

# ***X-ray Spectroscopy***

- Interaction of X-rays with matter
- XANES and EXAFS
- XANES analysis
- Pre-edge analysis
- EXAFS analysis

# *Why XAS?*

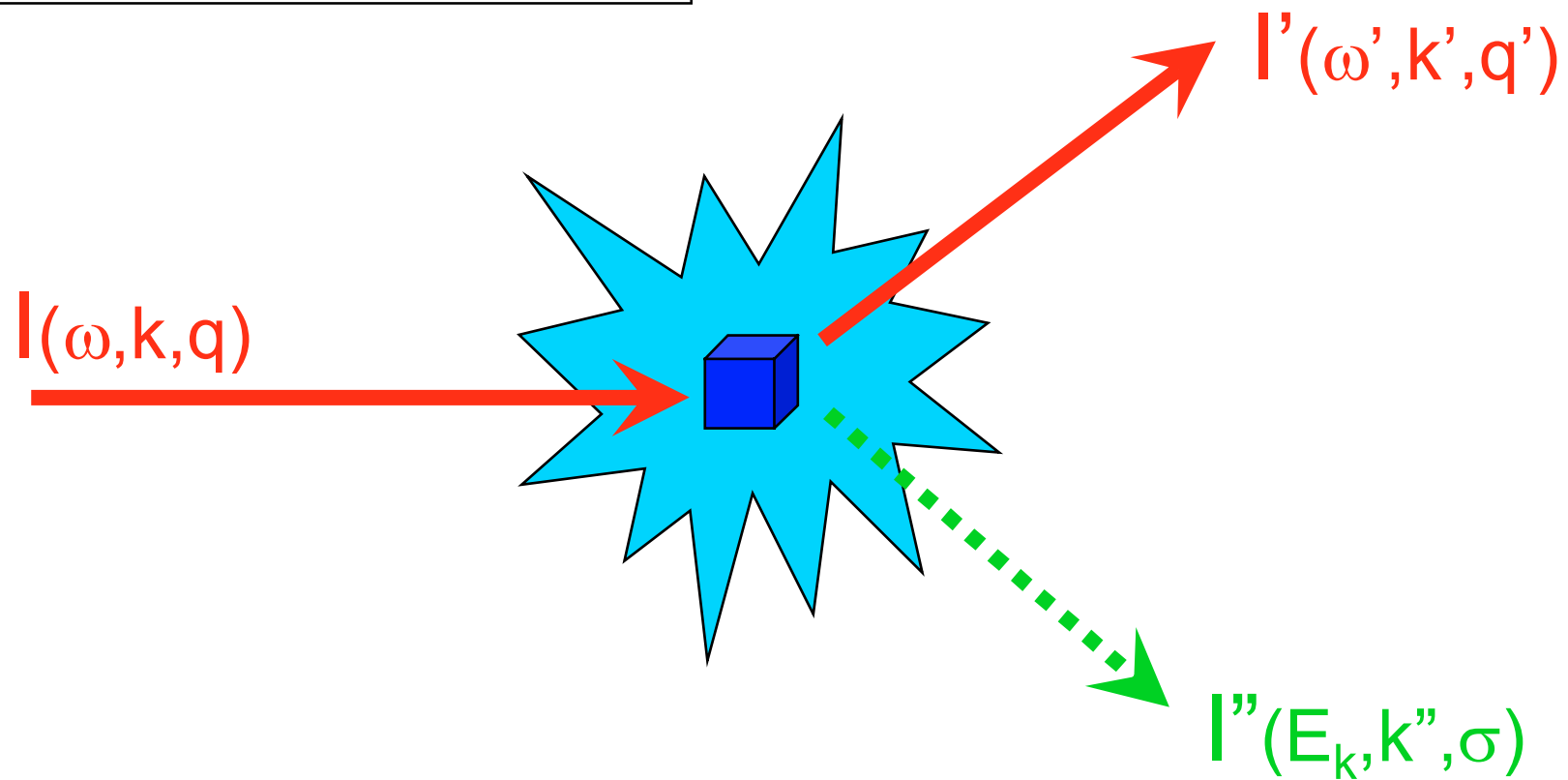
- Element specific
- Sensitive to low concentrations  
(0.01-0.1 %)
- Applicable under extreme conditions  
(high-pressure, high temperature, operando)
- Applicable to gasses, liquids and solids  
(+ surfaces, buried interfaces, impurities, etc.)
- Local geometric information
- Local electronic information

# ***What do we learn from XAS?***

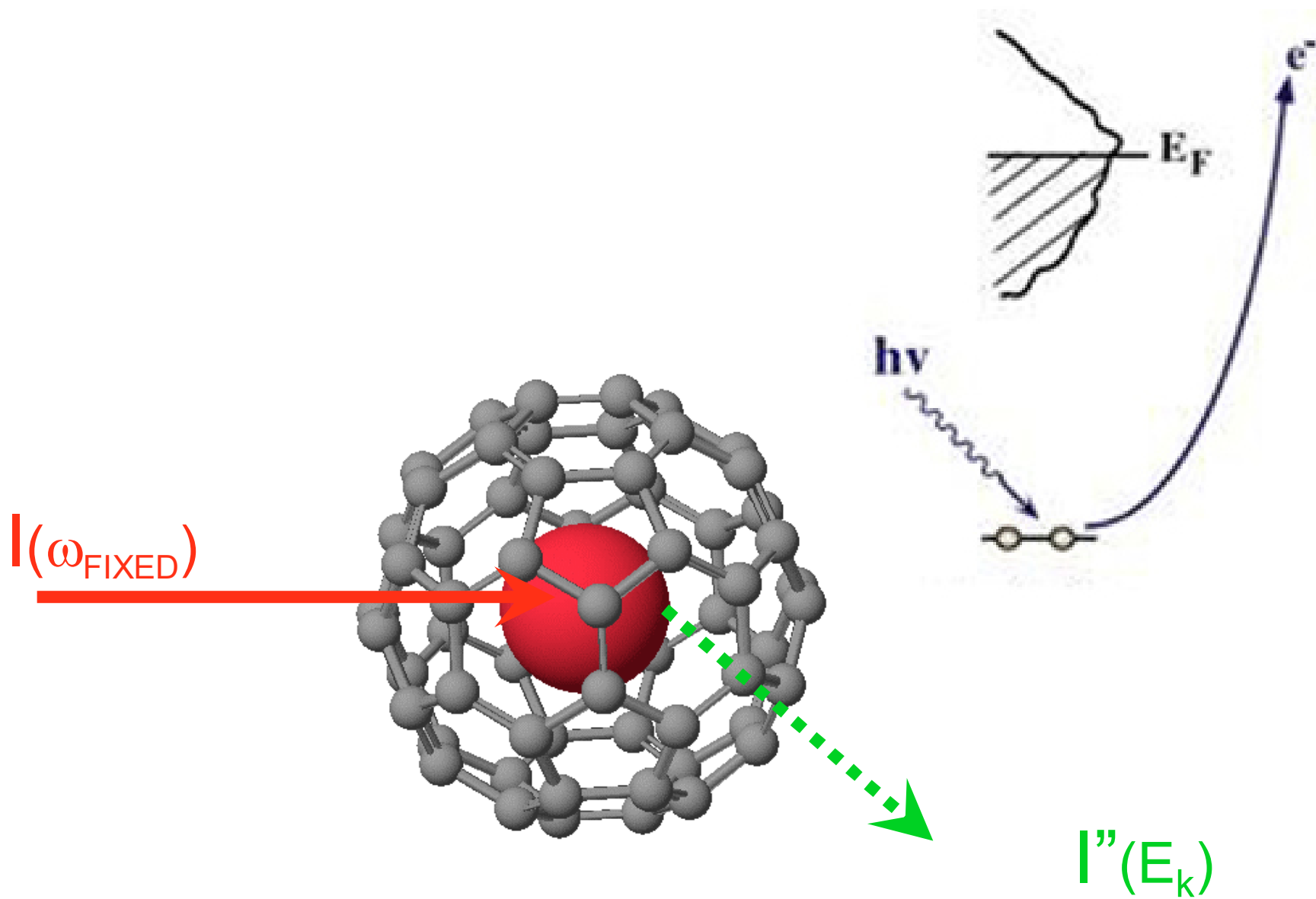
- Metal valence during synthesis and reaction
- Metal coordination
  - Binuclear centers, (very small) cluster sizes
- Metal site symmetry
- d-band occupation
  - (3d, 4d or 5d; metal versus oxide, valence)
- Energy positions of empty bands of adsorbates
  - (CO, H<sub>2</sub>, on Pt, nature of adsorption site)
- 20 nm microscopy, 50 ps time-resolved

# *Interaction of x-rays with matter*

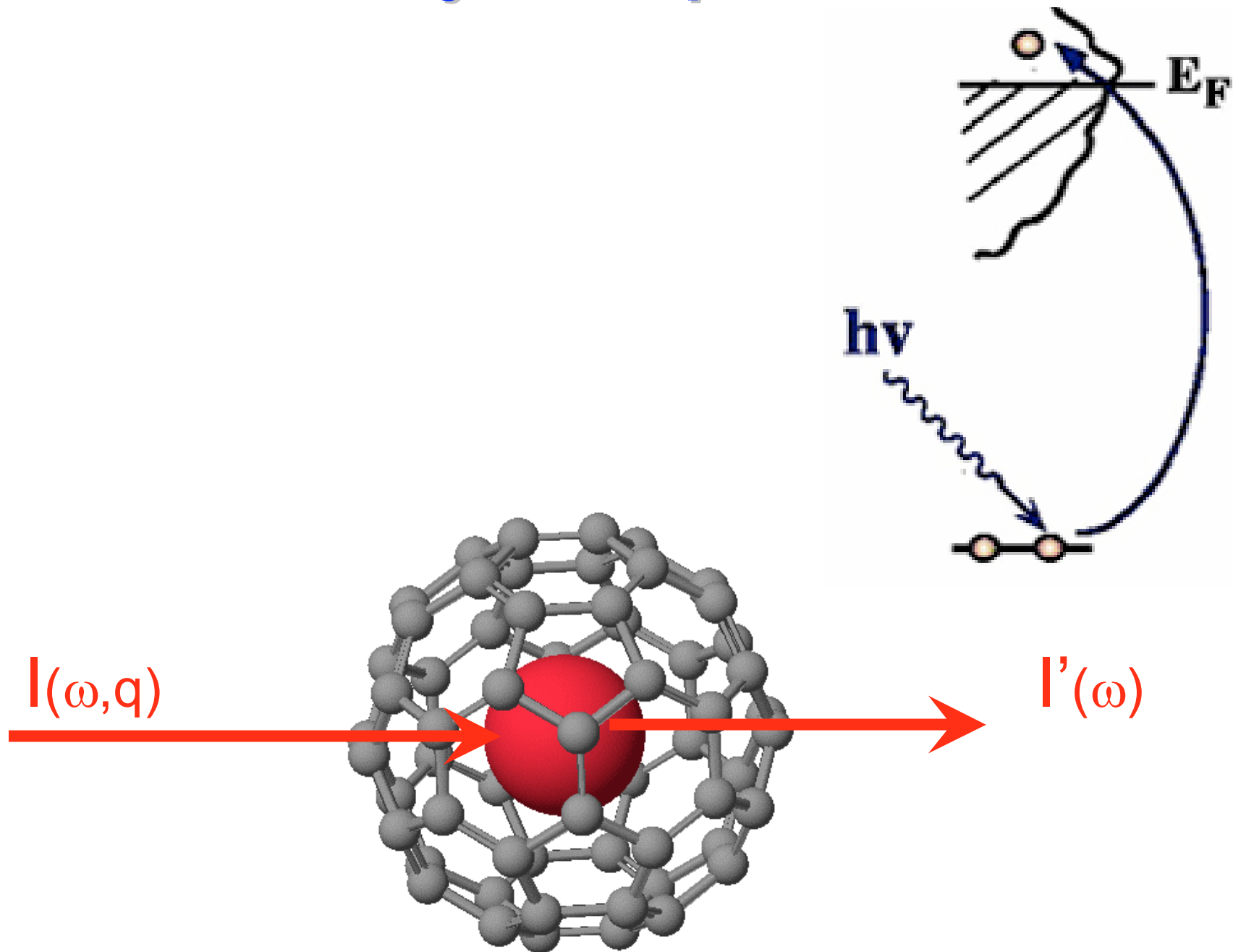
Energy → Spectroscopy  
Direction → Structure  
Polarization → Magnetism



# *X-ray photoemission*










# *X-ray absorption*



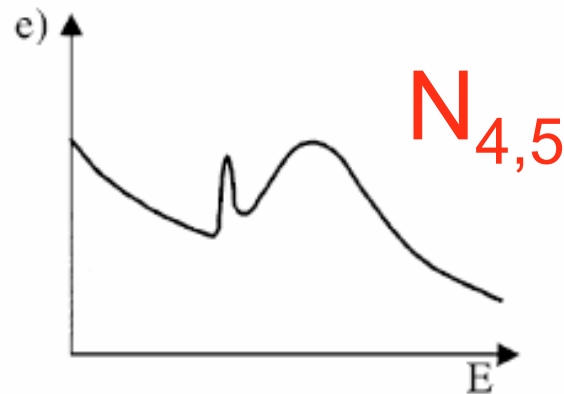
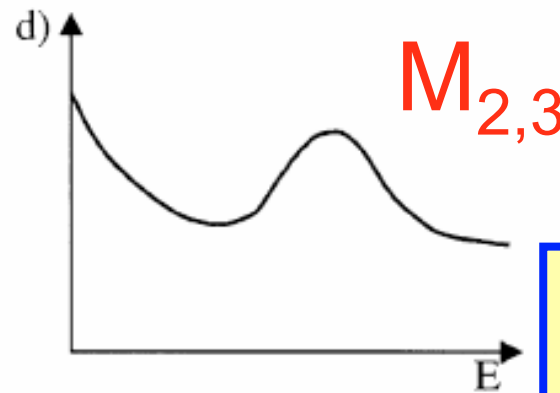
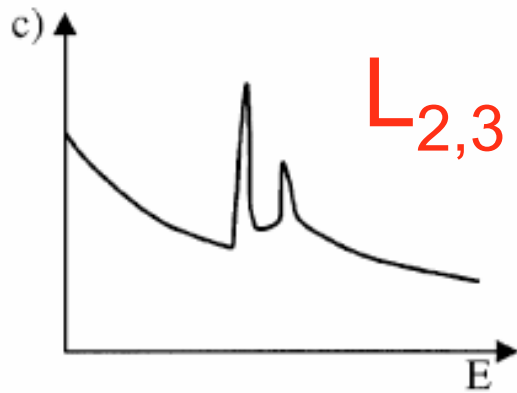
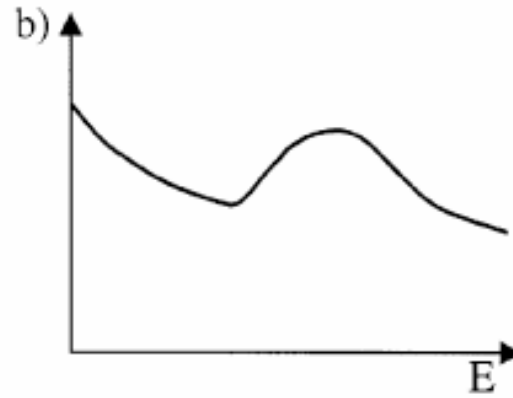
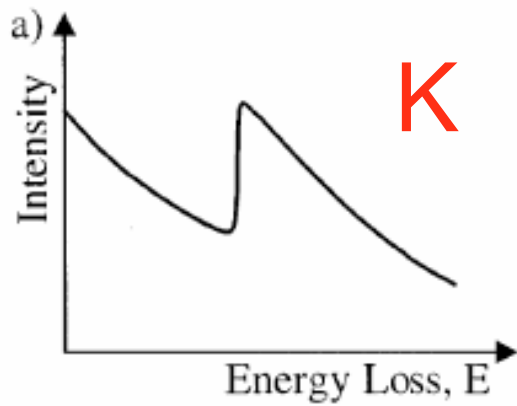
# X-ray absorption edges

## Manganese Electron binding energies

	Label	Orbital	eV [literature reference]
	K	<u>1s</u>	6539 [1]
	L <sub>I</sub>	<u>2s</u>	769.1 [3]
	L <sub>II</sub>	<u>2p<sub>1/2</sub></u>	649.9 [3]
	L <sub>III</sub>	<u>2p<sub>3/2</sub></u>	638.7 [3]
	M <sub>I</sub>	<u>3s</u>	82.3 [3]
	M <sub>II</sub>	<u>3p<sub>1/2</sub></u>	47.2 [3]
	M <sub>III</sub>	<u>3p<sub>3/2</sub></u>	47.2 [3]

<http://www.webelements.com/>

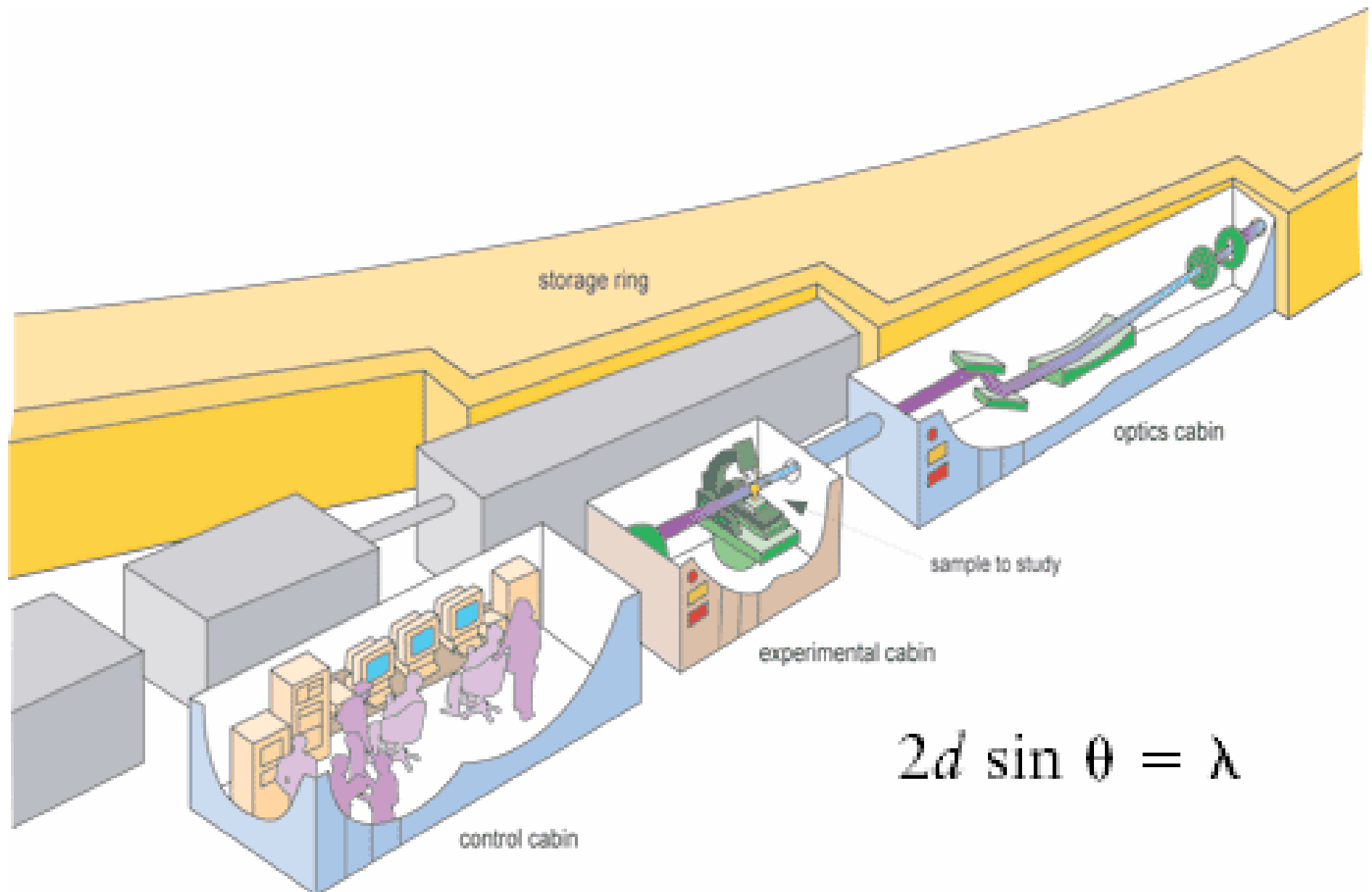
# X-ray absorption



<b>K</b>	1s → p (3d)
<b>L<sub>2,3</sub></b>	2p → 3d (3d)
<b>M<sub>2,3</sub></b>	3p → 3d (3d)
<b>N<sub>4,5</sub></b>	4d → 4f (4f)

