

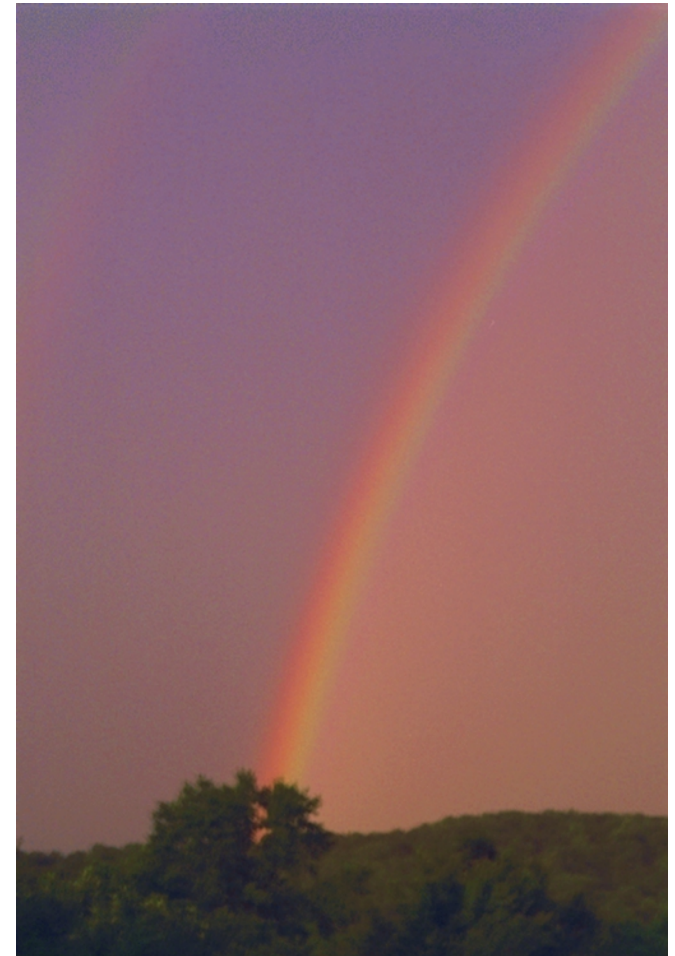
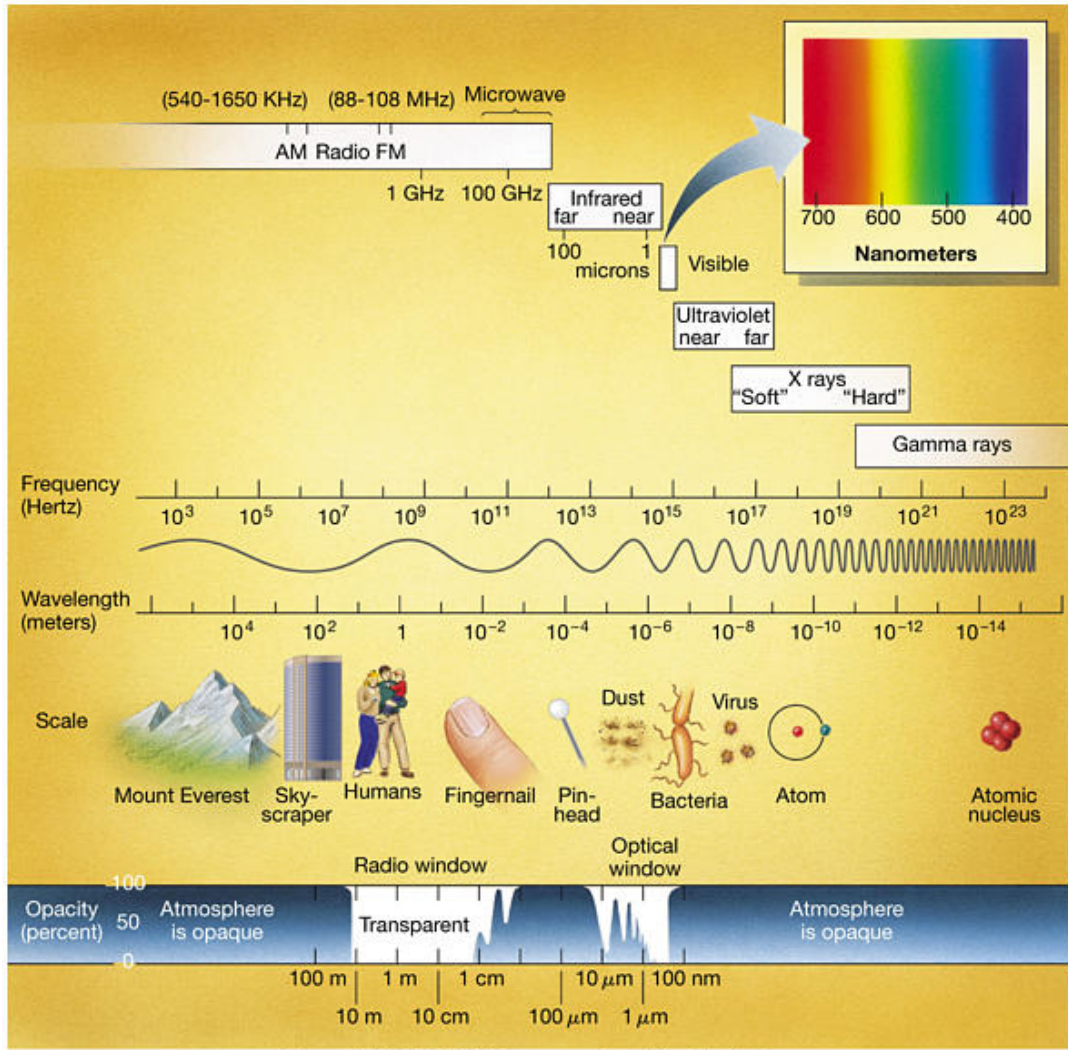
X-ray absorption spectroscopy

