Introduction to XAFS

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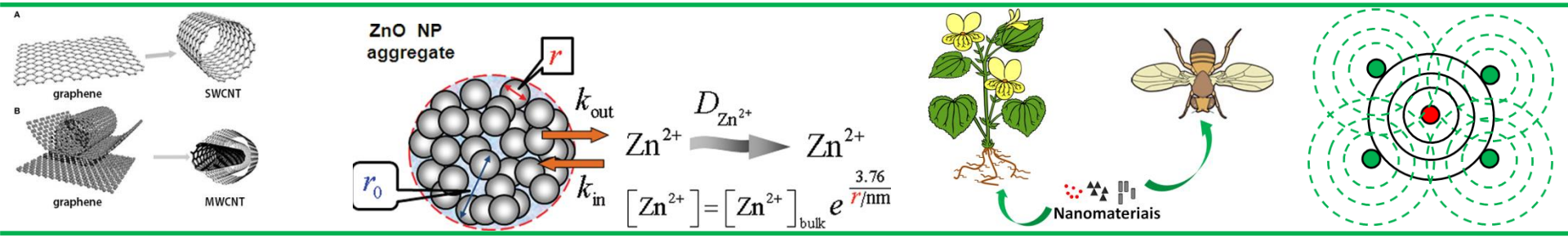
Grupo de Espectroscopia Aplicada ao Estudo de Nanomateriais na Agricultura e no Ambiente
Laboratório de Instrumentação Nuclear



Basics of XAFS

Revista Brasileira de Ensino de Física, vol. 22, no. 3, Setembro, 2000

Aplicação de Técnicas de Absorção de Raios X no Estudo de Materiais Magnéticos

(Study of magnetic materials by means of x-ray absorption techniques)

J.C. Cezar[1,2], F.C. Vicentin[1], H.C.N. Tolentino[1]

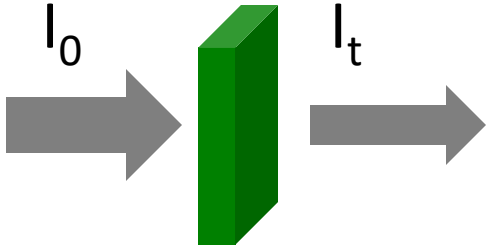
1 - Laboratório Nacional de Luz Síncrotron

CP. 6192 - Campinas - SP - 13083-970

2 - IFGW - UNICAMP

Principles of XAS - absorption edges

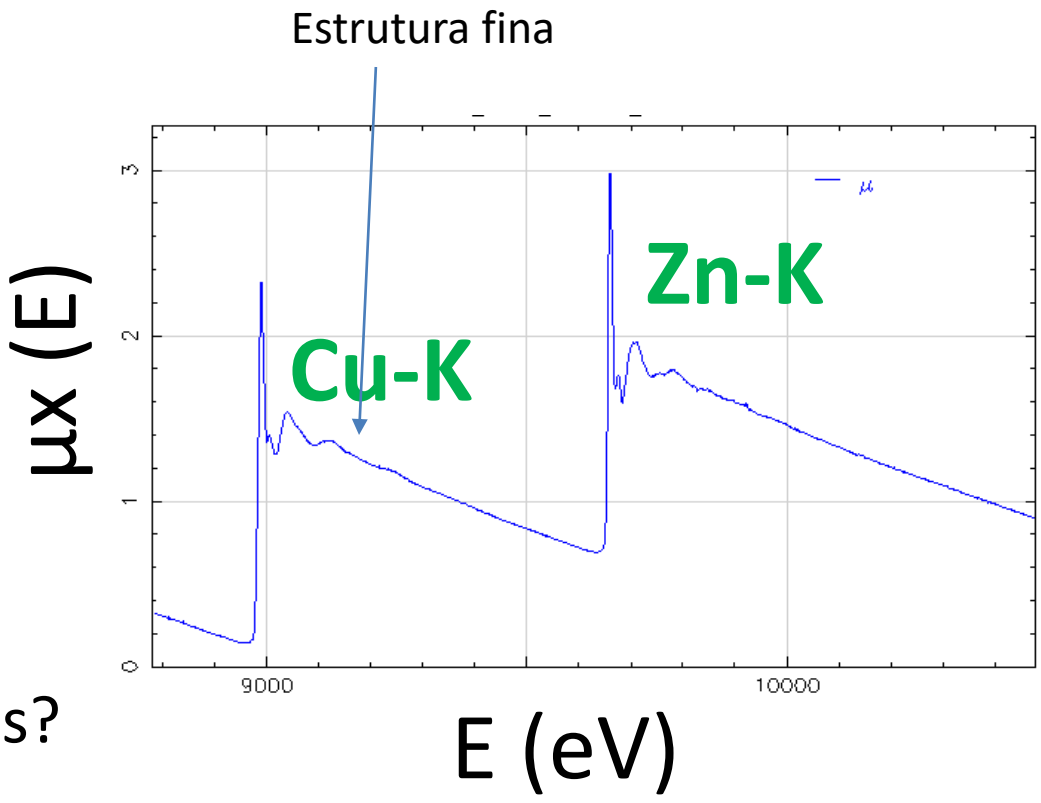
- The absorption edges and fine structure
  - The measurement is pretty simple



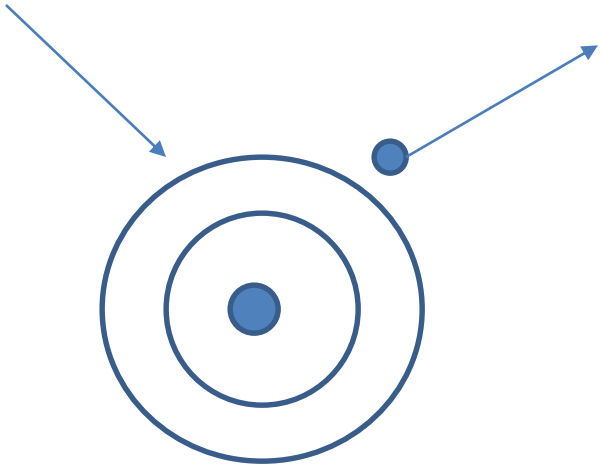
$$T = I_t/I_0$$

$$I_t = I_0 e^{-\mu x}$$

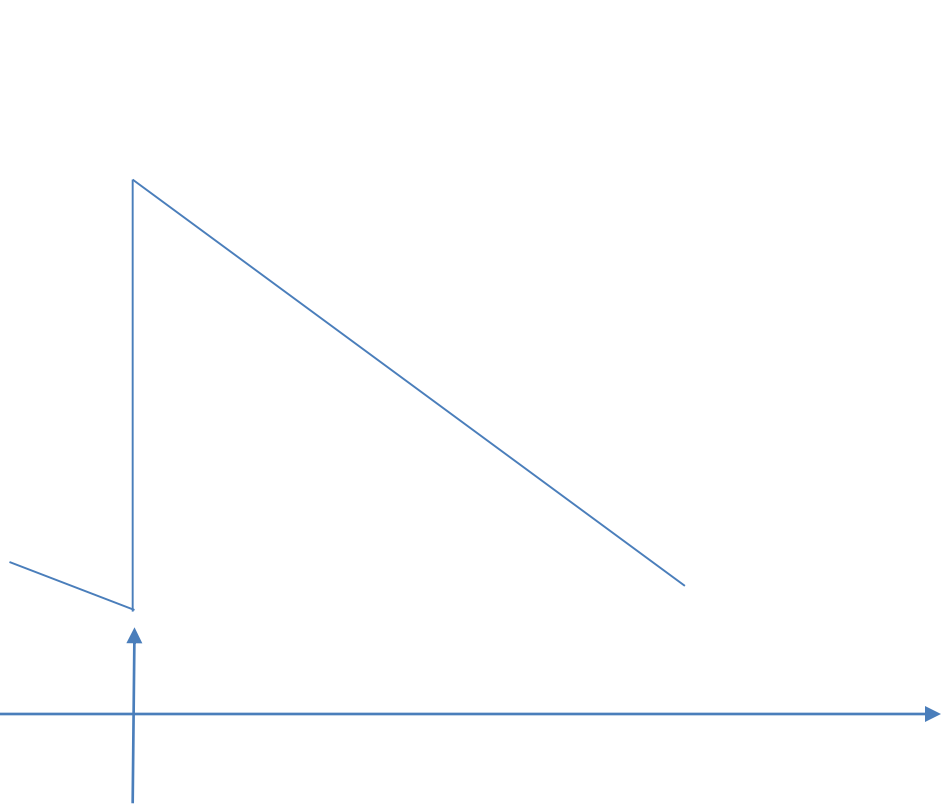
$$A = \ln(I_0/I_t) = \mu x$$

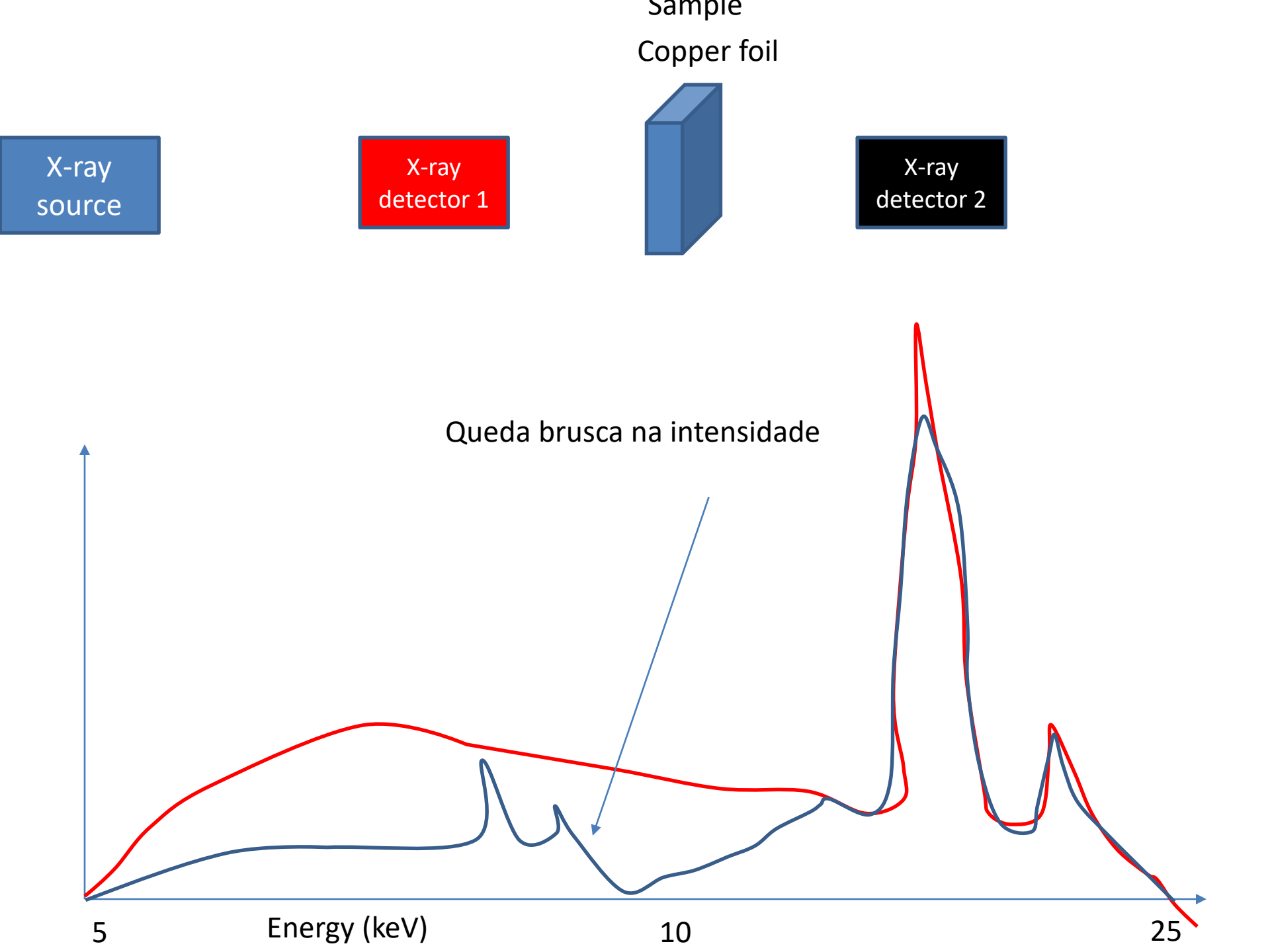


- What are these edges?



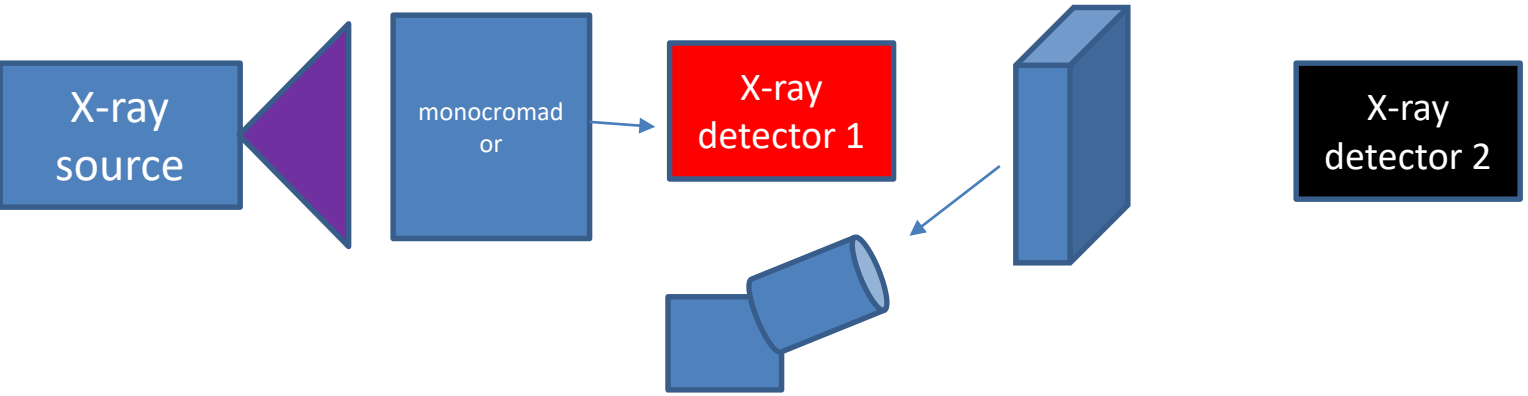
Um elétron é removido após a absorção do fóton. A energia do fóton > do que a energia de ligação do elétron



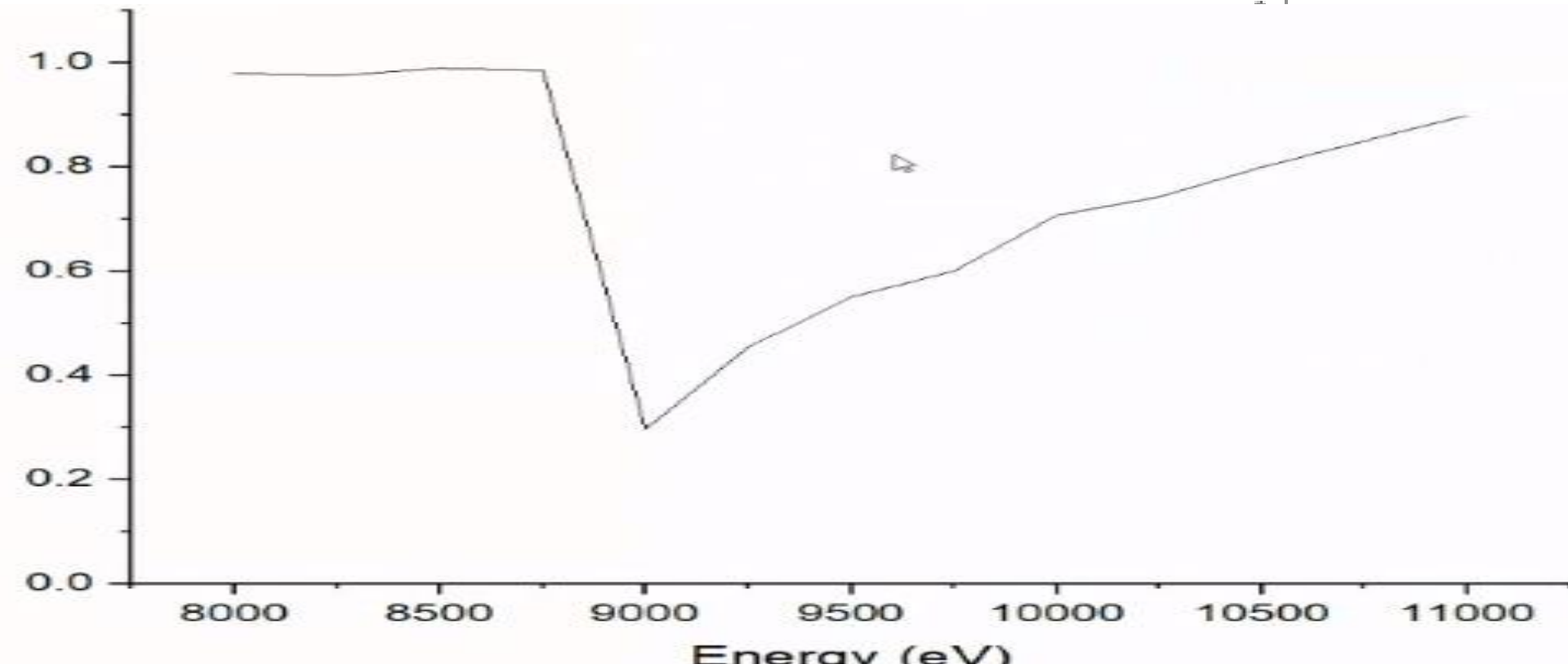

Sample
Copper foil
X-ray source
X-ray detector 1
X-ray detector 2
Queda brusca na intensidade
5
Energy (keV)
10
25

Sample

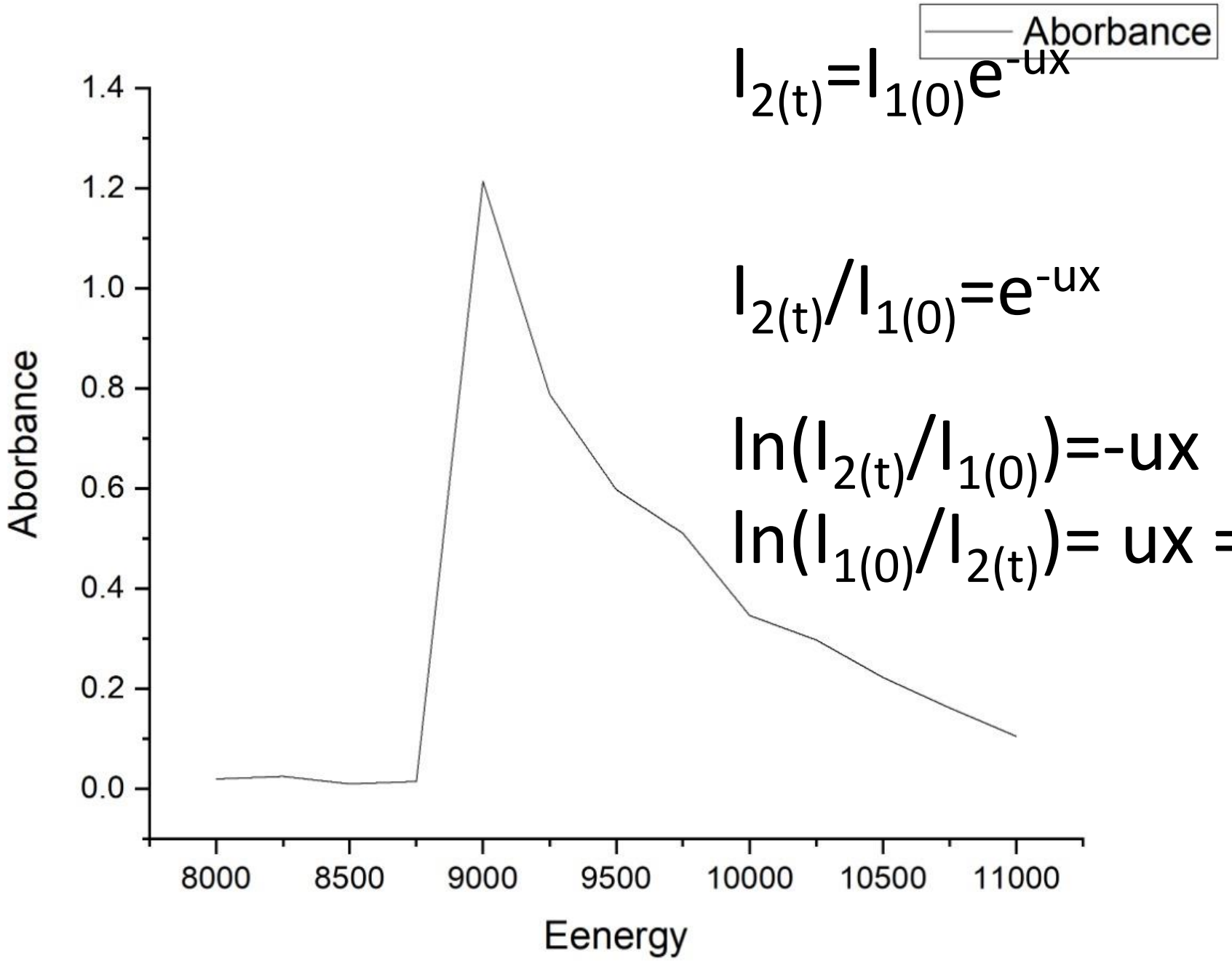
Copper foil



XRF detector



energia	Detector 1	Detector 2
8000	1000	980
8250	1010	985
8500	990	980
8750	1000	985
9000	1010	300
9250	990	450
9500	1000	550
9750	1000	600
10000	9090	700
10250	1010	750
10500	1000	800
10750	1000	850
11000	1000	900