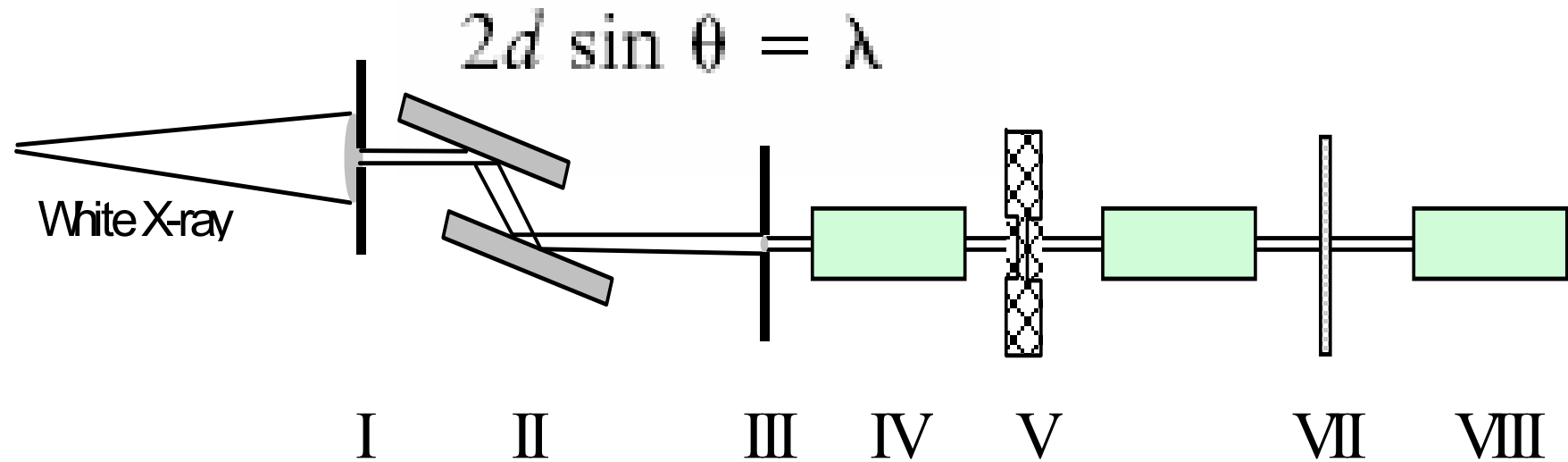


# *X-rays from synchrotrons*



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

# *X-ray absorption beamline (transmission)*



I Entrance slits

II Monochromator

III Exit slits

IV Ionisation chamber

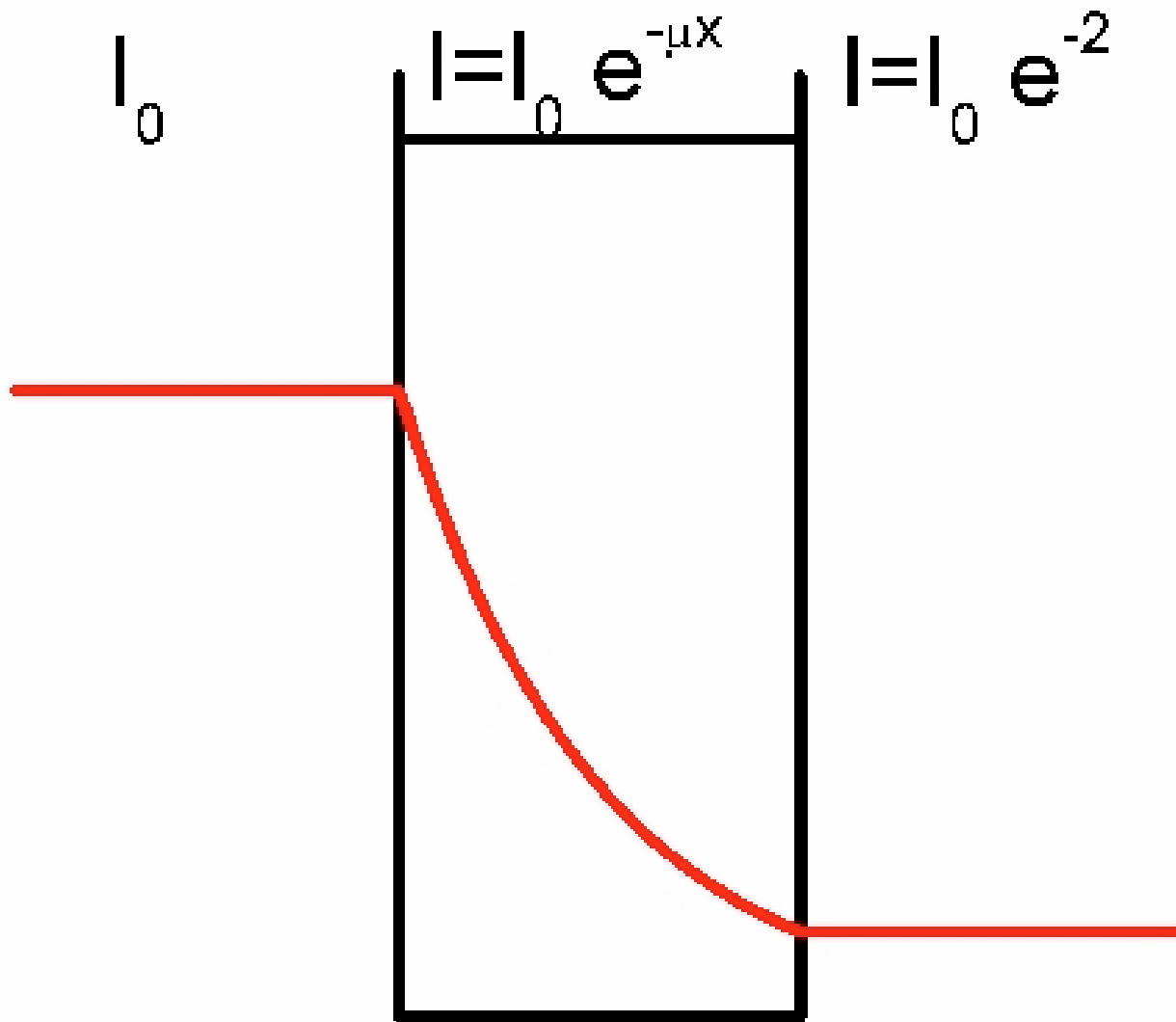
V Sample

VI Ionisation chamber

VII Reference material

VIII Ionisation chamber

# *X-ray absorption*



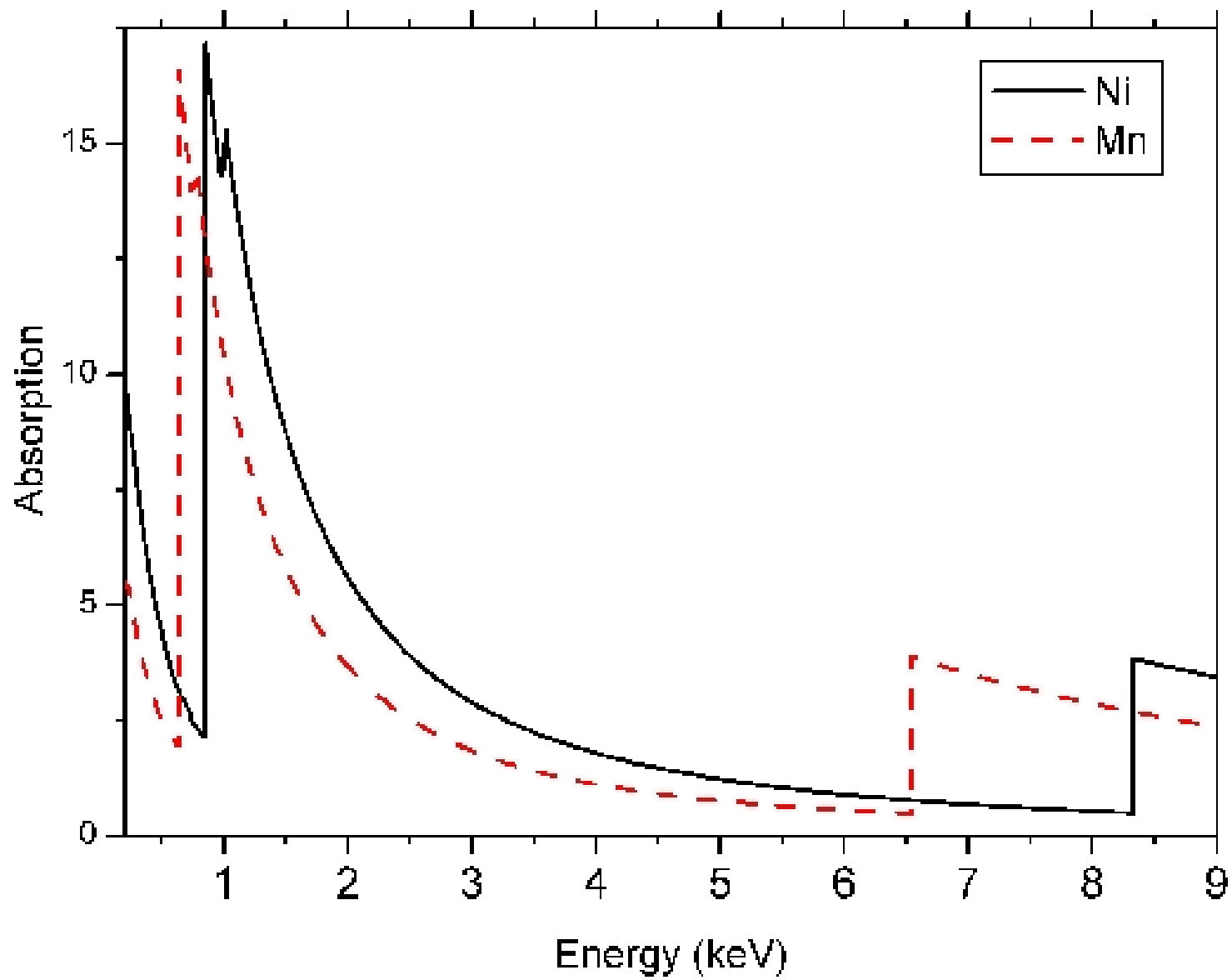
# *X-ray absorption*

$$\ln \frac{I_0}{I_t} = \varepsilon \cdot c \cdot l$$

$$\mu = \frac{1}{x} \ln \frac{I_0}{I_t}$$

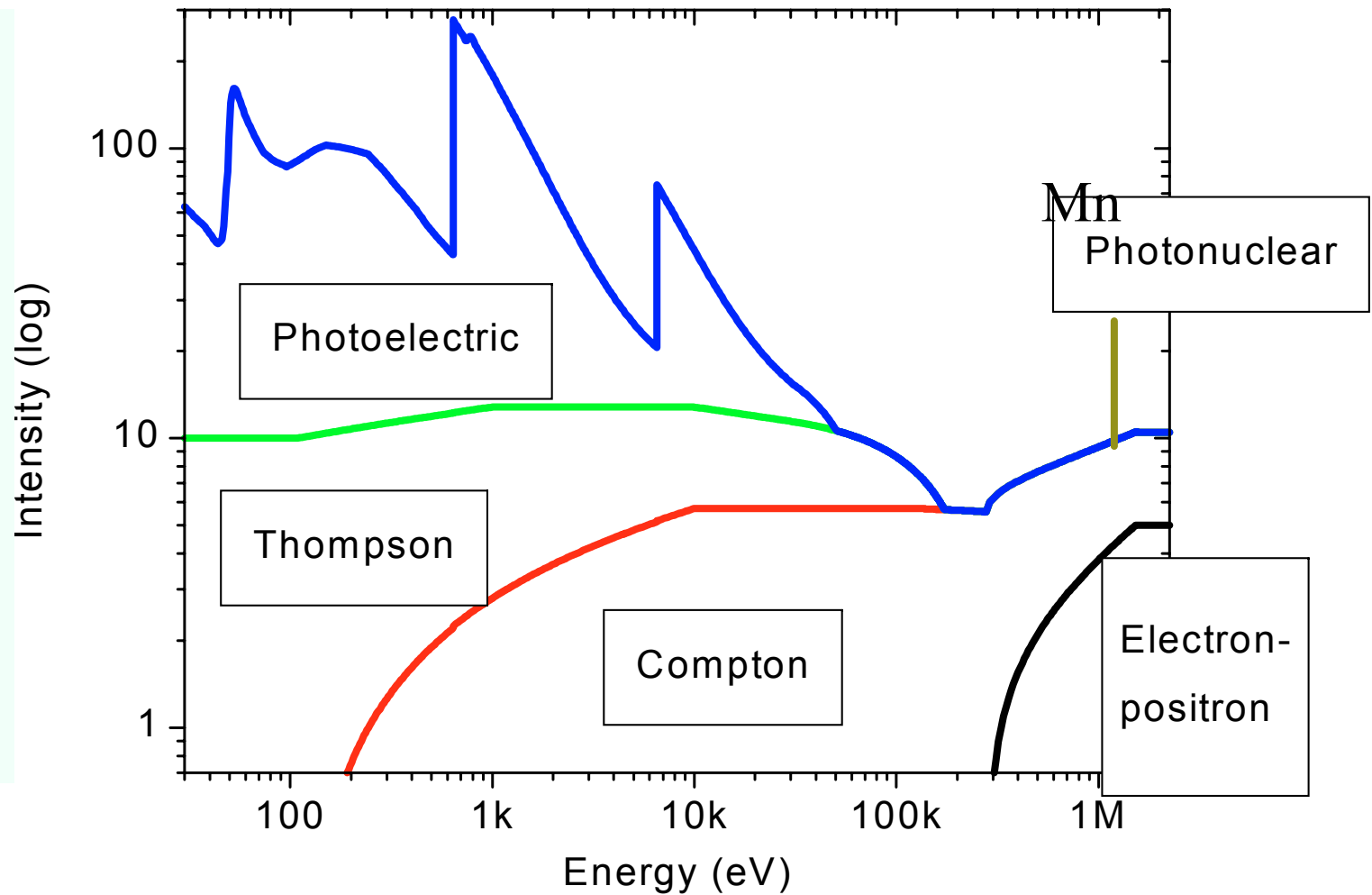
- Lambert-Beer
- $\mu$  = absorption coefficient
- $x$  = sample thickness
- Measure x-ray intensity before and after sample

# *X-ray absorption*

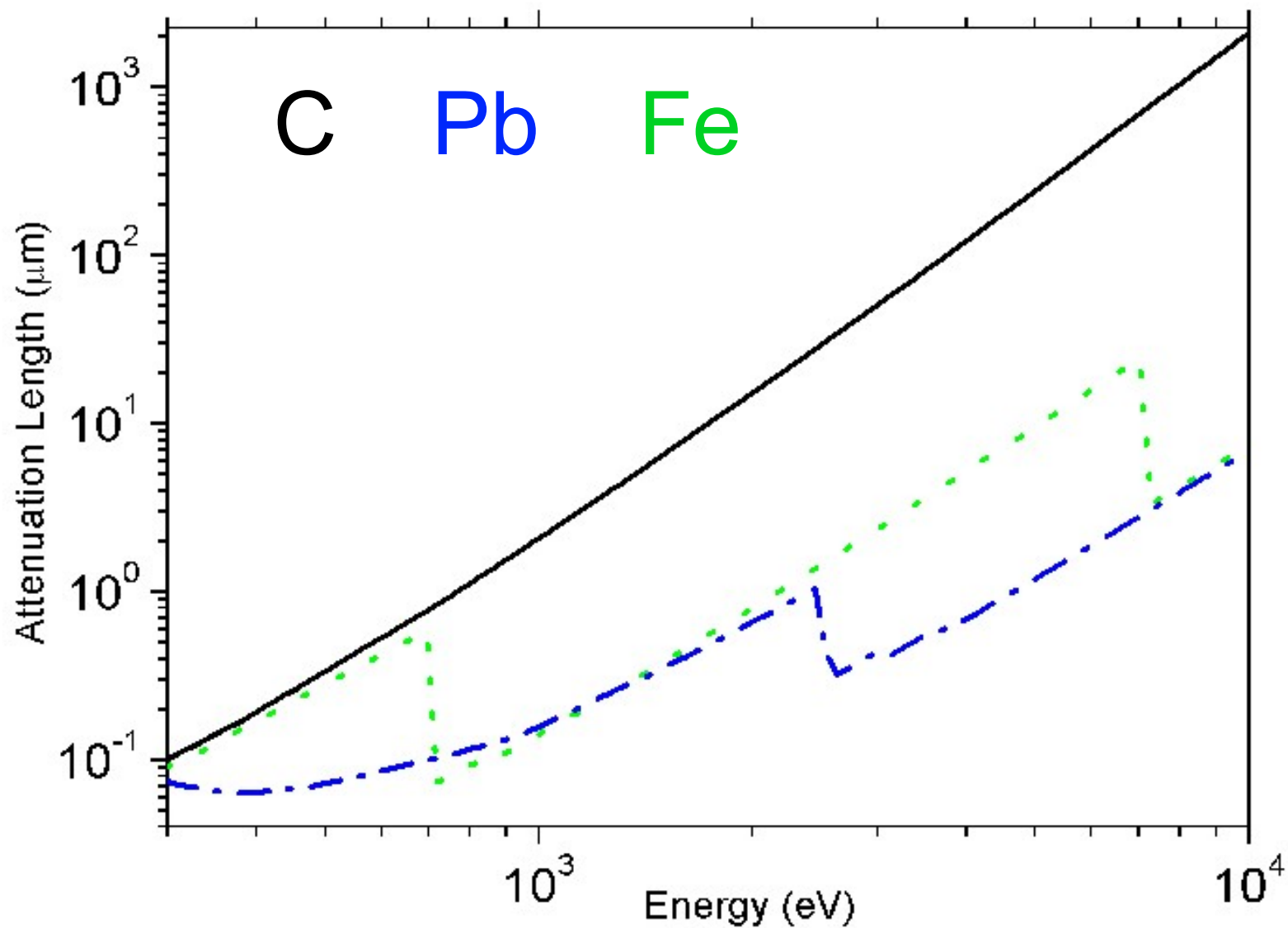


# Interaction of x-rays with matter

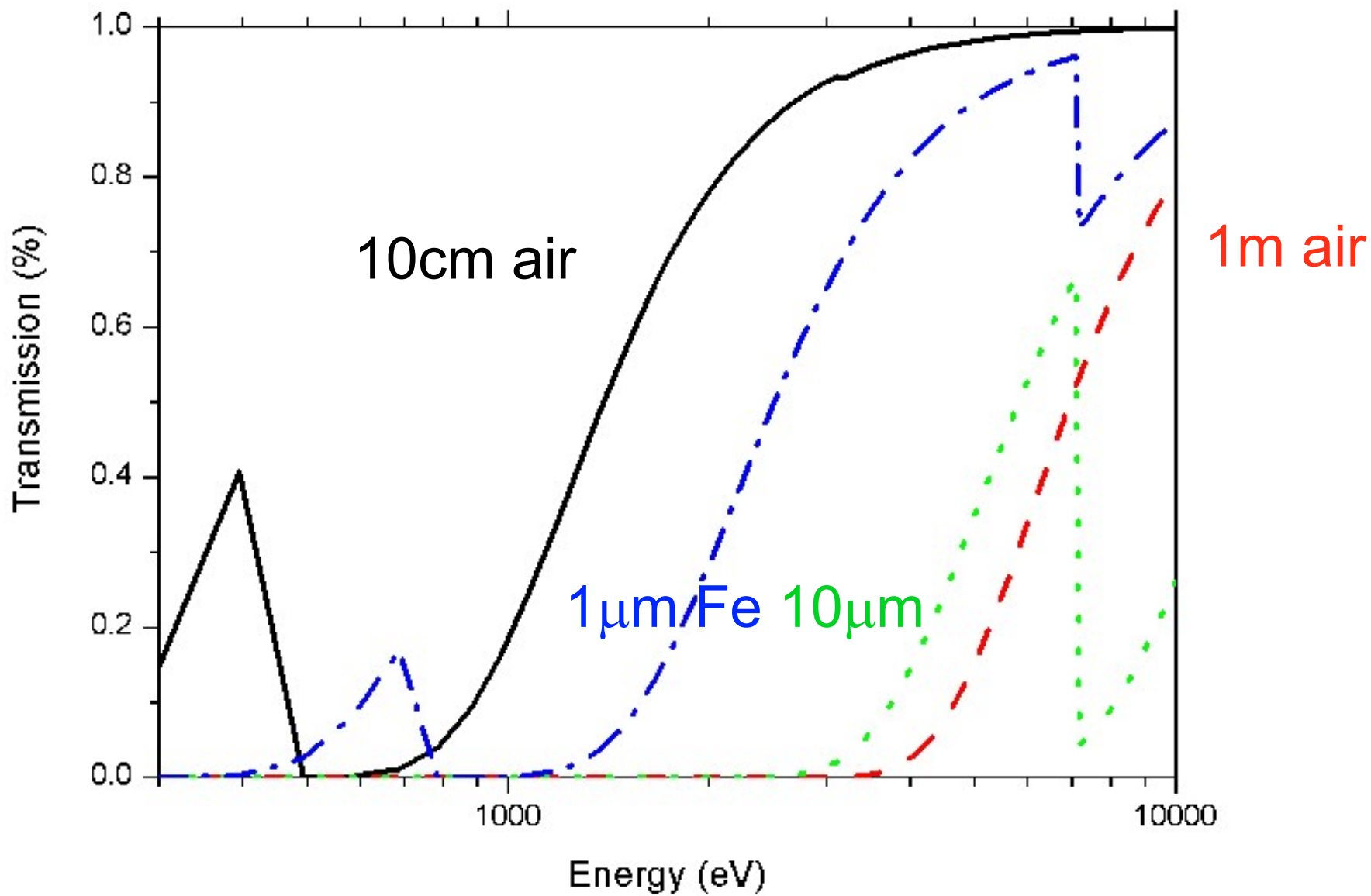
- XAFS studies photoelectric absorption
- Thompson scattering (Diffraction)
- Compton scattering
- Photonuclear scattering (Mössbauer)



# *X-ray attenuation*



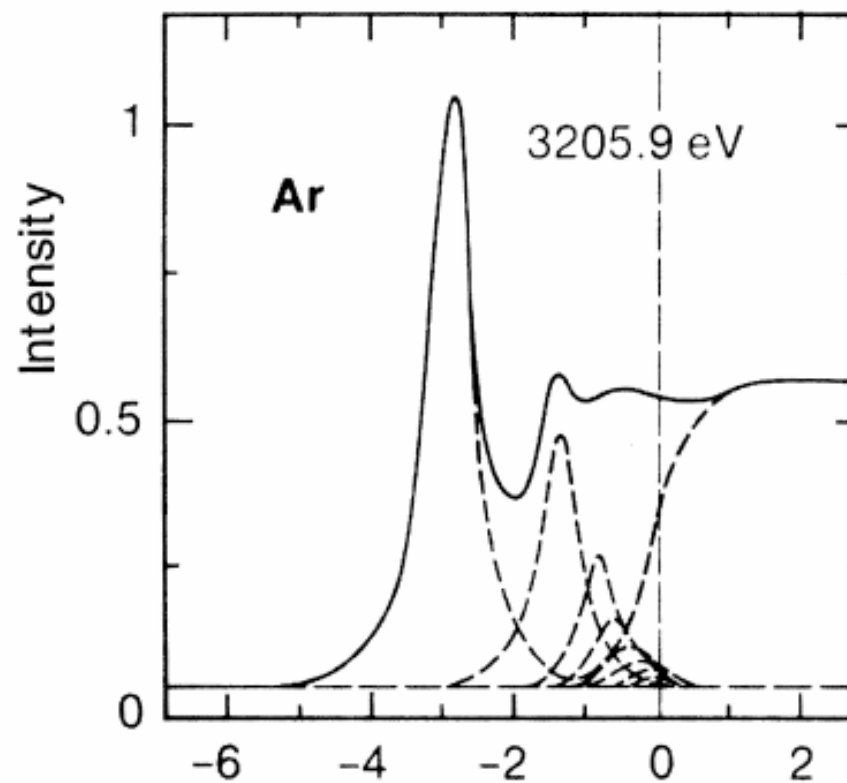
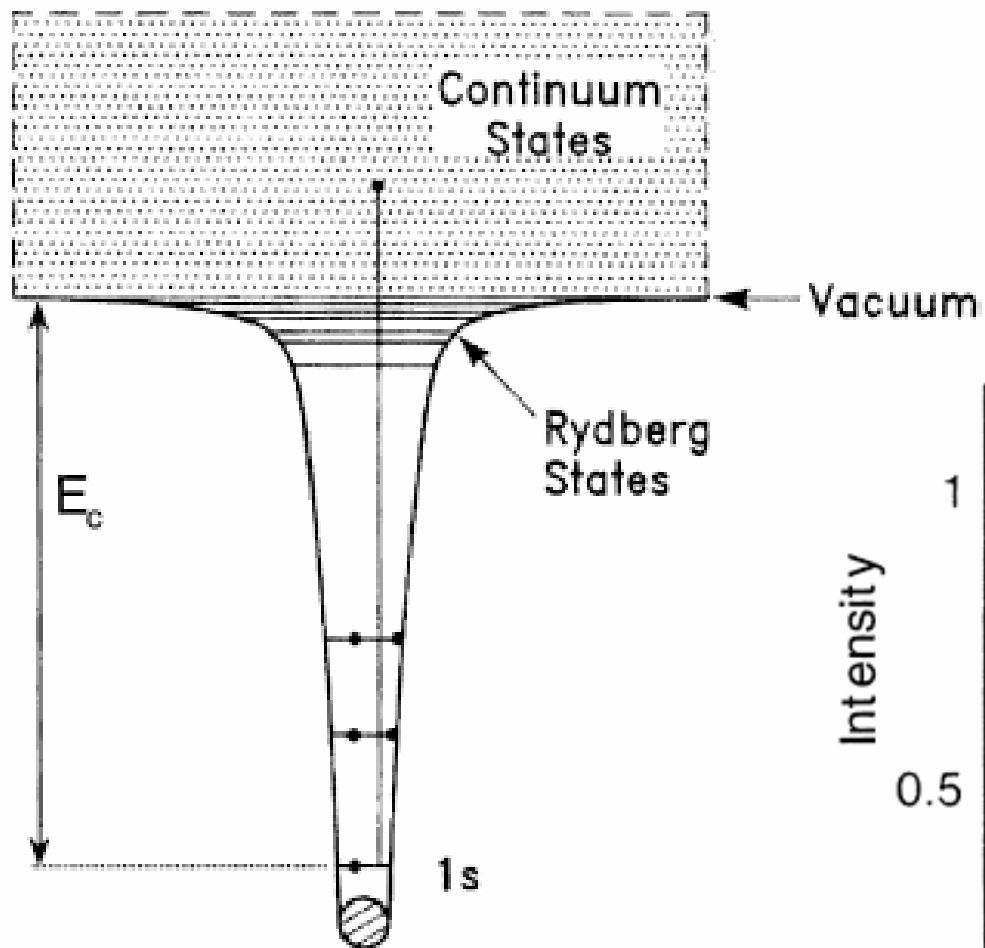
# *X-ray attenuation*



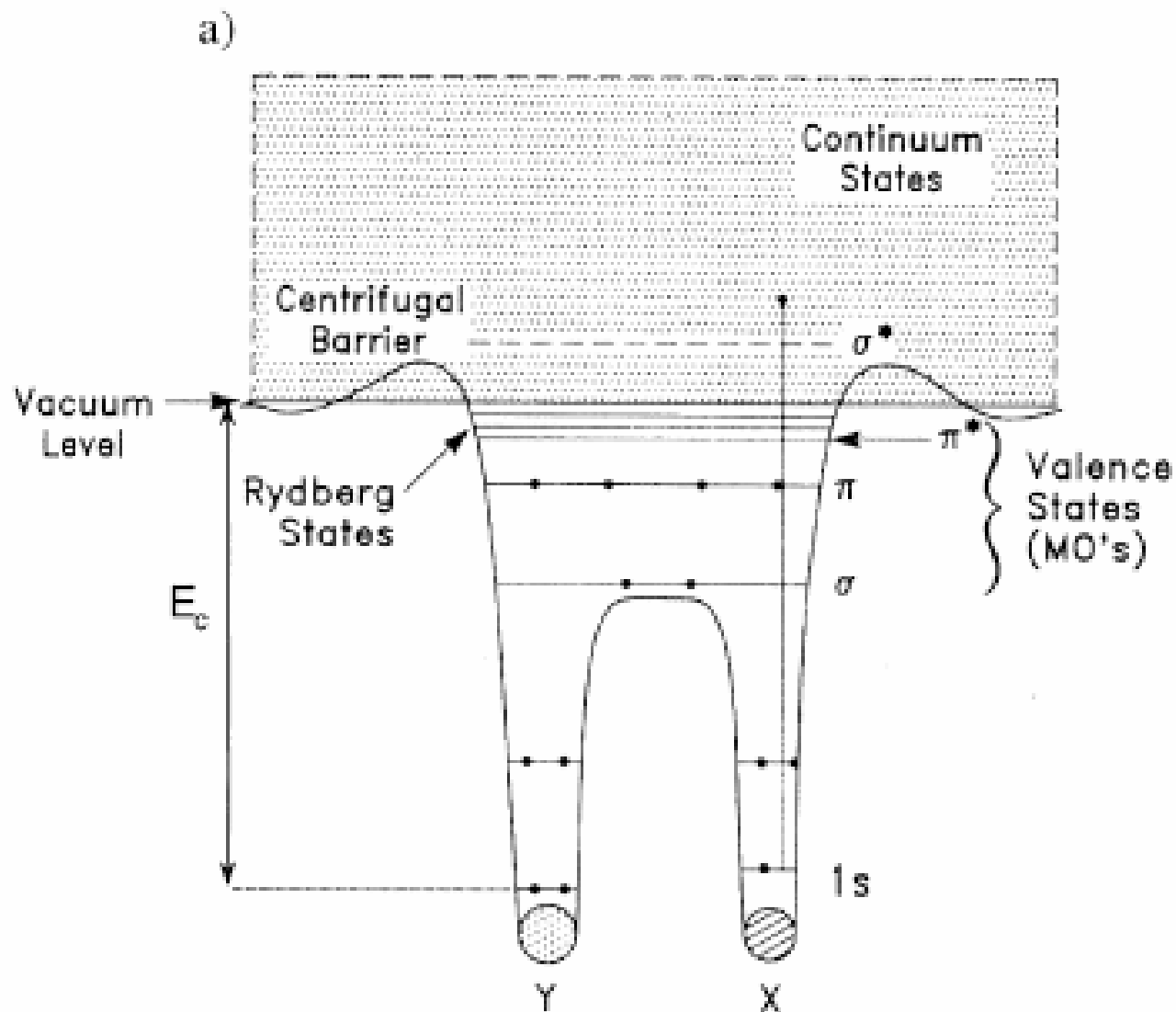


# X-ray absorption of an atom

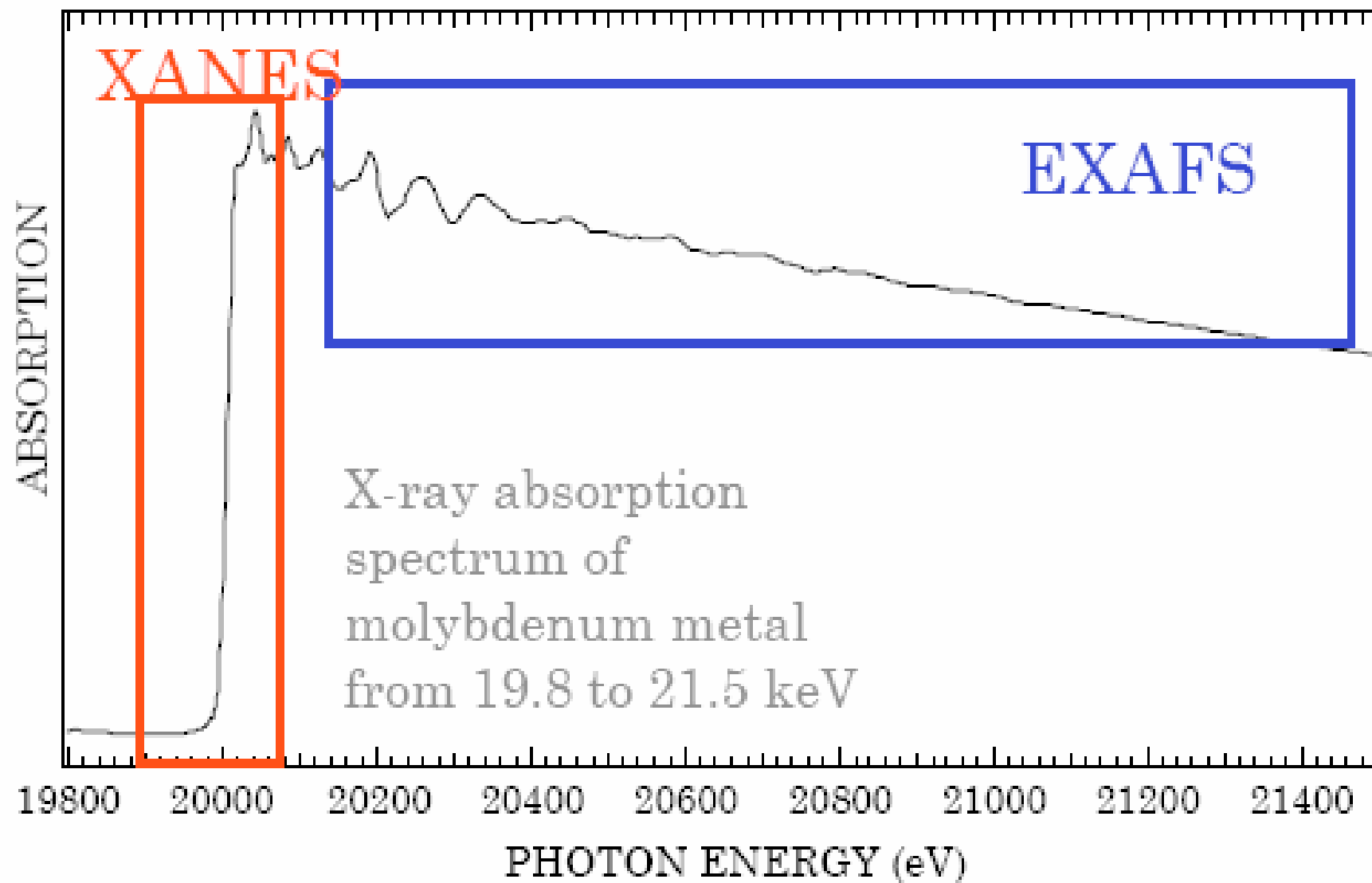
a)



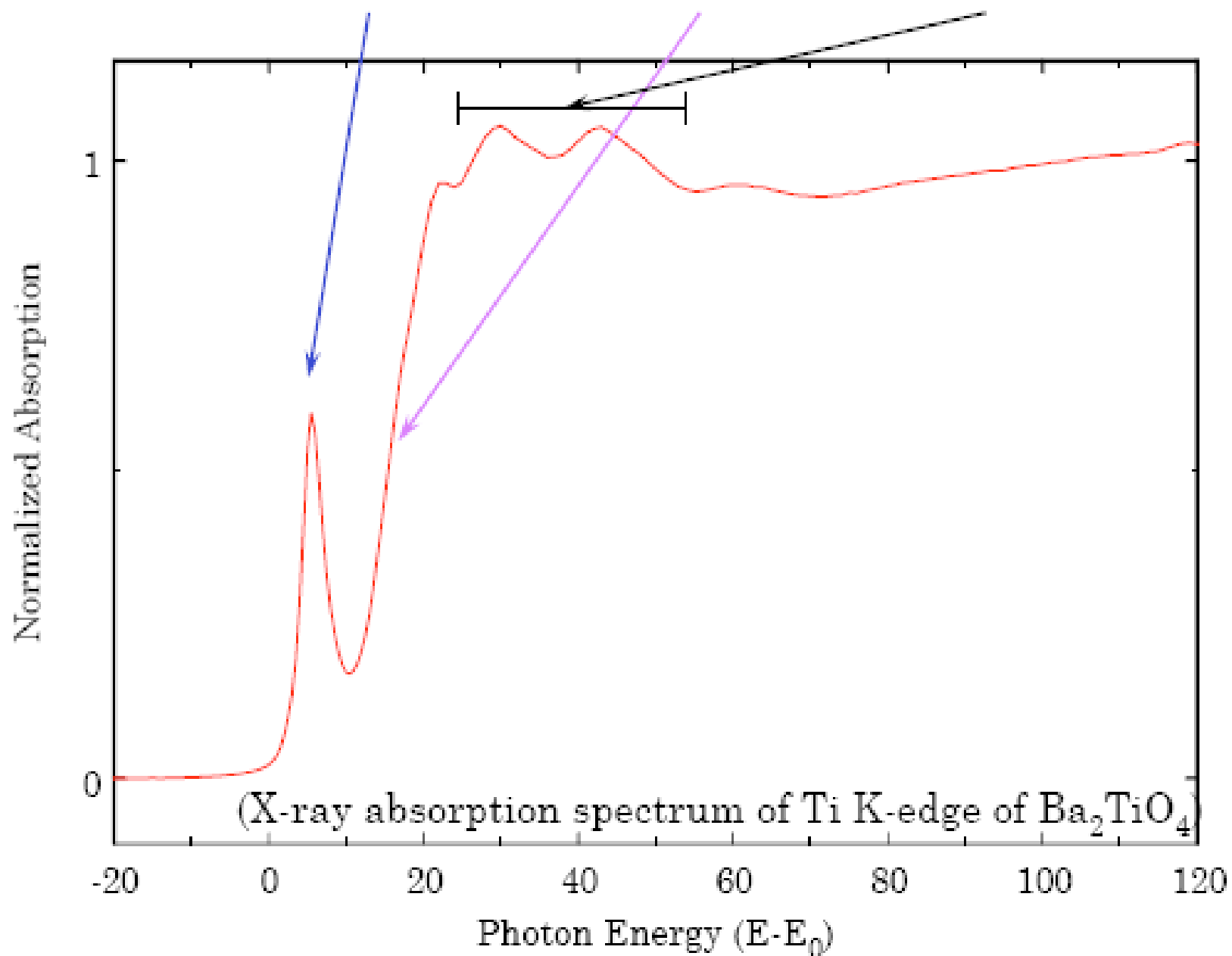
# X-ray absorption of a molecule



# *X-ray absorption*



**XANES= Pre-edge + Edge + XANES**



# ***X-ray absorption***

Excitation of core electrons to empty states.