Literature recommendations

- J.C. Vickerman (editor), "Surface Analysis – The Principal Techniques", Wiley, 1997
- J. W. Niemantsverdriet, "Spectroscopy in Catalysis – An Introduction", VCH, 1993
- B. K. Teo, "EXAFS Spectroscopy: Principles and Applications", Plenum Pub Corp, 1981

Jagdeep Singh

Jeroen A. van Bokhoven



Nice and handy abbreviations

XAS	X-ray Absorption Spectroscopy
EXAFS	Extended X-ray Absorption Fine Structure
XANES	X-ray Absorption Near Edge Structure
NEXAFS	Near Edge X-ray Absorption Fine Structure

Historical development

- 1895 Discovery of X-rays (Röntgen)
- 1920 Discovery of EXAFS Phenomenon
- 1970 Synchrotrons become available as synchrotron source
- 1971 Theoretical description by Sayers, Stern, Lytle
- 80'ies Application in catalysis
- 90'ies First *in situ* studies and combination with other techniques
- 2004 First hard X-ray beam at an EXAFS beamline in CH at the SLS



Outline of the Technique

Advantages / Applications

- **Wide range of applications**
- Structural information (EXAFS)
- Electronic information (XANES)
- Capable of in-situ application

Disadvantages

- Synchrotron needed
- Careful planning of experiments necessary
- Data interpretation sometimes difficult

Synchrotron needed

ESRF (Grenoble)



DESY (Hamburg)



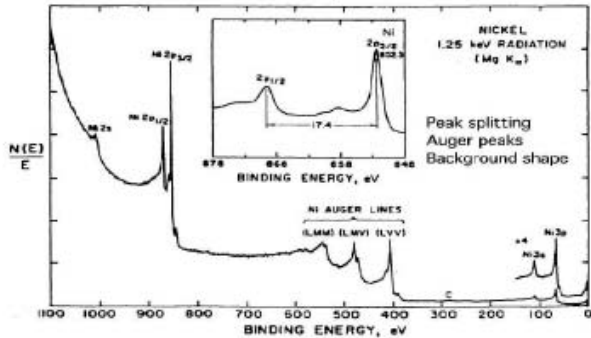
SLS (Villigen)



APS (Chicago)

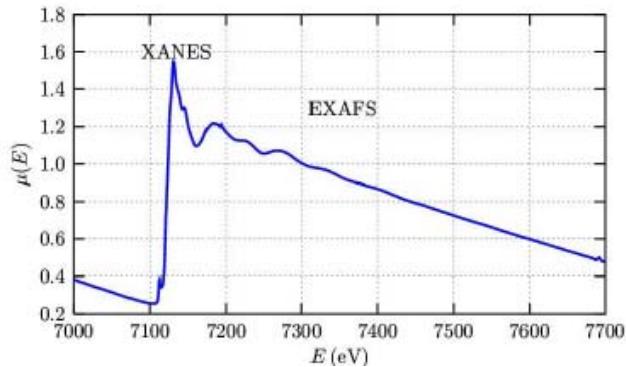
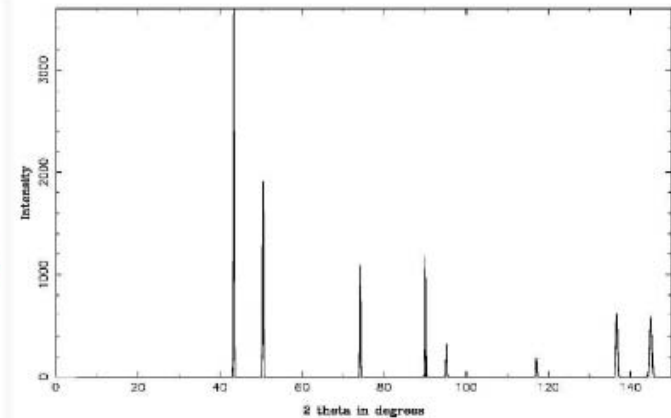


Comparison: XPS, XRD, XAS



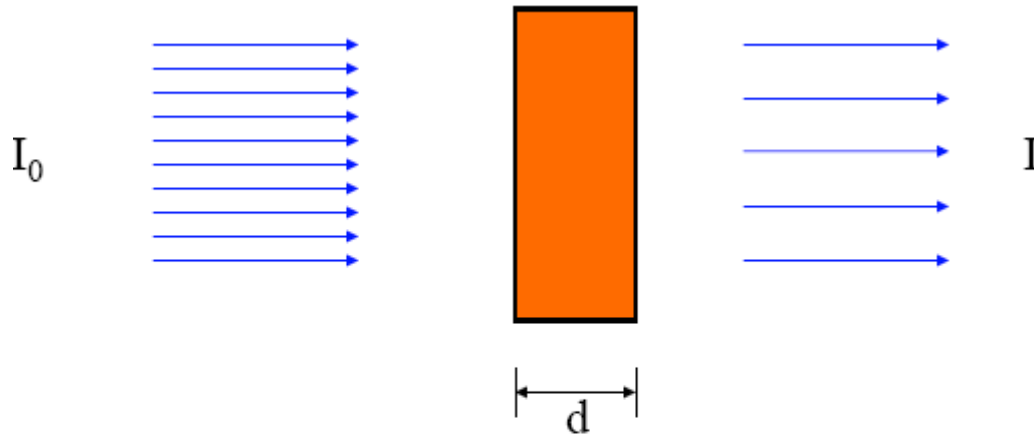
- Yields electronic information
- Surface sensitive
- In-situ application difficult
- Needs UHV