$I_{2(t)}=I_{1(0)}e^{-ux}$

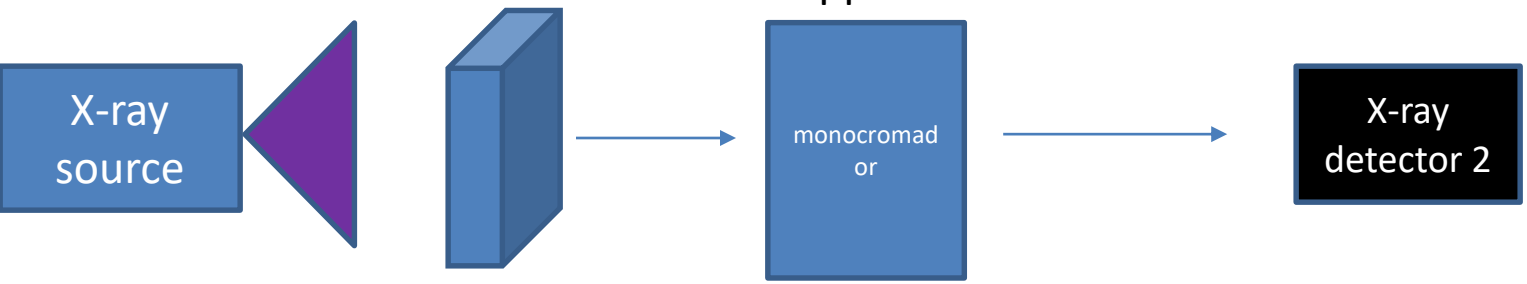
$I_{2(t)}/I_{1(0)}=e^{-ux}$

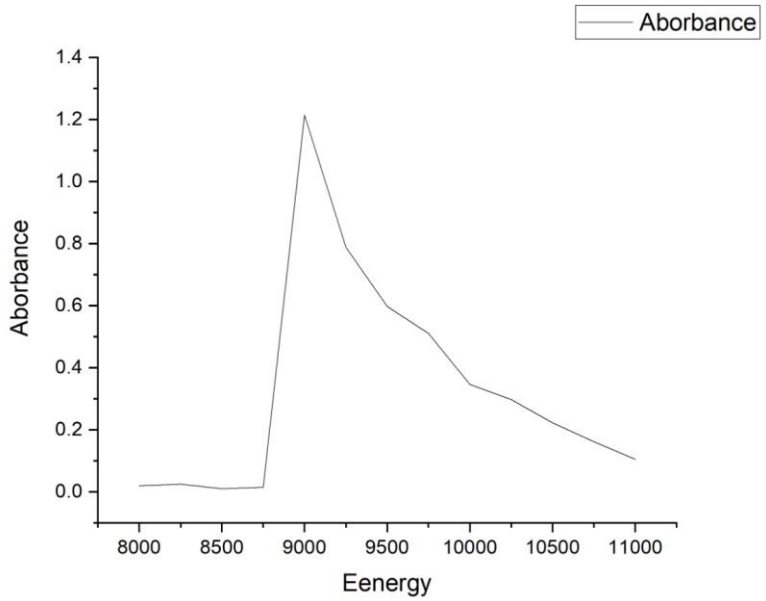
$\ln(I_{2(t)}/I_{1(0)})=-ux$

$\ln(I_{1(0)}/I_{2(t)})= ux = A$

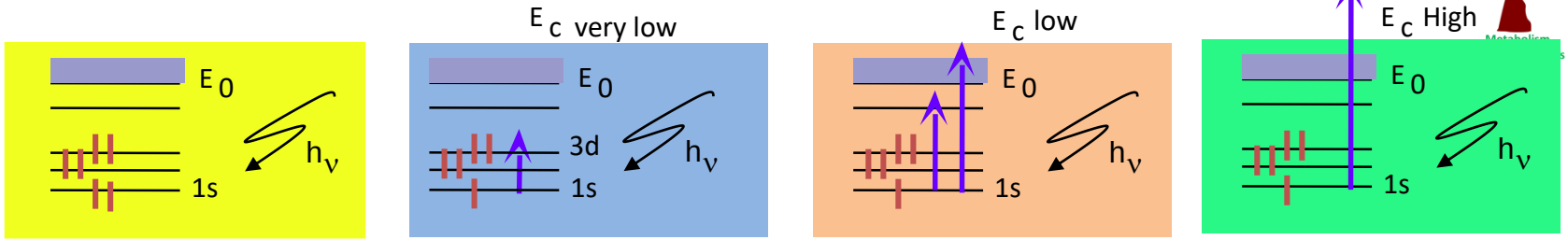
Sample

Copper foil

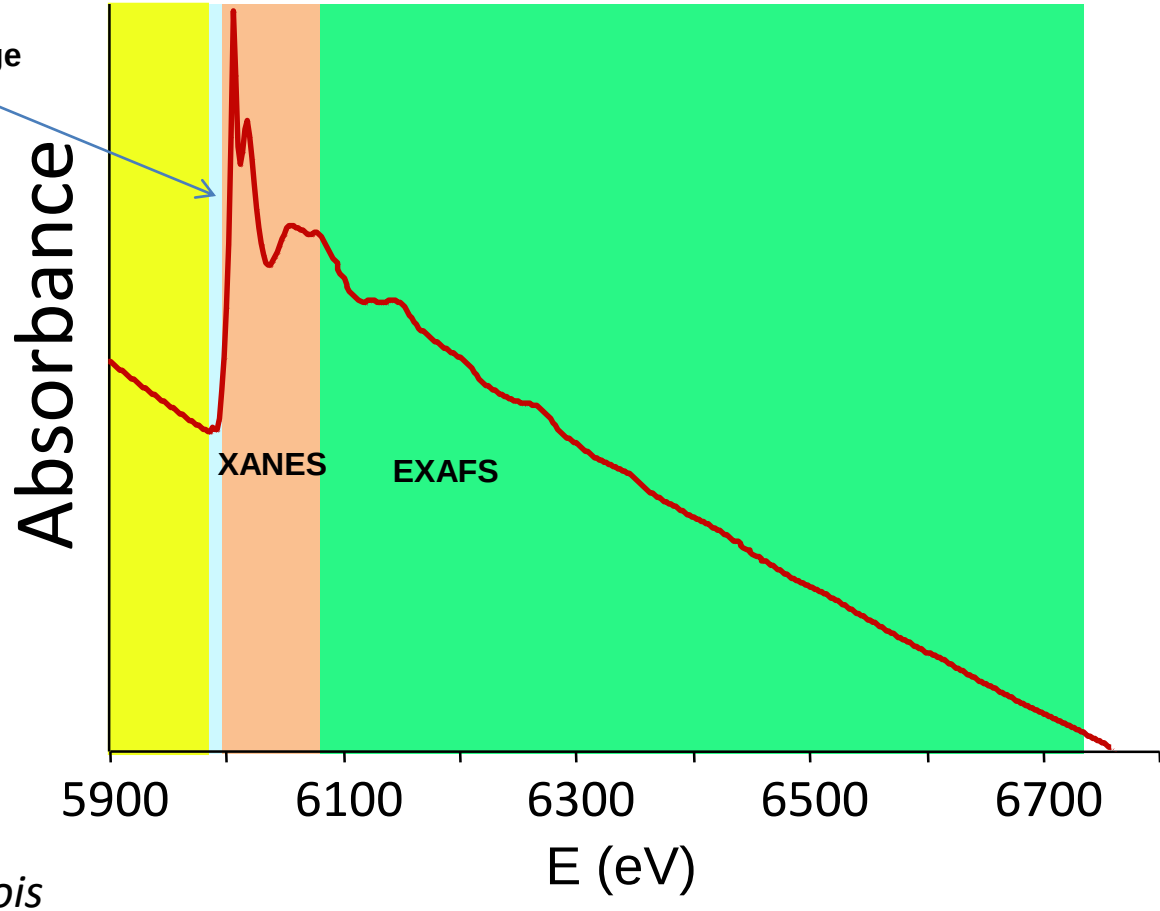




Principles of XAS- spectral regions



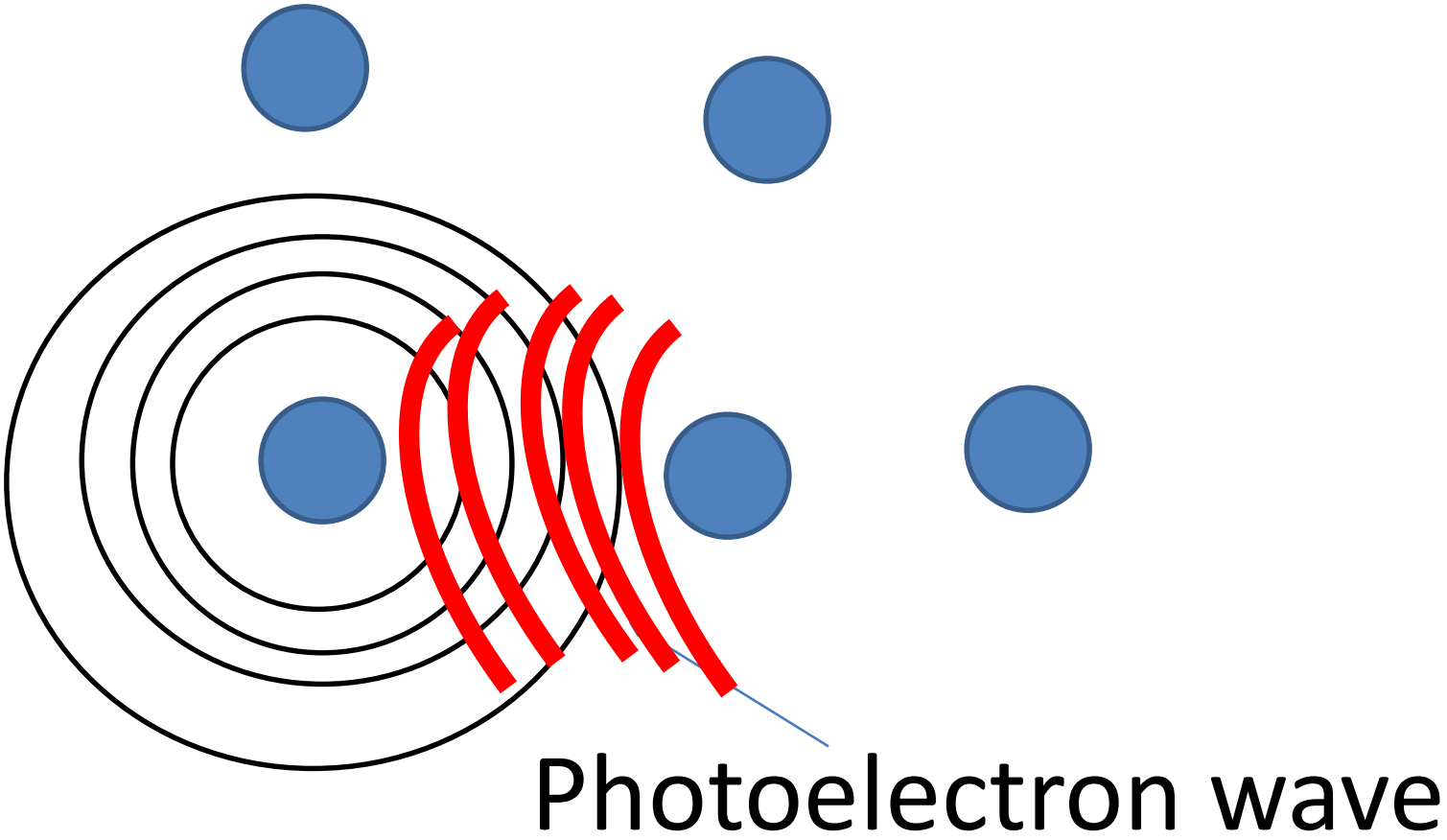
- Cr XAS spectrum
- ≠ theories for ≠ regions
- The electron fate after ejection



Modified from Dr. Valerie Briois

Ec= photoelectron's kinetic energy

Ec= h*v (photon energy)* – $E_{binding}$ – work function (very small)



λ(wavelenght) = h (Plank constant)/p (momentum)

$p = mv$

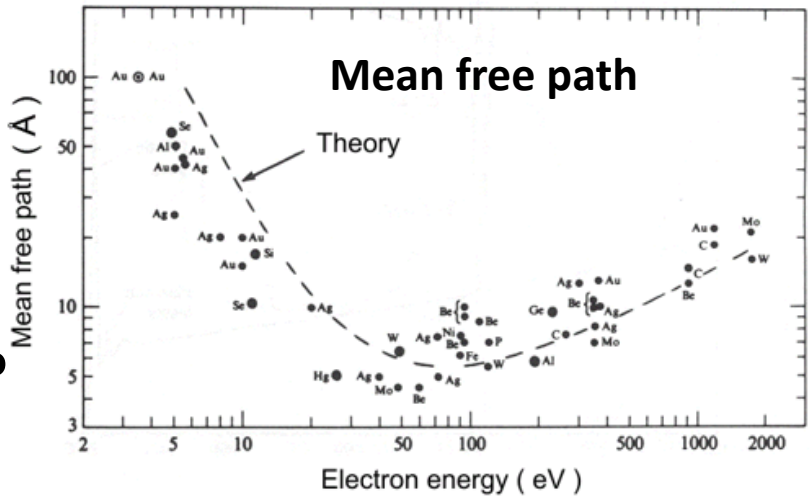
$Ec = 1/2mv^2$

De Broglie relationship

https://br.pinterest.com/pin/658792251723477724/

Principles of XAS- XANES *versus* EXAFS

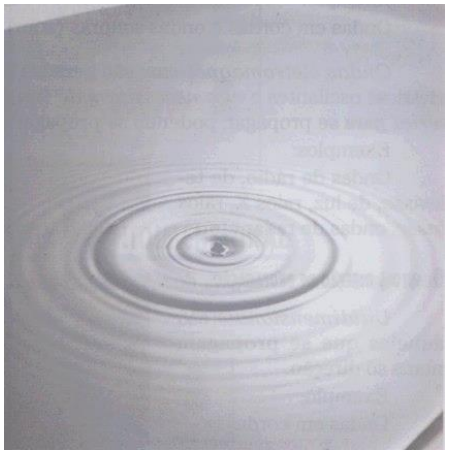
- **Multiple scattering approach**



http://users.uj.edu.pl/~ufpostaw/2_Pracownia/D1/images/jak_ba1_eng.png

- The photoelectron is regarded as a wave
- May the wave find any obstacles?

One wave

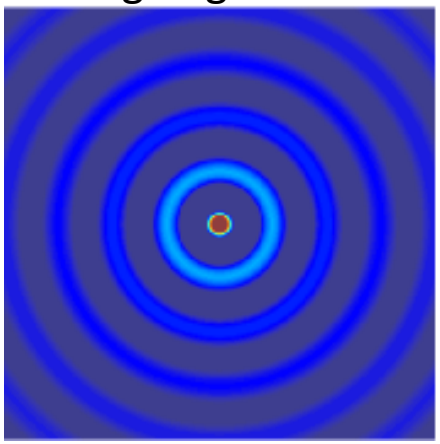


Two interfering waves

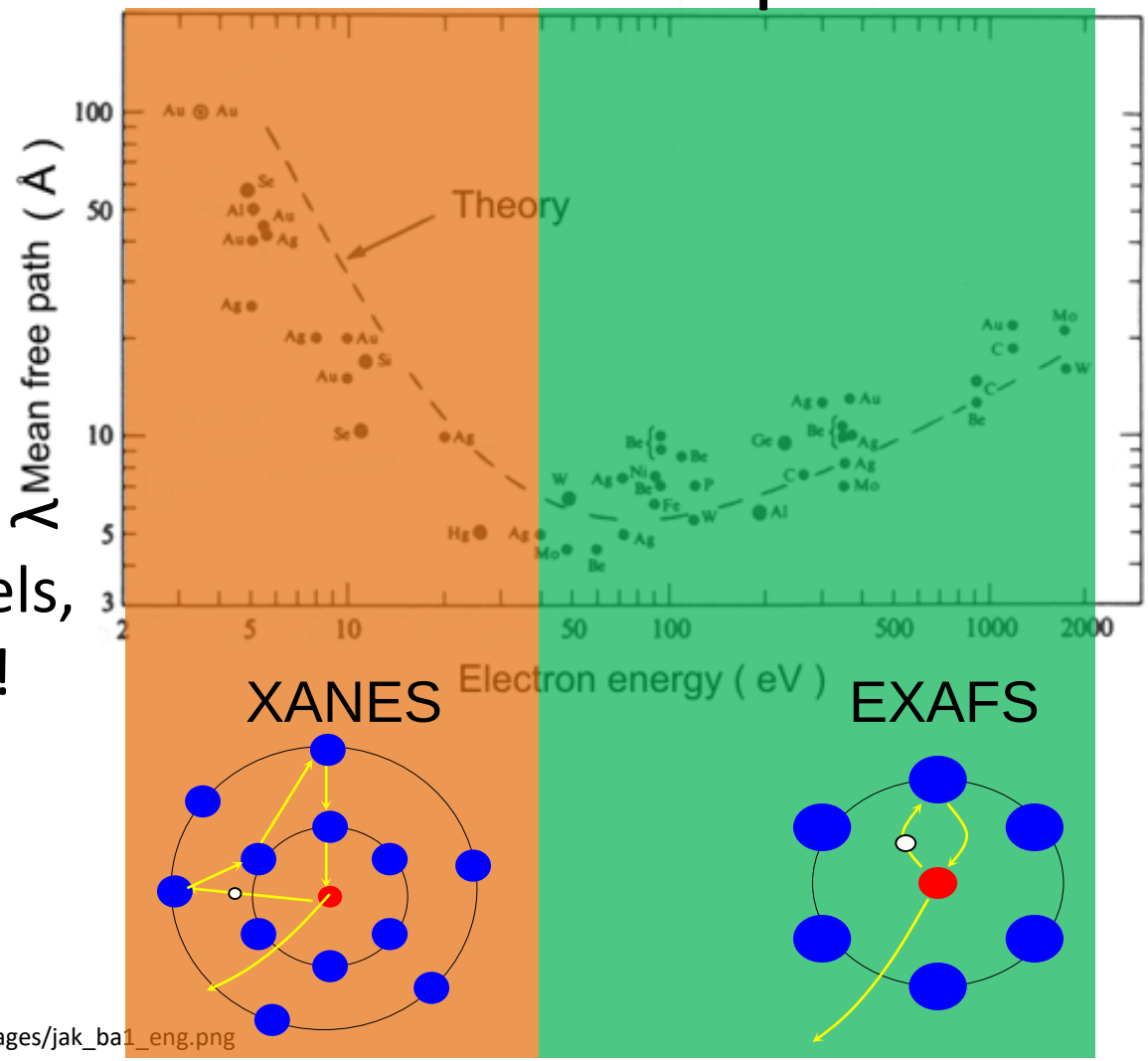
Principles of XAS- XANES *versus* EXAFS

- Multiple scattering approach

outgoing wave



Electron mean free path λ



- The electron travels, and brings info back!
- Low Ec = long λ
- High Ec = short λ

http://users.uj.edu.pl/~ufpostaw/2_Pracownia/D1/images/jak_ba1_eng.png

The Paper by H. Fricke

- Any questions?

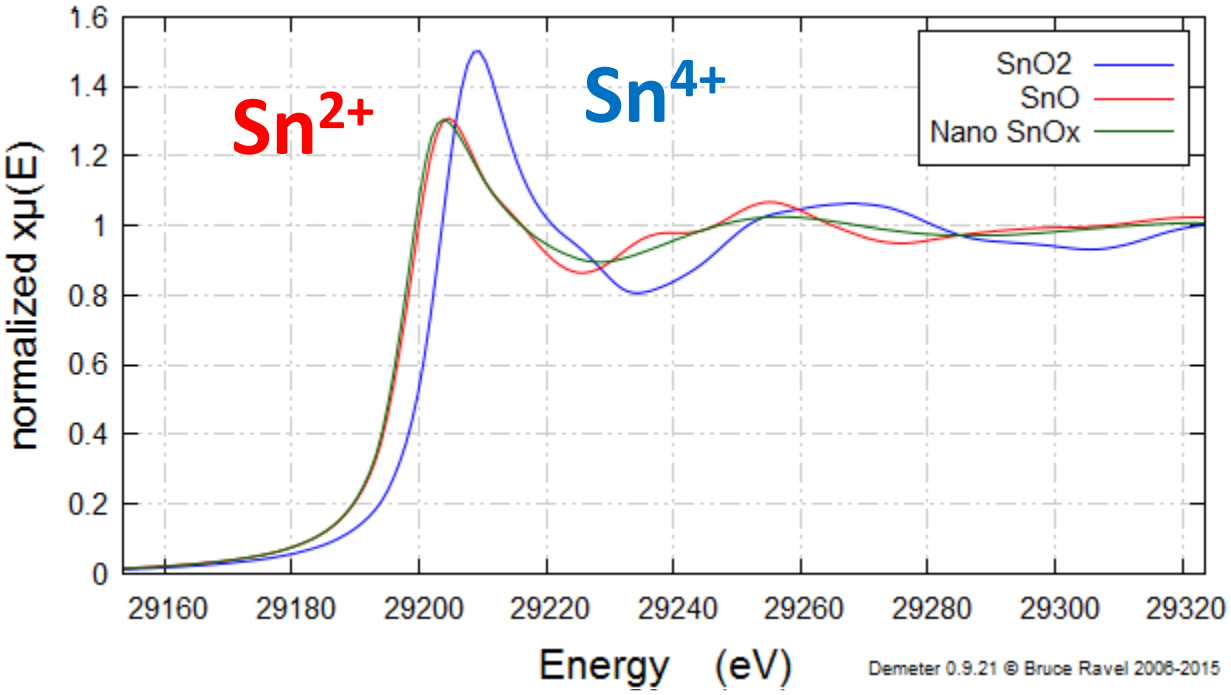
Applications and Theory of XANES

- The information that one gets:
  - Oxidation state
  - Semi quantitative speciation
  - Symmetry, *e.g*. Td ou Oh
  - Nature and distance of ligands

Finger print

XANES Data analysis

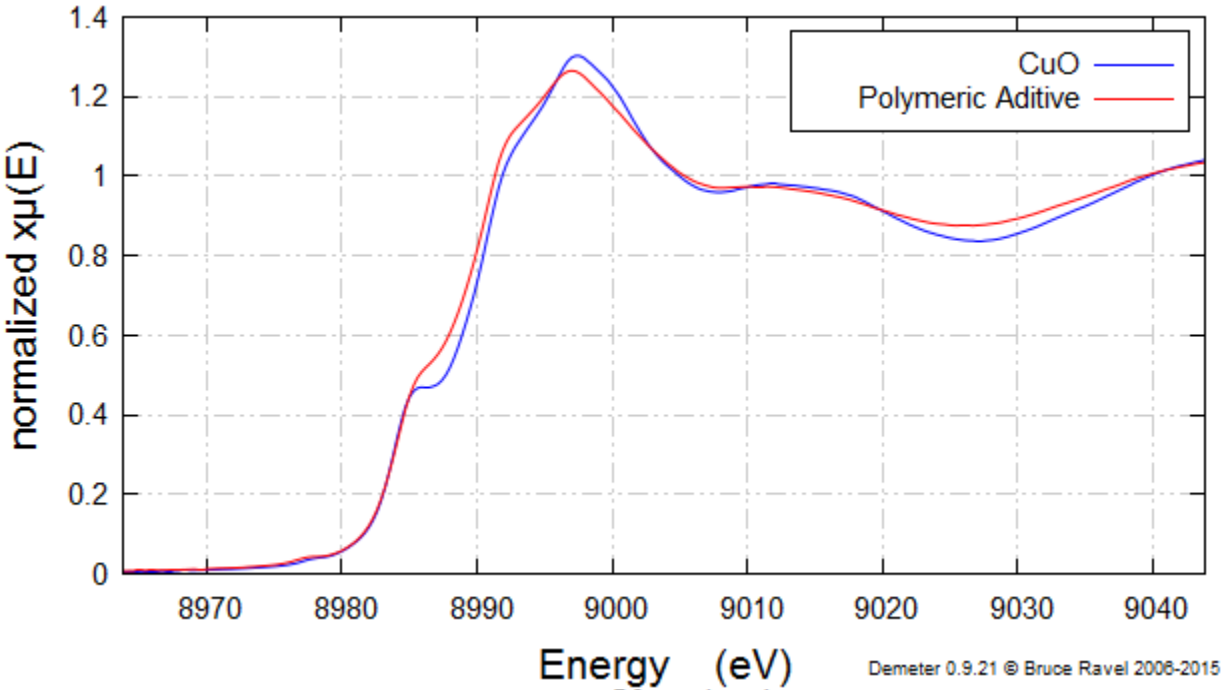
- XANES
  - Finger print
  - Semi quantitative analysis
- Finding out the oxidation state of Sn based semi conductor
- Oxidation plays on the edge intensity and position



Data recorded at DORIS X1 (Germany)

XANES Data analysis

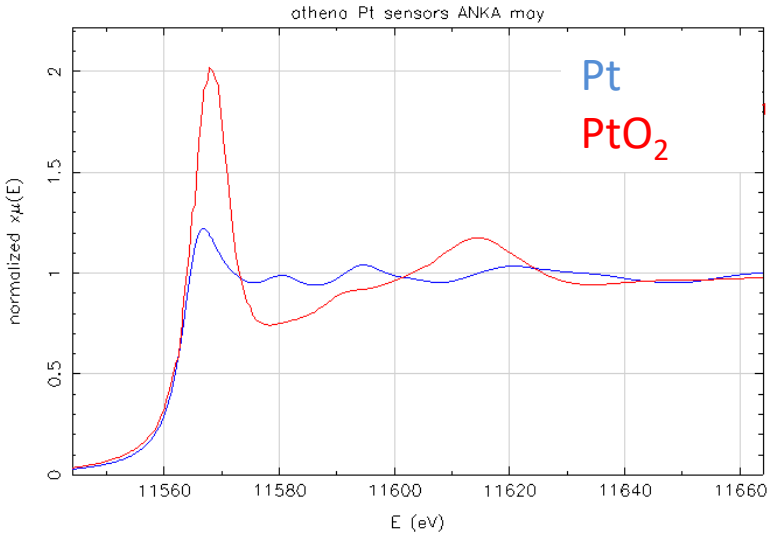
- XANES
  - Finger print
- Cu based polymeric additive state after burning

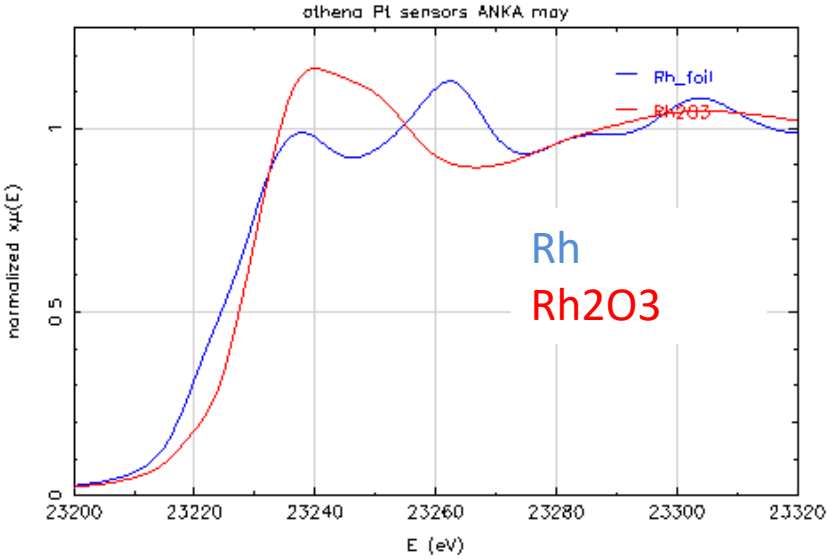


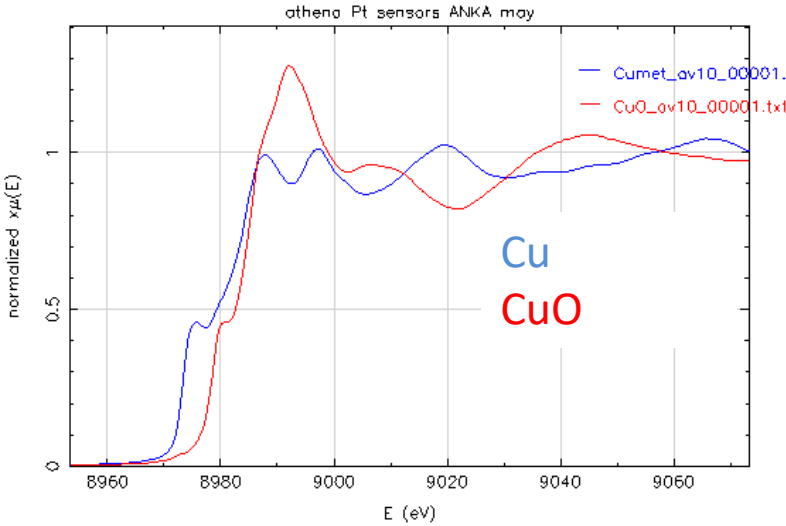
Data recorded at SOLEIL SAMBA (France)

