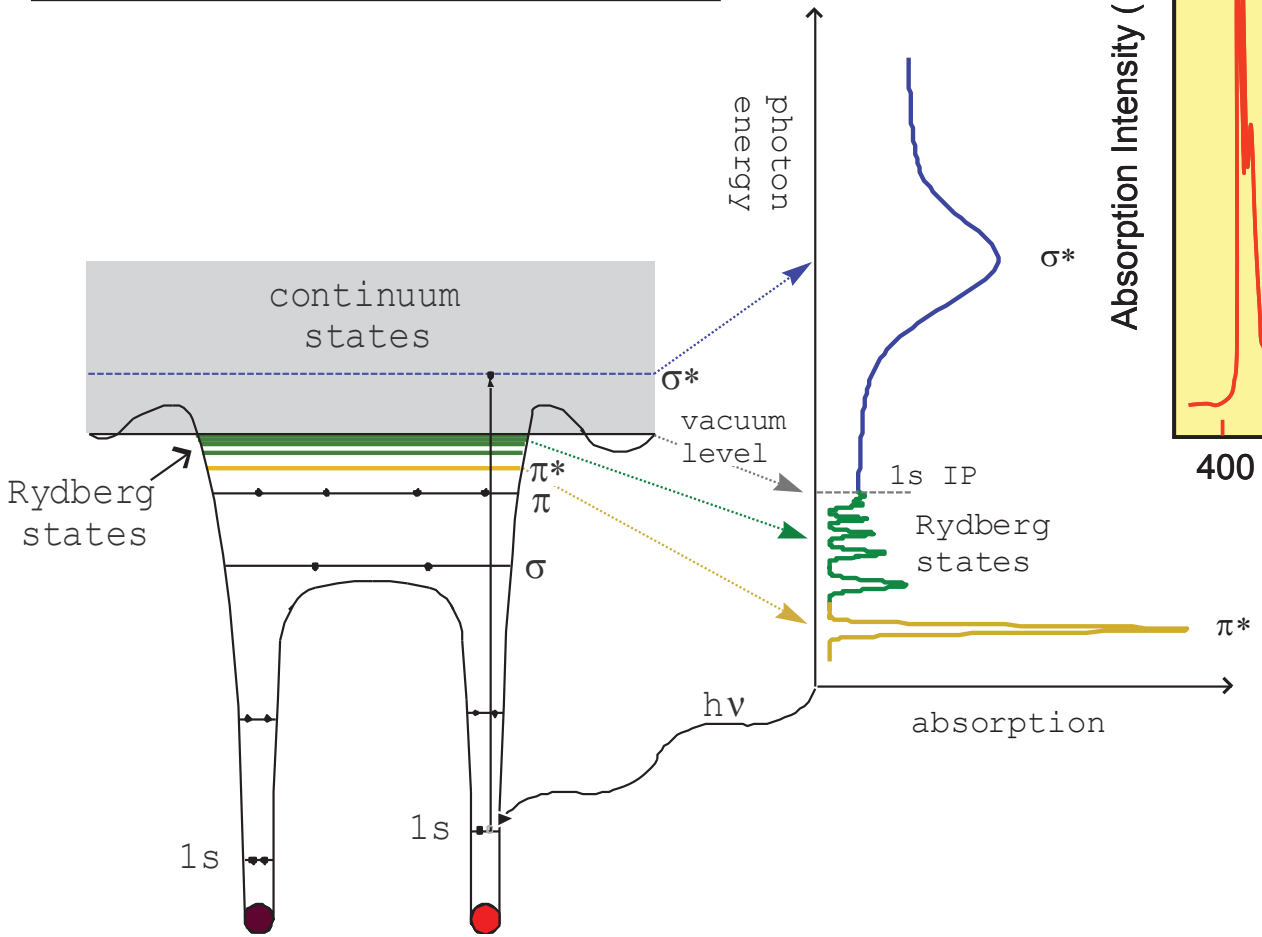


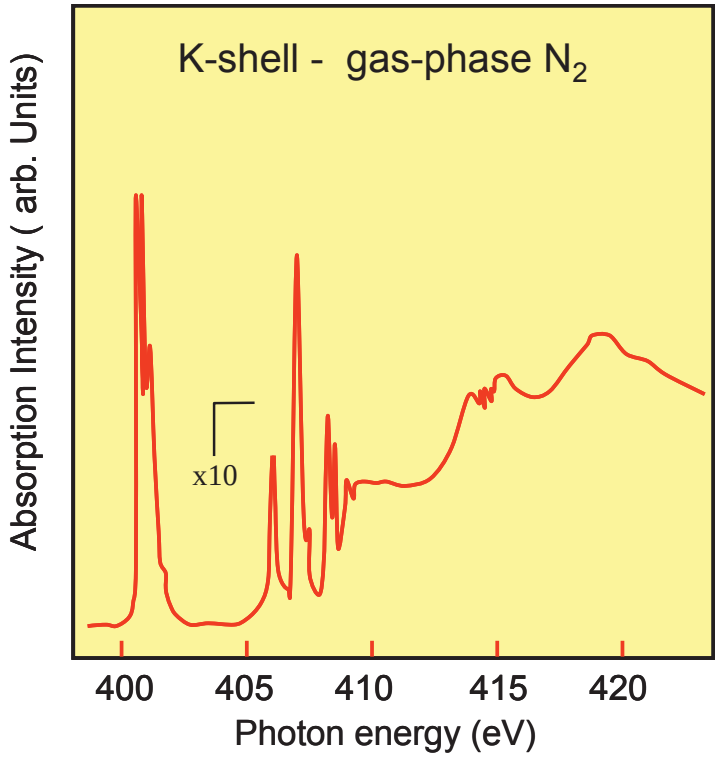
⇨ smooth function



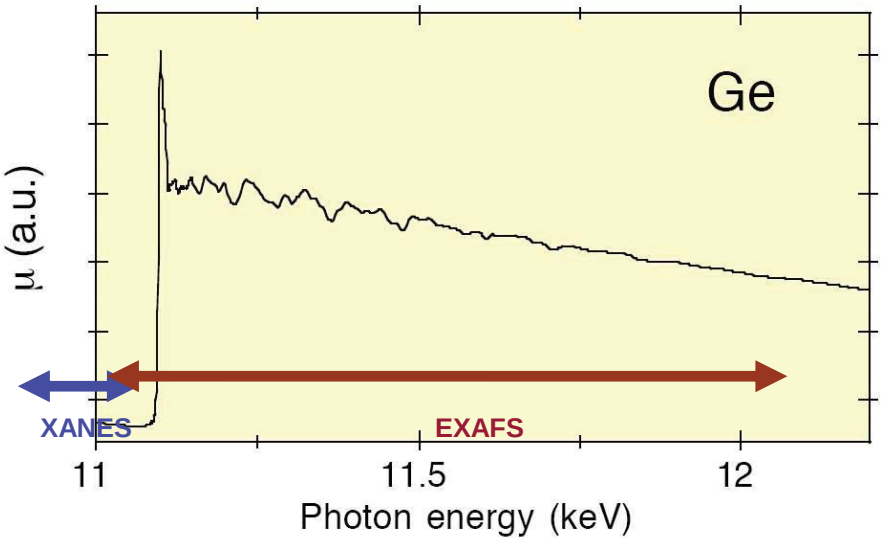
Near Edge Fine Structure – origin - molecules

For molecules the predominant features are unfilled molecular orbitals σ* and π* (resonances).



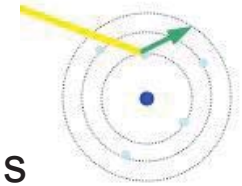


Near Edge Fine Structure – origin
Condensed systems

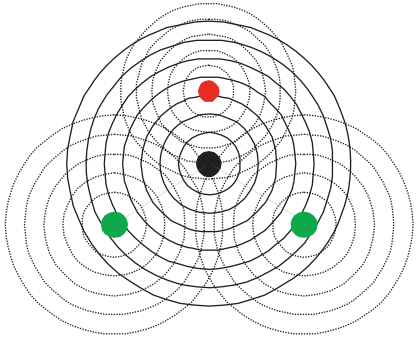


$E_{ph} \sim E_b$

Core electron → unoccupied levels



⇨ Edge fine structure
(XANES or NEXAFS)

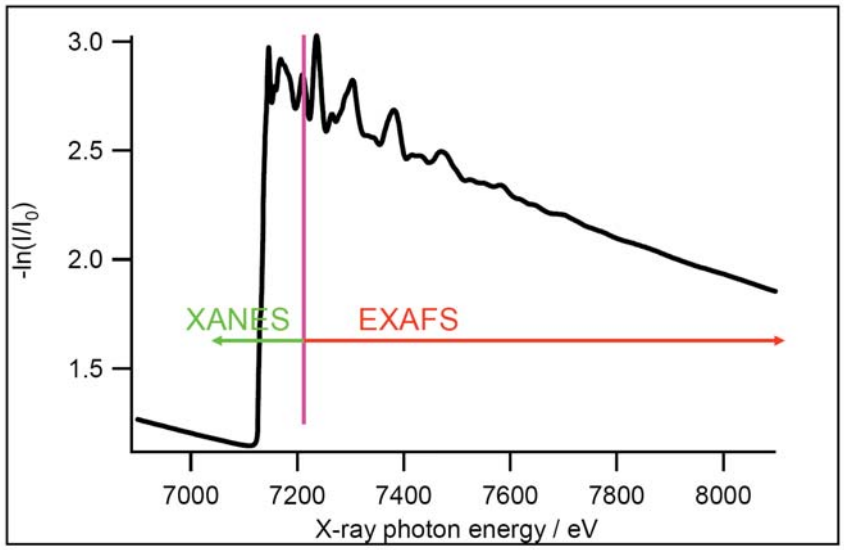


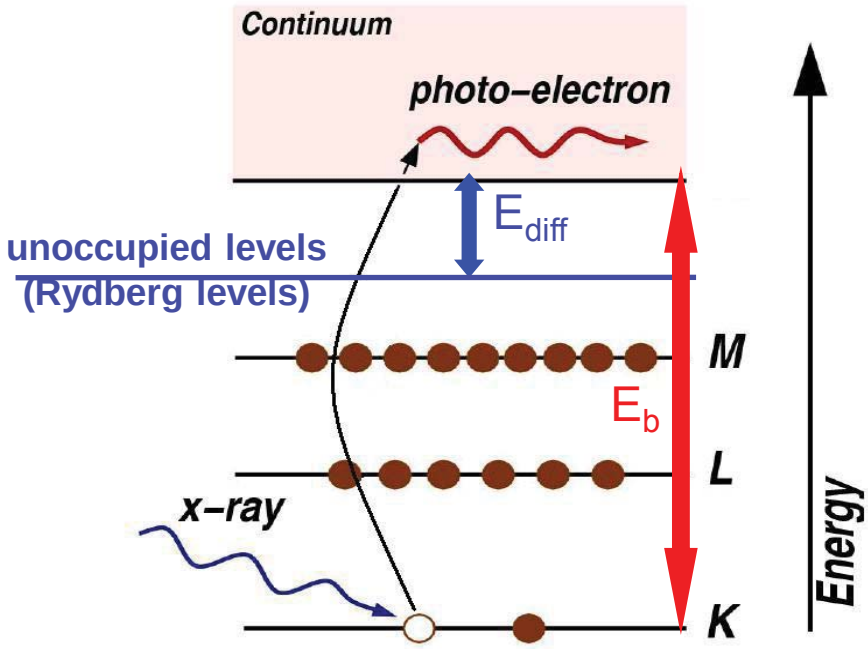
$E_{ph} > E_b$

Core electron → continuum → *outgoing wavefunction* → Backscattering from neighbouring atoms

incoming wavefunction → INTERFERENCE → Extended fine structure (EXAFS)

Near Edge Fine Structure





XANES: **X**-Ray **A**bsorption **N**ear **E**dge **S**tructure, ends 50-100 eV above the edgefd

EXAFS: **E**xtended **X**-Ray **A**bsorption **F**ine **S**tructure, starts 50 - 100 eV above the edge

NEXAFS: **N**ear **E**dge **X**-Ray **A**bsorption **F**ine **S**tructure, typically used for moleules and the soft x-ray range

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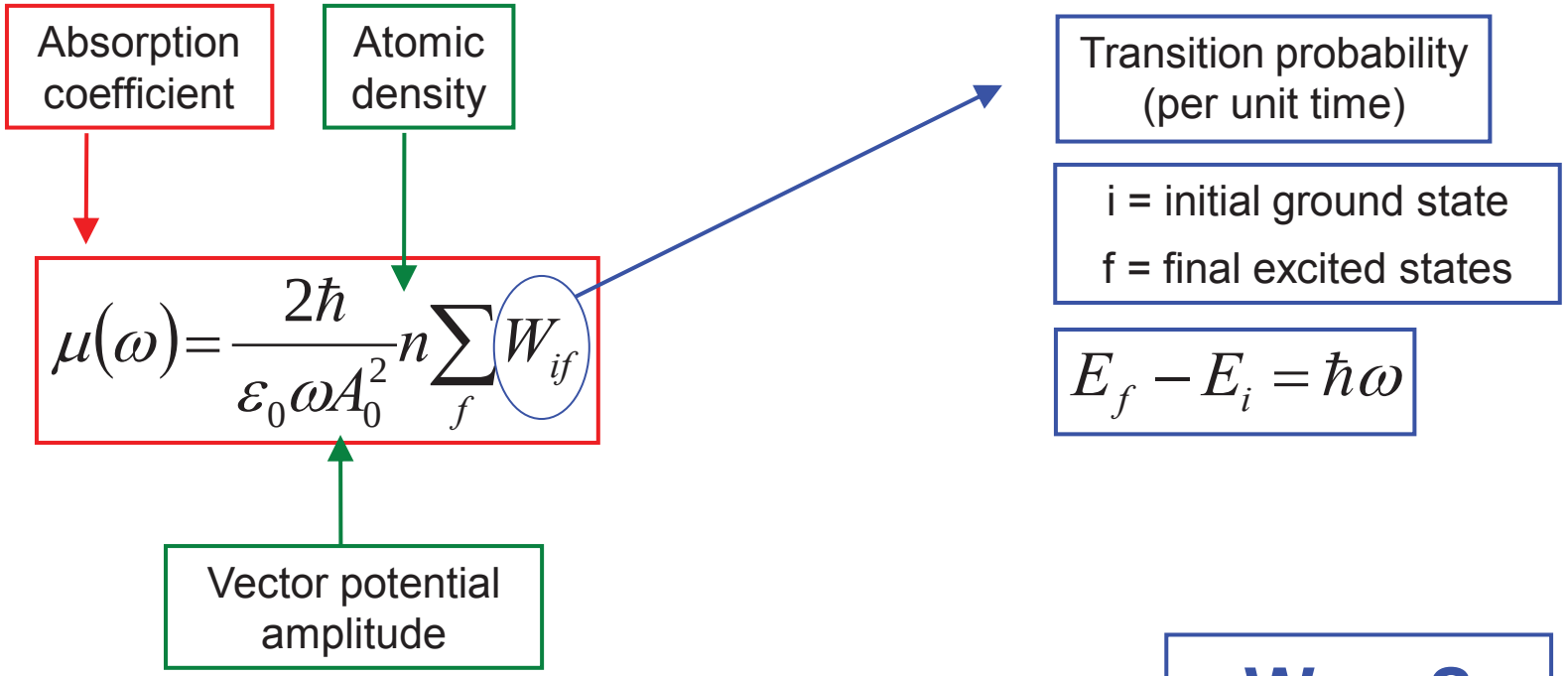
Near Edge Fine Structure

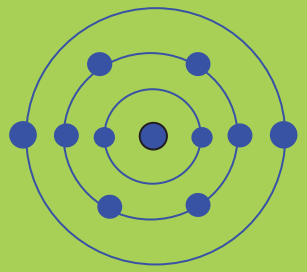
Theoretical description

XAS theory – absorption coefficient



XAS theory – transition probability

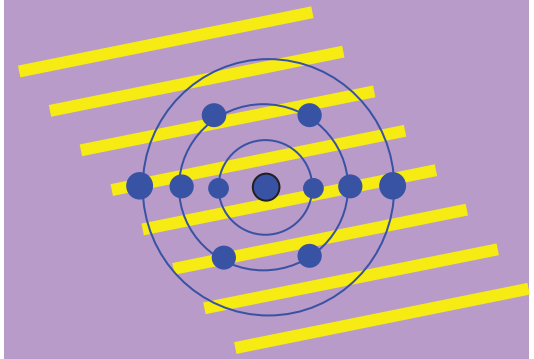
Initial atomic state



$|\Psi_i\rangle$

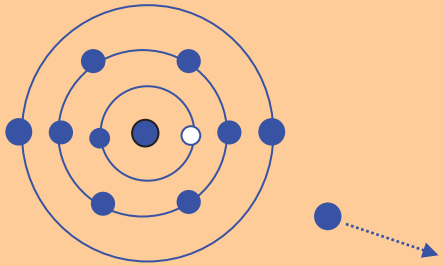
Stationary ground state

Interaction



$|\Psi(t)\rangle$

Final atomic state



$|\Psi_f\rangle$

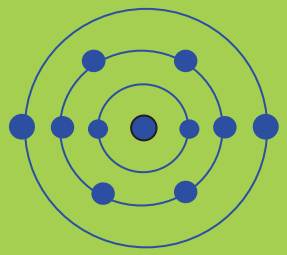
Stationary excited state

$W_{if} = ?$

Fermi Golden Rule

Time-dependent perturbation theory (1st-order)

Initial atomic state



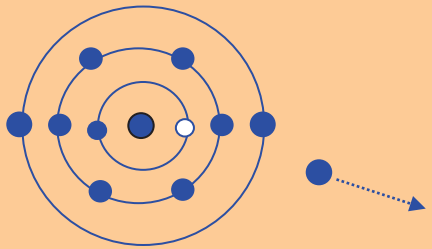
$|\Psi_i\rangle$

Stationary ground state

H_I

Interaction with e.m. field

Final atomic state



$|\Psi_f\rangle$

Stationary excited state

EXAFS **XANES**

$$W_{if} \propto \left| \langle \Psi_i | H_I | \Psi_f \rangle \right|^2 \rho(E_f)$$

matrix element

density of final states

$$E_f - E_i = \hbar\omega$$

Interaction Hamiltonian

Coulomb gauge

$$\vec{\nabla}\cdot\vec{A}=0 \qquad \vec{E}=\partial\vec{A}/\partial t$$
$$\Phi=0 \qquad \vec{B}=\vec{\nabla}\times\vec{A}$$
$$\vec{J}=0 \qquad \vec{\nabla}\cdot\vec{A}=\vec{A}\cdot\vec{\nabla}$$

