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

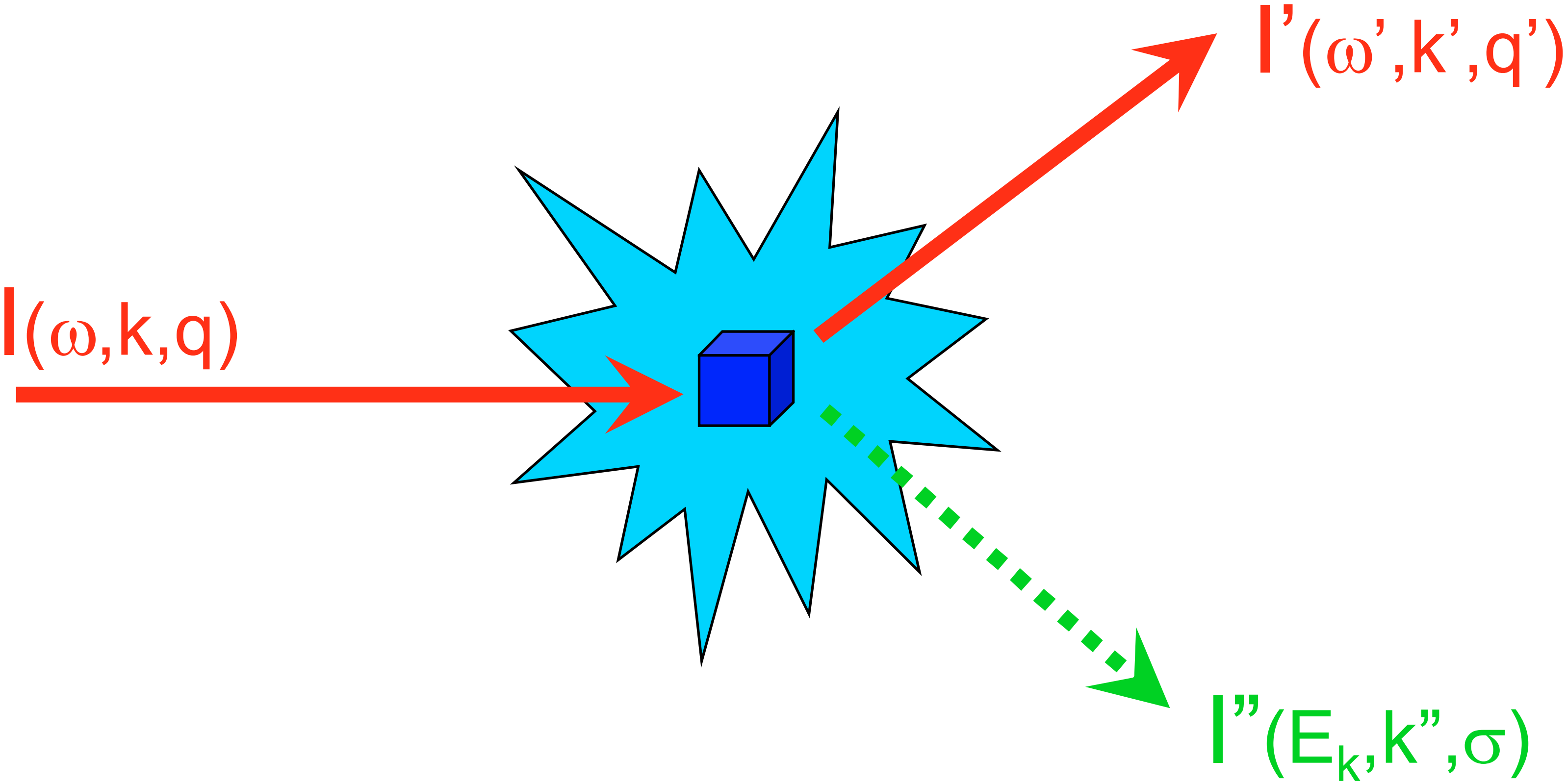
  Binuclear centers, (very small) cluster sizes
- Metal site symmetry
- d-band occupation

  (3d, 4d or 5d; metal versus oxide, valence)
- Energy positions of empty bands of adsorbates

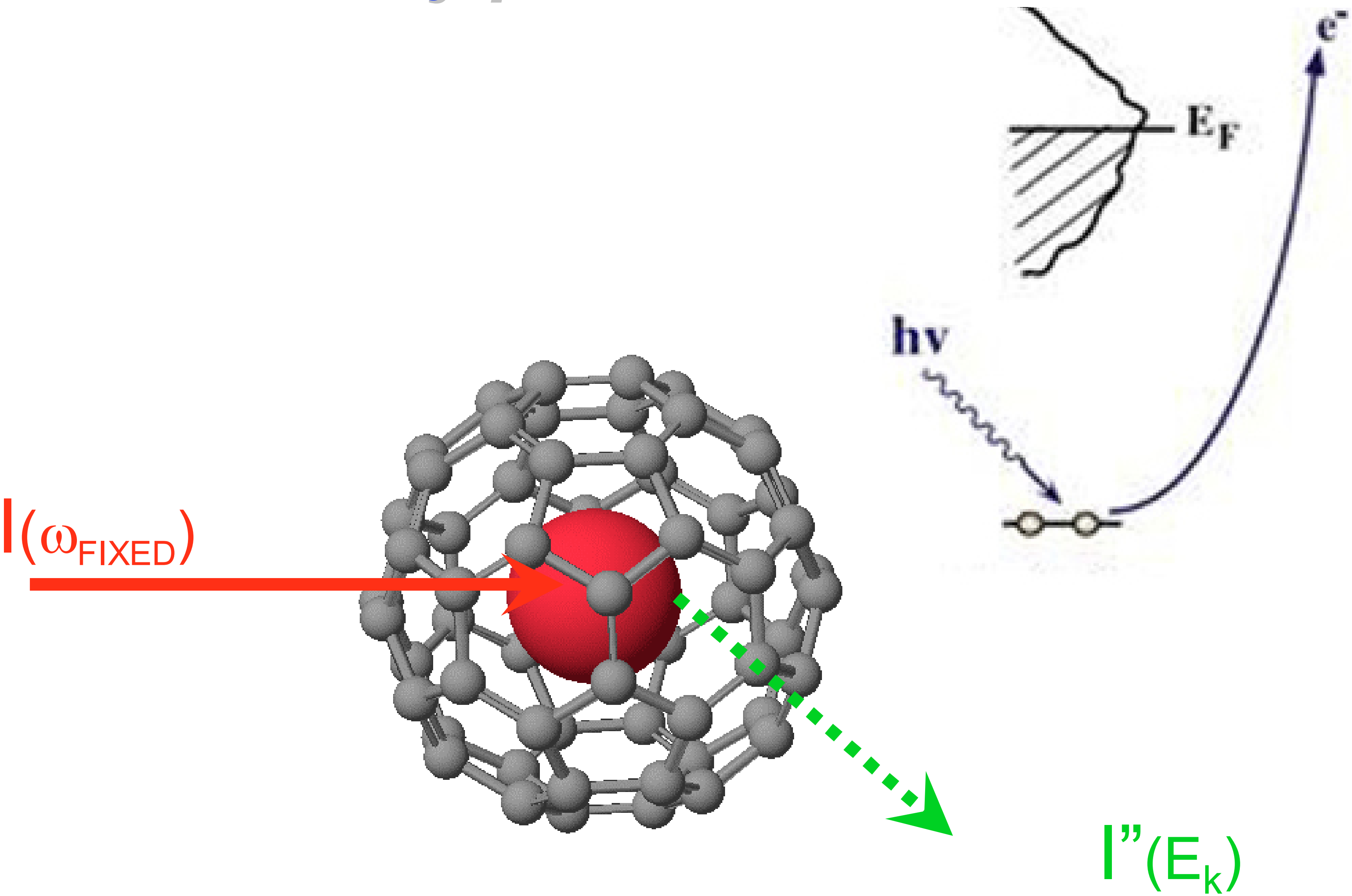
  (CO, H_2, on Pt, nature of adsorption site)
- 20 nm microscopy, 50 ps time-resolved

Interaction of x-rays with matter

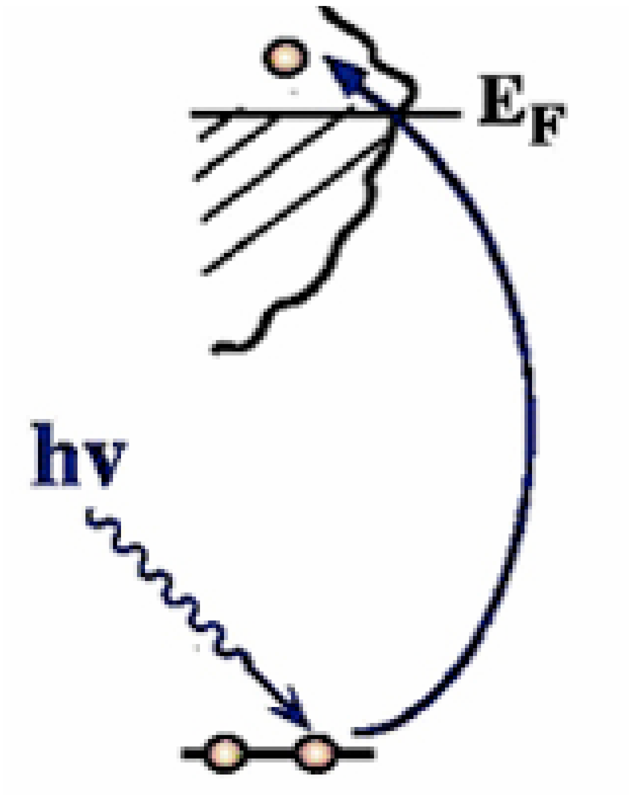
Energy → Spectroscopy
Direction → Structure
Polarization → Magnetism

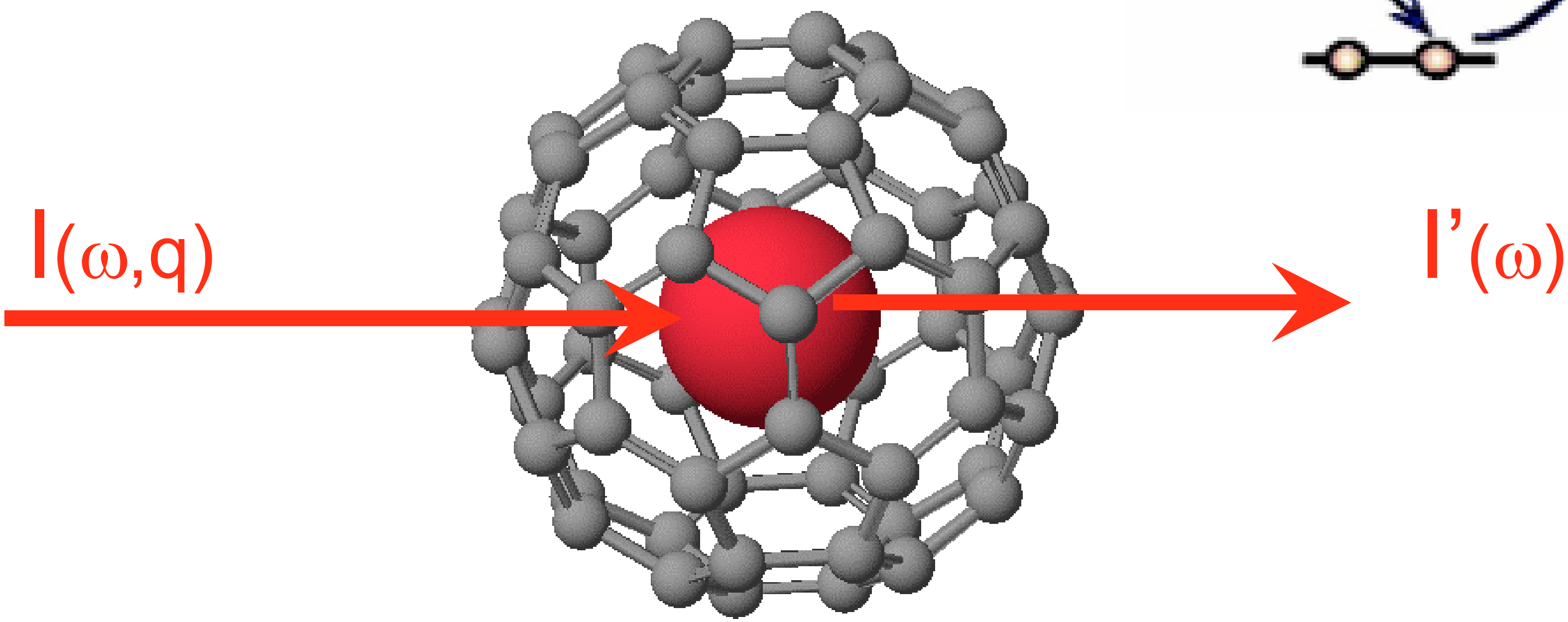


X-ray photoemission



X-ray absorption





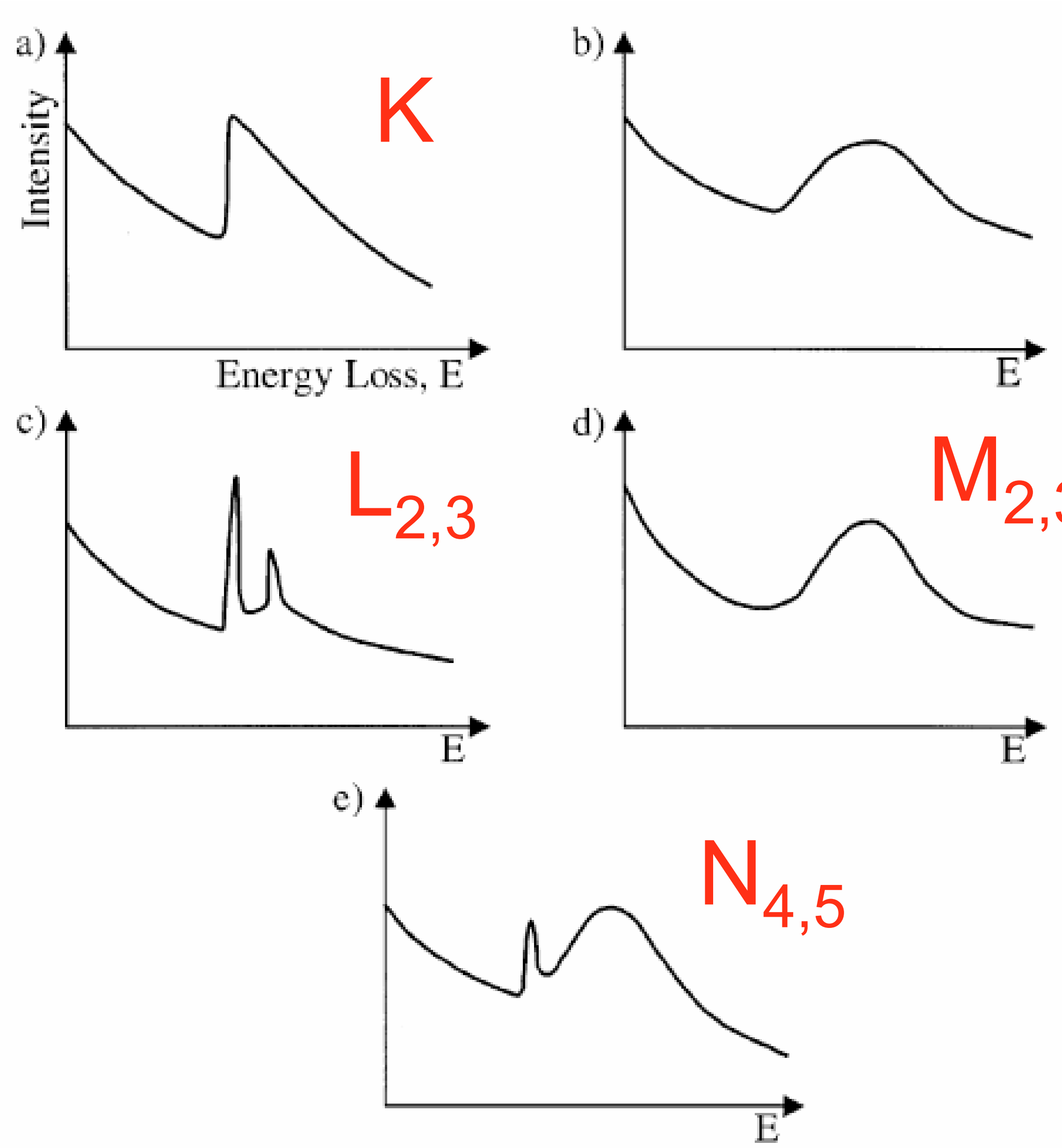
X-ray absorption edges

Manganese Electron binding energies

	Label	Orbital	eV [literature reference]
view	K	1s	6539 [1]
view	L_{I}	2s	769.1 [3]
view	L_{II}	$2p_{1/2}$	649.9 [3]
view	L_{III}	$2p_{3/2}$	638.7 [3]
view	M_{I}	3s	82.3 [3]
view	M_{II}	$3p_{1/2}$	47.2 [3]
view	M_{III}	$3p_{3/2}$	47.2 [3]

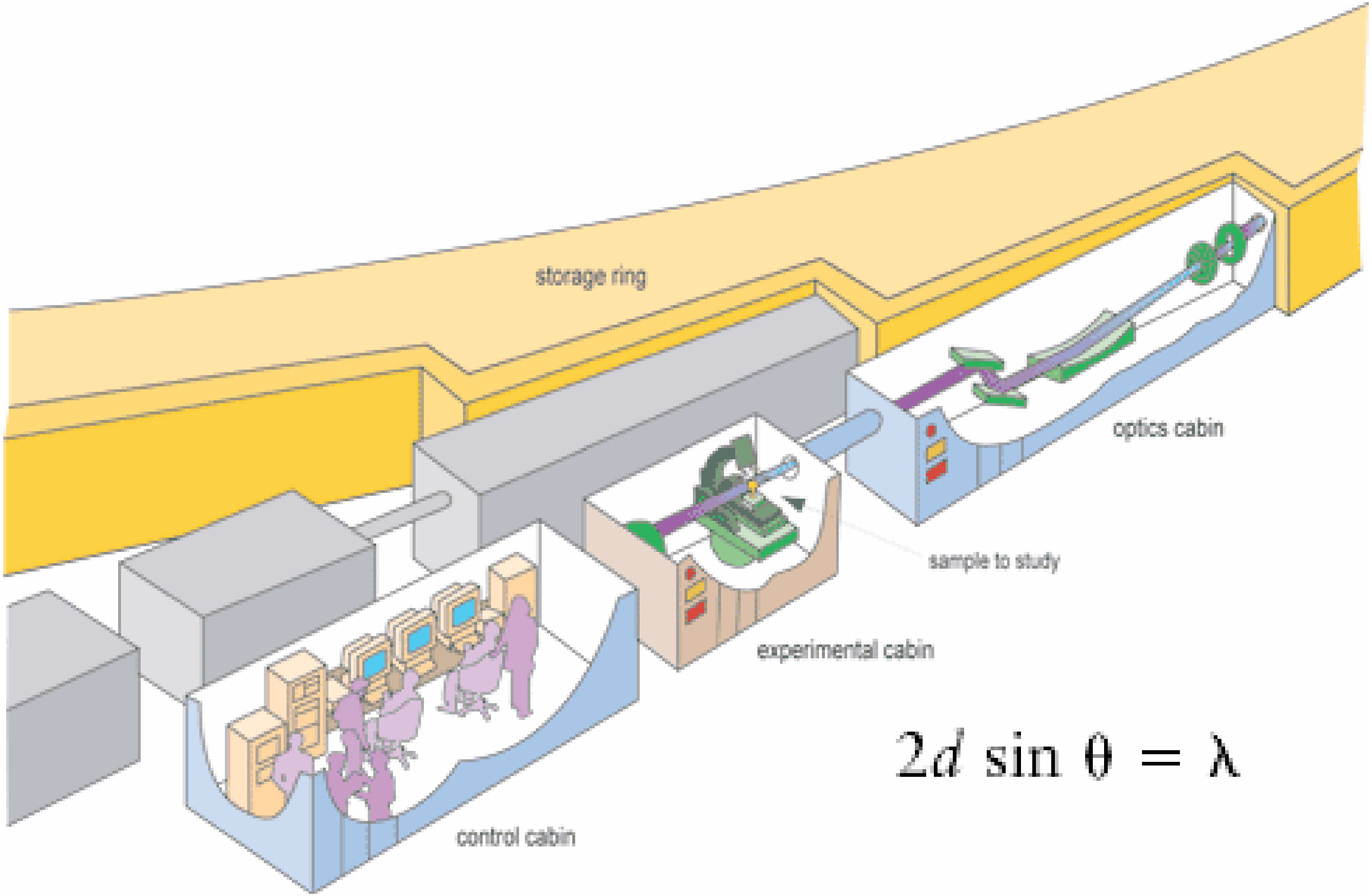
http://www.webelements.com/

X-ray absorption



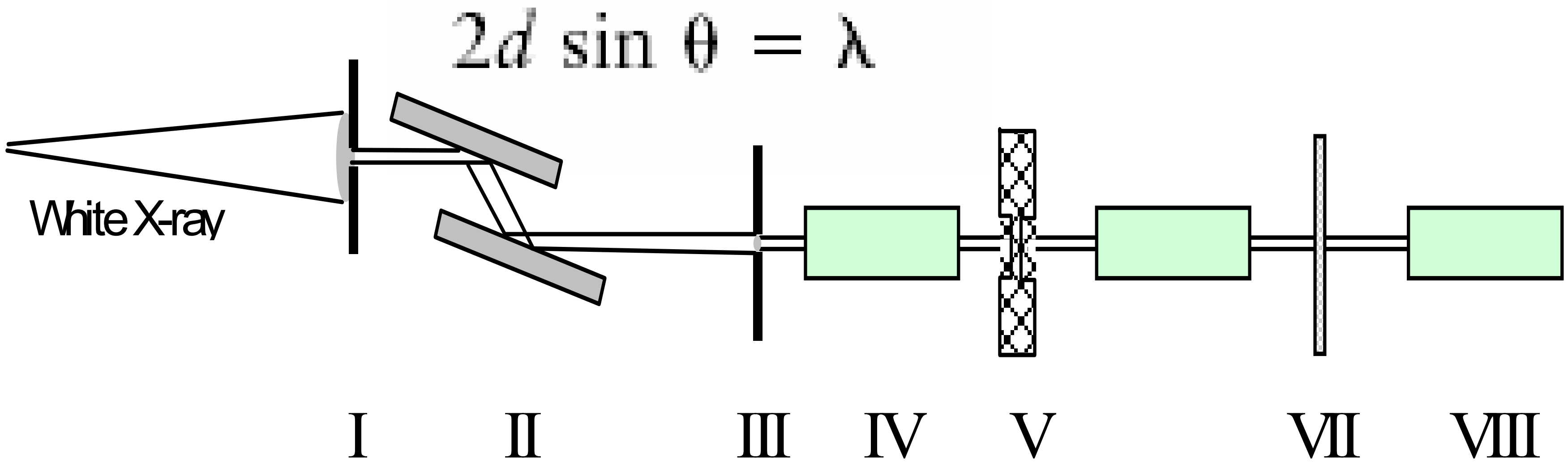
K	1s→p (3d)
$L_{2,3}$	2p→3d (3d)
$M_{2,3}$	3p→3d (3d)
$N_{4,5}$	4d→4f (4f)

X-rays from synchrotrons



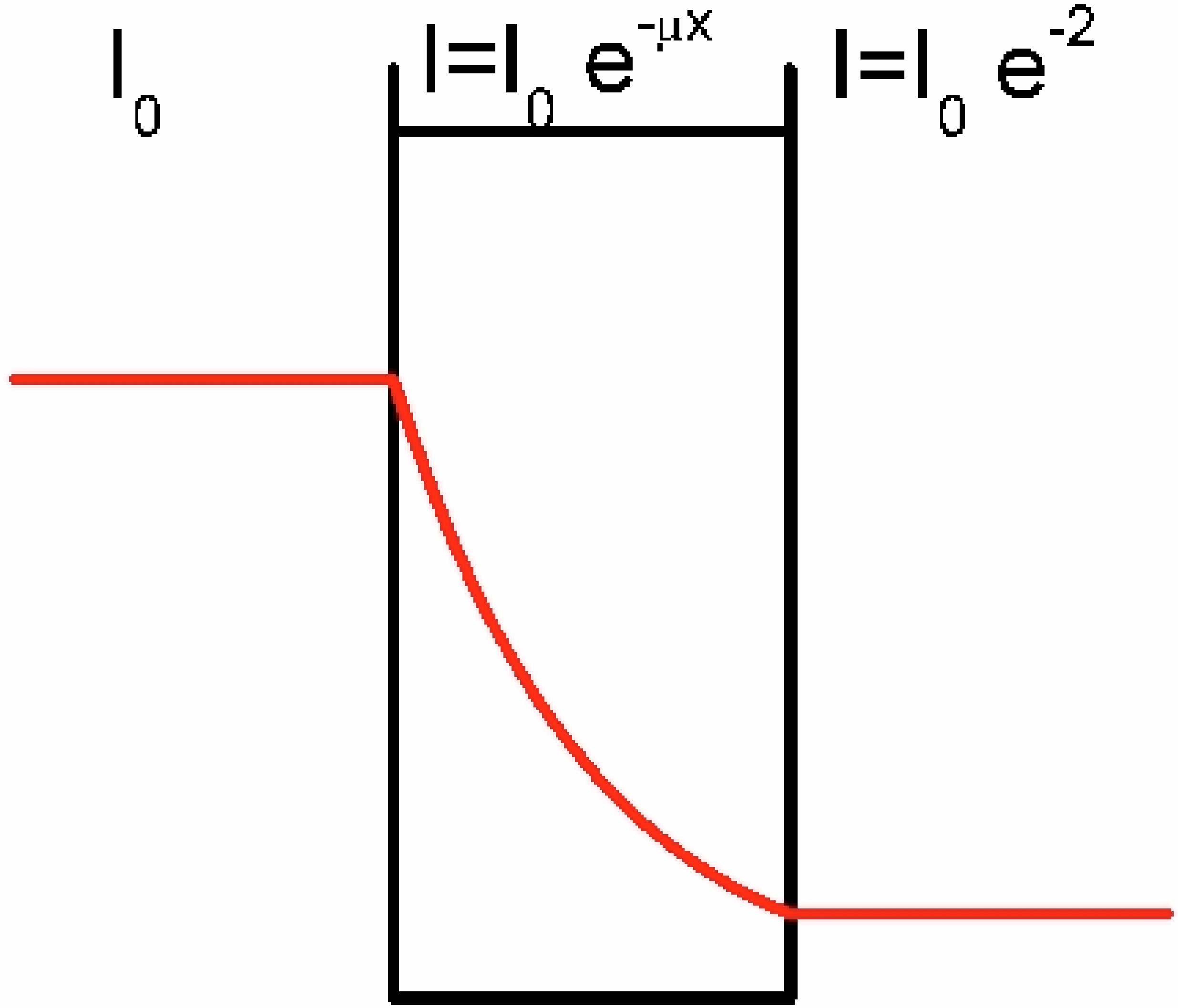
$$2d \sin \theta = \lambda$$

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

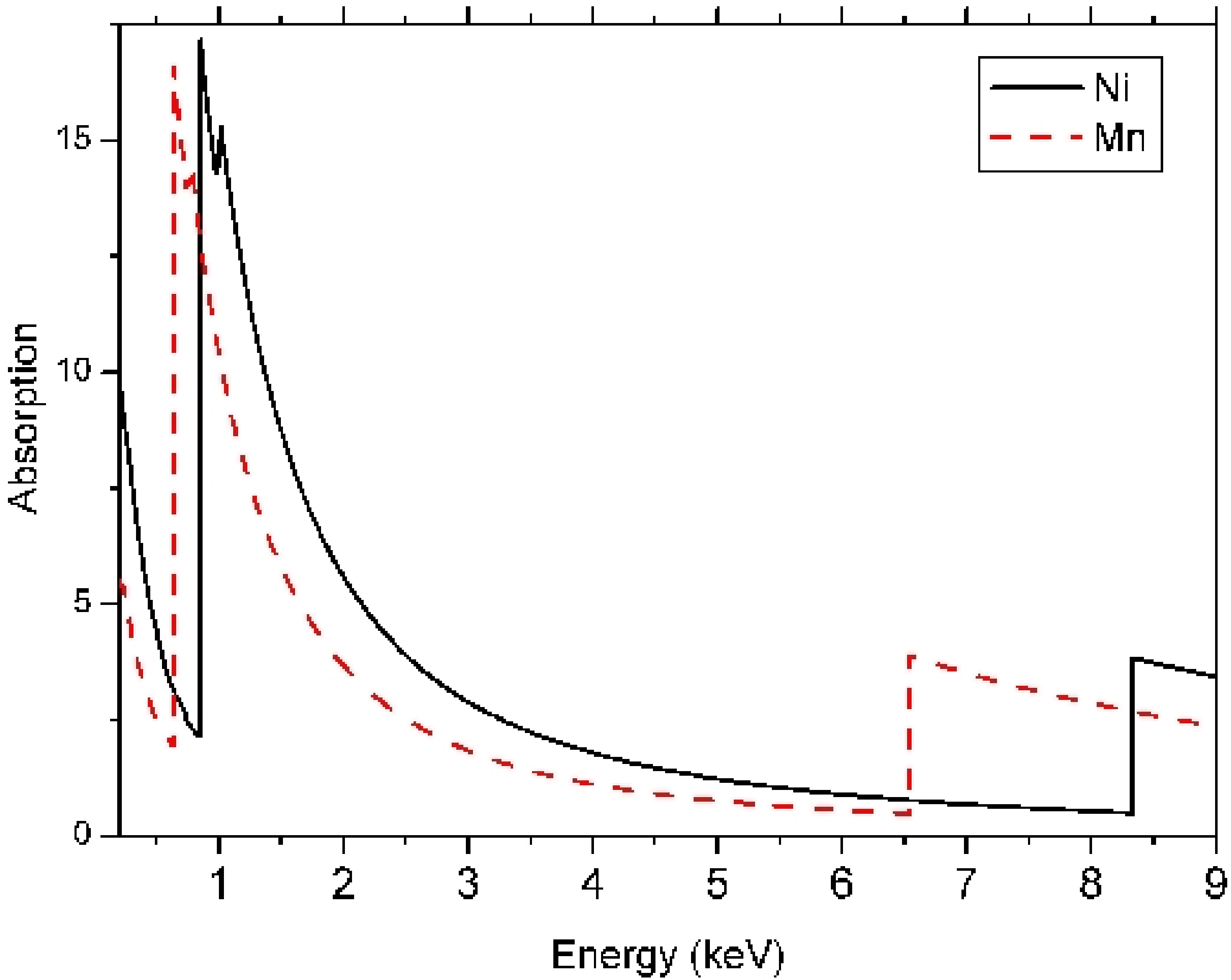
$$\ln \frac{I_0}{I_t} = \varepsilon \cdot c \cdot l$$