XANES Data analysis

- XANES
  - Finger print
- Oxidation state

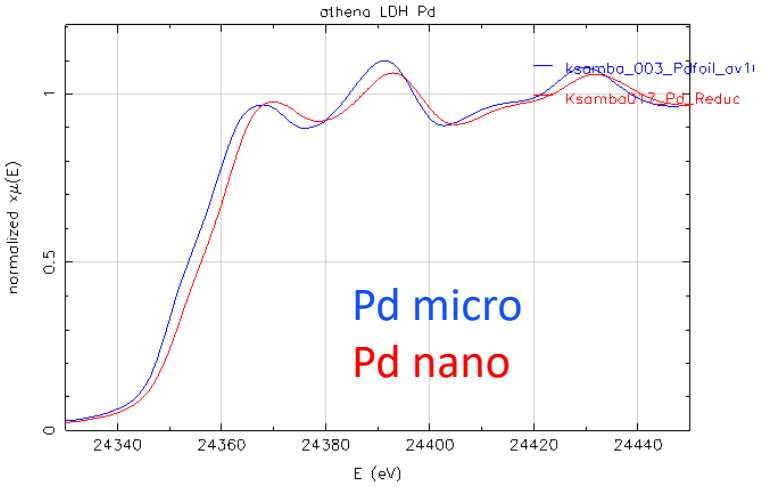


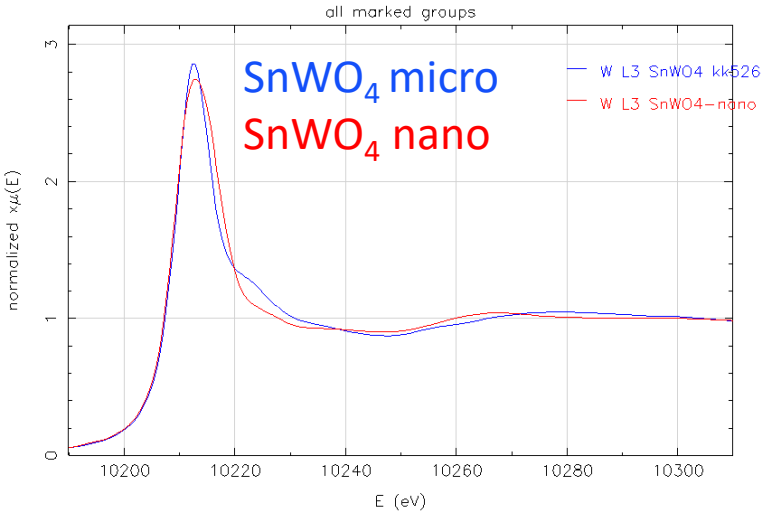


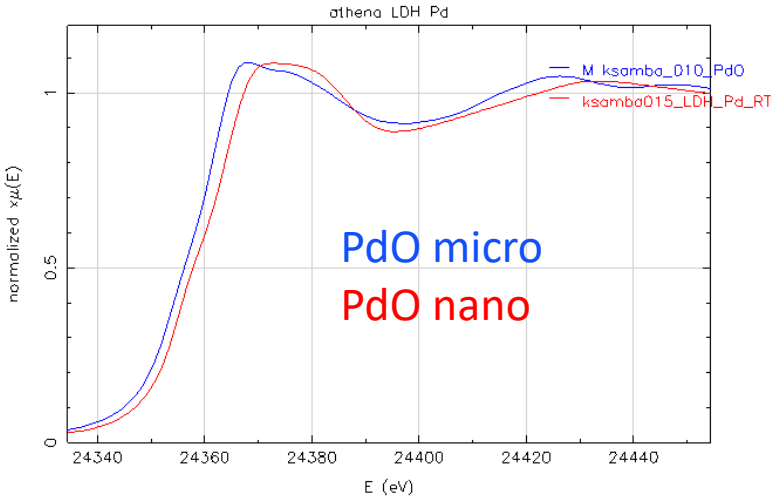


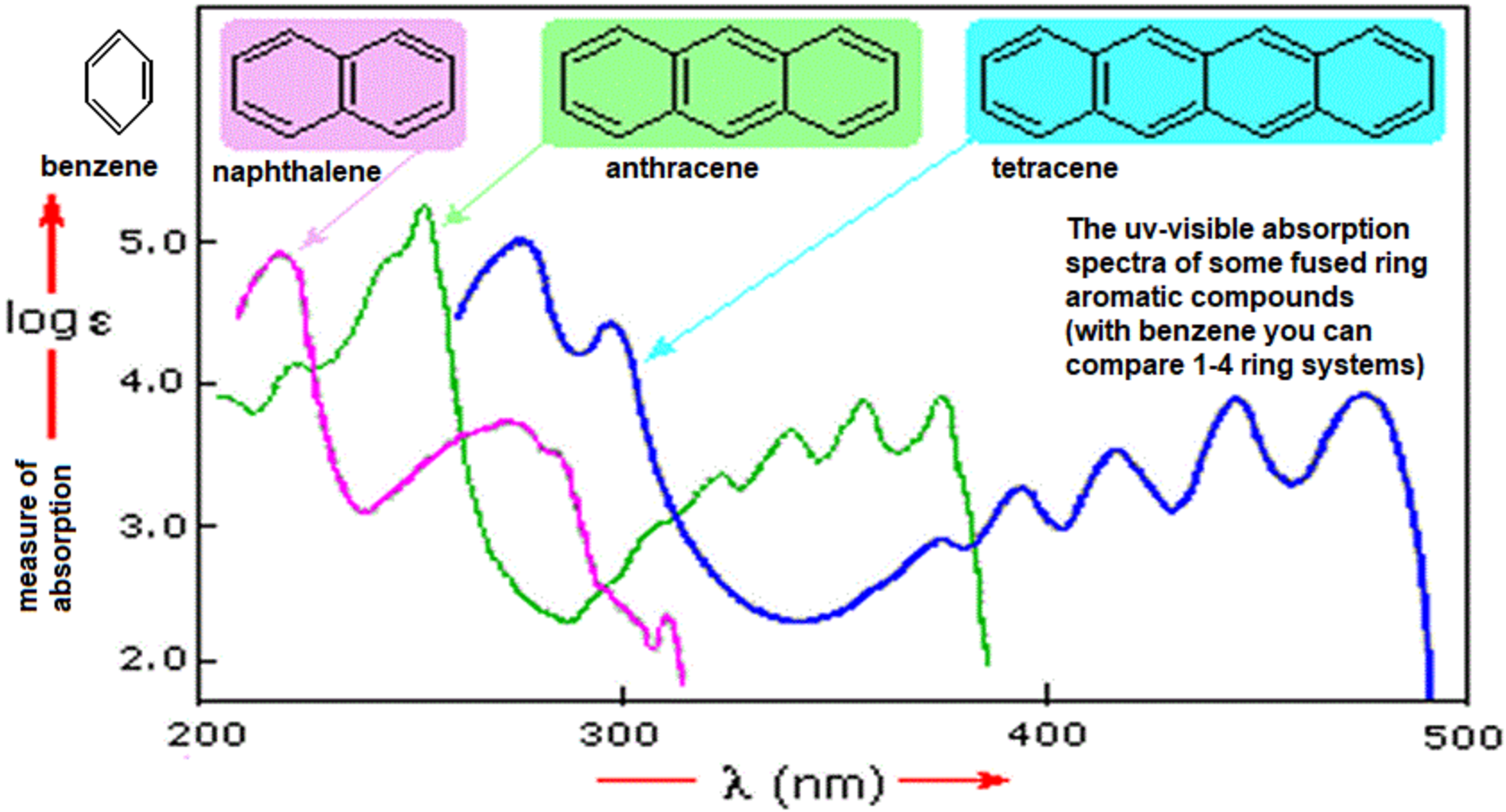
XANES Data analysis

- XANES
  - Input on Disorder









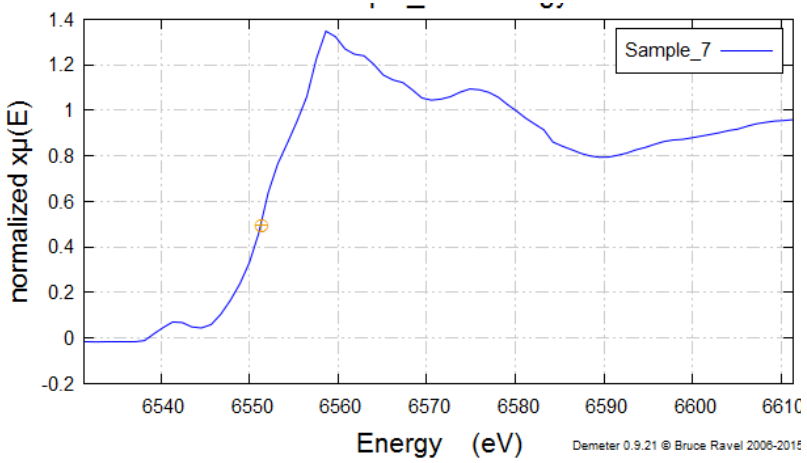
https://docbrown.info/page06/spectra/0uv-visible-spectra-07aroms.htm

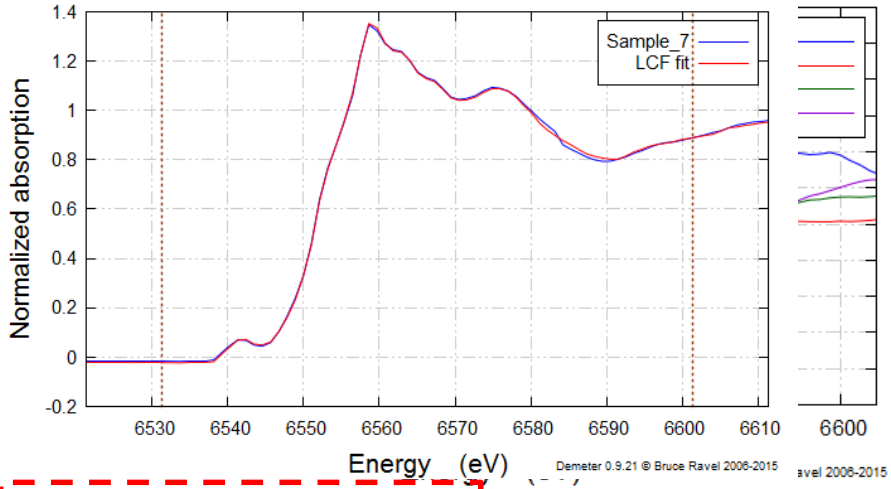
$$E = \frac{n^2 h^2}{8mL^2}$$

Linear combination

Data analysis

- XANES
  - Finger print
  - Semi quantitative analysis
- Mn in LaMnSrOx based electrodes





$$R = \frac{\sum_{i=1}^{N}(data_i - fit_i)^2}{\sum_{i=1}^{N}(data_i)^2}$$

R-factor = 0.0005594 X100 = 0.05594%

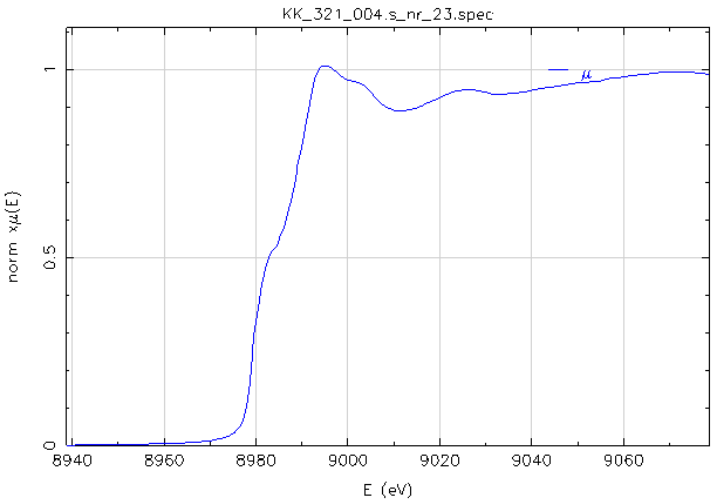
. MnO2	0.588 (0.010)
. Mn3O4	0.107 (0.015)
. Mn2O3	0.304 (0.023)

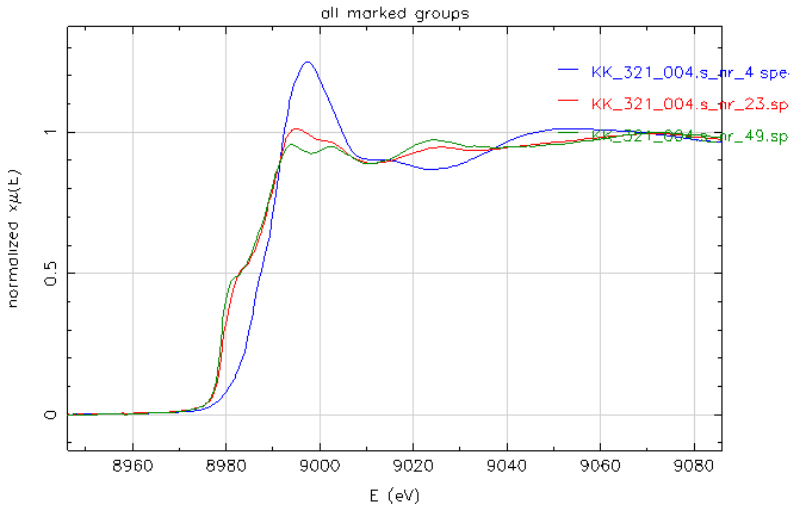
Data recorded at ESRF ID26 (France)

- Overall uncertainty ≈ 10%

Data analysis

- XANES
  - Finger print
  - Semi quantitative analysis
- Mn in LaMnSrOx based electrodes





$$R = \frac{\sum_{i=1}^{N}(data_i - fit_i)^2}{\sum_{i=1}^{N}(data_i)^2}$$

R-factor = 0.000471 X100 = 0.0471%

. CuO 0.17 (0.010)

. Cu 0.83 (0.010)

- Overall uncertainty ≈ 10%

Data recorded at ANKA XAS (Germany)

Data analysis

- XANES
- Semi quantitative analysis
- Ni based catalyst for hydrogenation of CO_2

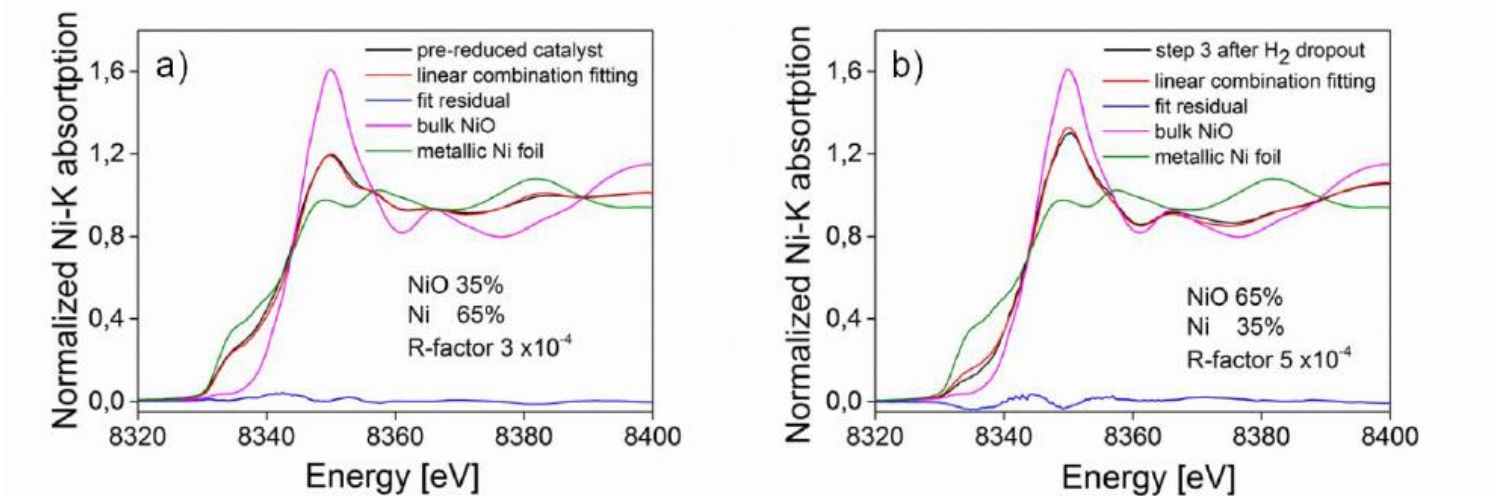


Figure S4: XANES spectra of the pre-reduced catalyst (a) and the catalyst under less reducing atmosphere (b) (measured *in situ* according to Figure 4, step 3) each in black, metallic Ni (green) and NiO (purple) references. Additionally, the result of the linear combination fitting (red) and the fit residual (blue) is shown. The linear combination of the pre-reduced catalyst revealed 35 % of an oxidic Ni phase, the catalyst after H_2 dropout revealed 65 % NiO.

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Methanation of CO_2: Structural response of a Ni-based catalyst under fluctuating reaction conditions unraveled by *operando* spectroscopy

Benjamin Mutz [a,b], Hudson W.P. Carvalho [a], Stefan Mangold [c], Wolfgang Kleist [a,b], Jan-Dierk Grunwaldt [a,b,*]

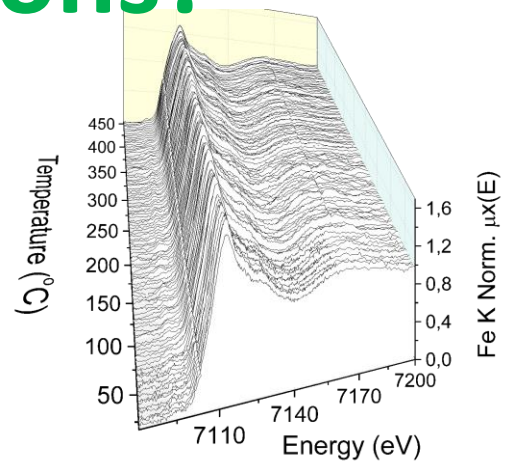
[a] Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany
[b] Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany
[c] Synchrotron Radiation Facility ANKA, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany

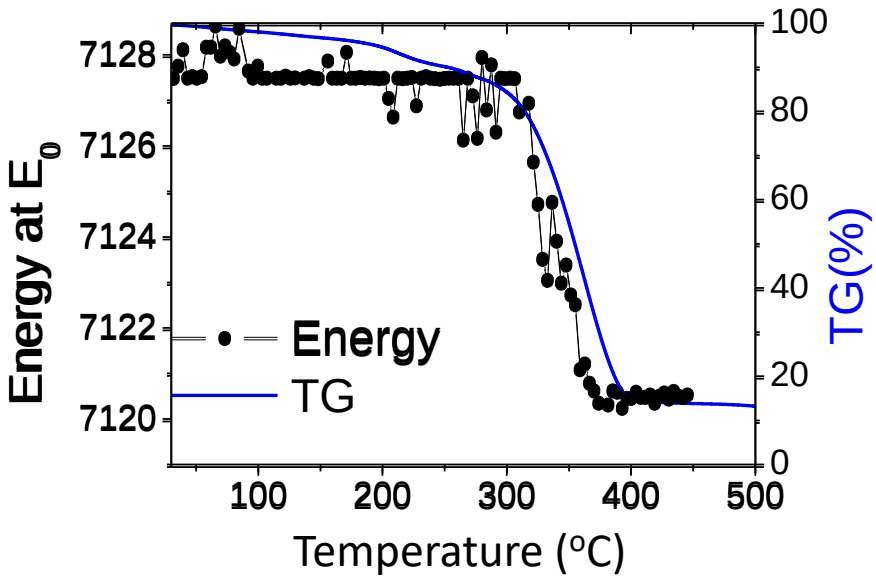
Data recorded at ANKA XAS (Germany)

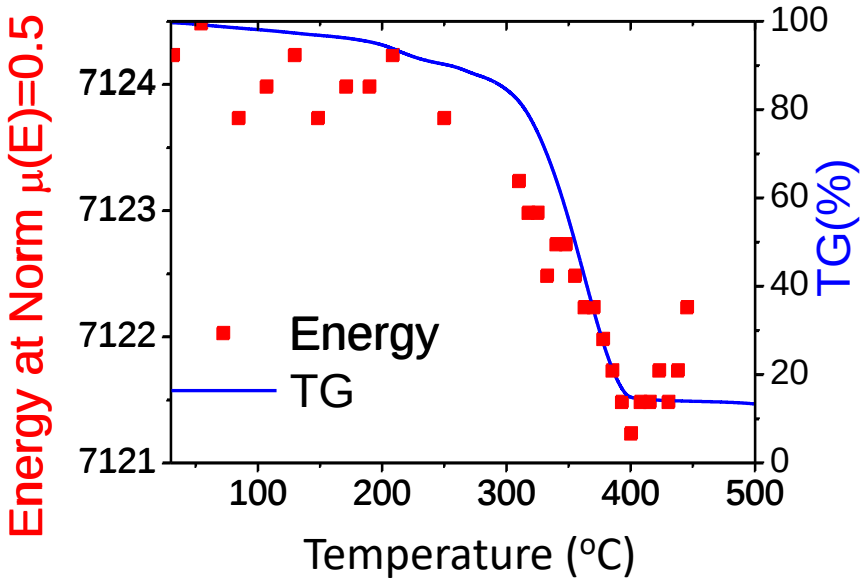
Following kinetics

What happens around Fe ions?

- The edge shifts
- This shift follows the TG curve
- It might mean:
  - Fe^{3+} is receiving electron density
  - **Fe^{3+} electron acceptance may stop the radicals**

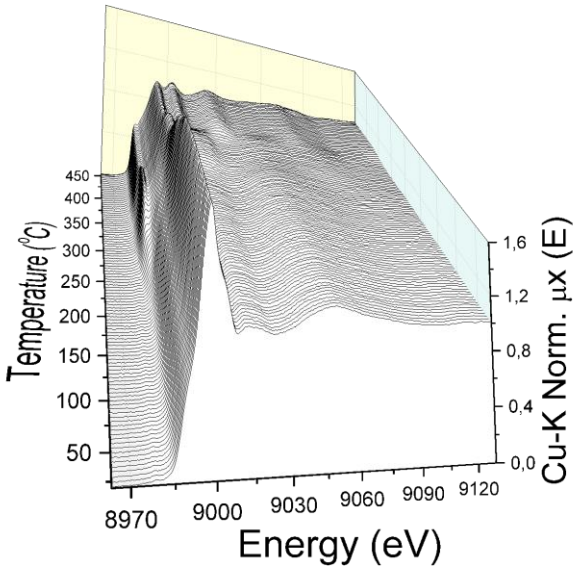


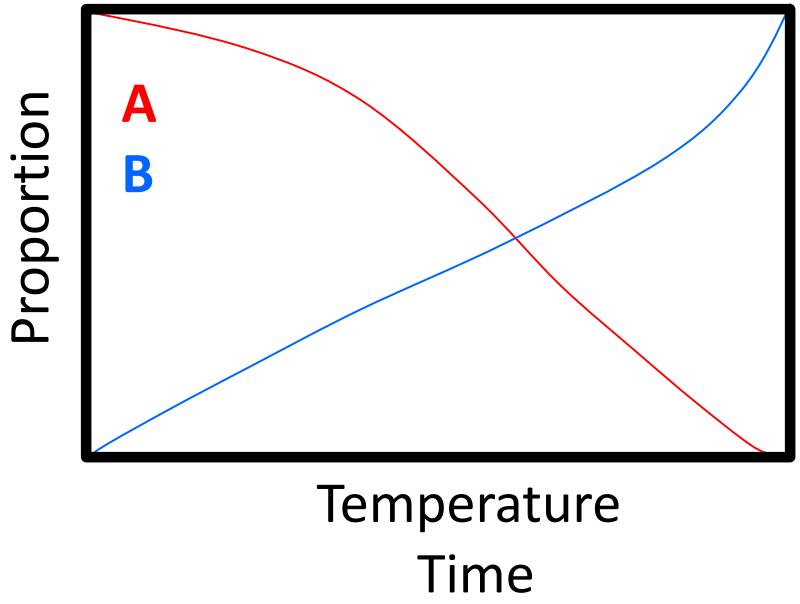




What happens around Cu ions?

- Cu looks more complex
- How to find the components?
- How to find the components' proportions?