Sum over electrons

$$\hat{H}_I=\sum_j\left[\frac{e}{m}\vec{p}_j\cdot\vec{A}(r_j,t)-\frac{e^2}{2m}A^2(r_j,t)\right]$$

$$\vec{A}=A_0\hat{\eta}e^{i(\vec{k}\cdot\vec{r}-\omega t)}+c.c.$$

$$W_{if}=\frac{\pi\hbar e^2}{m^2}|A_o|^2\left|\left\langle\Psi_i\left|\sum_j e^{i\vec{k}\cdot\vec{r}_j}\,\hat{\eta}\cdot\vec{\nabla}_j\right|\Psi_f\right\rangle\right|^2\rho(E_f)$$

One electron approximation

$$\mu_{tot}(\omega) = \mu_{el}(\omega) + \mu_{inel}(\omega)$$

- 1 core electron excited
- N-1 passive electrons relaxed

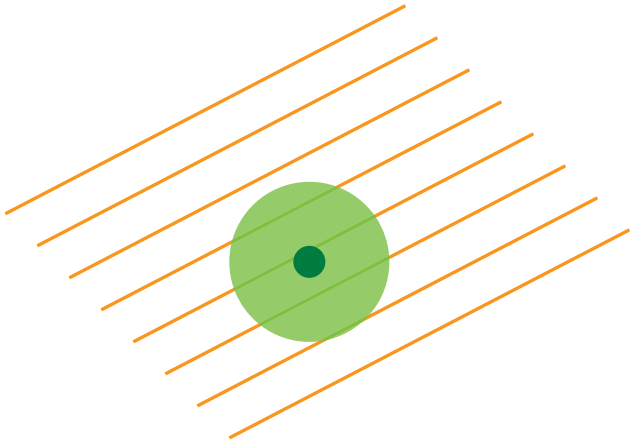
→ EXAFS coherent signal

- 1 core electron excited
- Other electrons excited

$$\mu_{el}(\omega) \propto \left| \left\langle \Psi_i^{N-1} \psi_i \right| e^{i\vec{k}\cdot\vec{r}} \hat{\eta} \cdot \vec{p} \left| \psi_f \Psi_f^{N-1} \right\rangle \right|^2 \rho(\varepsilon_f)$$

Electron dipole approximation

$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{r} - \ldots \approx 1$$

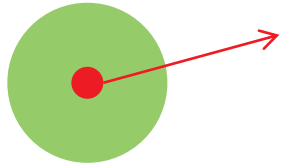


$$H_I \propto e^{i\vec{k}\cdot\vec{r}}\,\hat{\eta}\cdot\vec{p} \approx \hat{\eta}\cdot\vec{p} = \omega^2\,\hat{\eta}\cdot\vec{r}$$

$$\mu_{\mathrm{el}}(\omega) \propto \left|\left\langle \Psi_i^{N-1}\psi_i \right|\,\hat{\eta}\cdot\vec{r}\,\left|\psi_f \Psi_f^{N-1}\right\rangle\right|^2$$

Sudden approximation

No interaction between photoelectron and passive electrons



$$\left|\Psi^{N-1}\psi\right\rangle = \left|\Psi^{N-1}\right\rangle\left|\psi\right\rangle$$

1 active electron — N-1 passive electrons

$$\mu_{\mathrm{el}}(\omega) \propto \left|\langle\psi_i|\hat{\eta}\cdot\vec{r}|\psi_f\rangle\right|^2 \rho(\varepsilon_f)\left|\langle\Psi_i^{N-1}|\Psi_f^{N-1}\rangle\right|^2$$

$$S_0^2 \approx 0.6 \div 0.9$$

Structural information

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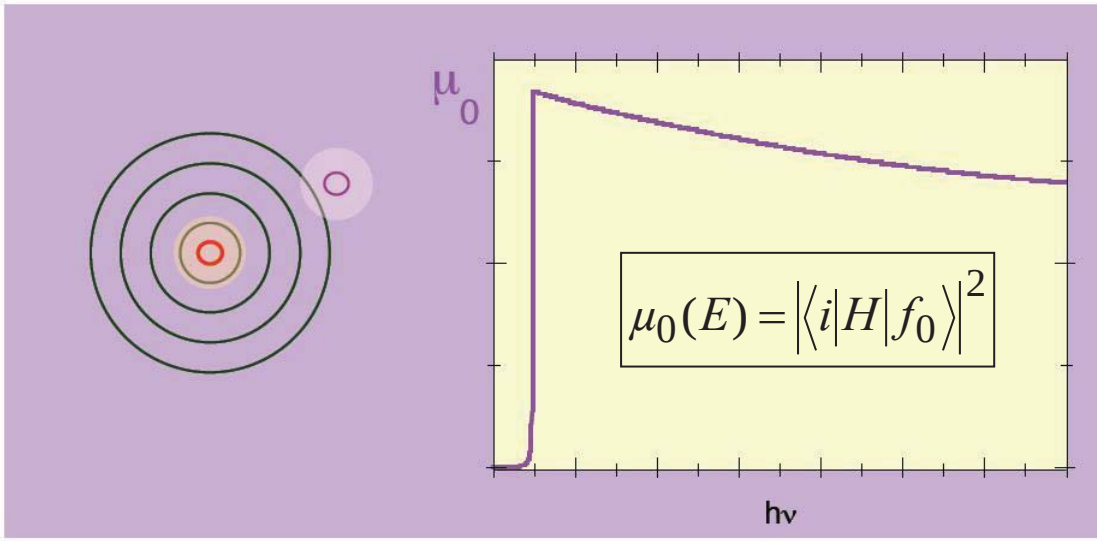
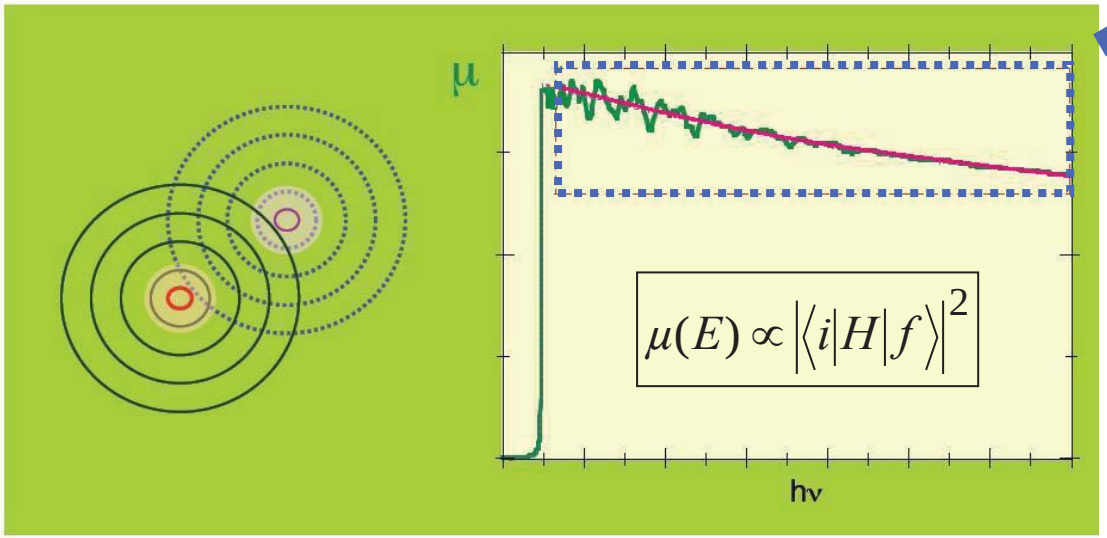
X-Ray Absorption Fine Structure

Perturbation of the absorption phenomena

The photoelectron is the real probe

the EXAFS function





EXAFS fine-structure function:

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

usually transformed to k-space with:

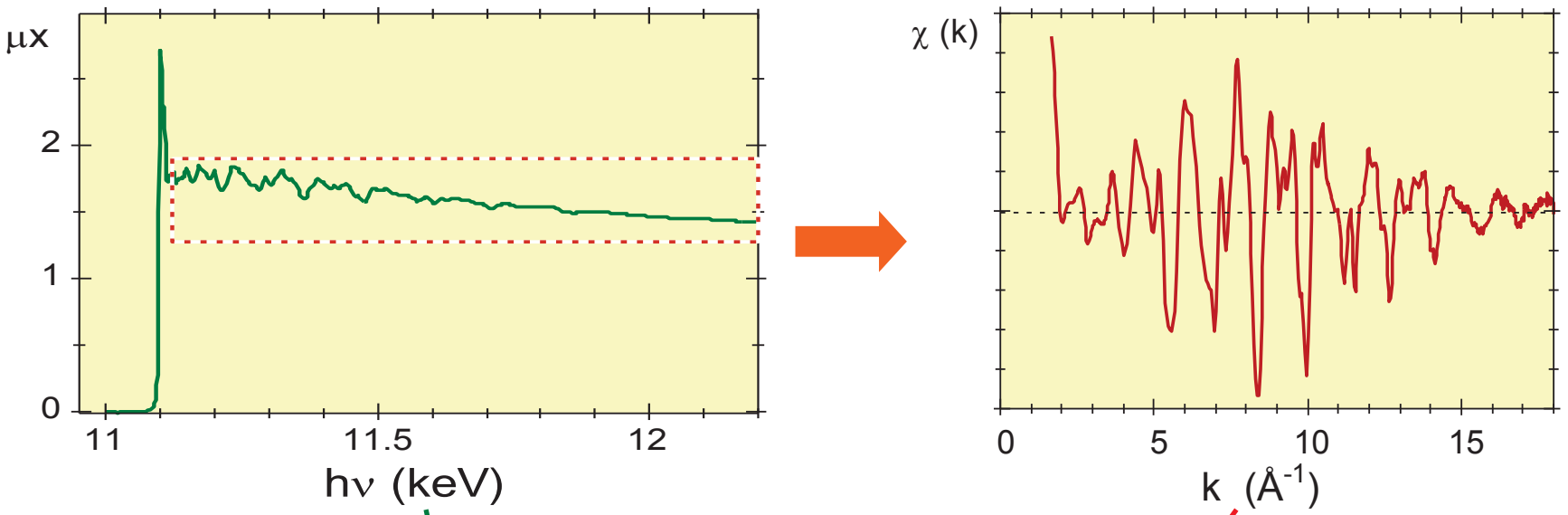
$$k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}}$$

k……photo electron wavenumber

m_e…..mass of electron

E_0…..binding energy

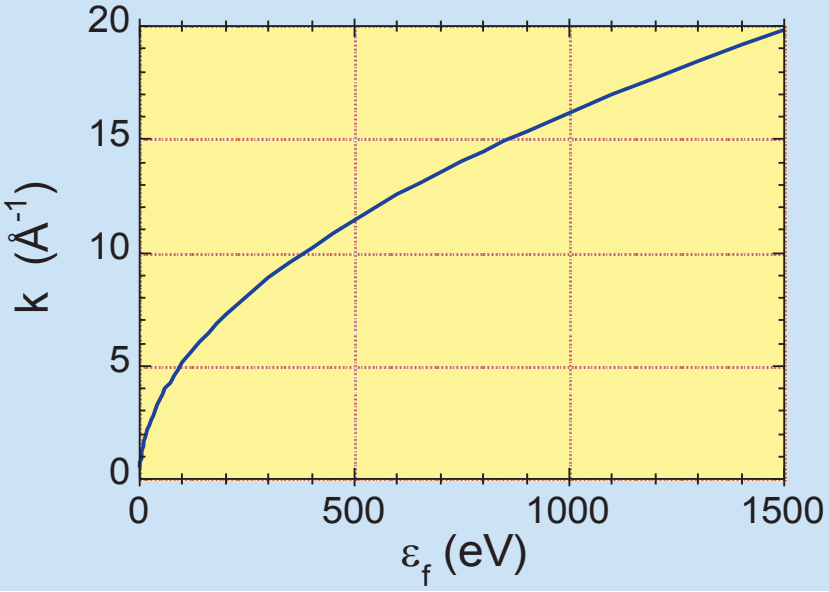
Photon ➔ photoelectron



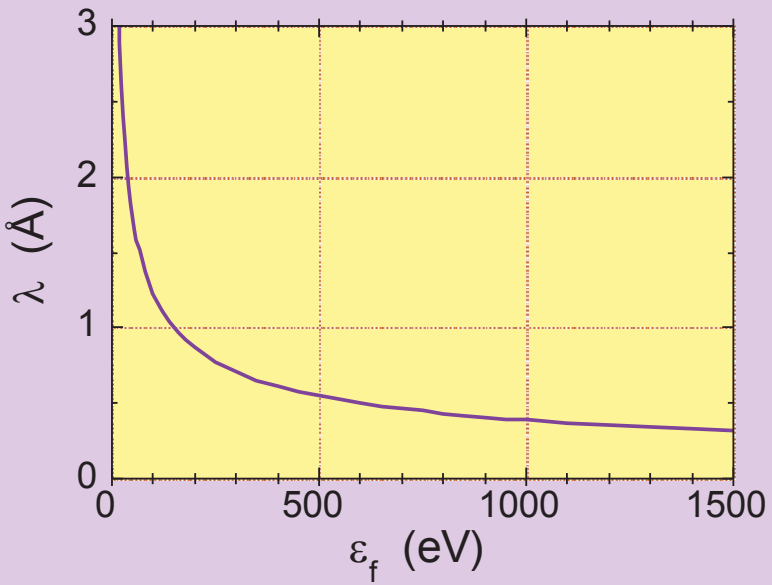
$$\sqrt{\frac{2m}{\hbar^2}(h\nu - E_b)} = \sqrt{\frac{2m}{\hbar^2}\varepsilon} = k = \frac{2\pi}{\lambda}$$

the photoelectron

Wave-number



Wave-length



Energy

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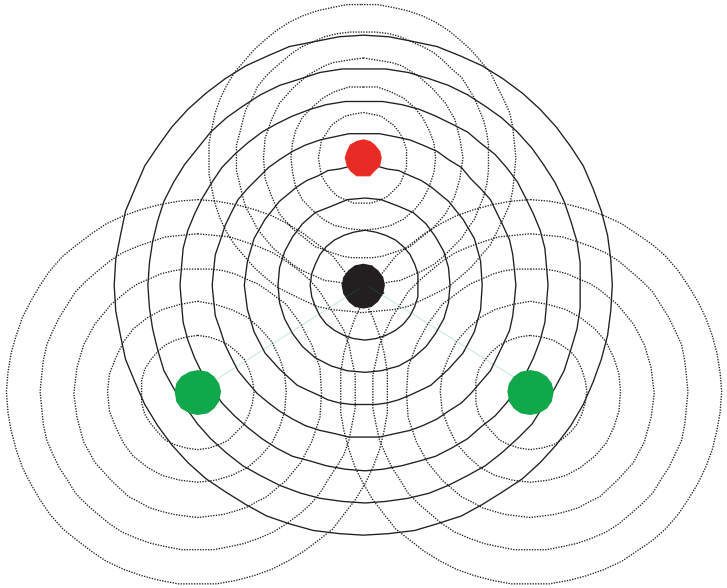
the near EDGE region
XANES

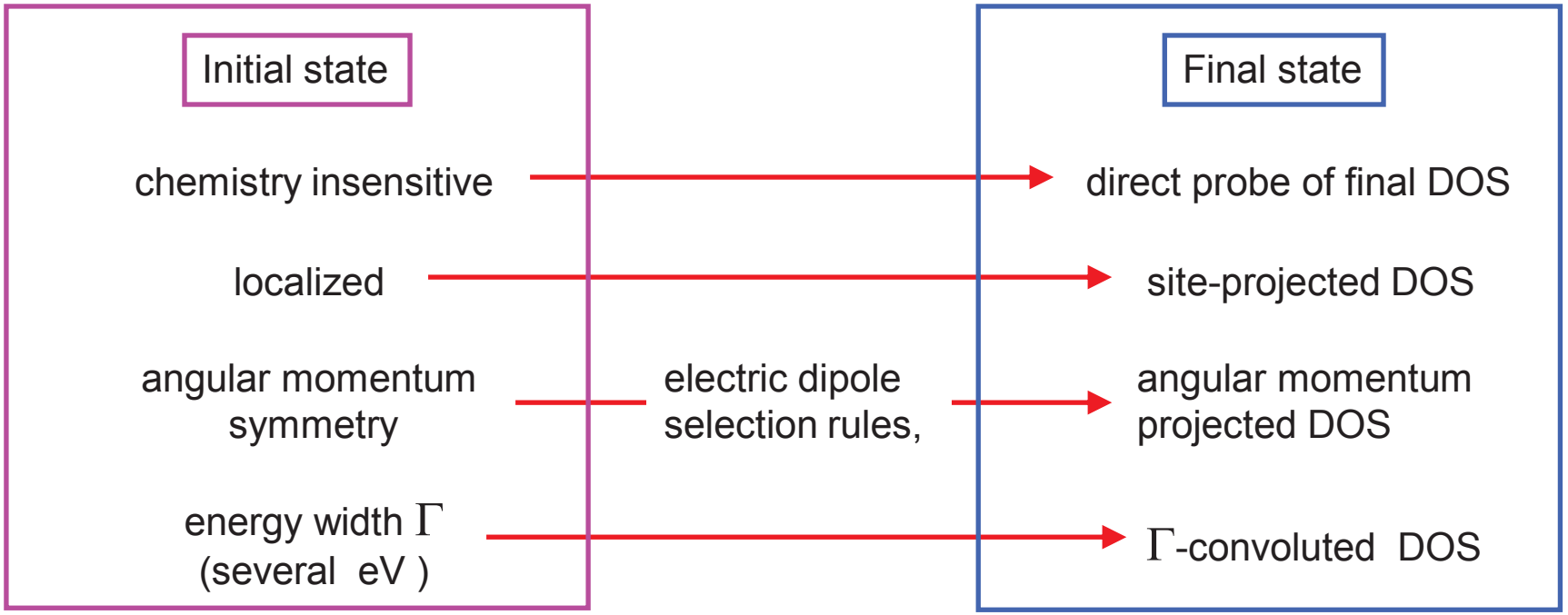


XANES

EXAFS XANES

$$W_{if} \propto \left| \langle \Psi_i | H_I | \Psi_f \rangle \right|^2 \rho(E_f)$$