- Yields structural information
- Bulk technique
- In-situ applications realizable
- Needs long range order to work



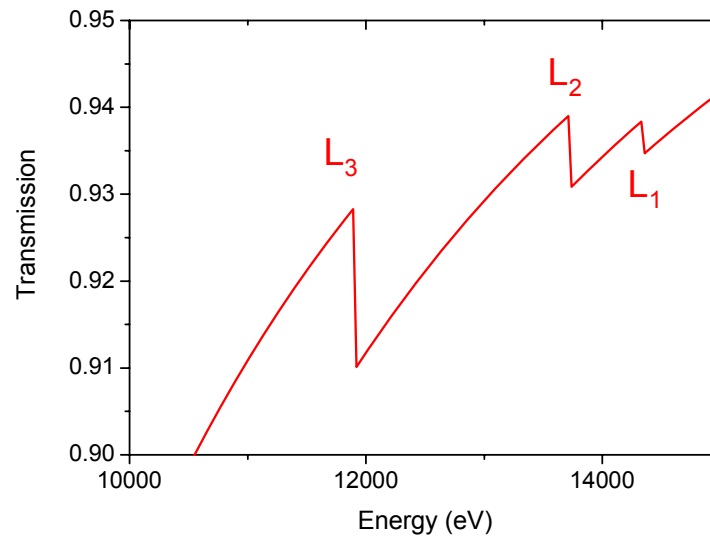
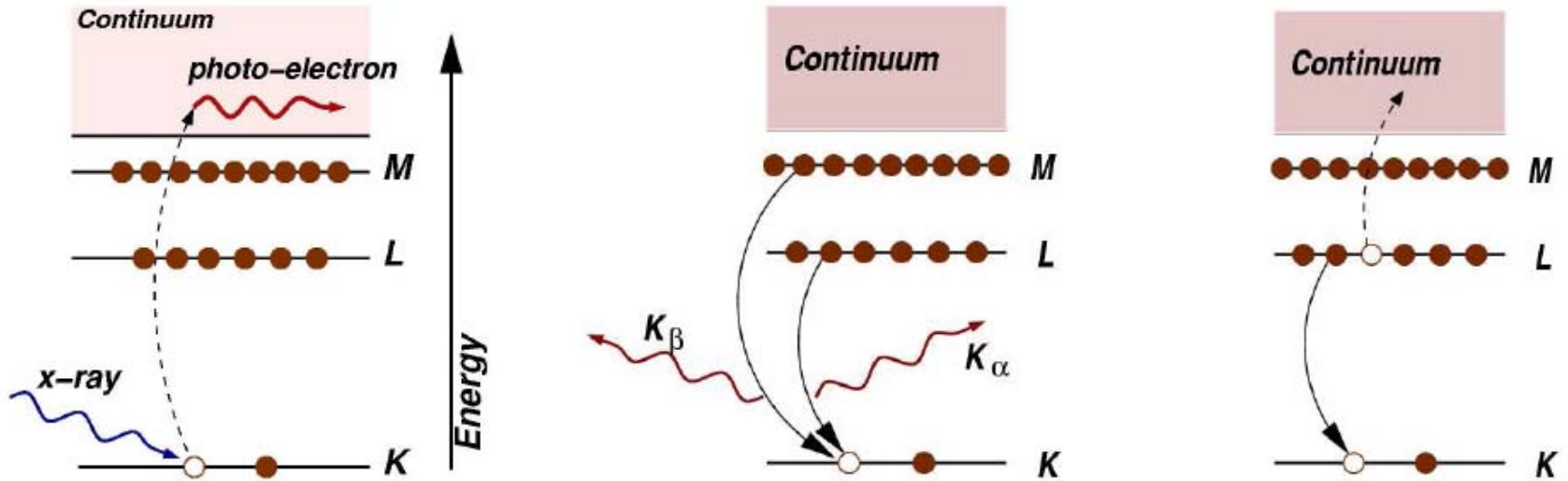
- Yields electronic and structural information
- In-situ application easy to realize
- Needs a synchrotron
- Data interpretation difficult

Absorption through matter



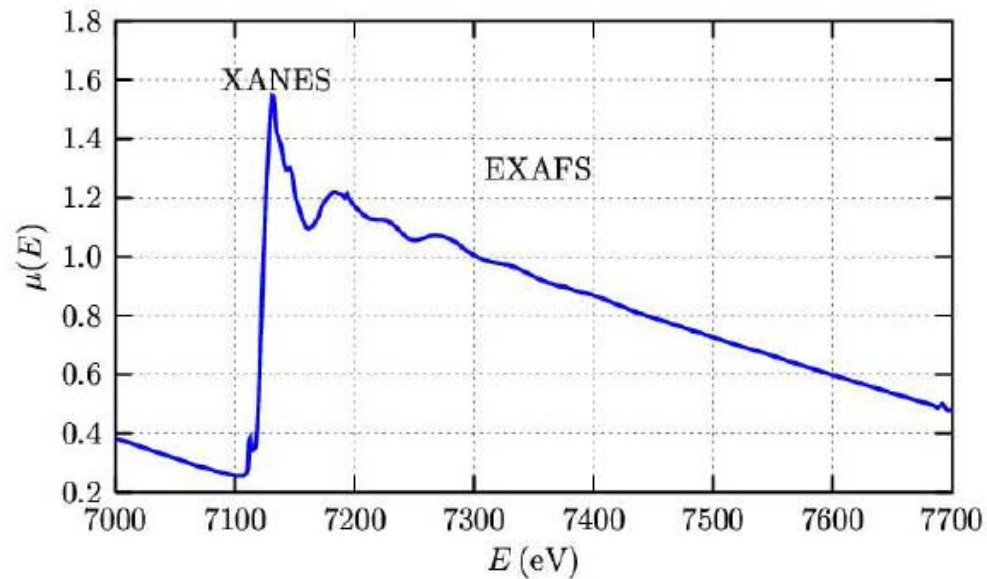
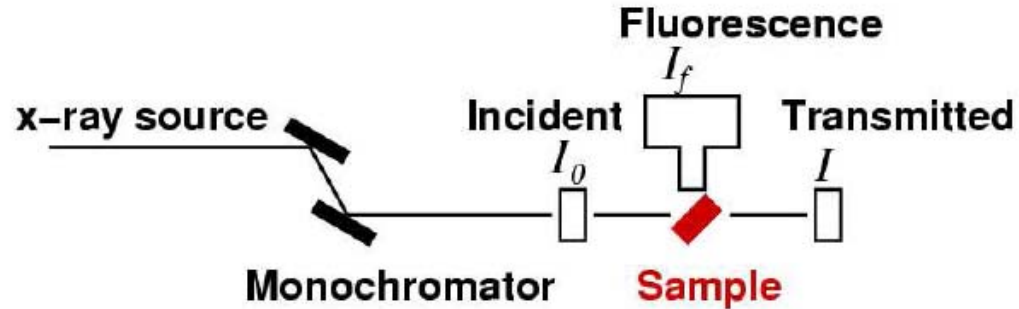
Lambert Beer's Law: $I = I_0 \cdot e^{-\mu d}$