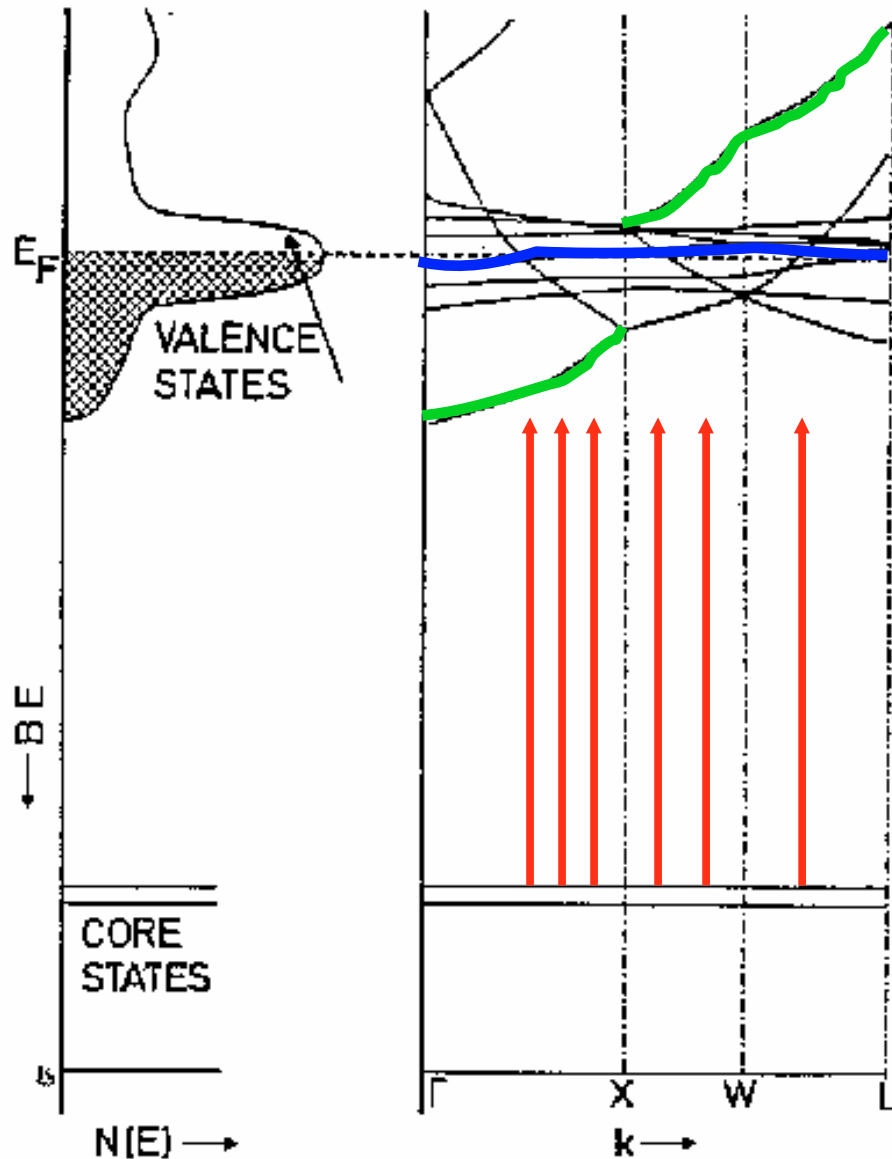
Spectrum given by the **Fermi Golden Rule**

(name Golden Rule given by Fermi; rule itself given by Dirac)

$$I_{XAS} \sim \sum_f \left| \langle \Phi_f | \hat{e} \cdot r | \Phi_i \rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

# *X-ray absorption*

## *(single particle interpretation)*

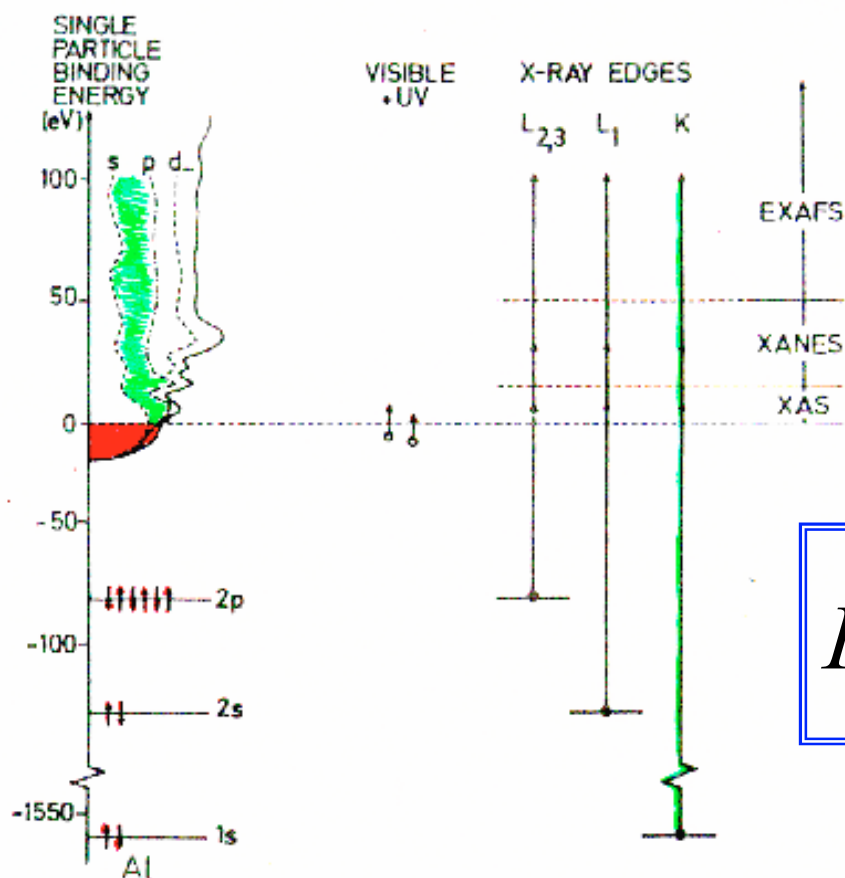
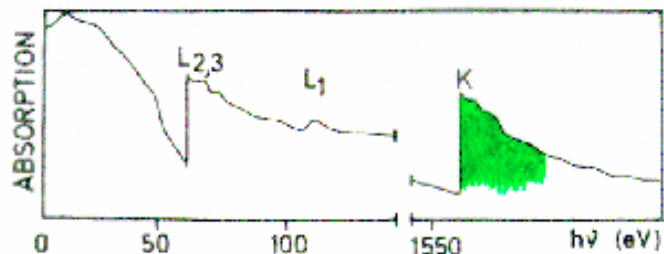


Density of States (DOS) is the integral over  $k$ -space of the band structure.

Core states have no dispersion.

XAS preserves momentum ( $k$ )

# X-ray absorption (single particle interpretation)

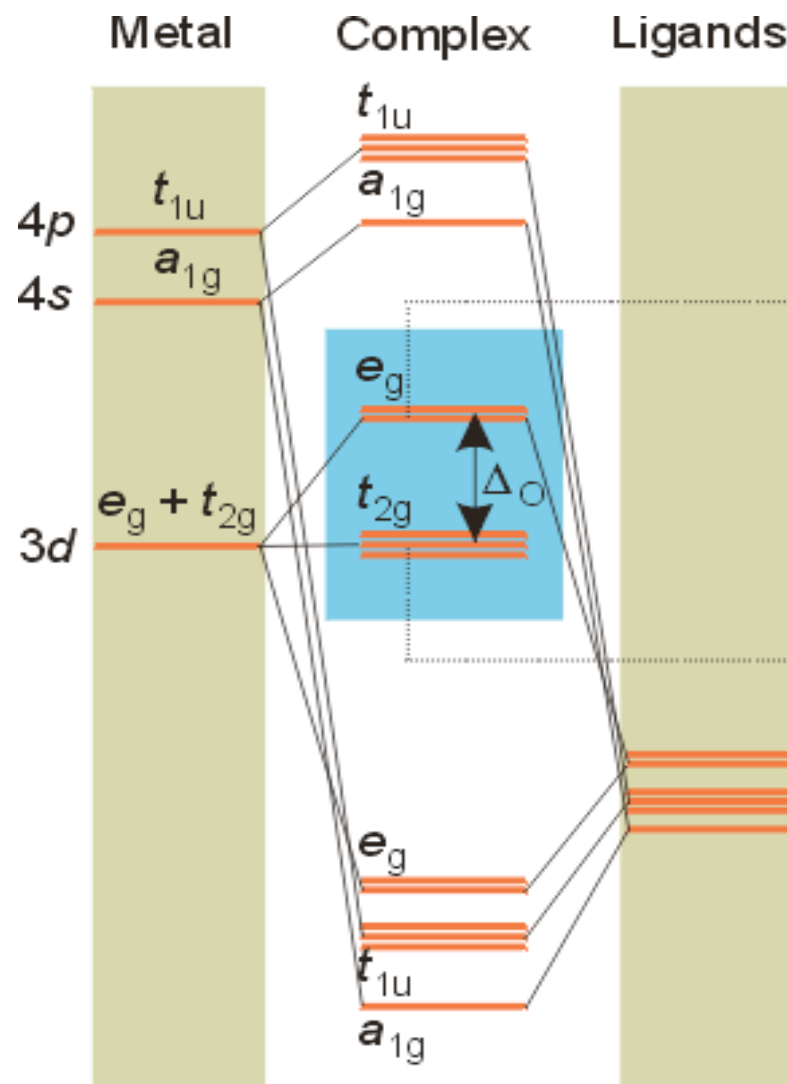
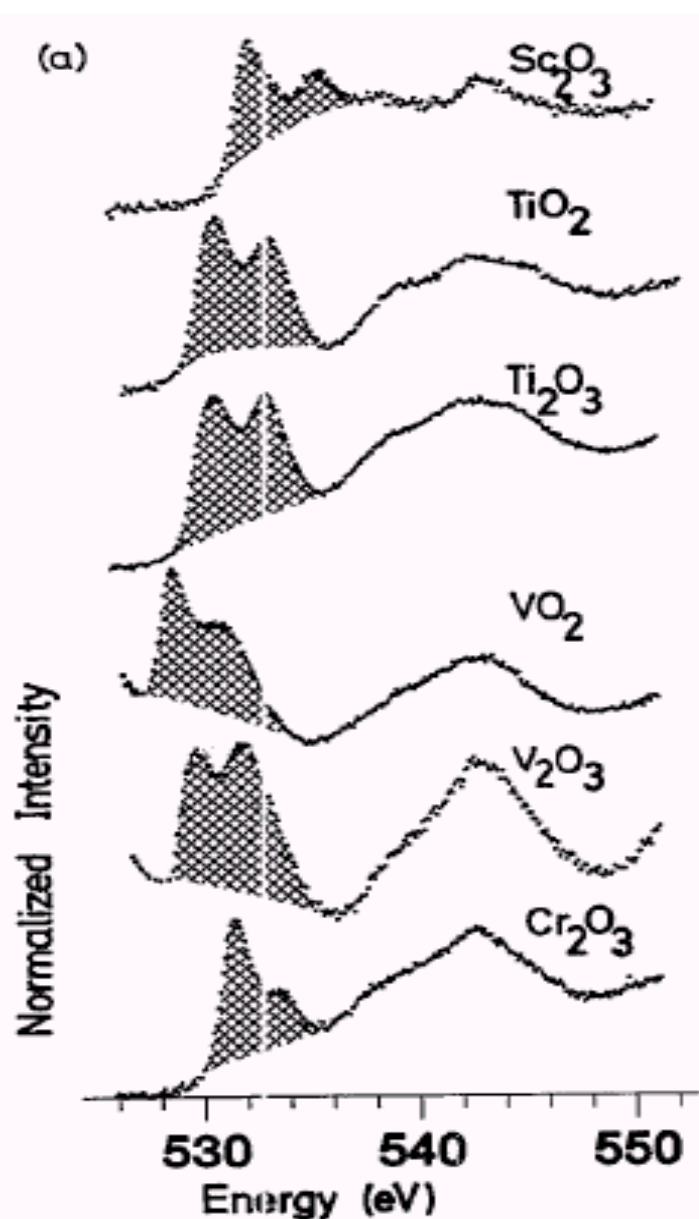


- Element specific DOS
- L specific DOS
- Dipole selection rule ( $\Delta L = \pm 1$ )

- Edge at binding energy of 2p, 2s and 1s states

$$I_{XAS} \sim \left| \left\langle \varepsilon | \hat{e} \cdot r | c \right\rangle \right|^2 \cdot \rho$$

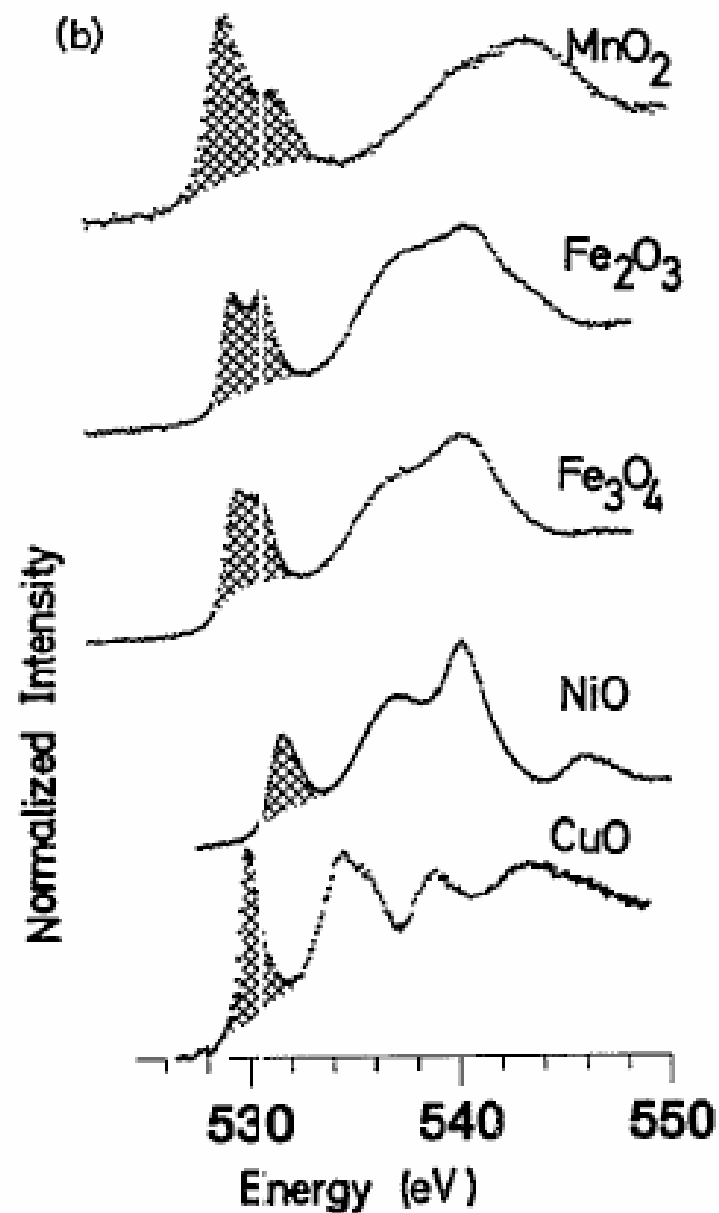
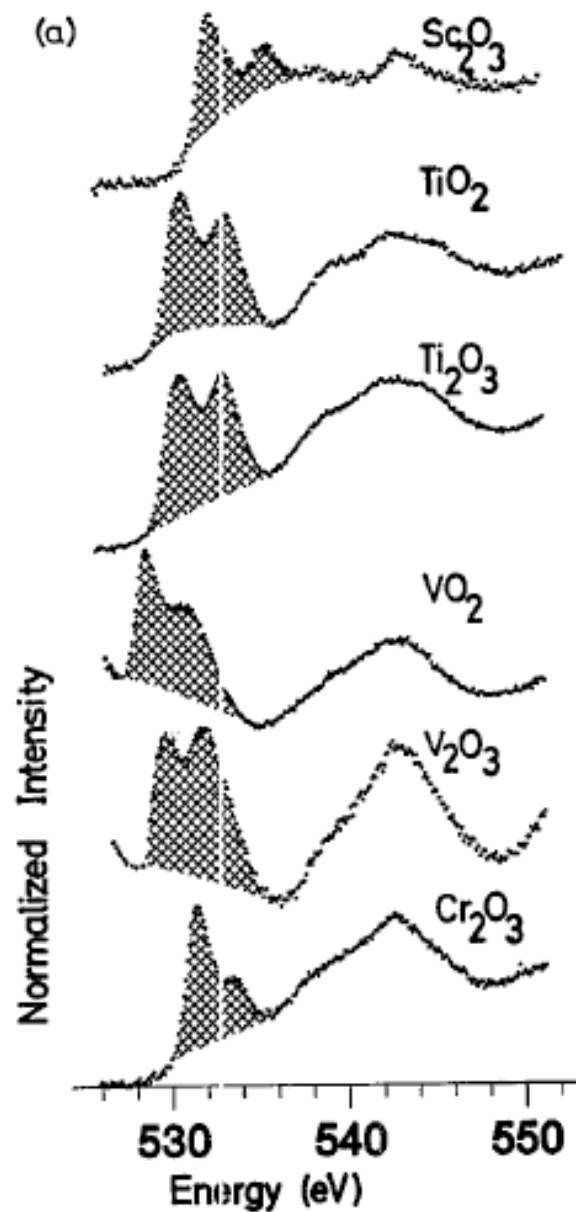
# X-ray Absorption Spectroscopy



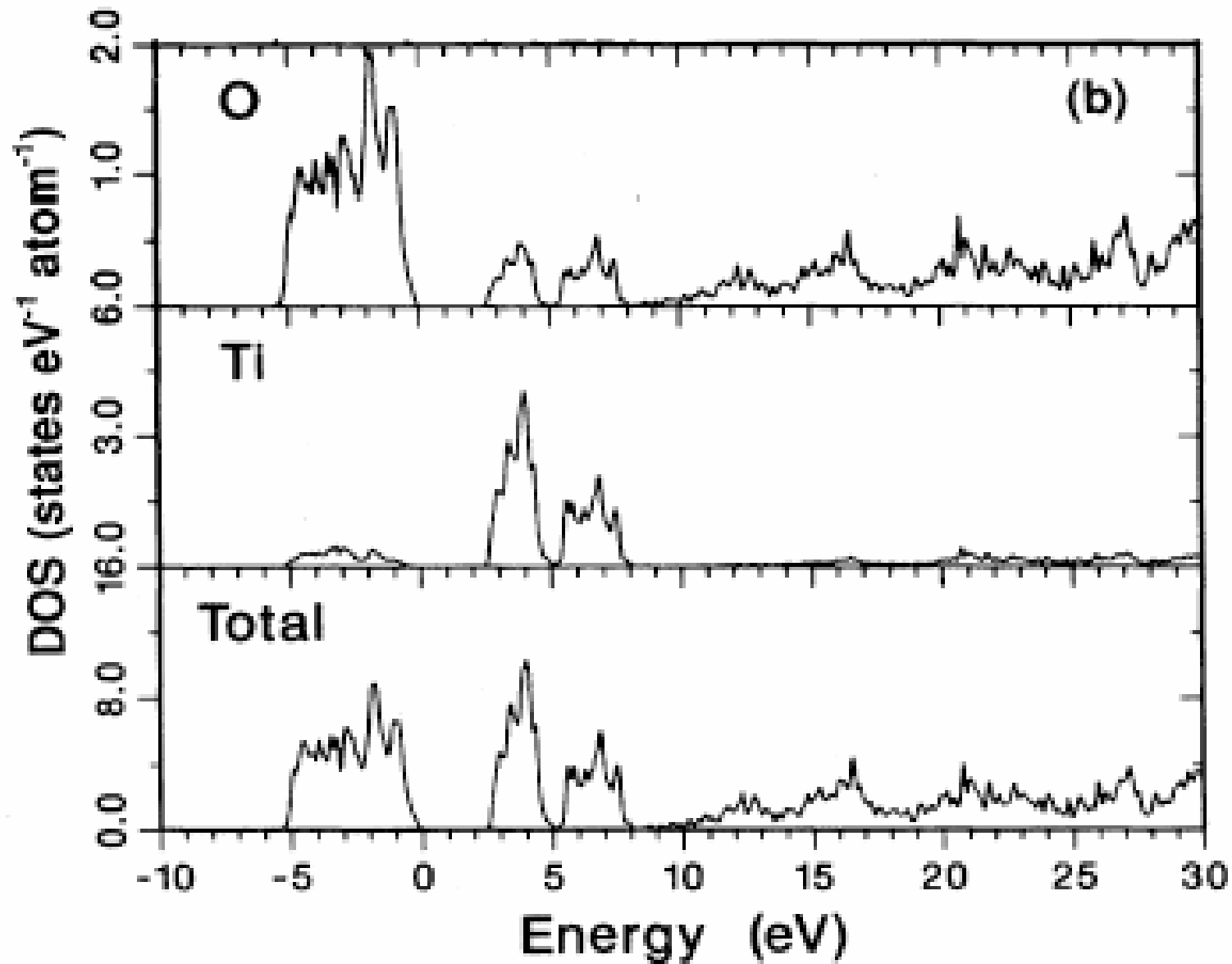
Phys. Rev. B.  
40, 5715 (1989) / 48, 2074 (1993)