The features of the absorption spectrum is dominated by the the density of final states



XANES

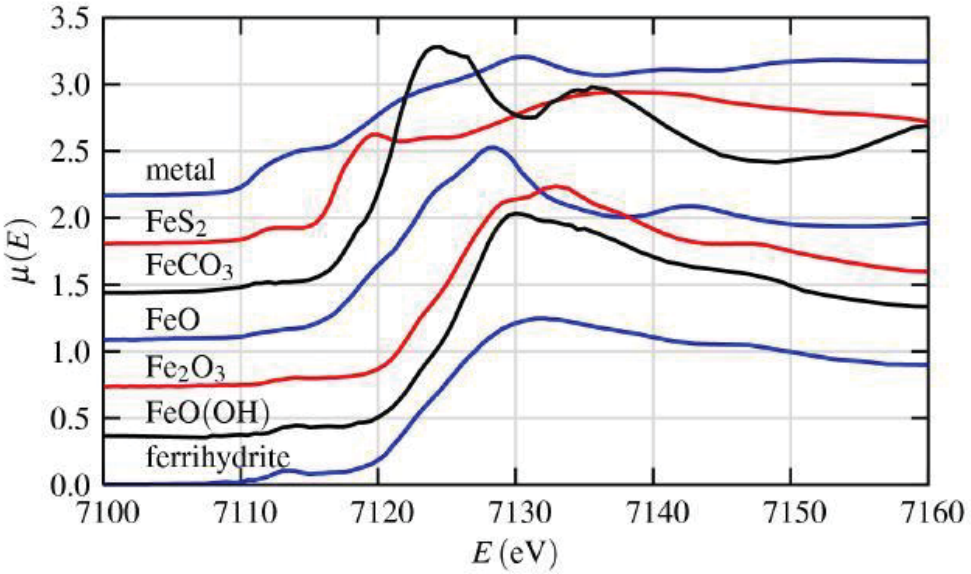
- XANES is a much larger signal than EXAFS

⇨ can be done at **lower concentrations**, and **less-than-perfect sample conditions**

- The interpretation of XANES is very complicated

⇔ there is **no simple analytic** (or even physical) **description** of XANES

- the EXAFS equation breaks down at low-k (**1/k term**) and the **increase in the mean-free-path** at very low-k



Still, there is much **chemical information** from the XANES region:

- the **edge position and shape** is sensitive to formal valence state, ligand type, and coordination environment

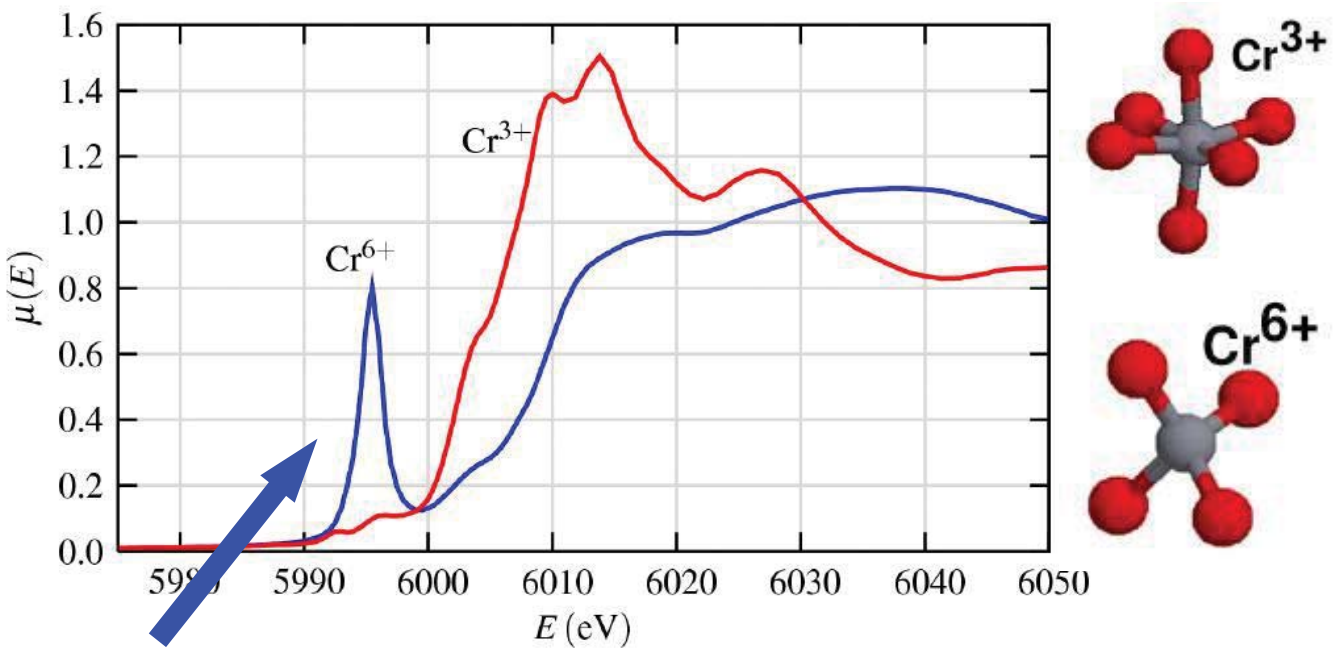
⇨ XANES can be used as a **fingerprint method** to identify phases.

XANES

An example: Chromium (Cr)

K edge XANES : edge energy = 5989.2 eV

- For ions with unfilled d-electrons bands, the **pd hybridization** is dramatically altered depending on the co-ordination environment.
- much stronger hybridization for tetrahedral coordination (Cr^{6+}) than for octahedral coordination.

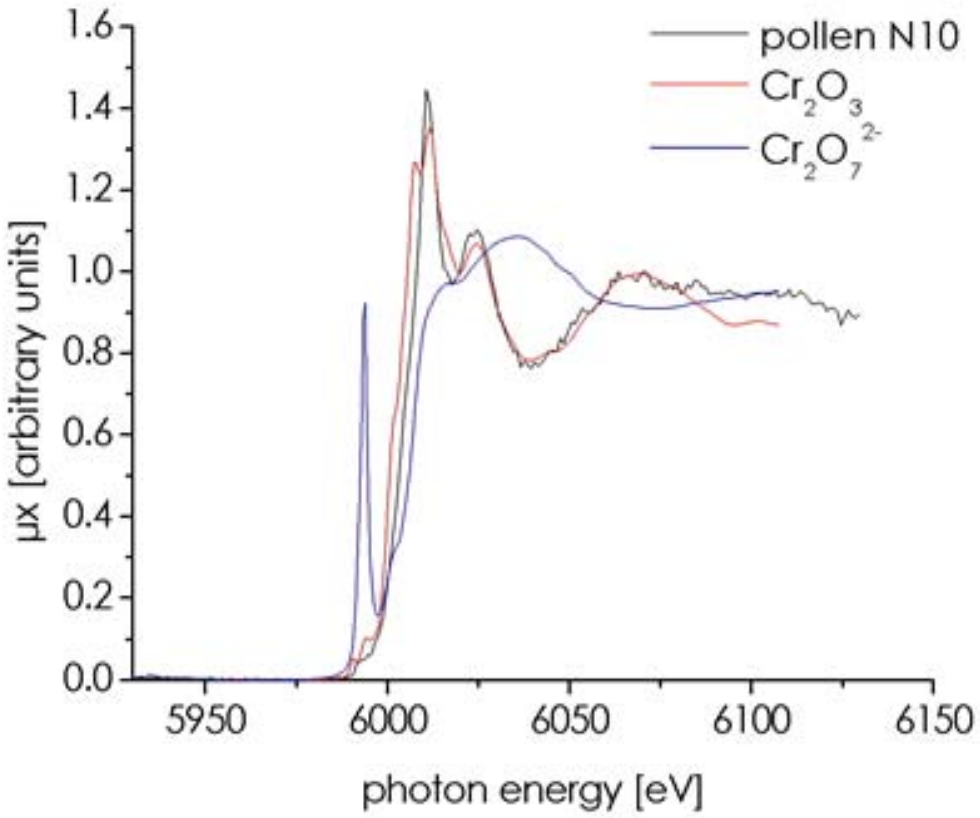


For the case of Cr^{6+} pd-hybridization results in a **highly localized molecular orbital state**, giving a well-defined peak below the main absorption edge, indicating a transition to a bound electronic state.

XANES

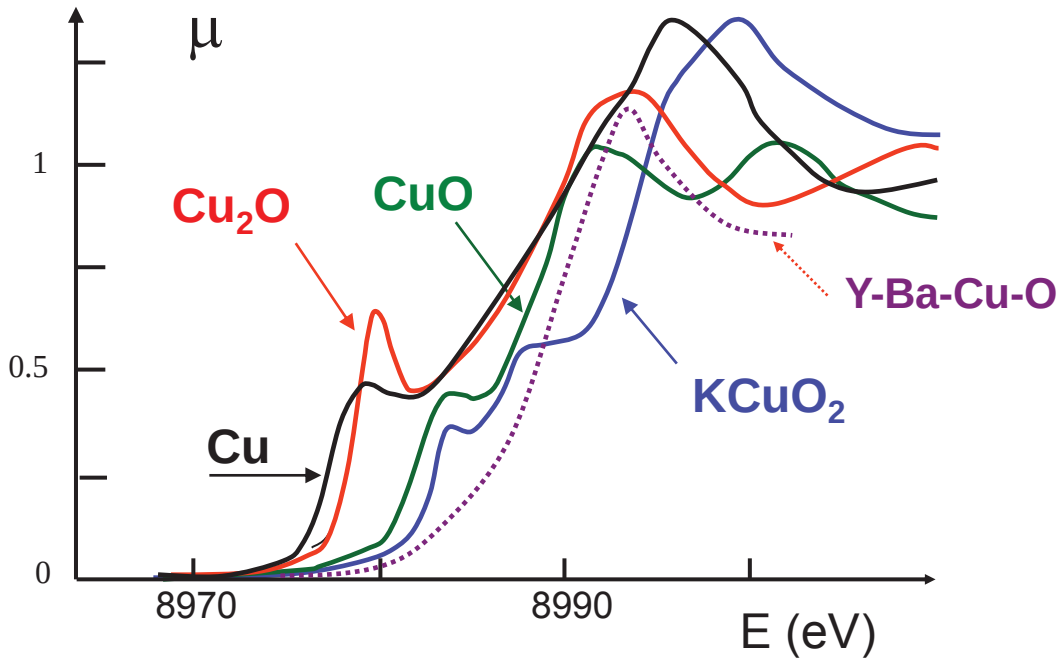
An example: Chromium (Cr)

K edge XANES : edge energy = 5989.2 eV



Pollen as an indicator of environmental pollution.

XANES



(J.B. Boyce et al.
Phys. Rev. B 1987)

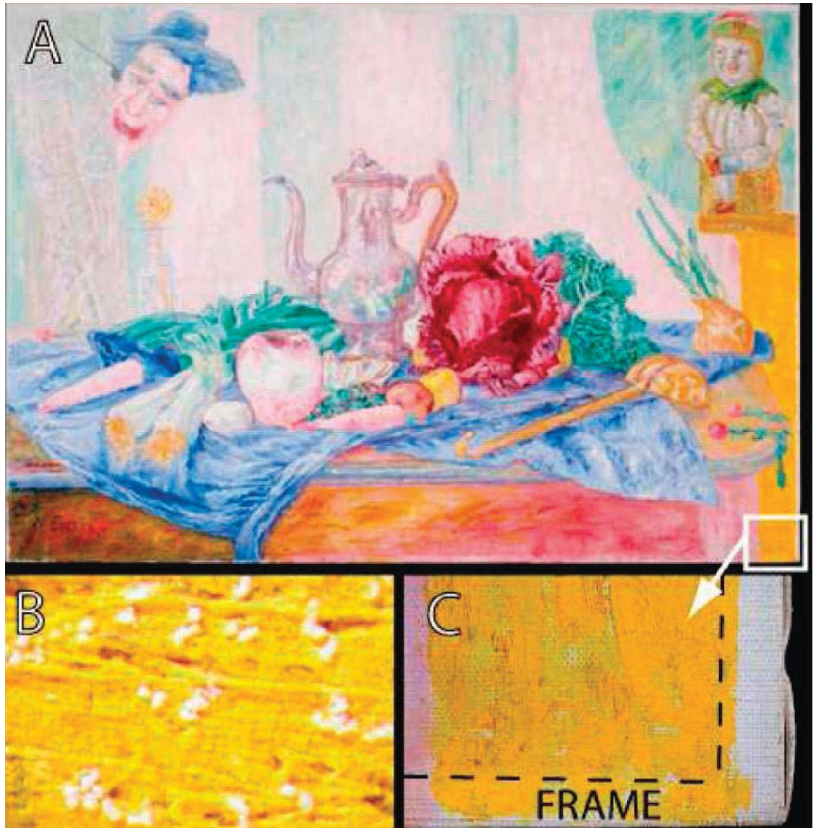
Oxidation Numbers (formal valences)

I Cu_2O
II CuO
III $KCuO_2$

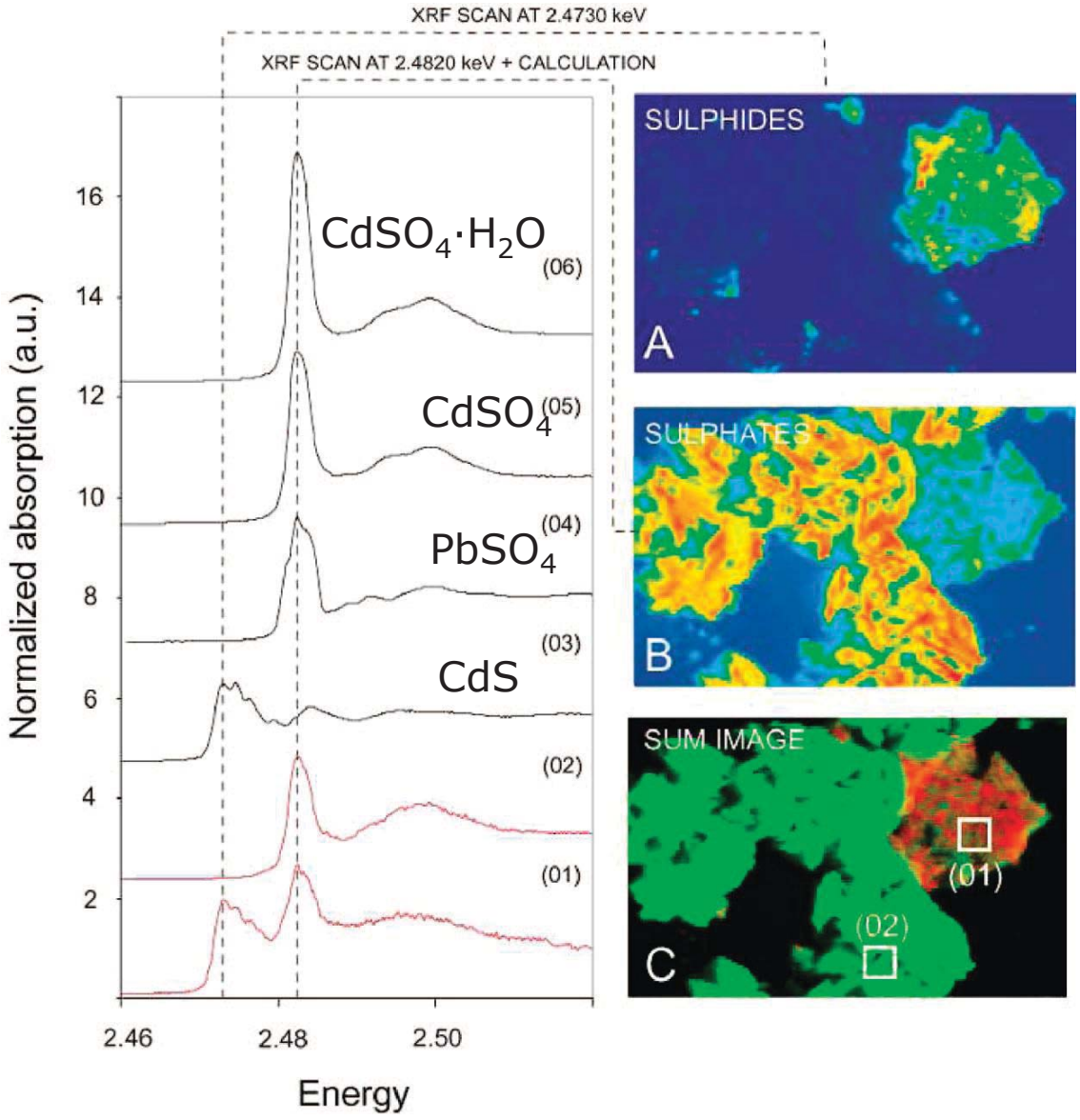
Higher transition energies are expected for higher valence states.