Reminder: Photoemission, Fluorescence, Auger Emission



Au Foil

What is XAS?



*Absorption as function of energy of the x-ray
Shape is structure dependent*

XAFS Theory: Absorption of a monoatomic substance

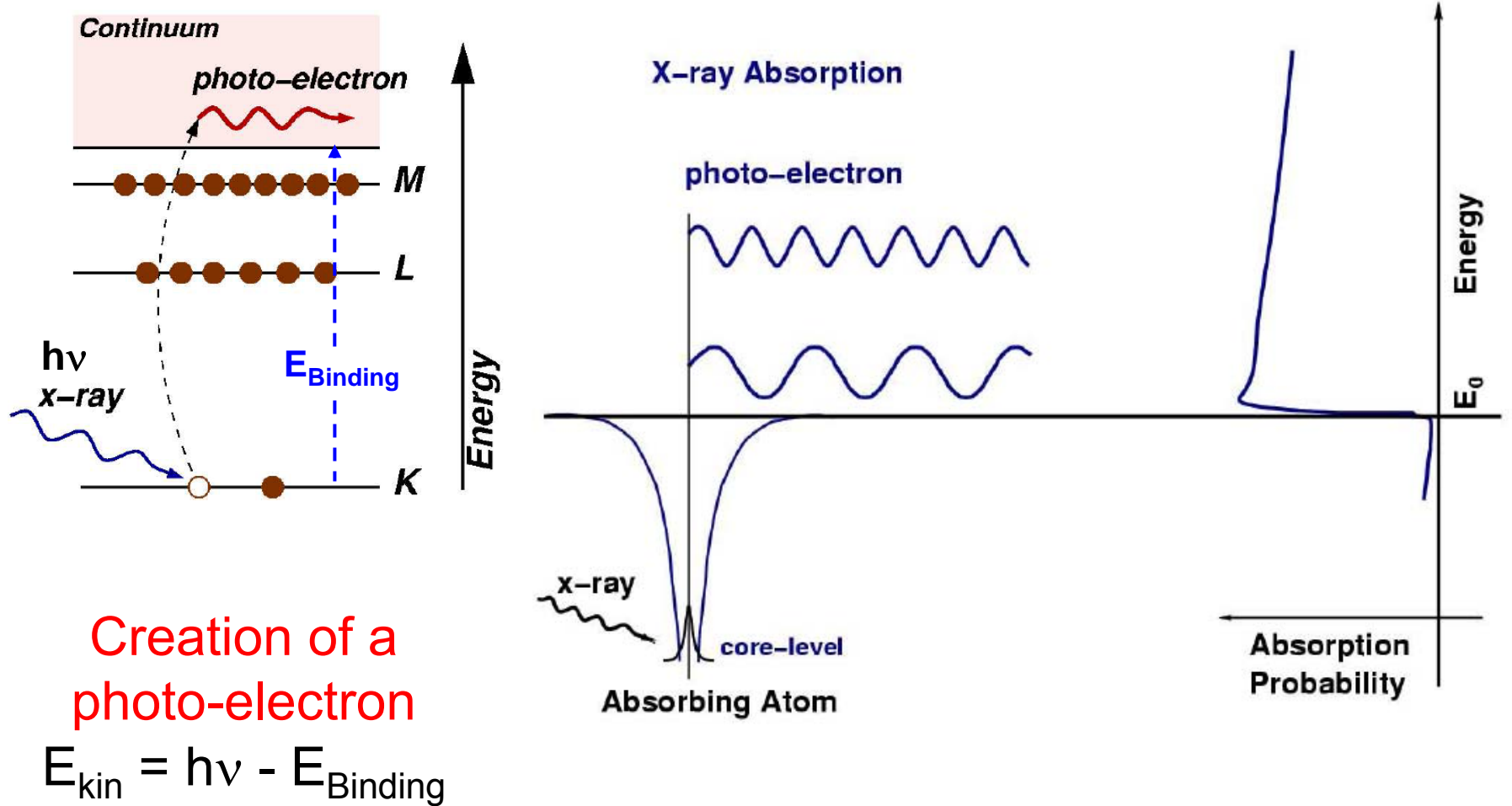


Photo-electron has kinetic energy