- Lambert-Beer

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

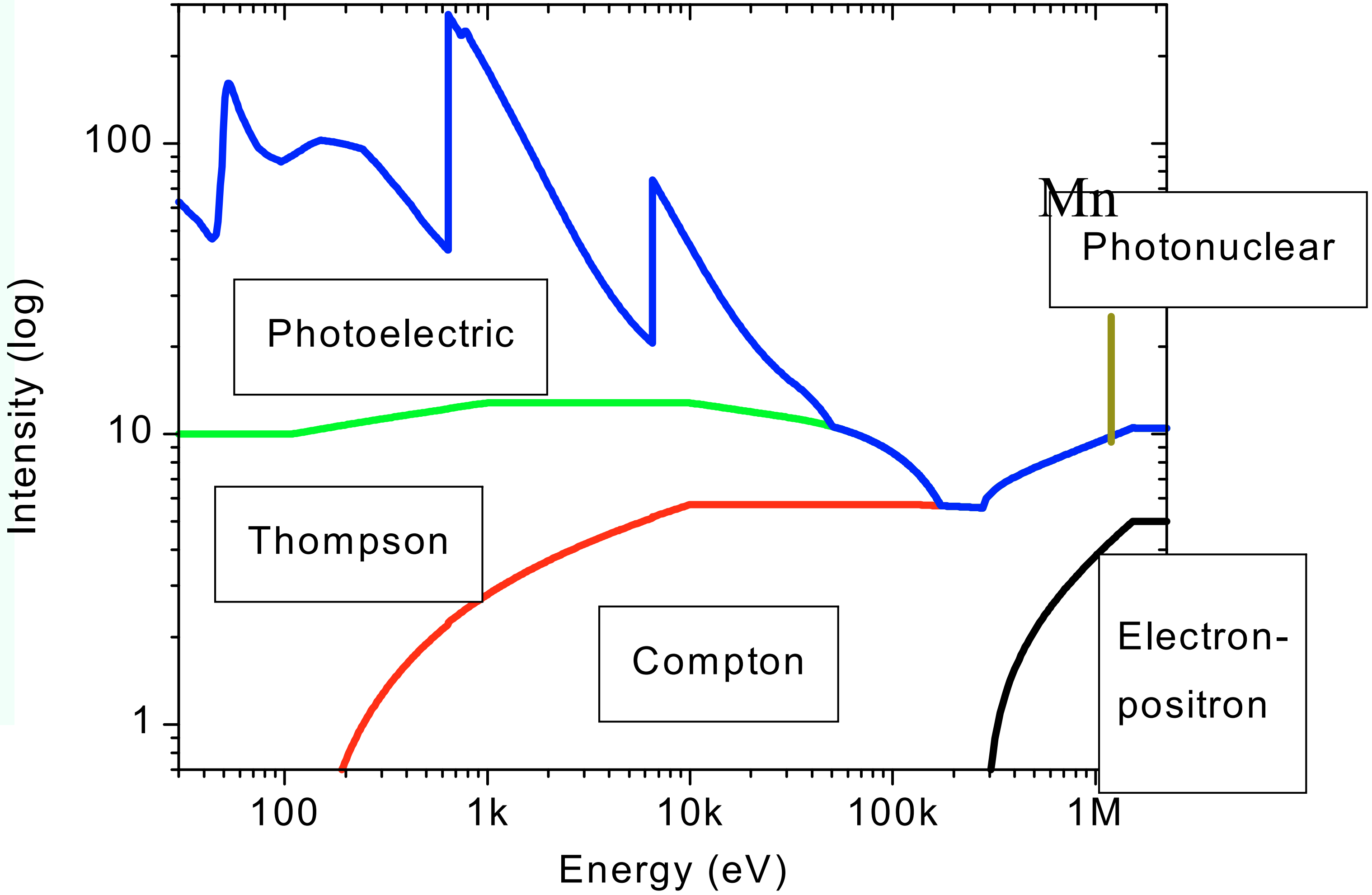
- μ = absorption coefficient
- x = sample thickness
- Measure x-ray intensity before and after sample

X-ray absorption

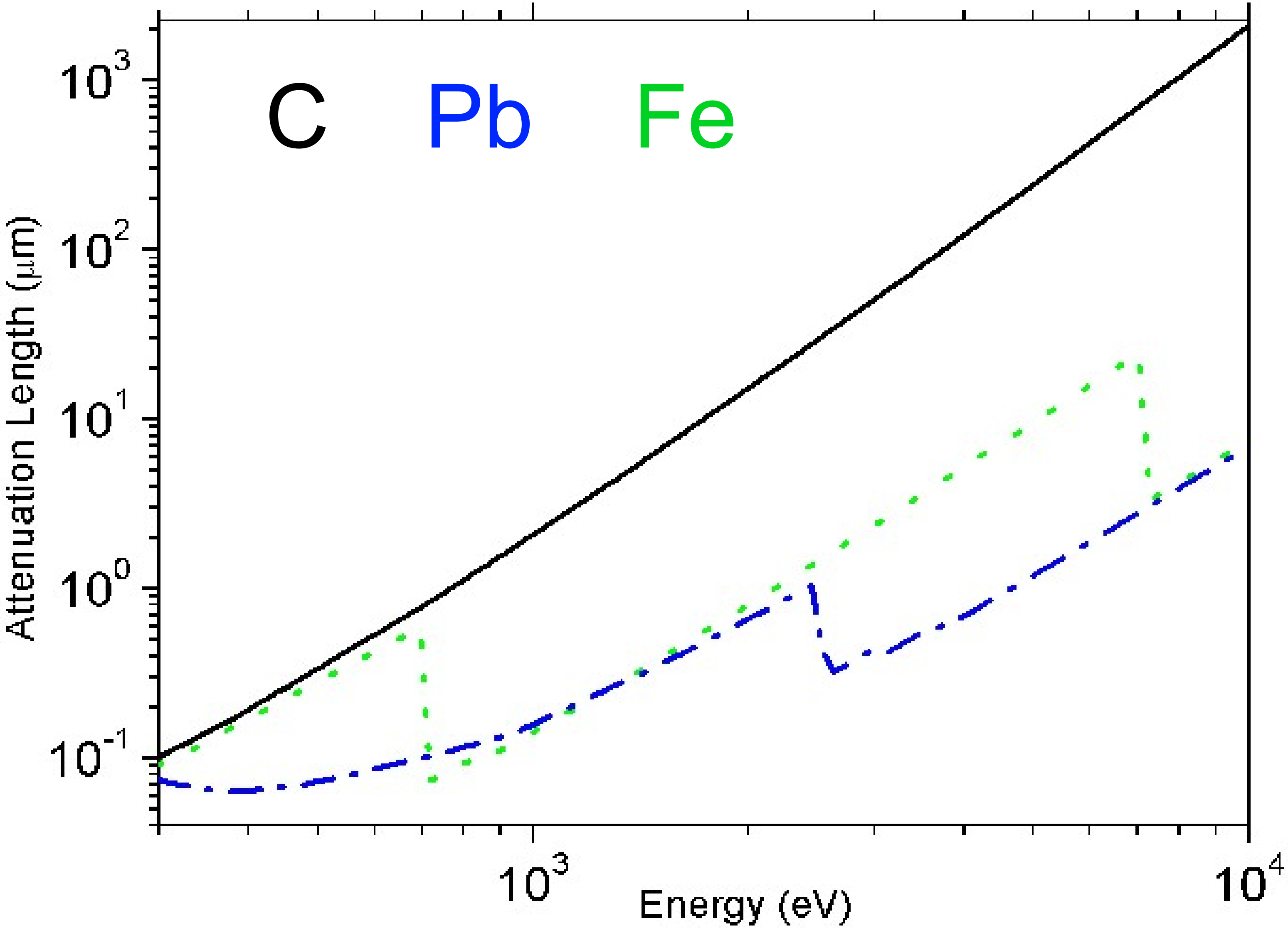


Interaction of x-rays with matter

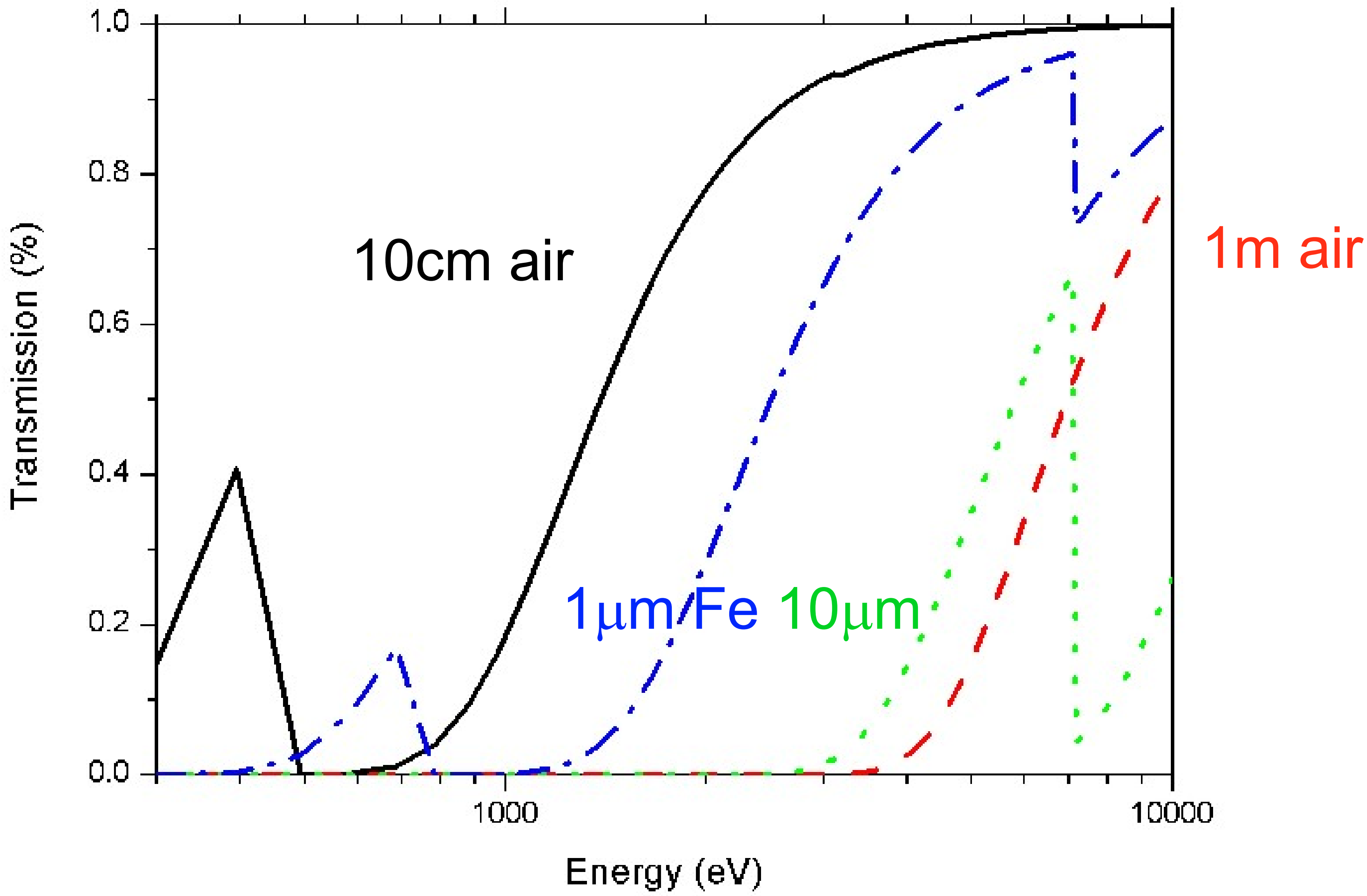
- XAFS studies photoelectric absorption
- Thompson scattering (Diffraction)
- Compton scattering
- Photonuclear scattering (Mössbauer)