XANES – example – CdS degradation

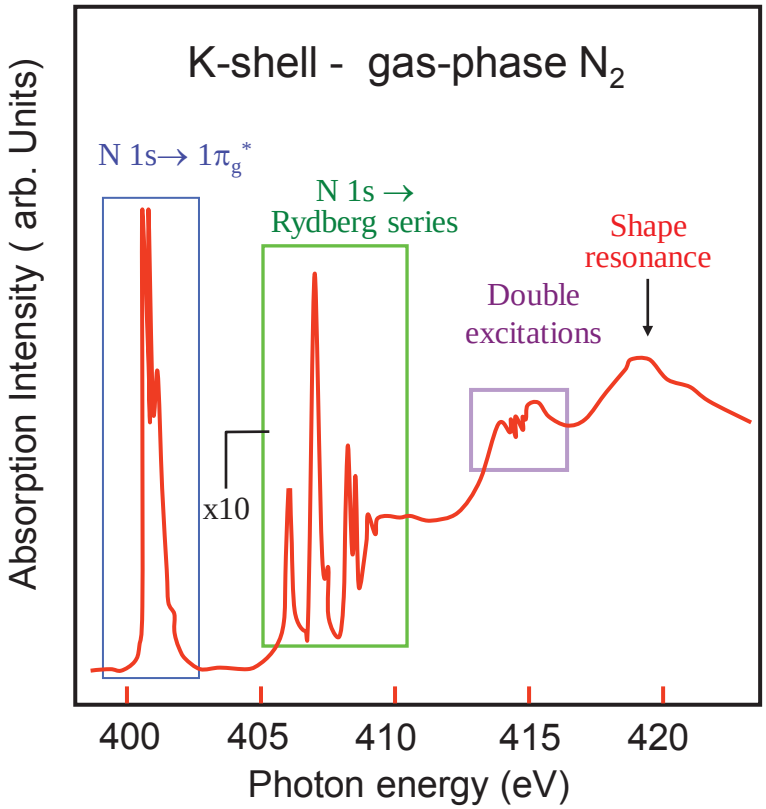
Characterization of a Degraded Cadmium Yellow (CdS) Pigment in an Oil Painting by Means of Synchrotron Radiation Based X-ray Techniques
Geert Van der Snickt et al., Analytical Chemistry, 2009

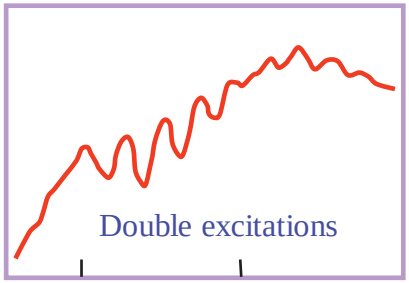


XANES – example – CdS degradation



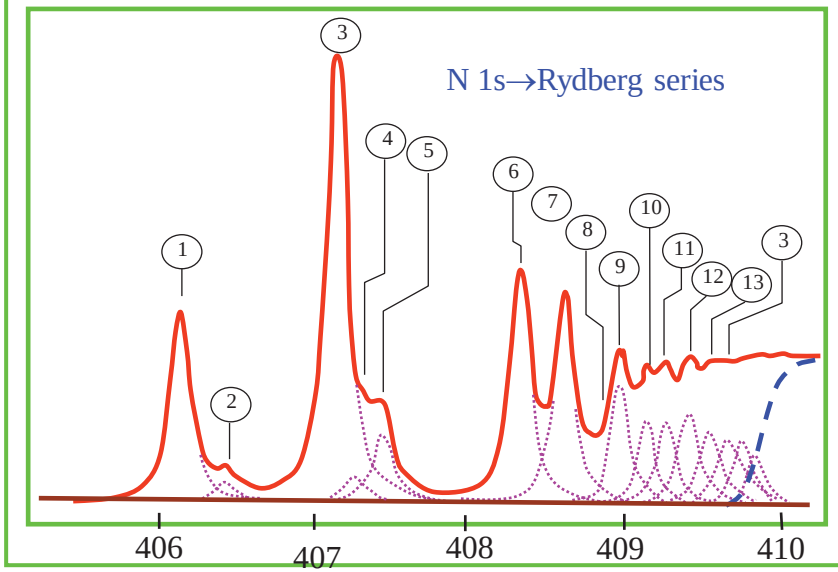
NEXAFS



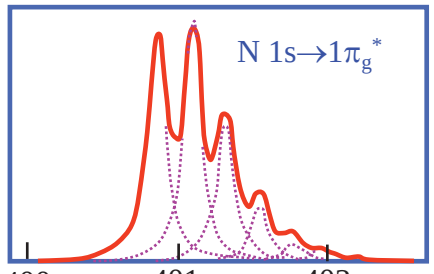


Double excitations associated to the $1s \rightarrow 1p_g^*$ transition.

1s → Rydberg series

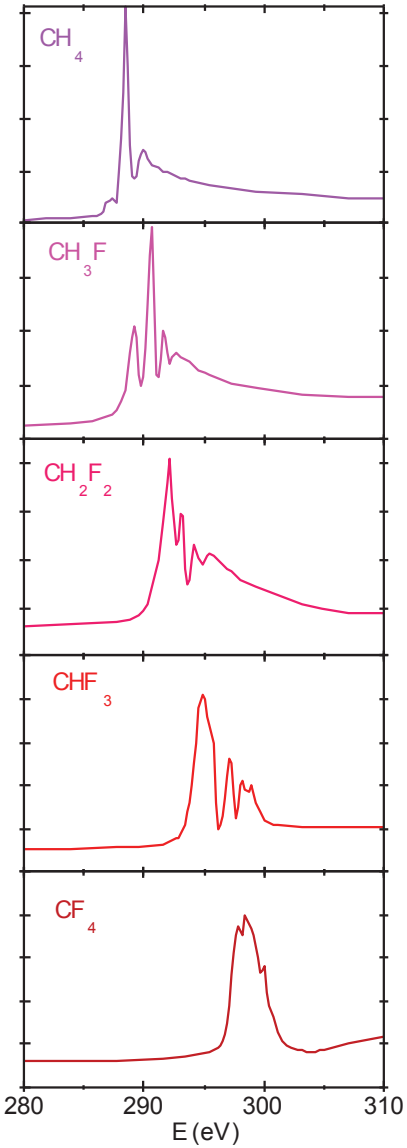


C.T. Chen and F. Sette, Phys. Rev. A 40 (1989)



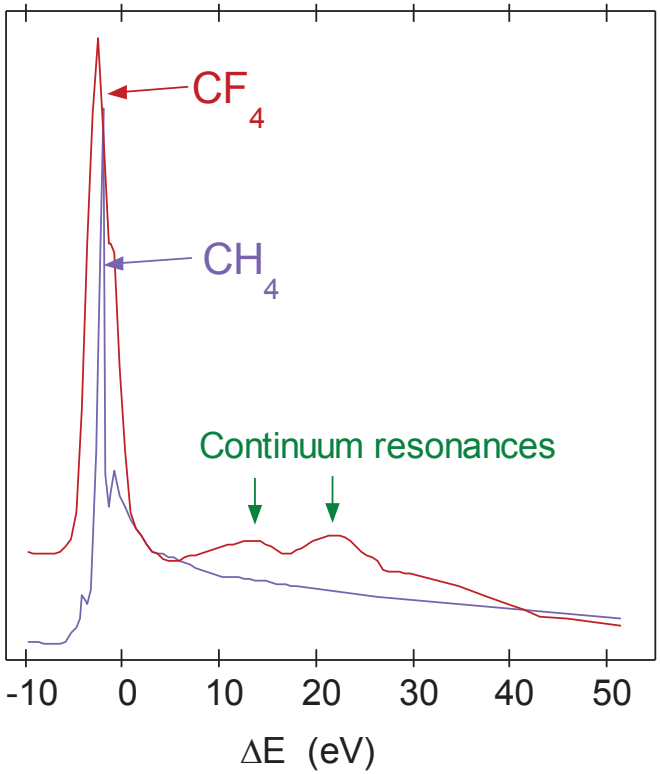
8 vibrational levels $1s \rightarrow 1\pi_g^*$

NEXAFS C – K edge



CH_4

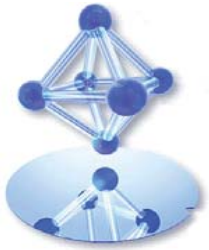
CF_4



Transitions to:

Rydberg states (narrow)
Valence orbitals (broad)
Resonances (broad)

Organic contamination on Si wafers

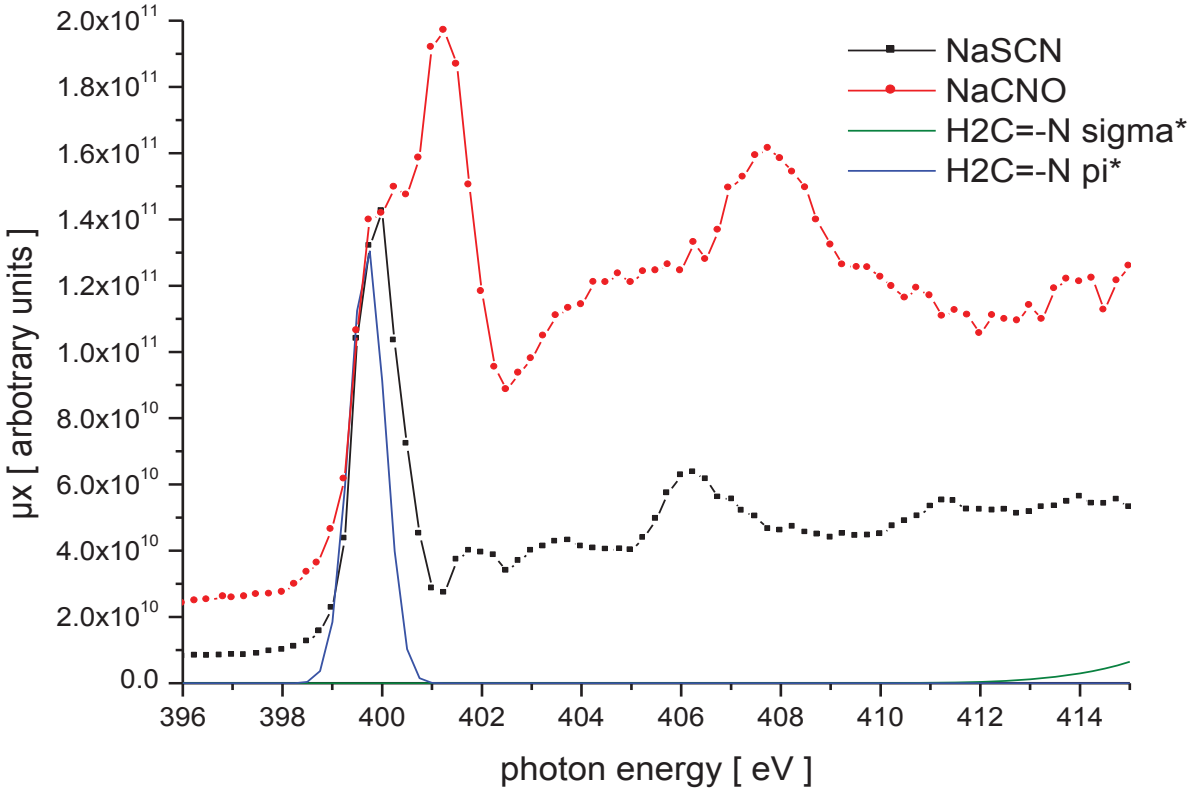


Motivation

- Si wafer contamination control is required by the semiconductor industry to produce high quality products with fast decreasing dimensions and prices. Contamination results in quantifiable yield losses.

- the worst are metallic contaminants but:
  ionic and molecular organic contaminants can affect the wetability and the microroughness of the wafer surface, leading either to crystalline defects in the epitaxial layer or even to carbonisation and formation of silicon carbide

NEXAFS - the systematic of resonance positions



$Na^+ \ ^-O-C\equiv N$

$Na^+ \ ^-S-C\equiv N$

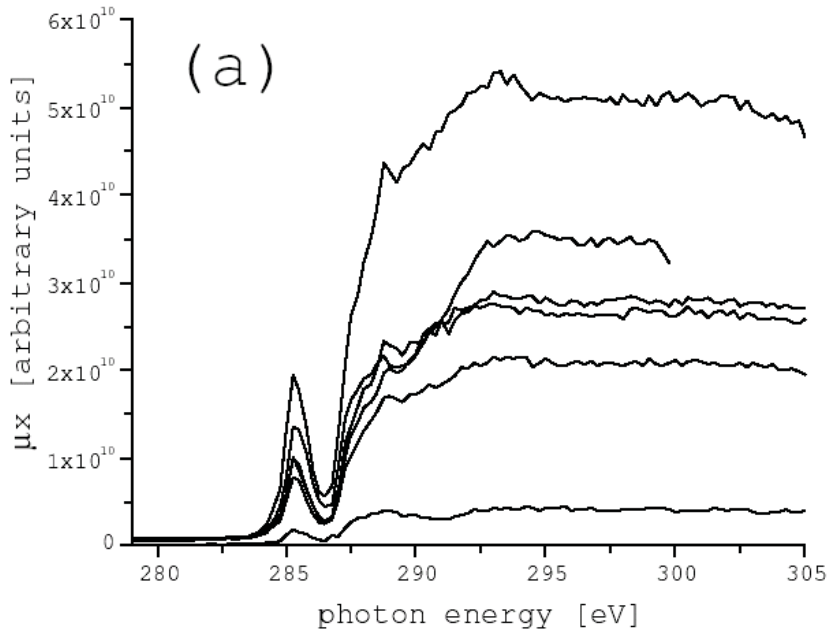
N edge

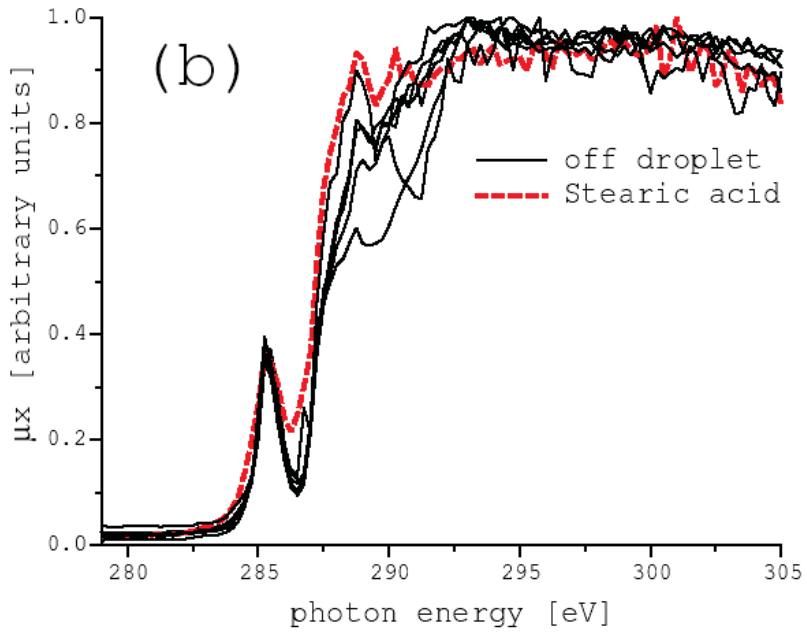
NEXAFS - the systematic of resonance positions

from J. Stöhr - NEXAFS Spectroscopy

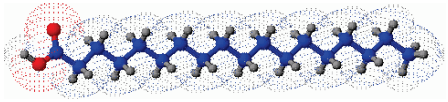
bond carbon	energy of resonance [eV] pi*	sigma*
HC≡CH	285.9	310
$H_2C=CH_2$	284.7	301
$H_3C–CH_3$		291.2
HC≡N	286.4	307.9
$H_3C–NH_2$		291.5
C≡O	287.3	304
$H_2C=O$	286	300.5
$H_3C–OH$		292
$H_3C–F$		289.1
nitrogen		
HC≡N	399.7	420.8
$H_3C–NH_2$		404.6
$F_3C–NO$		407.5
N≡N	401	418.9
$H_2N–NH_2$		405.1
N≡O	399.7	414.5
$F_3CN=O$	399.1	413.2
$N–F_3$		407.1
oxygen		
C≡O	534.1	550
$H_2C=O$	530.8	544
$H_3C–OH$		537.4
N≡O	532.7	546.3
O=O	530.8	540.5
HO–OH		533
$F_2–O$		534.6

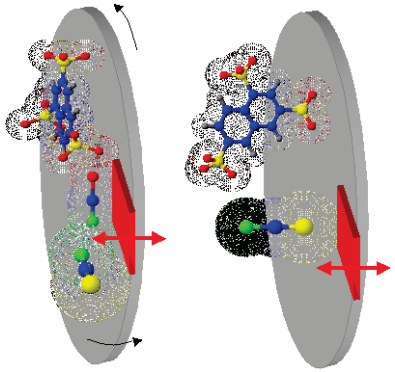
NEXAFS - organic contamination on wafers





Stearic acid





NB.
Polarise light
Bond (dipole) orientation

see J. Stöhr - NEXAFS Spectroscopy

G. Pepponi et al. SPECTROCHIMICA ACTA B, vol. 58,n. 12,2003

NEXAFS - speciation of fine atmospheric particulate

Ultratrace speciation of nitrogen compounds in aerosols collected on silicon wafer surfaces by means of TXRF-NEXAFS
S. Török et al., Powder Diffraction **19** (1), March 2004

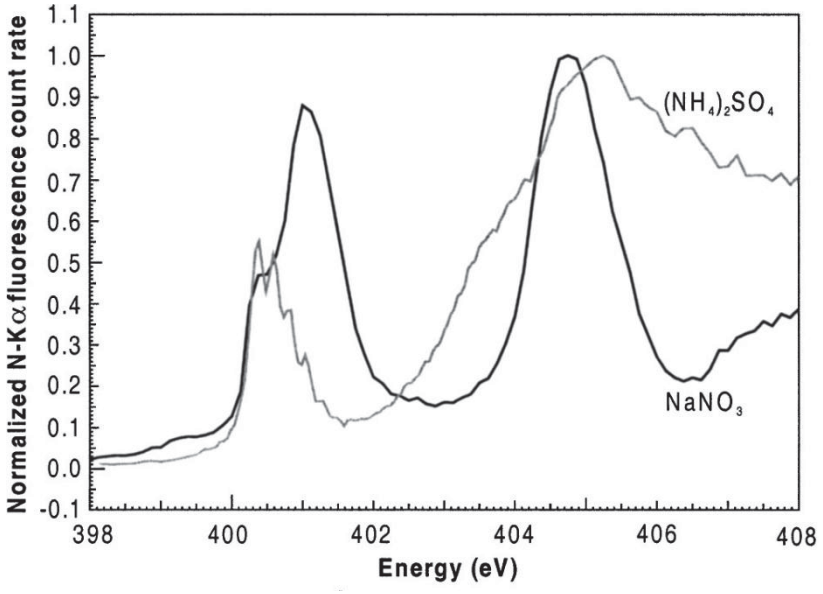


Figure 1. N K-edge TXRF-NEXAFS spectra of ammonium sulfate and sodium nitrate standards prepared on silicon wafers.