XAFS Theory: Substance with neighbor atoms present

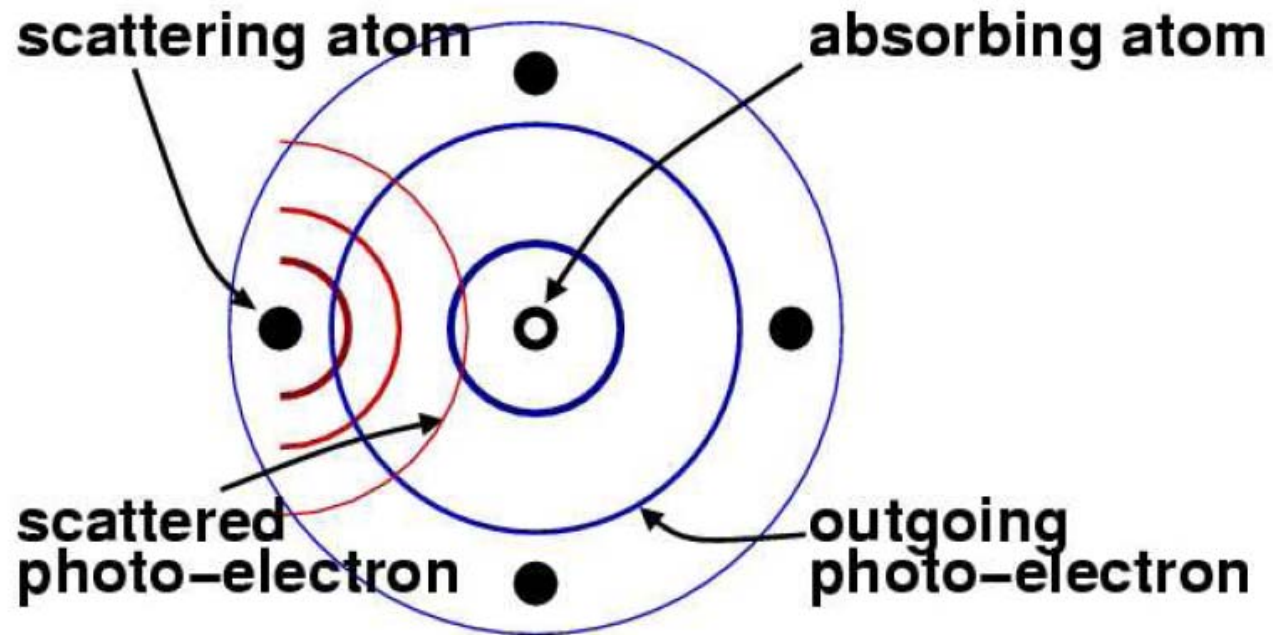


Photo-electron has kinetic energy

XANES

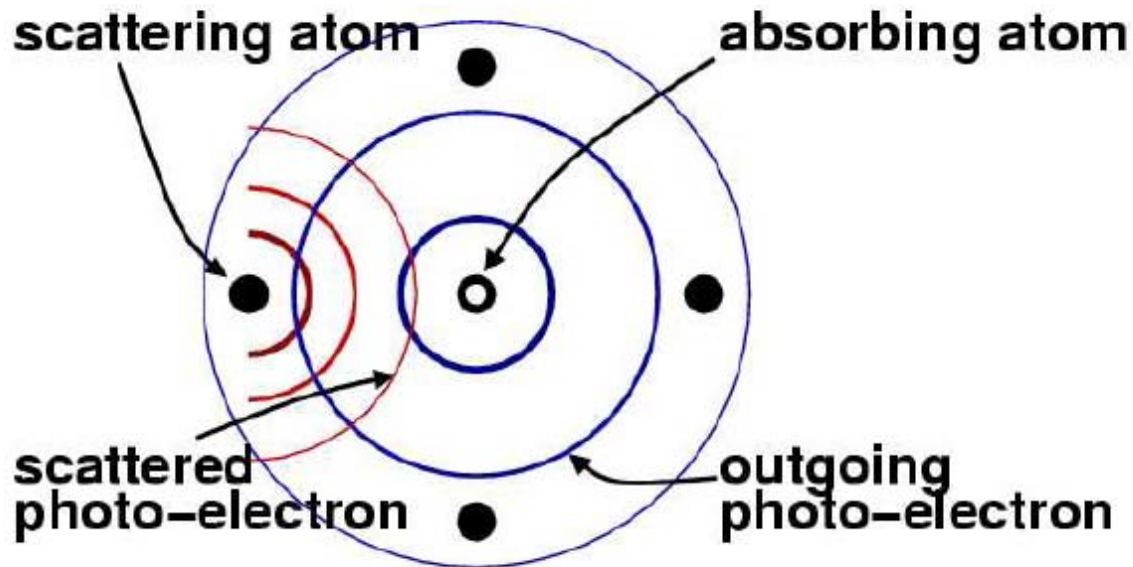
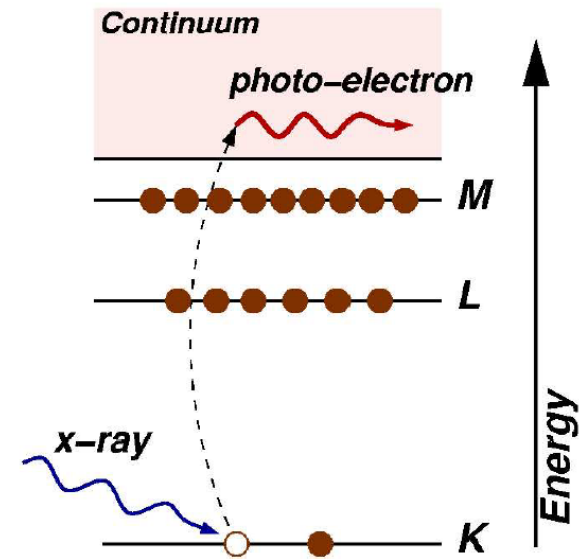
Fermi's Golden Rule

$$P \propto \left| \langle \Psi_i | T | \Psi_f \rangle \right|^2 \delta_{E_f - E_i - \hbar\nu}$$