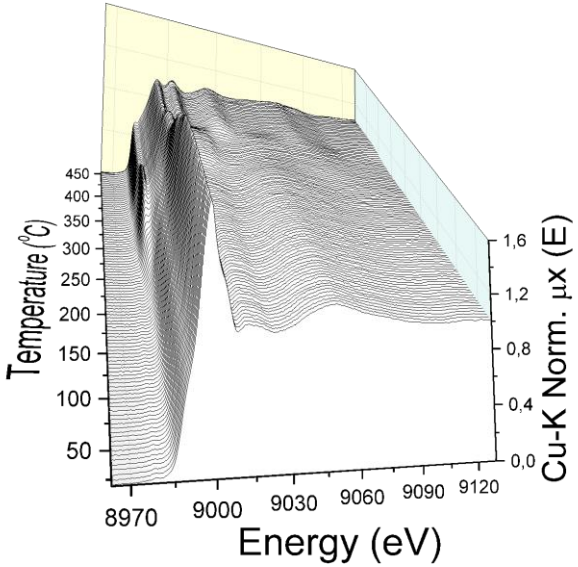


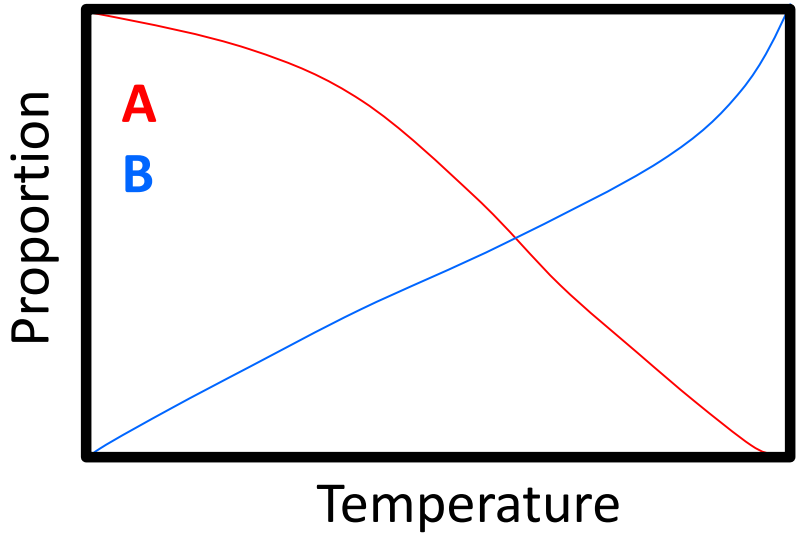


- A clever strategy:
  - PCA to uncover the "*number*" of phases
  - TT to find candidates to be references
  - Linear combination analysis

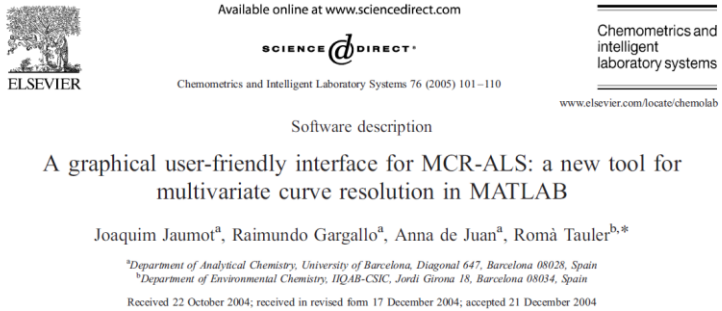
What happens around Cu ions?

- Cu looks more complex
- How to find the components?
- How to find the components' proportions?





- Another strategy:
  - Chemometrics MCR-ALS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SCIENCE DIRECT
Chemometrics and Intelligent Laboratory Systems 76 (2005) 101–110
Chemometrics and intelligent laboratory systems
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Software description

A graphical user-friendly interface for MCR-ALS: a new tool for multivariate curve resolution in MATLAB

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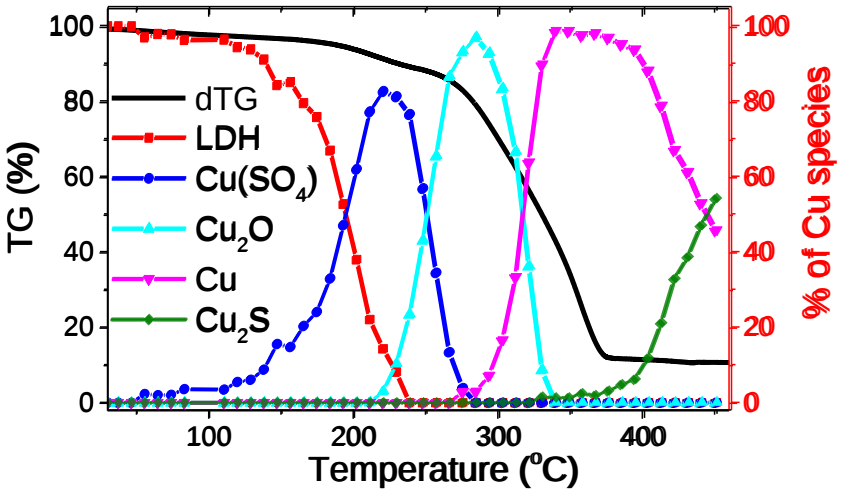
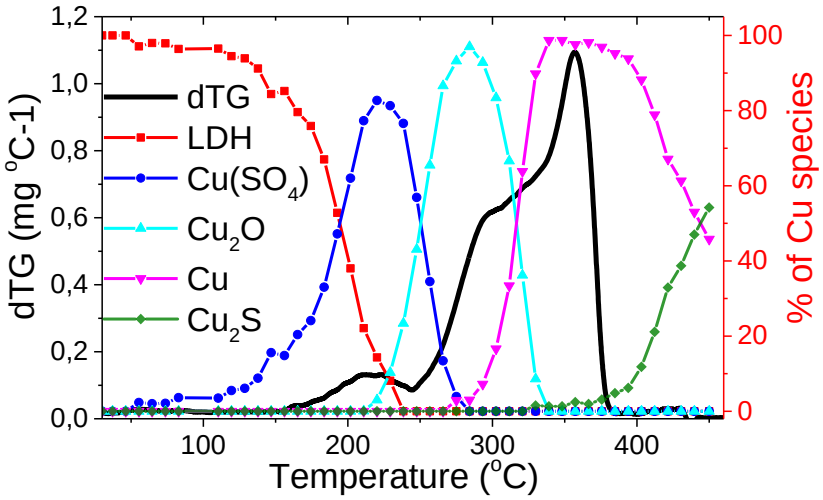
Received 22 October 2004; received in revised form 17 December 2004; accepted 21 December 2004

What happens around Cu ions?

- Speciation results:



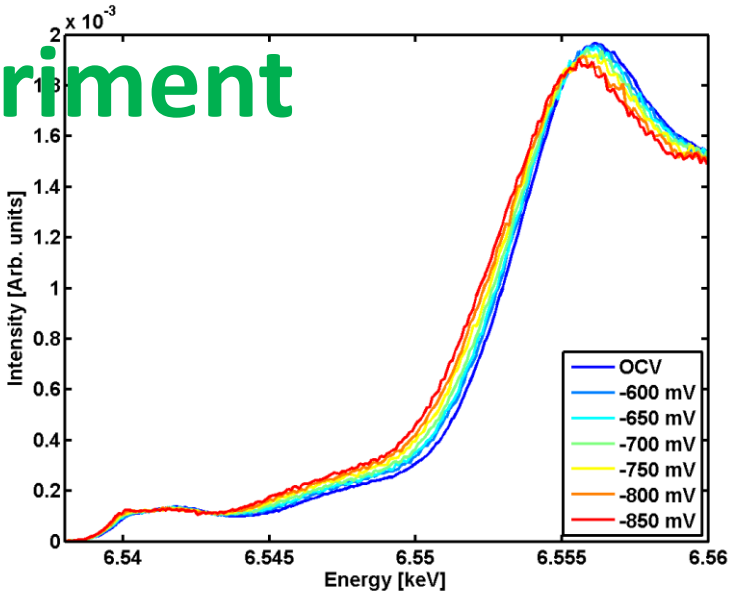


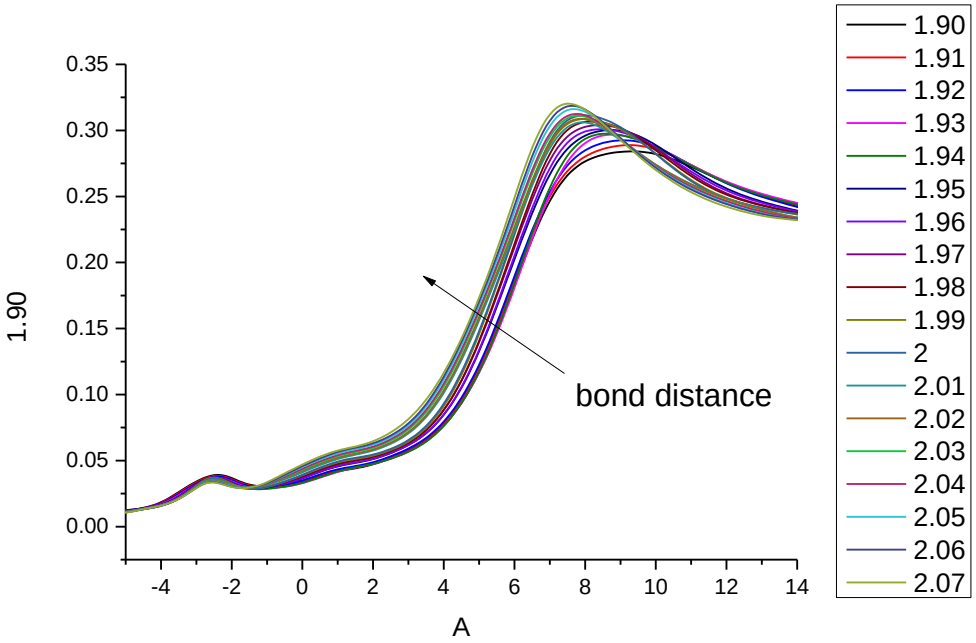
- Remarks:
  - Cu^{2+} reduction starts before the radical unzipping
  - Looks like it triggers the PMMA decomposition
  - Cu^{1+} accepts electrons and it slows down the weight loss
  - Once Cu^{1+} is completely consumed the slope increases

Theory *vs* experiment

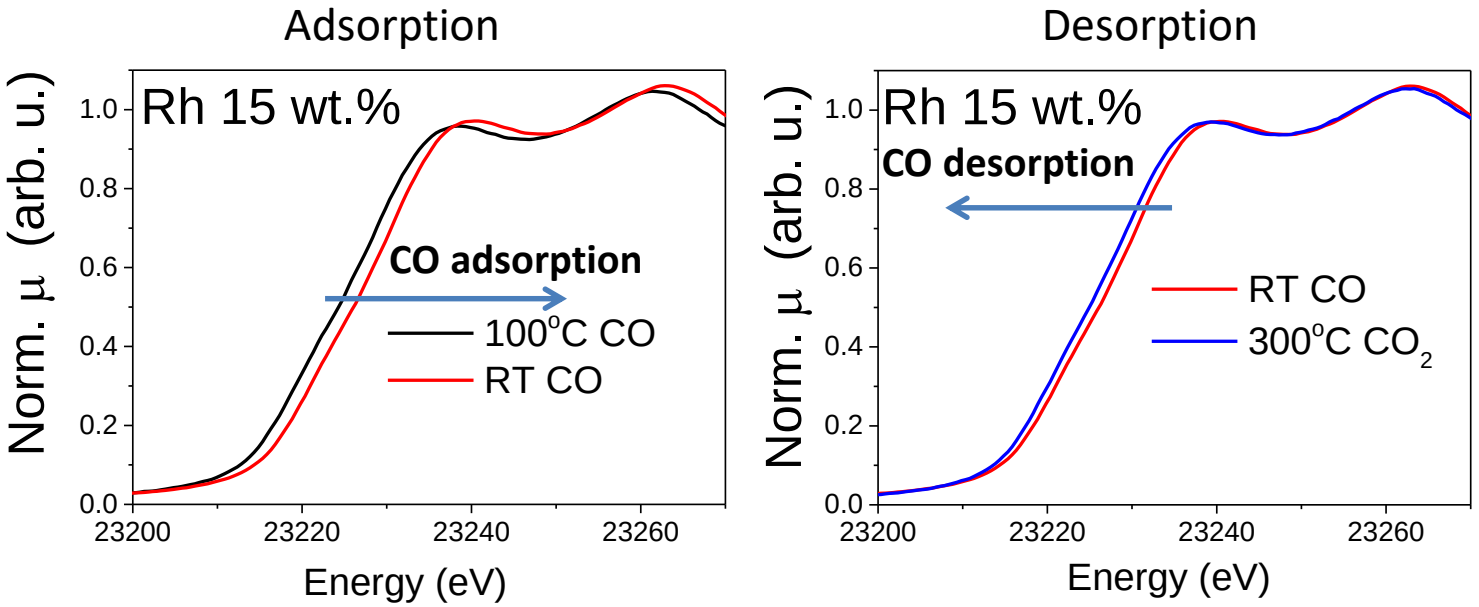
Theory *vs* experiment

Cell parameter a, b and c	Mn-O	Mn-La
5.28	1.90056	3.24
5.32	1.9100	
5.37	1.92188	
5.41	1.93140	
5.45,	1.94095	
5.5032, 5.5032 and 13.3675	1.95367	3.36
5.531, 5.531 and 13.3675	1.9603	
5.573, 5.573 and 13.3675	1.9704	
5.615, 5.615 and 13.3675	1.98054	
5.655, 6.655 and 13.3675	1.99020	
5.699, 5.699 and 13.3675	2.0008	
5.740, 5.740 and 13.3675	2.01079	
5.78, 5.78 and 13.3675	2.02051	
5.82, 5.82 and 13.3675	2.03026	
5.86	2.04002	
5.905	2.05103	
5.948	2.06157	
5.99	2.07189	3.63





Testing the CO adsorption on 15 wt.% Rh/CeO_2

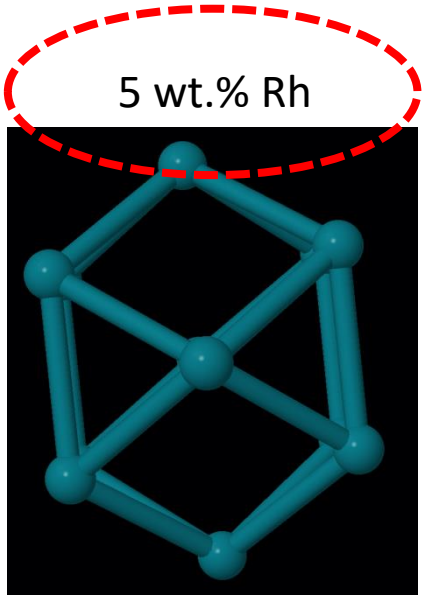


- CO adsorption shifted the spectrum towards higher energies

Bulding a model: inputs from EXAFS

Sample	Coordination number
15 wt.% Rh/CeO_2	7.0 ± 0.6
5 wt.% Rh/CeO_2	5.0 ± 0.5

- Coordination numbers depends on particle size

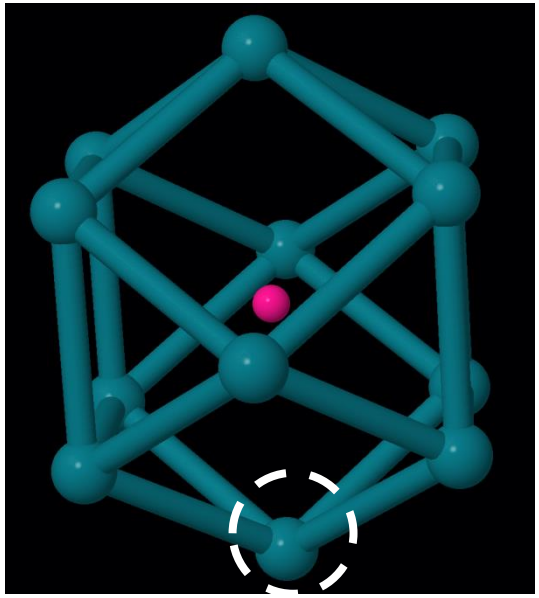


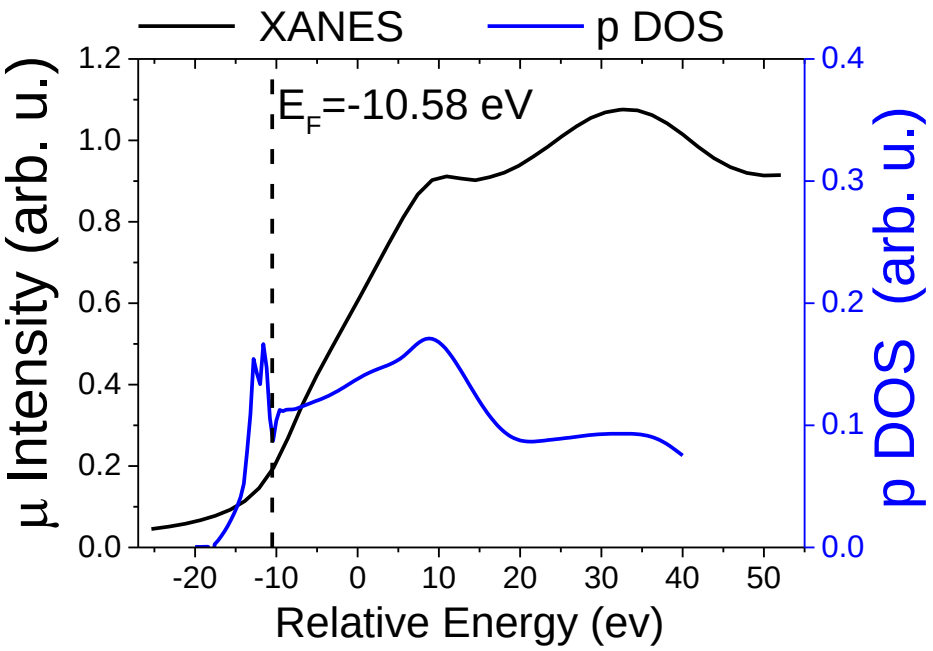
Smaller than 1.0 nm

The spectrum of a Rh cluster

- Simulated spectrum and p orbital density of states

  13 atoms cluster





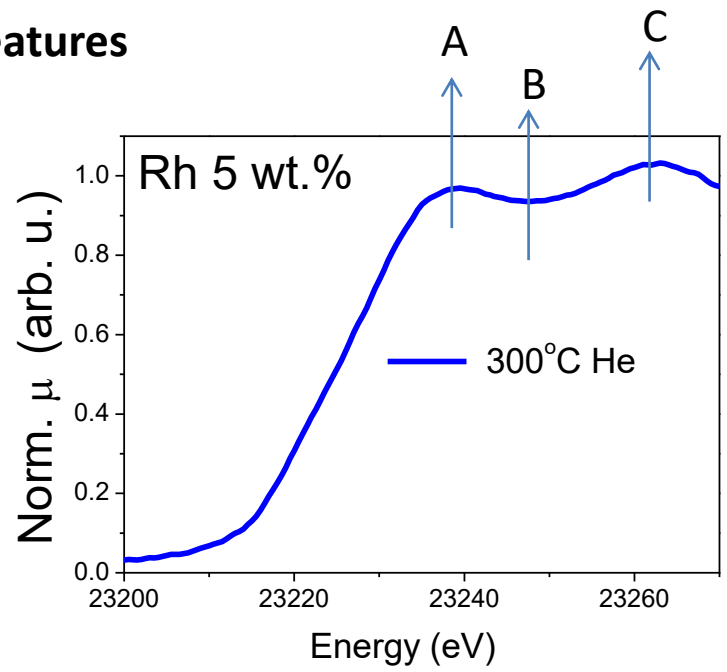
- 1s to 5p transition

How good is our theory?

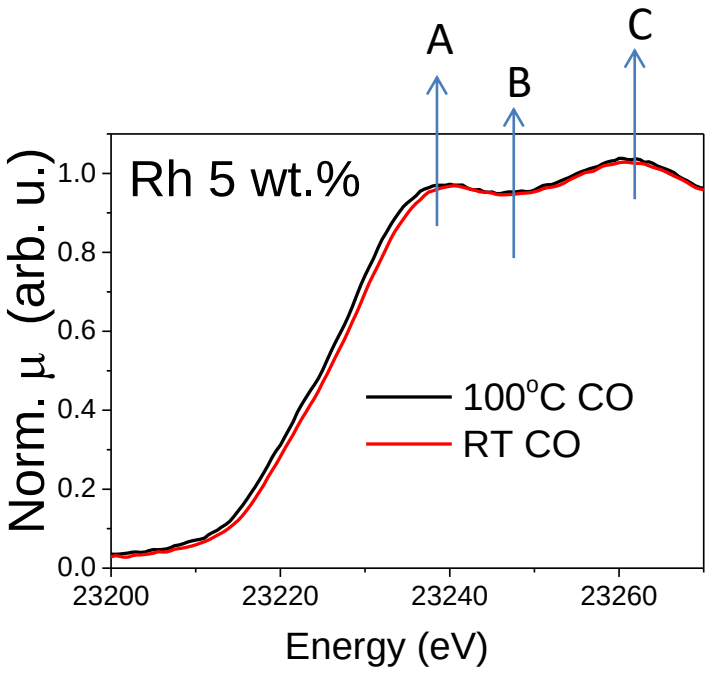
- We can reproduce the experimental spectrum

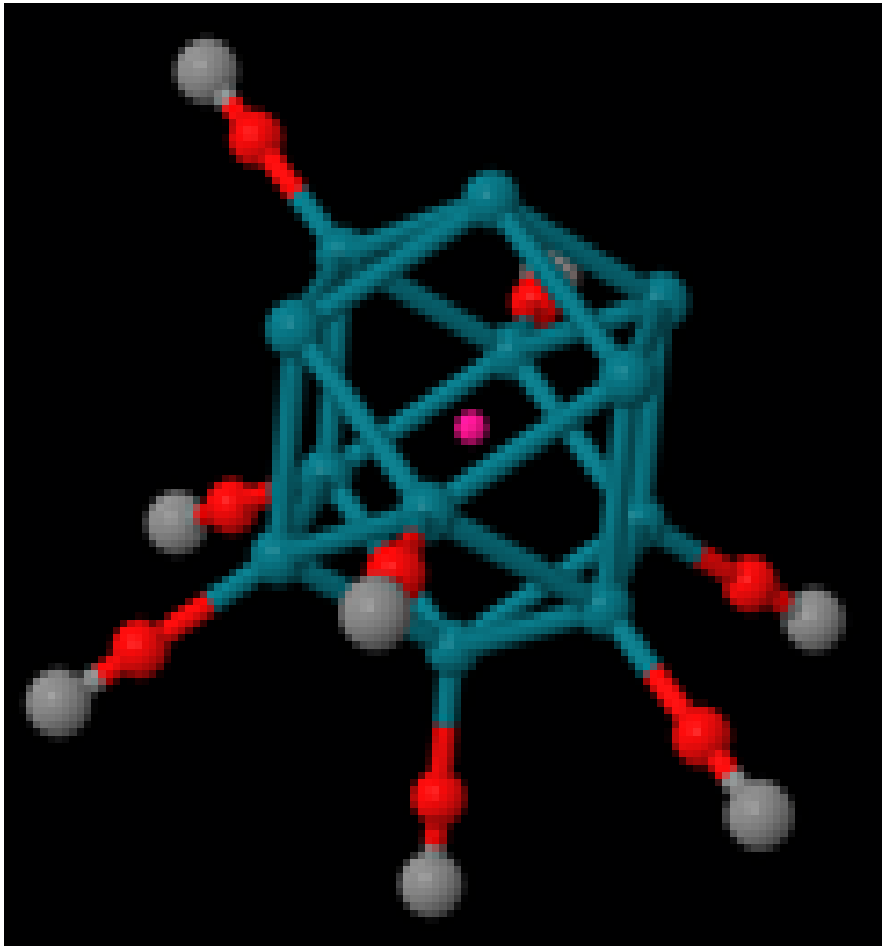
Theory

Features



Experiment

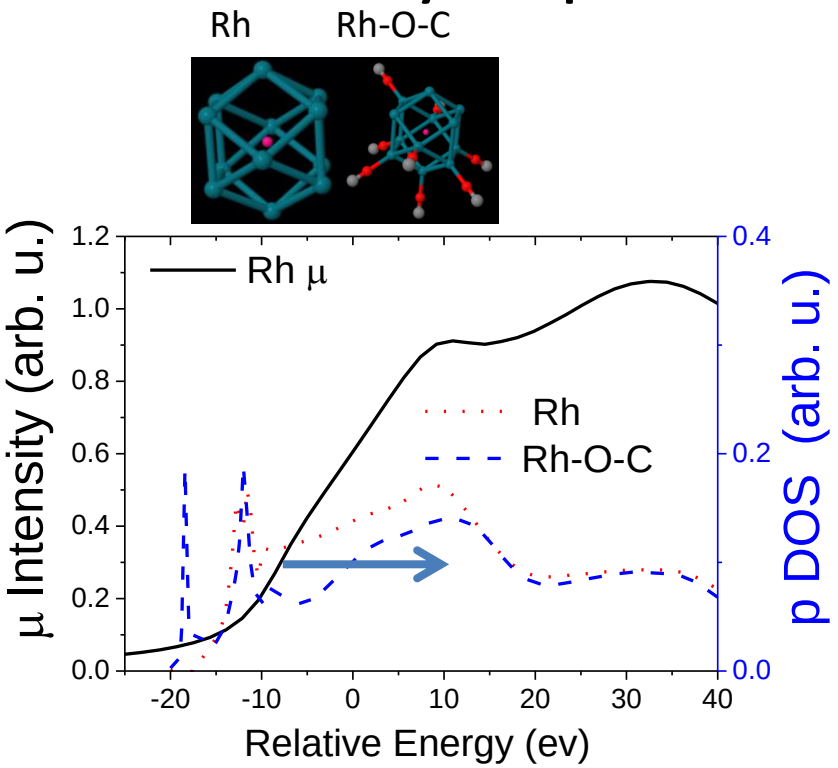


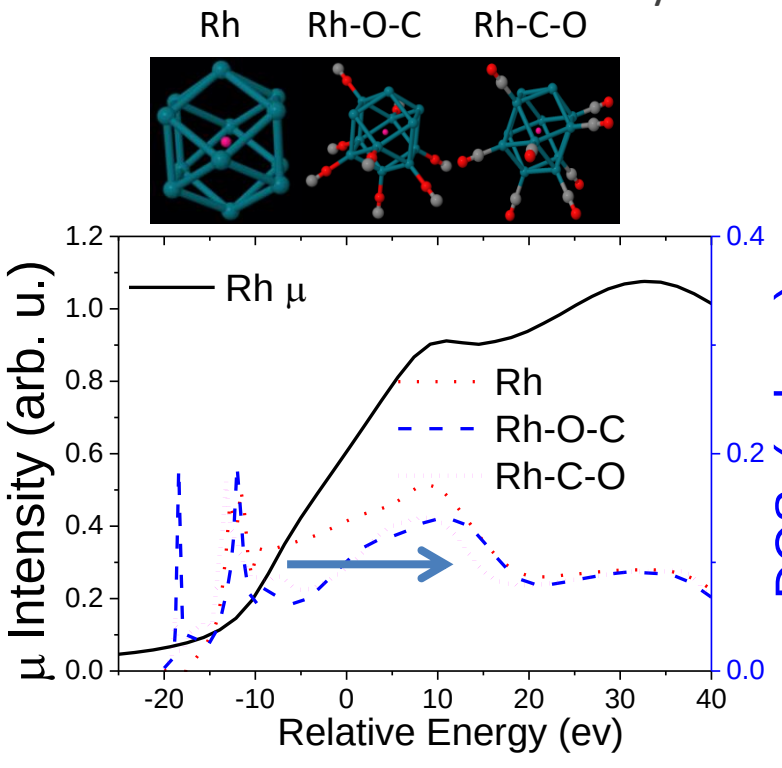


Why does the shift occur?