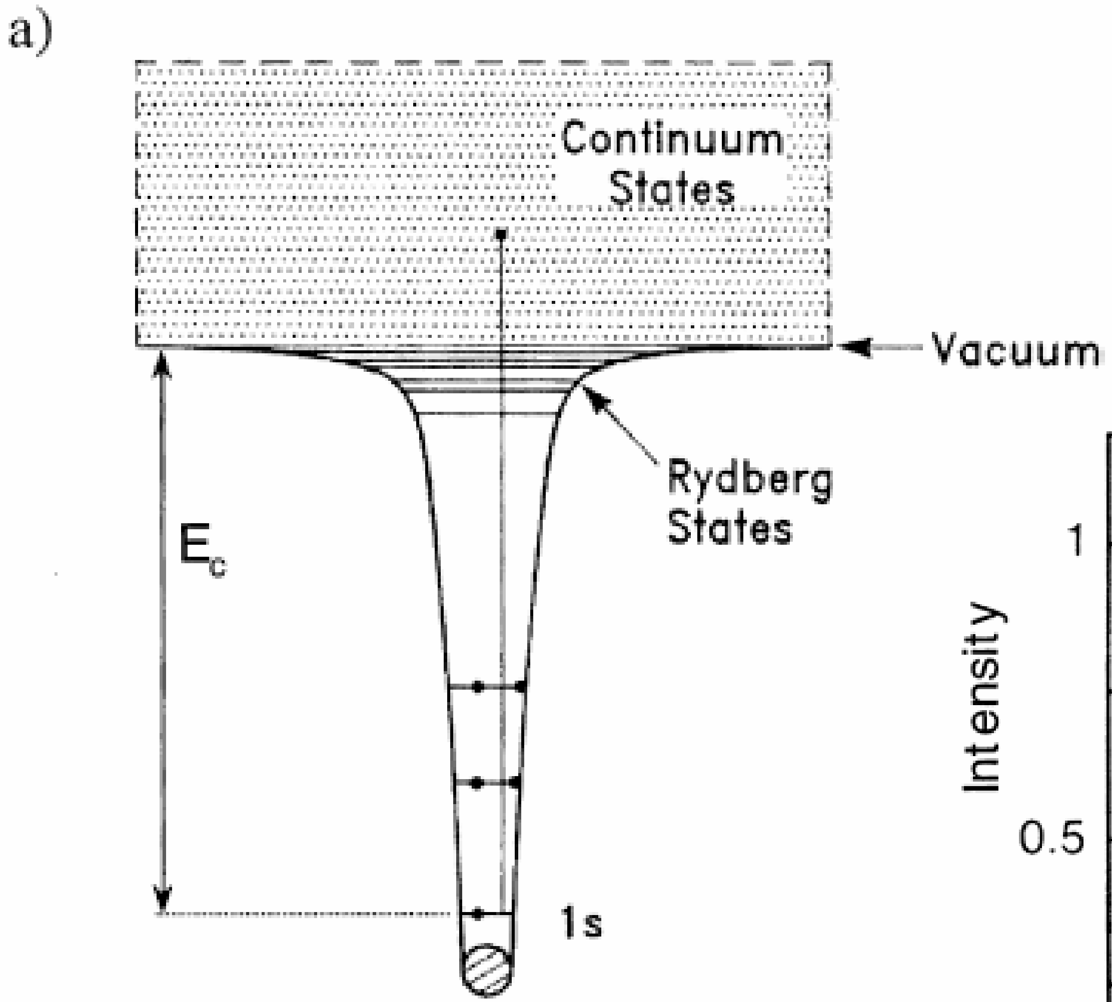
X-ray attenuation

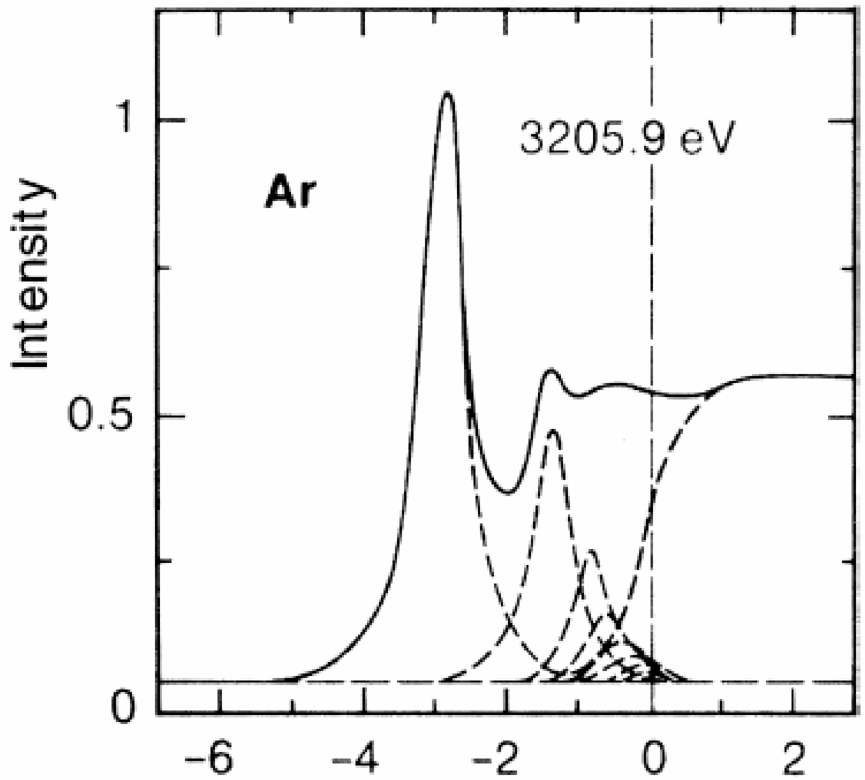


X-ray attenuation

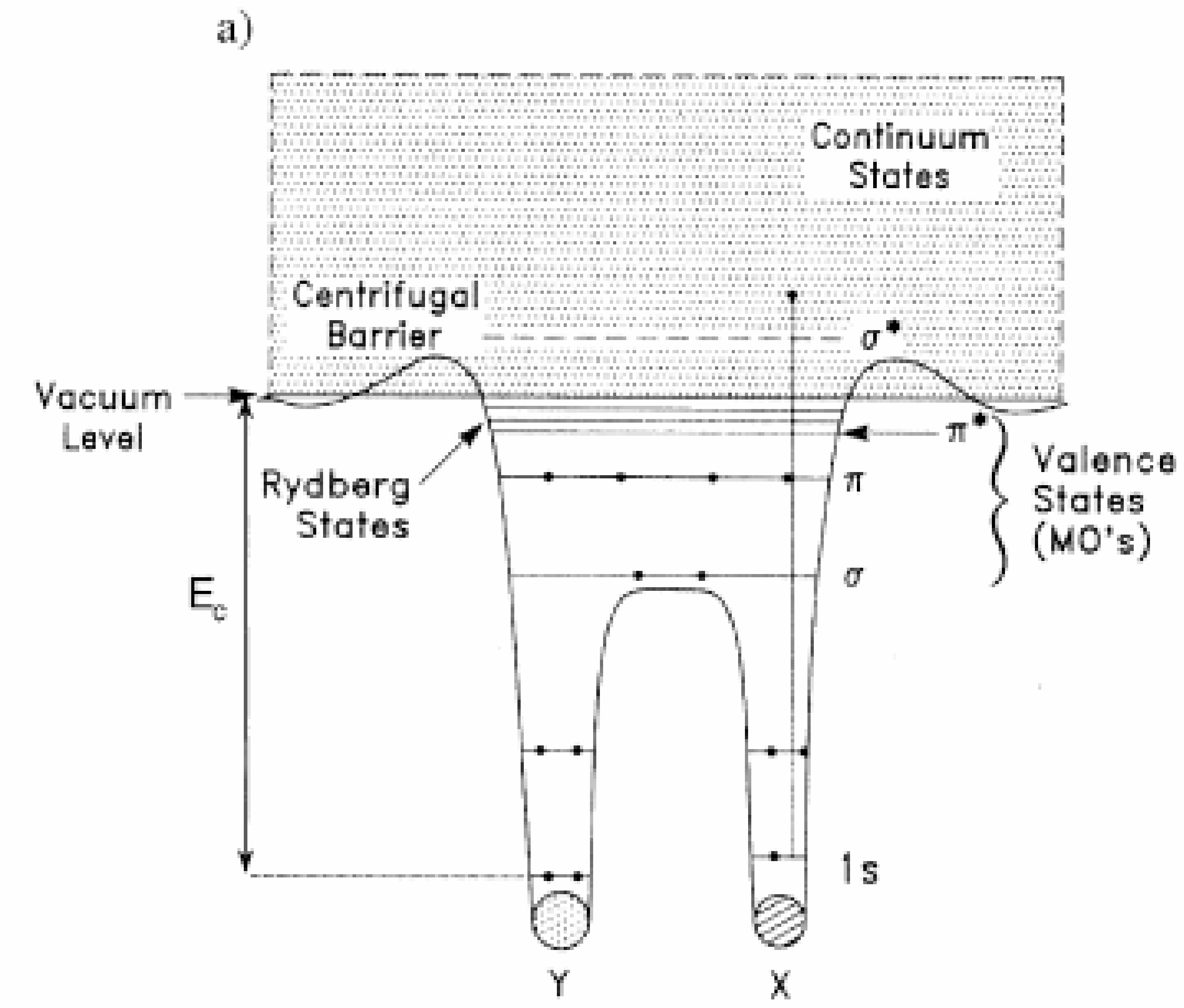


X-ray absorption of an atom

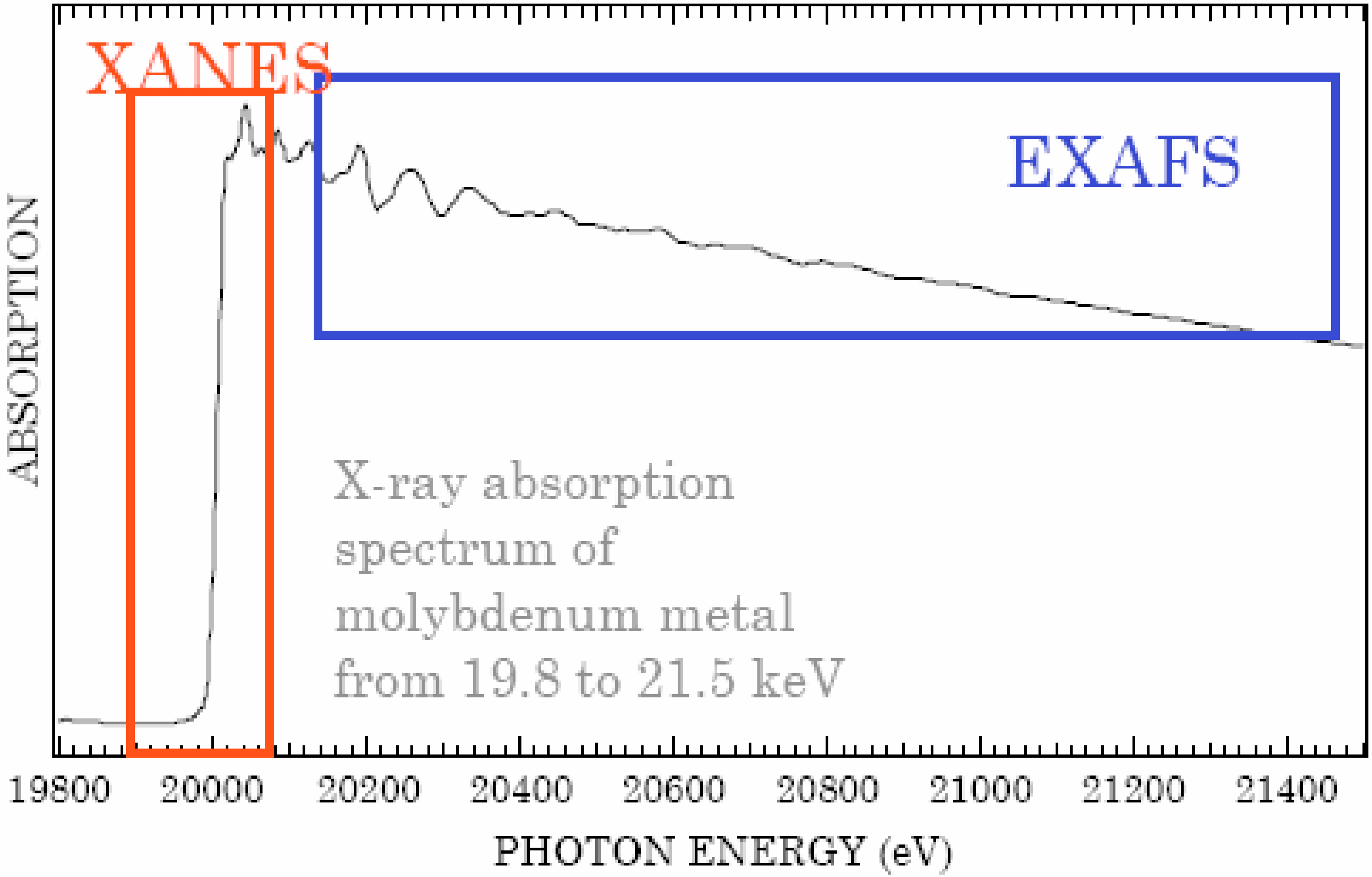




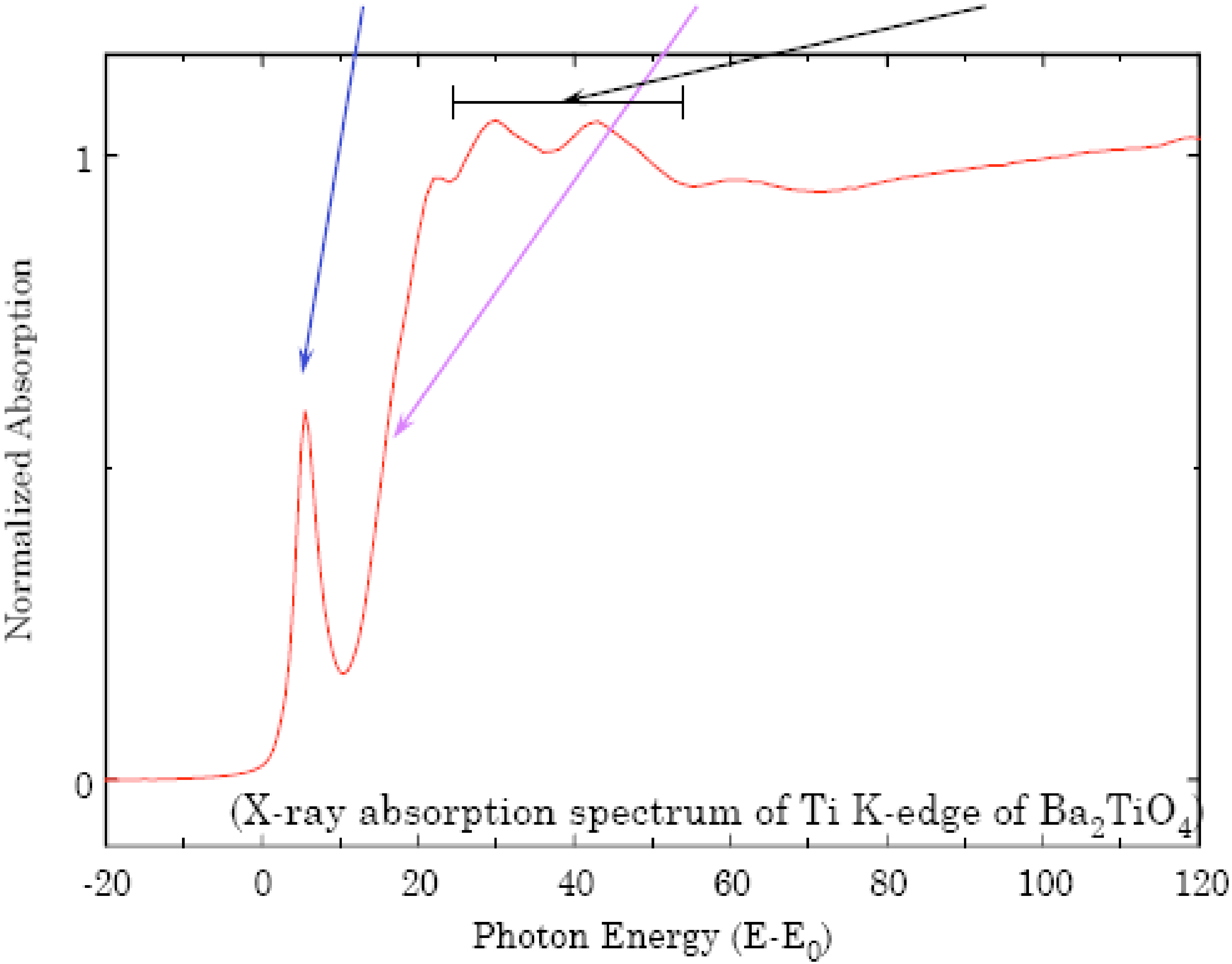
X-ray absorption of a molecule



X-ray absorption



XANES= Pre-edge + Edge + XANES



X-ray absorption

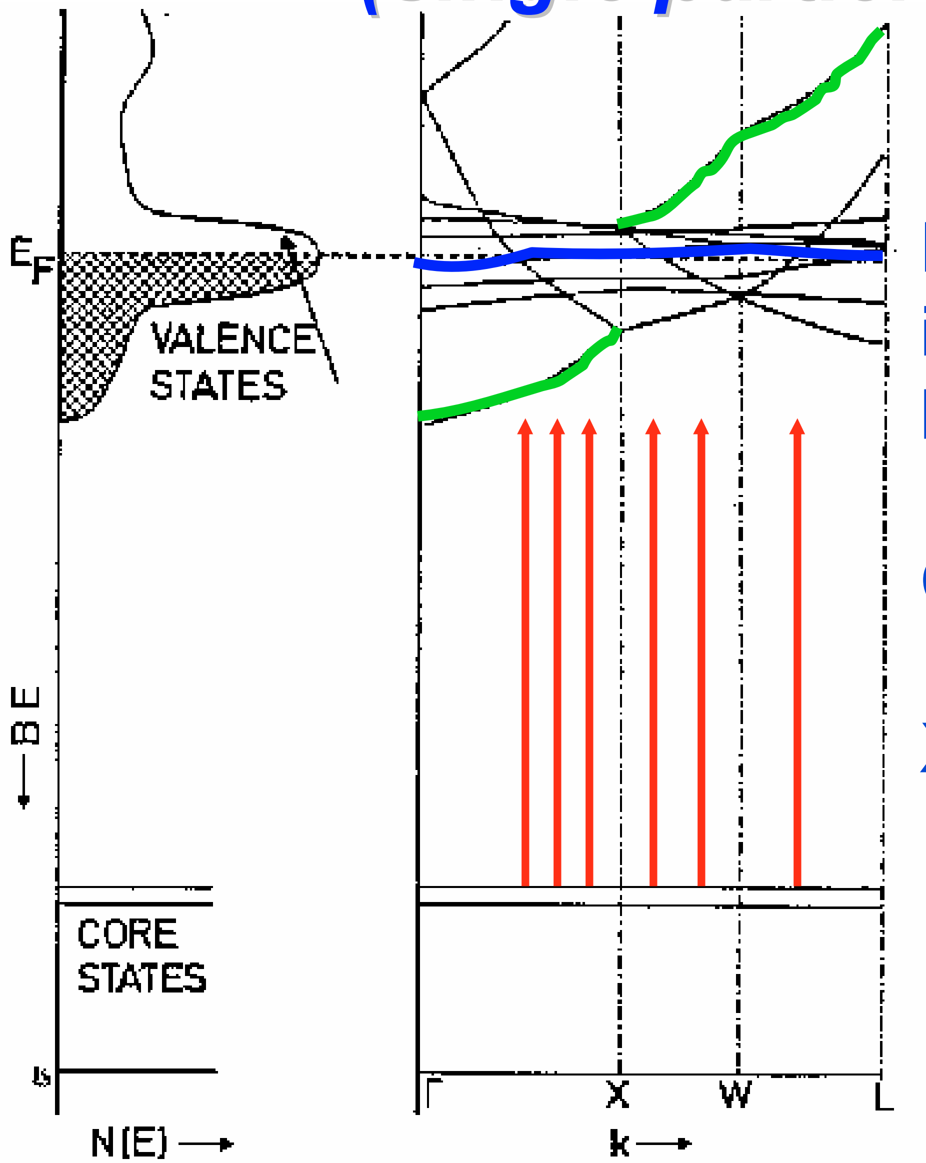
Excitation of core electrons to empty states.

Spectrum given by the **Fermi Golden Rule**

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

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

X-ray absorption
(single particle interpretation)

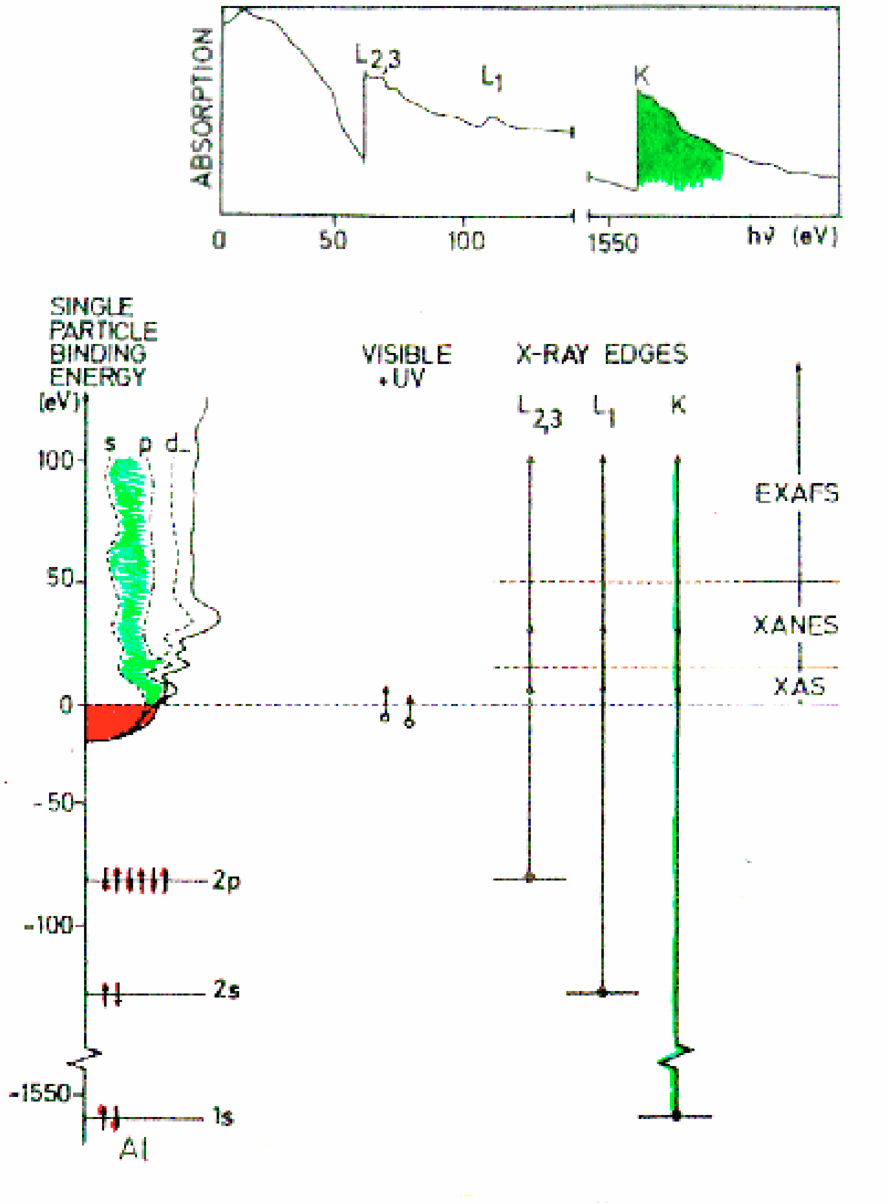


Density of States (DOS) is the integral over k-space of the band structure.

Core states have no dispersion.

XAS preserves momentum (k)

X-ray absorption
(single particle interpretation)

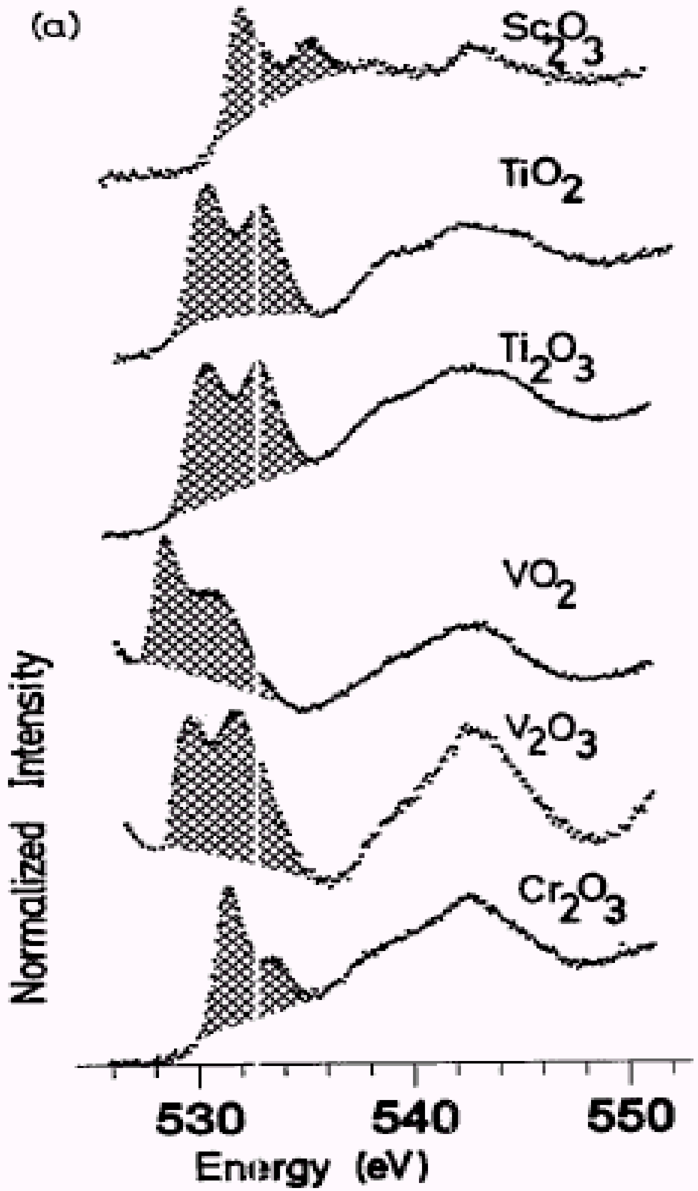


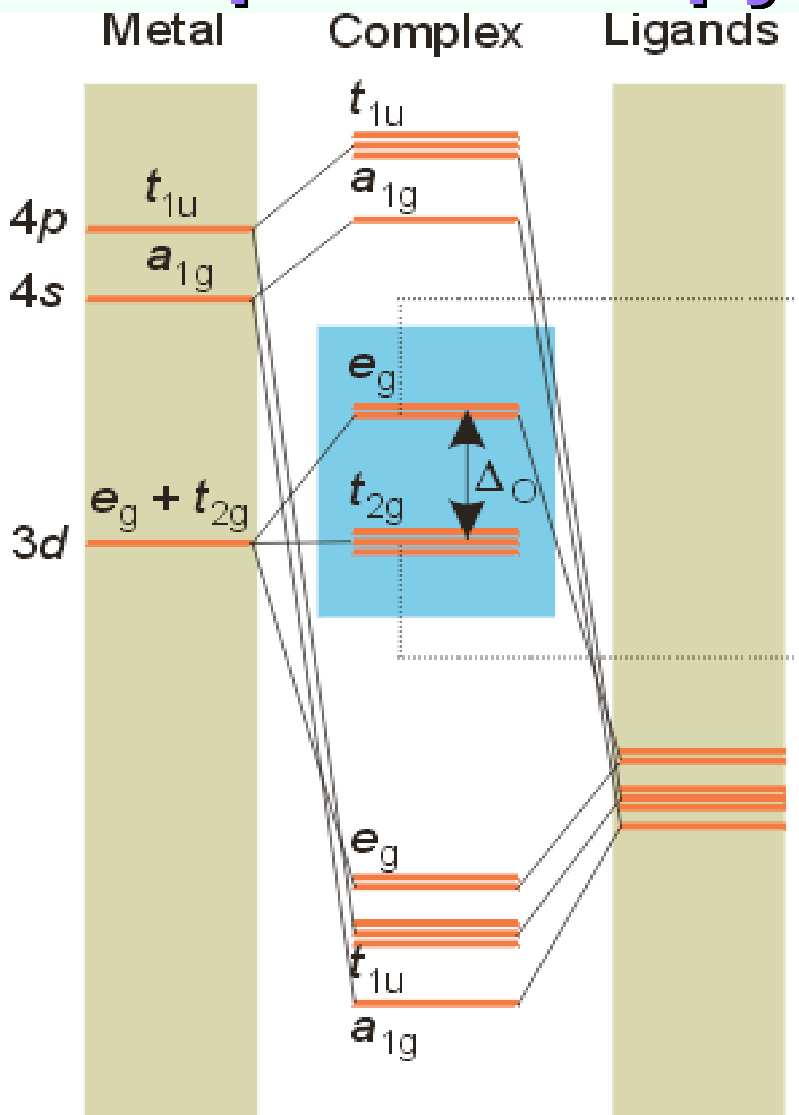
- Element specific DOS
- L specific DOS
- Dipole selection rule (ΔL= ±1)

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

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

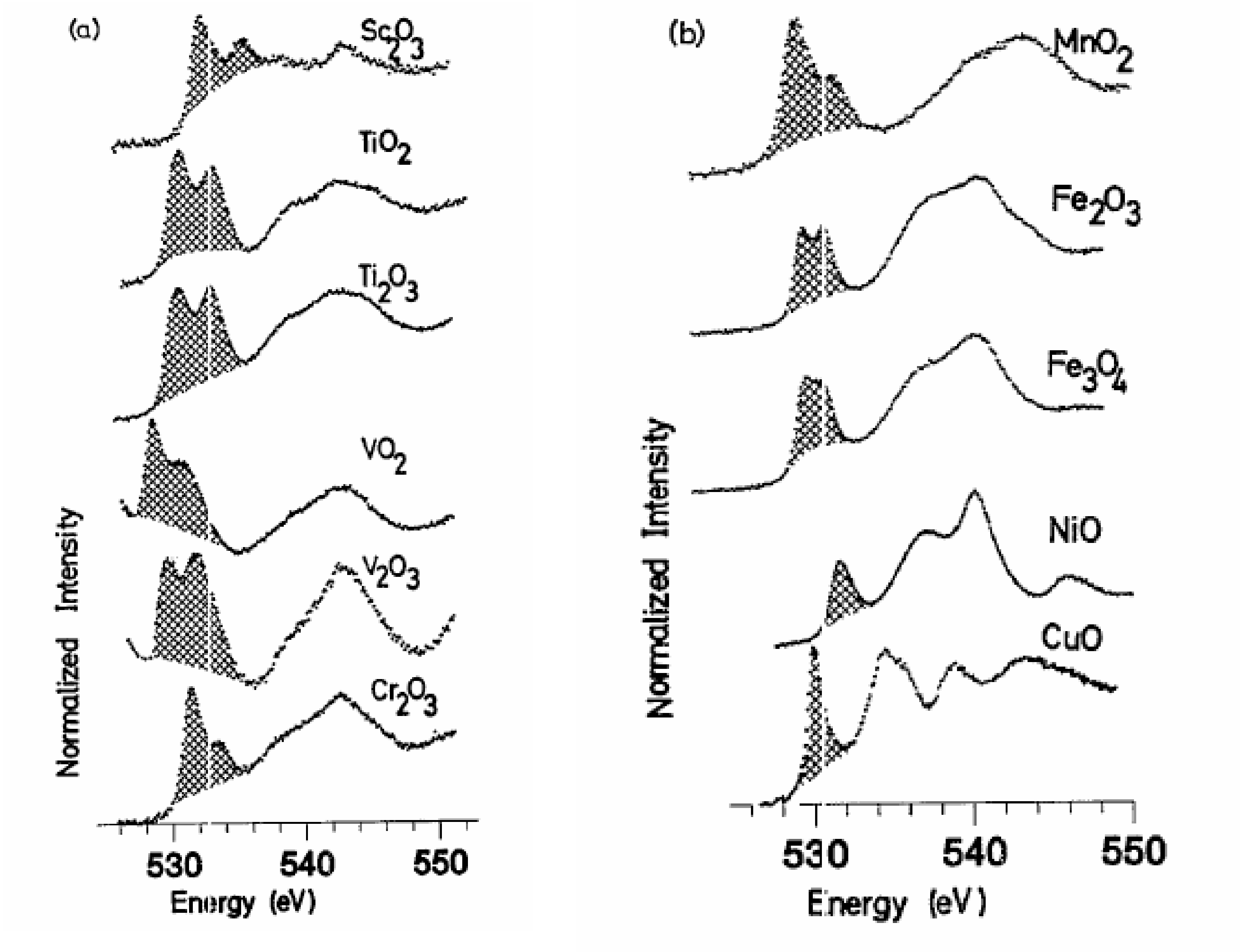
X-ray Absorption Spectroscopy



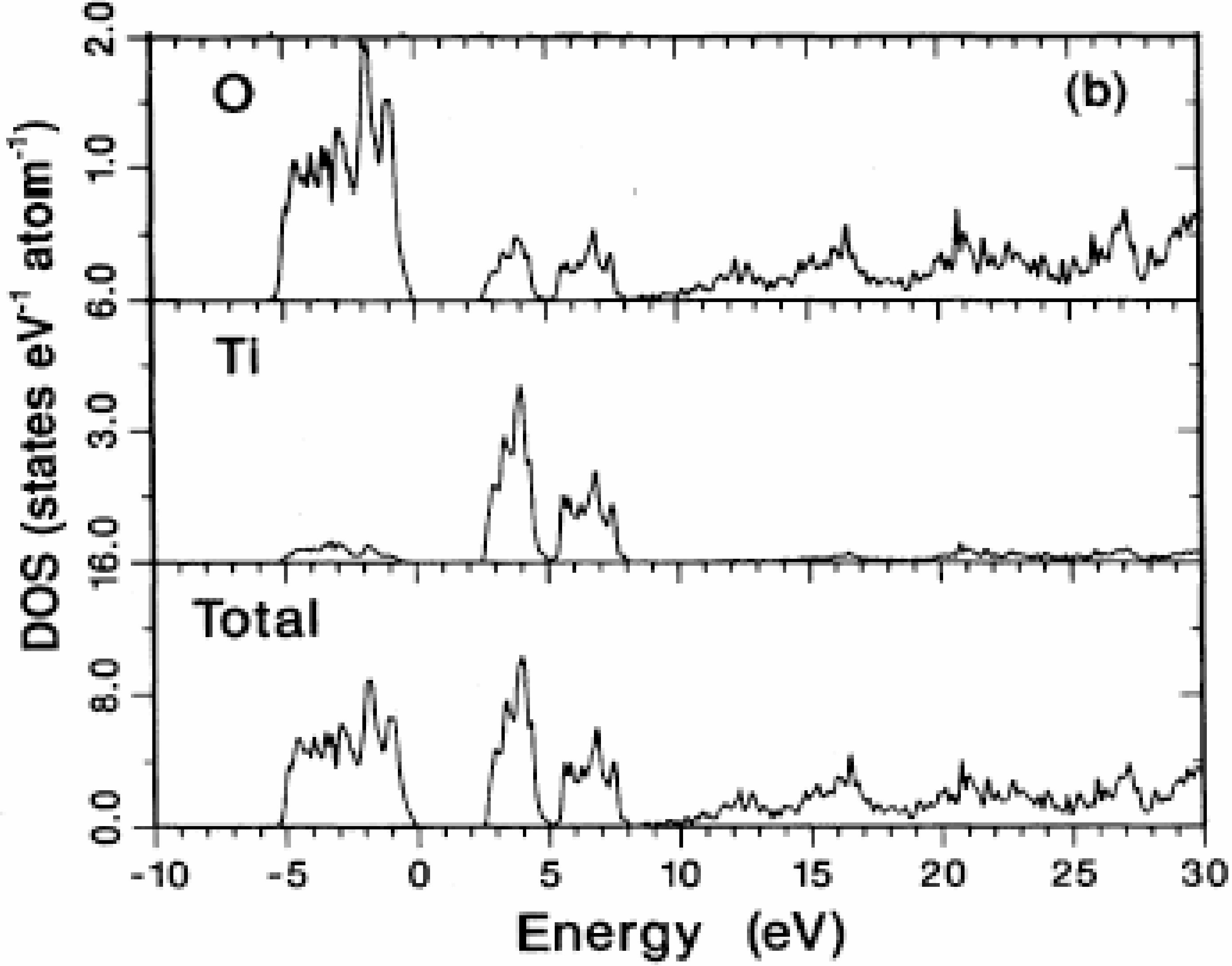


Phys. Rev. B.
40, 5715 (1989) / 48, 2074 (1993)