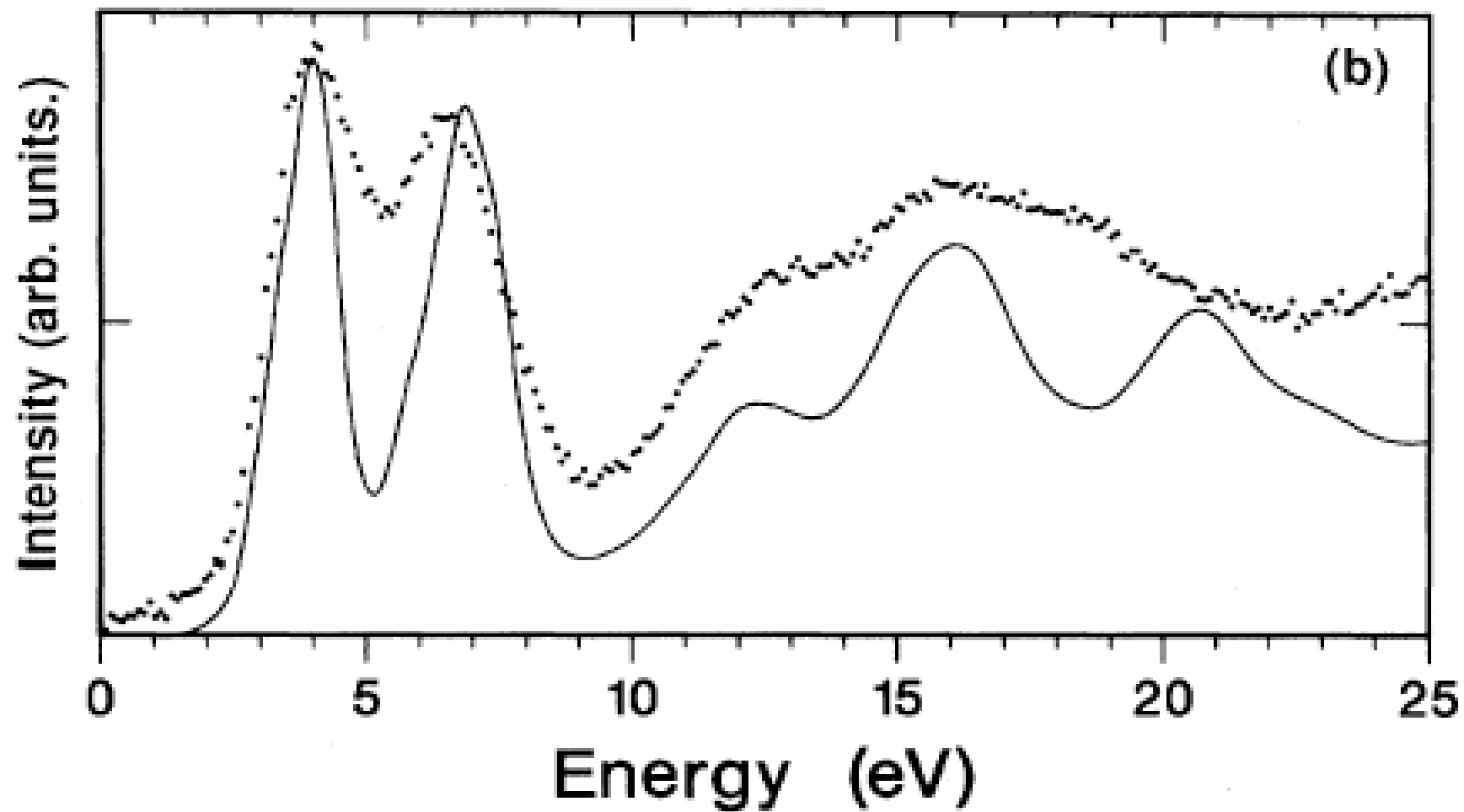
# X-ray absorption



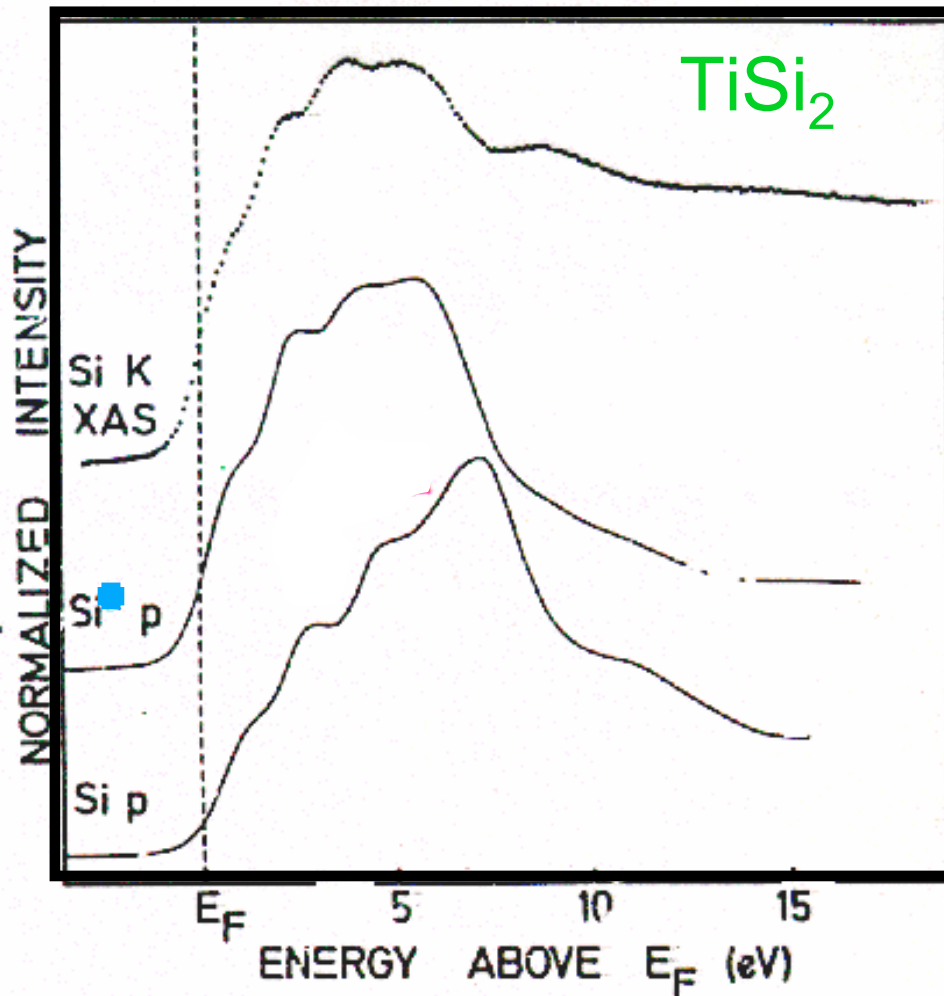
# *Electronic Structure*



# *Electronic Structure*



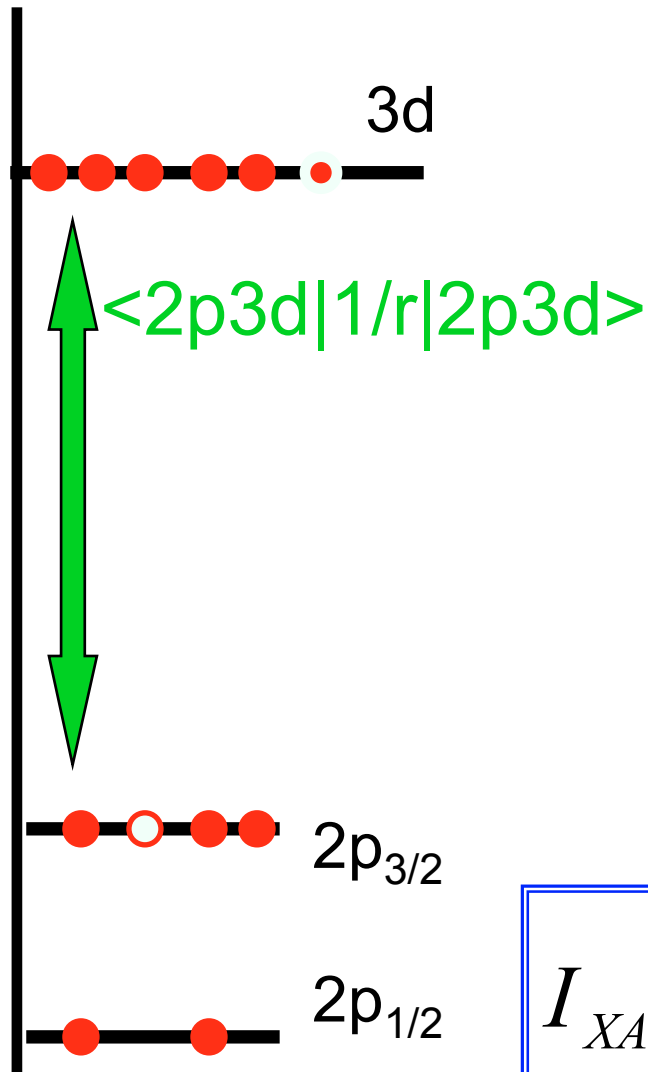
# *X-ray absorption: core hole effect*



- **Final State Rule:**  
Spectral shape of XAS looks like final state DOS
- **Initial State Rule:**  
Intensity of XAS is given by the initial state

Phys. Rev. B.  
41, 11899 (1991)

# X-ray absorption: multiplet effects



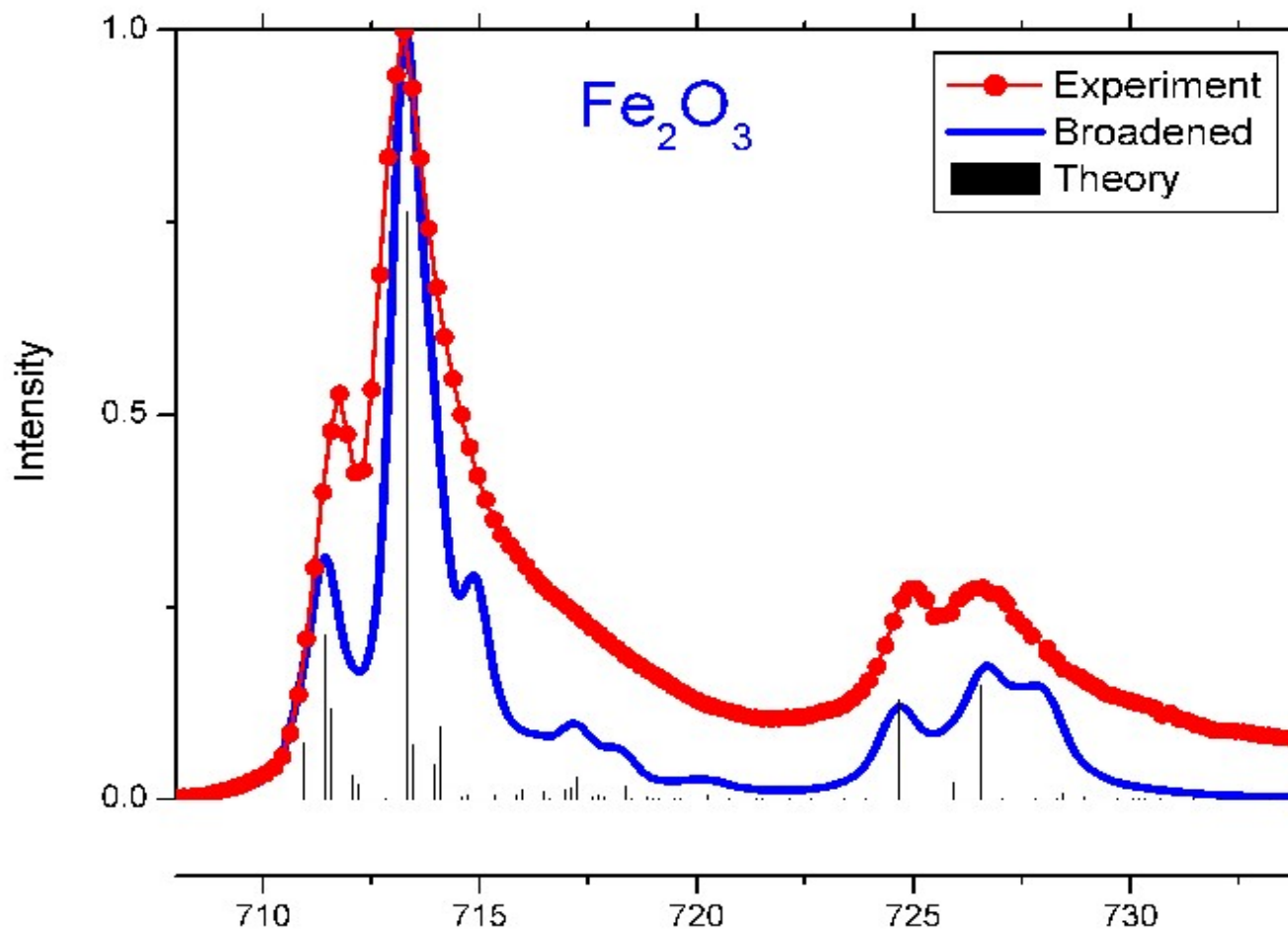
Strong overlap of core and valence wave functions

Single Particle model breaks down

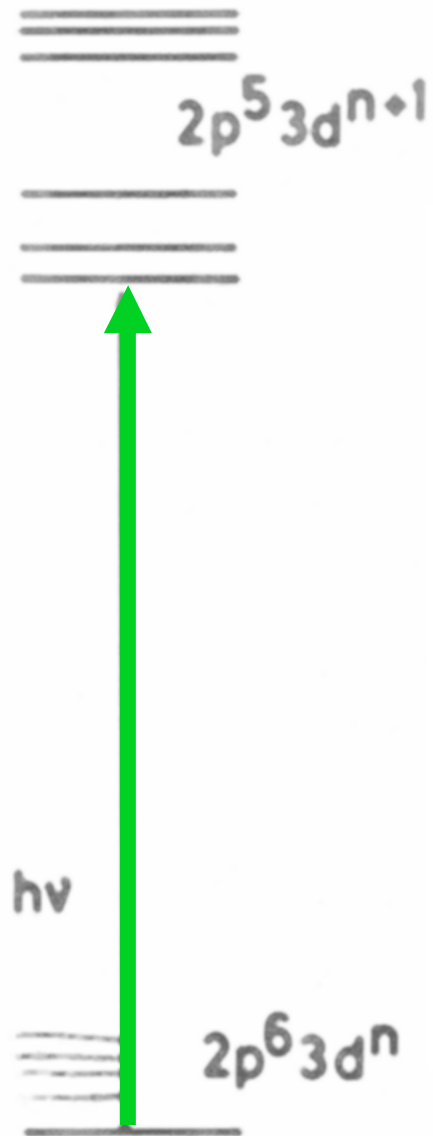
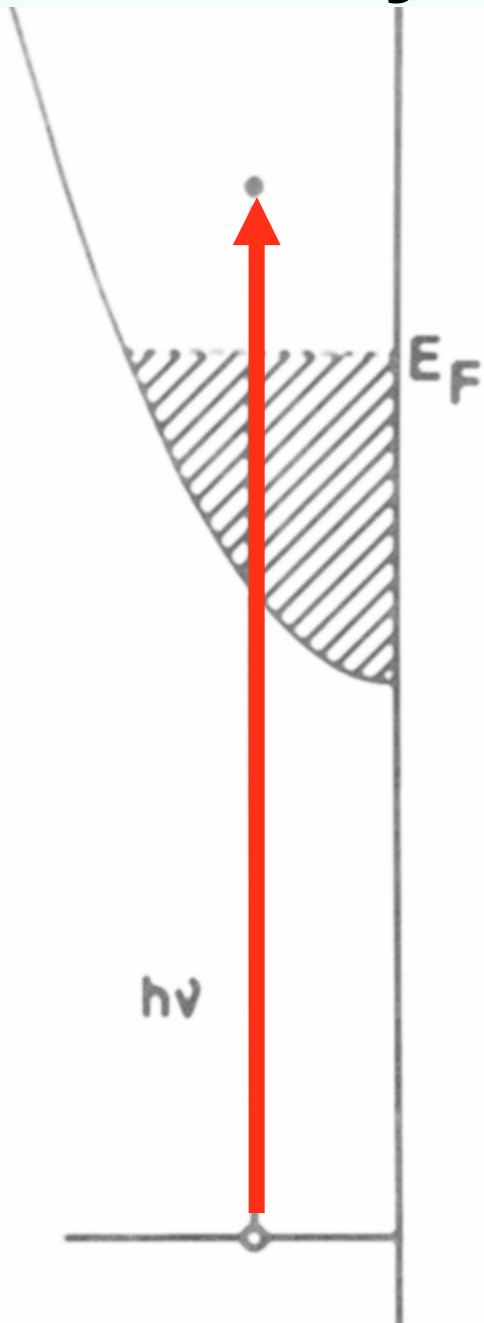
$$I_{XAS} \sim \left| \left\langle 2p^5 3d^6 \left| \hat{e} \cdot r \right| 3d^5 \right\rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

# *X-ray absorption: multiplet effects*

## Multiplet Effects in XAS



# X-ray Absorption Spectroscopy



## Single Particle:

1s edges

Hard x-rays

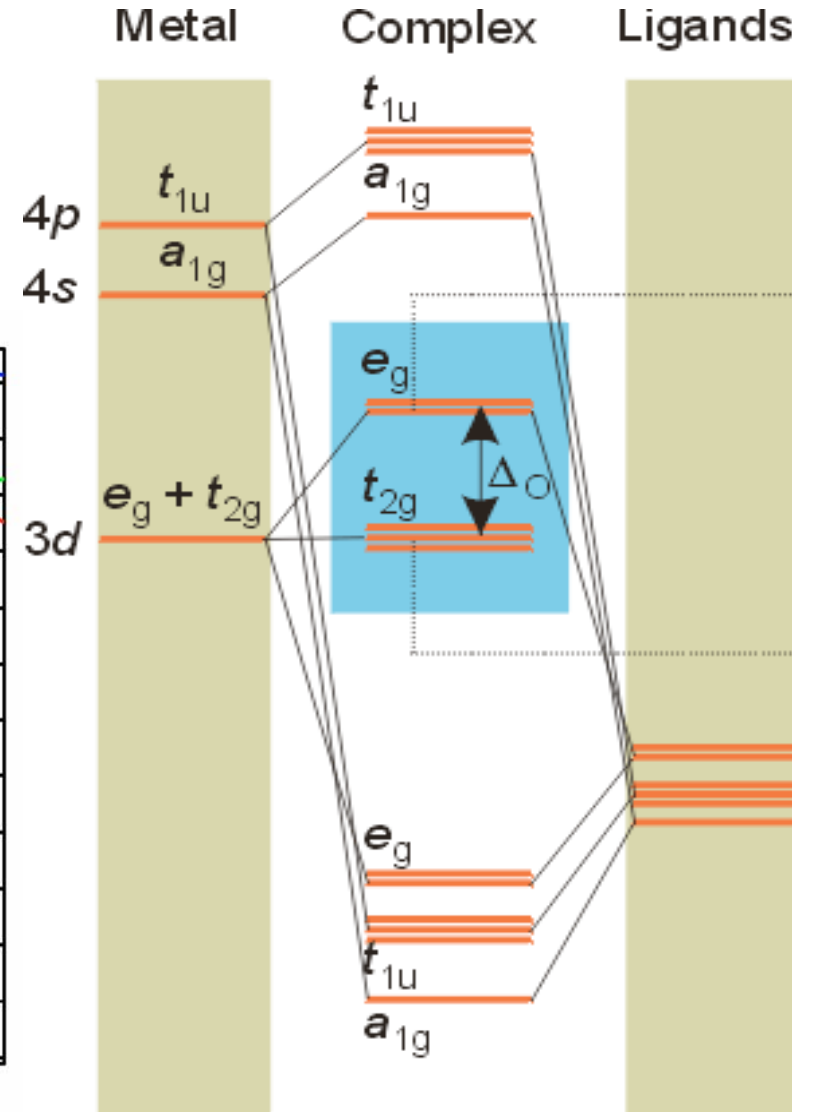
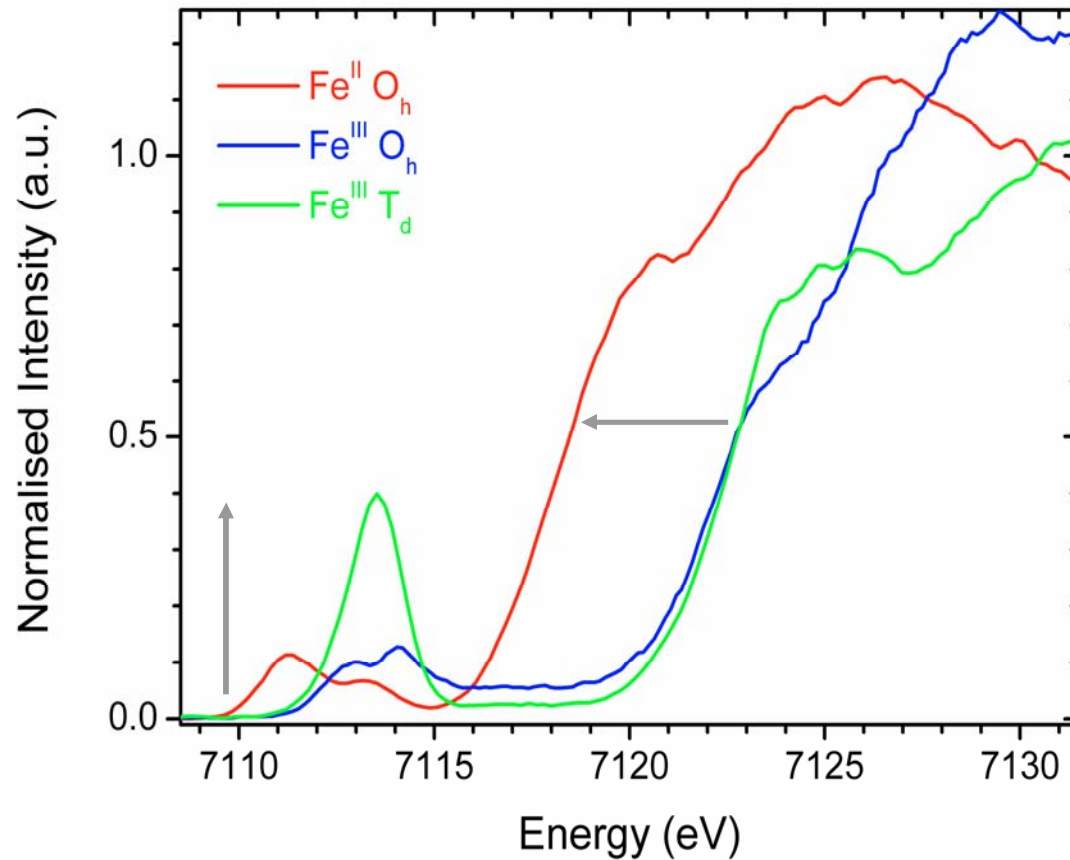
## Multiplets:

2p, 3s, 3p edges

Soft x-rays

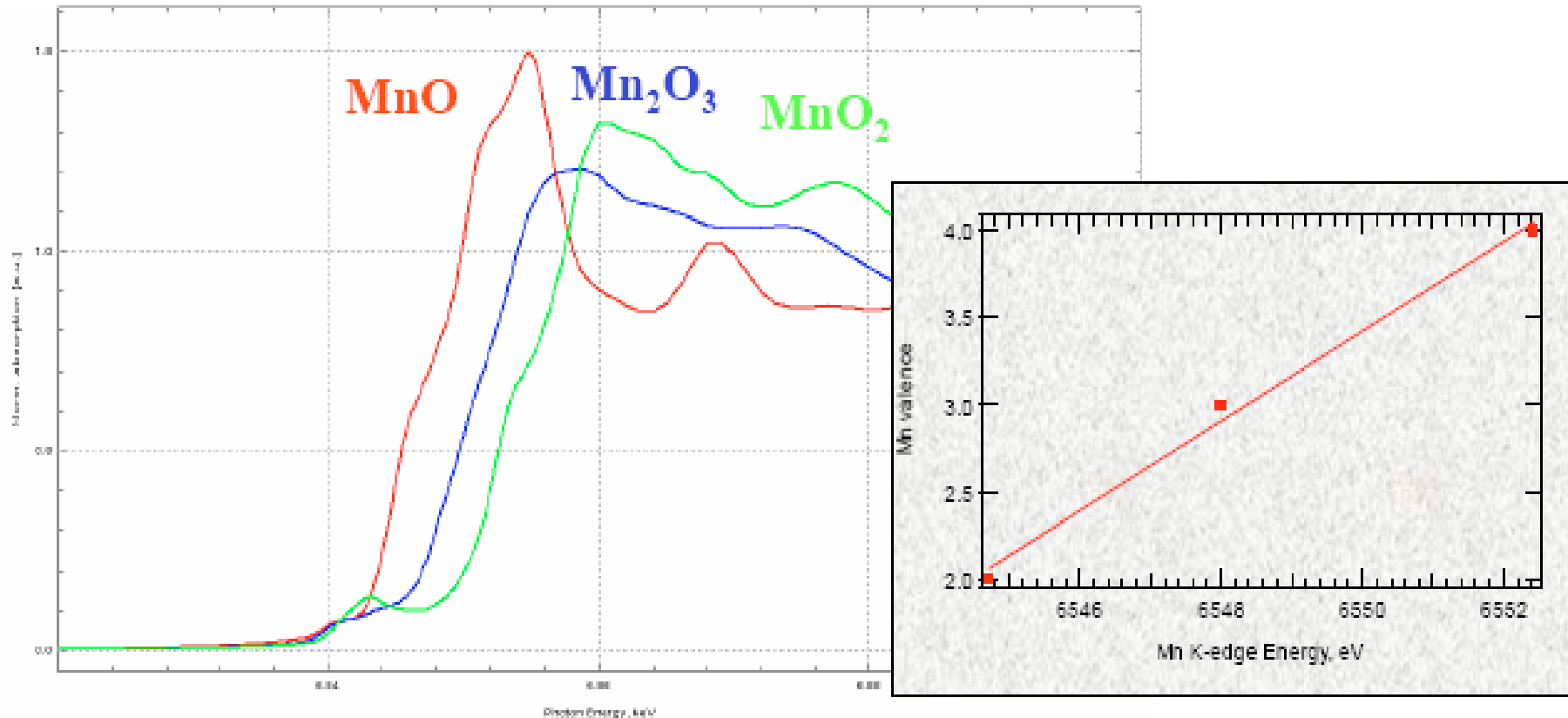
# K edge XANES

- Element specific DOS
- L specific DOS
- Dipole selection rule ( $\Delta L = \pm 1$ )





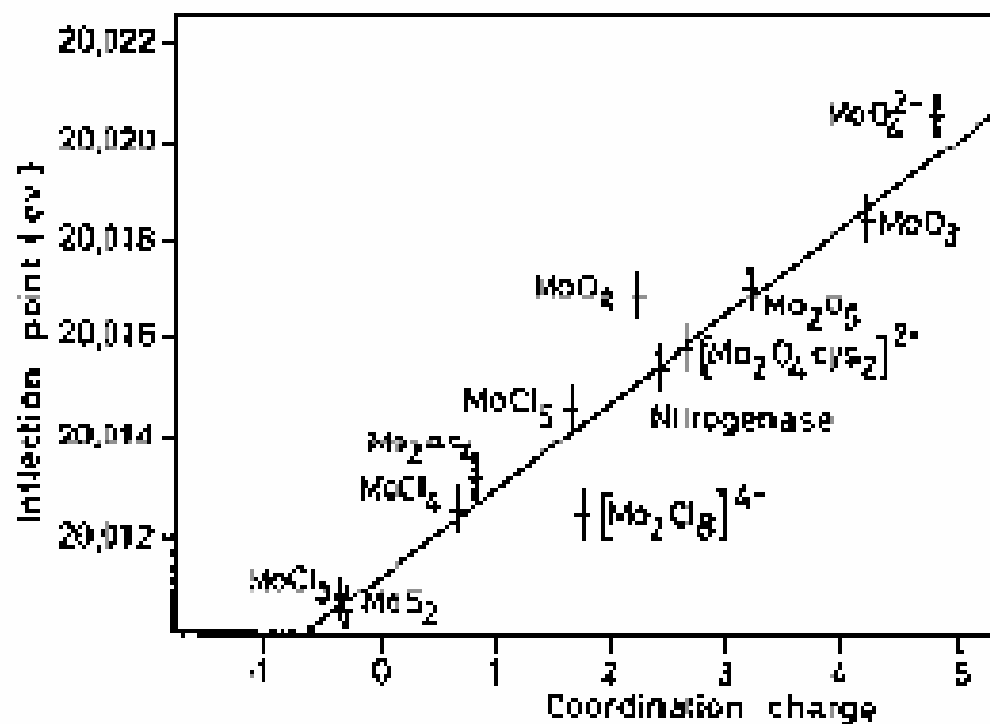
# ***XANES: qualitative analysis***



**Edge position gives valence**

# XANES: qualitative analysis

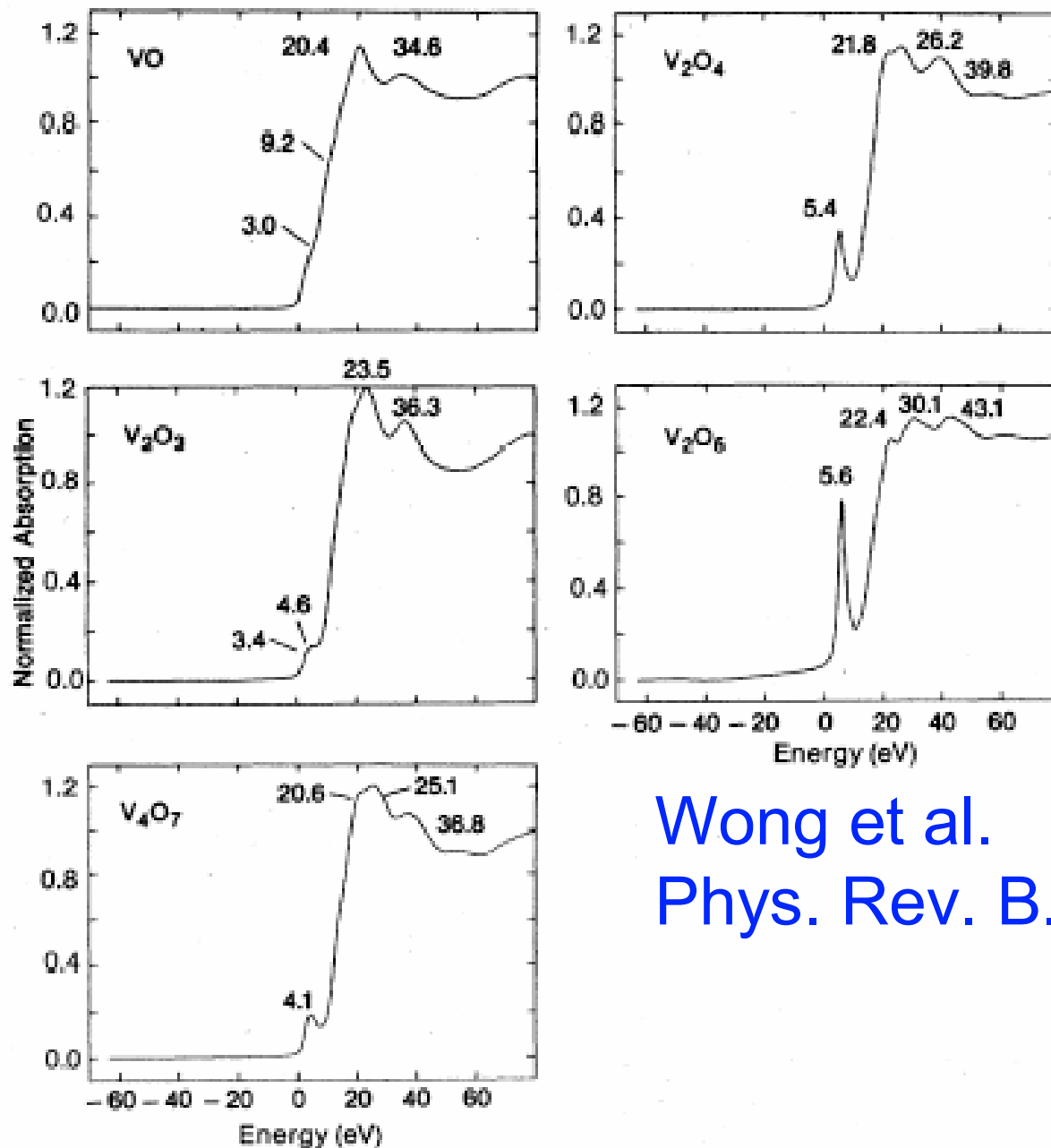
## Mo K-edge



Ref: Cramer et al., JACS, 98 (1976) 1287

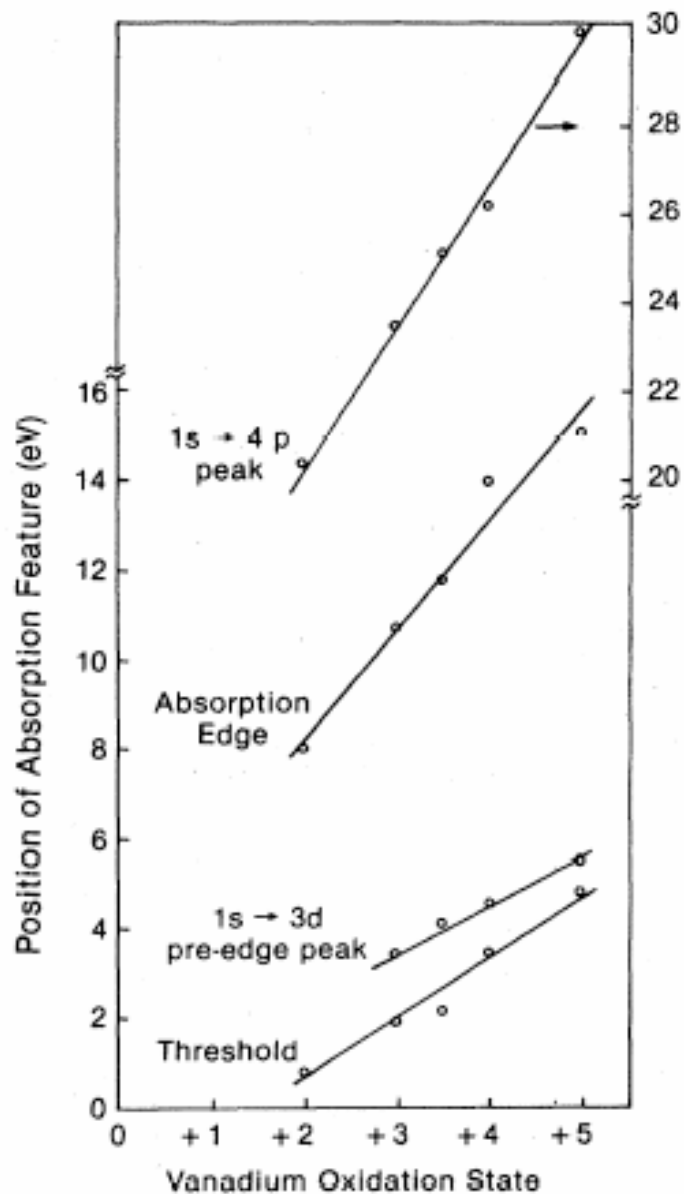
Edge position gives valence

# *XANES: qualitative analysis*



Wong et al.  
Phys. Rev. B. 30, 5596 (1984)