- Rh density of p unoccupied states

Red: oxyge
Grey: carb



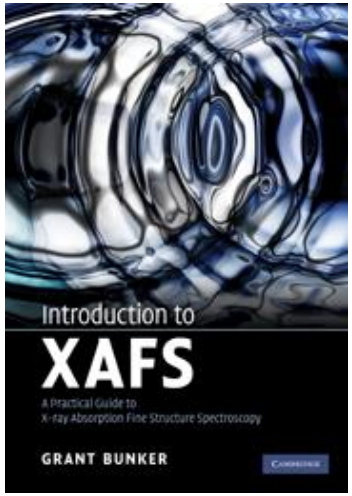


- The presence of C or O shifts **the Rh p orbitals** to higher energies!

XANES data analysis

- Finger print: simple comparison
- Liner combination: semi quantitative
- Following kinetics: semi quantitative
- *Ab initio*: comparing experiment with theory

XANES Theory



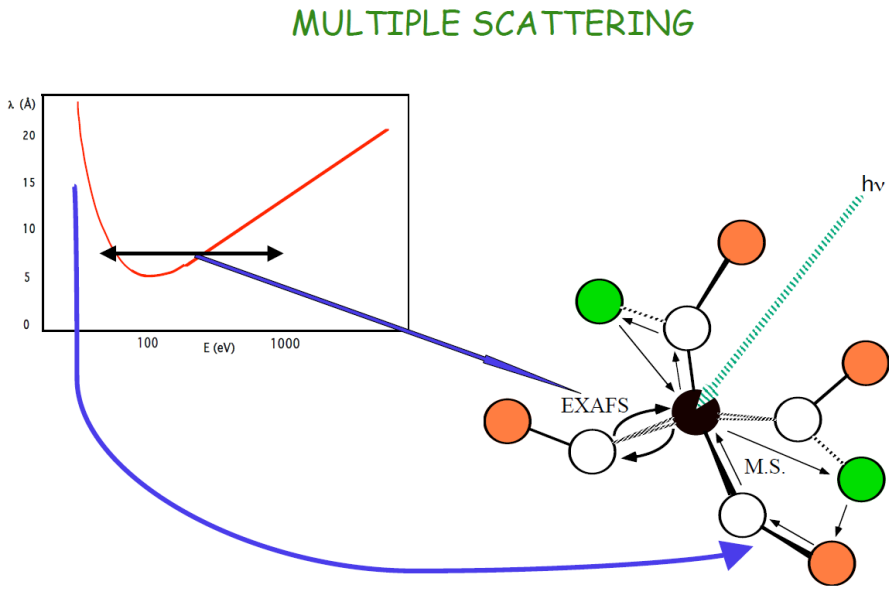
Pg 106-125
Pg 134-146

XANES spectroscopy
By Andrej Mihelic in 2002

http://www.ung.si/~arcon/xas/xanes/xanes-theory.pdf

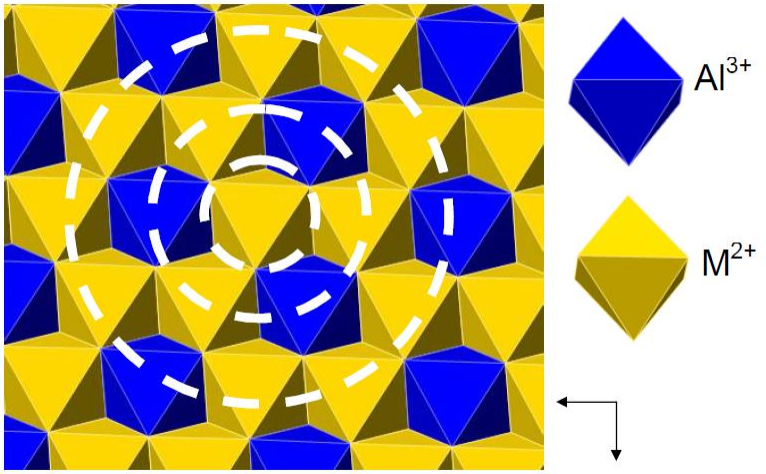
Multiple scattering *vs* single scattering

- In XANES the photon electron travels more than in EXAFS
- Let‘s see what kind of paths are possible:



What kind of information XANES can supply?

- Symmetry
- Charge
- Nature of ligands
- Bond lengths



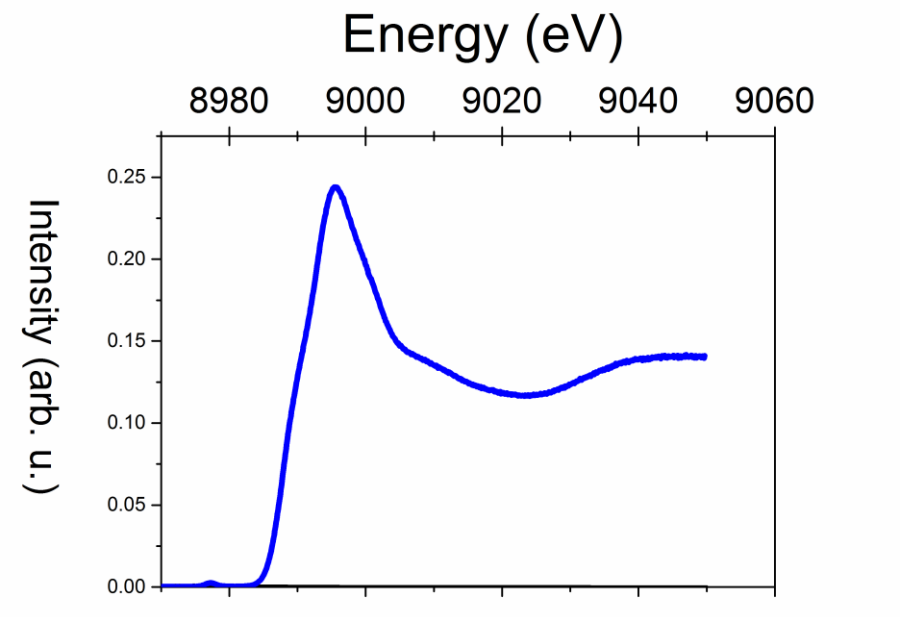
Layered double hydroxide top view

- Advantages over EXFAS:

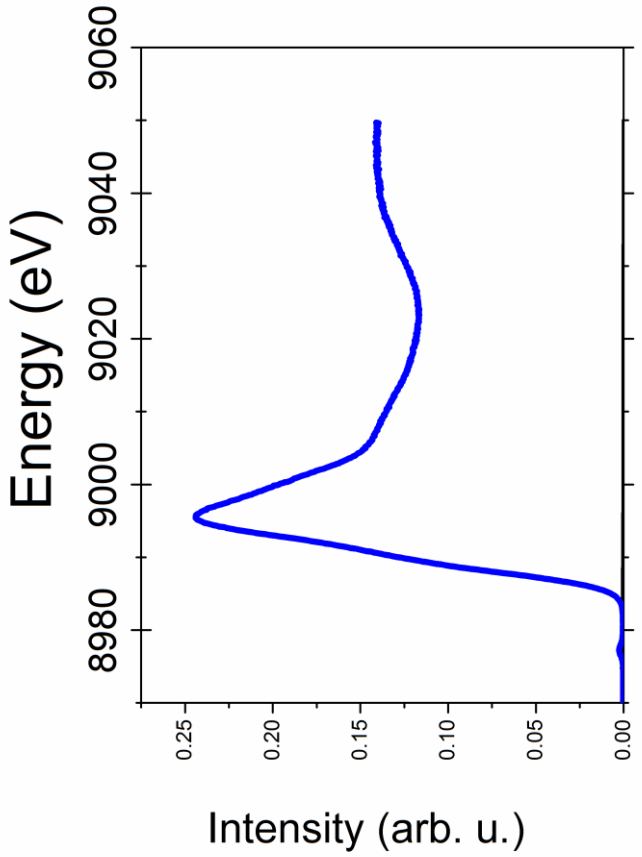
- Faster to record
- Lower influence of temperature
- Easier to extract qualitative information

The Origin of the Near Edge Features

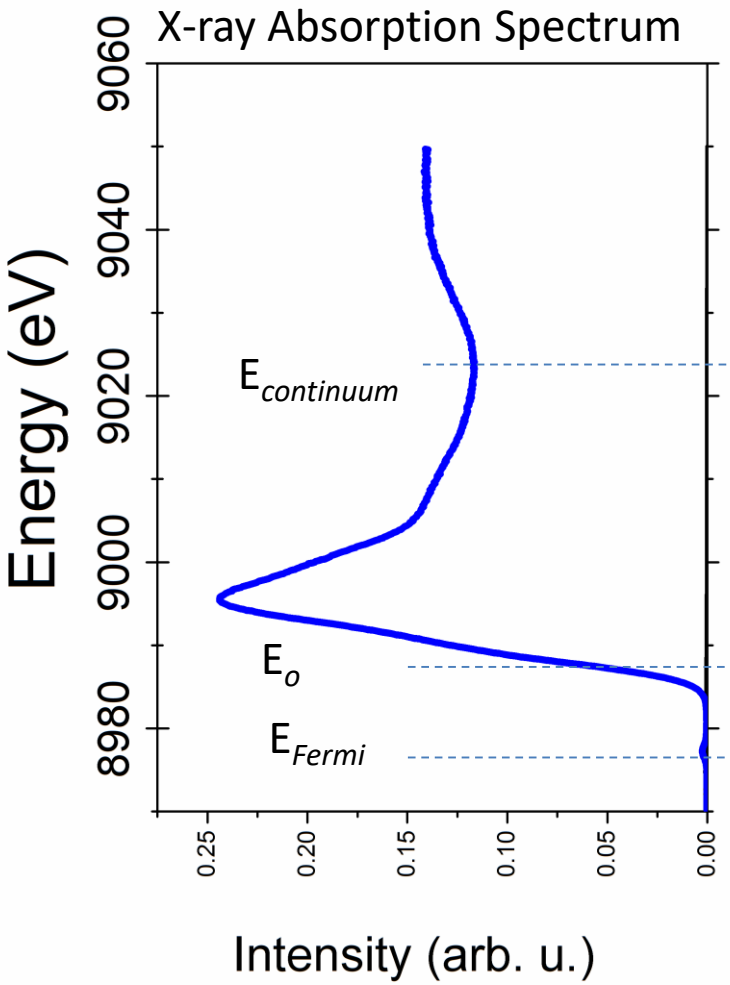
- We are used to see the X-ray absorption spectrum like that:



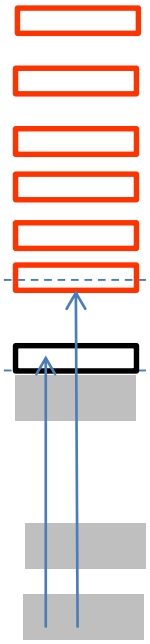
- Let‘s rotate it



The Origin of the Near Edge Features



- The config. of the empty states depends on:
- Nature of ligands
- Geometry
- Bond length
- Oxidation state of absorber



EXAFS

Empty p mixed states and empty **ligand states**

XANES

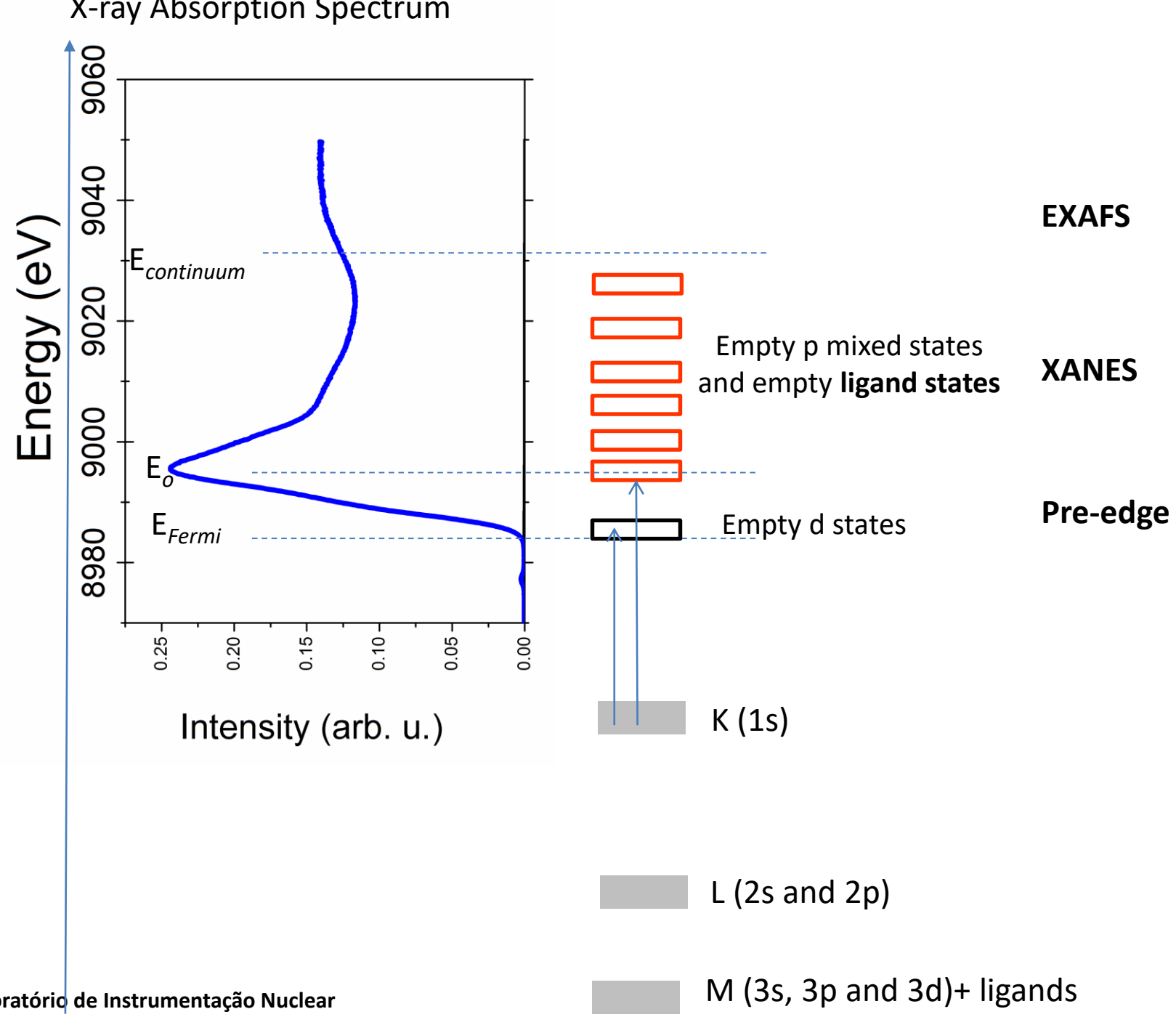
Empty d states

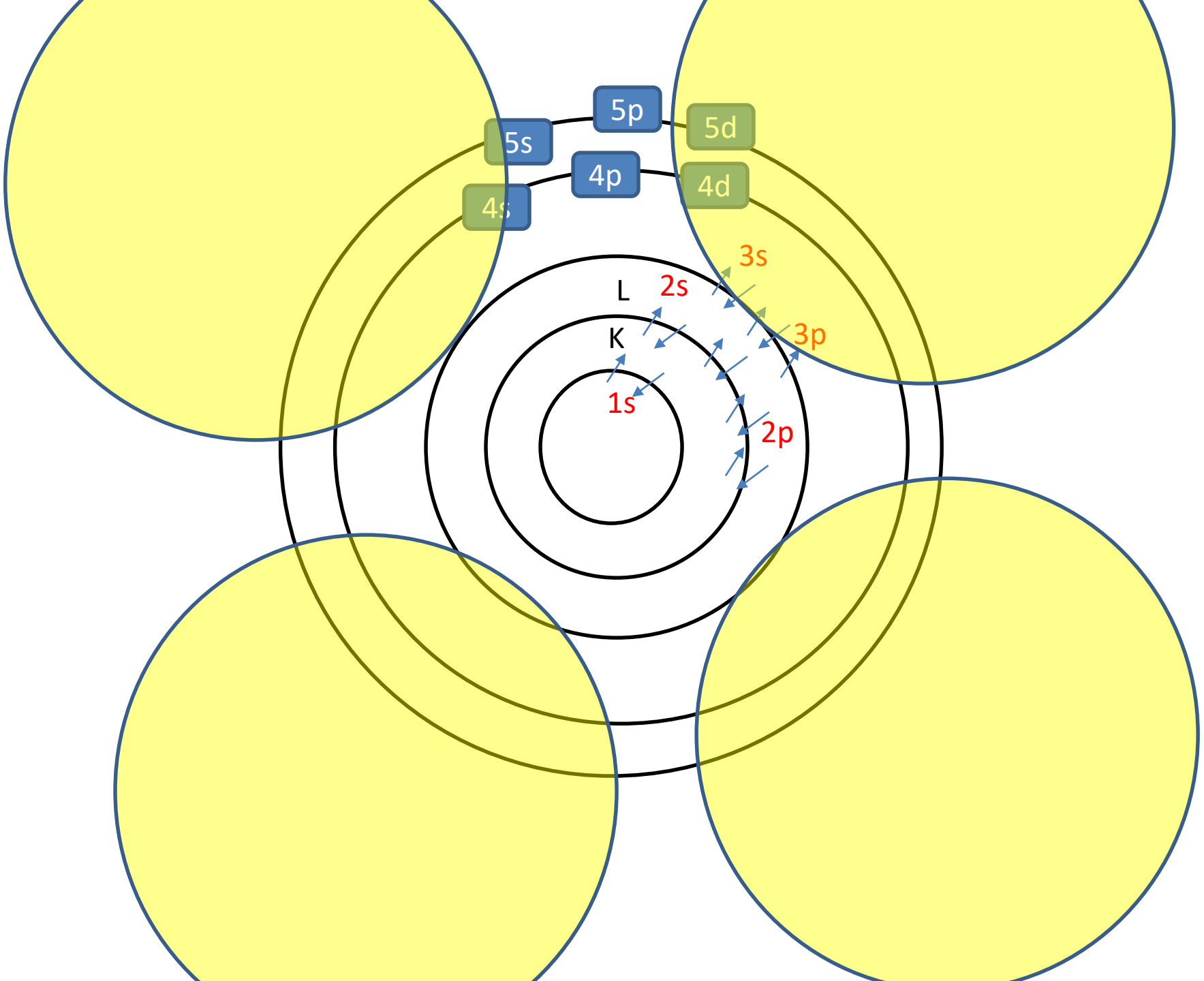
Pre-edge

M (3s, 3p and 3d)+ ligands

L (2s and 2p)

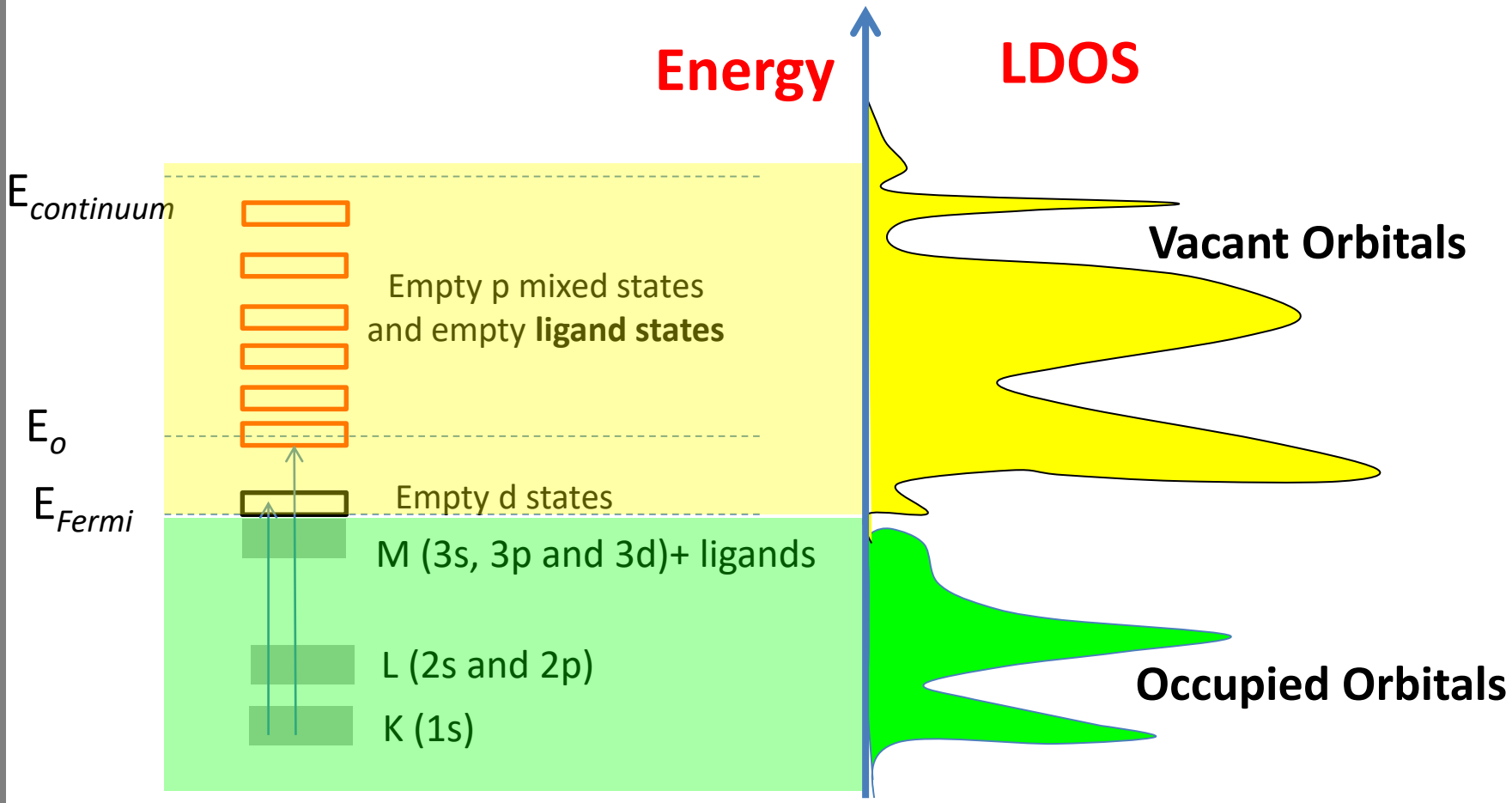
K (1s)


X-ray Absorption Spectrum
Energy (eV)
9060
9040
9020
9000
8980
E continuum
E o
E Fermi
0.25
0.20
0.15
0.10
0.05
0.00
Intensity (arb. u.)
EXAFS
Empty p mixed states
and empty ligand states
XANES
Empty d states
Pre-edge
K (1s)
L (2s and 2p)
M (3s, 3p and 3d)+ ligands


5p
5d
5s
4p
4d
4s
3s
L
2s
K
3p
1s
2p

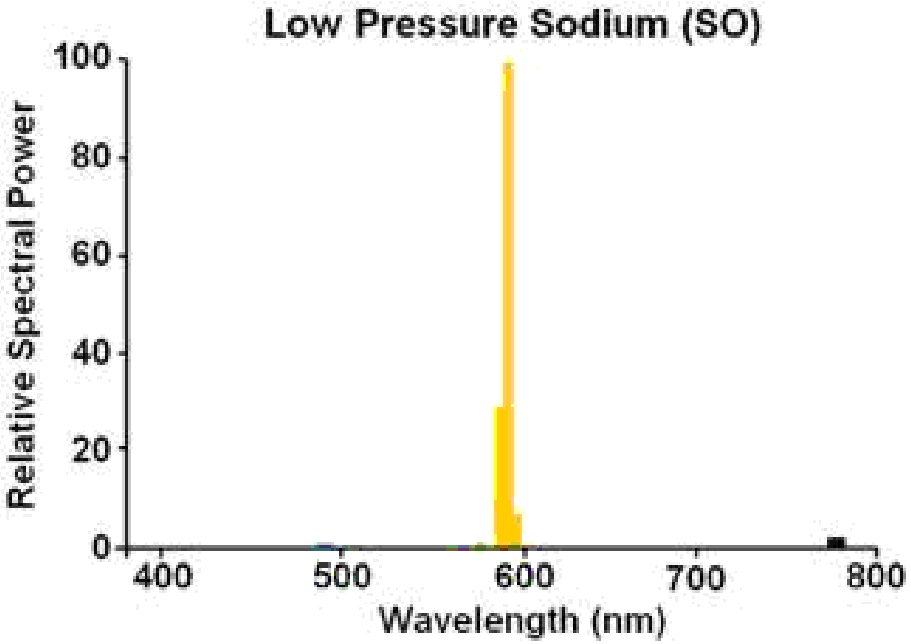
The spectrum is a projection of the electronic levels

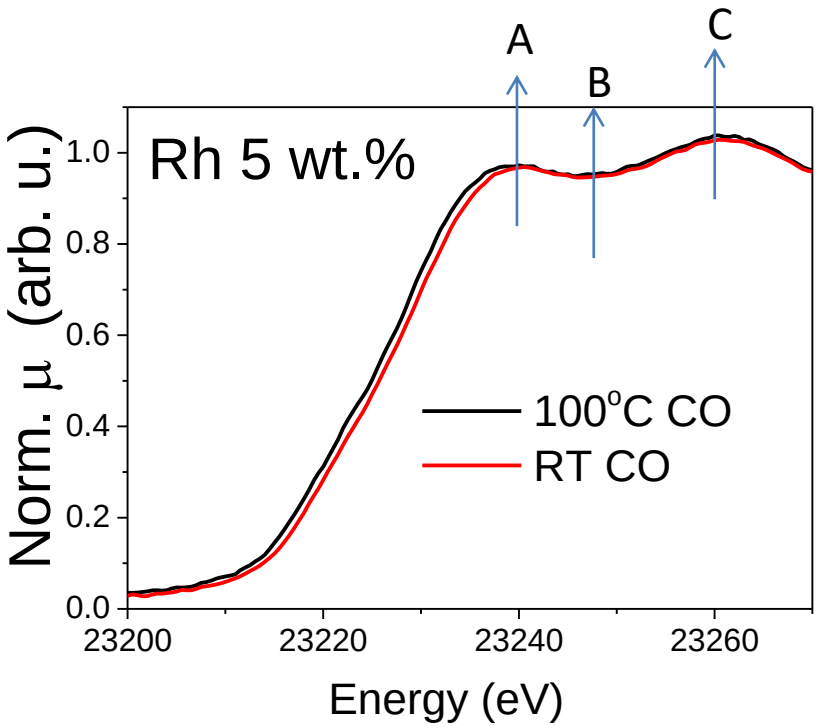
- The chemical environment defines the electronic structure



The million-dollar question:

Why some lines are brighter than others?