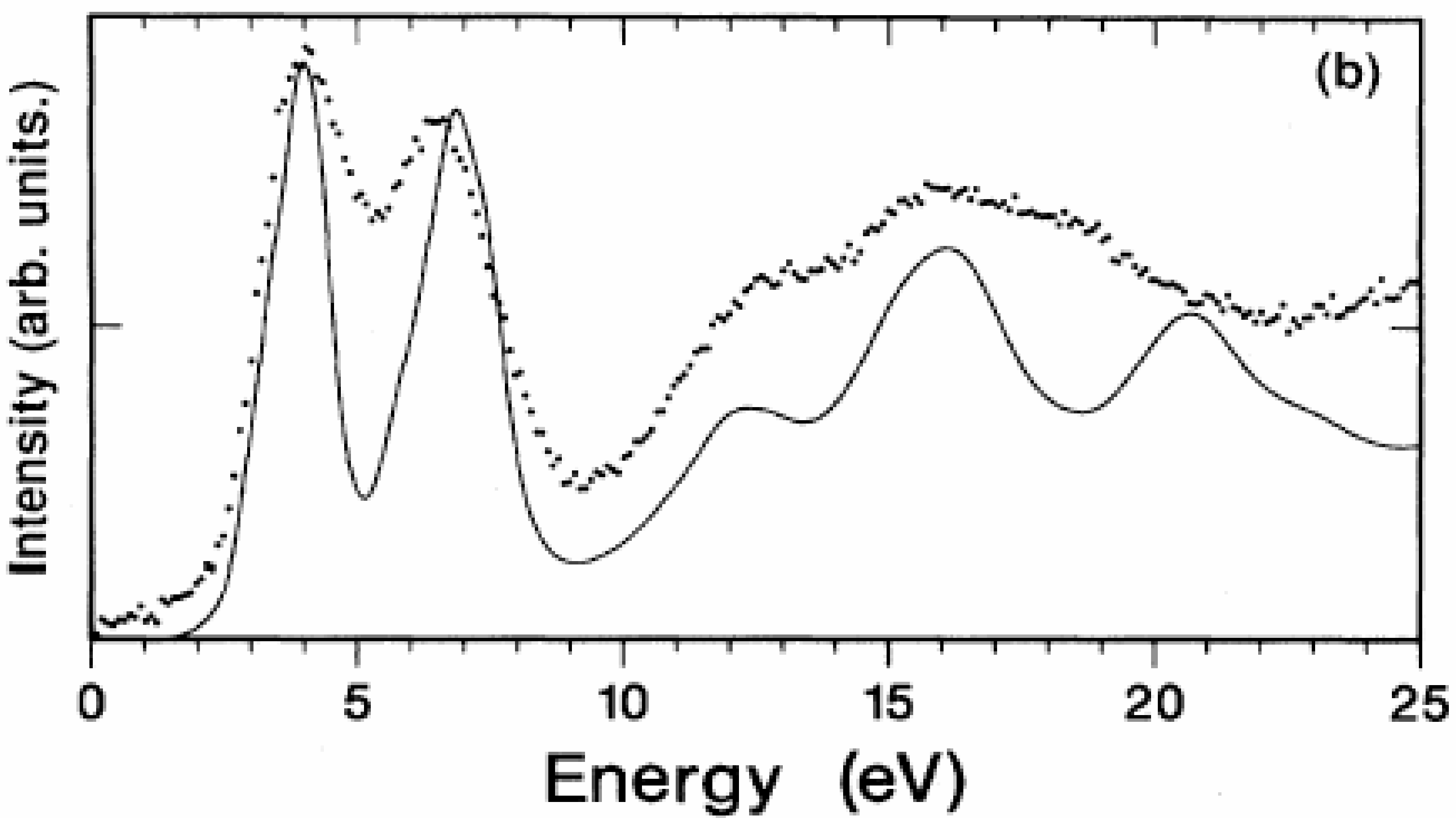
X-ray absorption



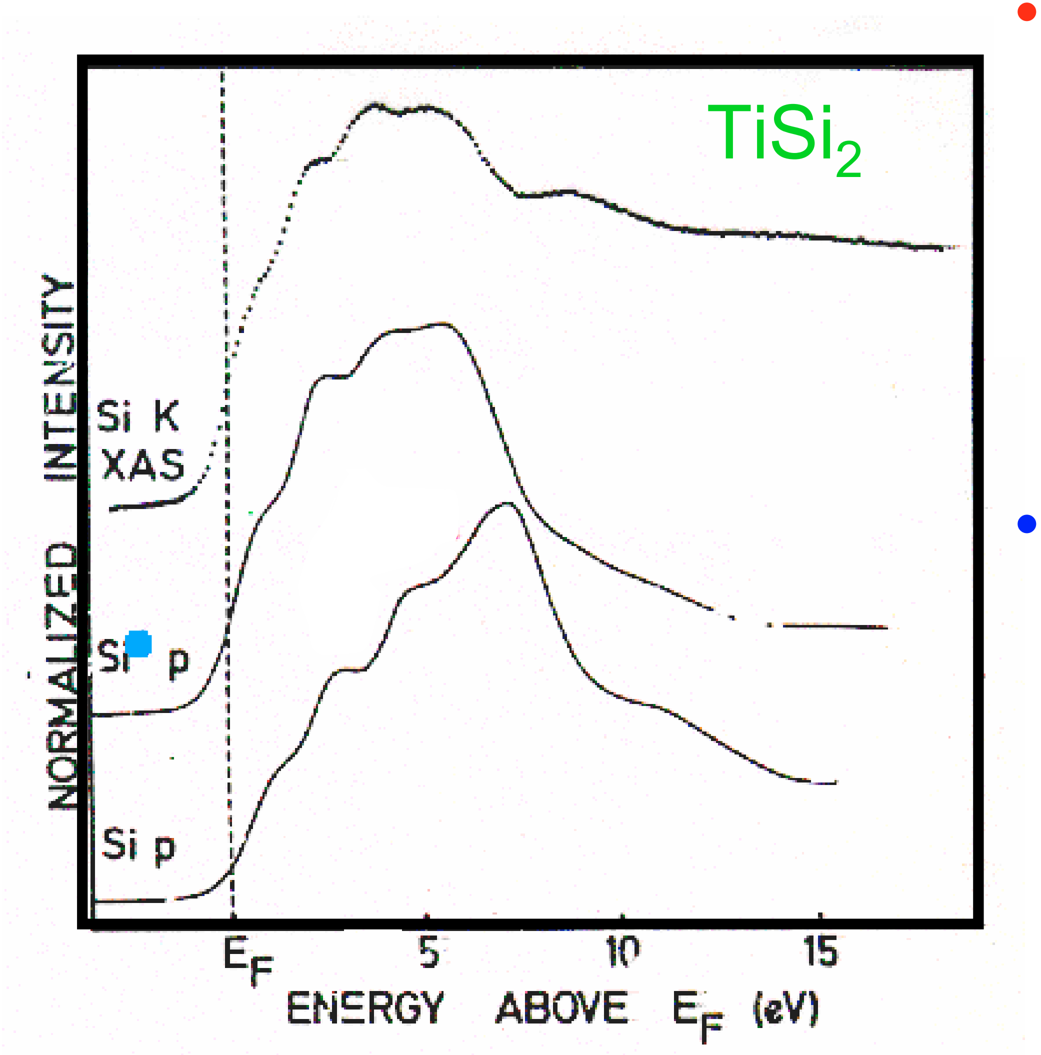
Electronic Structure



Electronic Structure



X-ray absorption: core hole effect

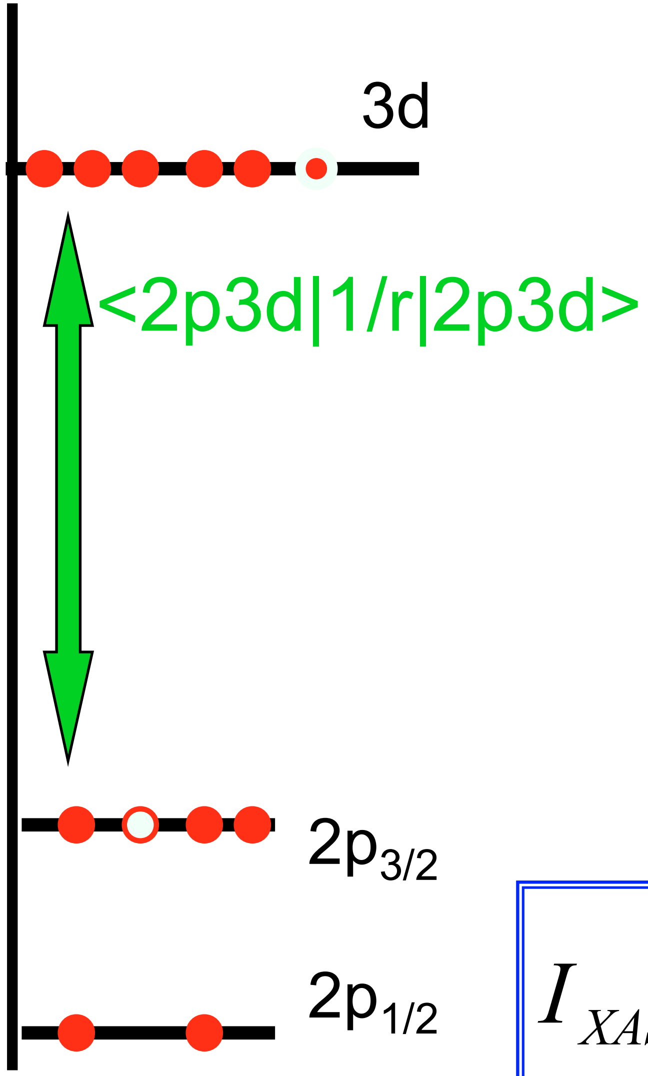


- **Final State Rule:** Spectral shape of XAS looks like final state DOS

- **Initial State Rule:** Intensity of XAS is given by the initial state

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

X-ray absorption: multiplet effects

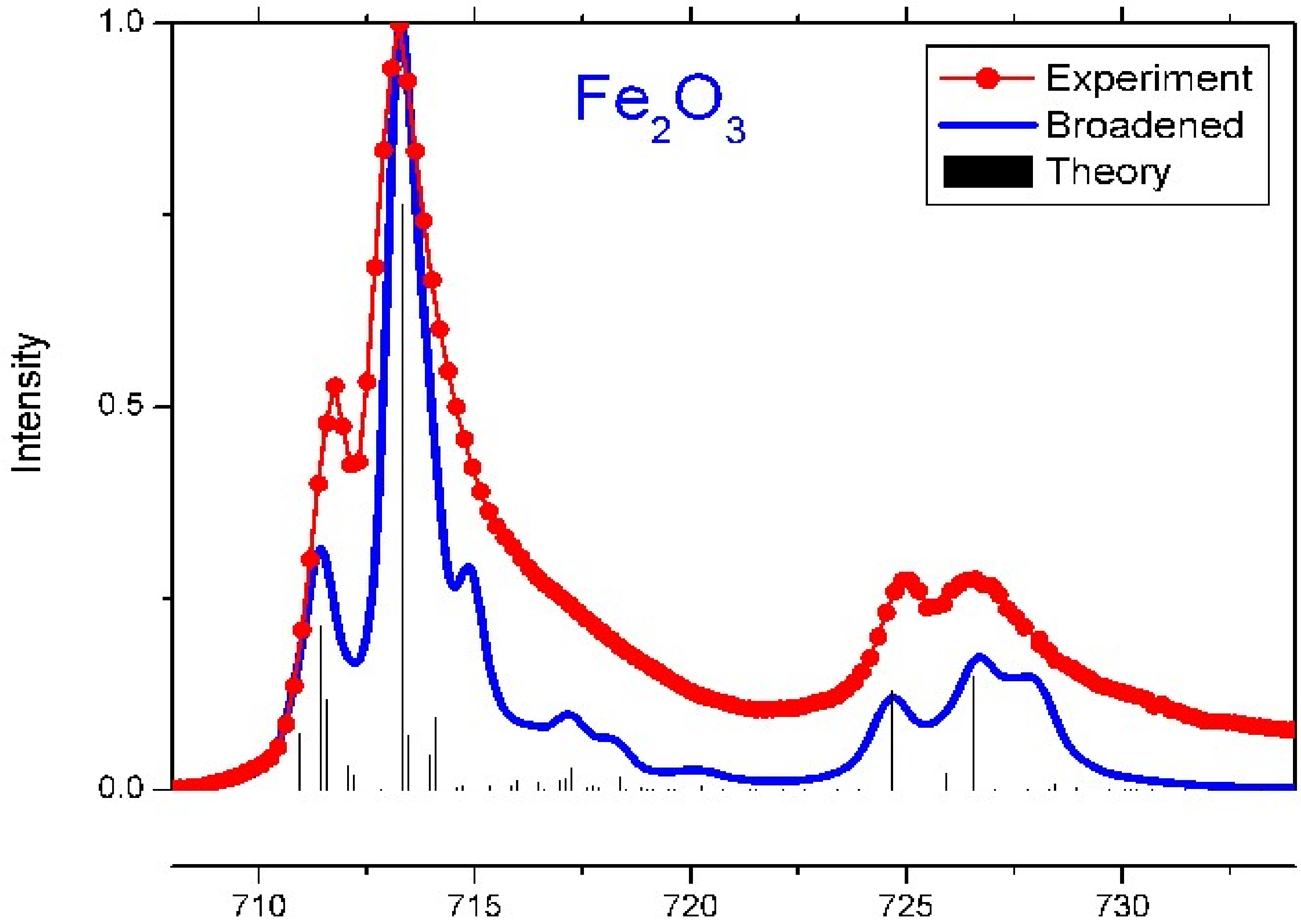


Strong overlap of core and valence wave functions

Single Particle model breaks down

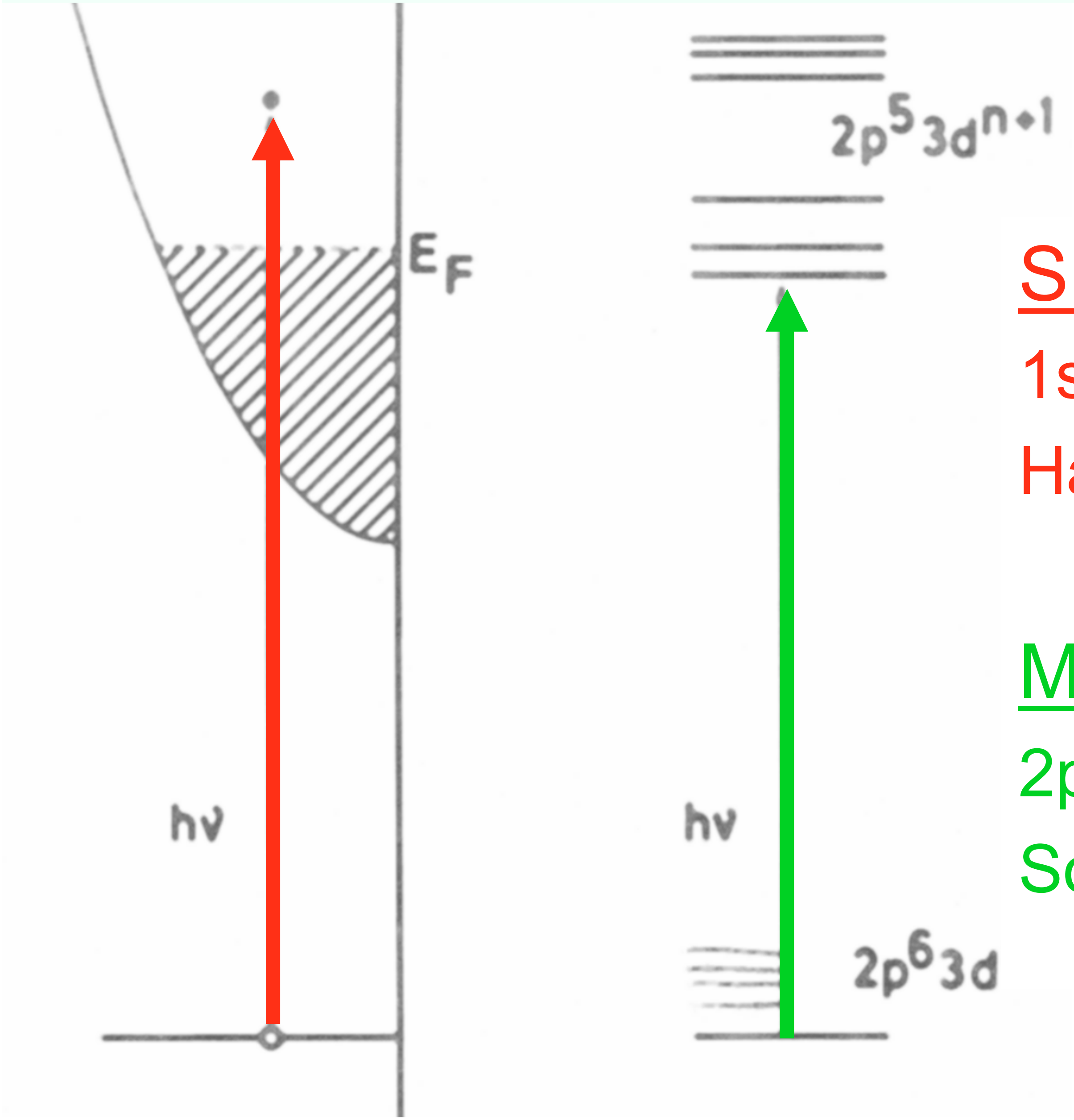
$$I_{XAS} \sim \left| \left\langle 2p^5 3d^6 \middle| \hat{e} \cdot r \middle| 3d^5 \right\rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

X-ray absorption: multiplet effects



www.anorg.chem.uu.nl/people/staff/FrankdeGroot/QCS.htm

X-ray Absorption Spectroscopy



Single Particle:

1s edges

Hard x-rays

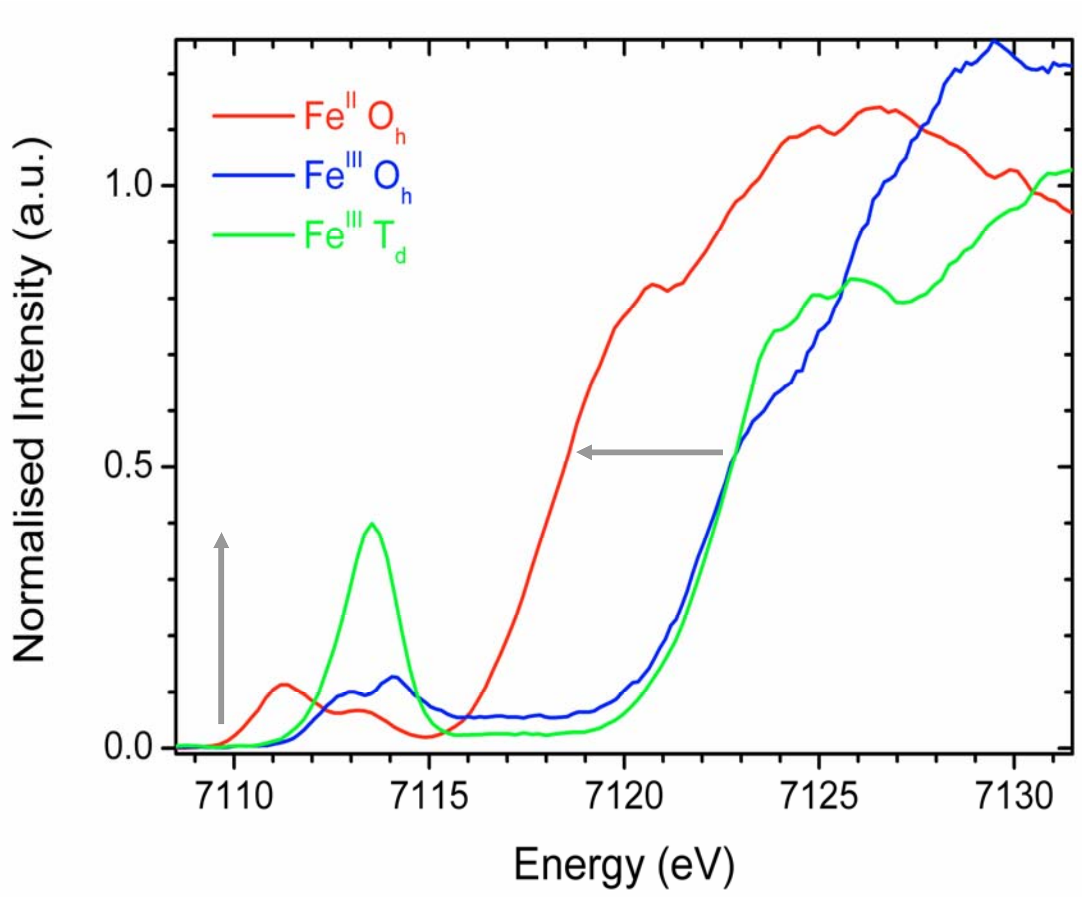
Multiplets:

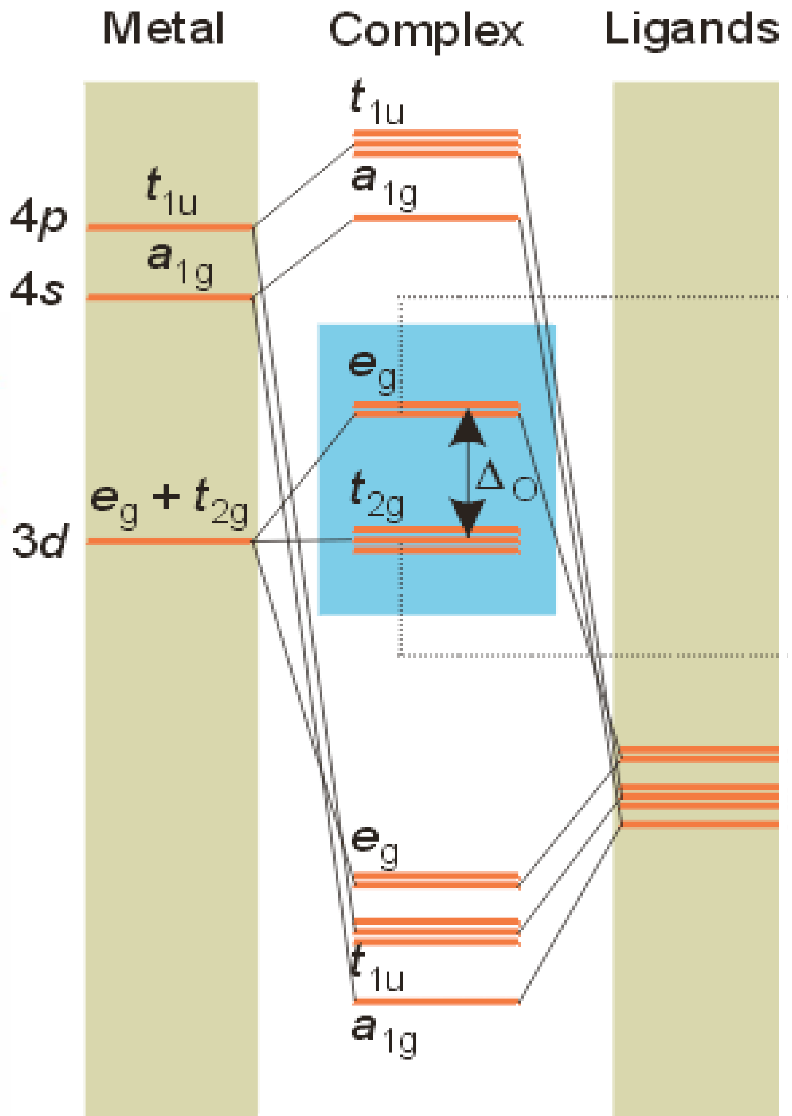
2p, 3s, 3p edges

Soft x-rays

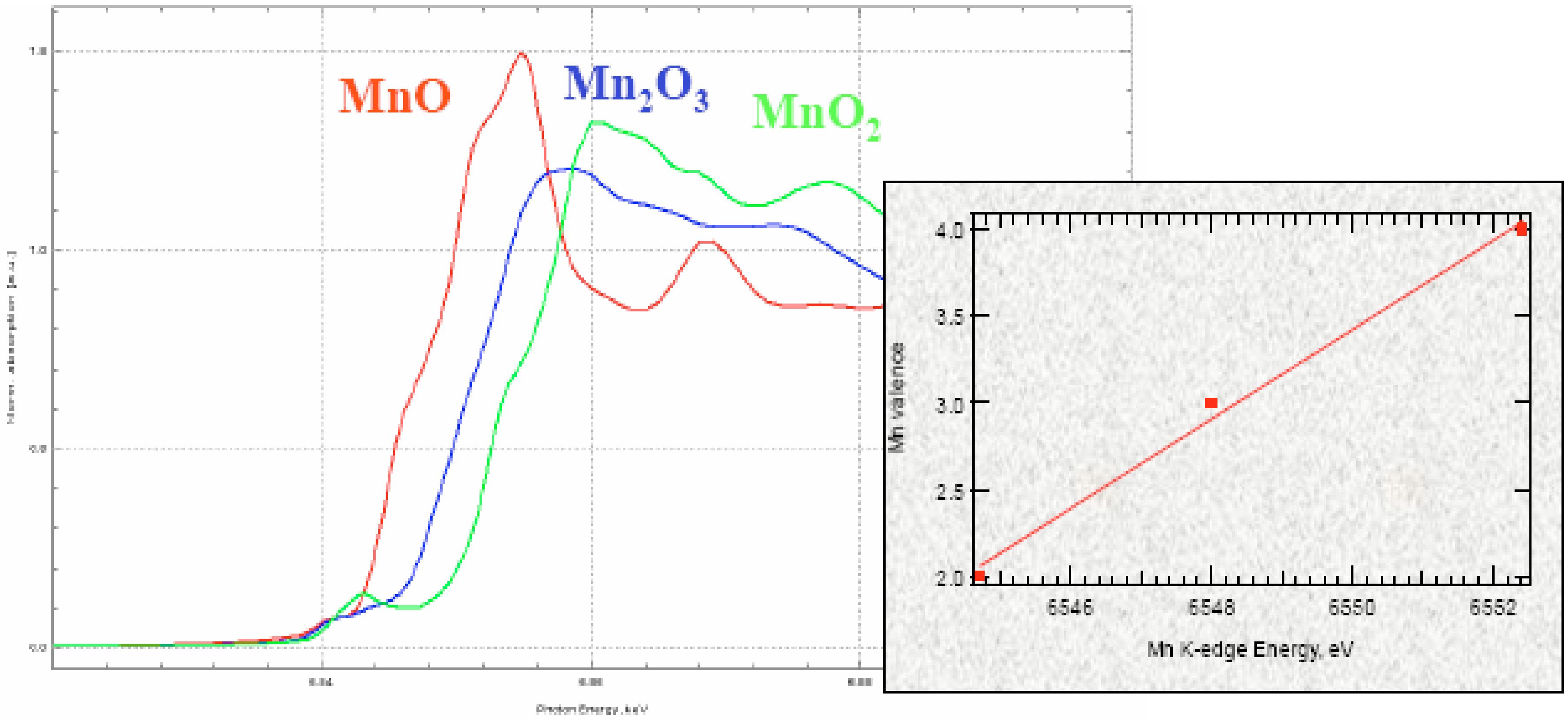
K edge XANES

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





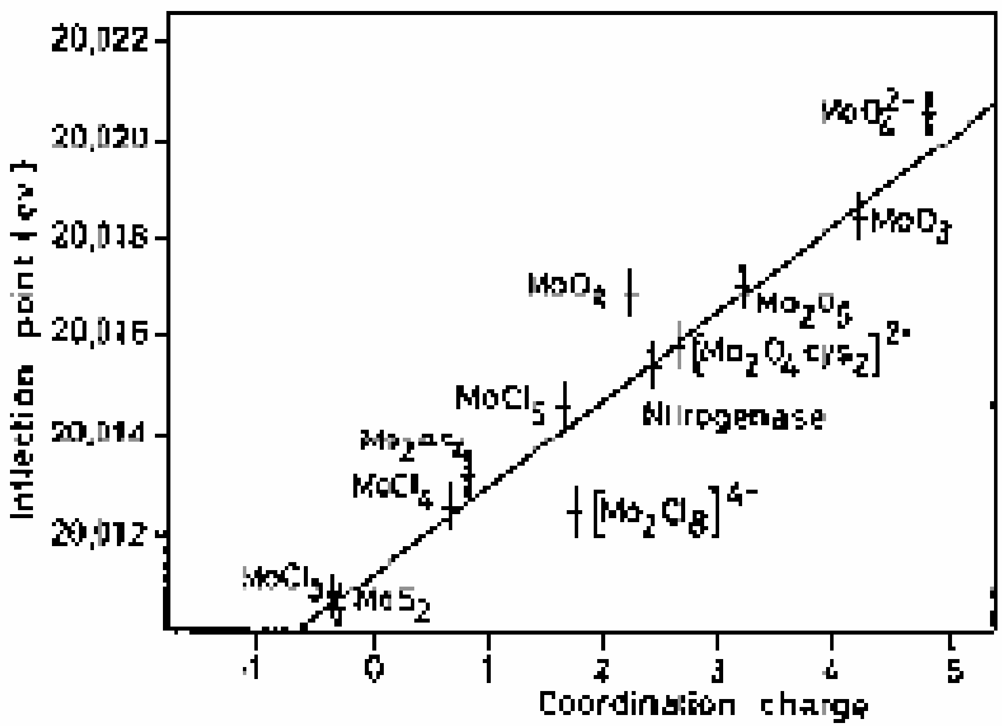
XANES: qualitative analysis



Edge position gives valence

XANES: qualitative analysis

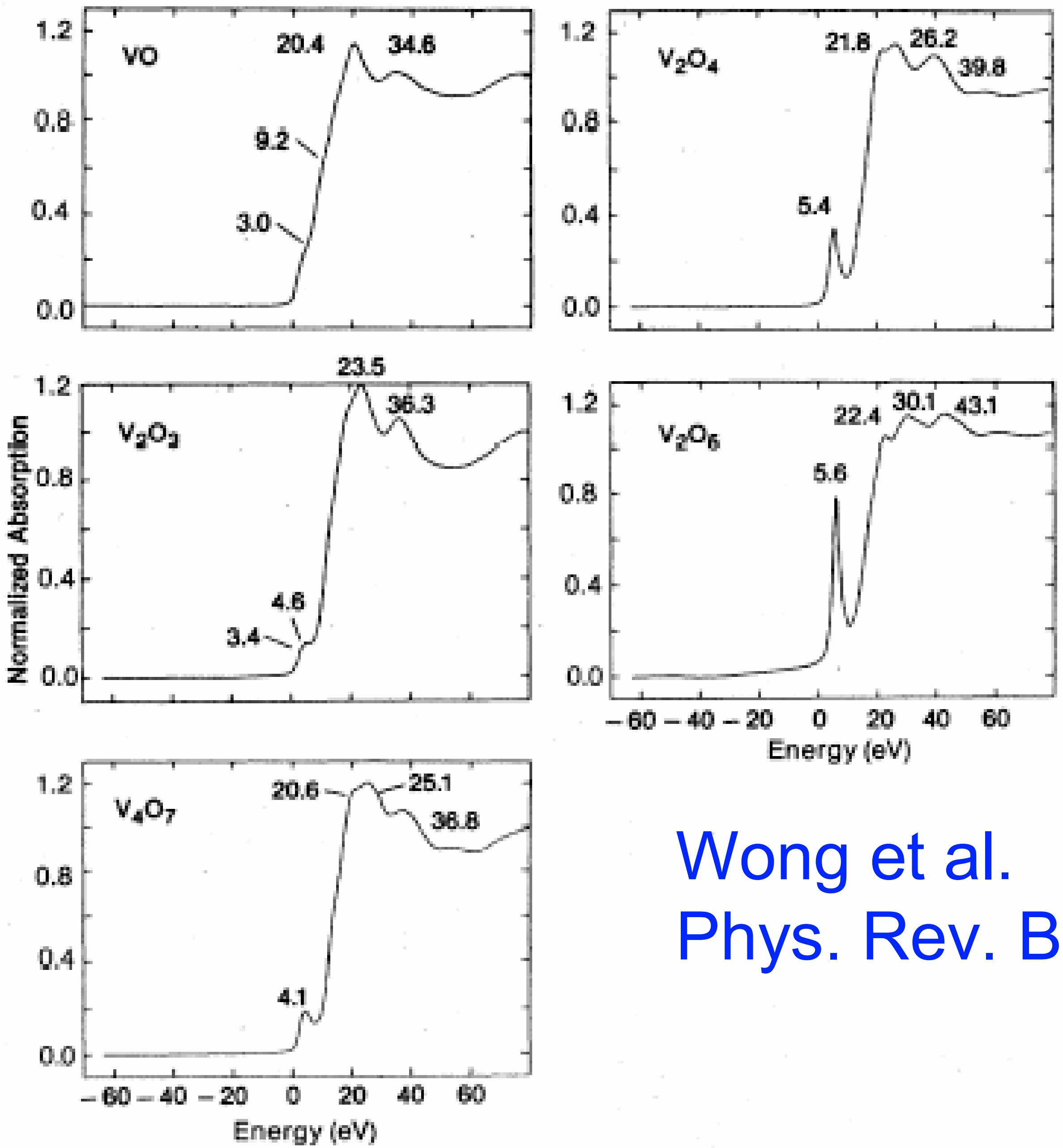
Mo K-edge



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

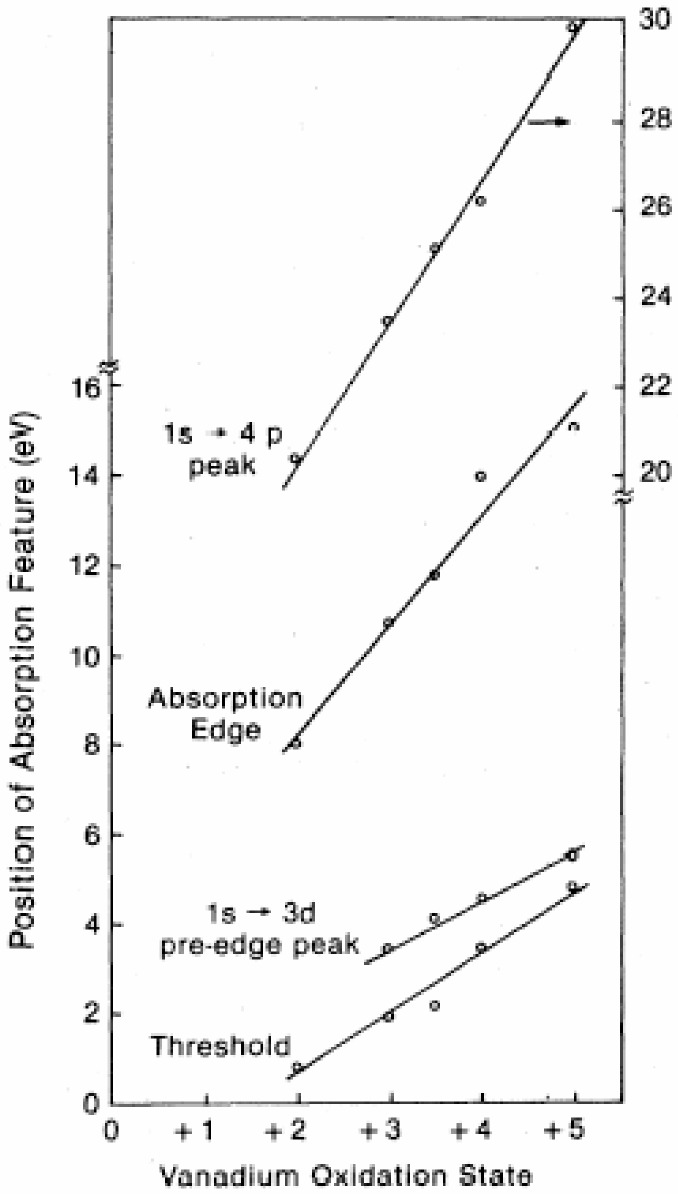
Edge position gives valence

XANES: qualitative analysis



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

XANES: qualitative analysis

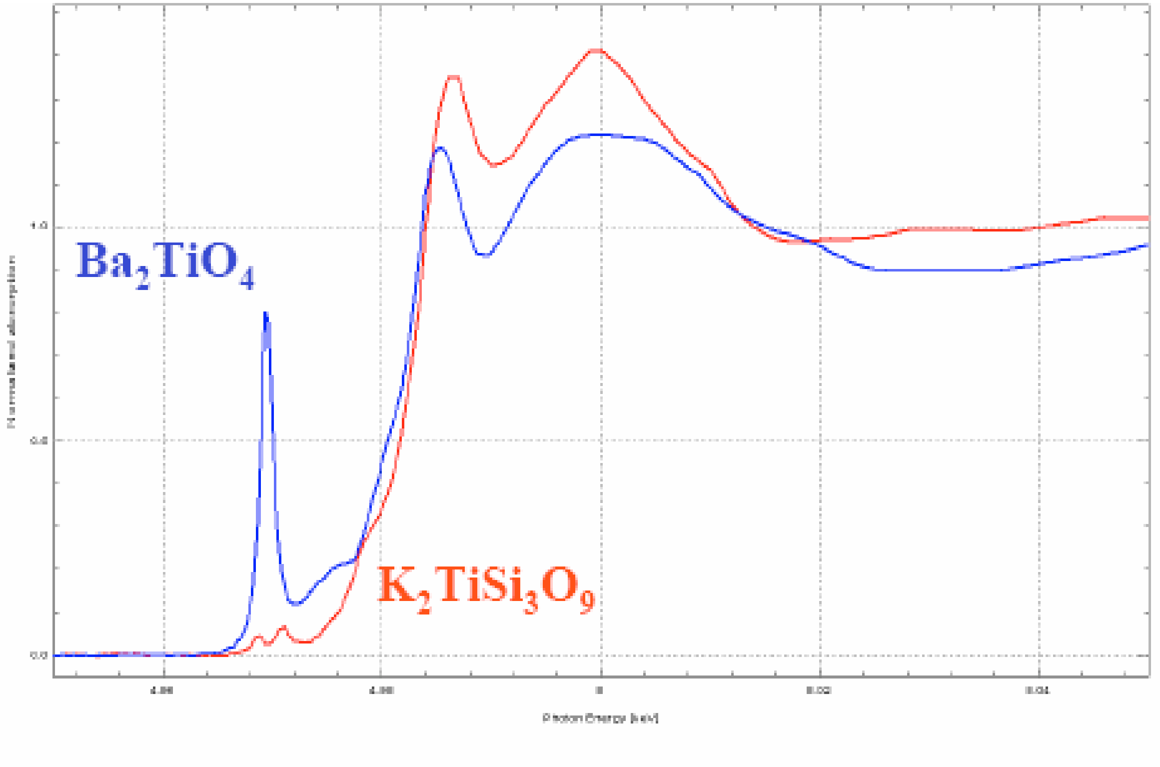


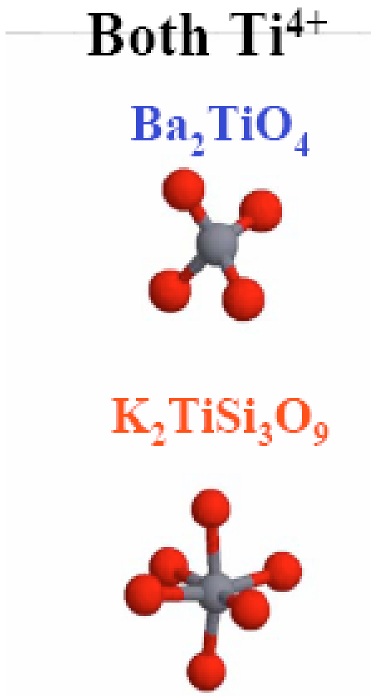
Edge position gives valence

Pre-edge gives valence

Different slopes

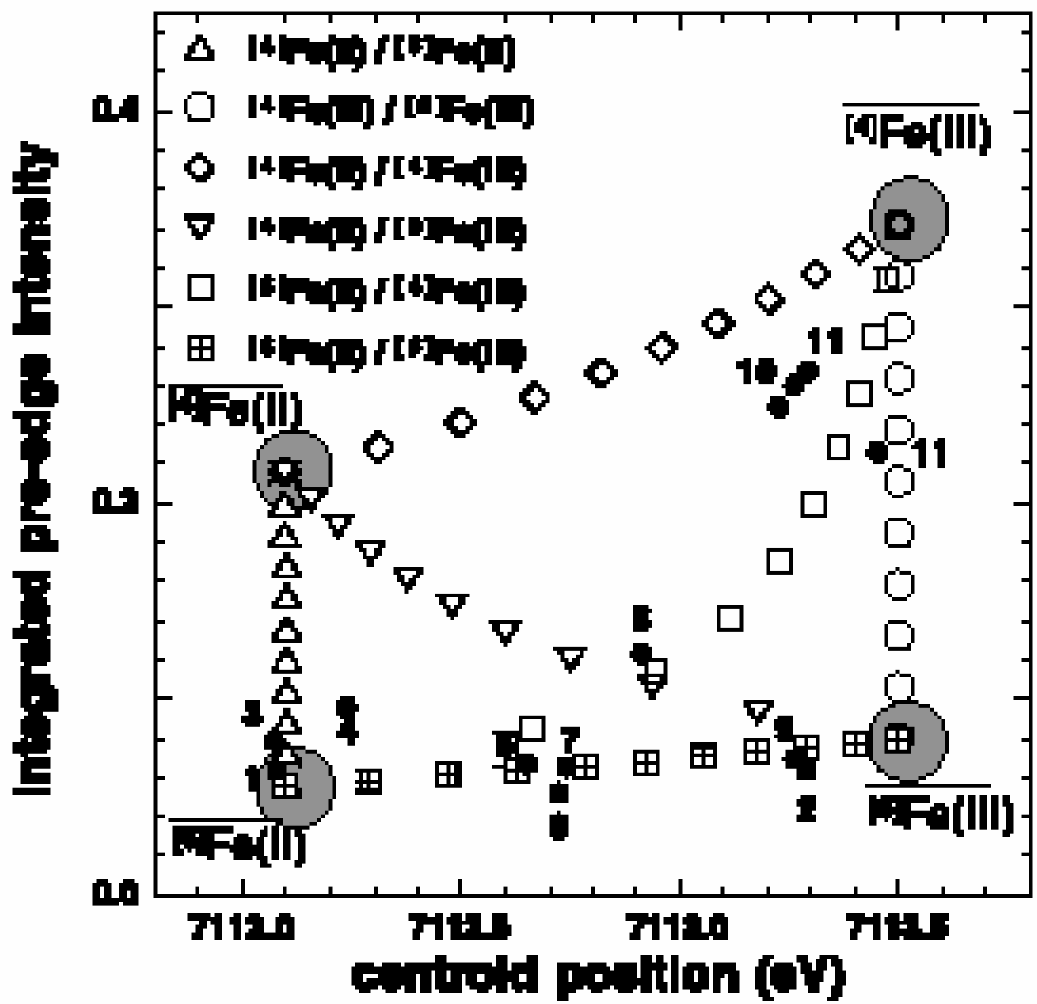
XANES: qualitative analysis





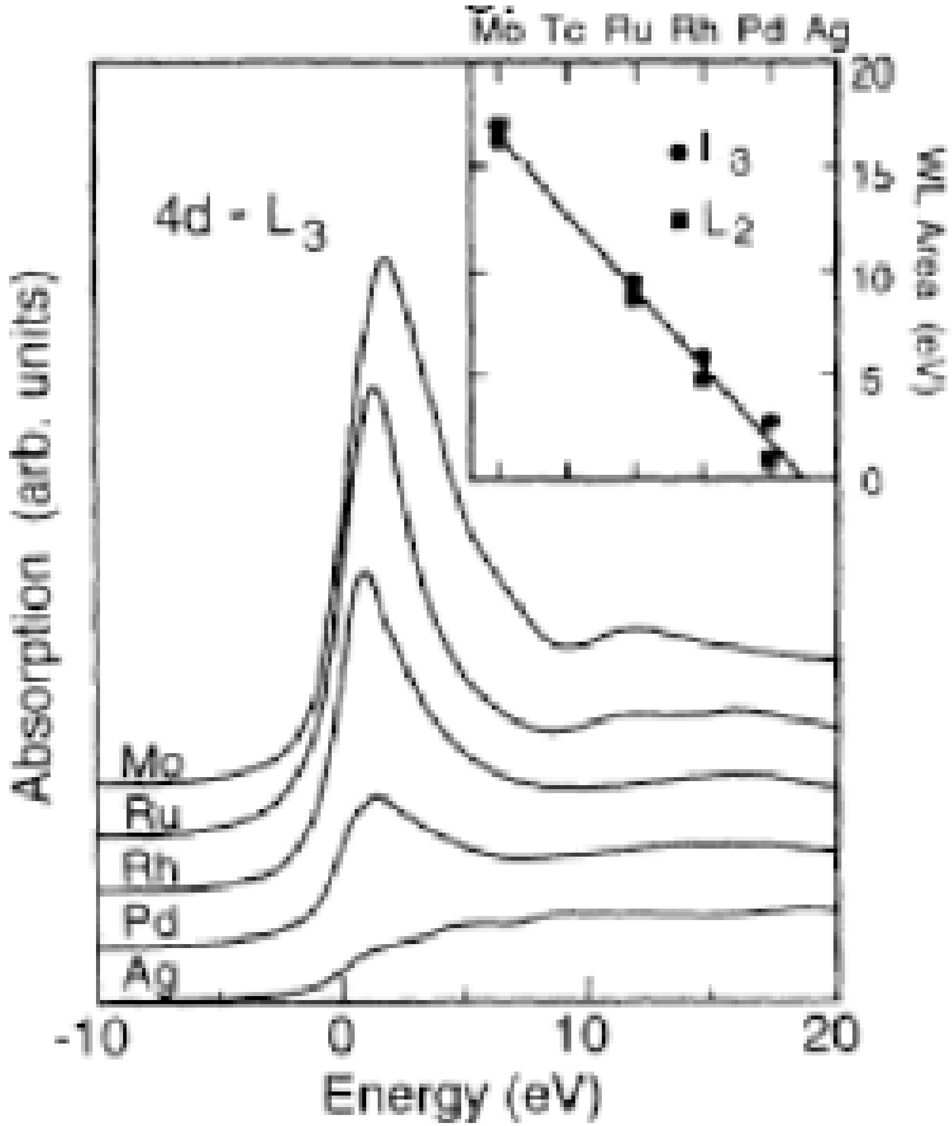
Pre-edge intensity gives site symmetry

XANES: qualitative analysis



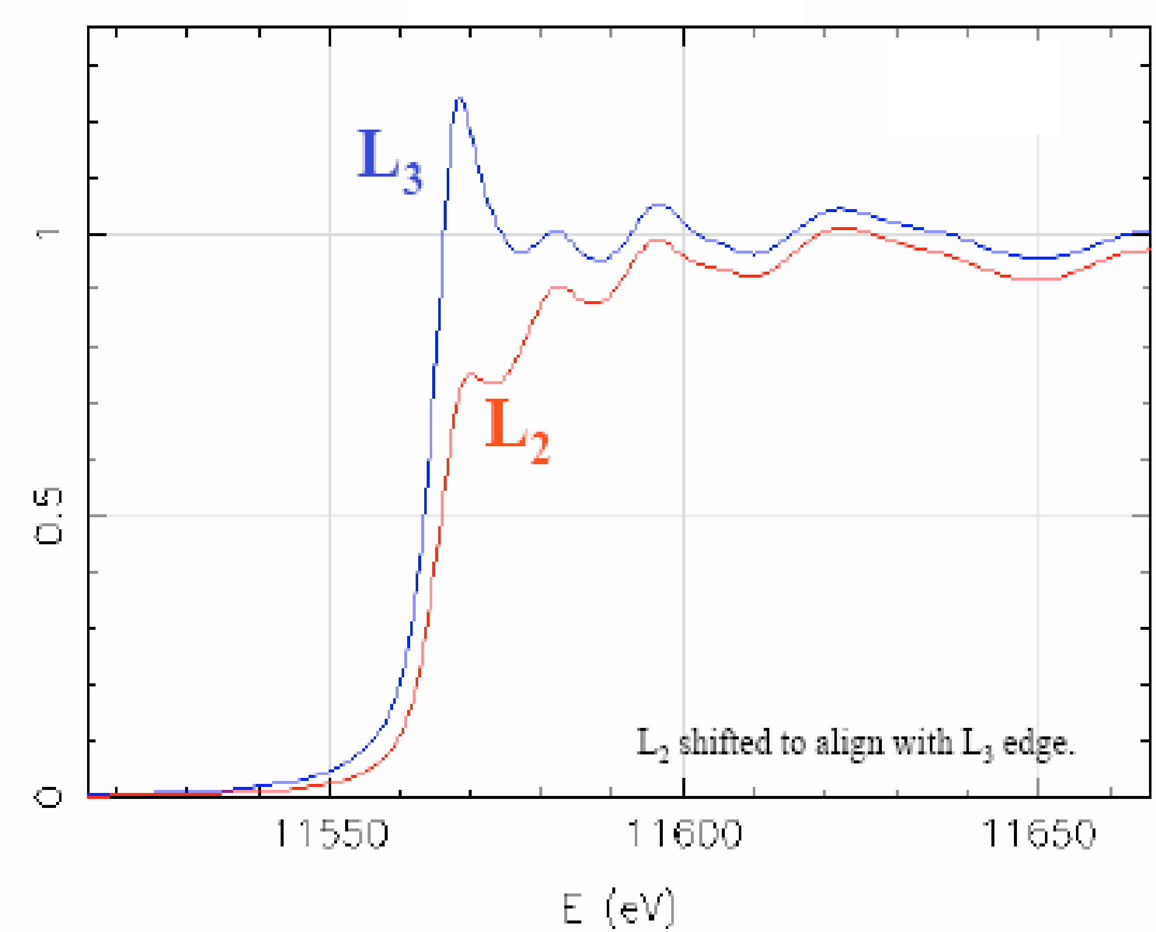
Pre-edge intensity and center

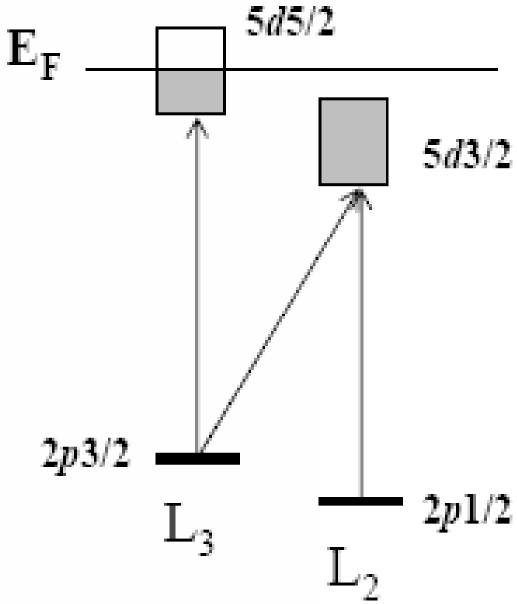
XANES: qualitative analysis



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

XANES: qualitative analysis



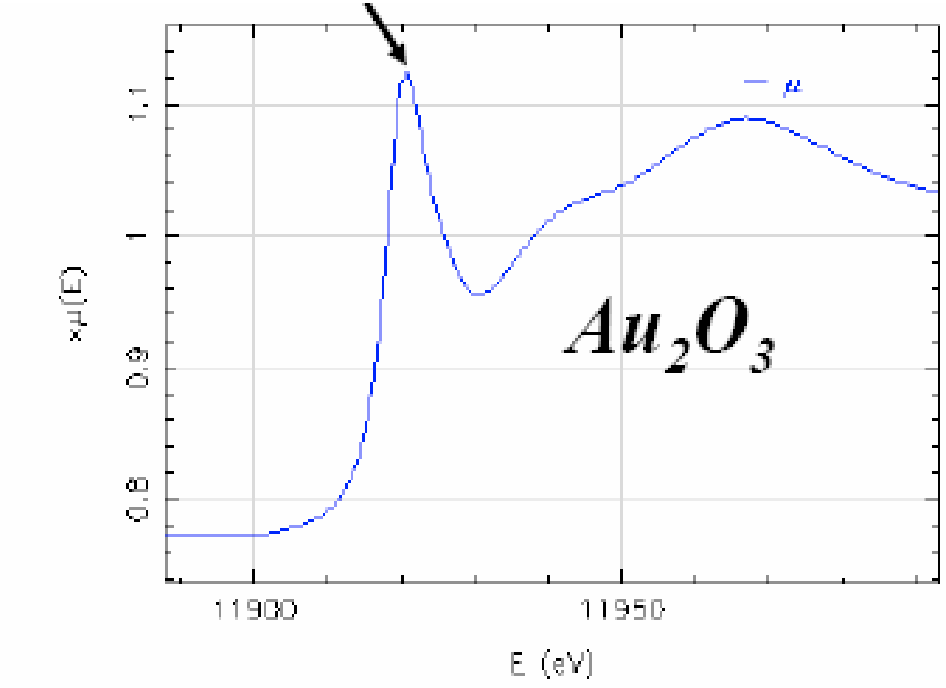


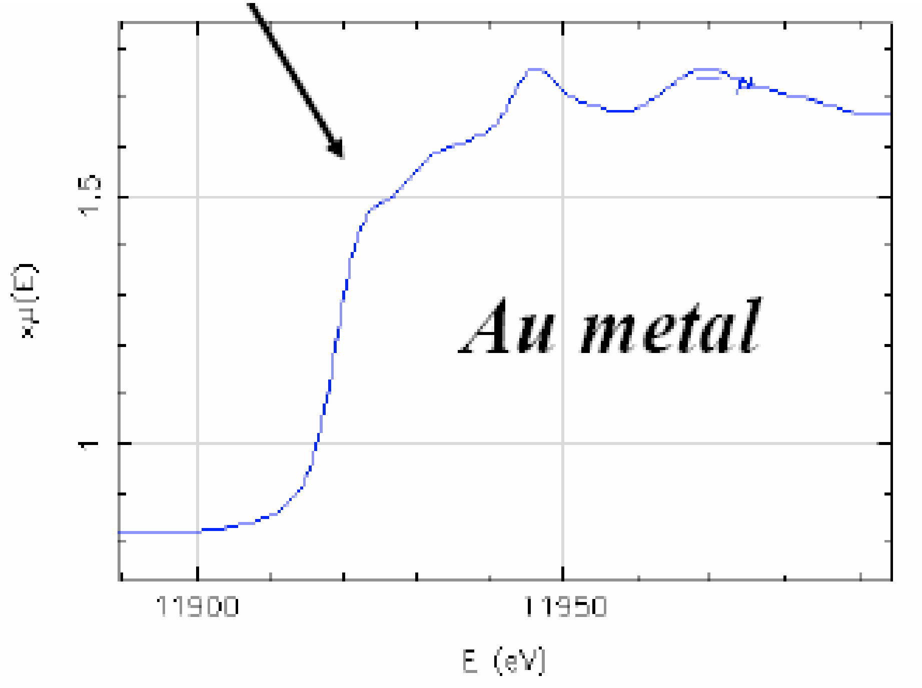
- Pt 5*d*3/2 filled, so no white line.