# ***XANES: qualitative analysis***

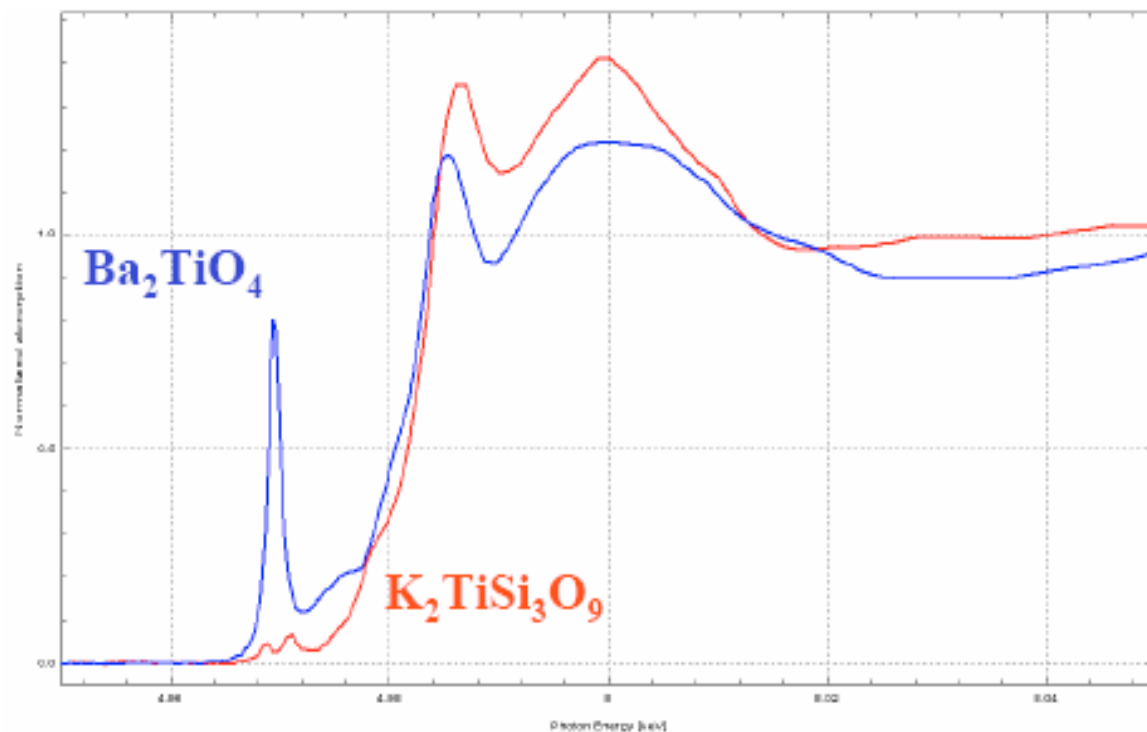


Edge position gives valence

Pre-edge gives valence

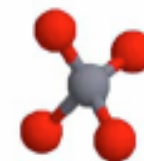
Different slopes

# ***XANES: qualitative analysis***



Both  $Ti^{4+}$

$Ba_2TiO_4$

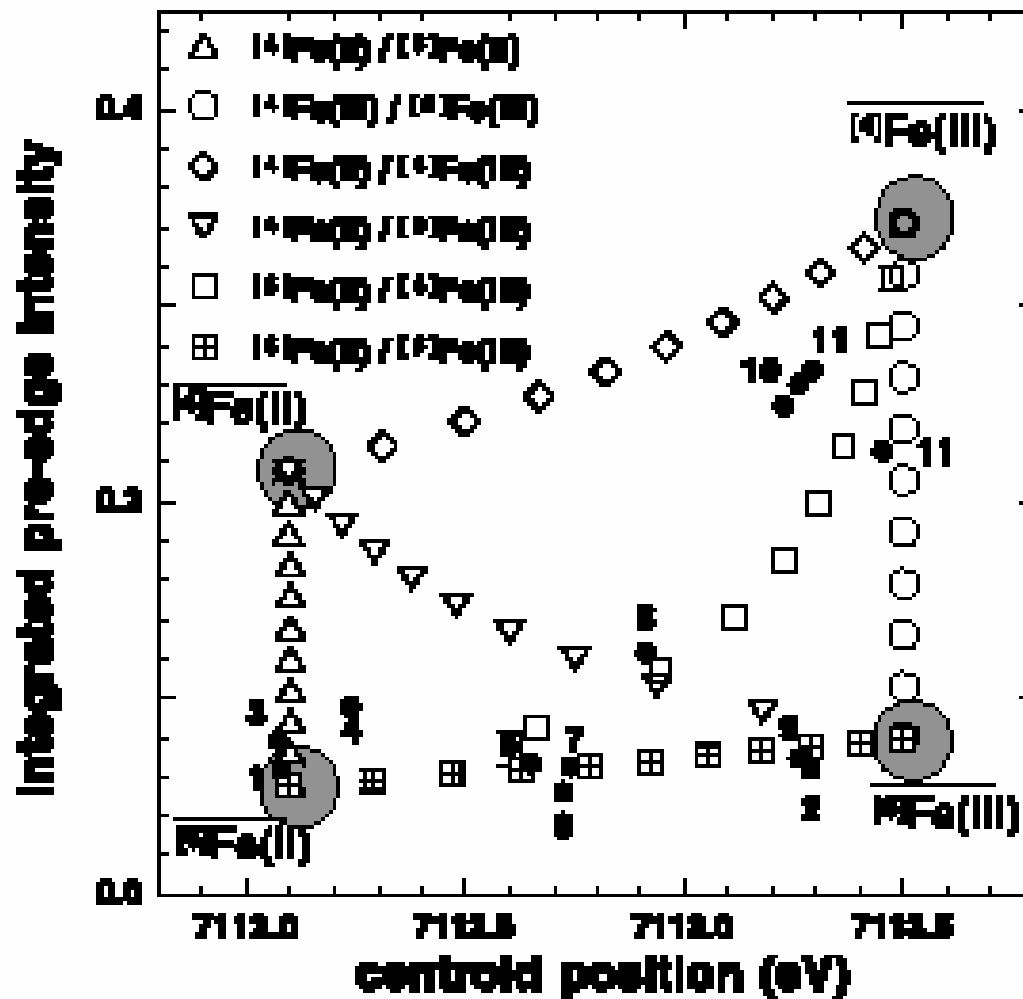


$K_2TiSi_3O_9$



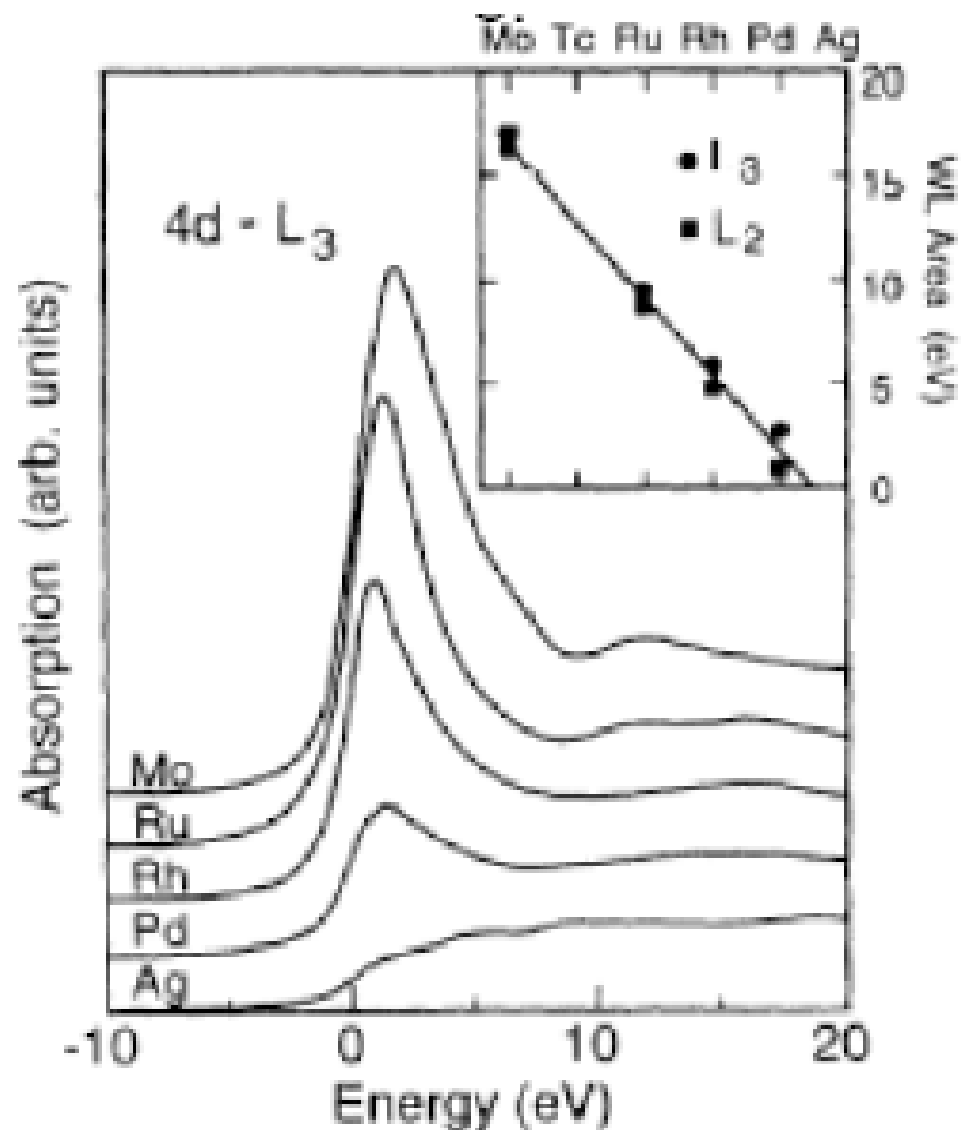
Pre-edge intensity gives site symmetry

# XANES: qualitative analysis



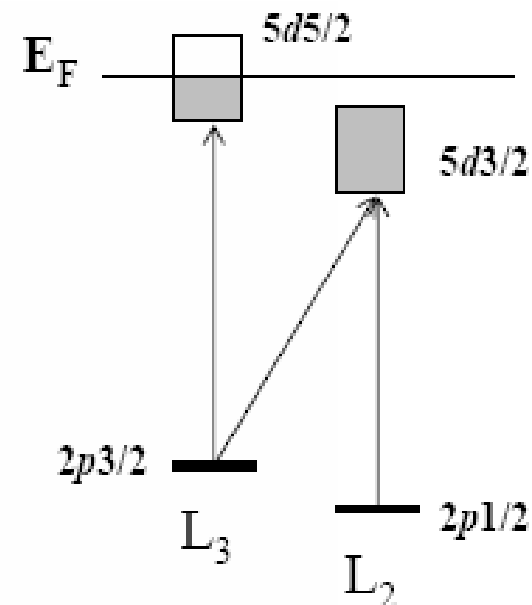
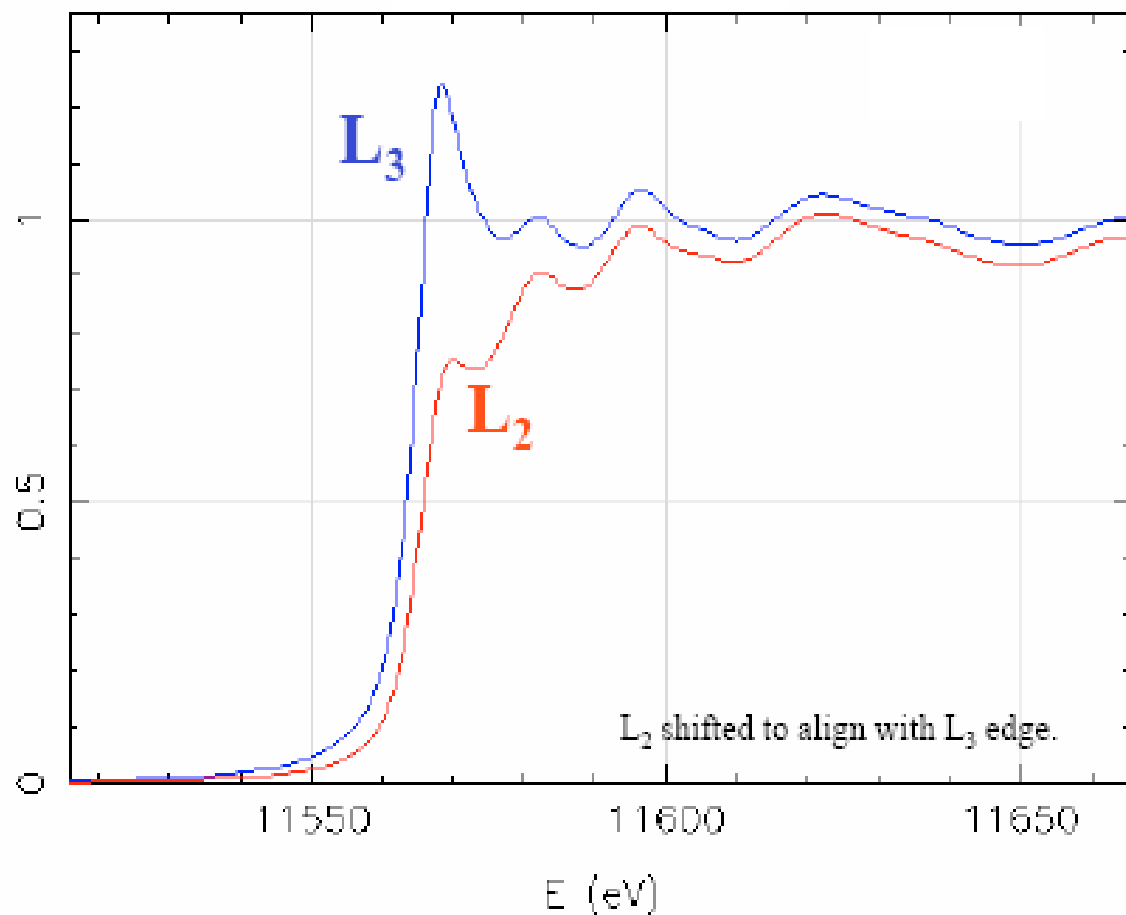
Pre-edge intensity and center

# ***XANES: qualitative analysis***



L edge of 4d-systems > number of empty 4d states

# ***XANES: qualitative analysis***



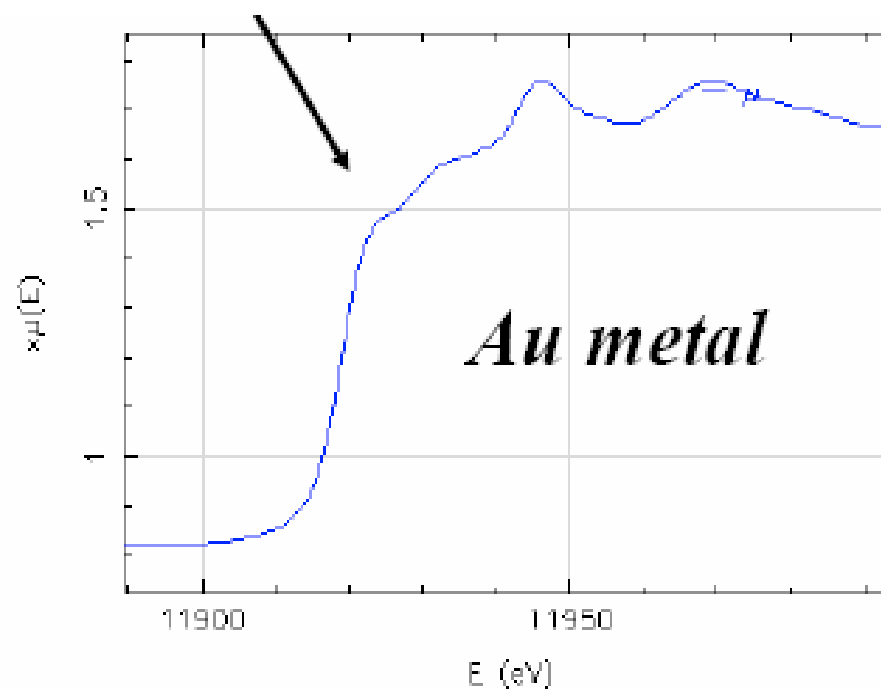
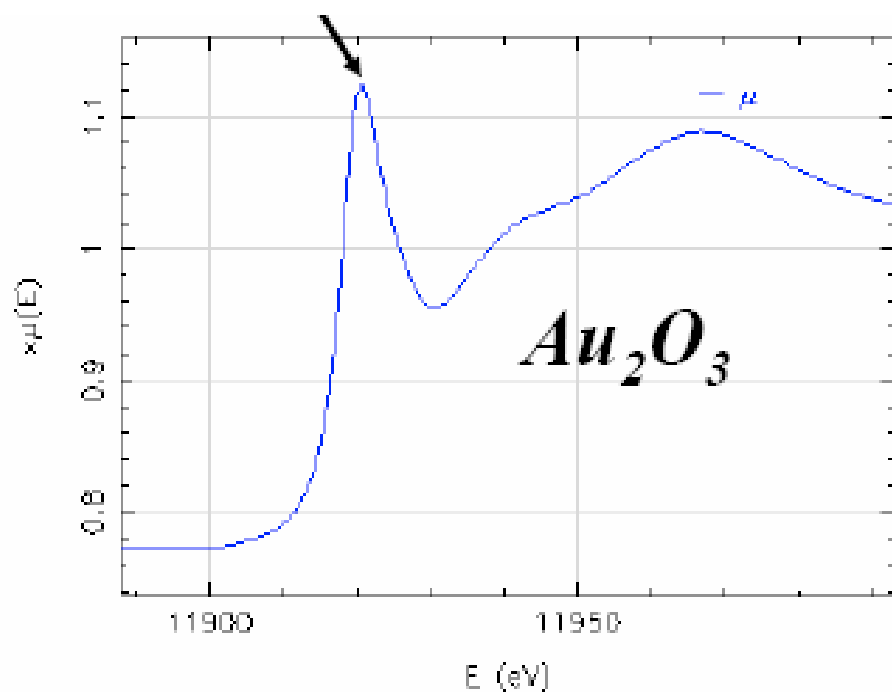
• Pt  $5d_{3/2}$  filled, so no white line.

**L edge of 5d-systems > number of empty 5d states**

**Difference between  $5d^{3/2}$  and  $5d^{5/2}$**



# ***XANES: qualitative analysis***

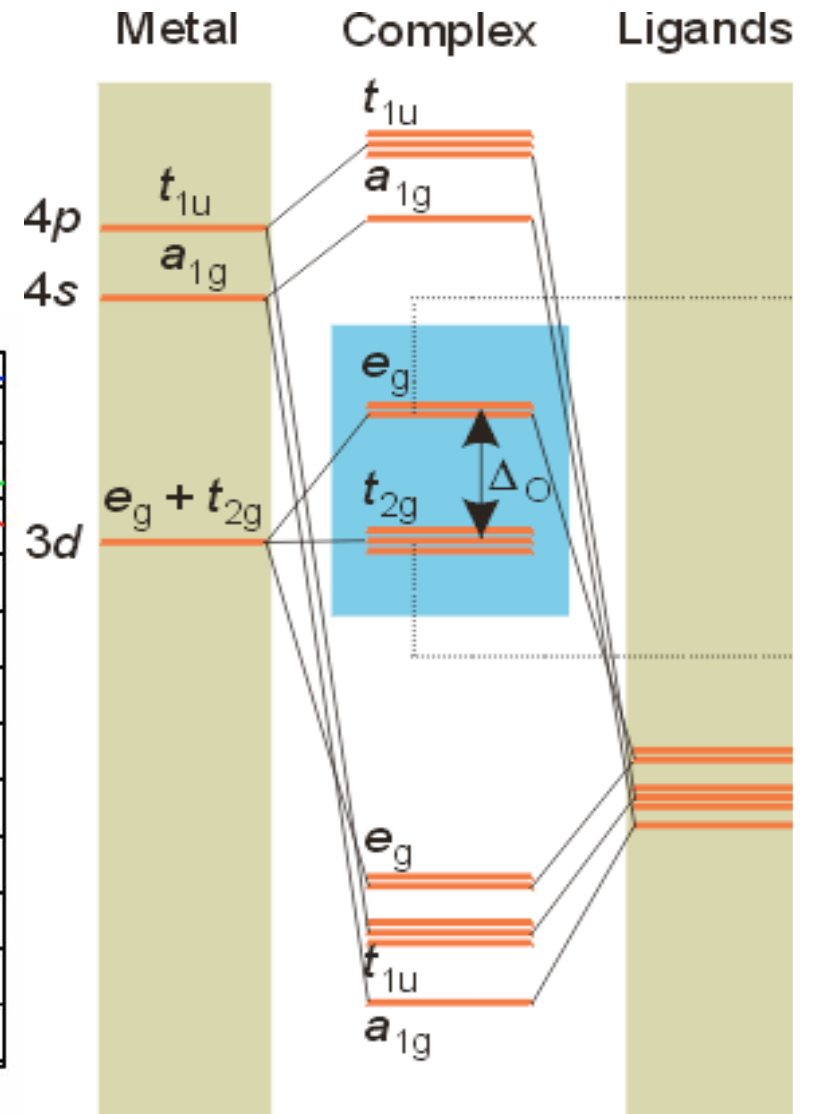
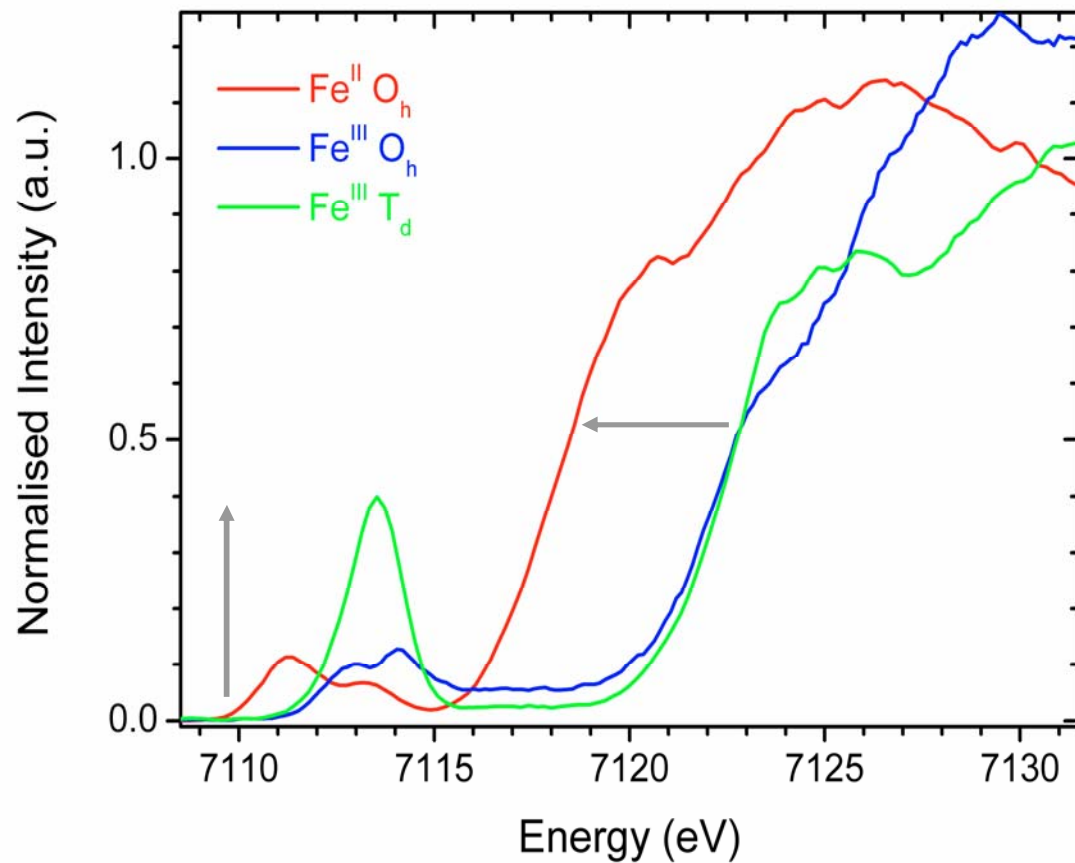