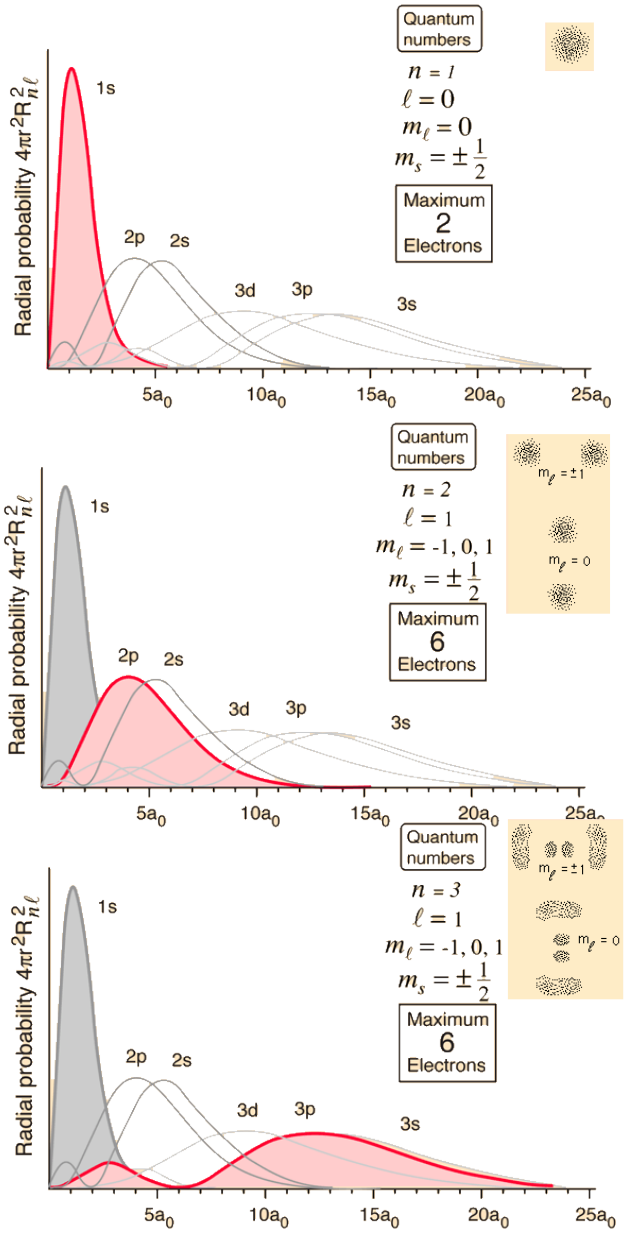


How does it work?
Why this Equation can foresee the spectrum?

$$\mu \propto \left\langle \psi_f \left| \vec{\varepsilon} \cdot \vec{R} \right| \psi_i \right\rangle$$

- **Let's invest some time here**

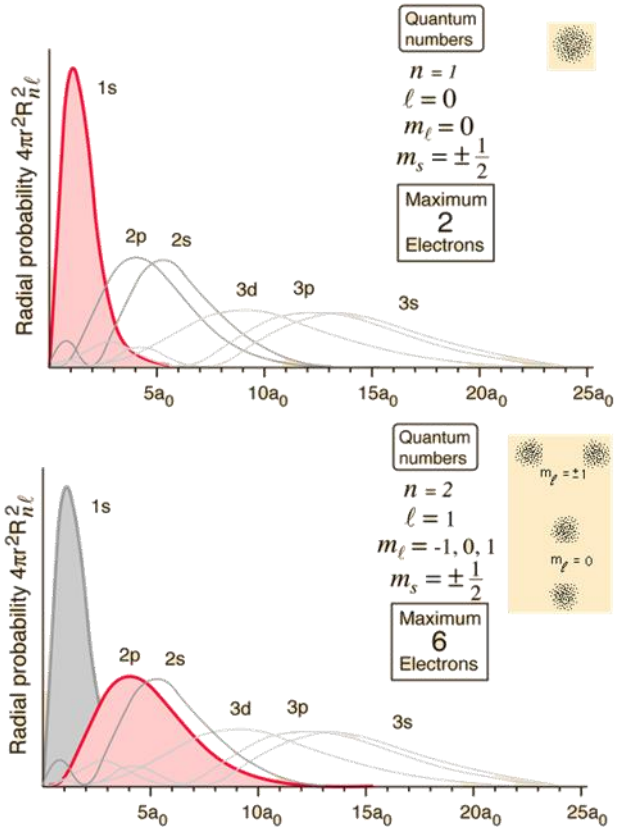
Orbital overlaping

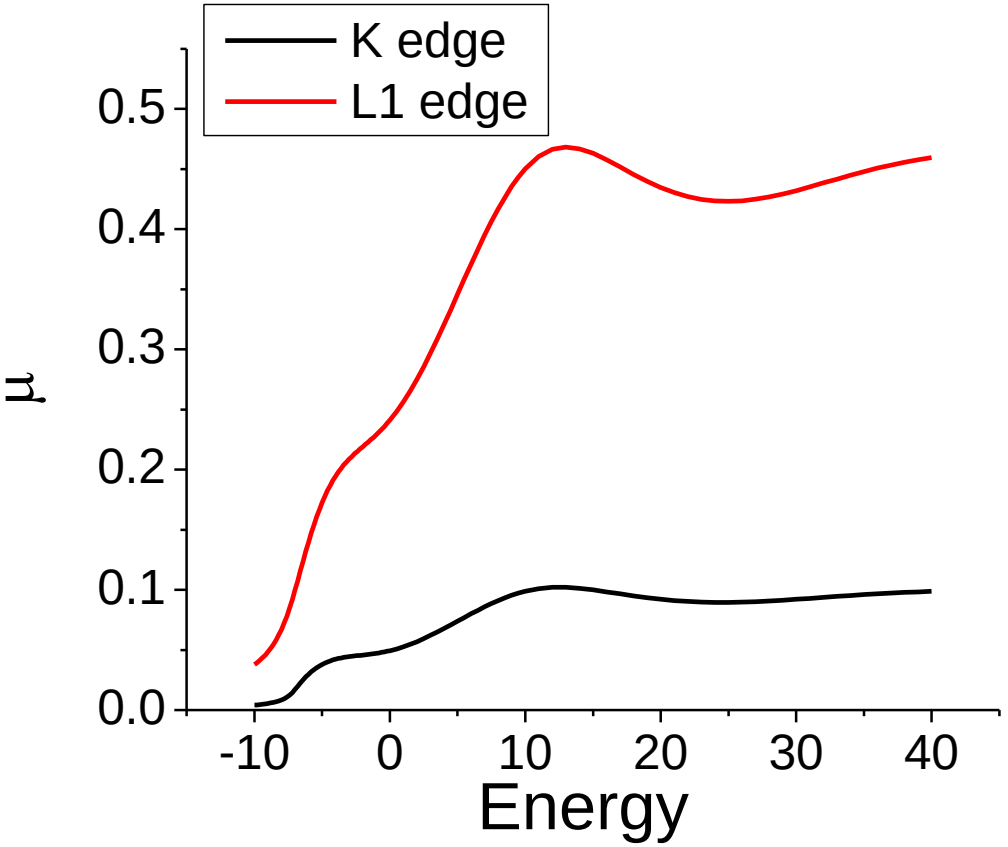


$$\mu \propto \langle \psi_f | \vec{\varepsilon} \cdot \vec{R} | \psi_i \rangle$$

How is it applied to spectroscopy?

Cu K edge *vs* L1 edge
Which one is more probable?
Why?





Why dependent on the neighboring atoms?

Fermi's Golden Rule: dependent on the initial and the final state

$$\mu \propto \left\langle \psi_f \left| \vec{\varepsilon} \cdot \vec{R} \right| \psi_i \right\rangle$$

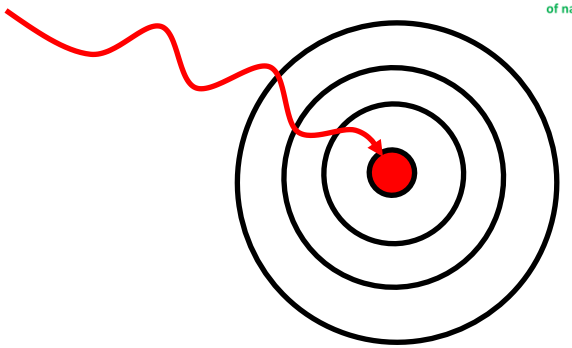
Ψi: initial state wave function of the bound electron
Ψ_f: final state wave function of the ejected photoelectron
ε: electric field vector
R: position vector of scatterer

NOTE: valid for all electronic transitions,see books for physical chemistry (perturbation theory in quantum mechanics)

$$\mu \propto \left\langle \psi_f \left| \vec{\varepsilon} \cdot \vec{R} \right| \psi_i \right\rangle$$

- **The initial state:**

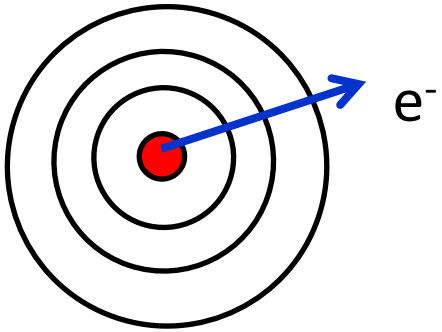
Ψ_i: bound electron



- **The final state:**

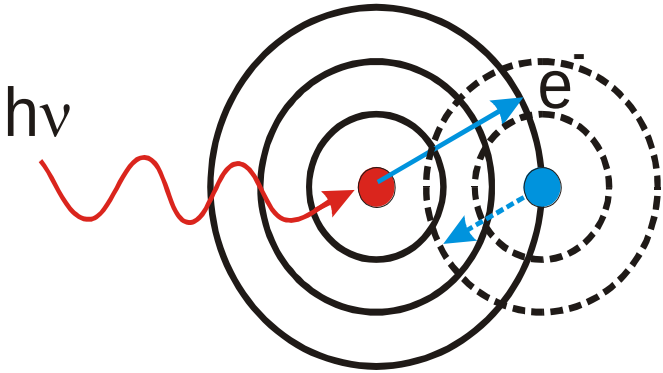
For an isolated atom:

Ψ_f: $\Psi_{outgoing\ wave}$



For a surrounded atom:

Ψ_f: $\Psi_{outgoing\ wave}$ + $\Psi_{backscattered\ wave}$



The initial state

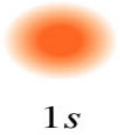
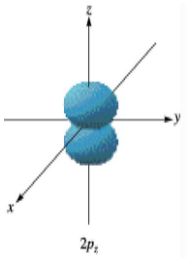
$$\mu \propto \left\langle \psi_f \left| \vec{\varepsilon} \cdot \vec{R} \right| \psi_i \right\rangle$$

The initial state

The final state

The initial state

- Ψ_i = absorption

n	l	m	ψ_{nlm}	Orbital Name		Edge
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}} e^{-\sigma}$	ψ_{1s}		K
2	0	0	$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}} (2-\sigma)e^{\frac{-\sigma}{2}}$	ψ_{2s}		L_1
	1	0	$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}} \sigma e^{\frac{-\sigma}{2}} cos\theta$	ψ_{2p_z}		
	1	±1	$\psi_{21\pm1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}} \sigma e^{\frac{-\sigma}{2}} sin\theta e^{\pm i\phi}$			L_2 and L_3

- Ψ_i is the orbital which the electron is leaving

http://www.udel.edu/pchem/C444/spLectures/04152008.pdf

The initial state

- Ψ_i or the absorption edge has a strong influence on the spectral features = absorption

L_3 edge

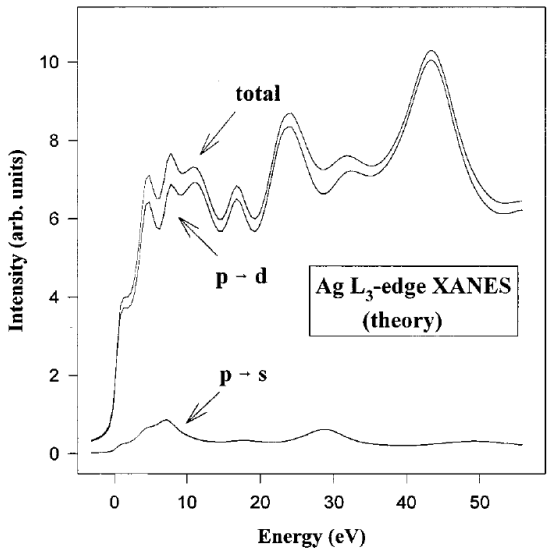
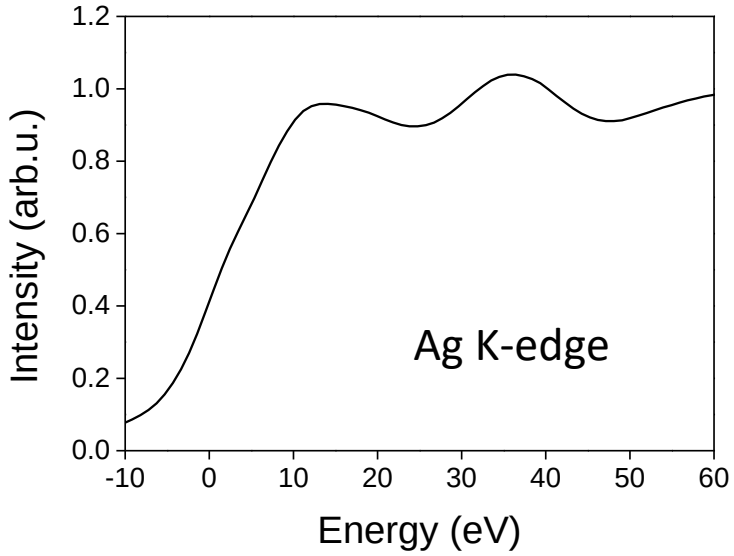


FIG. 2. Ag L_3-edge XANES for fcc Ag metal obtained with the multiple scattering calculation. The $p \rightarrow d$ and $p \rightarrow s$ channels are also shown separately.

K edge



- This effect is mainly due to the core hole life time and the selection rules

PHYSICAL REVIEW B VOLUME 58, NUMBER 11 15 SEPTEMBER 1998-I

Sublifetime-resolution Ag L_3-edge XANES studies of Ag-Au alloys

W. Drube and R. Treusch*
Hamburger Synchrotronstrahlungslabor HASYLAB am Deutschen Elektronen-Synchrotron DESY, Notkestrasse 85, D-22603 Hamburg, Germany

The final state

$$\mu \propto \left\langle \psi_f \left| \vec{\varepsilon} \cdot \vec{R} \right| \psi_i \right\rangle$$

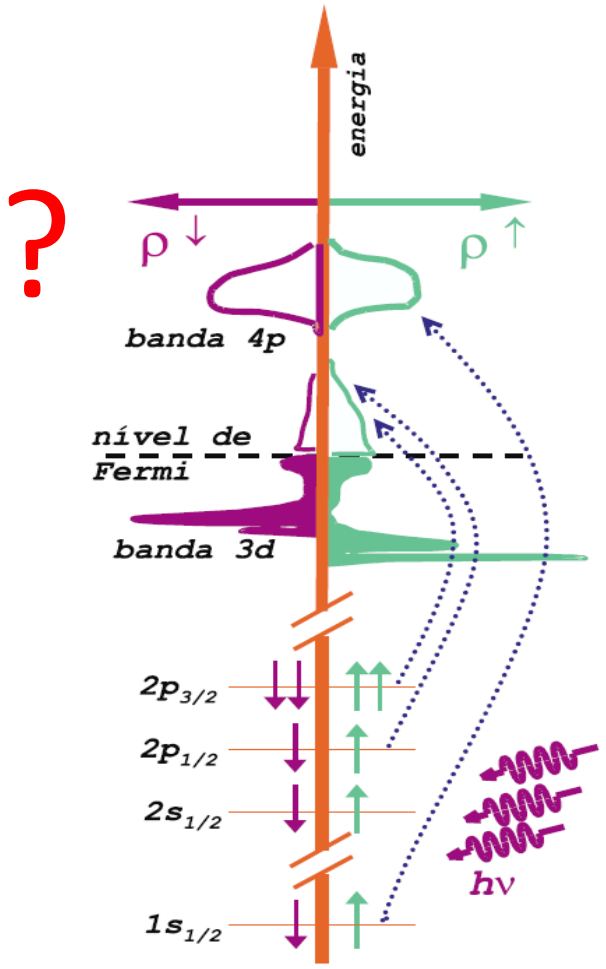
The initial state

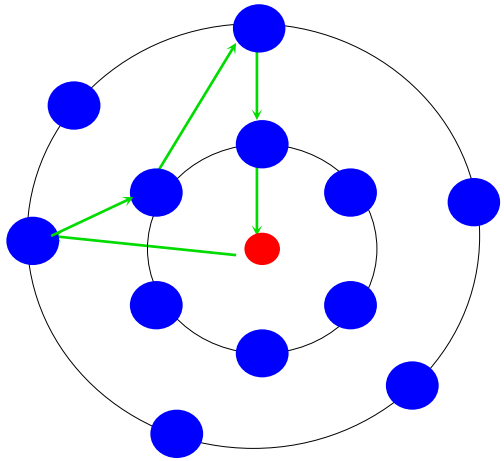
The final state

The final sate

- To simulate the XANES we have to find out all possible final states

Ψ_f = Final state





The most impotant difference between:

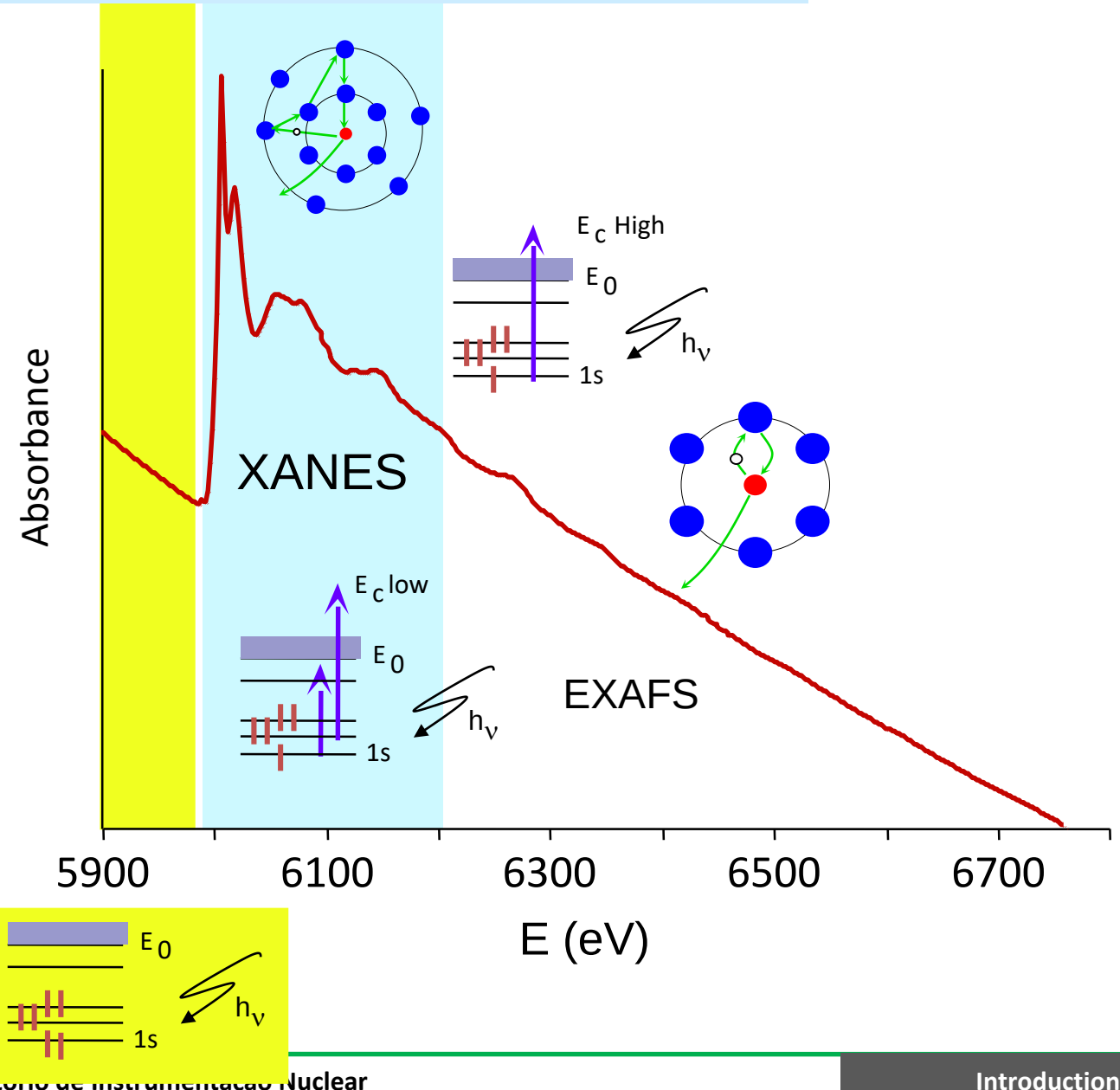
XANES, EXAFS and optical transitions:

The nature of the final states

The EXAFS phenomenon: a closer look

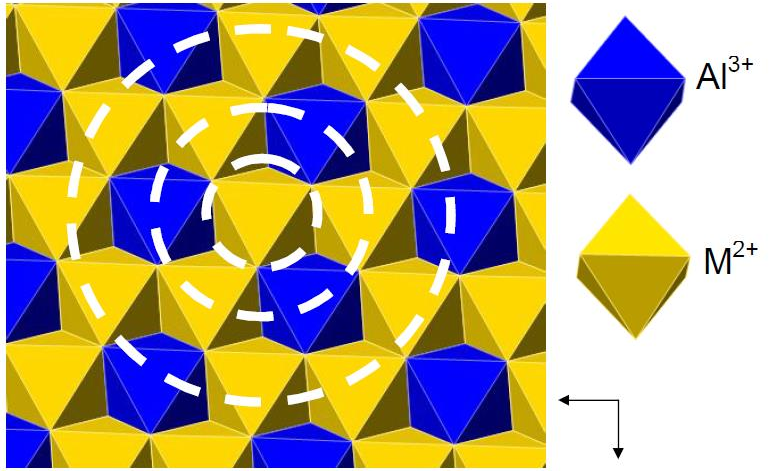
X-ray Absorption Spectroscopy

The EXAFS phenomenon: a closer look



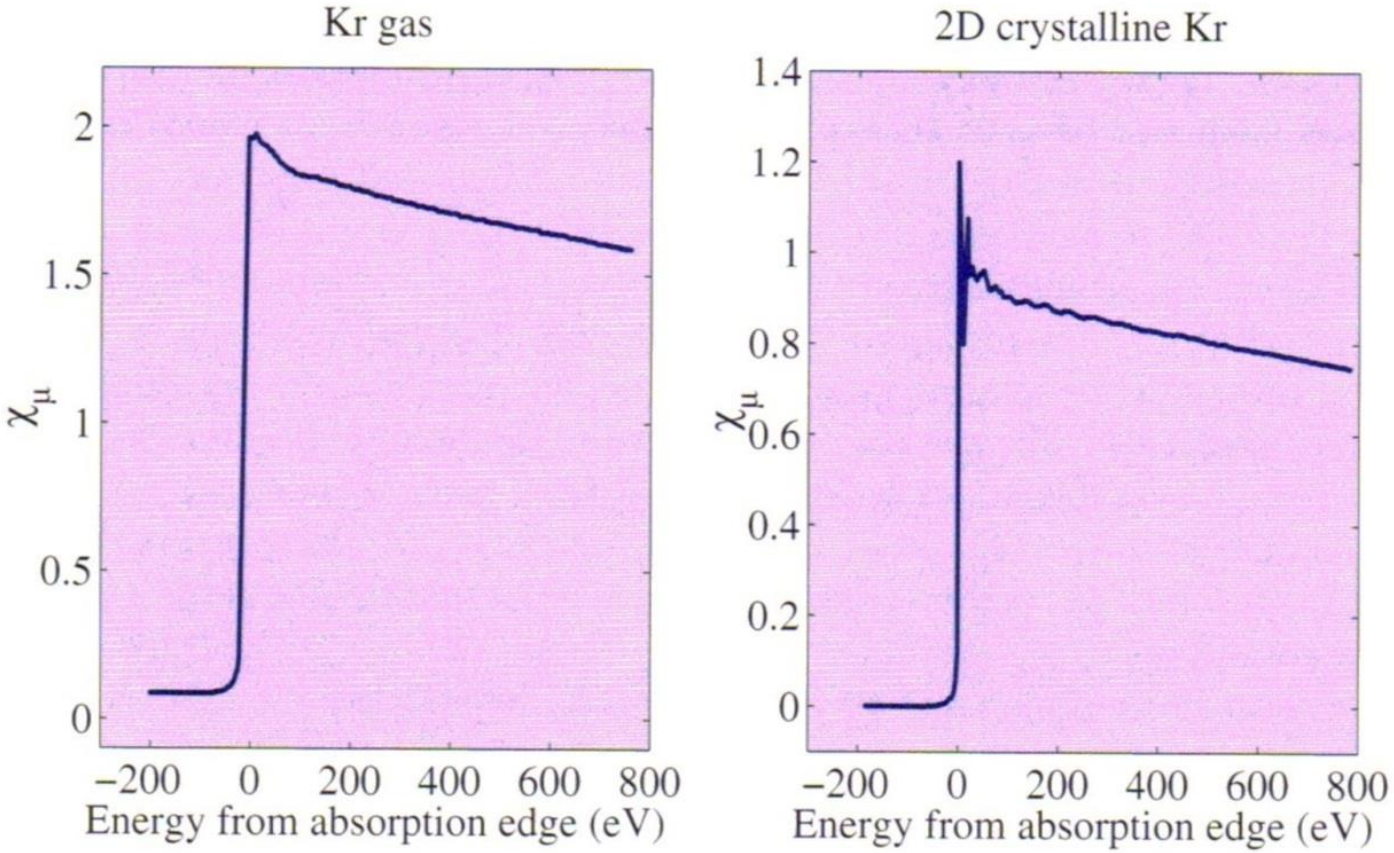
• What kind of information EXAFS can supply?

- Identify an absorbing atom
- Indentify which atoms sourround the absorber atom.
- Determine how many sourrounding atoms and their distances.
- An idea about how ordered those sourrounding atoms are.



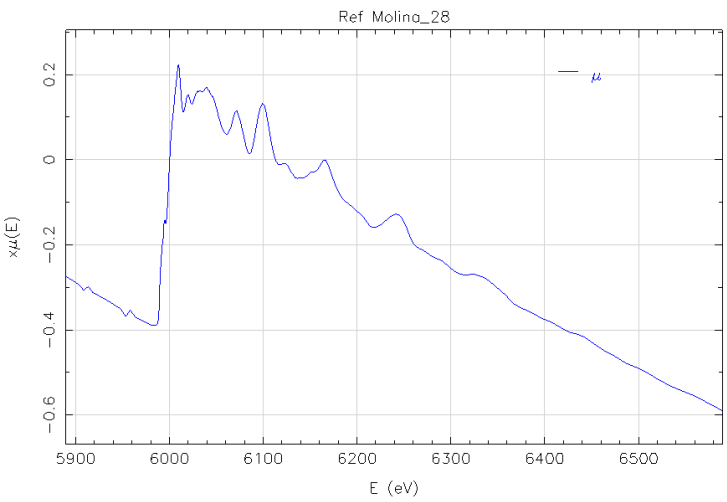
Layered double hydroxide top view

Hudson Wallace Pereira de Carvalho
ROLE DE L'ARGILE DANS LA STABILISATION THERMIQUE DE NANOCOMPOSITES : ETUDE DE L'ORDRE LOCAL ET DE L'ORDRE À MOYENNE DISTANCE

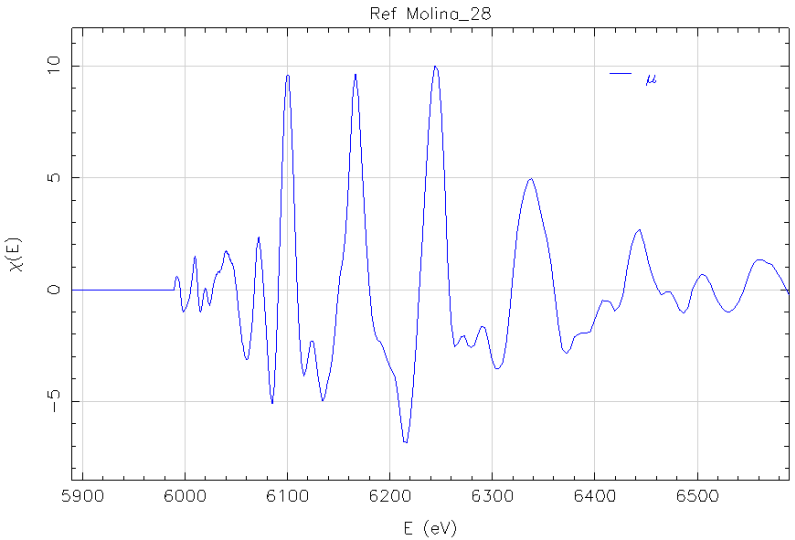

Kr gas
2D crystalline Kr
χ_μ
Energy from absorption edge (eV)
−200
0
200
400
600
800
0
0.5
1
1.5
2
0.2
0.4
0.6
0.8
1.2
1.4

- To get information one must isolate the oscillations.

Raw spectrum



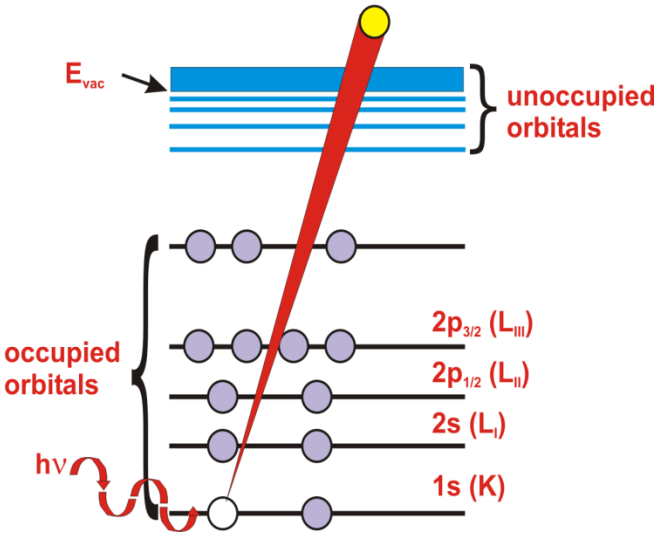
Isolated oscillations

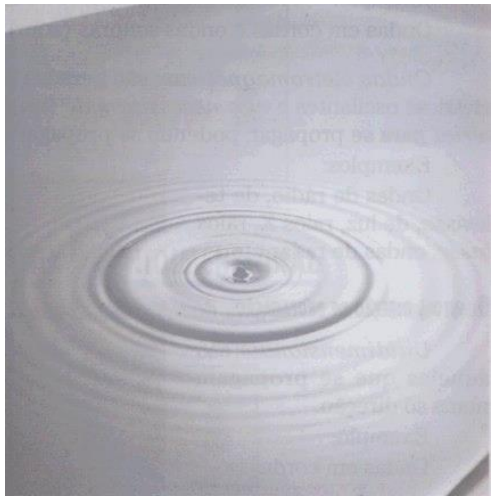


How to do it?

- The photon is absorbed, and its energy is tranfered to the electron

Wave-particle dualism





Remember that the electron can be regard either as particle or as wave

- Let´s follow a short reasoning:

- We can calculate the electron´s wavelength

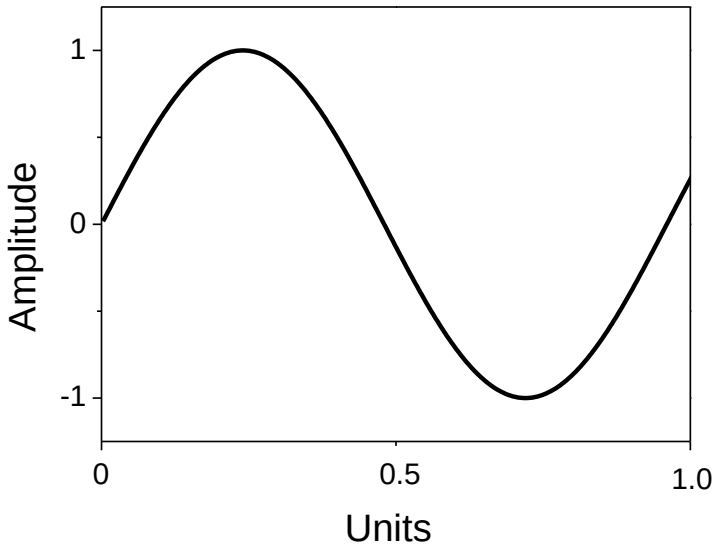
$$E = h\nu \longrightarrow \lambda = \frac{h}{p}$$ **(de Broglie)**

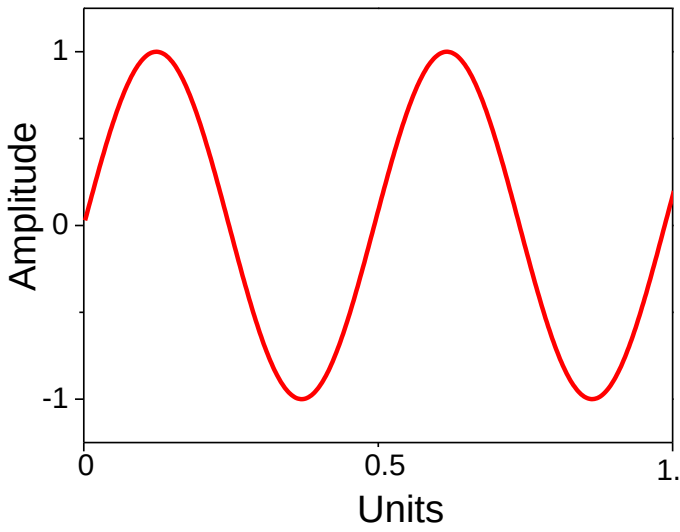
- We can also determine the electron´s wavenumber

Number of oscilations per unit e.g.

$$\nu = \frac{1}{\lambda}$$

$$k = \frac{2\pi}{\lambda}$$





- Let´s follow a short reasoning (perhaps not too short):

- Photoelectron´s energy balance:

$$E_{kin} = E_{x\text{-}ray} - E_{binding\ E} \quad \text{or} \quad E_{kin} = E - E_0$$

$$E_{kin} = \tfrac{1}{2}\, mv^2 = p^2/2m = E - E_0$$

$$p = (2m(E\text{-}E_0))\text{^}0.5$$

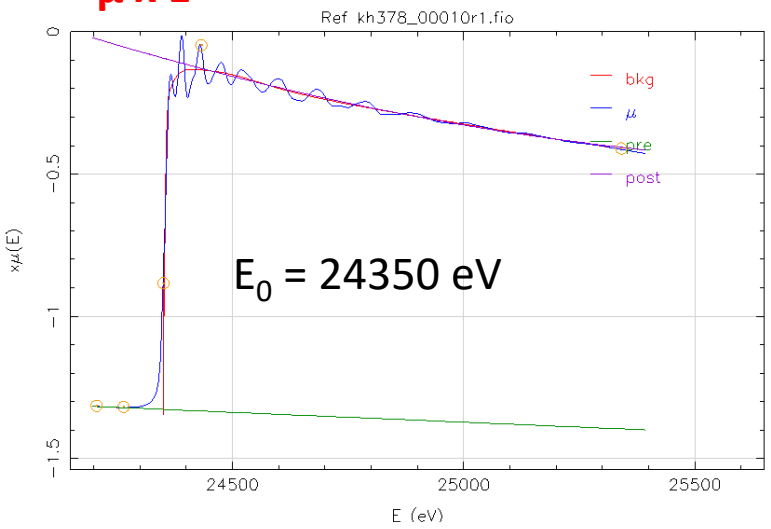
$$k = 2\pi/\lambda = 2\pi p/h$$

Photoelectron wave number:

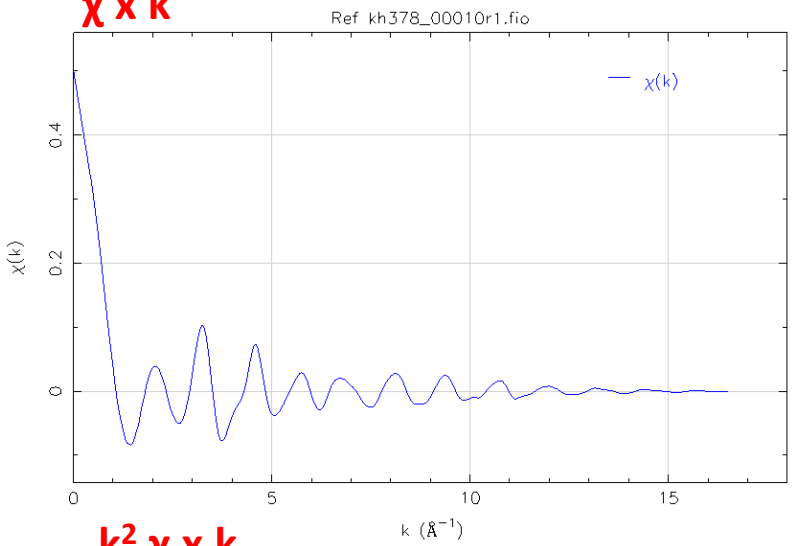
$$k = \frac{2\pi}{h} \cdot \sqrt{2m_e E_{kin}} = \frac{2\pi}{h} \cdot \sqrt{2m_e (E - E_0)}$$

When are we going to use k?

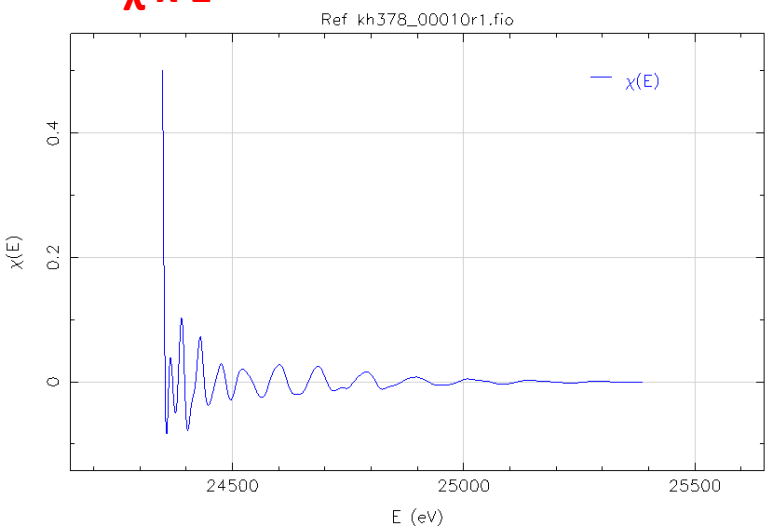
μ x E



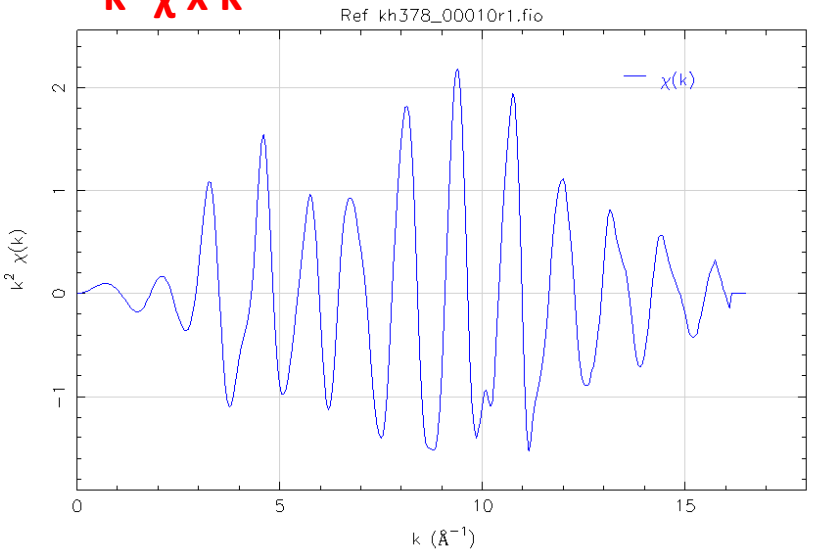
χ x k

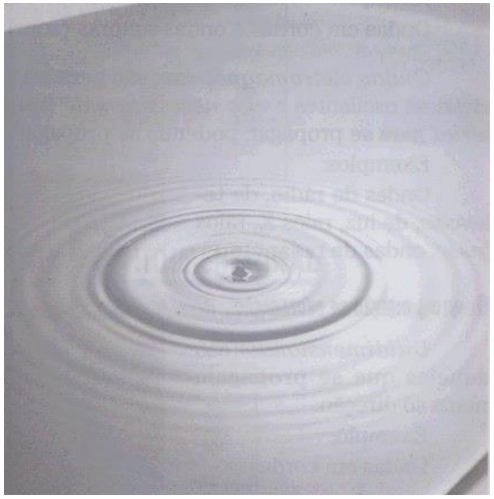


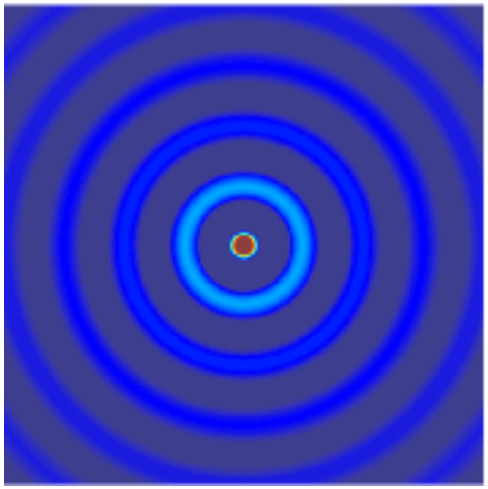
χ x E



k^2 χ x k







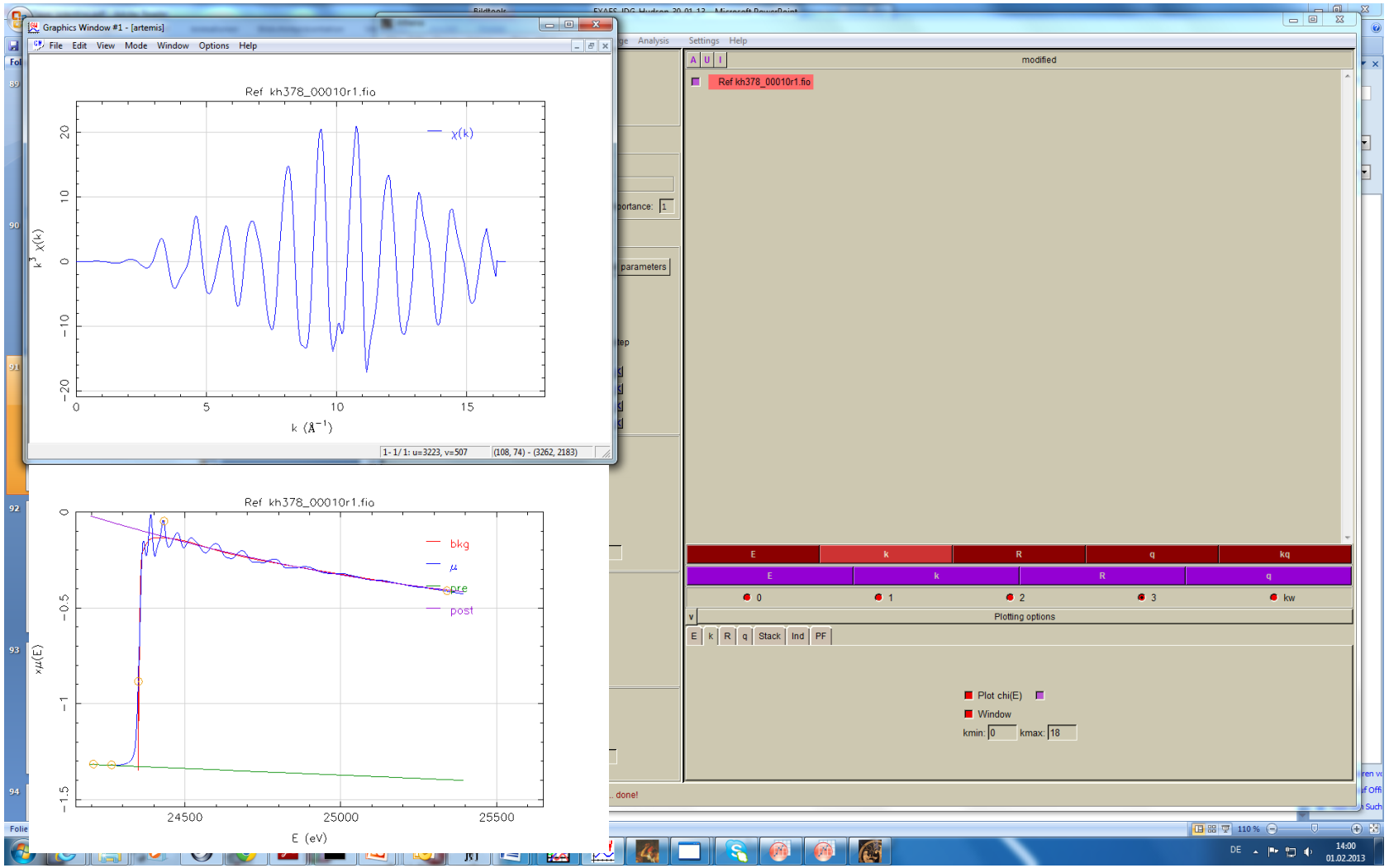
Photoelectron wave number:

$$k = \frac{2\pi}{h} \cdot \sqrt{2m_e E_{kin}} = \frac{2\pi}{h} \cdot \sqrt{2m_e (E - E_0)}$$

Solution of the wave equation:

$$u = A \sin(\vec{k}\,\vec{r} - w\,t)$$

A = amplitude
k= wave vector
r= postion
w= 2πf= angular frequency
t= time


Graphics Window #1 - [artemis]
File Edit View Mode Window Options Help
Ref kh378_00010r1.fio
χ(k)
k³ χ(k)
k (Å⁻¹)
Ref kh378_00010r1.fio
bkg
μ
pre
post
χμ(E)
E (eV)
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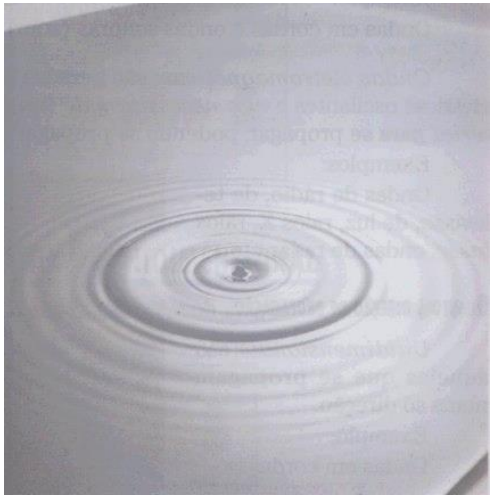
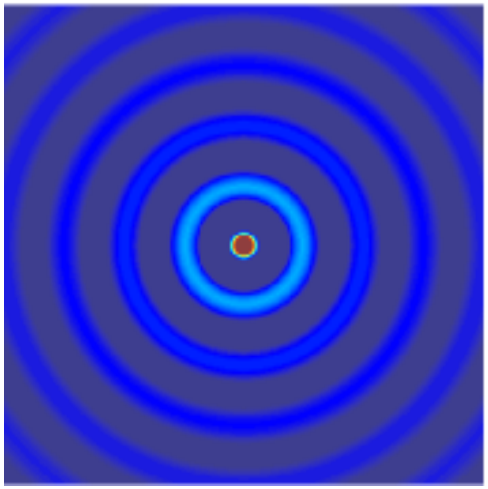
kmin: 0
kmax: 18