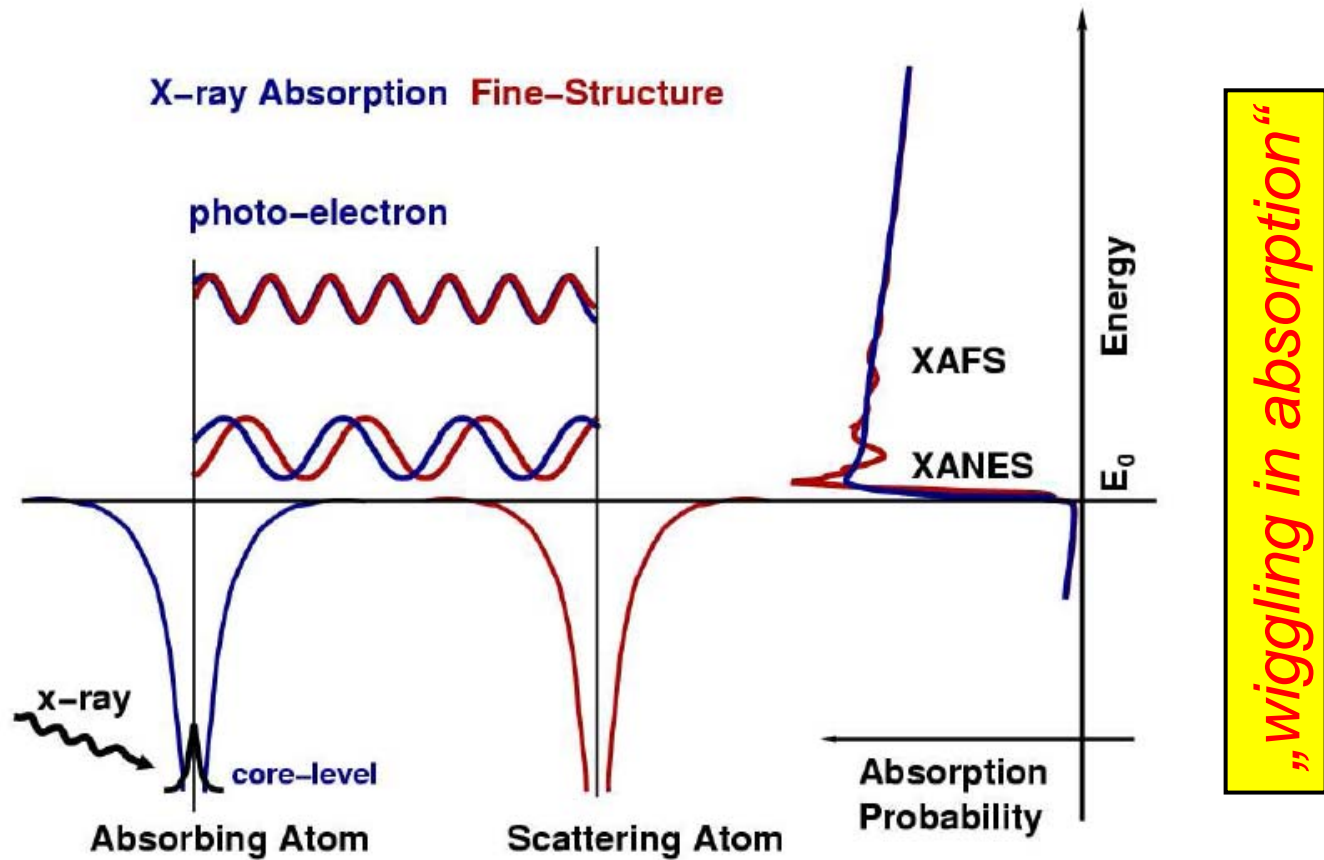
Initial state

Final state

Transition operator



XAFS Theory: Substance with neighbor atoms present



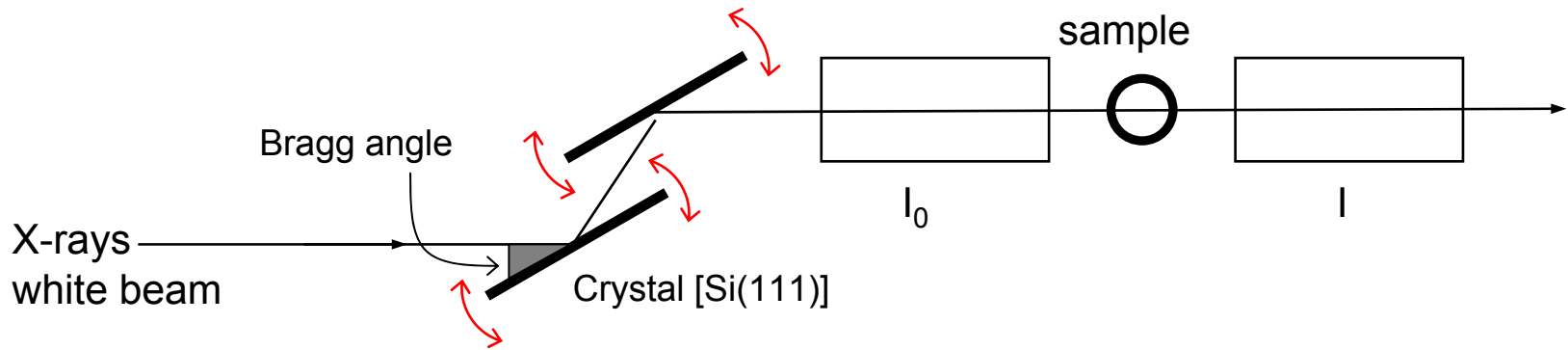
$$\Psi_{\text{final}} = \Psi_{\text{outgoing}} + \Psi_{\text{back scattering}}$$