L edge of 5d-systems  $>$  number of empty 5d states

Difference between metal and oxide

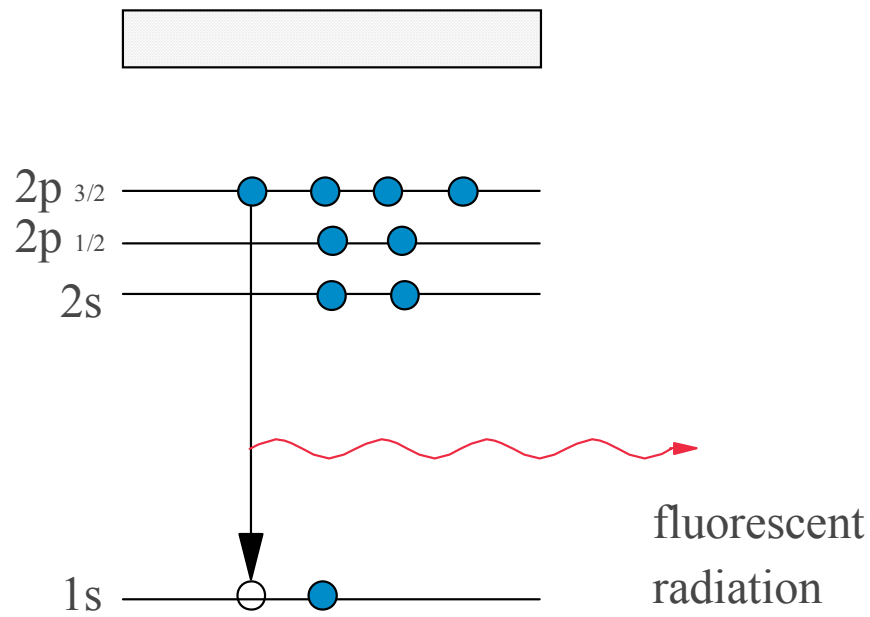
# K edge XANES

- Element specific DOS
- L specific DOS
- Dipole selection rule ( $\Delta L = \pm 1$ )

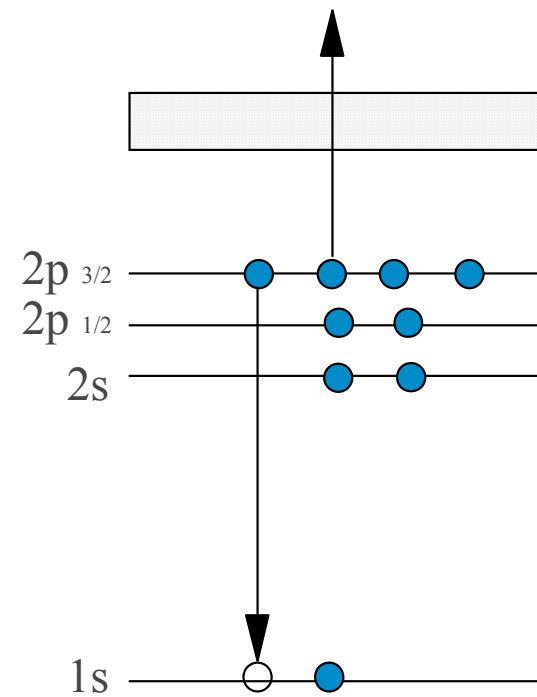


# Core Hole Decay

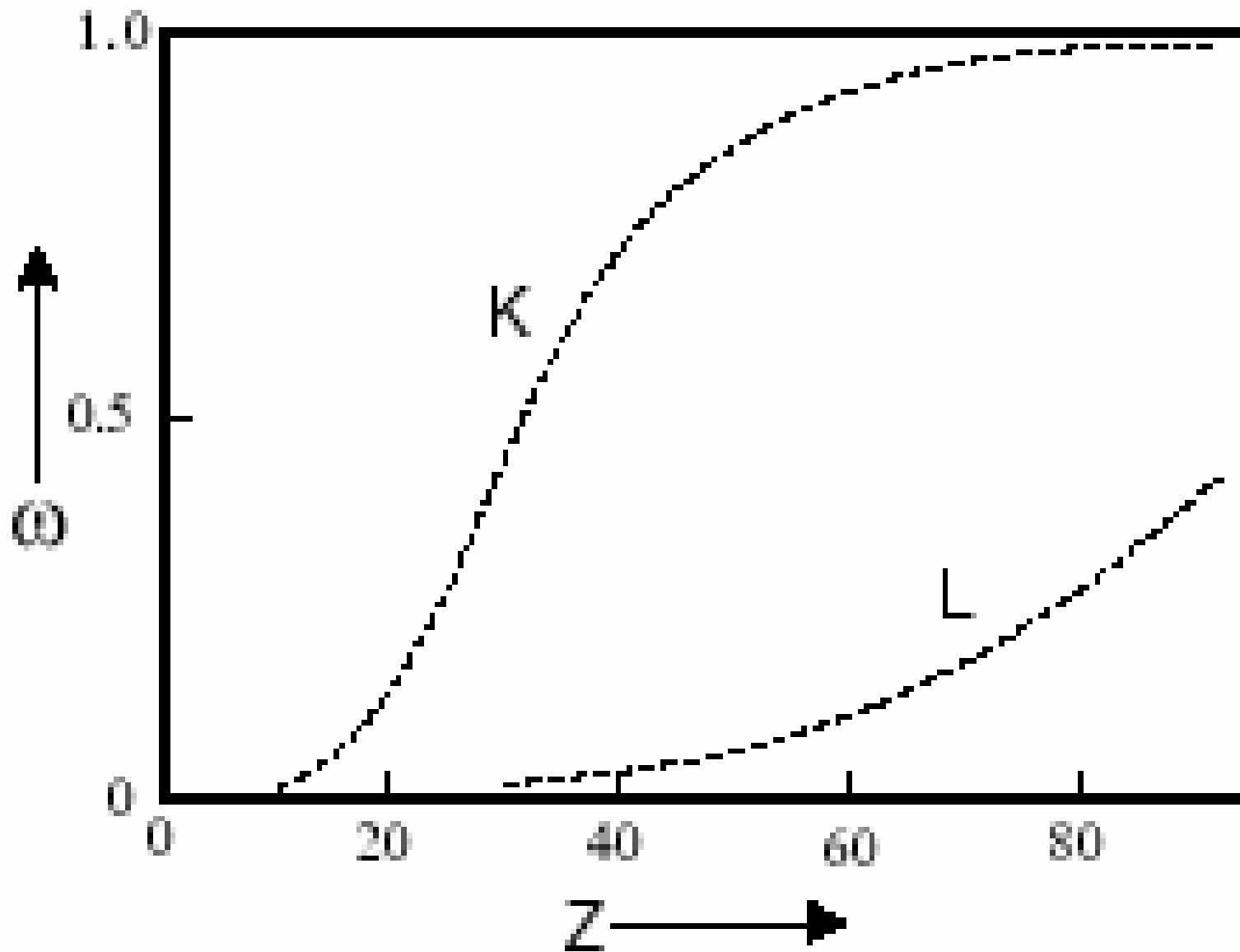
## Fluorescence



## Auger

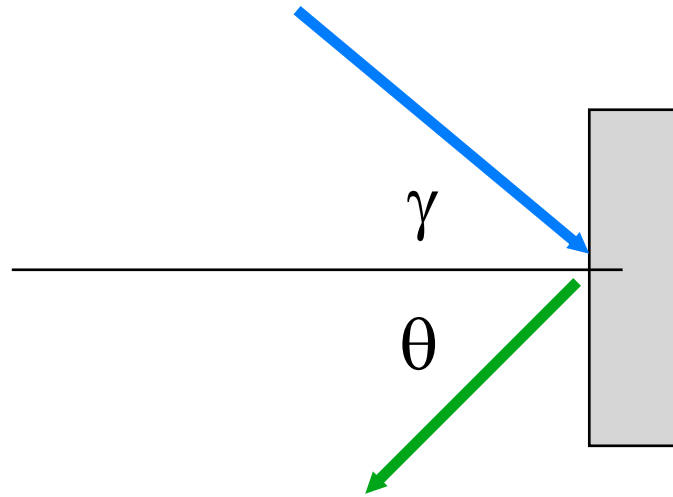


# *Fluorescence and Auger*



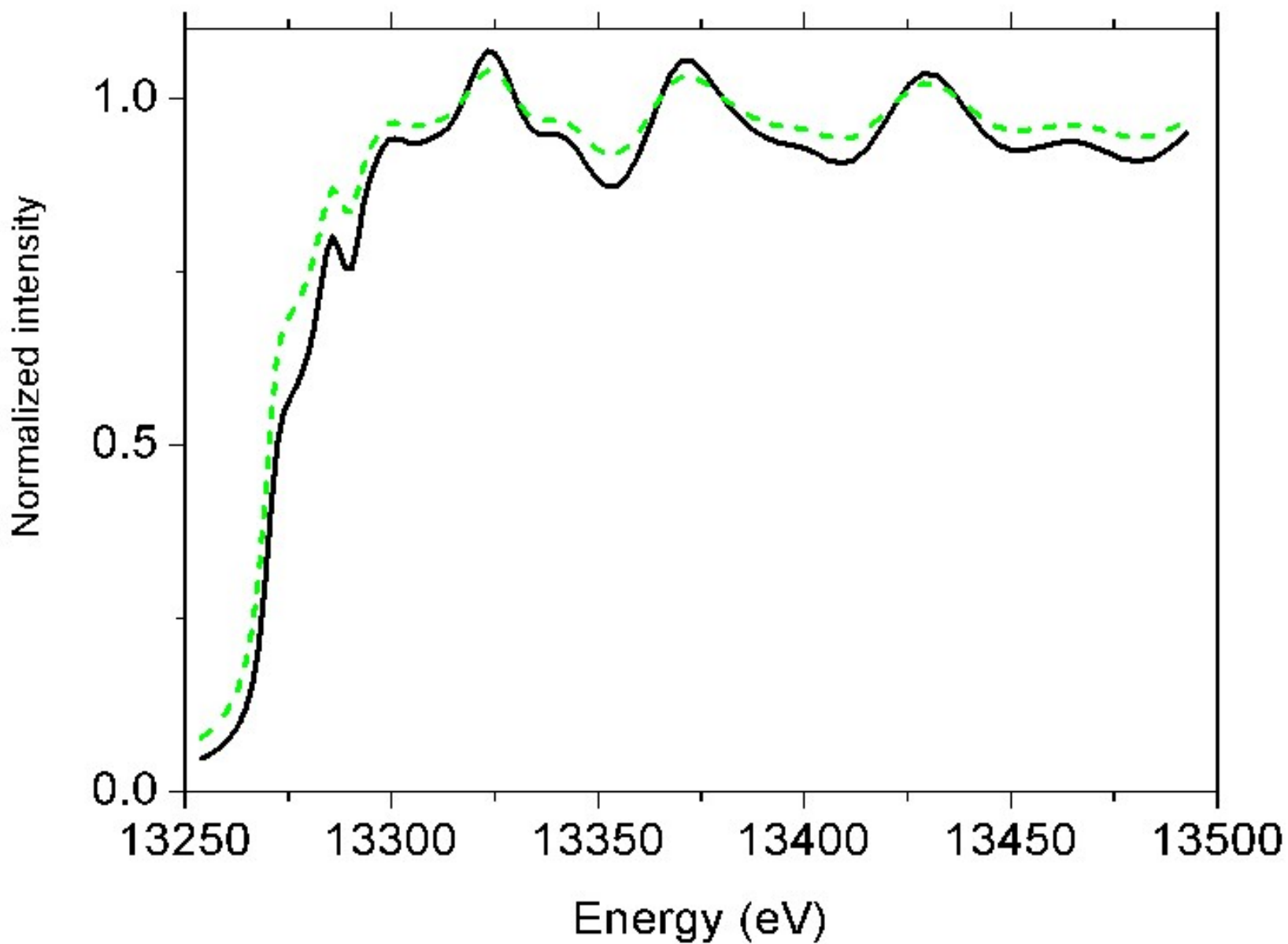
# *X-ray Fluorescence*

$$I_f(\omega) \propto \frac{\mu(\omega)}{[\mu(\omega) + \mu_B(\omega)] \sin \theta + [\mu(\omega_F) + \mu_B(\omega_F)] \sin \gamma}$$

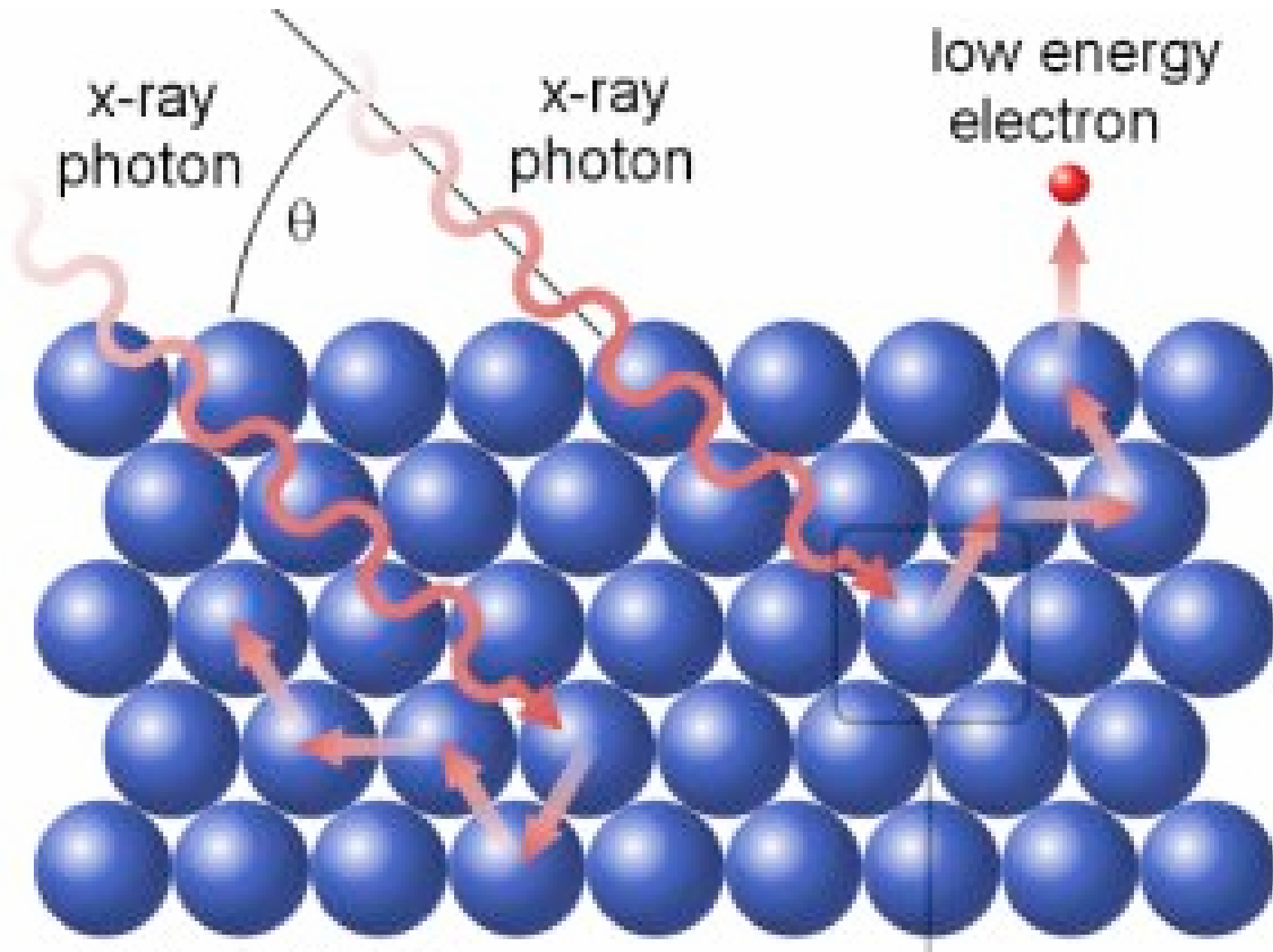


$$I_f(\omega) \propto \frac{\mu(\omega)}{\mu(\omega) \cdot \frac{1}{2} \sqrt{2} + \mu_B \sqrt{2}} \approx \frac{\mu(\omega)}{\mu(\omega) + 2\mu_B}$$

# *X-ray Fluorescence*



# *X-ray Detection*



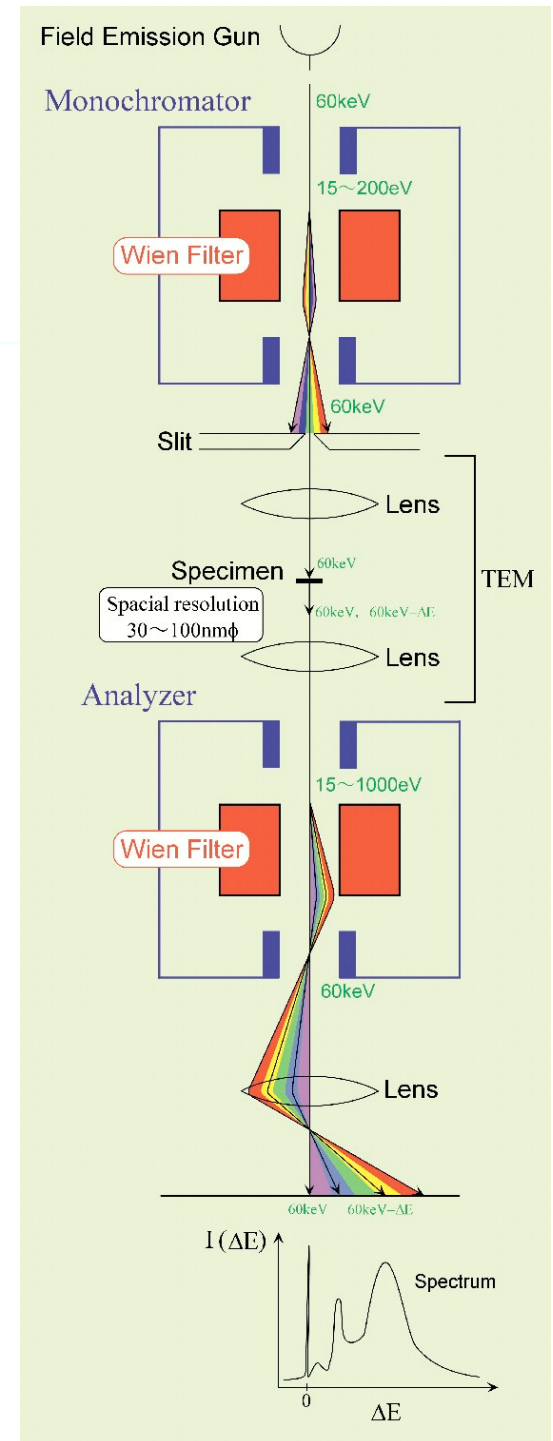
# ***What do we learn from XANES?***

- Edge position gives valence
- K pre-edge center gives valence
- K pre-edge intensity gives site symmetry
- L edge intensity gives empty d-states
- HERFD-XANES gives details anti-bonding bands of adsorbates



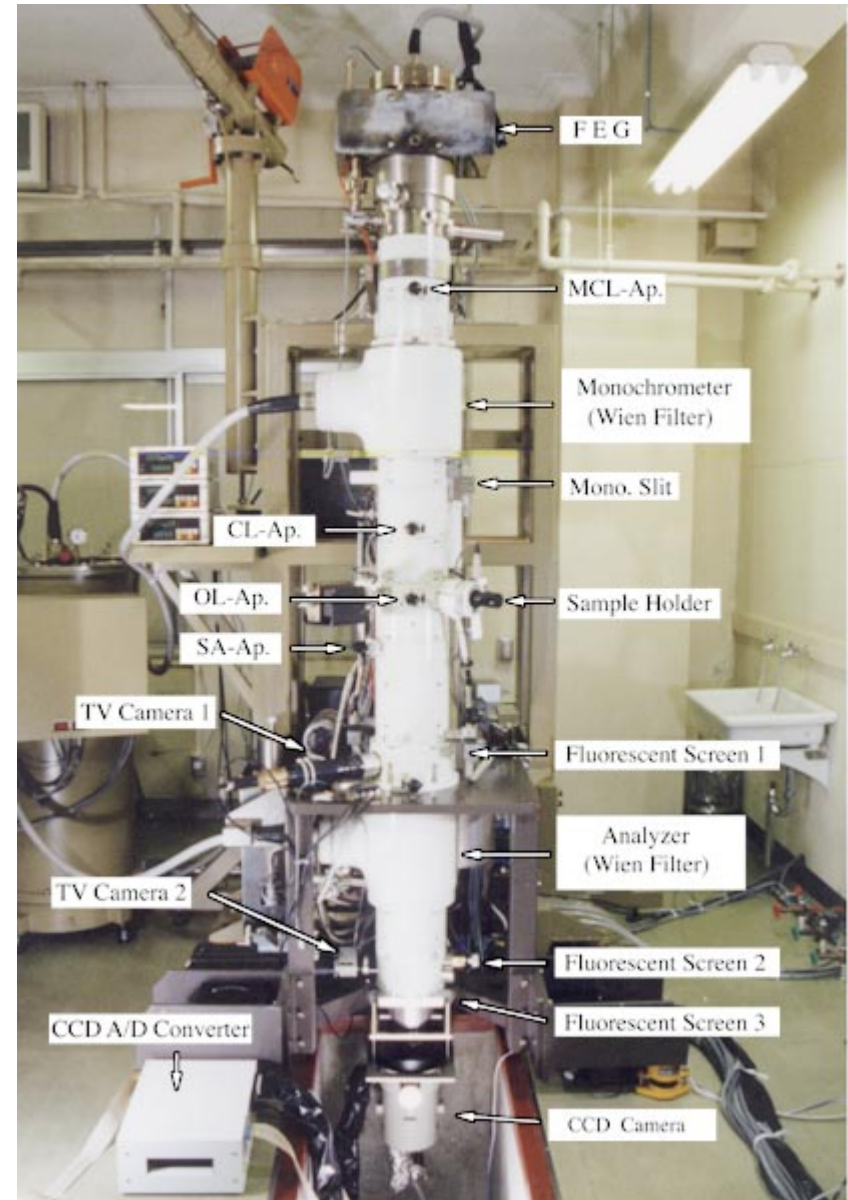
# XAS and EELS

- Identical spectral shape  
(*only for soft x-ray edges!*)  
[If EELS uses small  $q$  and high  $E$ ]
- XAS at Synchrotron
- EELS with (S)TEM
- XAS: 0.1 eV with 20nm
- EELS: 0.3 eV with 0.5 nm
- XAS: extreme conditions
- EELS: vacuum

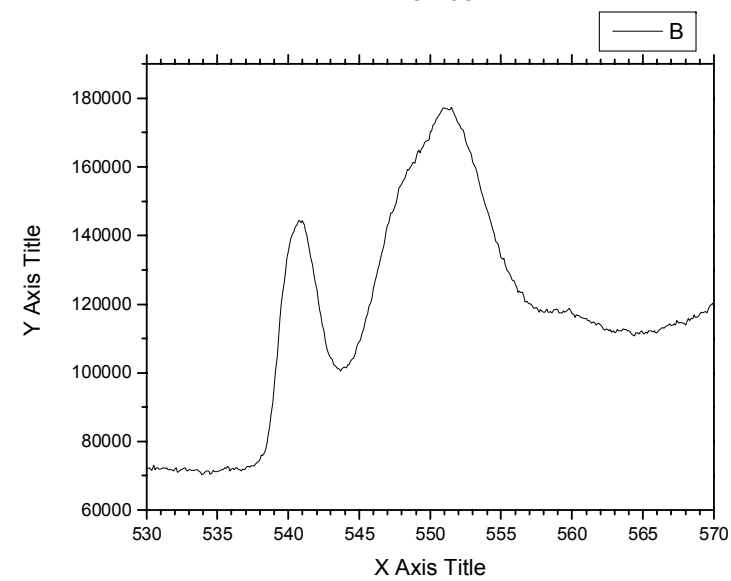
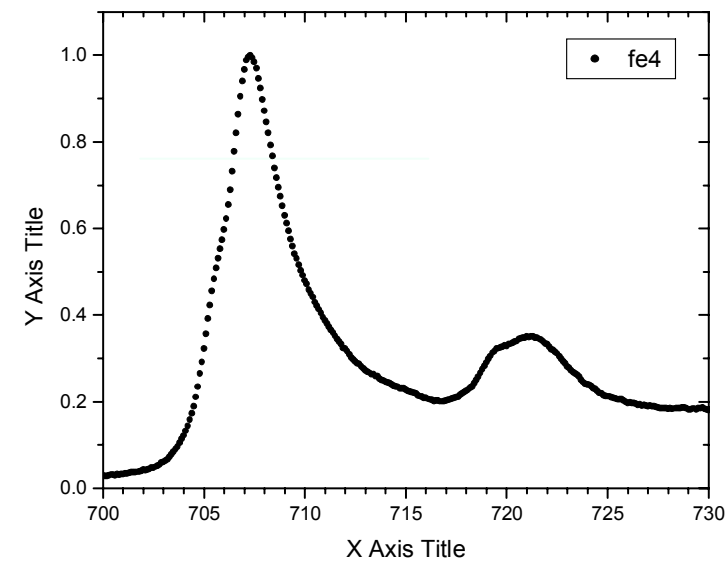
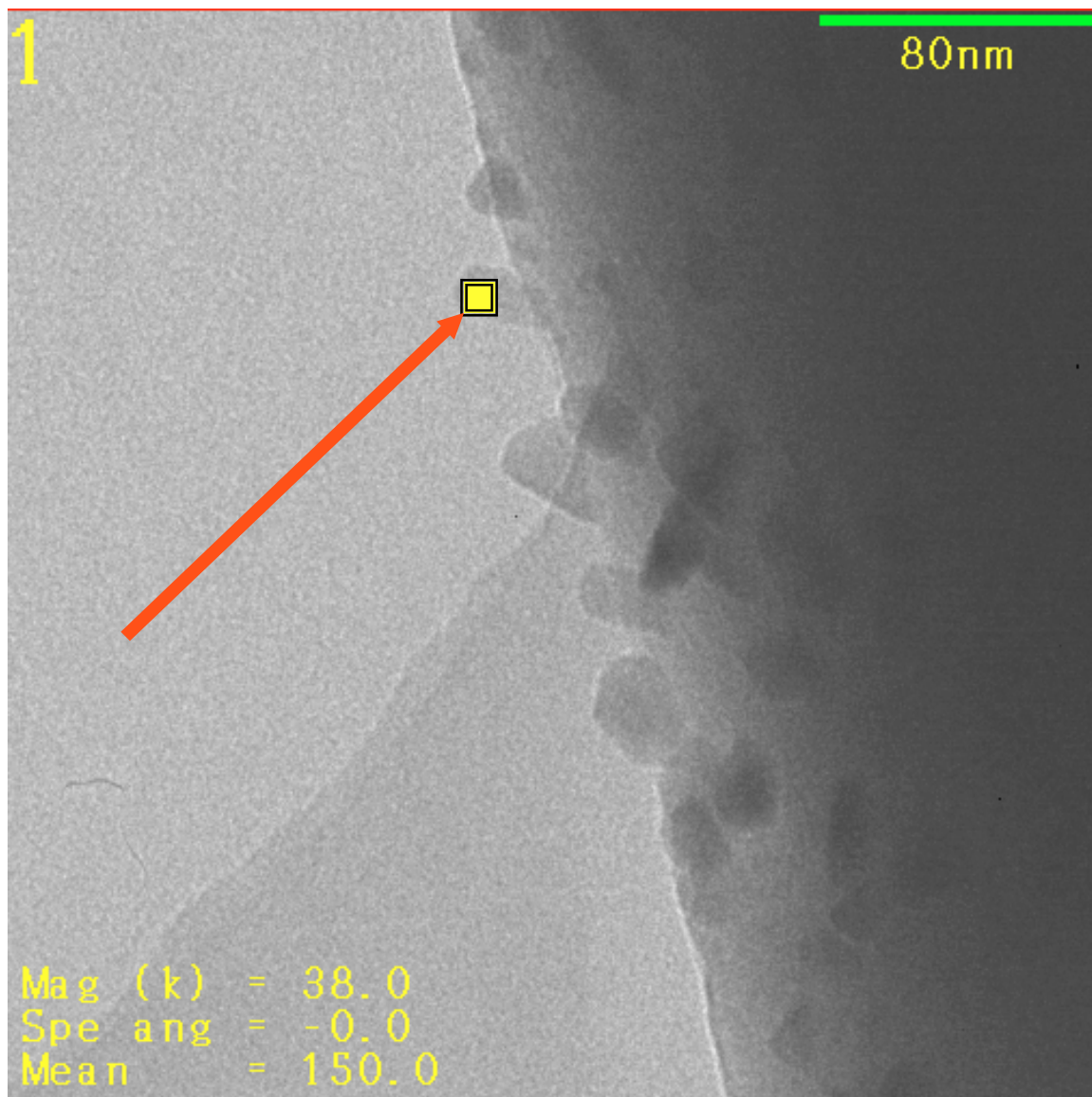