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

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

XANES: qualitative analysis



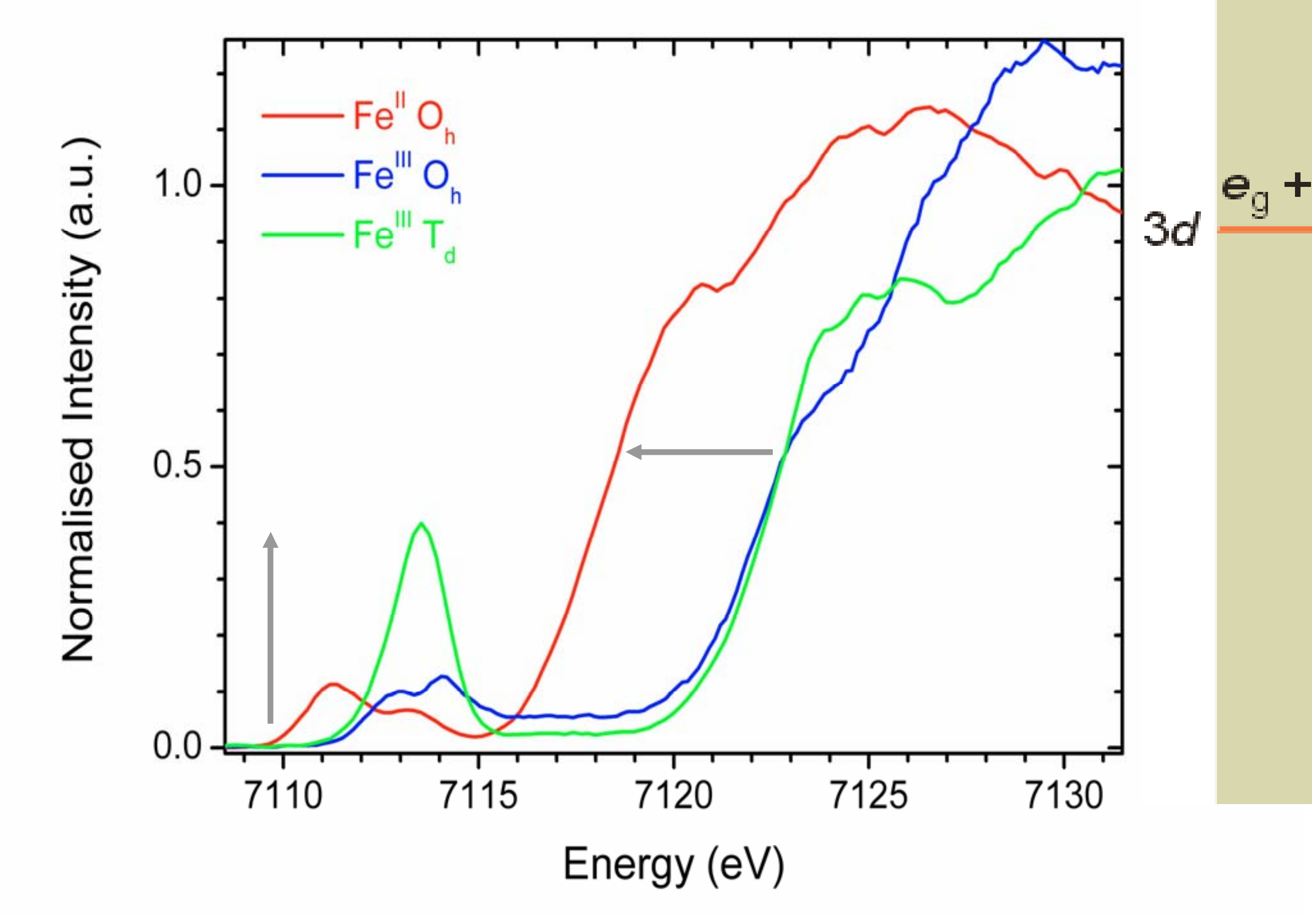


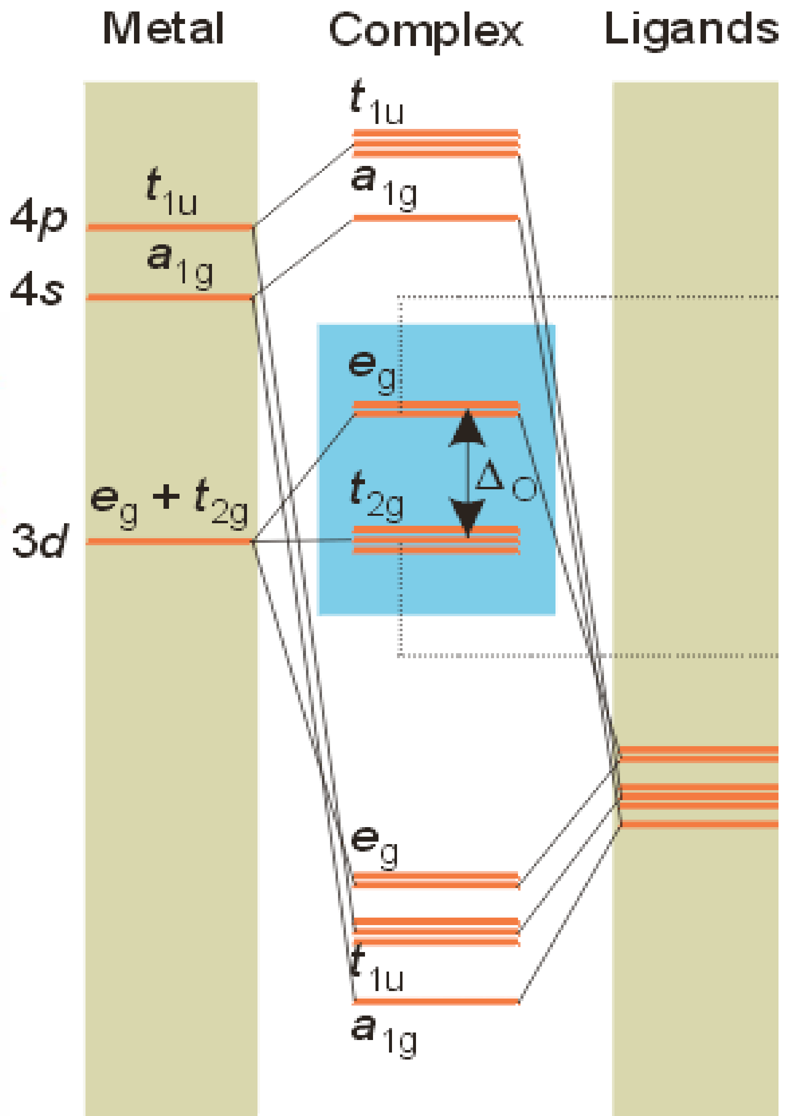
L edge of 5d-systems > number of empty 5d states

Difference between metal and oxide

K edge XANES

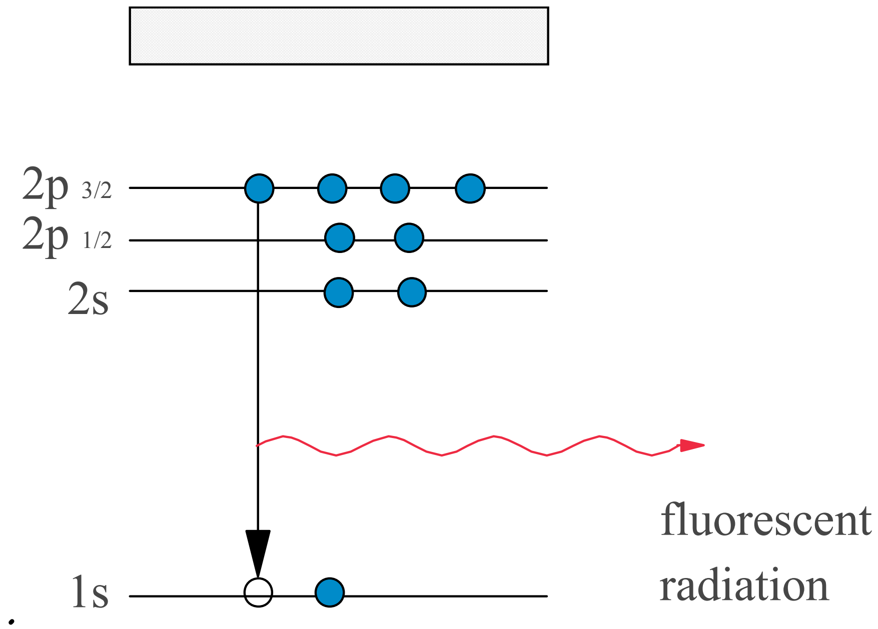
- Element specific DOS
- L specific DOS
- Dipole selection rule ($\Delta L = \pm 1$)



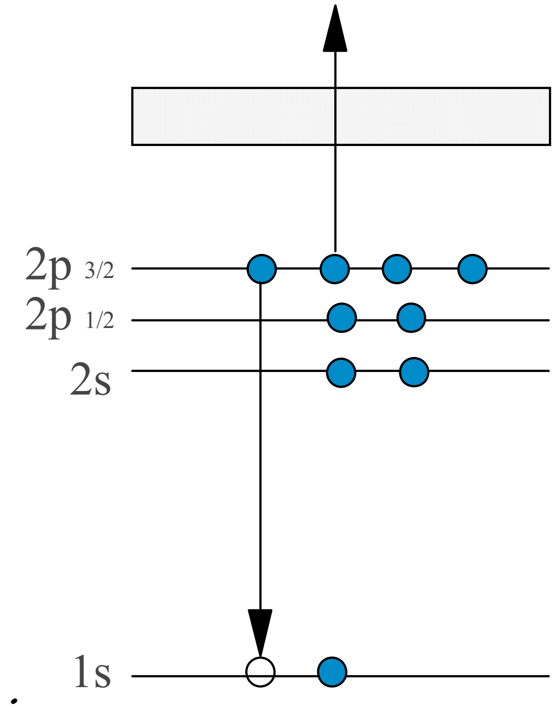


Core Hole Decay

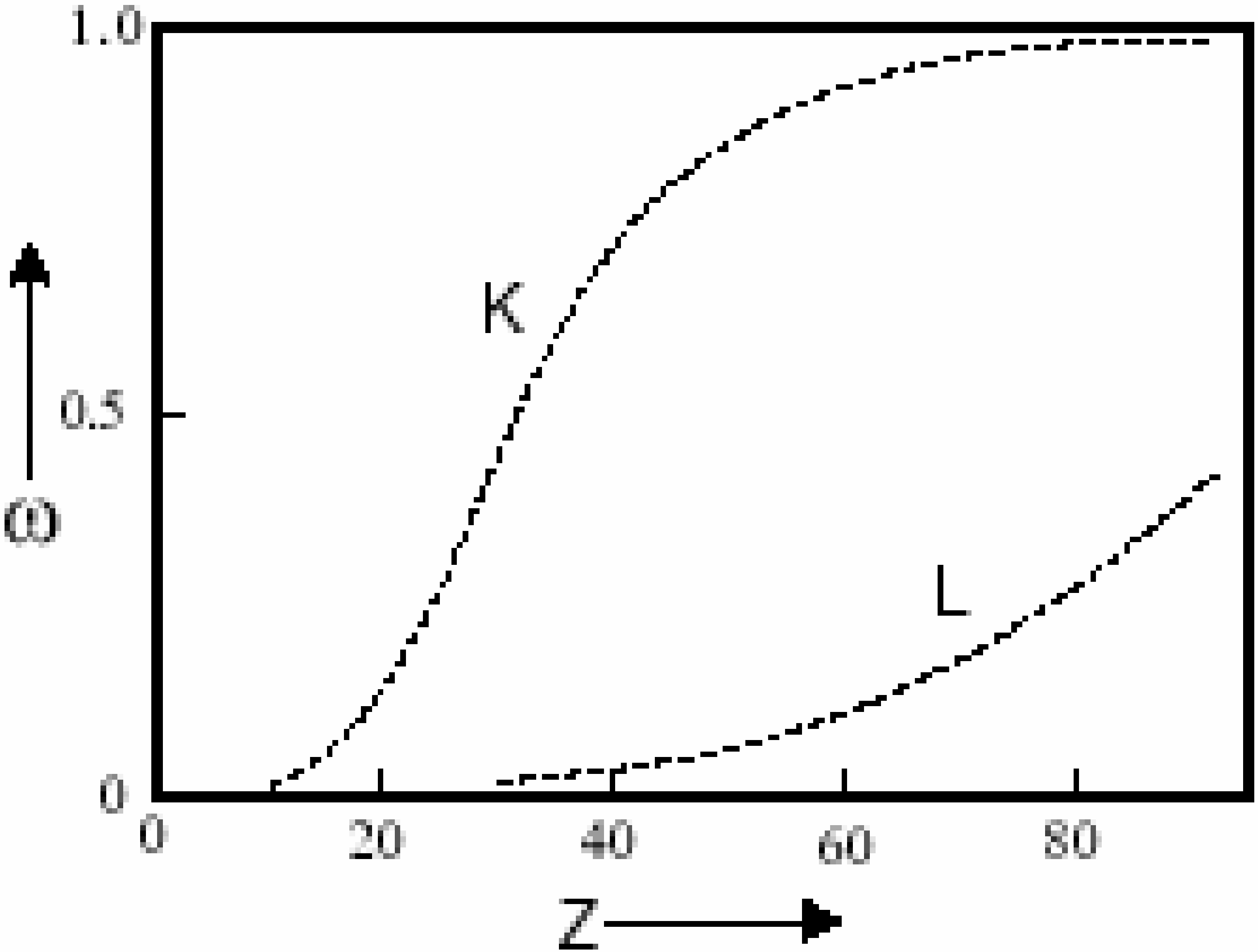
Fluorescence



Auger

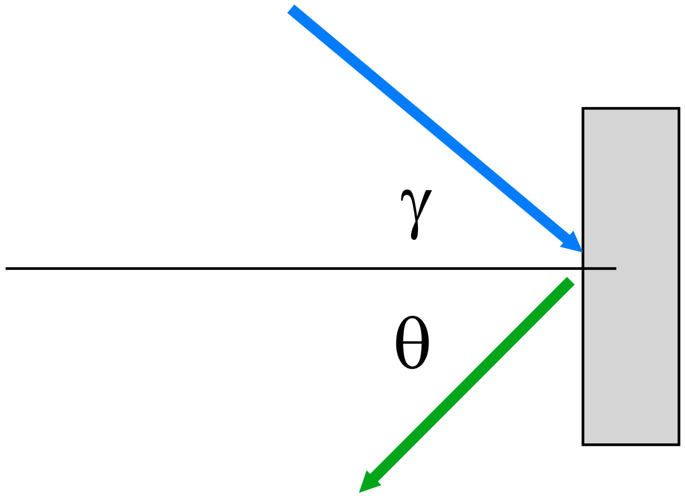


Fluorescence and Auger



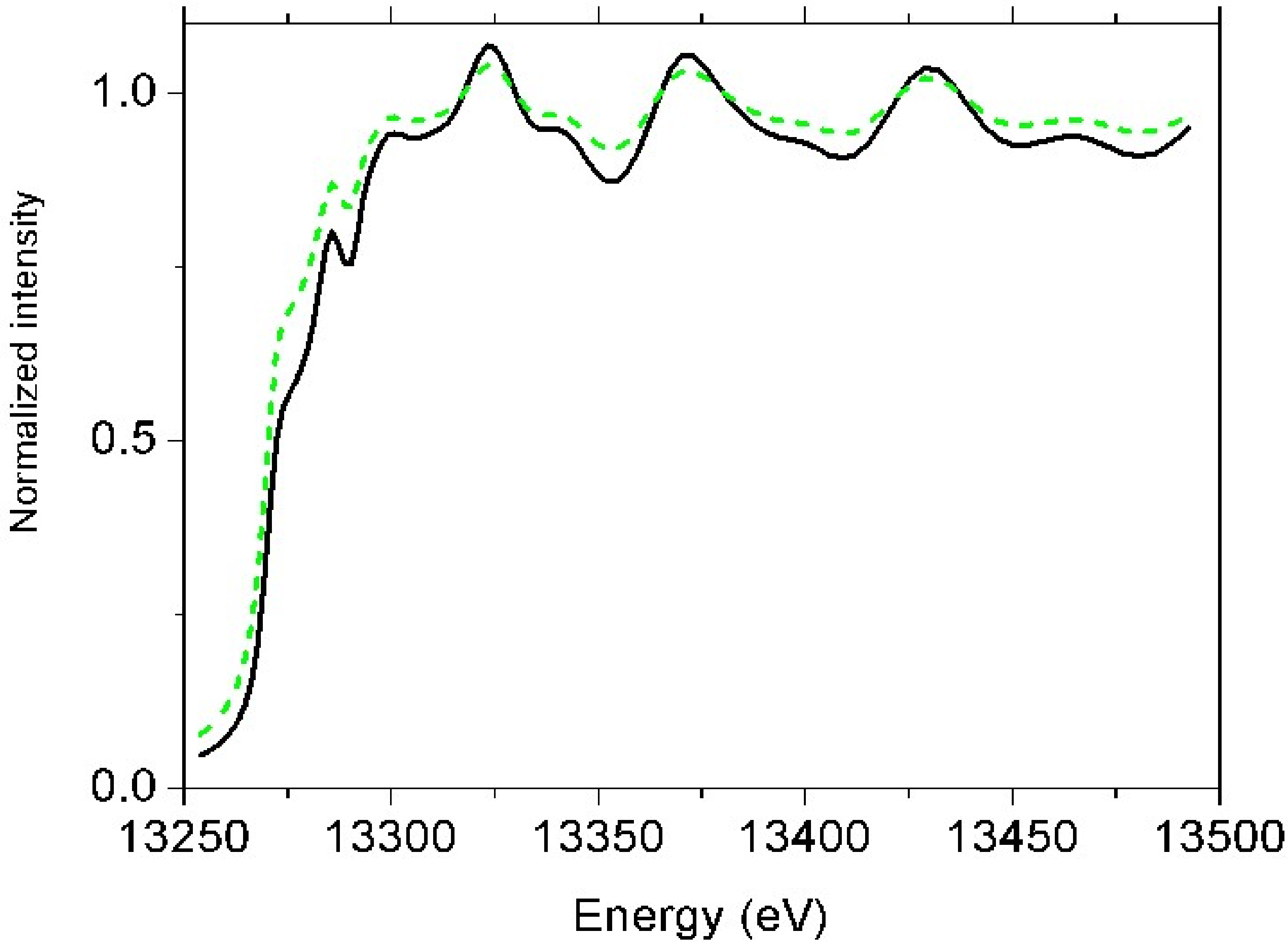
X-ray Fluorescence

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

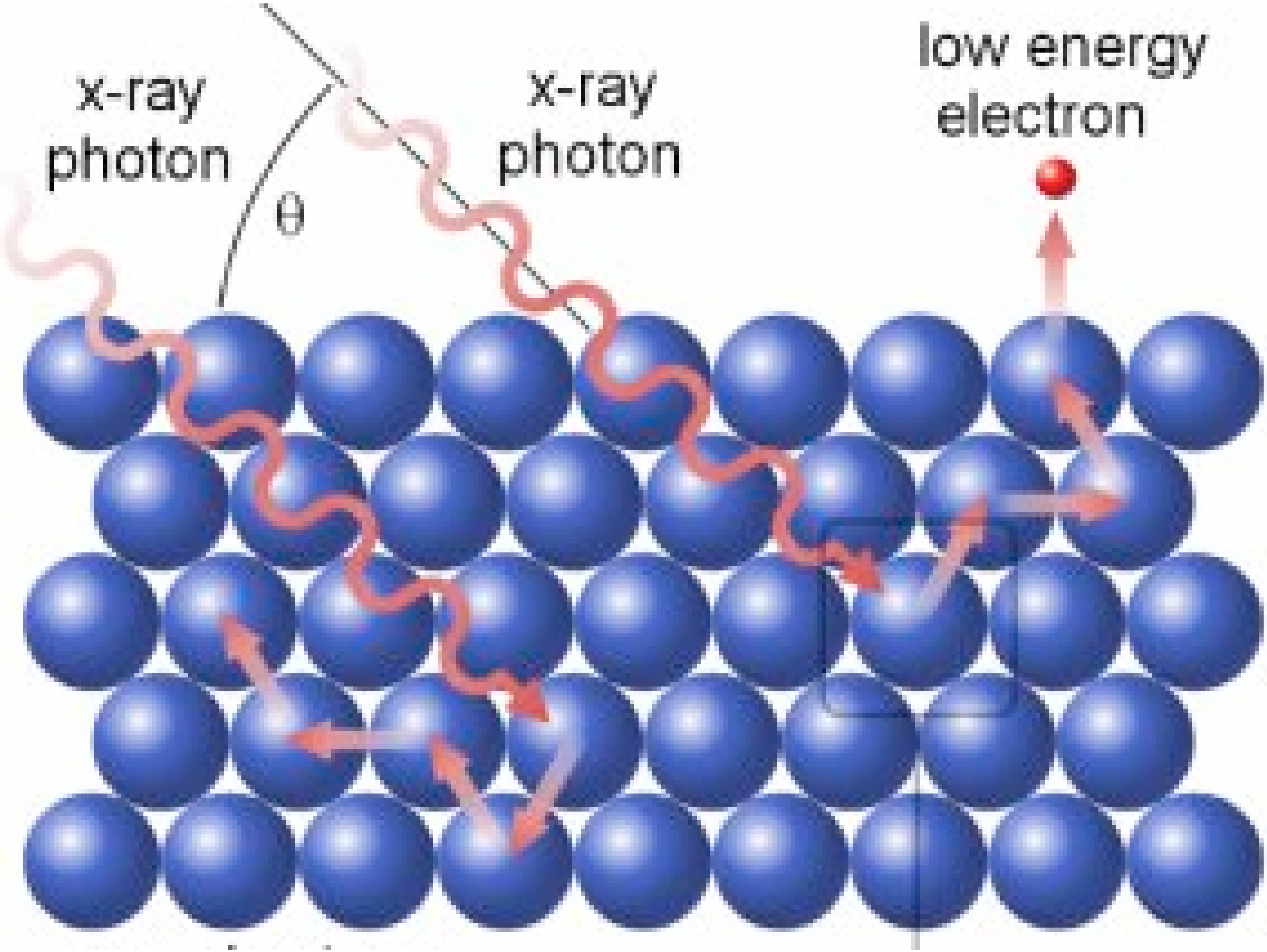


$$I_f(\omega) \propto \frac{\mu(\omega)}{\mu(\omega)\cdot\frac{1}{2}\sqrt{2}+\mu_B\sqrt{2}} \approx \frac{\mu(\omega)}{\mu(\omega)+2\mu_B}$$

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

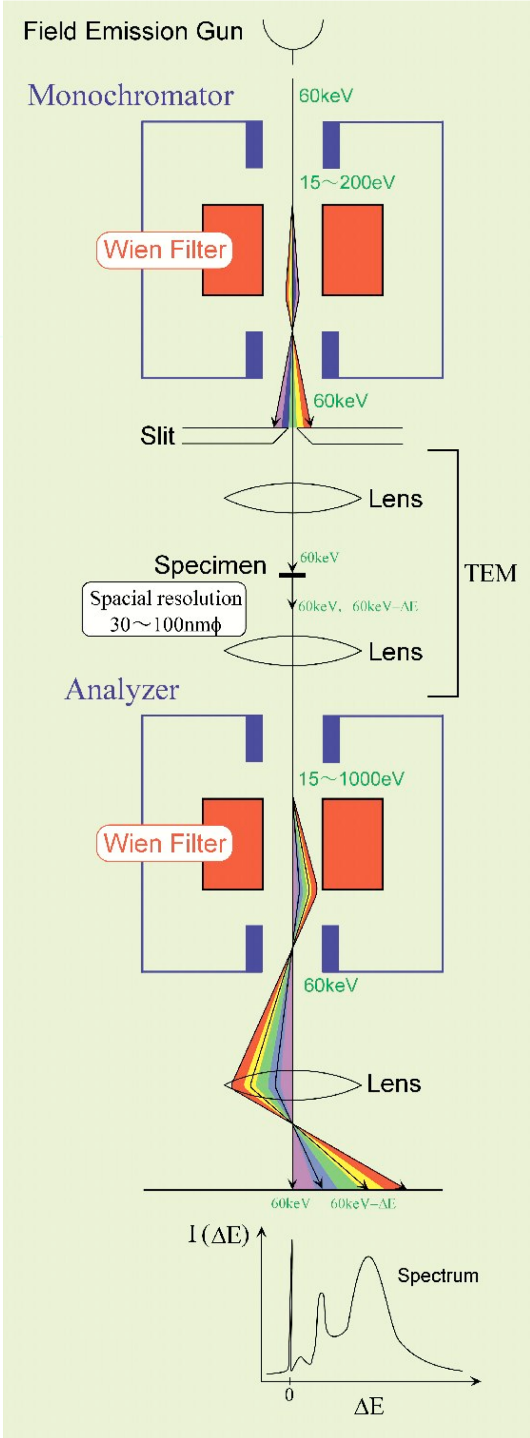
XAS and EELS

- Identical spectral shape
  (*only for soft x-ray edges*!)
  [If EELS uses small q and high E]

- XAS at Synchrotron
- EELS with (S)TEM

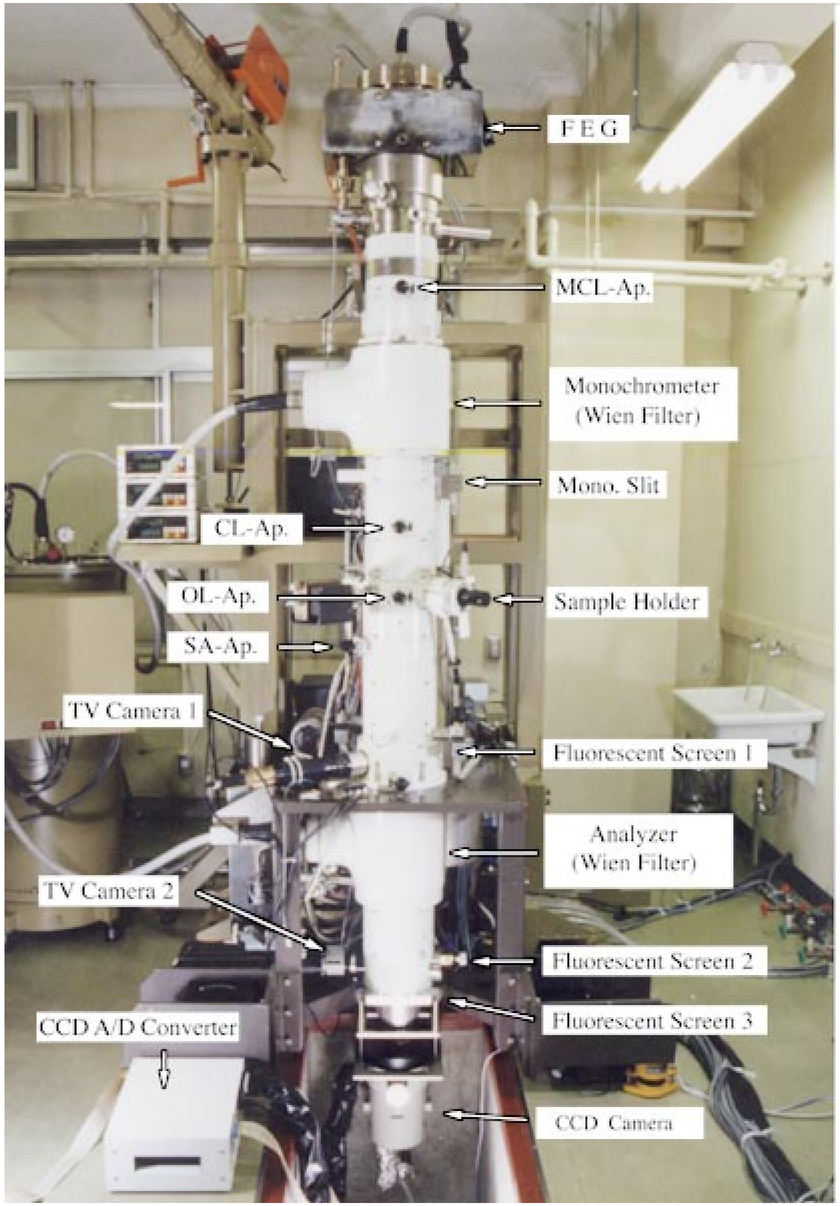
- XAS: 0.1 eV with 20nm
- EELS: 0.3 eV with 0.5 nm

- 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]

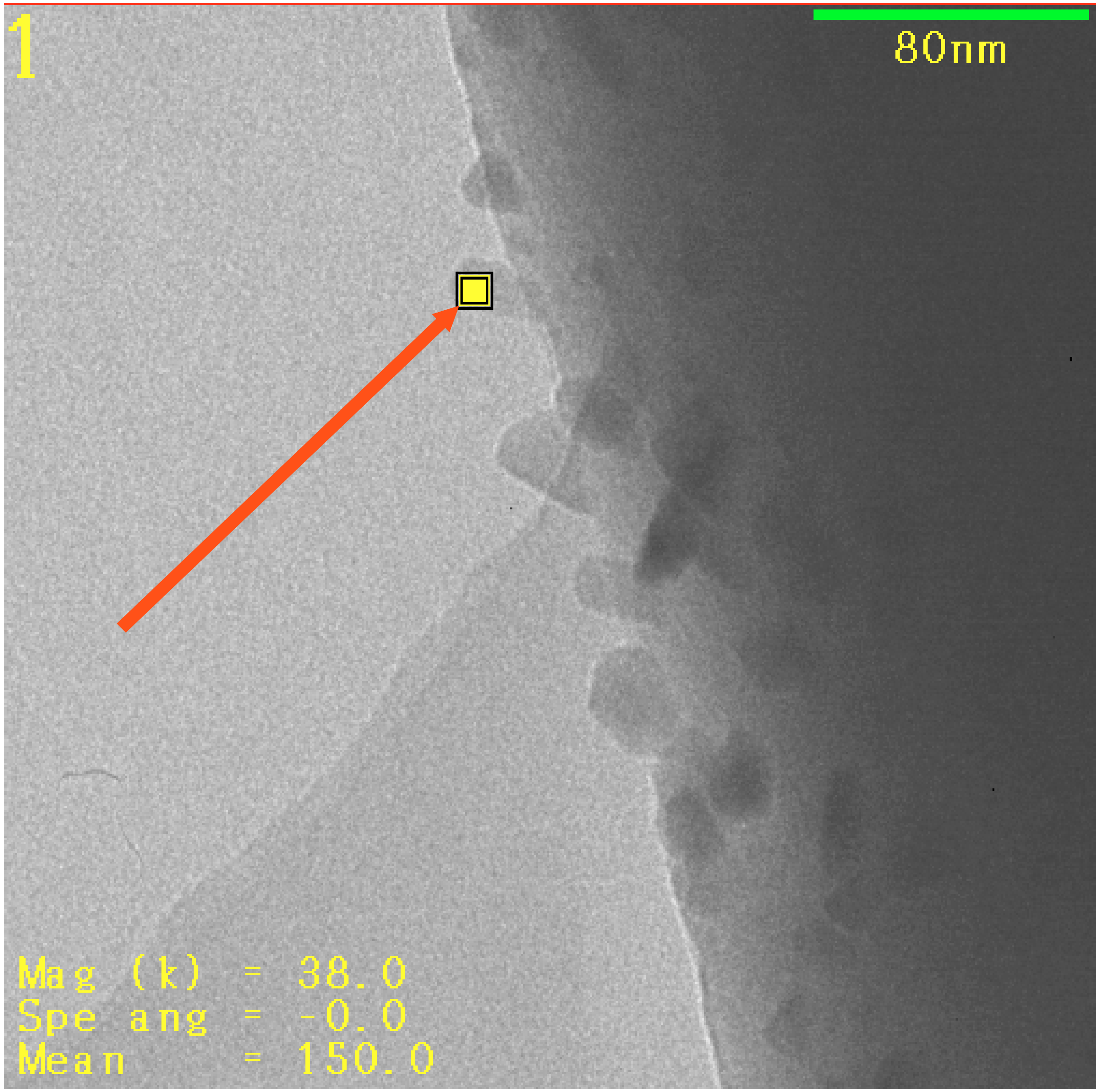


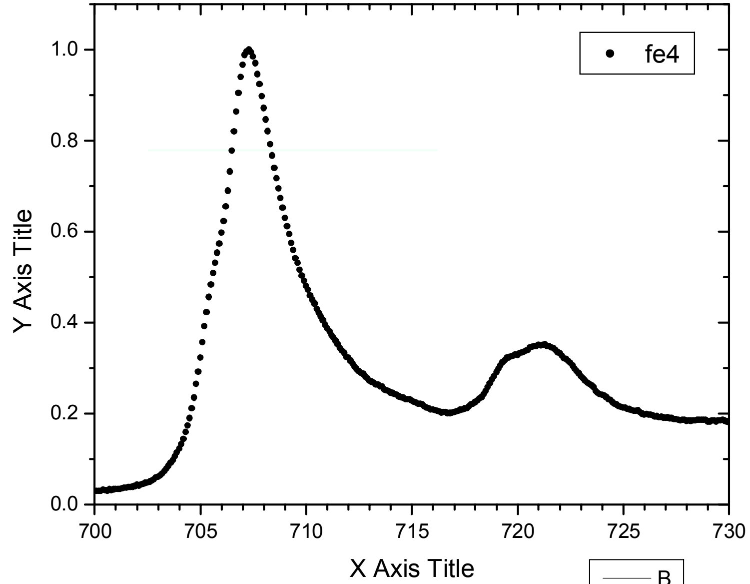
- XAS at Synchrotron
- EELS with (S)TEM

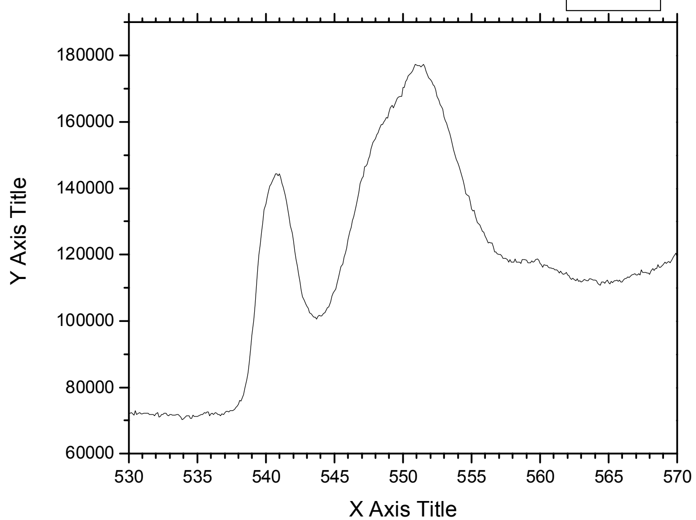
- XAS: 0.1 eV with 20nm
- EELS: 0.3 eV with 0.5 nm