Outgoing wave == backscattering == interference pattern
Constructive / destructive interference

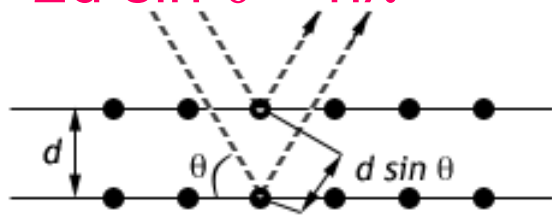
EXAFS is the wiggling part of the absorption

Tuning the energy

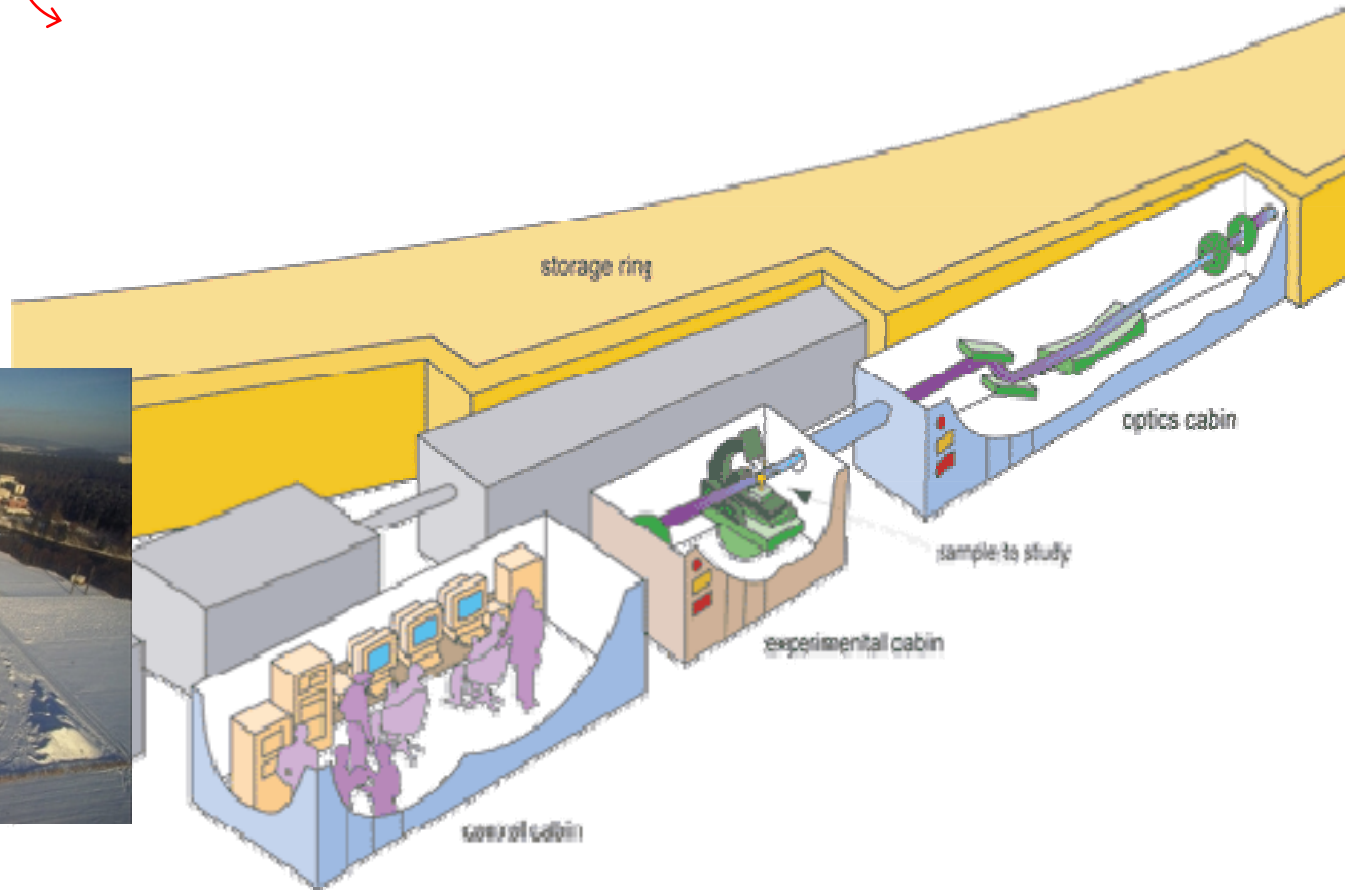
Double crystal monochromator