# XAS and EELS

- Identical spectral shape (*only for soft x-ray edges!*)  
[If EELS uses small  $q$  and high  $E$ ]
- XAS at Synchrotron
- EELS with (S)TEM
- XAS: 0.1 eV with 20nm
- EELS: 0.3 eV with 0.5 nm
- XAS: extreme conditions
- EELS: vacuum

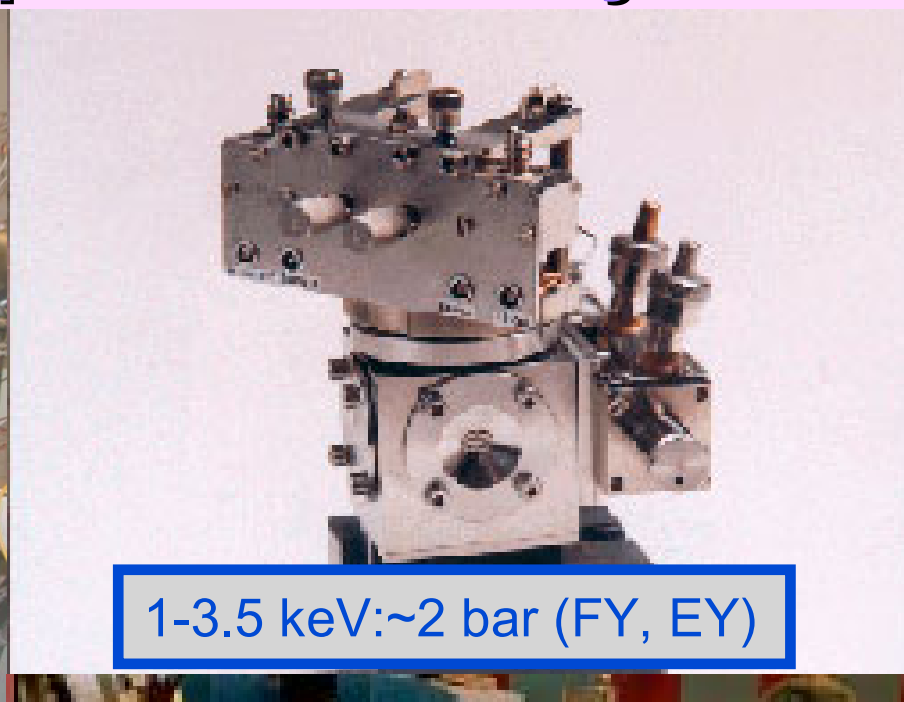
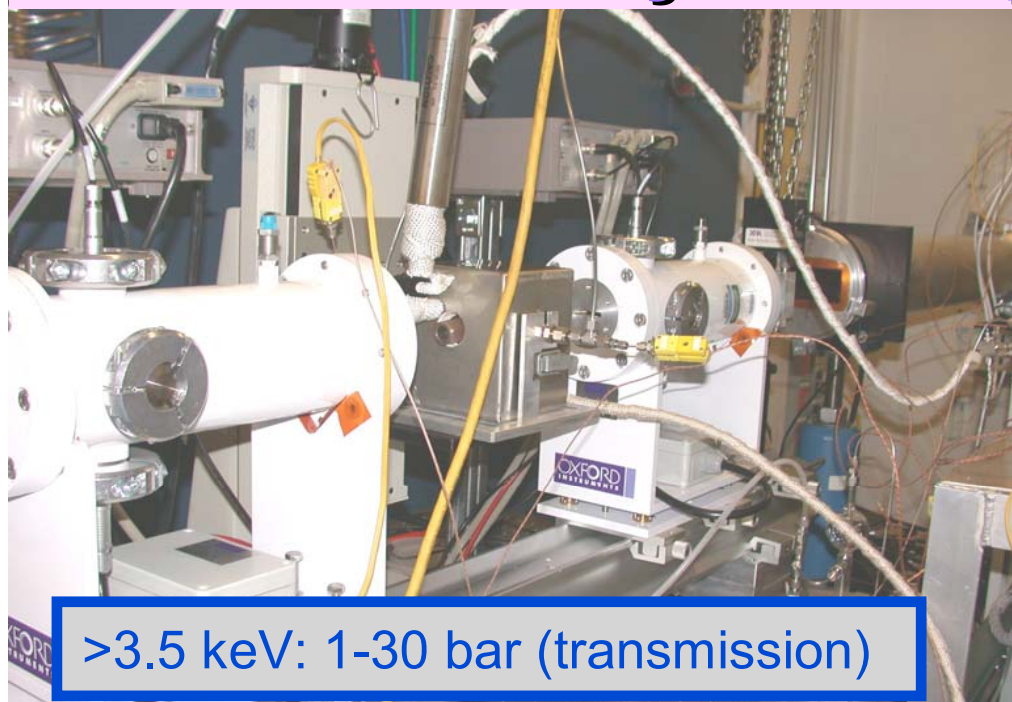


# TEM-EELS of FeZSM-5



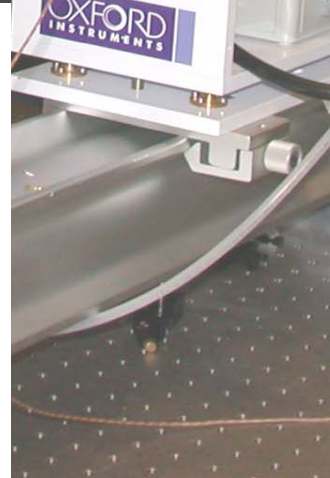
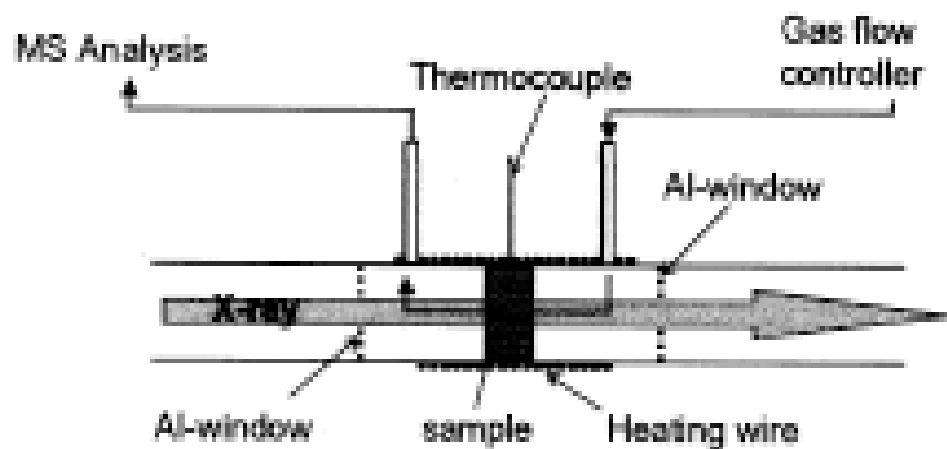
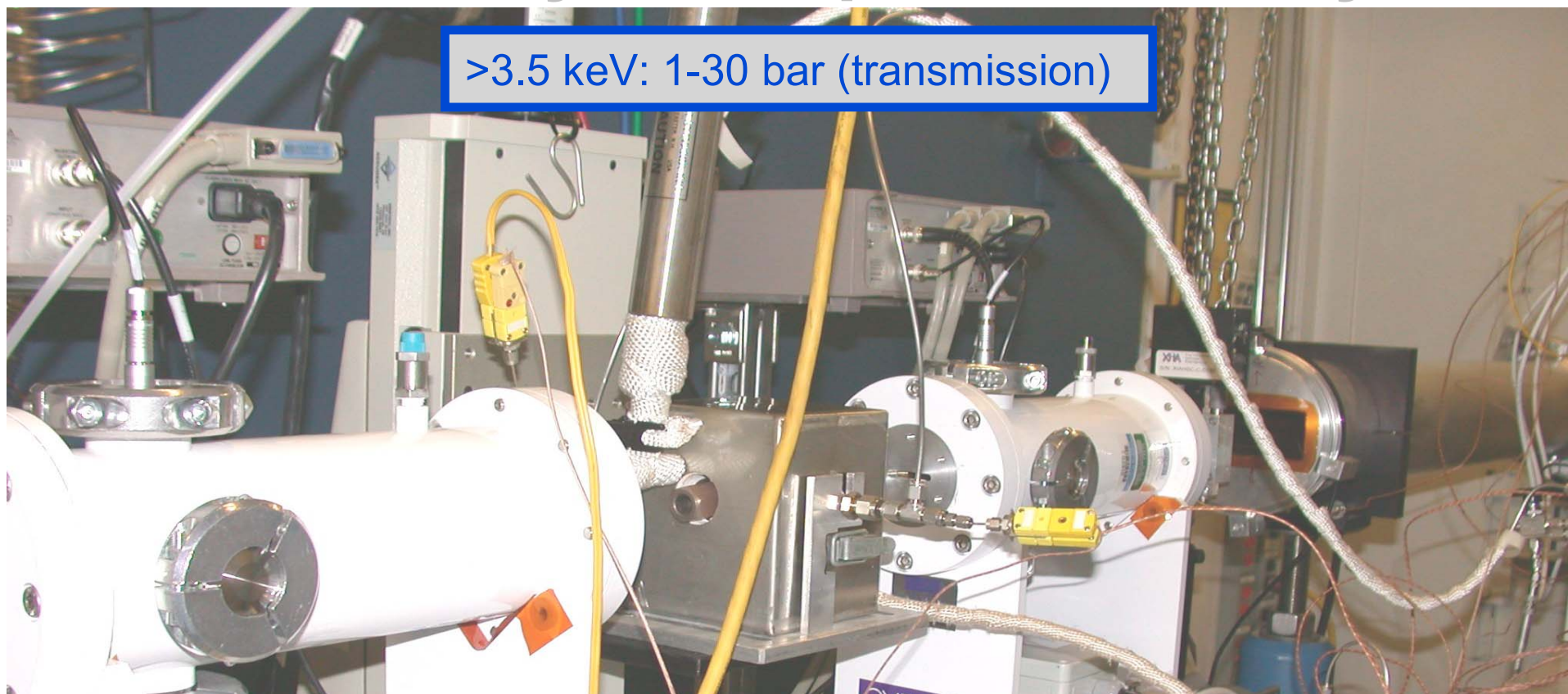


# In-situ X-ray Absorption in Catalysis



# In-situ X-ray Absorption in Catalysis

>3.5 keV: 1-30 bar (transmission)

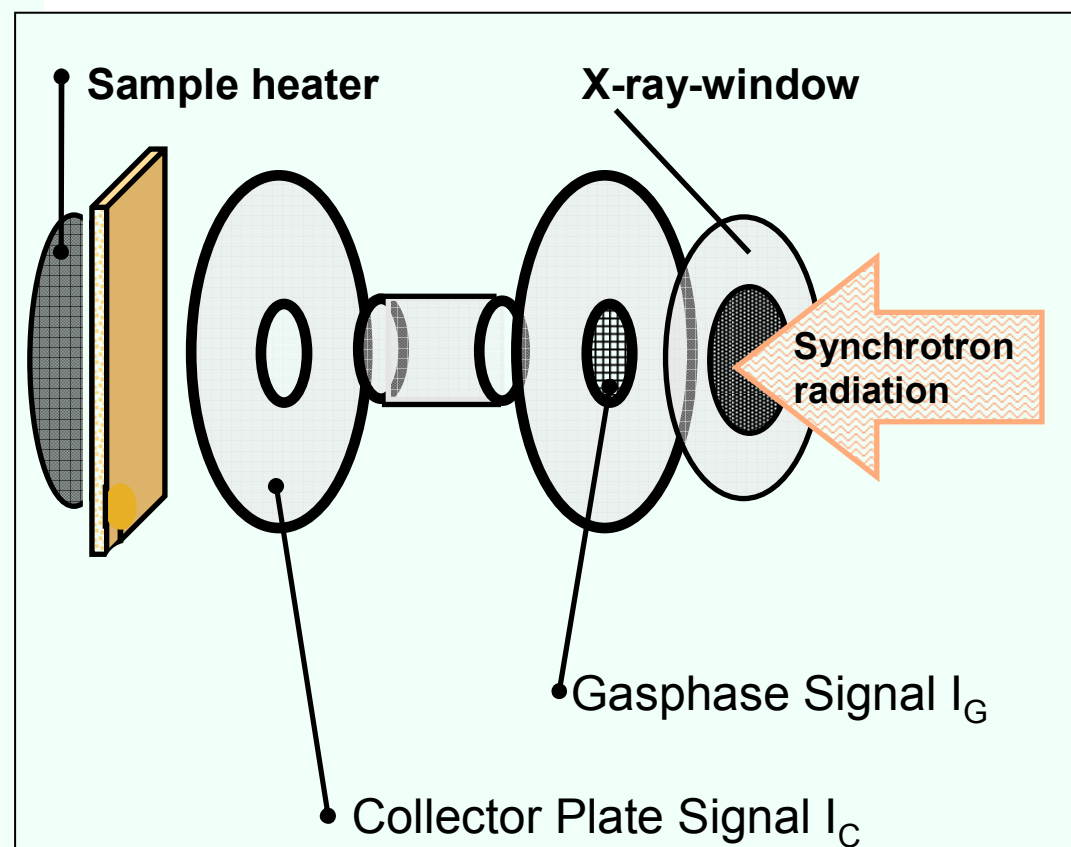
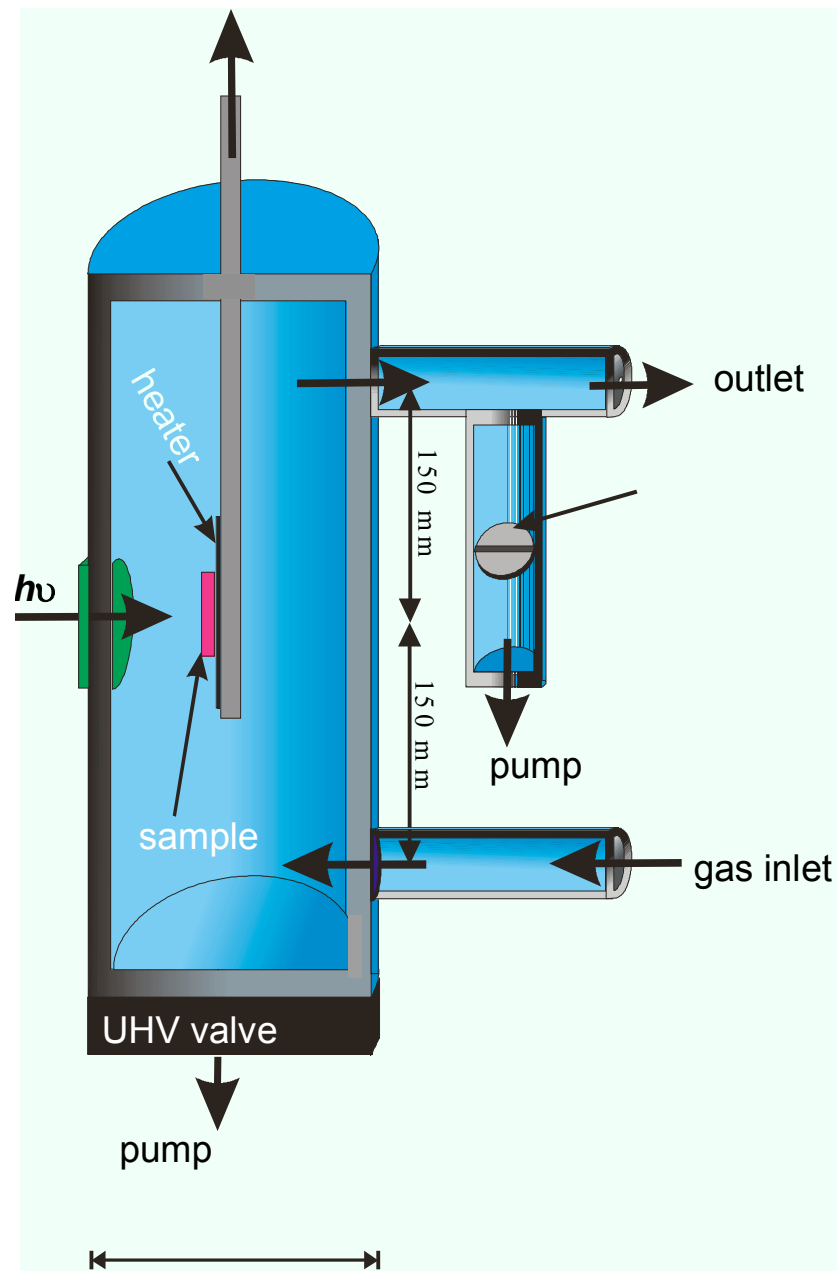




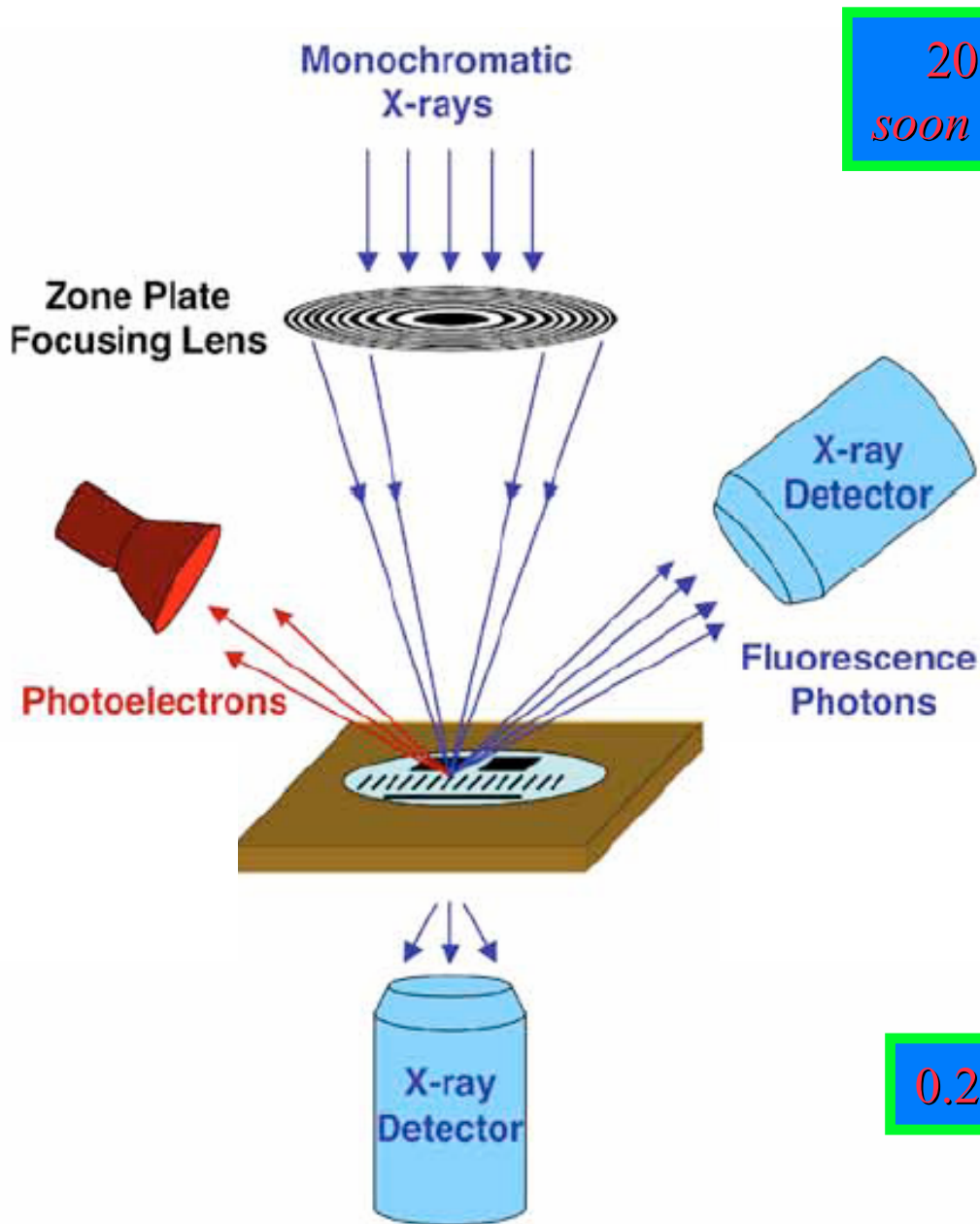
# In-situ X-ray Absorption in Catalysis



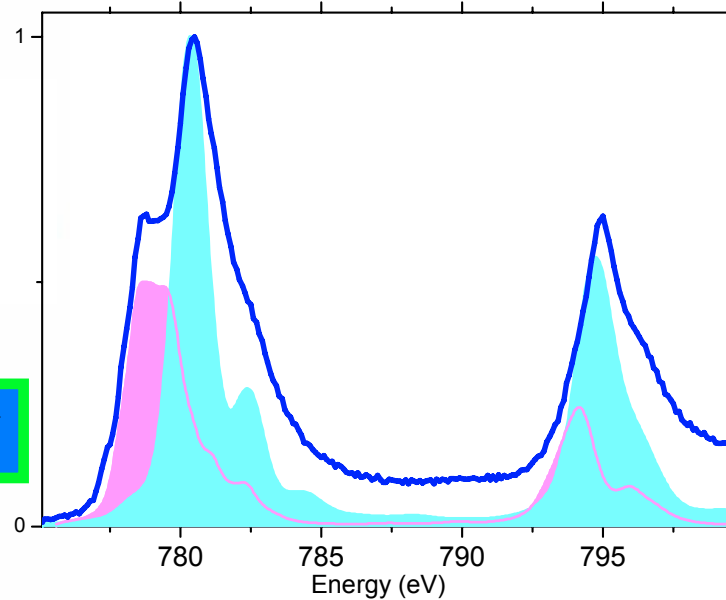
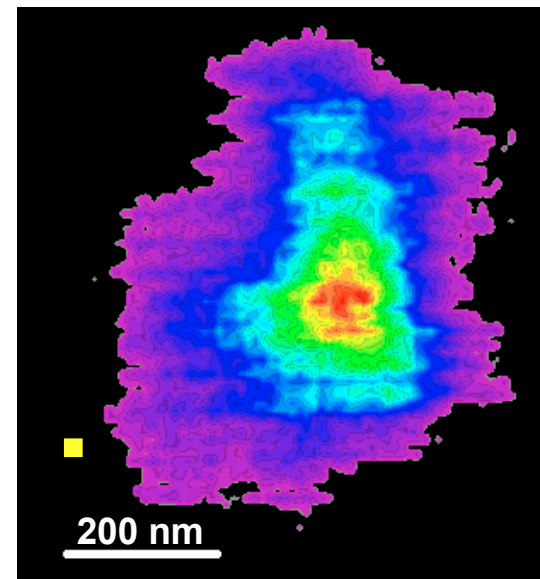
XAS at 5 mbar



# Transmission X-ray Microscopy (TXM)



20 nm  
*soon 10 nm*



0.2 eV

# ***Conditions XAS***

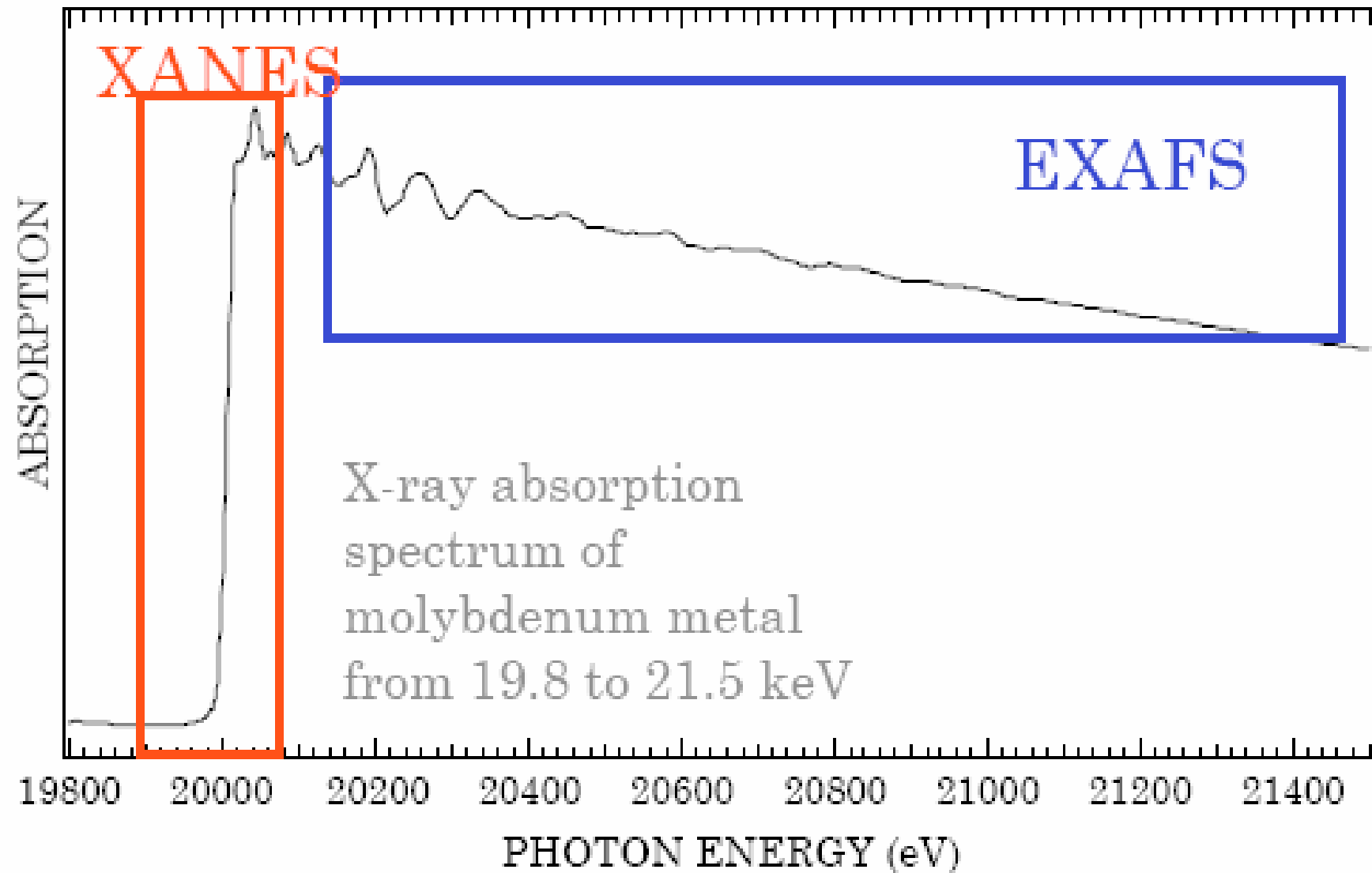
- Hard x-ray XAS:  
extreme conditions > operando catalysis
- Soft x-ray XAS:  
1 bar and  $\sim 250^{\circ}\text{C}$  (TXM) > in-situ catalysis  
10 mbar and  $\sim 500^{\circ}\text{C}$  (electron yield)
- EELS:  
vacuum