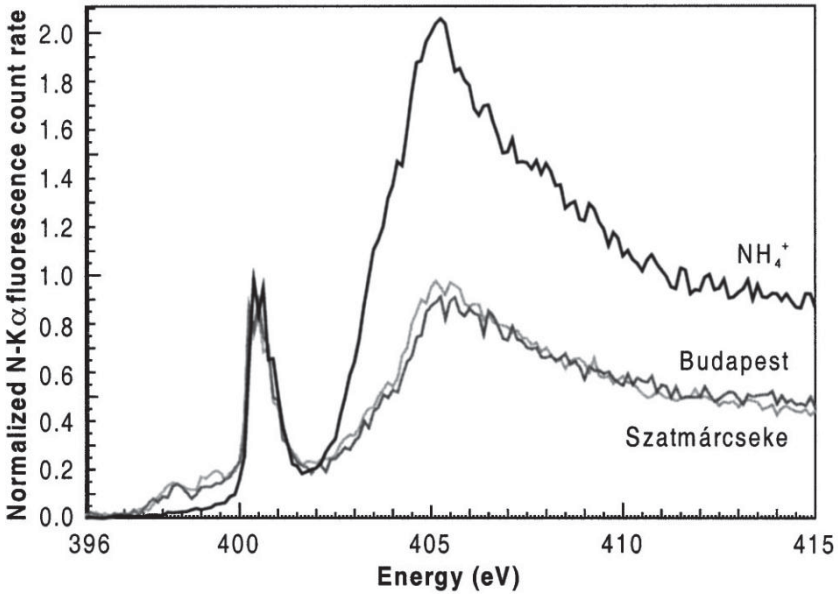


Figure 2. A comparison of N K-edge TXRF-NEXAFS spectra of the submicrometer aerosol samples and of the ammonium sulfate standard.

NEXAFS - speciation of fine atmospheric particulate

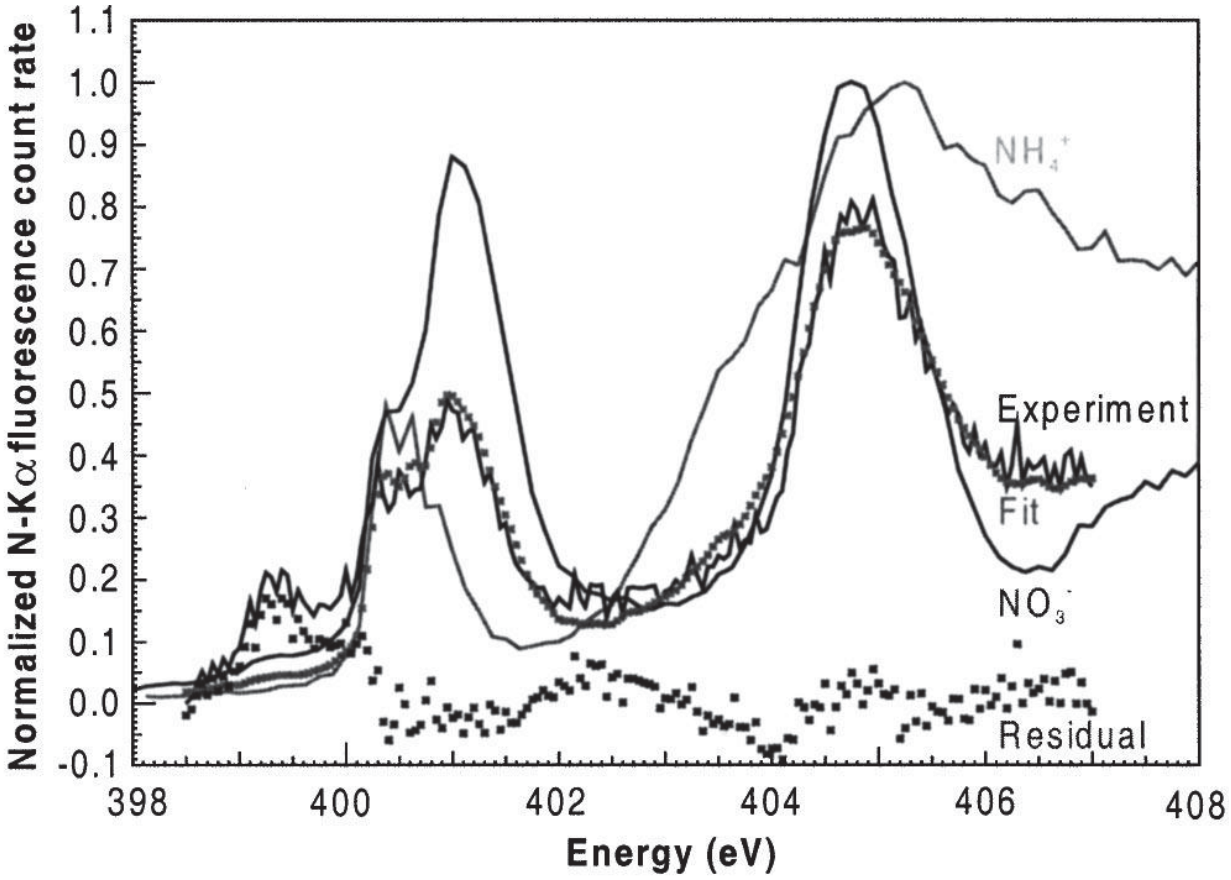


Figure 3. An evaluation of the N K-edge TXRF-NEXAFS spectrum of the 1–2 μm aerosol fraction collected at Szatmarcseke, using a linear combination of the standard spectra of ammonium and nitrate.

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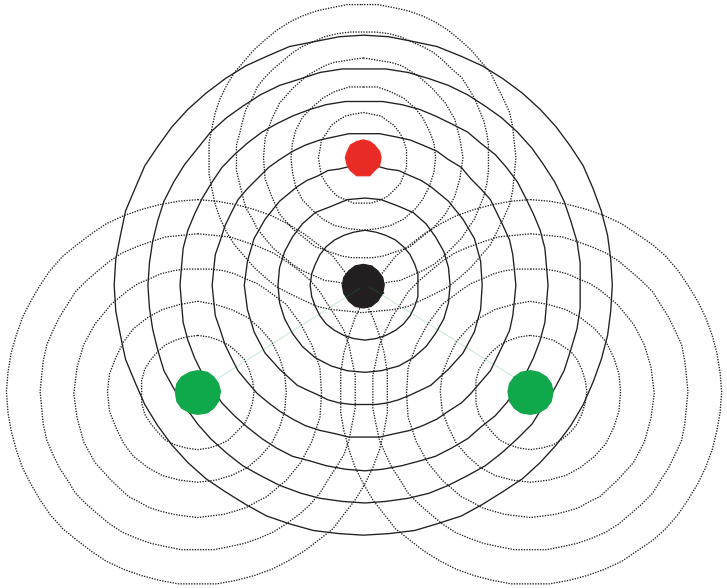
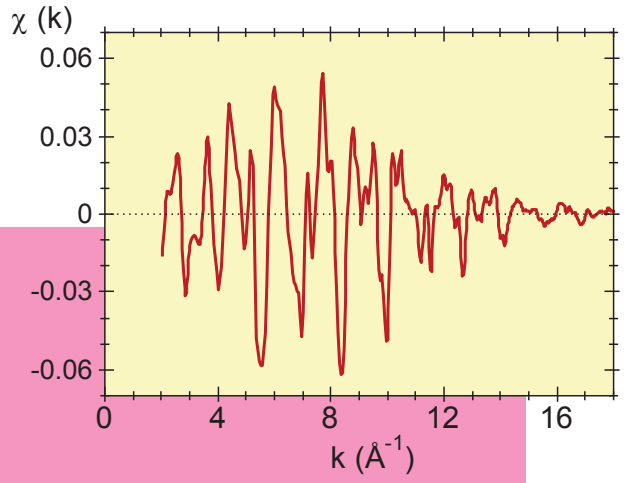
BRUNO KESSLER

the extended region
EXAFS



the EXAFS function



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

$$\mu_0(\omega) \propto \left| \langle \psi_i | \hat{\eta} \cdot \vec{r} | \psi_f^0 \rangle \right|^2$$

$$\mu(\omega) \propto \left| \langle \psi_i | \hat{\eta} \cdot \vec{r} | \psi_f \rangle \right|^2$$

(weak interaction)

$$|\psi_f\rangle = |\psi_f^0 + \delta\psi_f\rangle$$

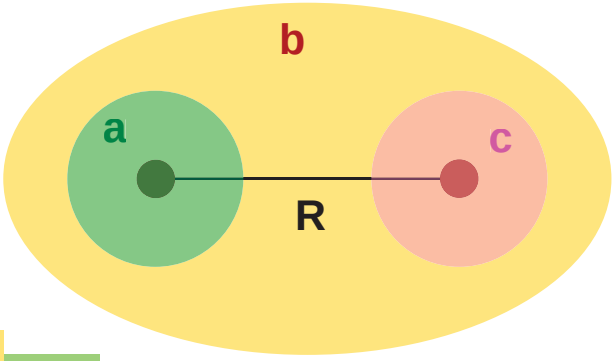
?

Quantum states → wavefunctions

$$\chi(k) = \frac{2\,\mathrm{Re} \int d\vec{r} \left(\psi_i\ \hat{\eta} \cdot \vec{r}\ \psi_f^{0*}\right)\left(\psi_i^*\ \hat{\eta} \cdot \vec{r}\ \delta\psi_f\right)}{\int d\vec{r} \left|\psi_i^*\ \hat{\eta} \cdot \vec{r}\ \psi_f^0\right|^2}$$

the EXAFS function

Scattering theory
in plane-wave approximation



$$\delta\psi_f \propto \psi_f^0 \; \mathrm{i}\, e^{i\delta} \frac{\exp(\mathrm{i}kR)}{2kR} f(k,\pi) \frac{\exp(\mathrm{i}kR)}{R} e^{i\delta}$$

polarisation

back-scattering amplitude

central atom phase-shift

$$\chi(k) = 3 \left|\hat{\eta}\cdot\hat{R}\right|^2 \frac{1}{kR^2} \mathrm{Im}\left[f(k,\pi)\, \exp(2\mathrm{i}\delta_1)\, \exp(2\mathrm{i}kR)\right]$$

spherical wave attenuation

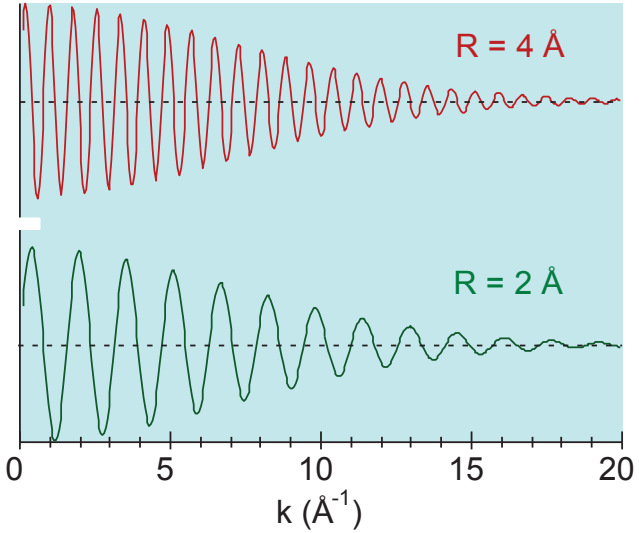
back & forth path

the EXAFS function

$$\chi(k) = 3\left|\hat{\eta}\cdot\vec{R}\right|\frac{1}{kR^2}\,\mathrm{Im}\left[f(k,\pi)\exp(2i\delta_1)\exp(2ikR)\right]$$

$$f(k,\pi)e^{2i\delta} = \left|f(k,\pi)\right|e^{i\phi}$$

$$\chi(k) = 3\left|\hat{\eta}\cdot\hat{R}\right|^2\frac{1}{kR^2}\left|f(k,\pi)\right|\sin\left[2kR+\phi(k)\right]$$



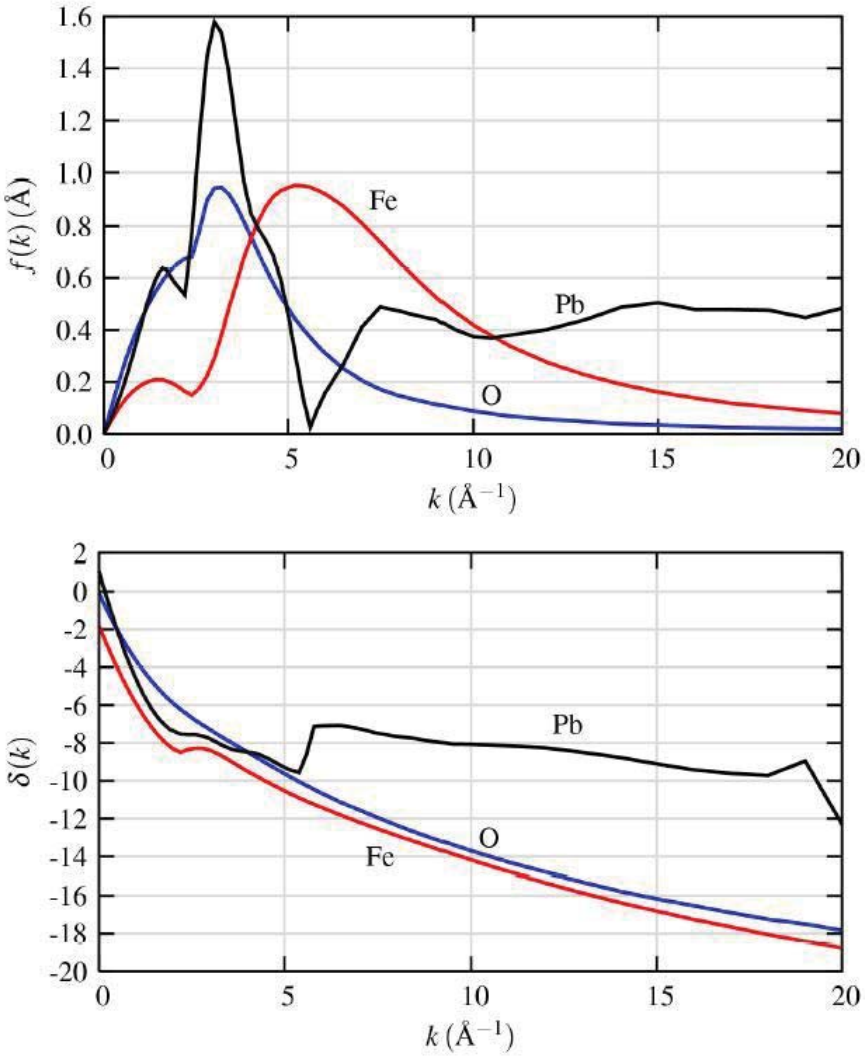
EXAFS frequency ⟷ Inter-atomic distance

Scattering amplitude aqnd phase shift

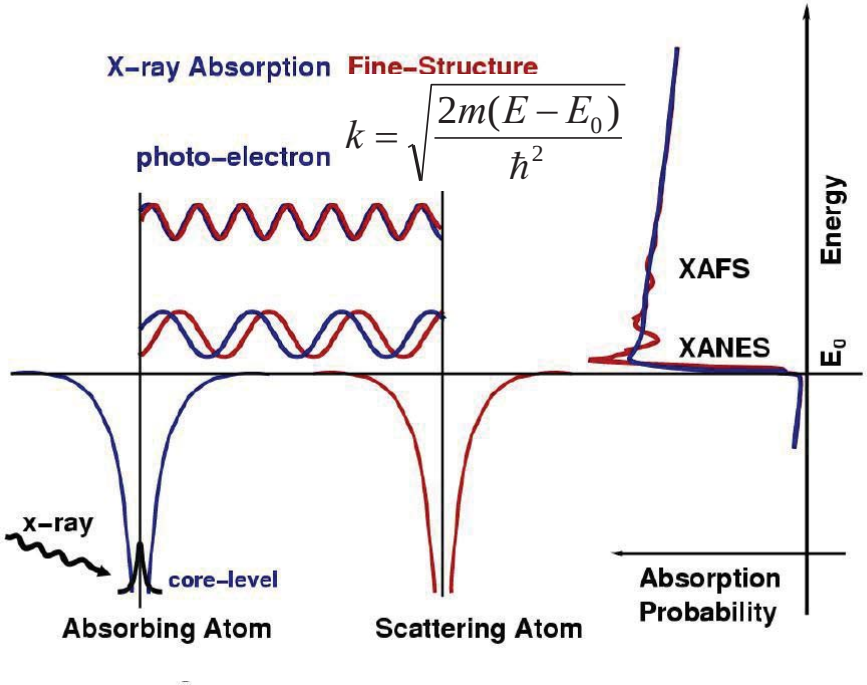
Examples: scattering properties

f(k) (top) and δ(k) (bottom)

for O, Fe, and Pb showing the dependence of these terms on atomic number Z



the EXAFS function



1. Absorption only takes place if there is an **available state** for the photo-electron:
   i.e. a quantum state at exactly the right energy, and also the right angular momentum state
2. A photo-electron with **wave number k** is created and propagates away from the atom
3. the photo-electron can **scatter from the electrons of a neighboring atom**, and return to the absorbing atom
4. considering point 1. we see that the presence of the photo-electron scattered back from the neighboring atom **will alter the absorption coefficient**:

This is the origin of XAFS

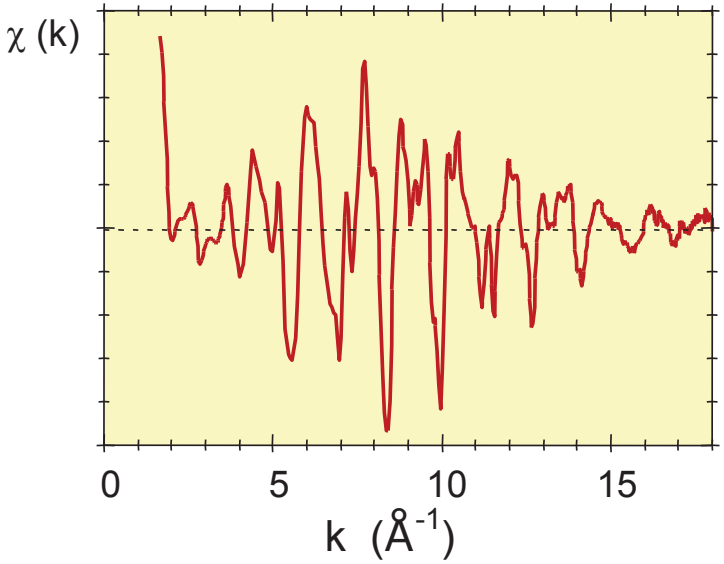
Inelastic effects – dumping

Intrinsic inelastic effects

Photo-electron mean-free-path

$$\chi(k) = \frac{S_0^2}{k} \sum_{shell} N_s \, \mathrm{Im}\left[f_s(k,\pi)\, e^{2i\delta_1} \, \frac{e^{-2R_s/\lambda(k)}}{R_s^2} \exp(2ikR_s) \right]$$

Atoms frozen in equilibrium positions !