- XAS: extreme conditions
- EELS: vacuum

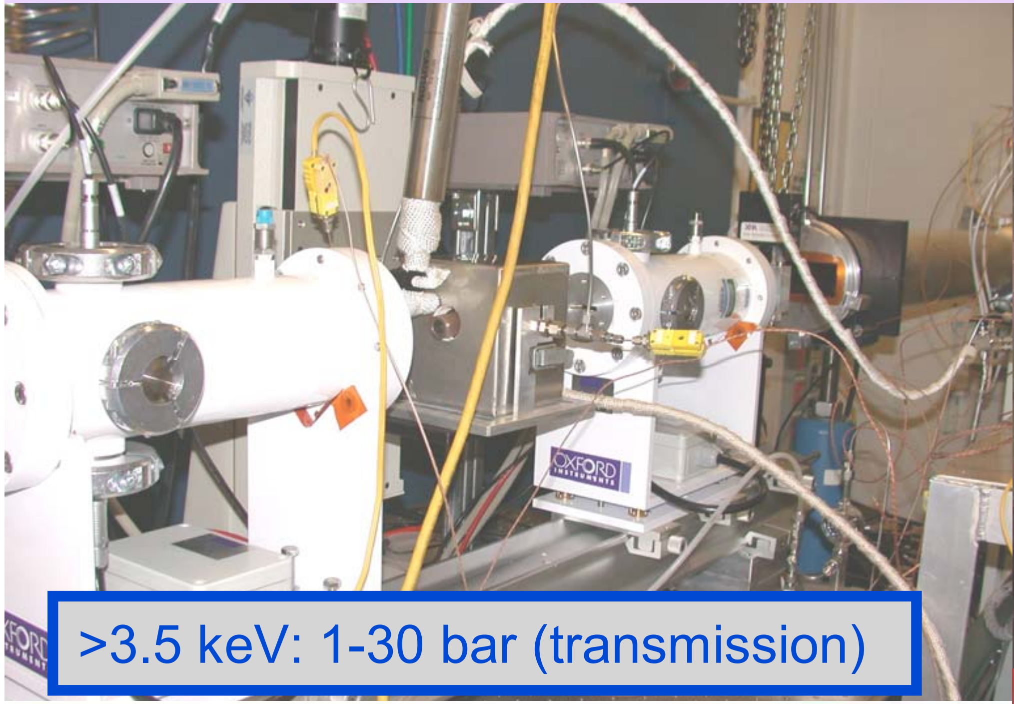
TEM-EELS of FeZSM-5



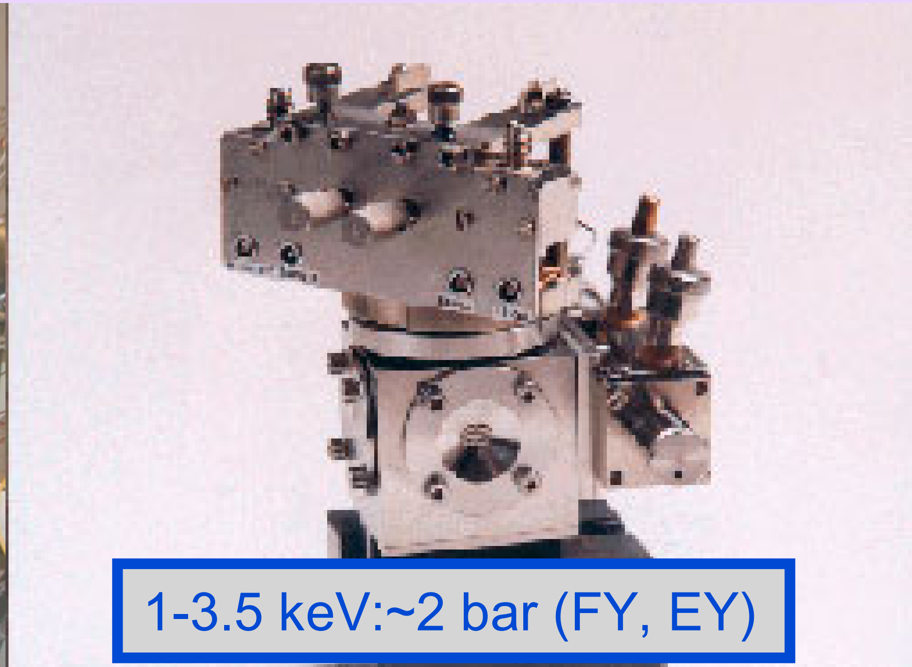




In-situ X-ray Absorption in Catalysis



>3.5 keV: 1-30 bar (transmission)



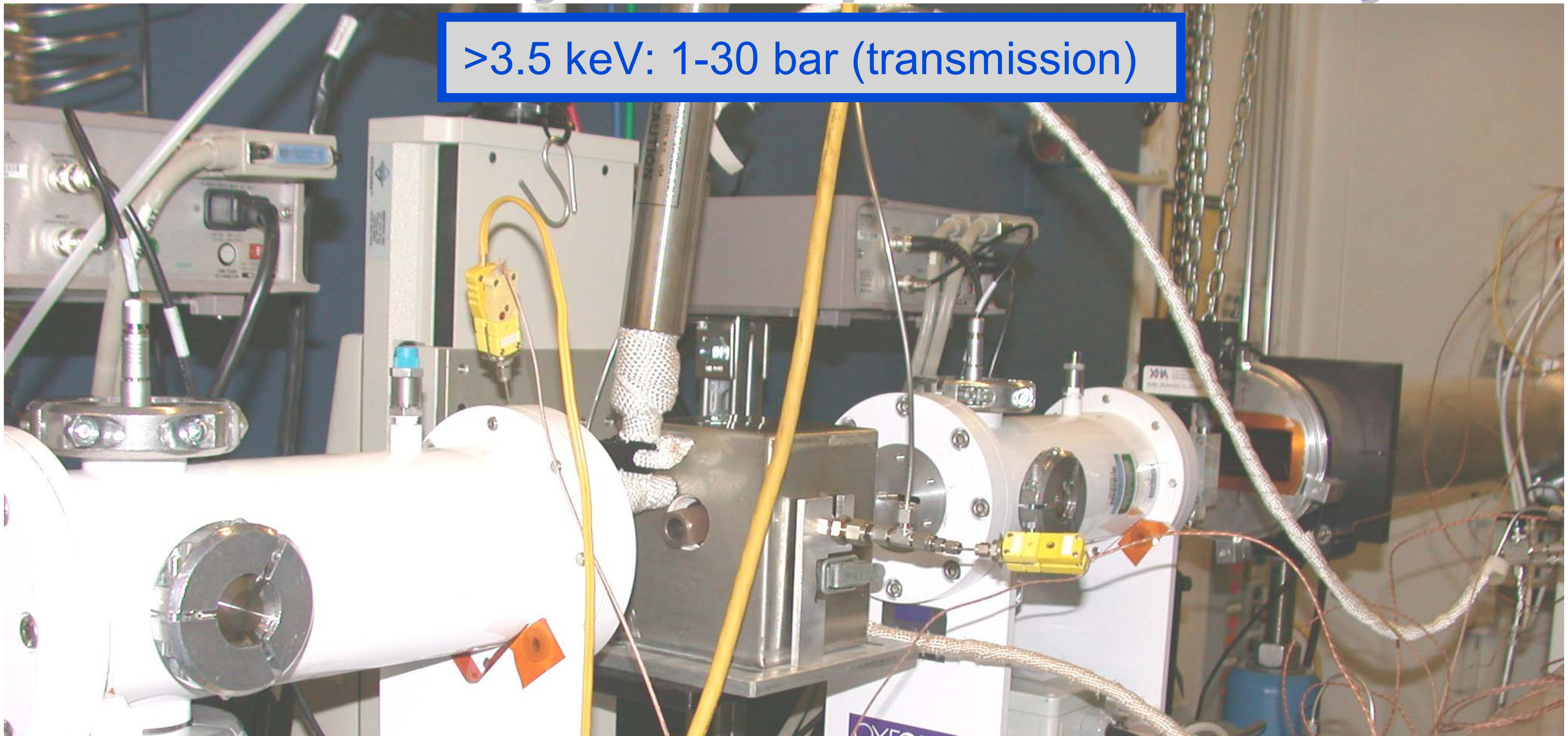
1-3.5 keV:~2 bar (FY, EY)

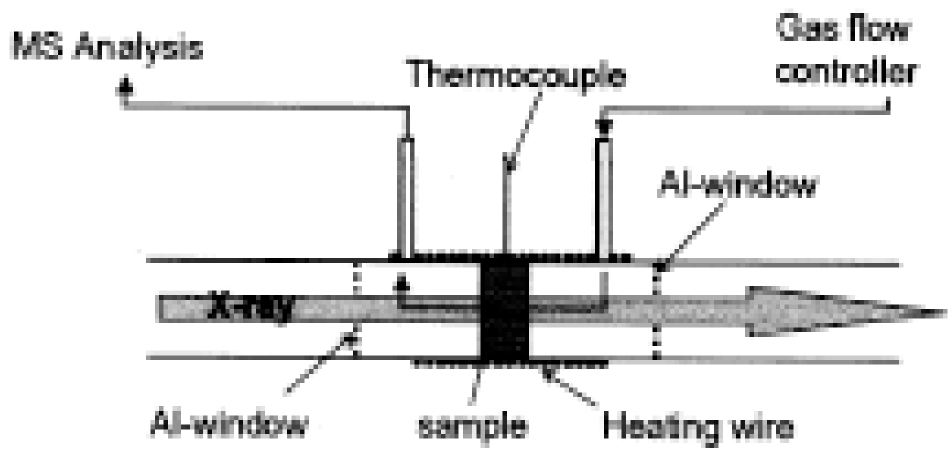
<1 keV: 5 mbar (conversion EY)

<1 keV: 1 bar (FY)

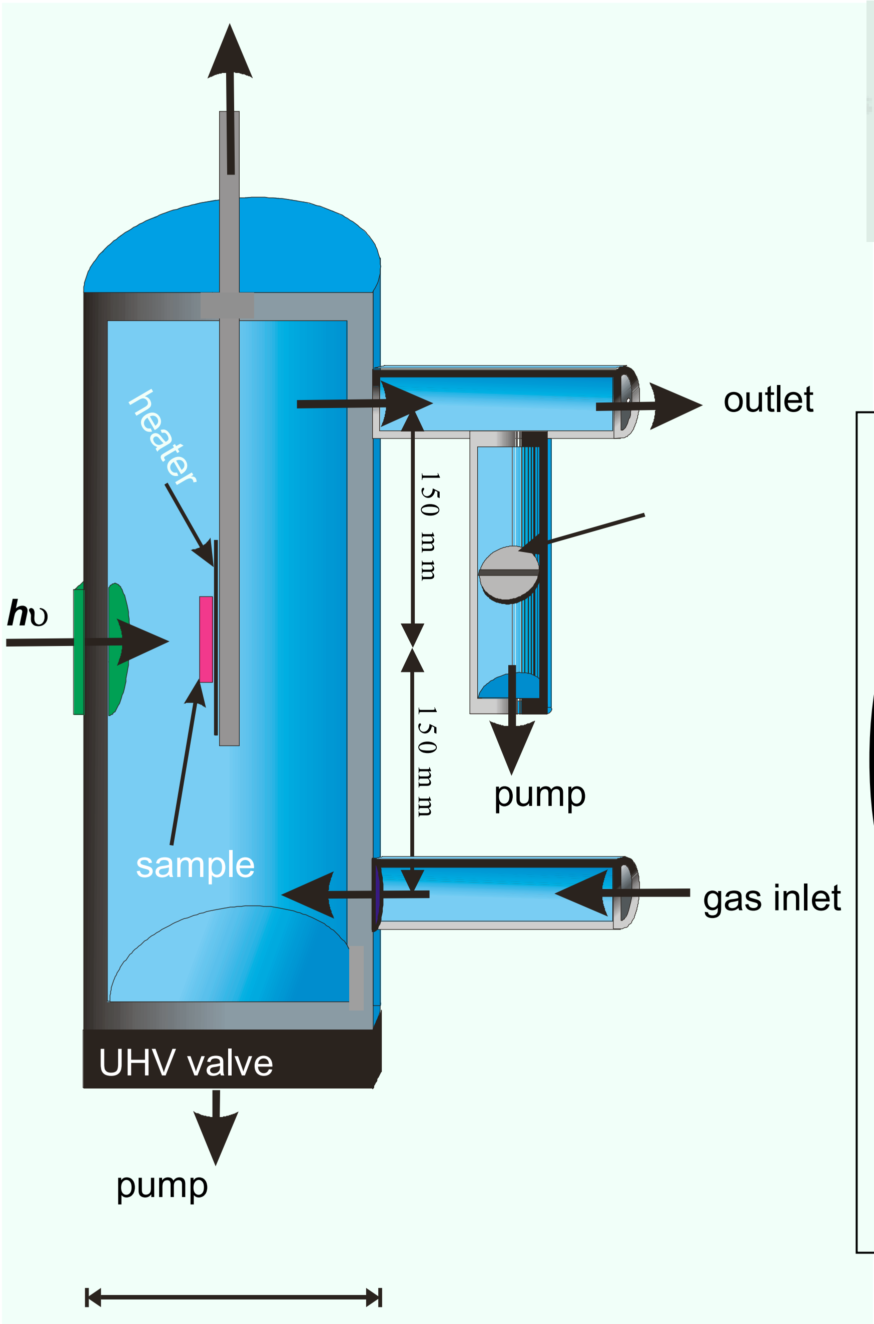
In-situ X-ray Absorption in Catalysis

>3.5 keV: 1-30 bar (transmission)

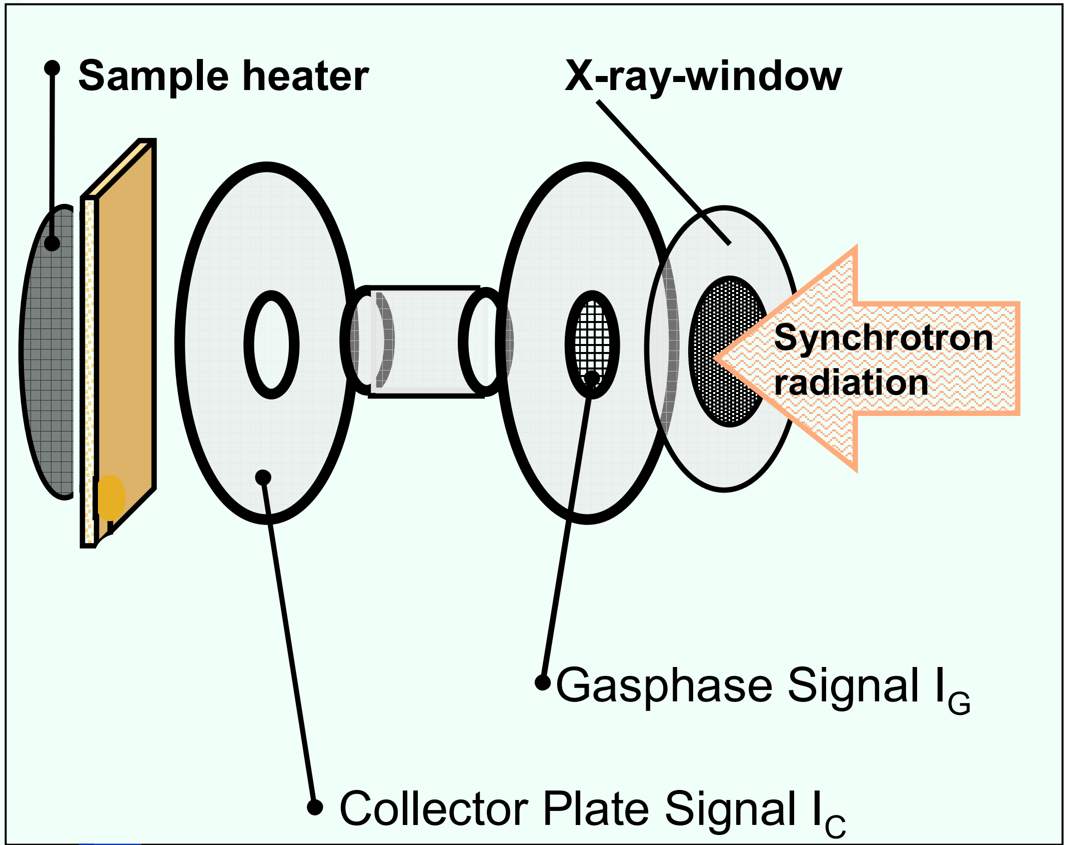




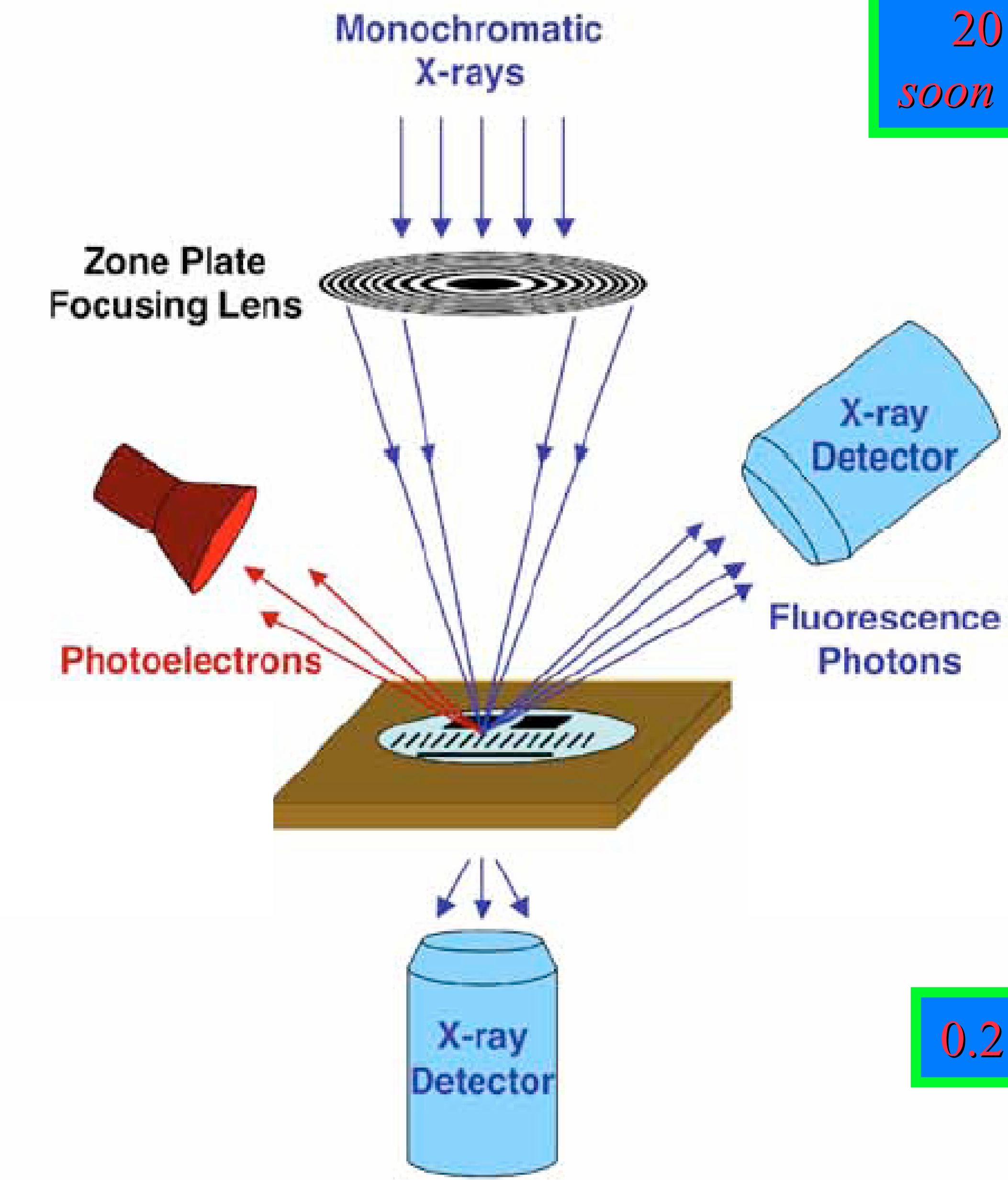
In-situ X-ray Absorption in Catalysis



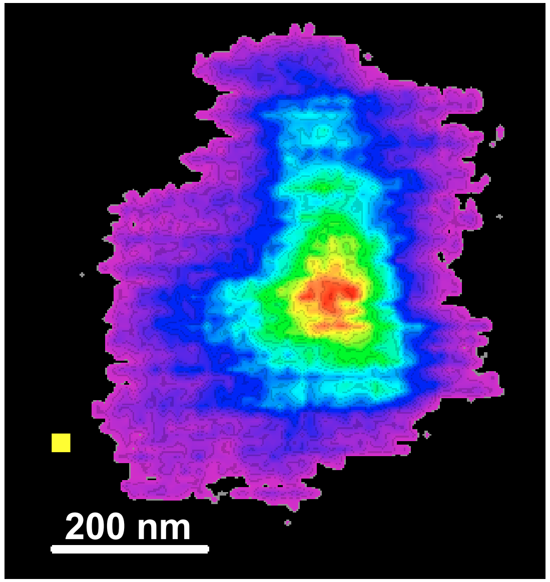
XAS at 5 mbar



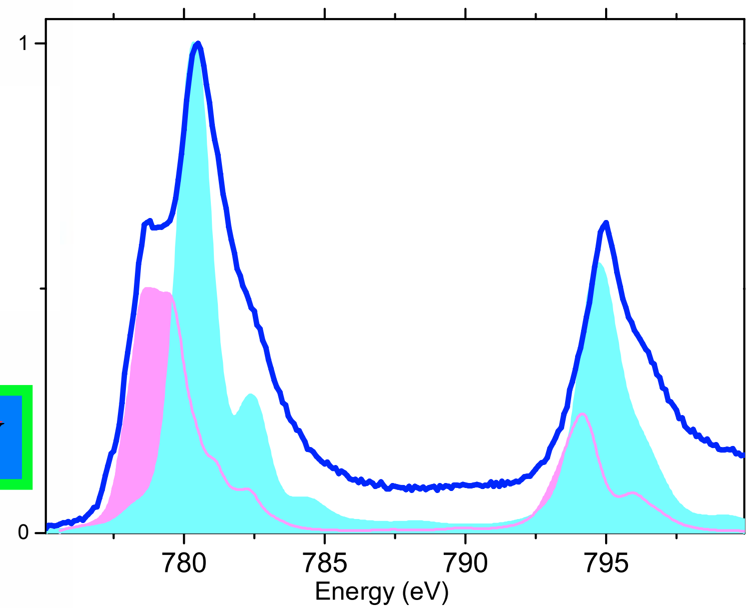
Transmission X-ray Microscopy (TXM)



20 nm
soon 10 nm



0.2 eV



Conditions XAS

- Hard x-ray XAS:
  extreme conditions > operando catalysis

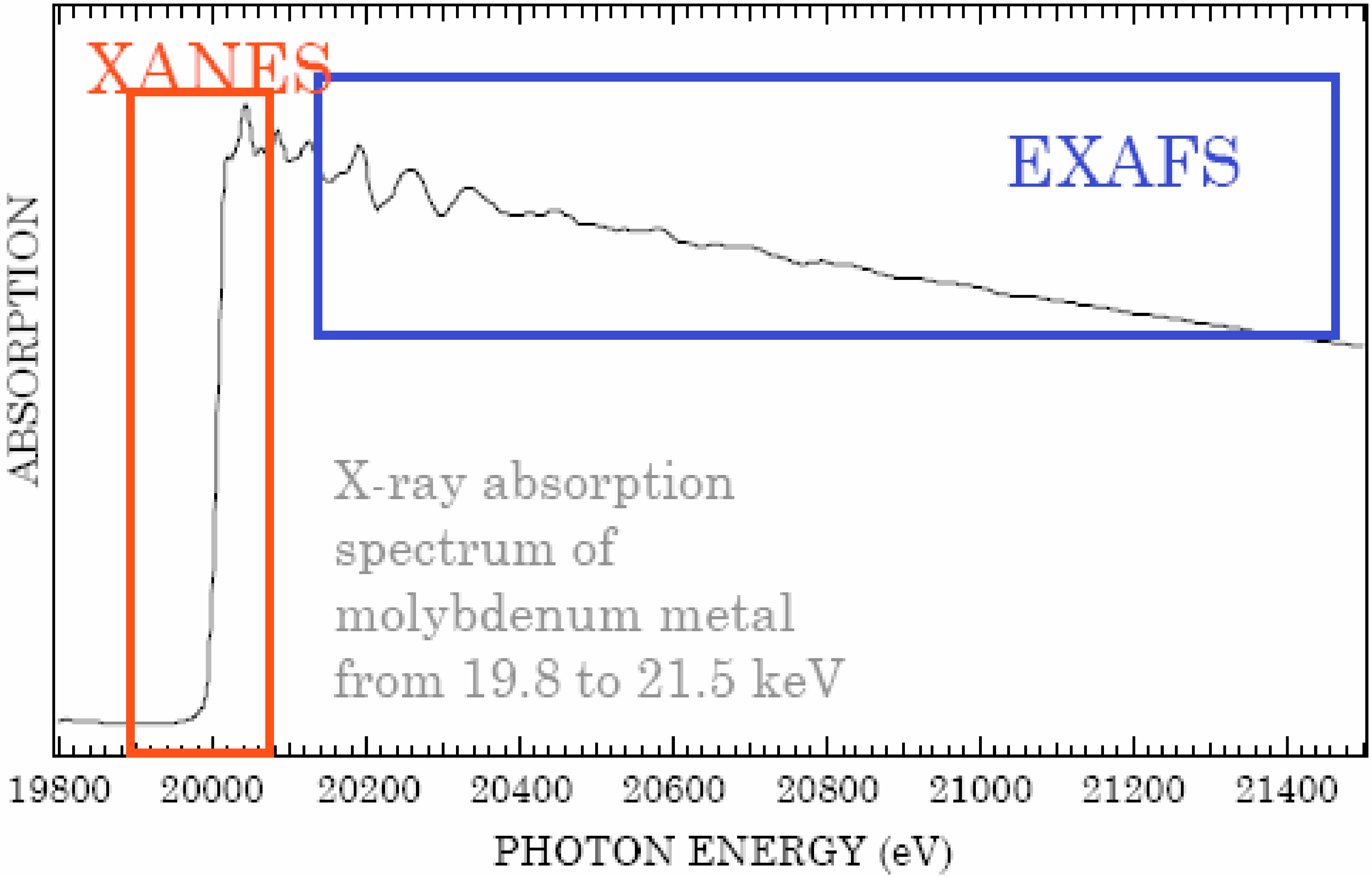
- Soft x-ray XAS:
  1 bar and ~250°C (TXM) > in-situ catalysis
  10 mbar and ~500°C (electron yield)