Photoelectron wave number:

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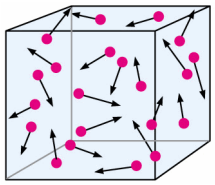
Solution of the wave equation:

$$u = A \sin(\vec{k}\,\vec{r} - w\,t)$$

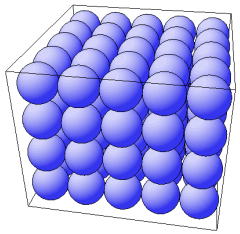
A = amplitude
k= wave vector
r= postion
w= 2πf= angular frequency
t= time

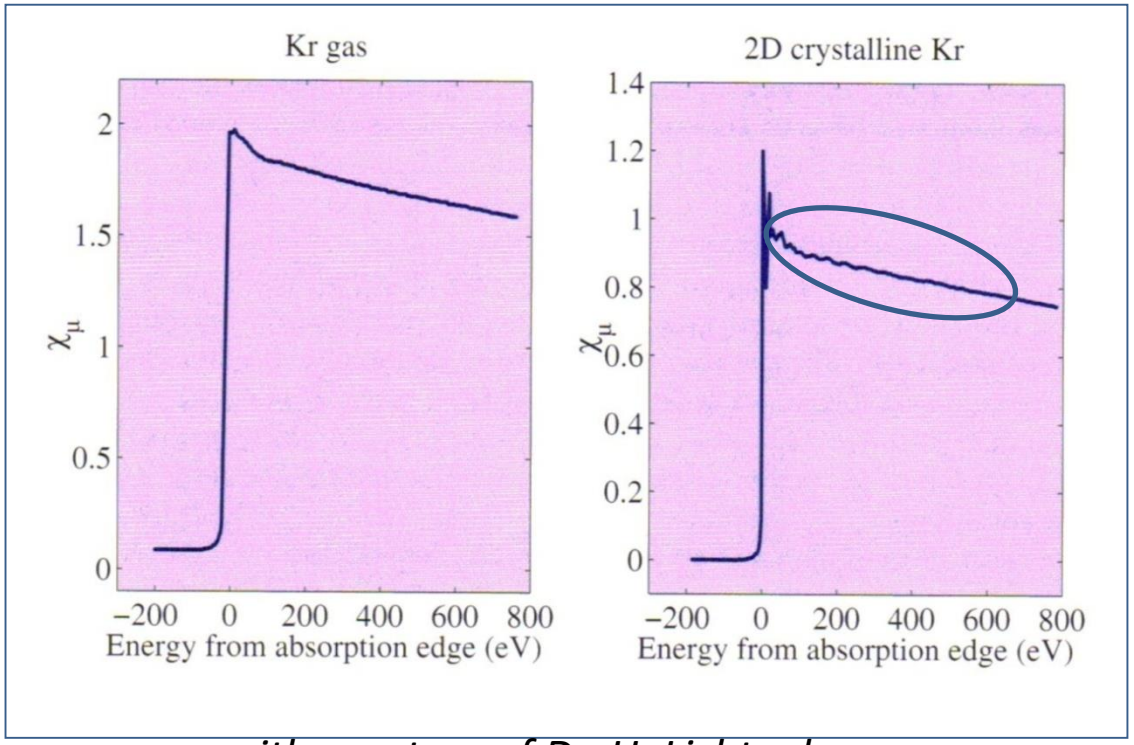
- Remembering: Where does the fine structure come from?

- What is a gas?



- What is solid?





with courtesy of Dr. H. Lichtenberg

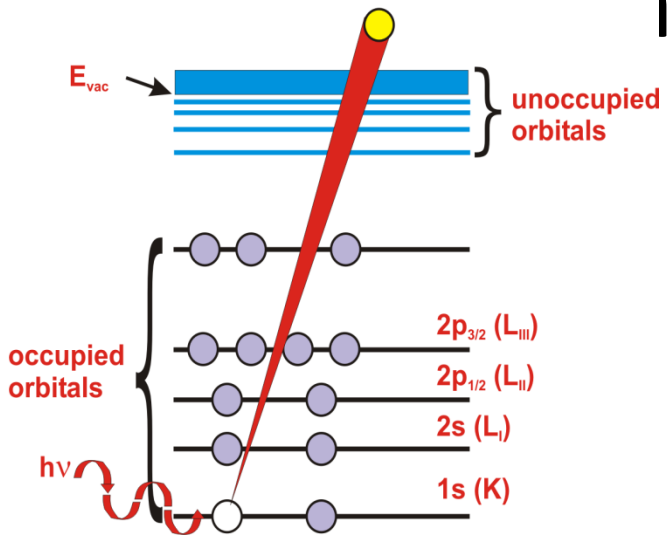
- What happens if the outgoing electron wave finds a hindrance?

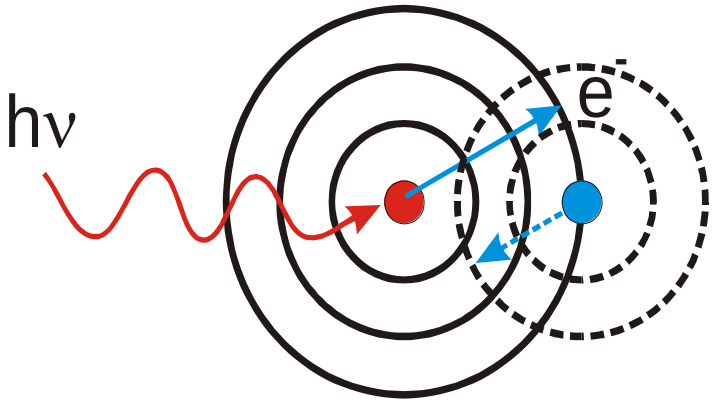
Software:

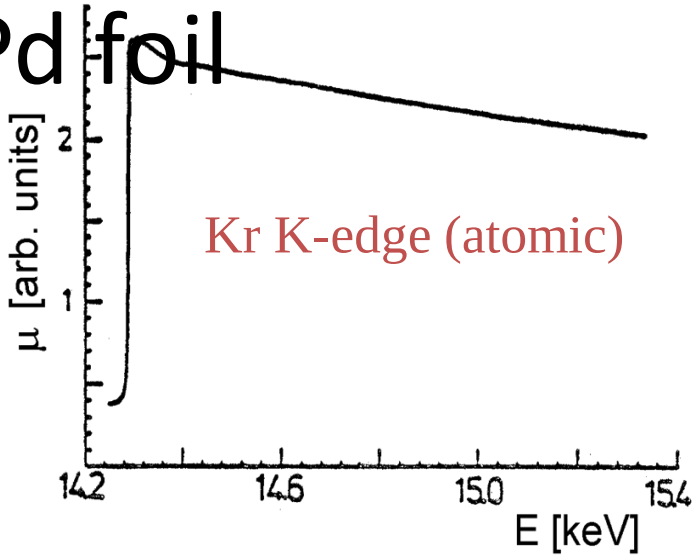
There is an backscattered wave!
Which does not exist in the monoatomic gas!

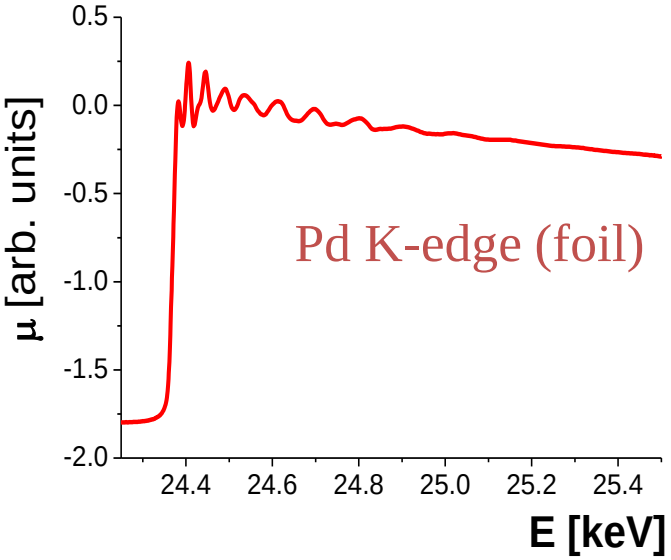
This is a more complicate scenario

X-ray absorption spectrum of Kr gas and Pd foil









Why dependent on the neighbouring atoms?

Fermi‘s Golden Rule: dependent on the initial and the final state

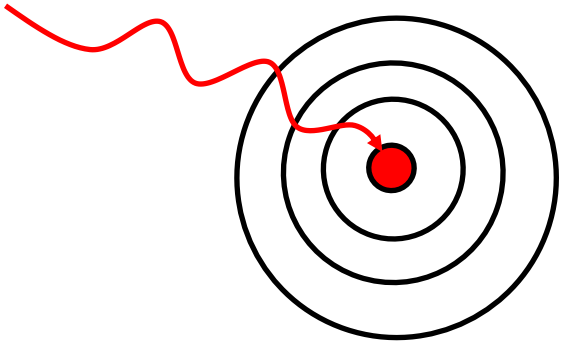
$$\mu \propto \left\langle \psi_f \left| \vec{\varepsilon} \cdot \vec{R} \right| \psi_i \right\rangle$$

Ψi: initial state wave function of the bound electron
Ψ_f: final state wave function of the ejected photoelectron
ε: electric field vector
R: position vector of scatterer

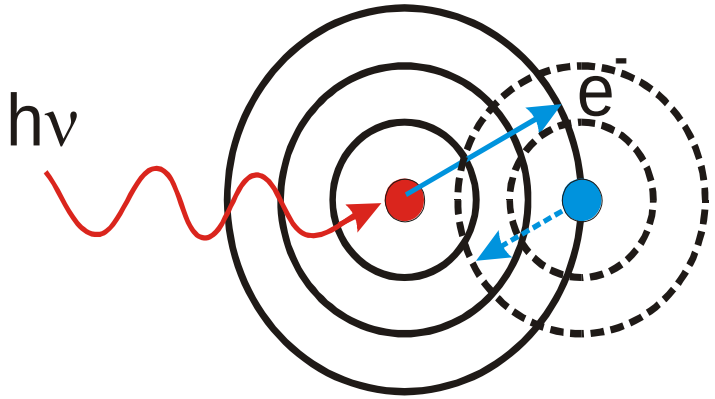
NOTE: valid for all electronic transitions,see books for physical chemistry (perturbation theory in quantum mechanics)

$$\mu \propto \left\langle \psi_f \left| \vec{\varepsilon} \cdot \vec{R} \right| \psi_i \right\rangle$$

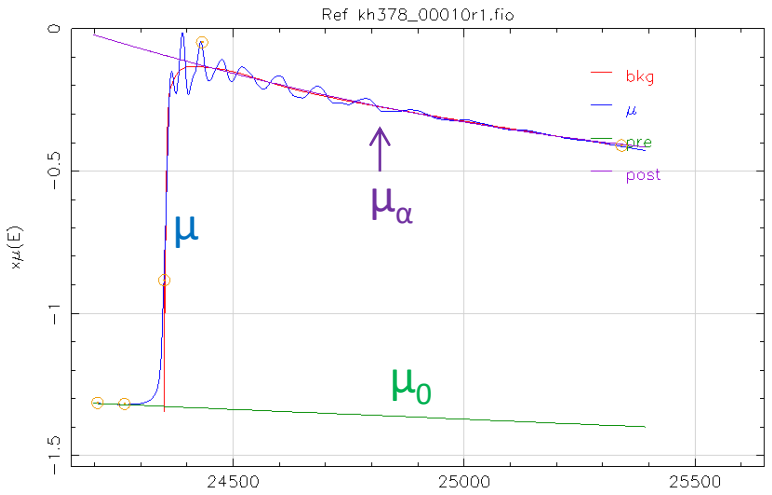
Ψ_f: $\Psi_{\text{outgoing wave}}$



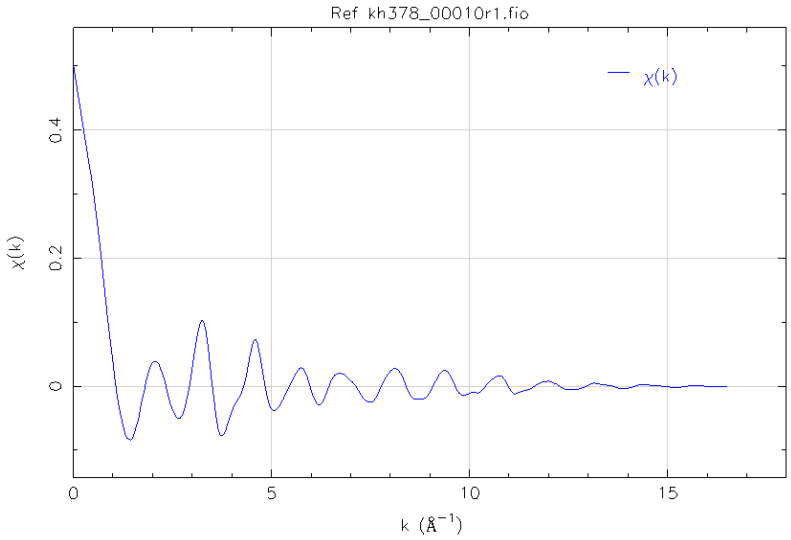
Ψ_f: $\Psi_{\text{outgoing wave}}$ + $\Psi_{\text{backscattered wave}}$



$$\mu \propto \left\langle \psi_f \left| \vec{\varepsilon} \cdot \vec{R} \right| \psi_i \right\rangle$$



$$\chi(k) = \frac{\mu - \mu_\alpha}{\mu_\alpha - \mu_0} = \frac{\mu - \mu_{backg}}{\Delta\mu_{edge\,step}}$$



Fine structure or EXAFS!

Modern EXAFS Equation

- Modern EXAFS theory 1971: Lytlle, Sayers and Stern

EXAFS

$$\chi(k) = \sum_j A_j(k) \sin(\Phi_j(k))$$

amplitude

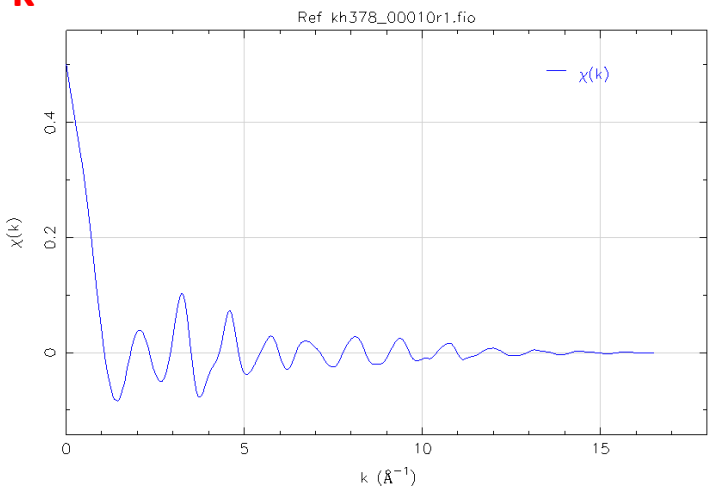
Interference pattern

Regular wave eq. solution

$$u = A \sin(\vec{k}\vec{r} - wt)$$

A = amplitude
k= wave vector
r= position
w= 2πf= angular freq
t= time

χ x k



Other way to present it

EXAFS

$$\chi_i(k) = \left(\frac{N_i S_0^2 F_i(k)}{kR_i^2} \sin(2kR_i + \varphi_i(k)) \exp(-2\sigma_i^2 k^2) \exp(-2R_i/\lambda(k)) \right)$$

$$R_i = R_0 + \Delta R$$

$$k^2 = 2\, m_e (E - E_0)/\hbar$$

Or

EXAFS

$$\chi(k) = \sum_j A_j(k) \sin(\Phi_j(k))$$

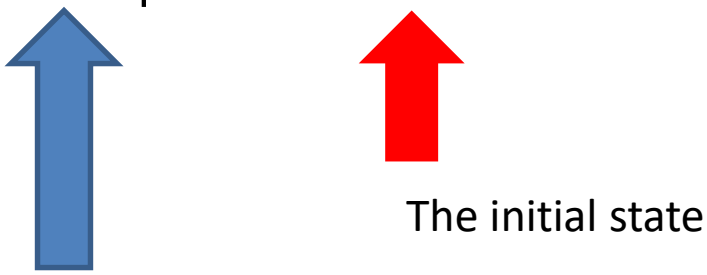
amplitude

Interference pattern

X-ray Absorption Spectroscopy

XANES phenomenon in two steps: the initial and final states

$$\mu \propto \left\langle \psi_f \left| \vec{\varepsilon} \cdot \vec{R} \right| \psi_i \right\rangle$$



The initial state

The final state

X-ray Absorption Spectroscopy

- The selection rules

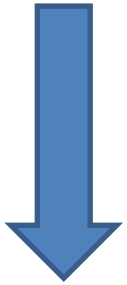
  -They depend on both initial and final states

  ΔS (spin)= 0

  ΔL (orbital momentum)= ±1

  ΔJ (total momentum L+S)= 0, ±1

Dipolar allowed transitions



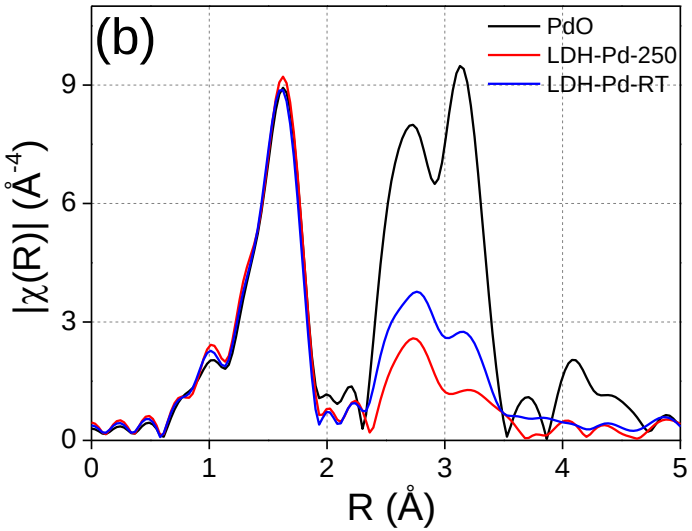
Forbiden trasitions may happen

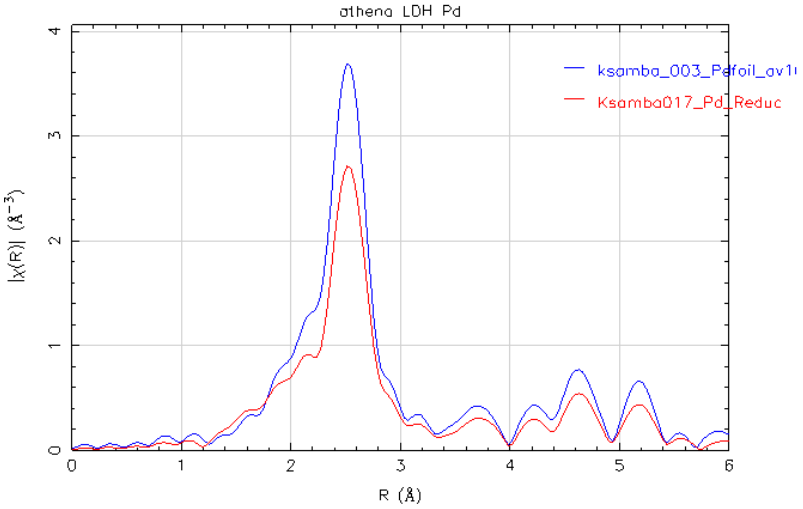
- Therefore it arises a double advantage:

  -one probes just one element per turn
  -one probes the orbitals selectively

What do with the spectrum?

- EXAFS
  - The effect of particle size





  - The effect of particle size

What do with the spectrum?

- EXAFS
  - The effect of particle size

What do with the spectrum?

- EXAFS
  - The effect of particle size

The thickness problem

A quick mind refresh from your XAS course

Beer-Lambert-Bouguer´s Law

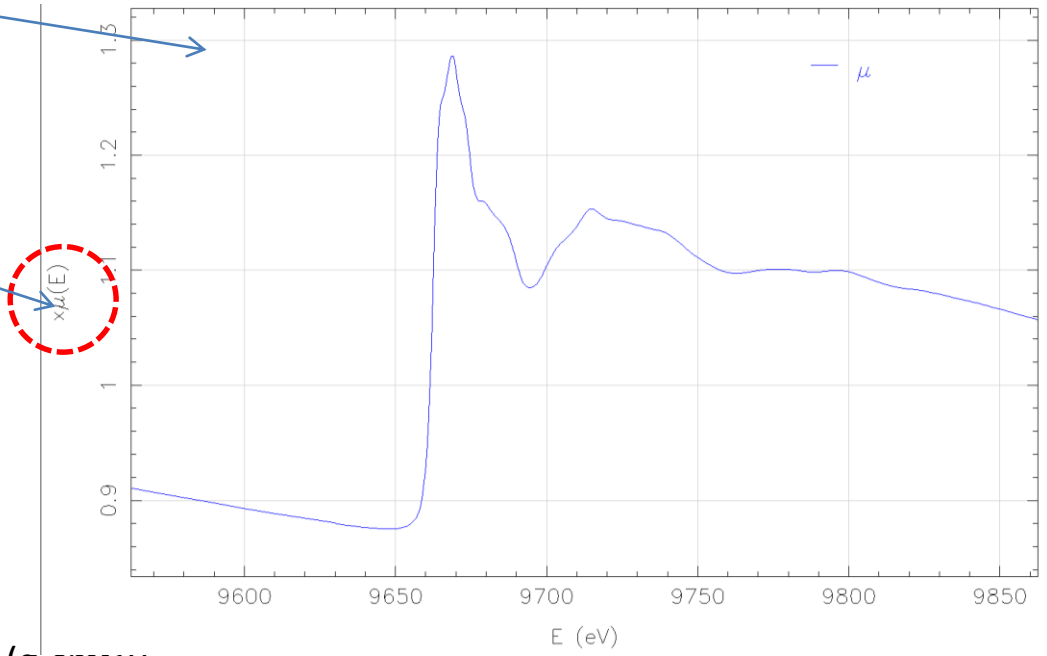
$$I_t = I_0 e^{-\mu x}$$

I_t = number of transmitted photons
I_0 = number of incident photons

i) In the beamline we measure I_0 and I_t
ii) Using Origin, Athena or other program we perform the **ln (I_0/I_t)** operation
iii) Thus: $\ln(I_0/I_t) = \mu x$
iv) Then we plot our data as:
v) Have you ever paied attention to this x here?
We did not plot the absorption coeficient.
We do plot the absorption length.

$$\mu x(E)$$

vi) What is the optimal μx ?



μ(cm^{-1}) = absorption coeficient [μ_m (cm^2.g^{-1}).ρ(g.cm^{-3})]
x(cm) = thickness of the absorbing sample

The thickness problem

The optimum tickness for transmission

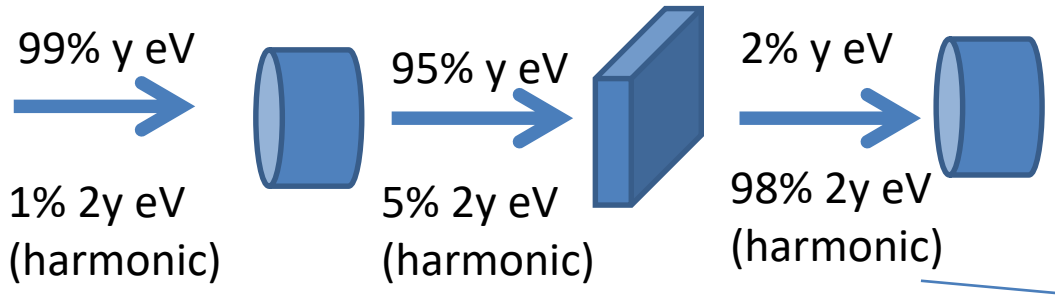
i) If the sample is too thin, e.g. μx = 0.01
Only 1% of the photons are absorbed. The signal to noise ratio becomes to low.

ii) In the microreactor case, the challange
Was to avoid too much absorption. Remember the Several foils: Ni, Pd and the catalyst poweder!

TABLE 3.2

iii) What´s wrong with to high absorption?

a) the noise of I_t becomes to high, since few photons are passing trough the sample
b) **The ratio of harmonics in the transmitted beam will become important.**



The high ratio of harmonics suppress the amplitude of XAS

This important contribution continues to send signal to It. like whether ´no absorption happend´.
They are not affected by the fine structure.

The thickness problem

The optimum tickness for transmission

Table 3.3

Figure 3.2

The witheline means that absorption is happening.
If your detection system continues to count, looks like no absorption happened!

Figure 3.3

i) How does it fool you?
   a) wrong speciation in XANES
   b) wrong coordinatination numbers and disorder factor