Disorder effects ?

The EXAFS equation – short range

Core-hole lifetime $\tau_h \rightarrow \lambda_h$

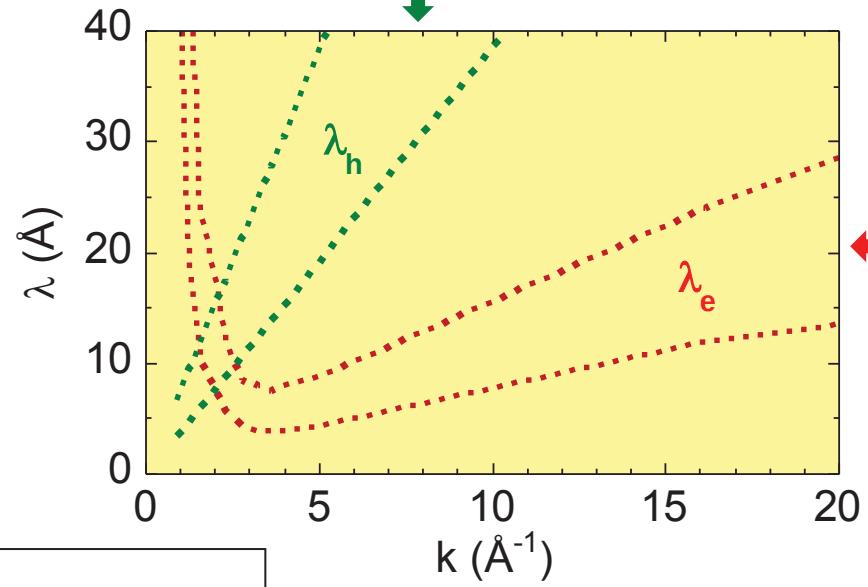


Photo-electron lifetime

$\tau_e \Leftrightarrow \lambda_e$

$$\frac{1}{\lambda} = \frac{1}{\lambda_h} + \frac{1}{\lambda_e}$$

$$\psi(k,r) = \frac{e^{ikr} e^{-2r/\lambda(k)}}{kr}$$

Photoelectron wavefunction

Attenuation factors

EXAFS Equation

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

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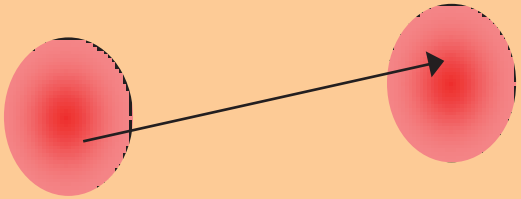
Disorder

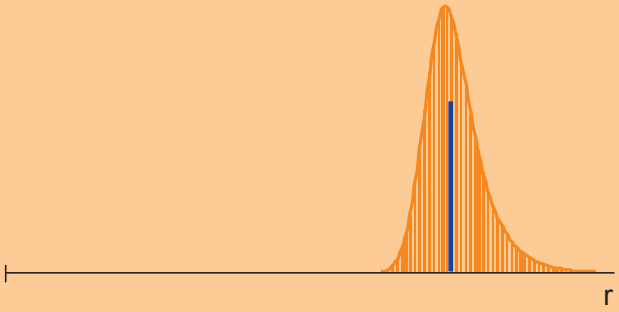
$$\chi(k) = \sum_j \frac{N_j \cdot e^{-2k^2\sigma_j^2} \cdot e^{-2R_j/\lambda(k)} \cdot f_j(k)}{kR_j^{\,2}} \sin\left[2kR_j + \delta_j(k)\right]$$

Thermal disorder



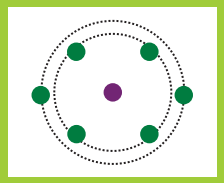
$\tau_{vib} \approx 10^{-12}$ s

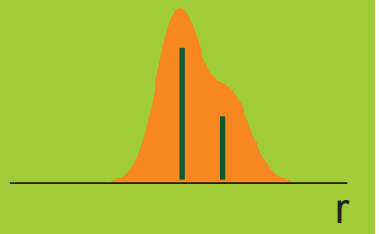
$\tau_{exafs} \approx 10^{-15}$ s



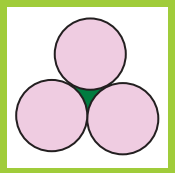
Structural disorder

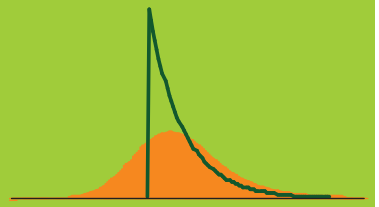
- Distorted coordination shells



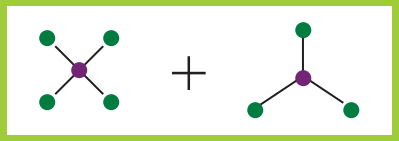


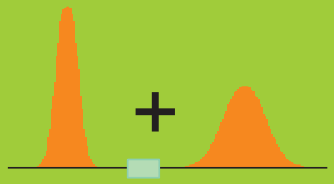
- Free-volume models





- Sites disorder



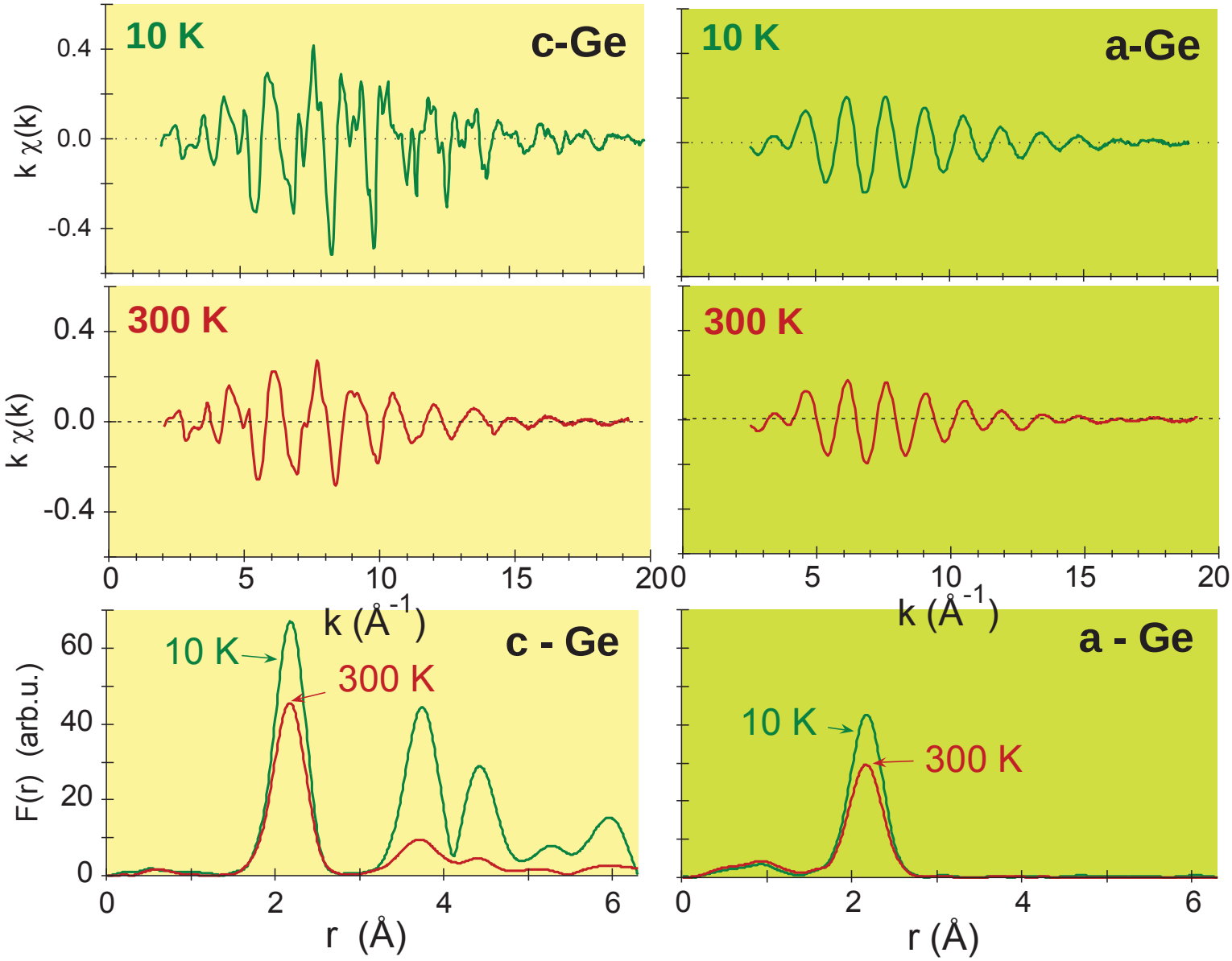


Distance → **Distribution of distances**

Disorder

EXAFS signals

Fourier transforms

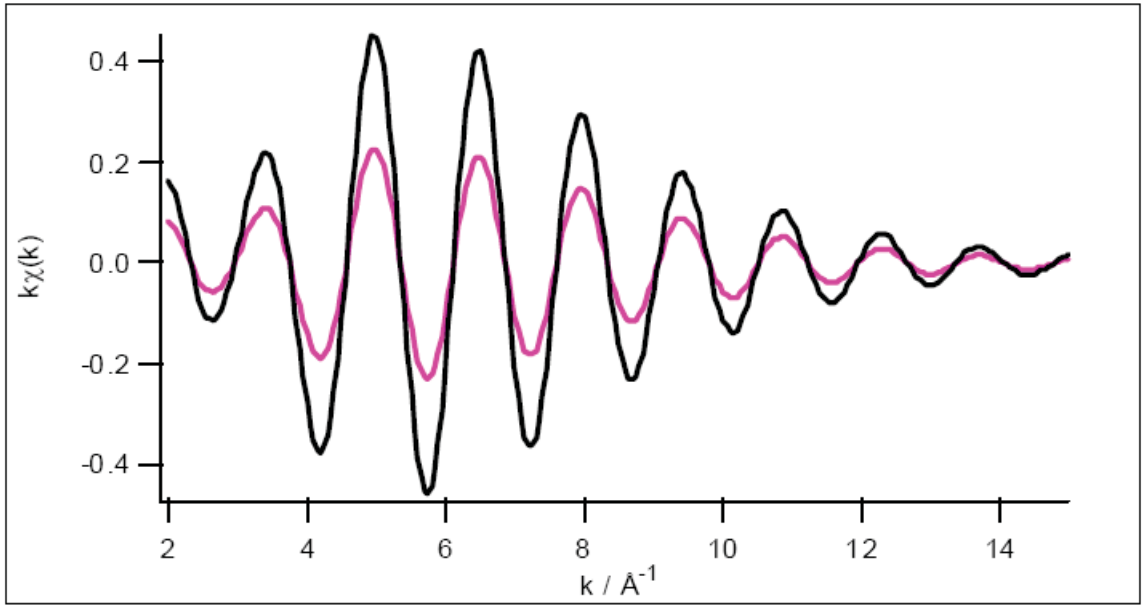


The EXAFS equation

Theoretical Fe-Fe XAFS, R = 2.4855 Å σ^2=0.005 Å^2

N = 4 compared to N = 8

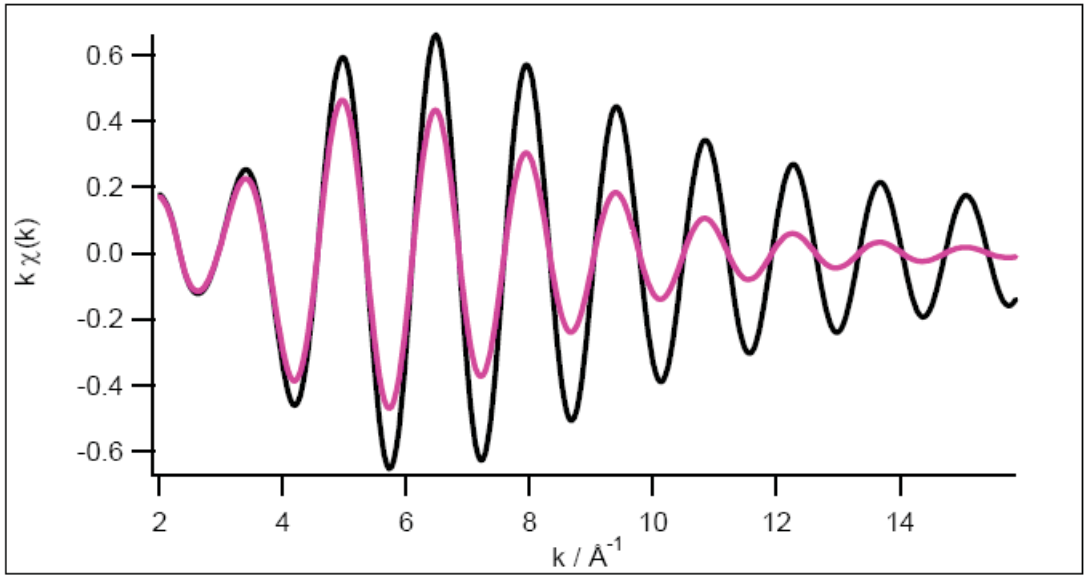
The EXAFS amplitude is proportional to the co-ordination number



$$\chi(k) = \sum_{j}^{n} N_j \times S_i(k) \times F_j(k) \times e^{-2\sigma_j^2 \times k^2} \times e^{-(2r_j/\lambda_j(k))} \times \frac{\sin(2kr_j + \phi_{ij}(k))}{kr_j^2}$$

The EXAFS equation

Theoretical Fe-Fe XAFS, N=8 and R = 2.4855 Å
σ^2=0.000 Å² compared to 0.005 Å²

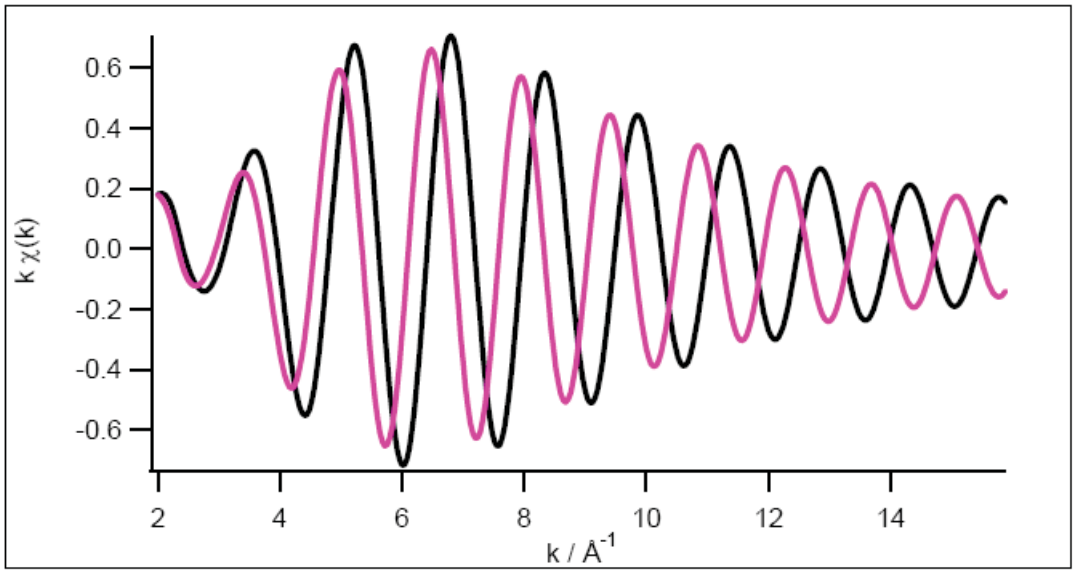


The EXAFS means square displacement dampens the oscillations exponentially

$$\chi(k) = \sum_j^n N_j \times S_i(k) \times F_j(k) \times e^{-2\sigma_j^2 \times k^2} \times e^{-(2r_j/\lambda_j(k))} \times \frac{\sin(2kr_j + \phi_{ij}(k))}{kr_j^2}$$

The EXAFS equation

Theoretical Fe-Fe XAFS for N=8 and R=2.3855 compared to R = 2.4855 Å, σ^2=0.000



Longer bond distances result in a shorter periodicity of their EXAFS oscillations

$$\chi(k) = \sum_j^n N_j \times S_i(k) \times F_j(k) \times e^{-2\sigma_j^2 \times k^2} \times e^{-(2r_j/\lambda_j(k))} \times \frac{\sin(2kr_j + \phi_{ij}(k))}{kr_j^2}$$

XAS – experimental acquisition

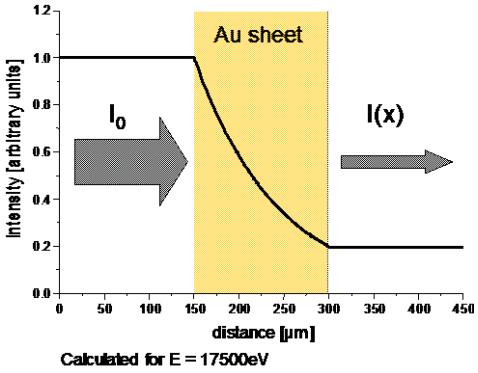
What do we need?