- EELS:
  vacuum

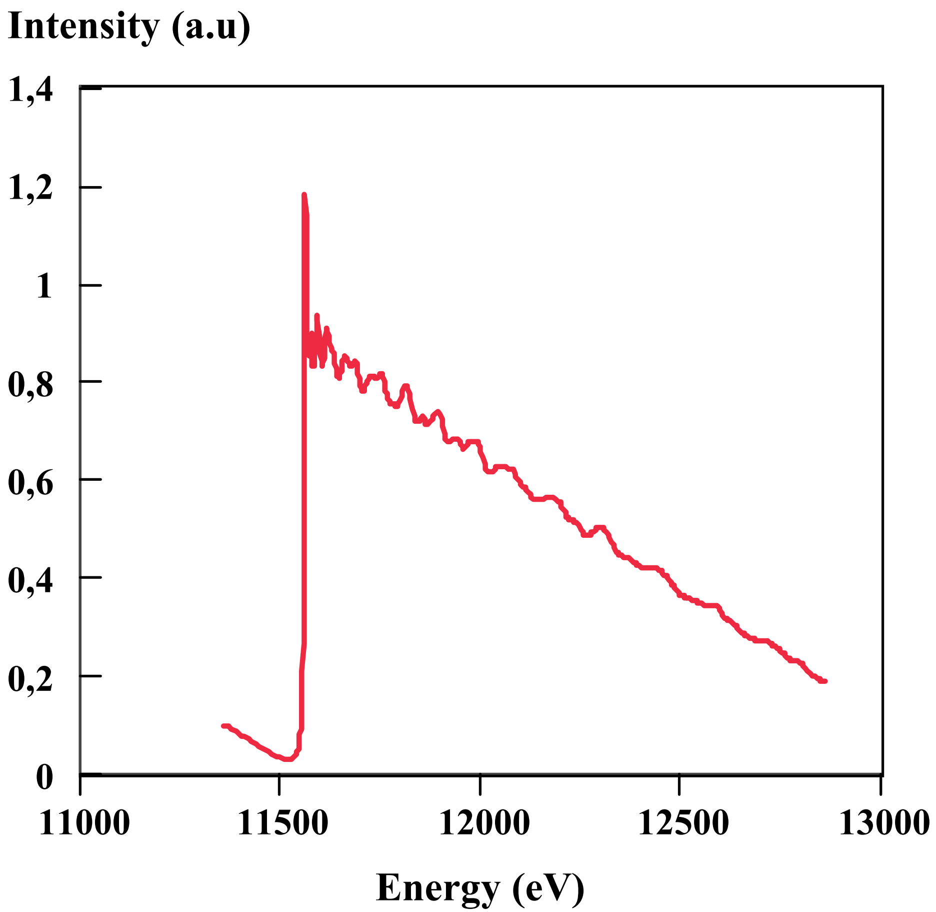
Why XAS?

- 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

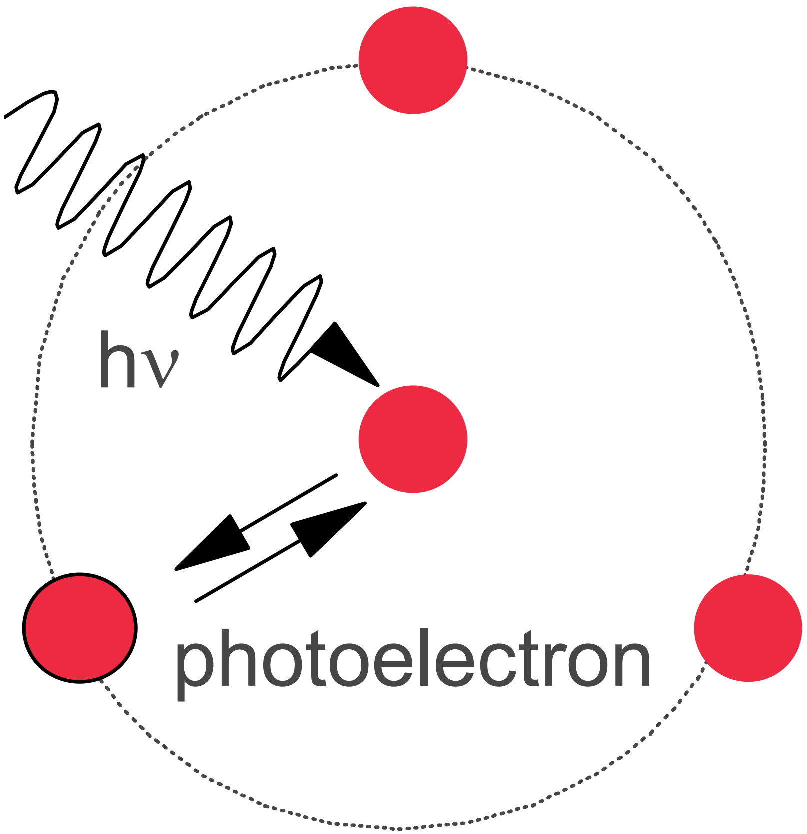


EXAFS



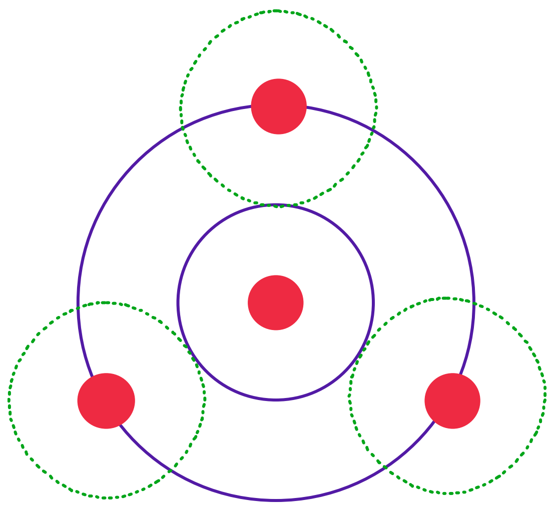
- Decreasing background with increasing energy
- Oscillations present due to the presence of neighbours

EXAFS

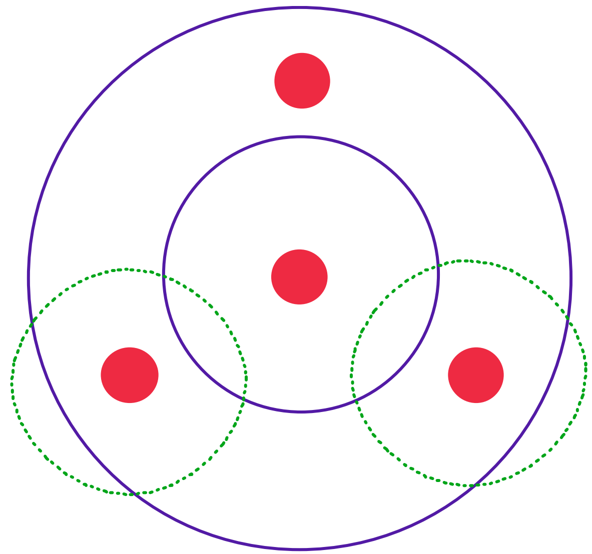


- Generation of photoelectrons (electron wave).
- Backscattering against neighbouring atoms.
- Interference with outgoing wave

EXAFS



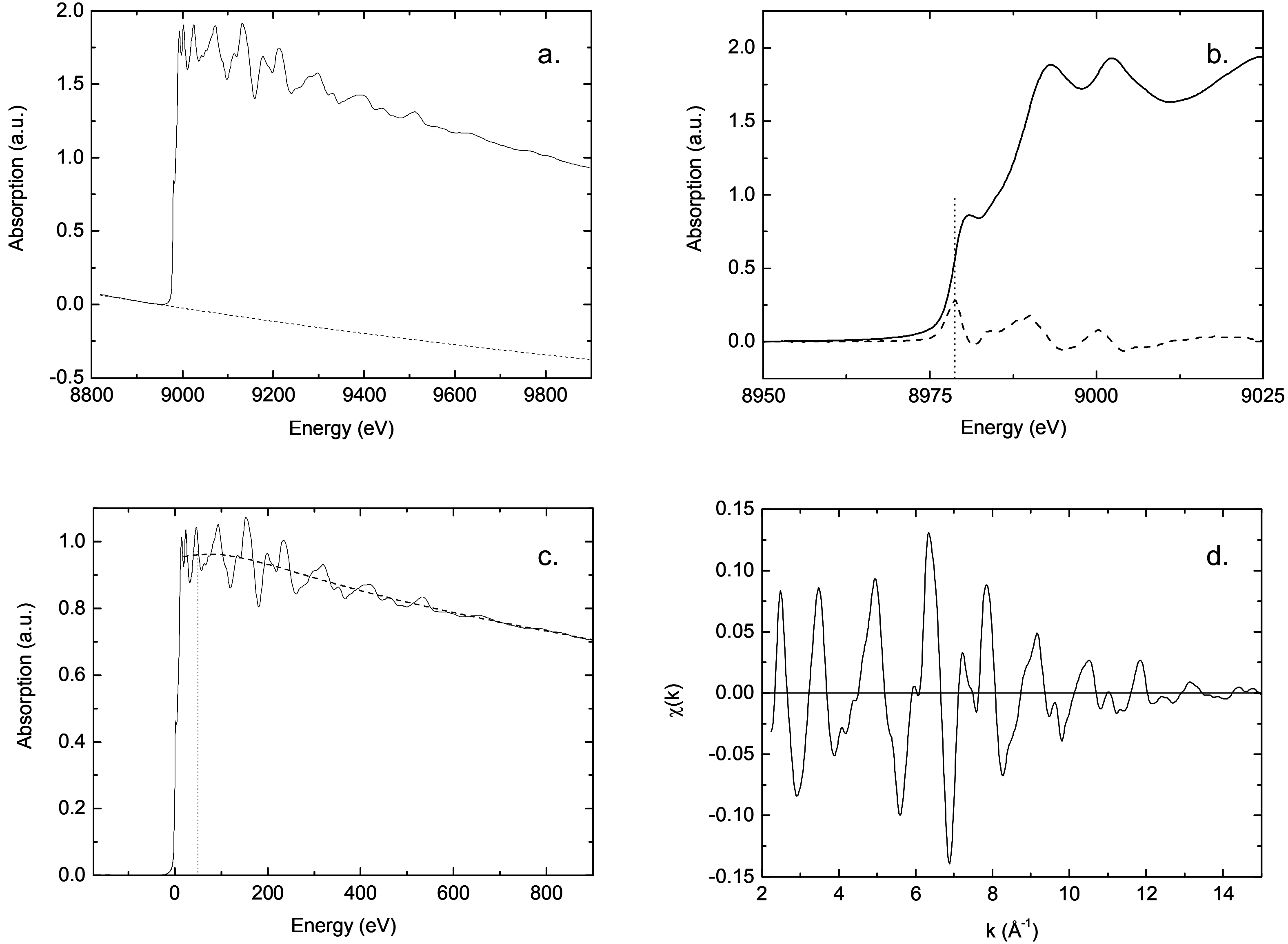
Constructive
(in phase)



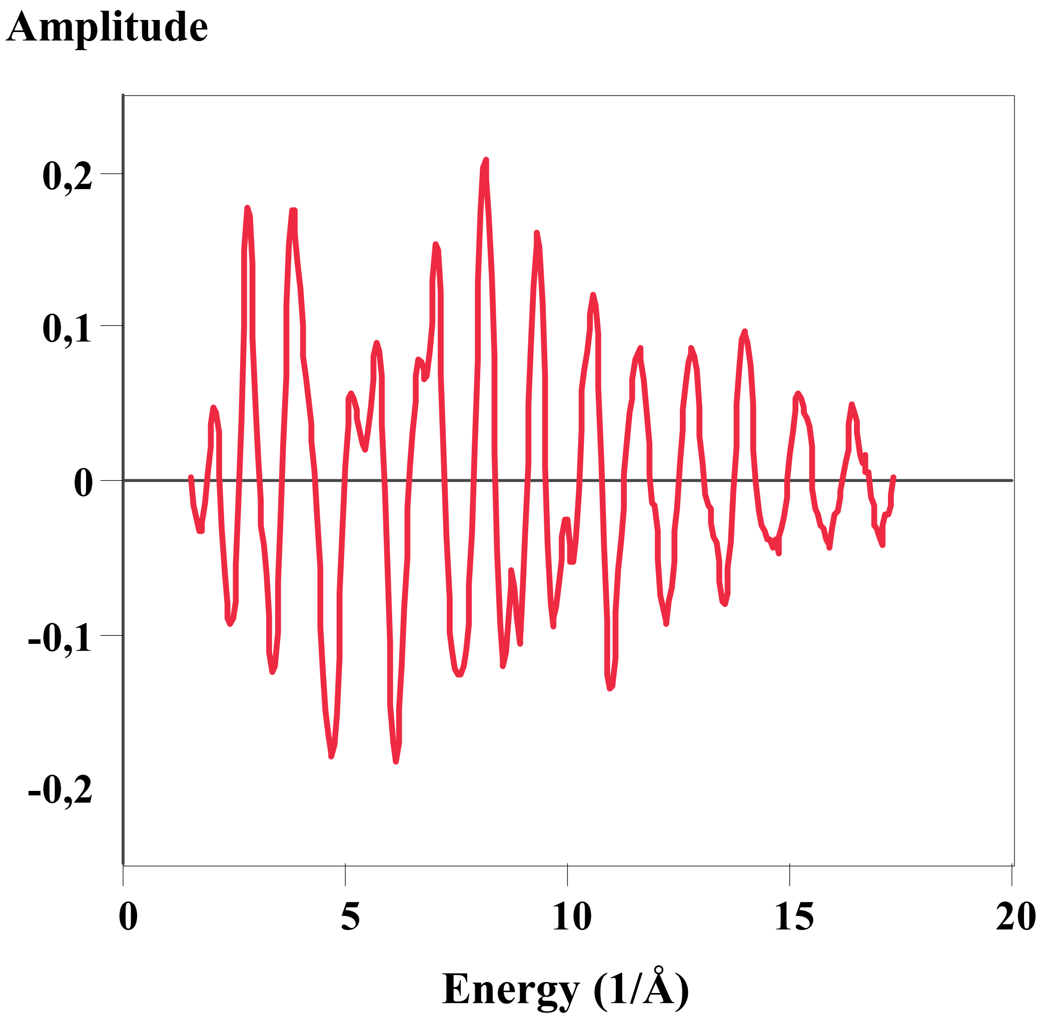
Destructive
(out of phase)

$$\Psi = \Psi out + \Psi back$$

EXAFS


a.
Absorption (a.u.)
Energy (eV)
2.0
1.5
1.0
0.5
0.0
-0.5
8800
9000
9200
9400
9600
9800
b.
2.0
1.5
1.0
0.5
0.0
8950
8975
9000
9025
c.
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
d.
χ(k)
k (Å^{-1})
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
2
4
6
8
10
12
14

EXAFS



- 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

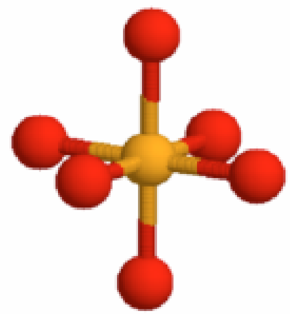
$$\chi_{\text{sim}}(k) = \sum_{j=1}^{Shells} N_j F_j \frac{e^{-2R_j/\lambda}}{k'_j R_j^2} S_0^2(k) e^{-2\sigma_j^2 k'^2} \sin\left[2kR_j + \varphi_j(k)\right]$$

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

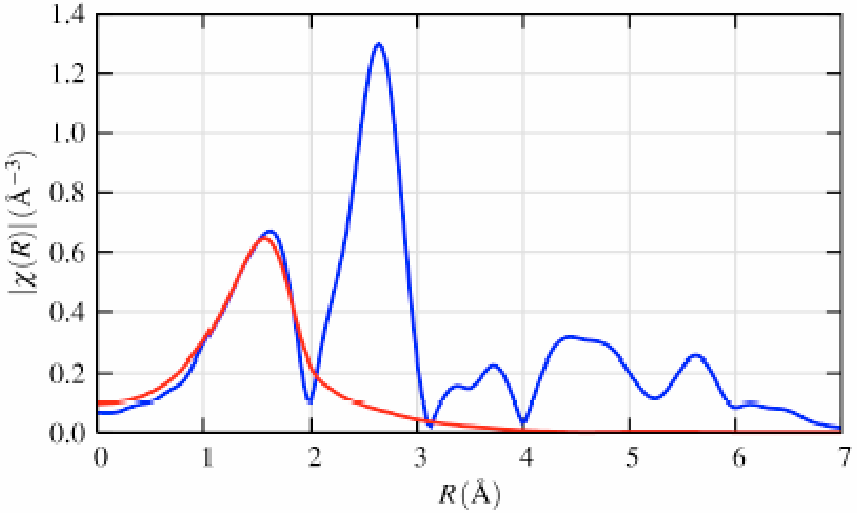
EXAFS Analysis: Modeling the 1st Shell of FeO

FeO has a rock-salt structure.

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



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

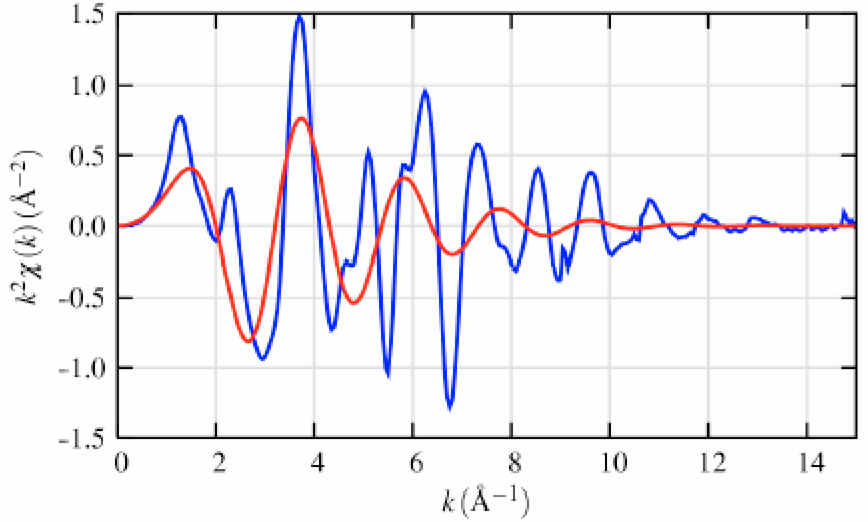


$|\chi(R)|$ for FeO (blue), and a 1st shell fit (red).

Fit results:

N	= 5.8 $\pm$ 1.8
R	= 2.10 $\pm$ 0.02Å
ΔE_0	= -3.1 $\pm$ 2.5 eV
σ^2	= 0.015 $\pm$ 0.005 Å^2.

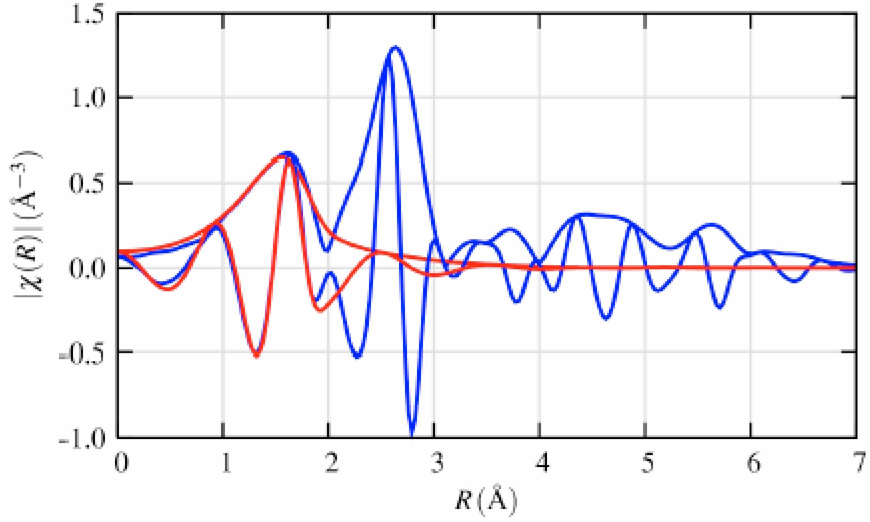
EXAFS Analysis: 1st Shell of FeO



1^{st} shell fit in k space.

The 1^{st} shell fit to FeO in k space.

There is clearly another component in the XAFS!



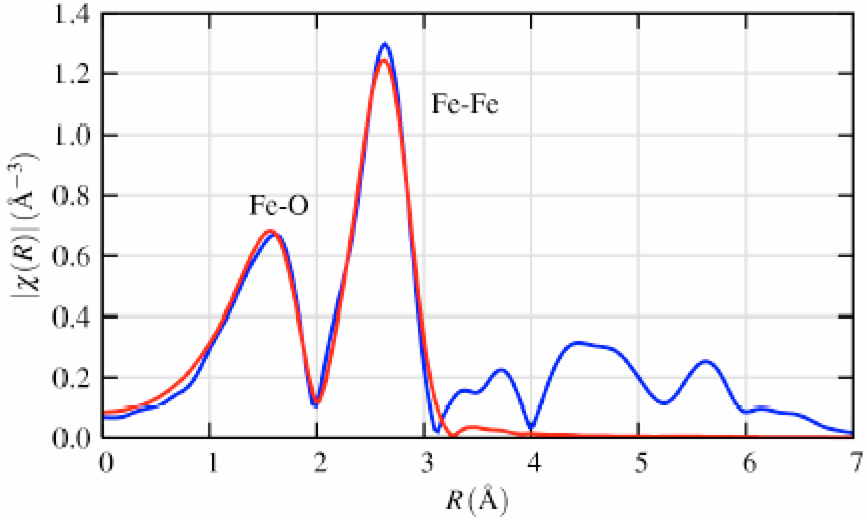
1^{st} shell fit in R space.

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

Though the fit to the magnitude didn't look great, the fit to 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 $\mathrm{f(k)}$ and $\delta(\mathrm{k})$ based on a guess of the Fe-Fe distance, and refine the values $\mathbf{R}$, $\mathbf{N}$, σ^2.
Such a fit gives a result like this:



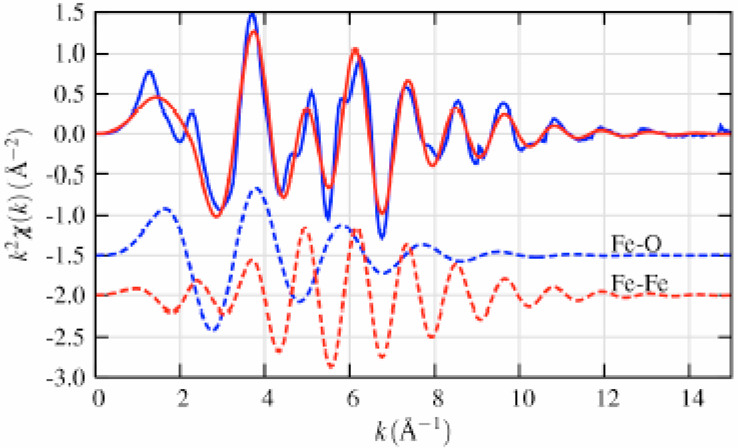
$|\chi(\mathbf{R})|$ data for FeO (blue), and fit of 1st and 2nd shells (red).
The results are fairly consistent with the known values for crystalline FeO:
6 O at 2.13Å, 12 Fe at 3.02Å.

Fit results (uncertainties in parentheses):

Shell	N	R (Å)	σ^2 (Å^2)	ΔE_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:

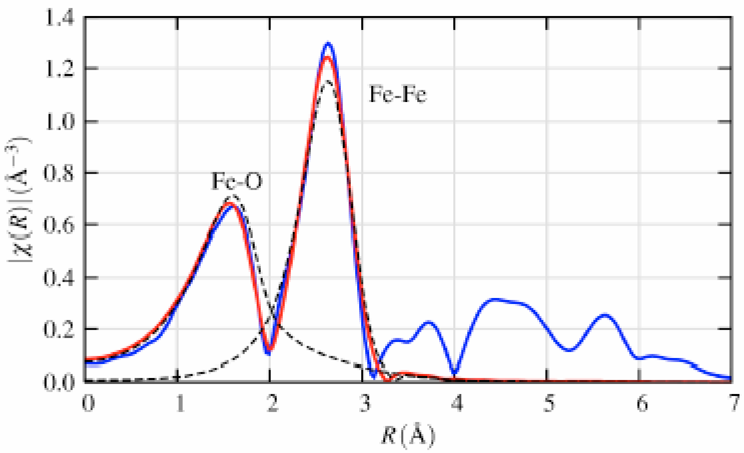


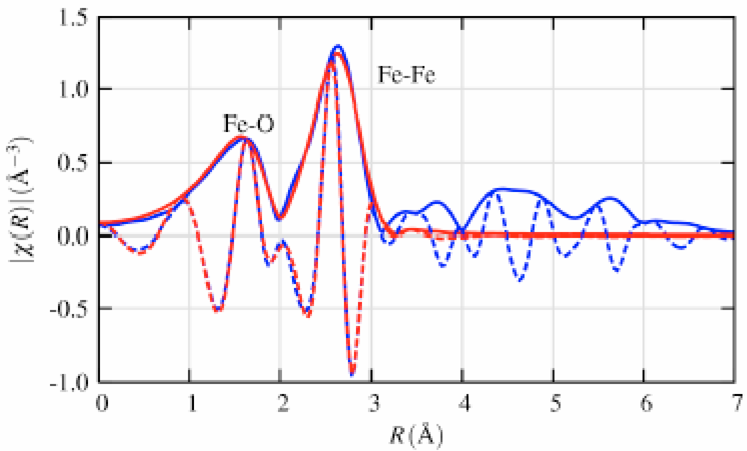
The Fe-Fe EXAFS extends to higher-k than the Fe-O EXAFS.

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

The agreement in Re$[\chi(\mathrm{R})]$ 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, σ)
- 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