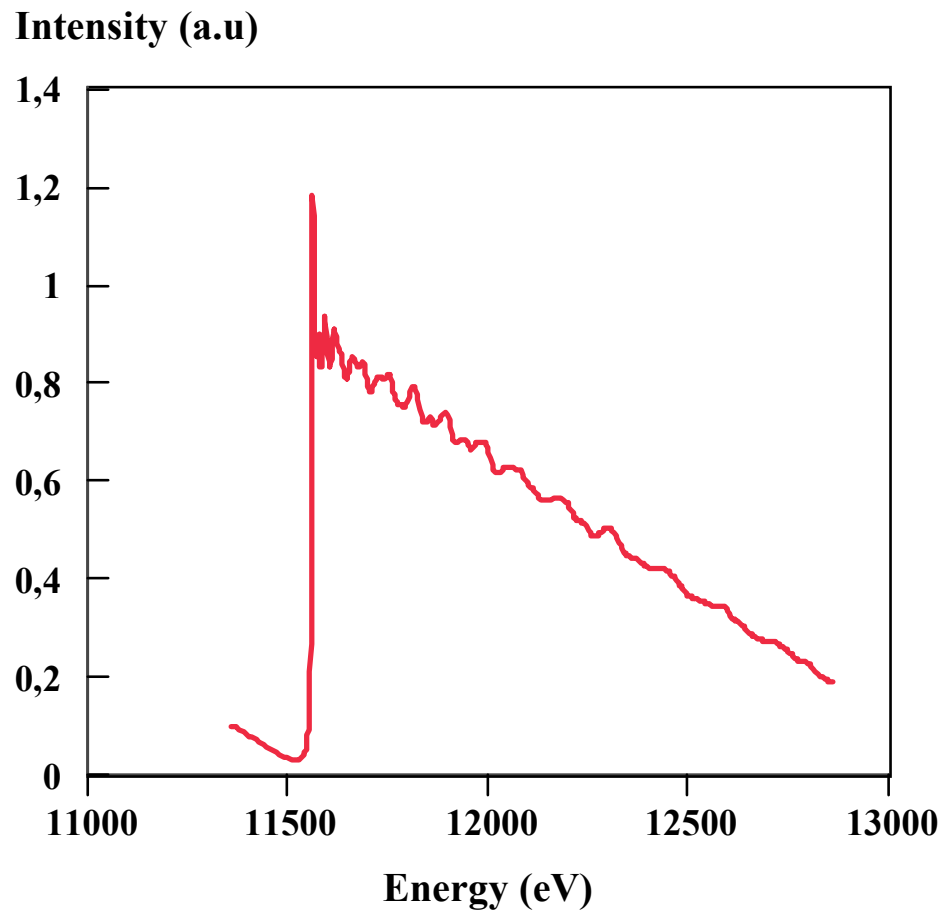
# *Why XAS?*

- Element specific
- Sensitive to low concentrations  
(0.01-0.1 %)
- Applicable under extreme conditions  
(high-pressure, high temperature, operando)
- Applicable to gasses, liquids and solids  
(+ surfaces, buried interfaces, impurities, etc.)
- Local geometric information
- Local electronic information

# *X-ray absorption*

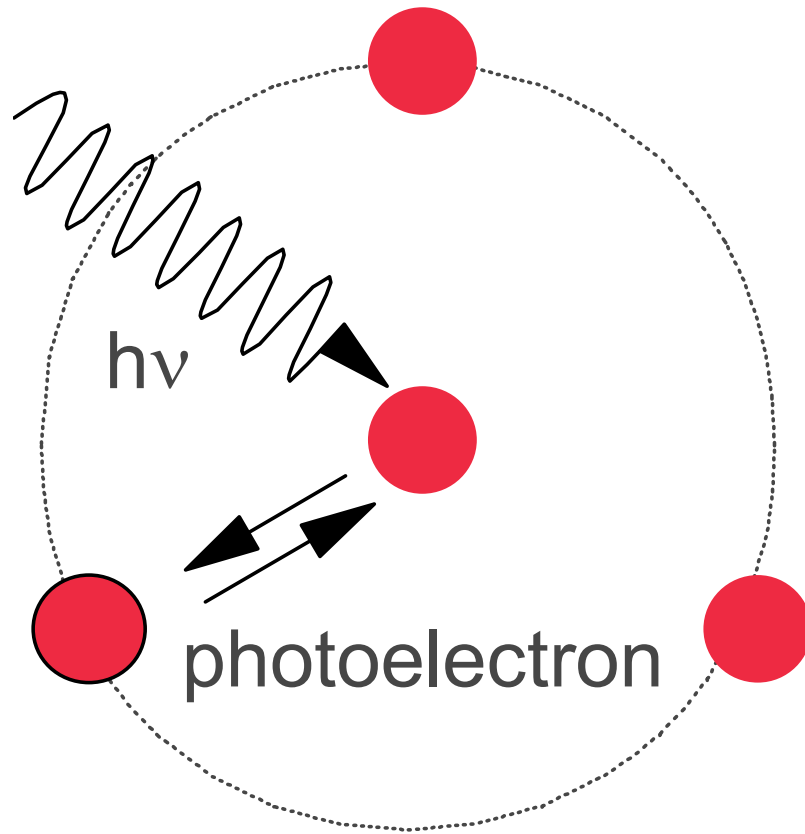


# EXAFS



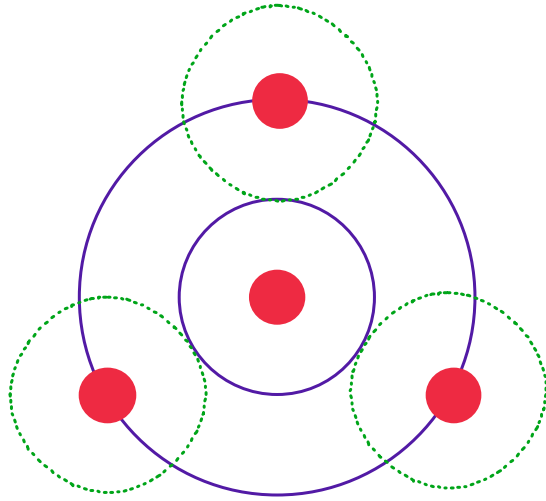
- Decreasing background with increasing energy
- Oscillations present due to the presence of neighbours

# EXAFS

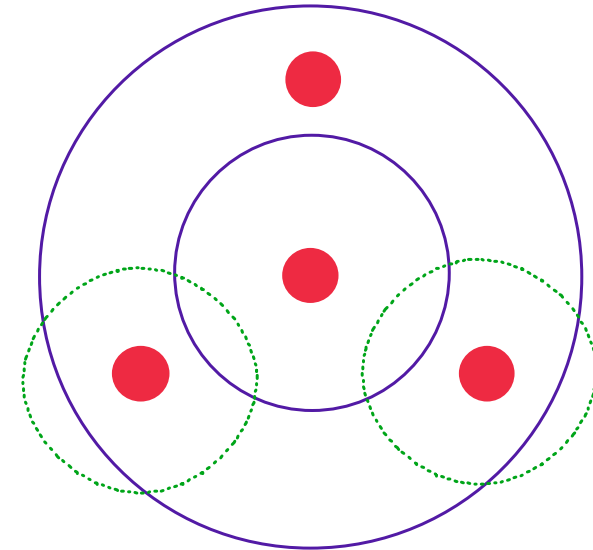


- Generation of photoelectrons (electron wave).
- Backscattering against neighbouring atoms.
- Interference with outgoing wave

# EXAFS



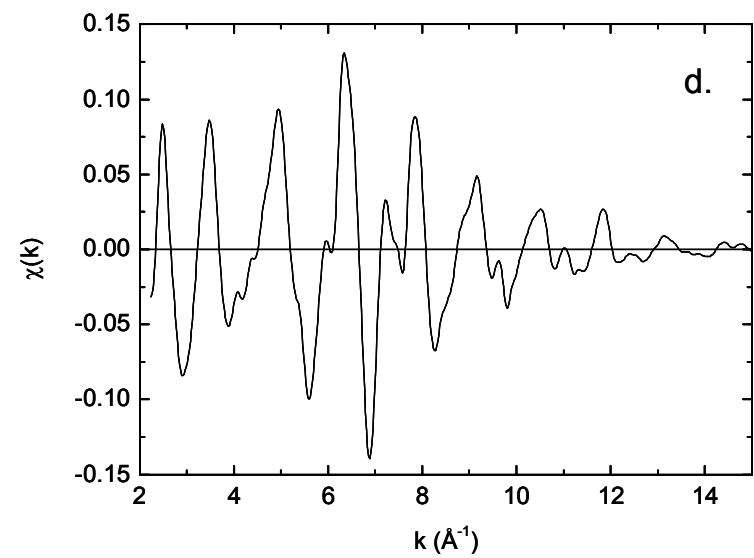
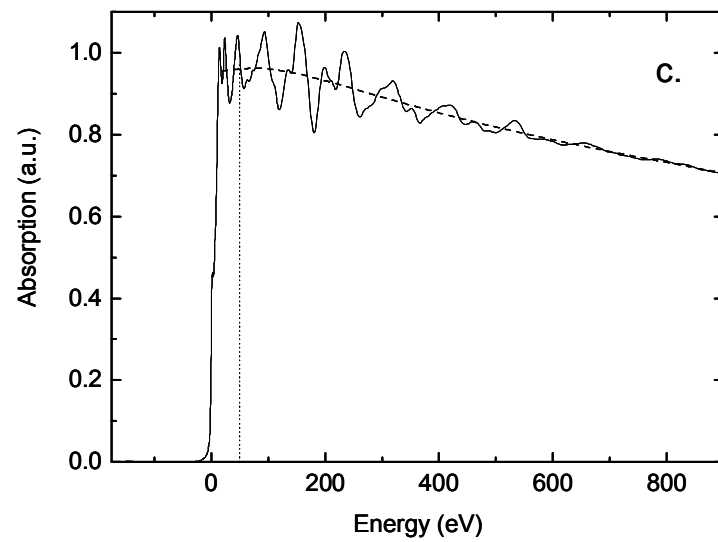
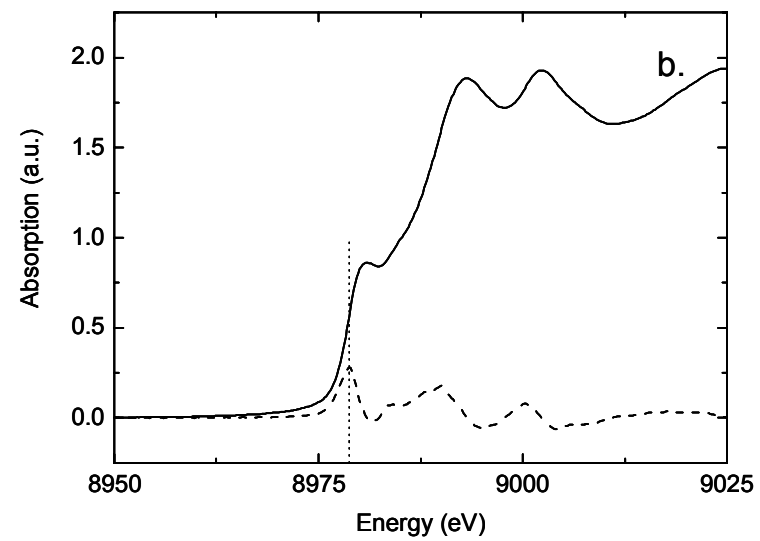
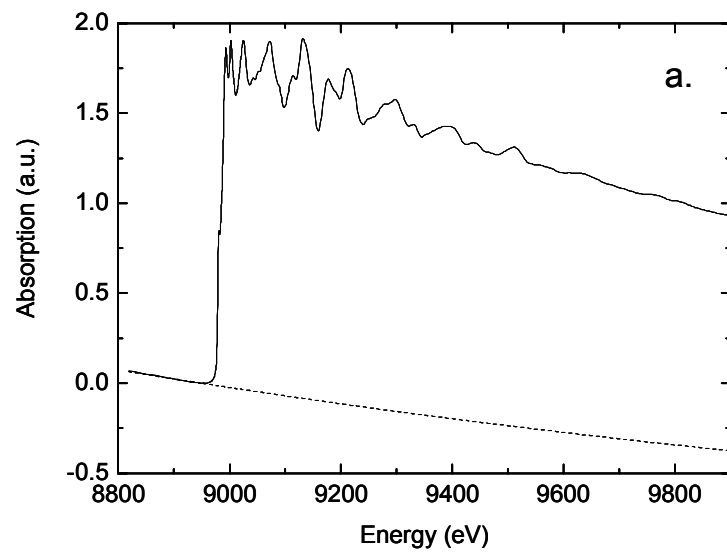
Constructive  
(in phase)



Destructive  
(out of phase)

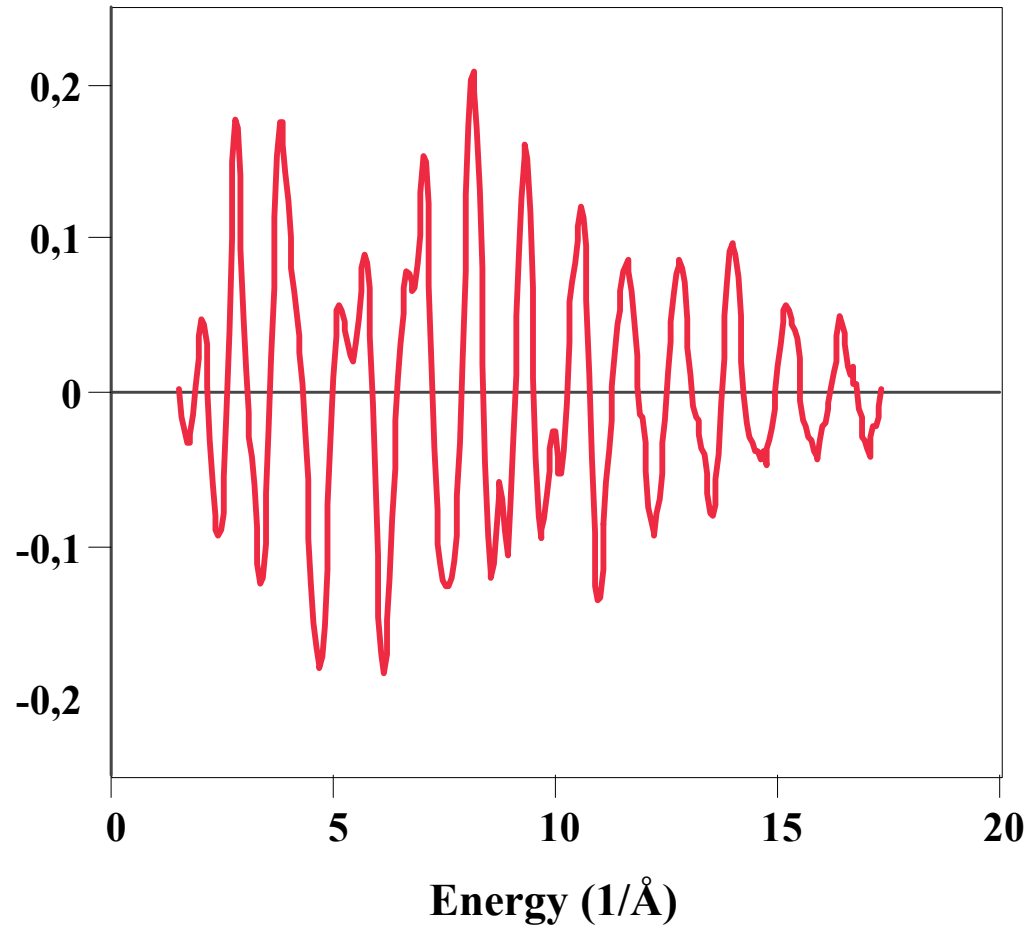
$$\Psi = \Psi_{\text{out}} + \Psi_{\text{back}}$$

# EXAFS



# EXAFS

Amplitude



- Remove step at edge
- Remove slope
- Change x-axis from energy to wave vector

# EXAFS formula

$$\chi(k) = \sum_{j=1}^{Shells} \chi_j(k) = \sum_{j=1}^{Shells} A_j(k) \sin \phi_j(k)$$

Oscillations depend on

- Energy
- Distance and type of neighbours (j)
- Disorder (Debye Waller factor)

The observed oscillations are the sum of different contributions from each shell of atoms around the absorber atom



# EXAFS

$$\chi_{\text{sim}}(k) = \sum_{j=1}^{\text{Shells}} N_j F_j \frac{e^{-2R_j/\lambda}}{k_j^2 R_j^2} S_0^2(k) e^{-2\sigma_j^2 k^2} \sin[2kR_j + \varphi_j(k)]$$

- Distance R
- Number of neighbours N
- Disorder: Debye-Waller factor, dependent on temperature.

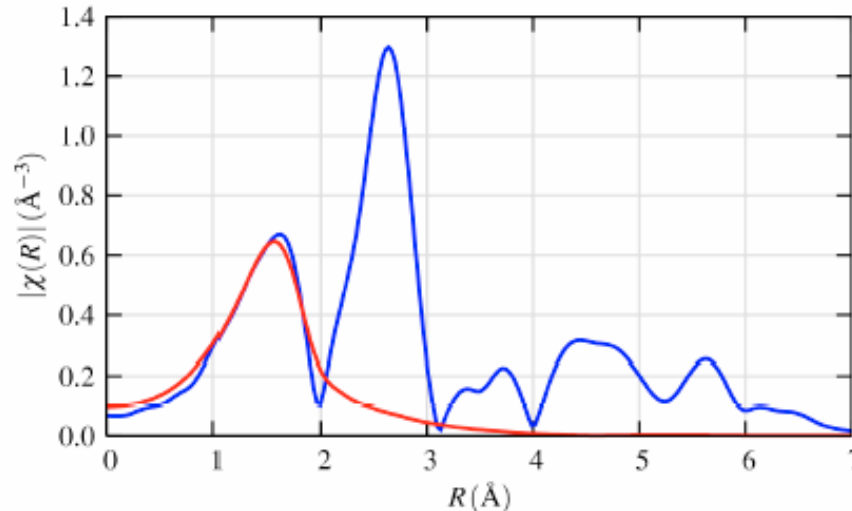
## EXAFS Analysis: Modeling the 1st Shell of FeO

FeO has a rock-salt structure.

To model the FeO EXAFS, we calculate the scattering amplitude  $f(\mathbf{k})$  and phase-shift  $\delta(\mathbf{k})$ , based on a guess of the structure, with Fe-O distance  $R = 2.14 \text{ \AA}$  (a regular octahedral coordination).



We'll use these functions to *refine* the values  $R$ ,  $N$ ,  $\sigma^2$ , and  $E_0$  so our model EXAFS function matches our data.



$|\chi(\mathbf{R})|$  for FeO (blue), and a 1<sup>st</sup> shell fit (red).

Fit results:

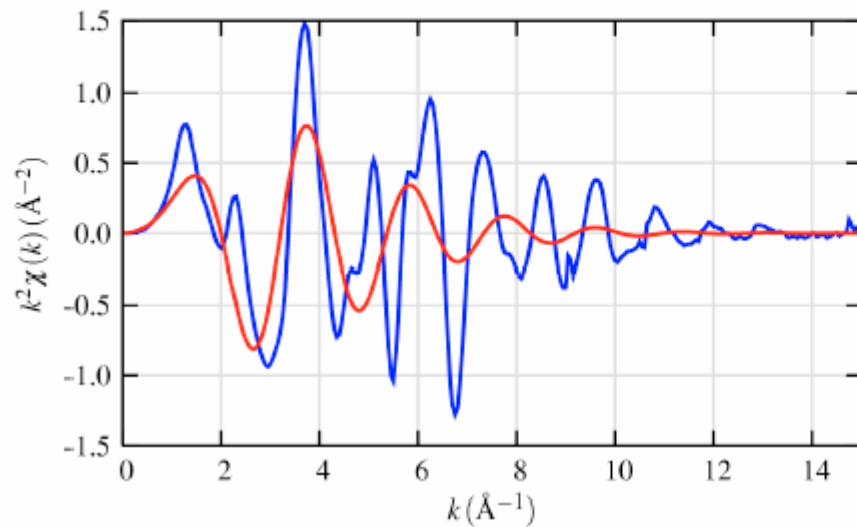
$$N = 5.8 \pm 1.8$$

$$R = 2.10 \pm 0.02 \text{ \AA}$$

$$\Delta E_0 = -3.1 \pm 2.5 \text{ eV}$$

$$\sigma^2 = 0.015 \pm 0.005 \text{ \AA}^2.$$

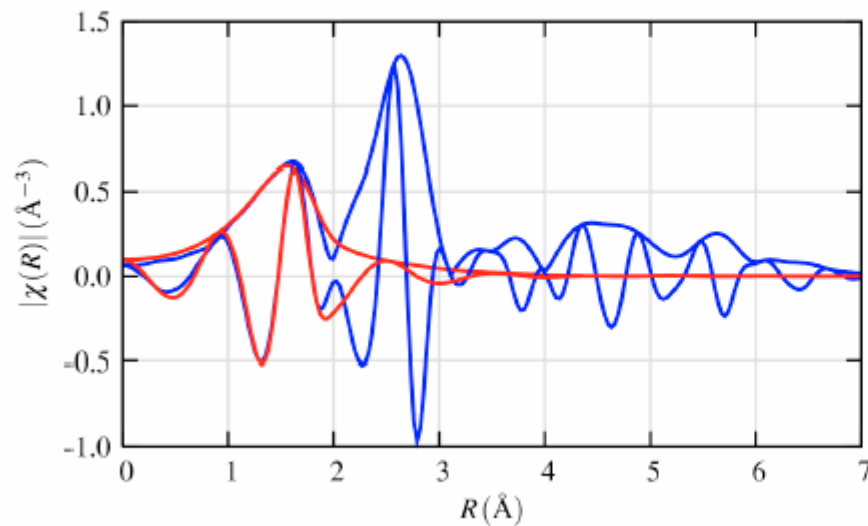
## EXAFS Analysis: 1st Shell of FeO



**1<sup>st</sup> shell fit in  $k$  space.**

The 1<sup>st</sup> shell fit to FeO in  $k$  space.

There is clearly another component in the XAFS!



**1<sup>st</sup> shell fit in  $R$  space.**

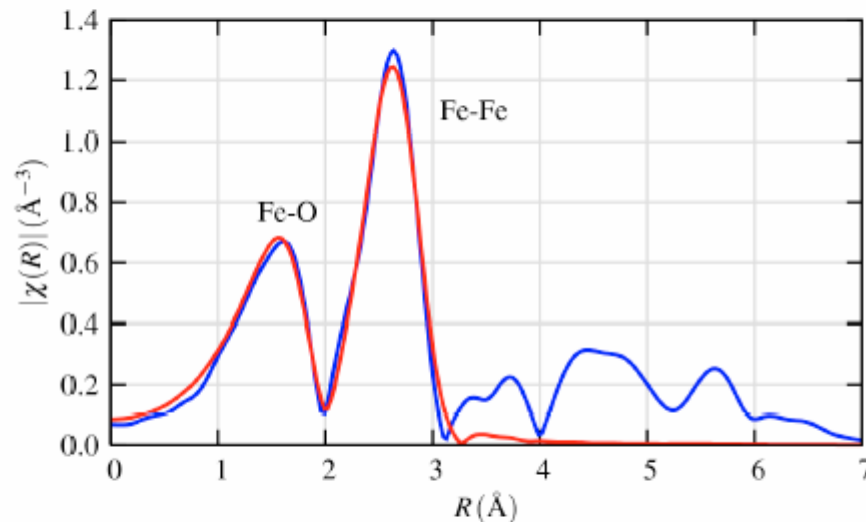
$|\chi(R)|$  and  $\text{Re}[\chi(R)]$  for FeO (blue), and a 1<sup>st</sup> shell fit (red).

Though the fit to the magnitude didn't look great, the fit to  $\text{Re}[\chi(R)]$  looks very good.

## EXAFS Analysis: Second Shell of FeO

To add the second shell Fe to the model, we use calculation for  $f(\mathbf{k})$  and  $\delta(\mathbf{k})$  based on a guess of the Fe-Fe distance, and refine the values  $R$ ,  $N$ ,  $\sigma^2$ .

Such a fit gives a result like this:



$|\chi(R)|$  data for FeO (blue), and fit of 1<sup>st</sup> and 2<sup>nd</sup> shells (red).

The results are fairly consistent with the known values for crystalline FeO:

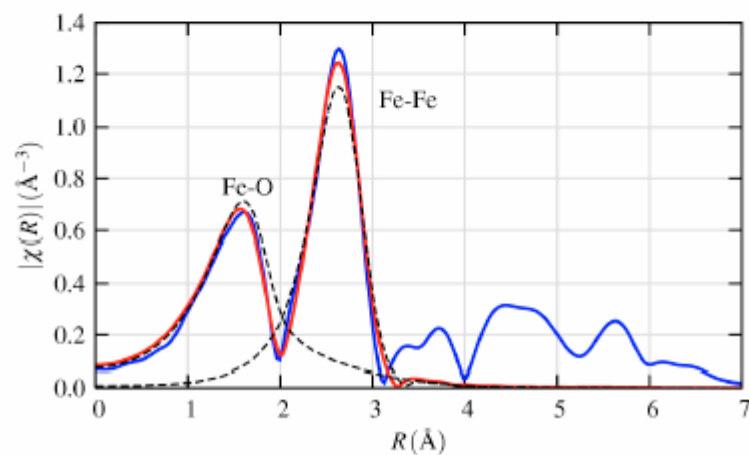
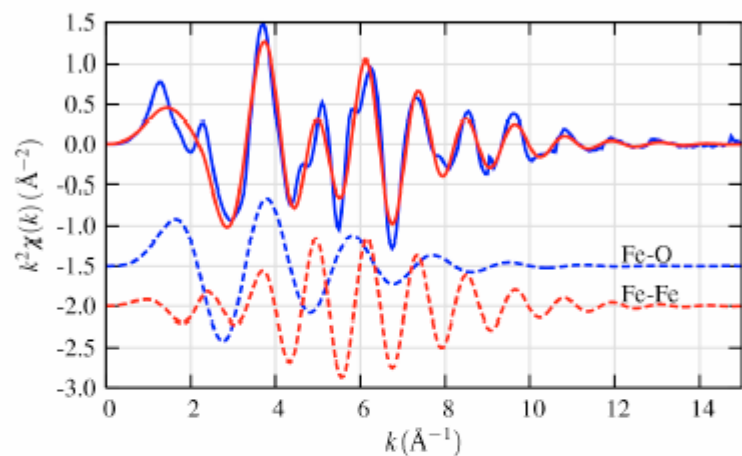
6 O at 2.13Å, 12 Fe at 3.02Å.

Fit results (uncertainties in parentheses):

Shell	N	R (Å)	$\sigma^2$ (Å <sup>2</sup> )	$\Delta E_0$ (eV)
Fe-O	6.0(1.0)	2.10(.02)	0.015(.003)	-2.1(0.8)
Fe-Fe	11.7(1.3)	3.05(.02)	0.014(.002)	-2.1(0.8)

## EXAFS Analysis: Second Shell of FeO

Other views of the data and two-shell fit:

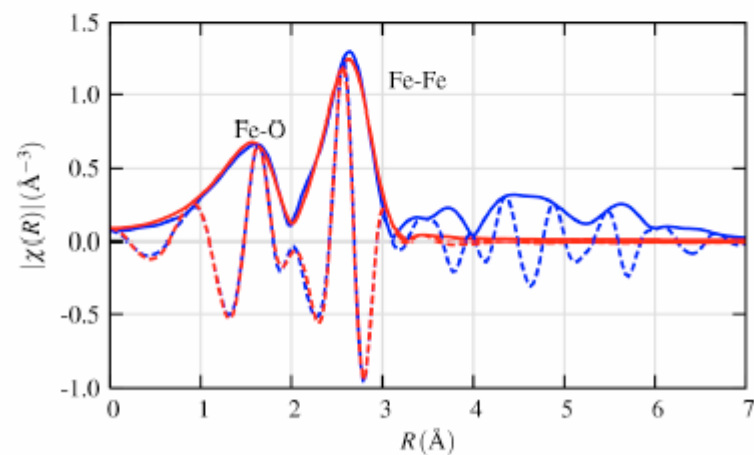


The Fe-Fe EXAFS extends to higher- $k$  than the Fe-O EXAFS.

Even in this simple system, there is some *overlap* of shells in  $R$ -space.

The agreement in  $\text{Re}[\chi(R)]$  look especially good – this is how the fits are done.

Of course, the modeling can get more complicated than this!



# ***XANES versus EXAFS***

- EXAFS: local geometry (N, R,  $\sigma$ )
- XANES: valence, site symmetry
  
- XANES much easier/faster to measure
- XANES easier to crudely interpret
- XANES more difficult to interpret 'ab-initio'
- HERFD-XANES gives many new possibilities
- XANES easier at high-temperature