- a "highly" (~dE/E 10^{-4}) monochromatic but adjustable (in energy) X-ray source (Polychromatic source + monochromator)

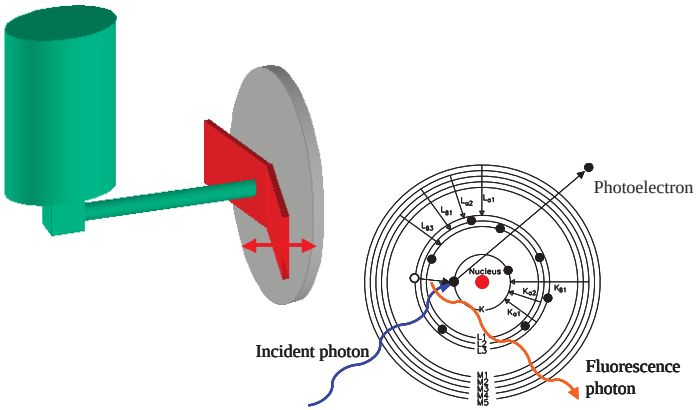
- loads of photons

→ A synchrotron would be good

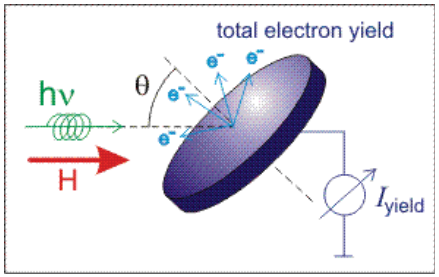
transmitted photons



fluorescence



electrons



http://www.fkf.mpg.de/kern/facilities/xmcd.html

XAS – experimental acquisition transmission

OK

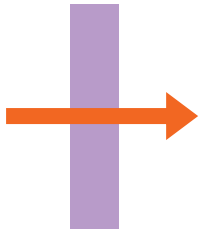
Bulk information
(not fom surface)
from:

Thin samples

Non-diluted samples

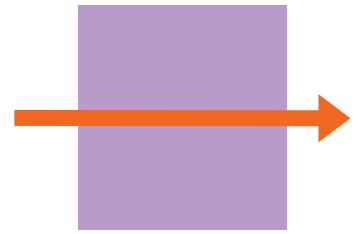
Homogeneous samples

High accuracy attainable

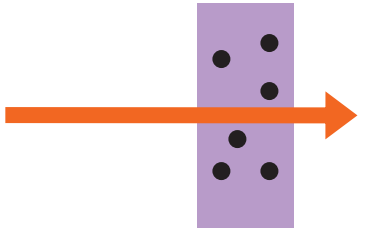


NO

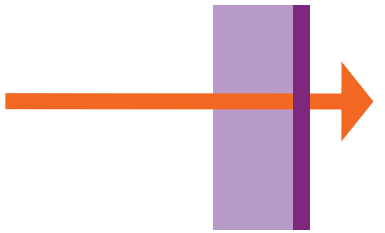
Thick samples



Diluted samples



Surface
information

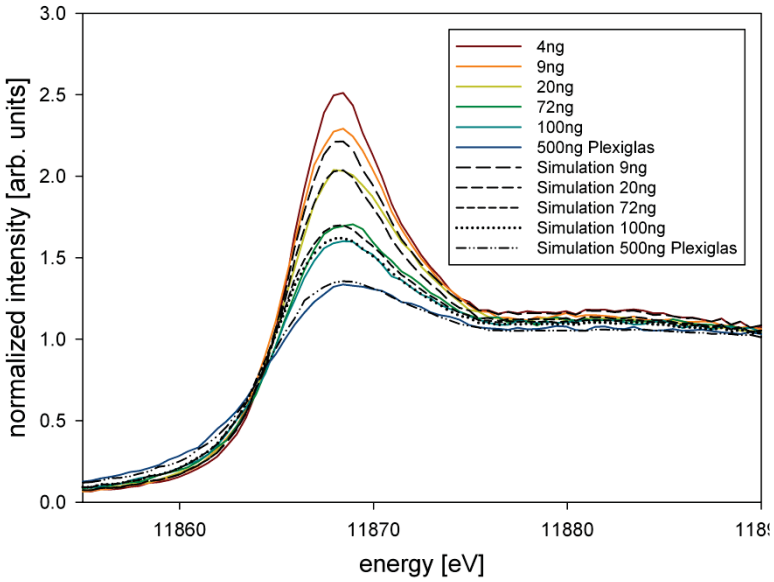


XAS – experimental acquisition fluorescence

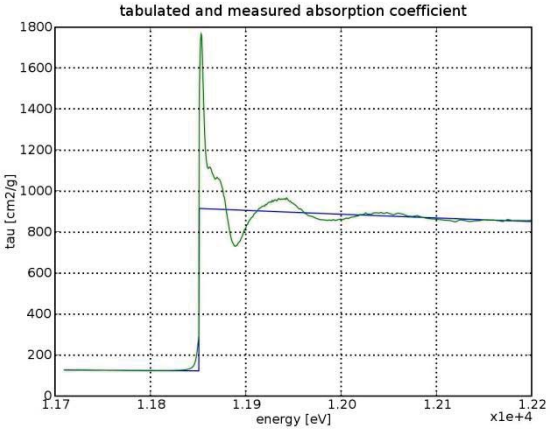
Good for diluted samples!

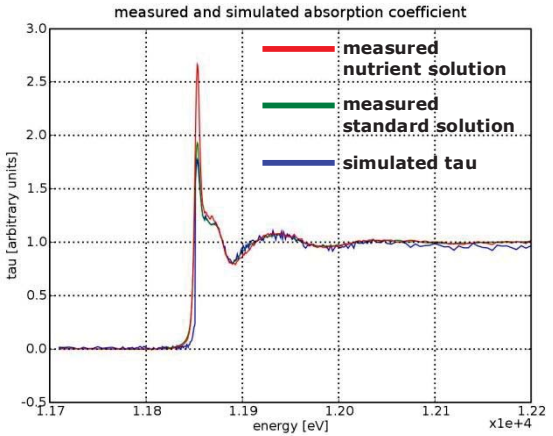
BUT: watch out for self absorption in "concentrated samples"

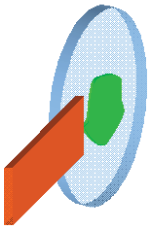
Arsenic standard solutions
TXRF geomertry



"Simple"
MONTE
CARLO
simulation





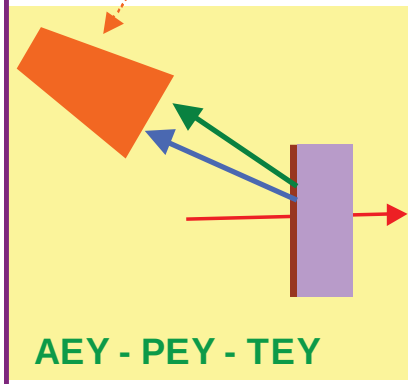


Sample (droplet) size becomes thickness, i.e. path that the primary beam crosses

F. Meirer et al., SPECTROCHIMICA ACTA B,vol. 63,n. 12,2008, pp. 1496-1502

XAS – experimental acquisition electrons

XAFS of adsorbates



AEY - PEY - TEY

AEY = **Auger Electron Yield**
- narrow energy window
- only direct Auger electrons
- spurious structures from photoelectrons

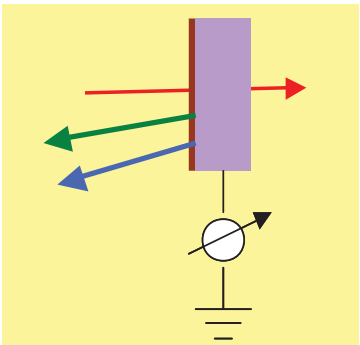
PEY = **Partial Eletron Yield**
- large energy window
- Auger (direct + secondary) = XAFS signal
- Photoel. (direct + secondary) = background

TEY = **Total Electron Yield**
- all electrons collected

- Auger (direct + second.) = XAFS signal
- Photoel. (direct + second.) = background

- XAFS from Auger and photoel.

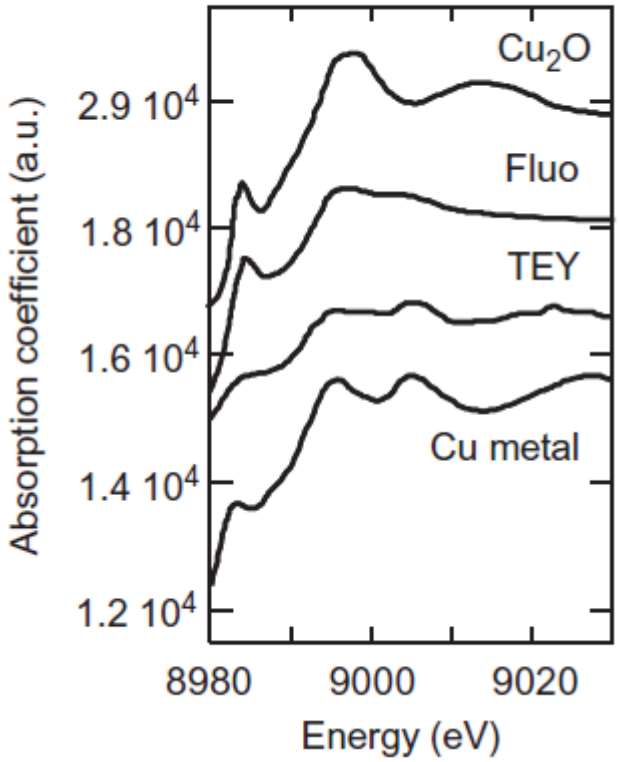
Bulk materials



TEY

XAS – experimental acquisition
Electrons vs. fluorescence

K. Janssens



XANES spectra obtained in fluorescence (fluo) and total electron yield (TEY) mode of the red lustre, compared to the XANES profiles of Cu2O and metallic Cu.

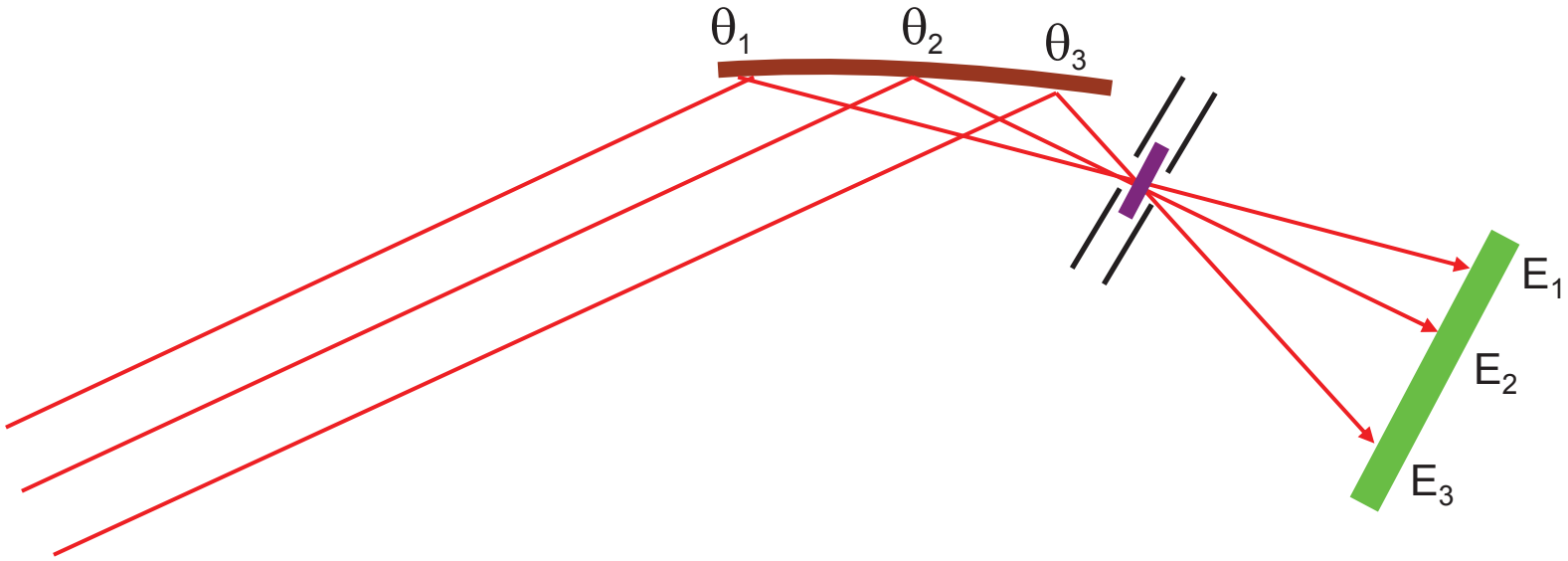
Copper in lustre

"When XANES data are recorded in the fluorescence mode of detection, where the lustre layer is probed down to a depth of 50 μm, Cu appears to be predominantly present under an oxidized form (i.e., as Cu^+ in Cu_2O, cuprite). However, if the TEY mode of detection is used, where only the top 100 nm of the same lustre layer is analysed, a different profile is obtained, showing the presence of Cu in the metallic state."

XAS – experimental acquisition
Dispersive EXAFS

Curved crystal monochromator

$$2d \sin\theta = \lambda$$



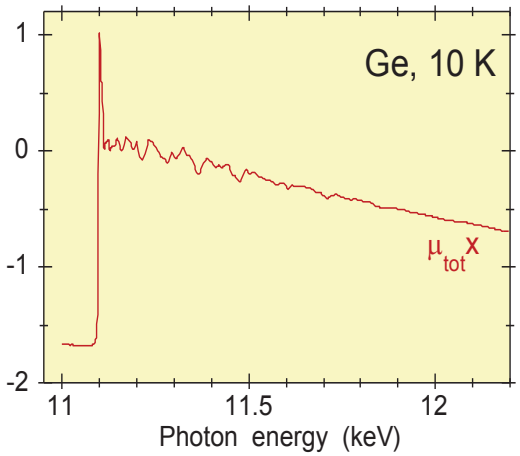
S.R. incoming white beam

Position-sensitive detector

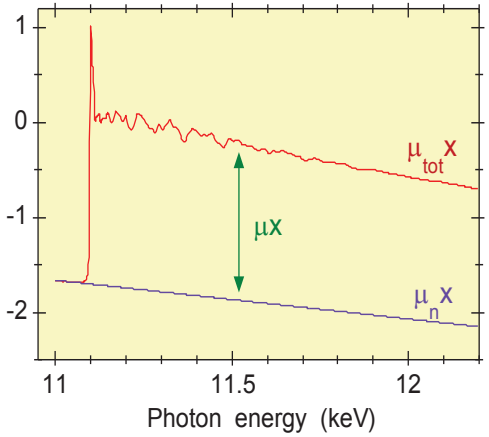
No high resolution nut very fast
Follow dynamics of non equilibrium systems

XAS – data analysis

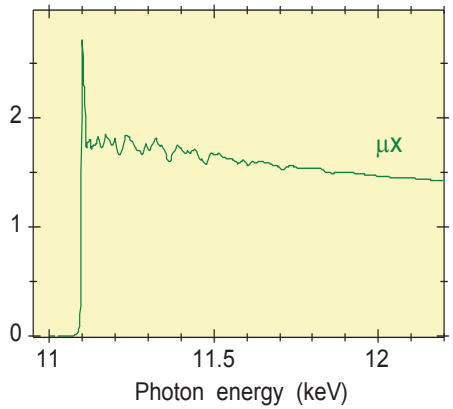
Experimental signal



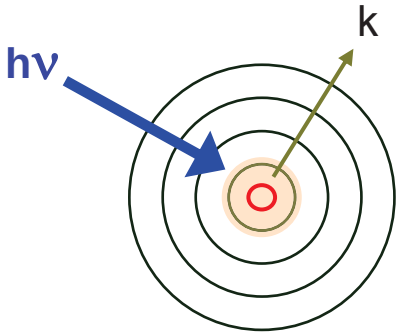
Extrapolation of pre-edge behaviour



Specific absorption coefficient



XAS – data analysis



Photoelectron wavenumber

$$k = \sqrt{\frac{2m}{\hbar^2}(h\nu - E_s)}$$

E = hν, photon energy

E_s

Edge energy

?

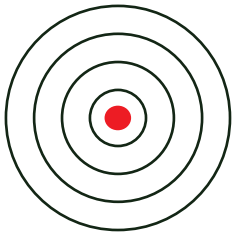
XAS – data analysis

EXAFS function

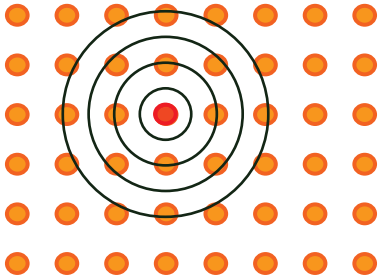
$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

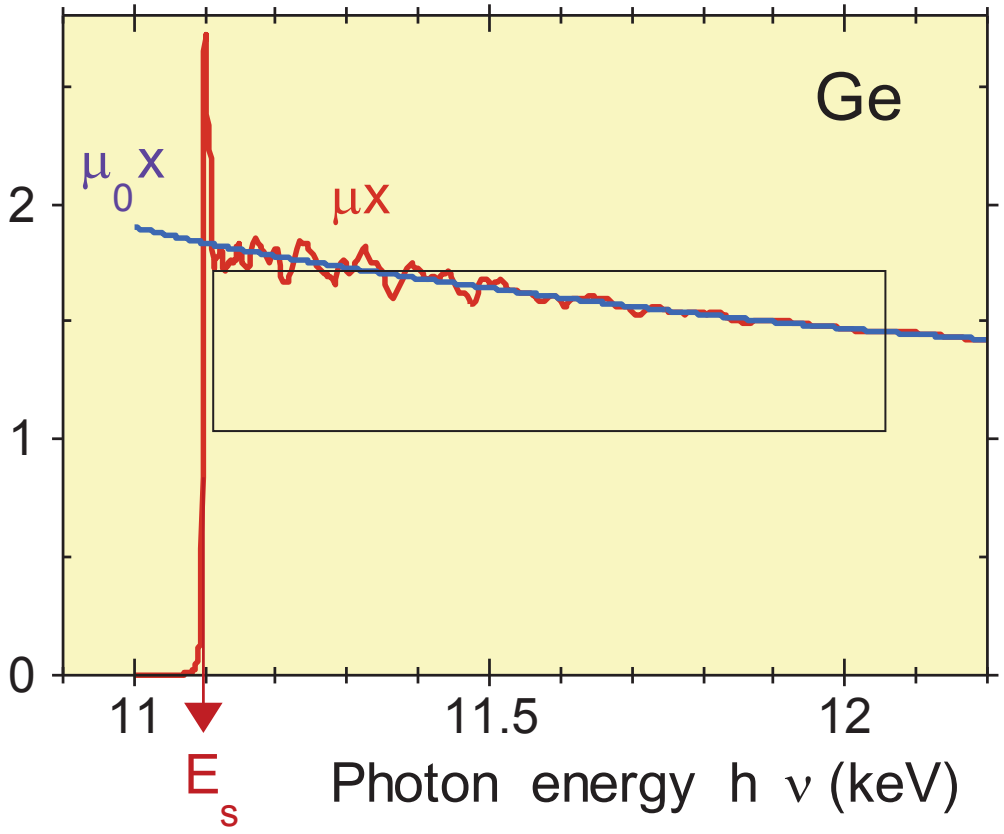
μ_0 ?

Isolated atom



Embedded atom



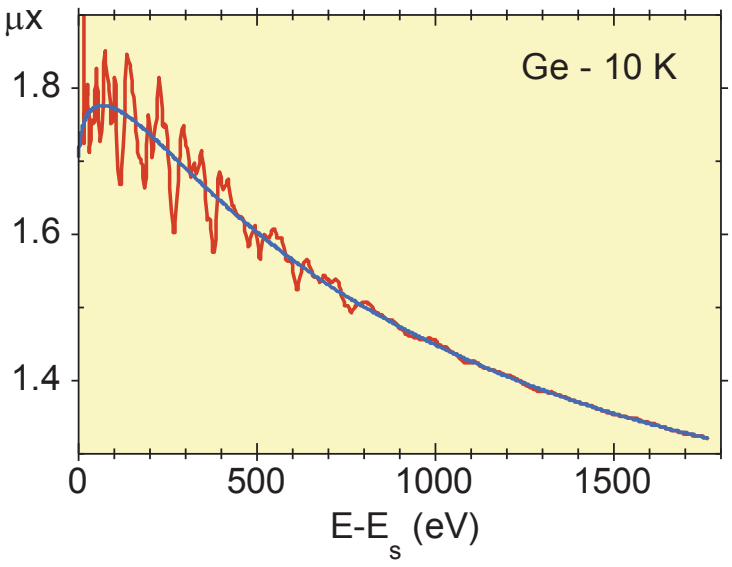


XAS – data analysis

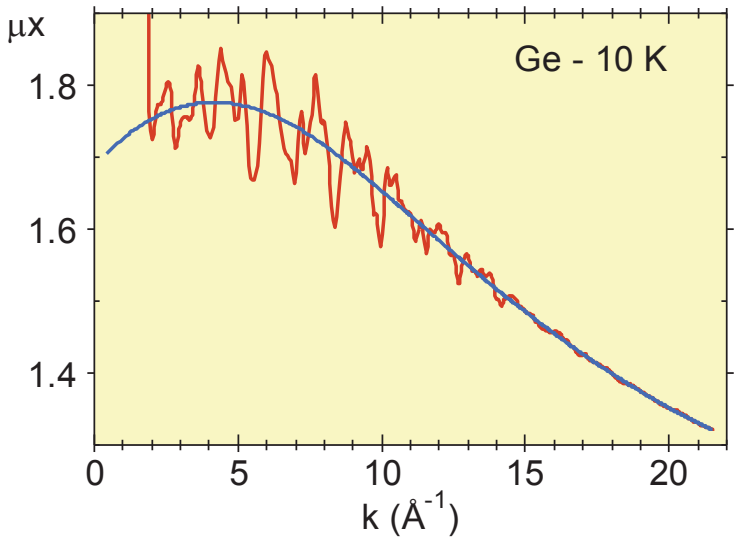
$$\chi(k) = \frac{\mu - \mu_0}{\mu_0}$$

Polynomial spline - best fit

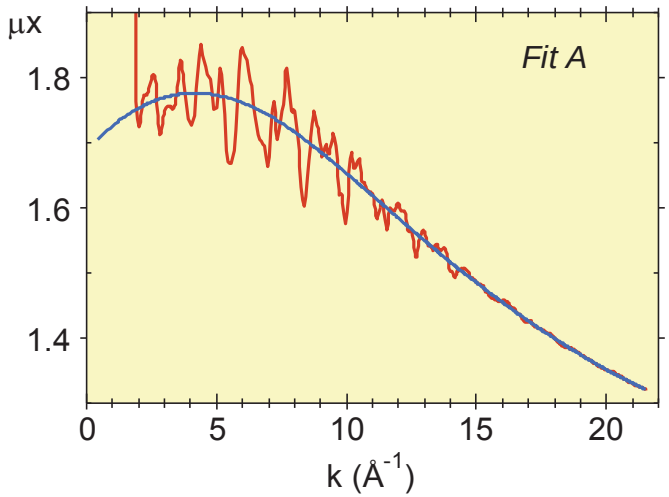
E space

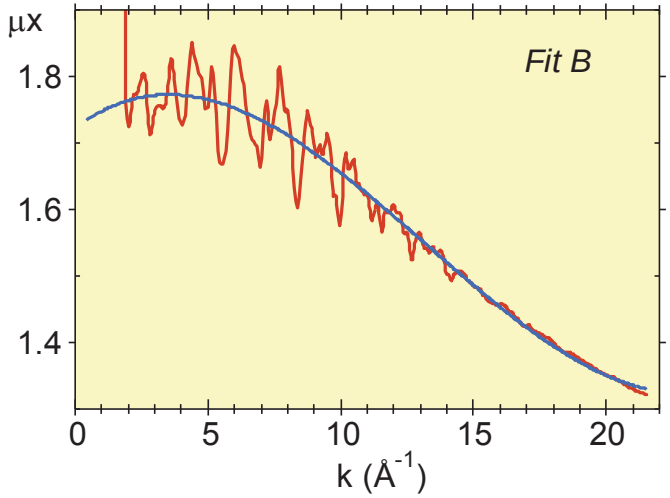


k space

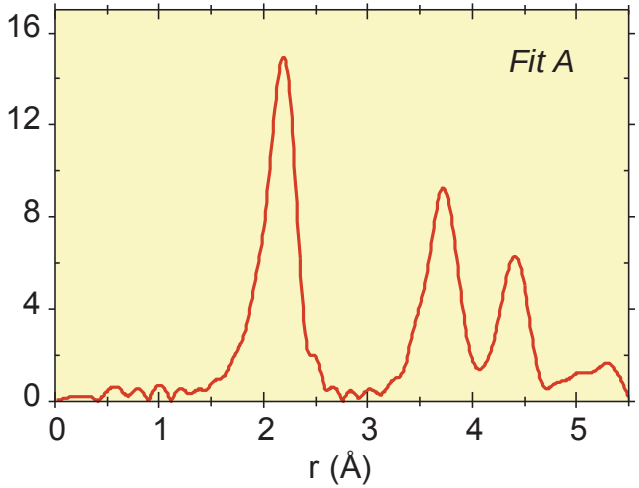


XAS – data analysis

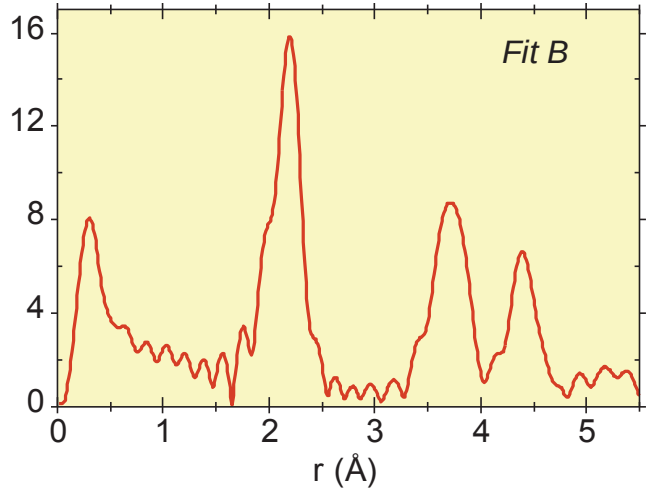




$\mu - \mu_0$

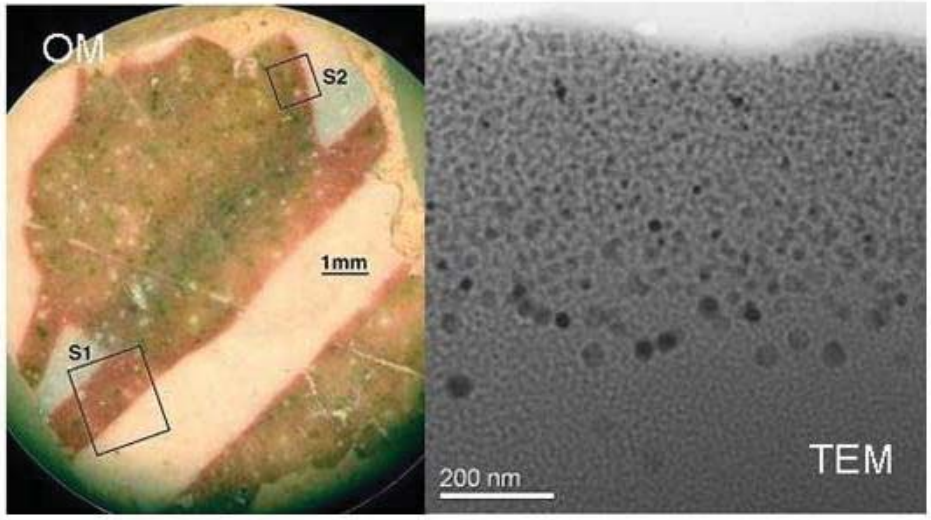


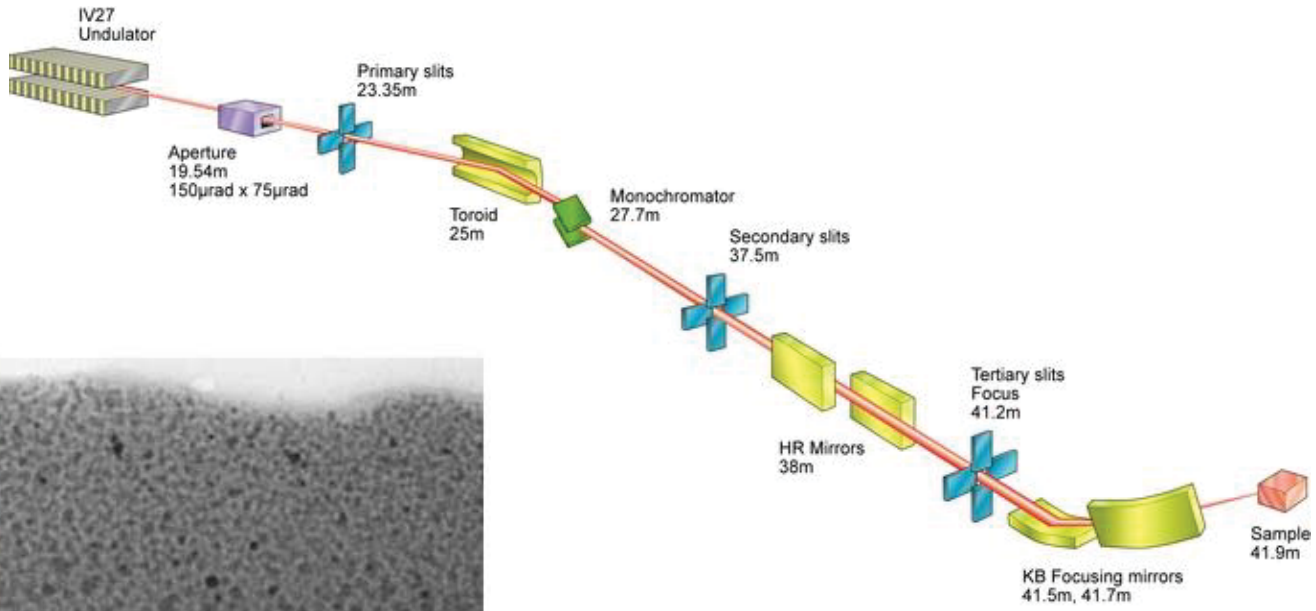
Fourier transf.



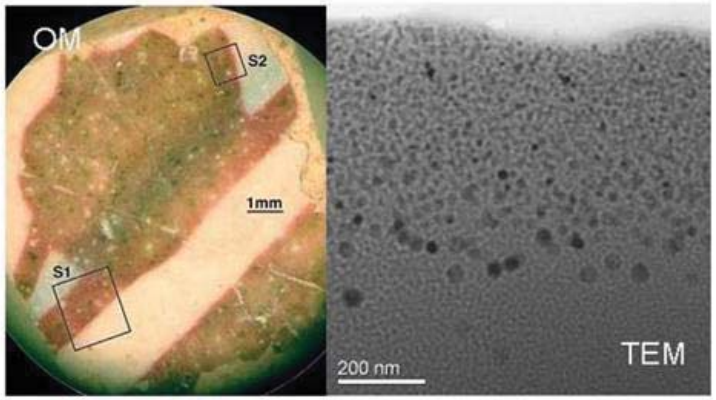
EXAFS example – Copper in lustre

Microfocus spectroscopy experiments on mineral deposits and in cultural heritage science at Diamond Light Source.
Josep Roque-Rosell1 et al.

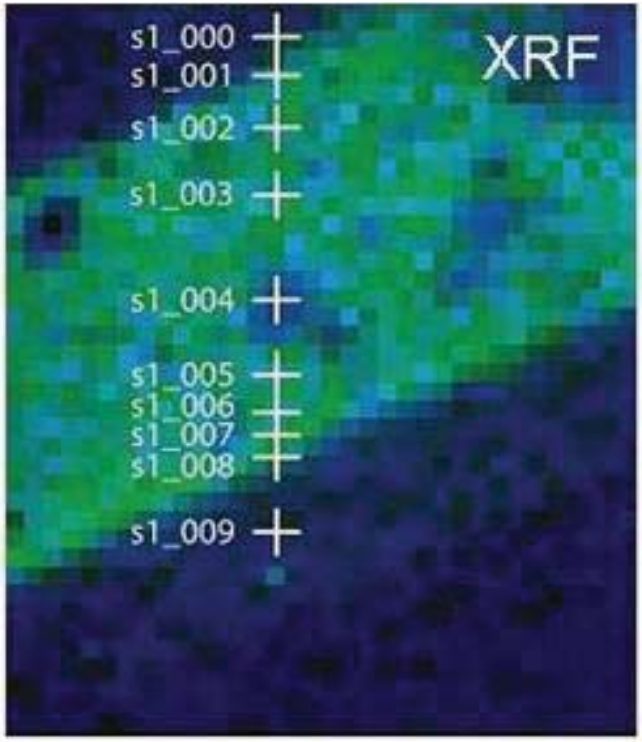


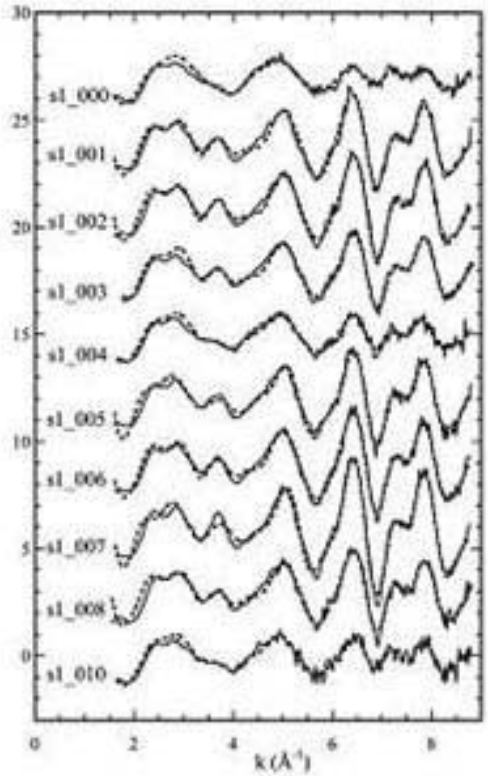


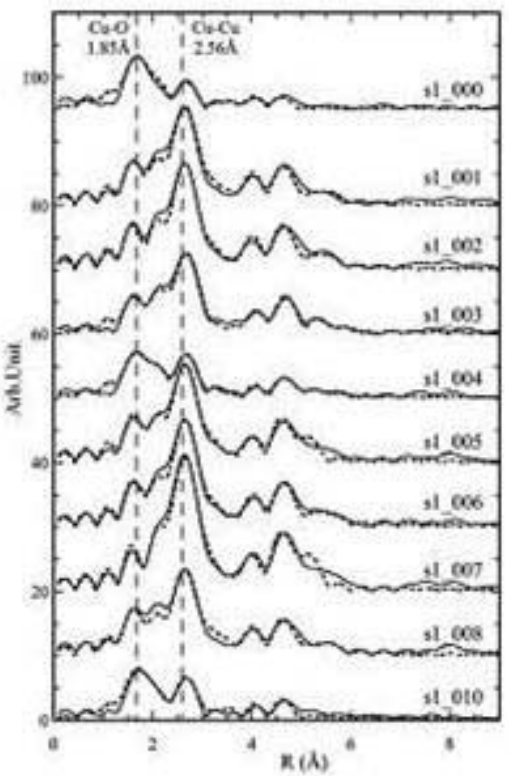
EXAFS example – Copper in lustre



Ceramic lustre from Paterna (Spain). Sampled region, TEM pictures showing copper nanoparticles, XRF mapping for Cu Ka, Cu K edge EXAFS spectra obtained across the lustre decoration and magnitude of the Fourier Transform of the EXAFS spectra.







XANES ↔ EXAFS
Multiple scattering

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

Single Scattering

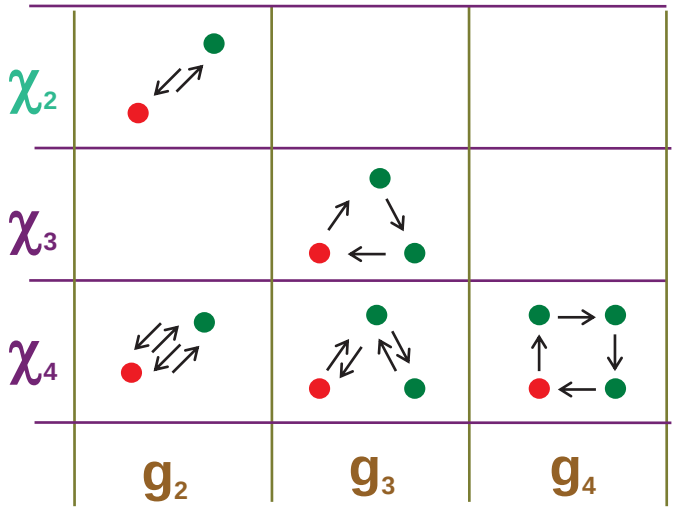
$$\mu(k) = \mu_0(k)[1 + \chi(k)]$$

Multiple Scattering

$$\mu(k) = \mu_0(k)[1 + \chi_2(k) + \chi_3(k) + \chi_4(k) + \ldots]$$

$\chi_n(k)$

Contribution from all n-order paths



g_n = n-body correlation function

XAS - References

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XAFS Society home page: http://ixs.csrri.iit.edu/IXS/

Software : ifeffit / Athena / Artemis/ Sixpack