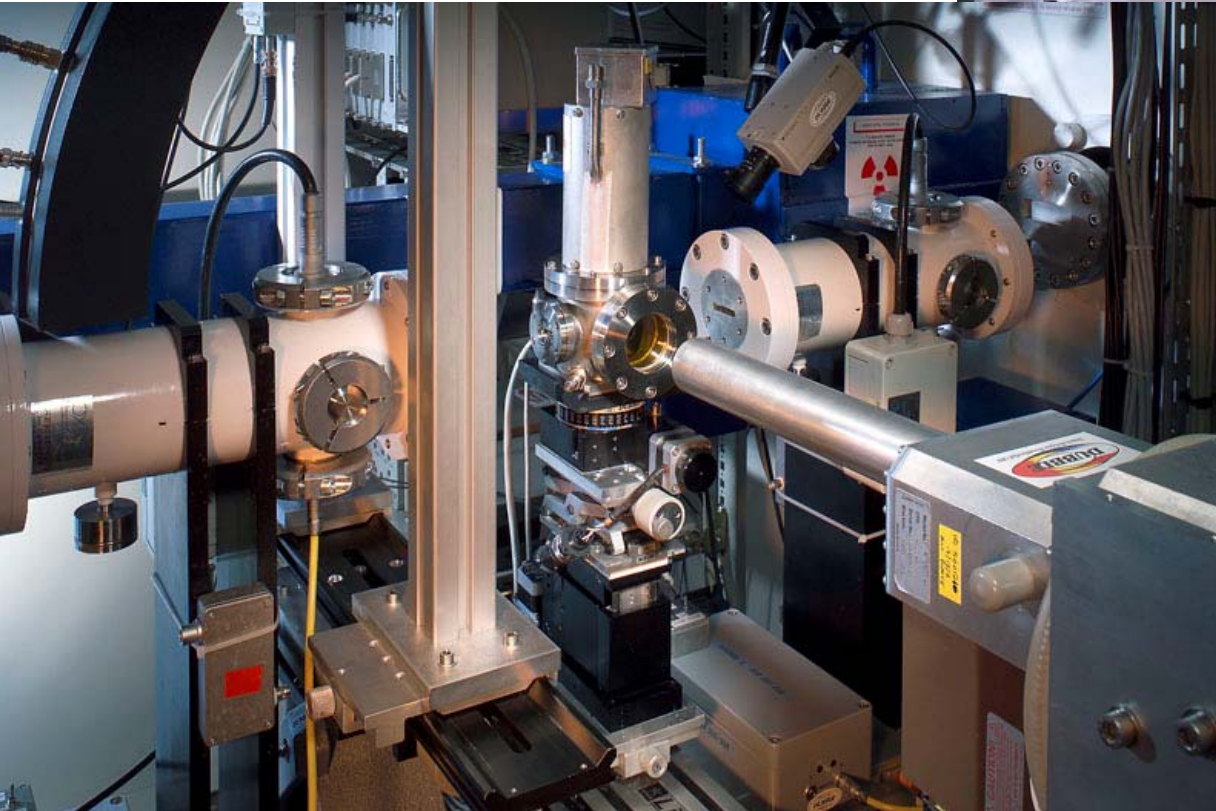
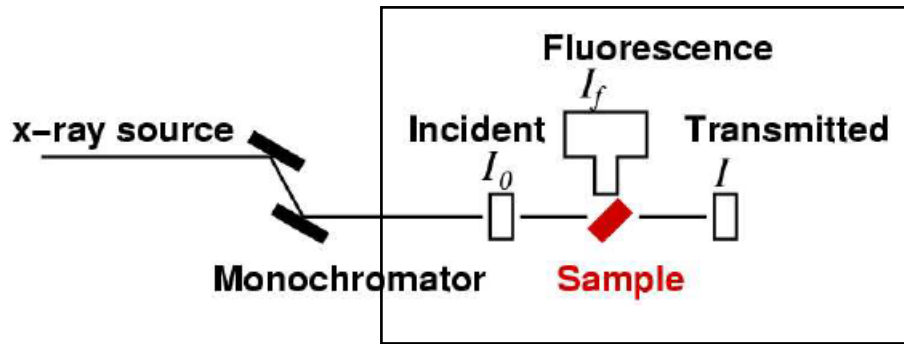
$$2d \sin \theta = n\lambda$$



SLS, Villigen

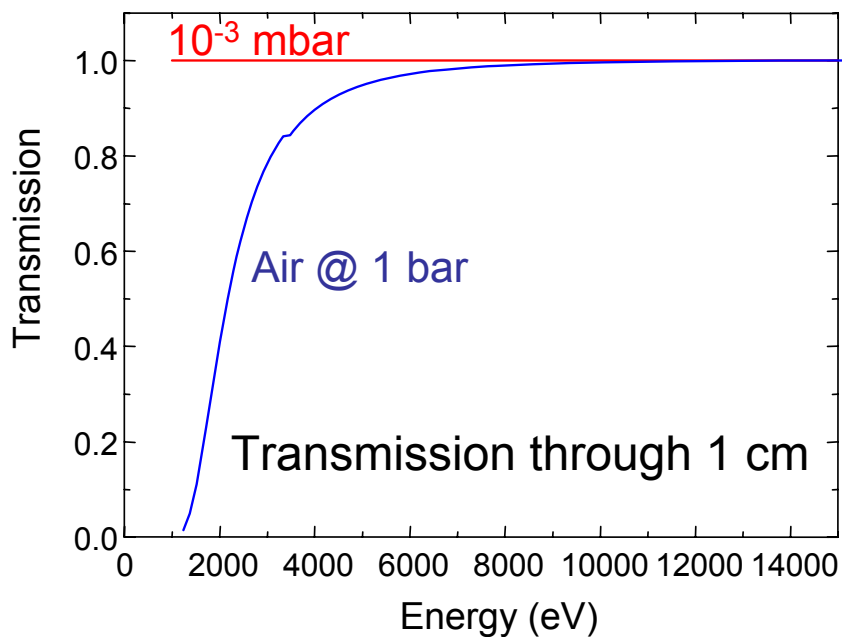
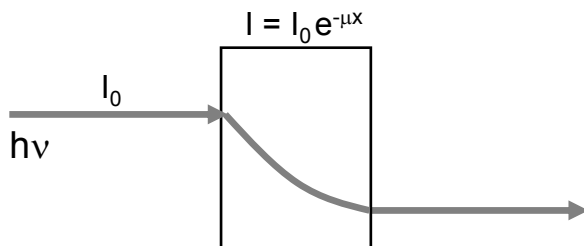


Experimental Hutch



BM26 (DUBBLE), ESRF Grenoble

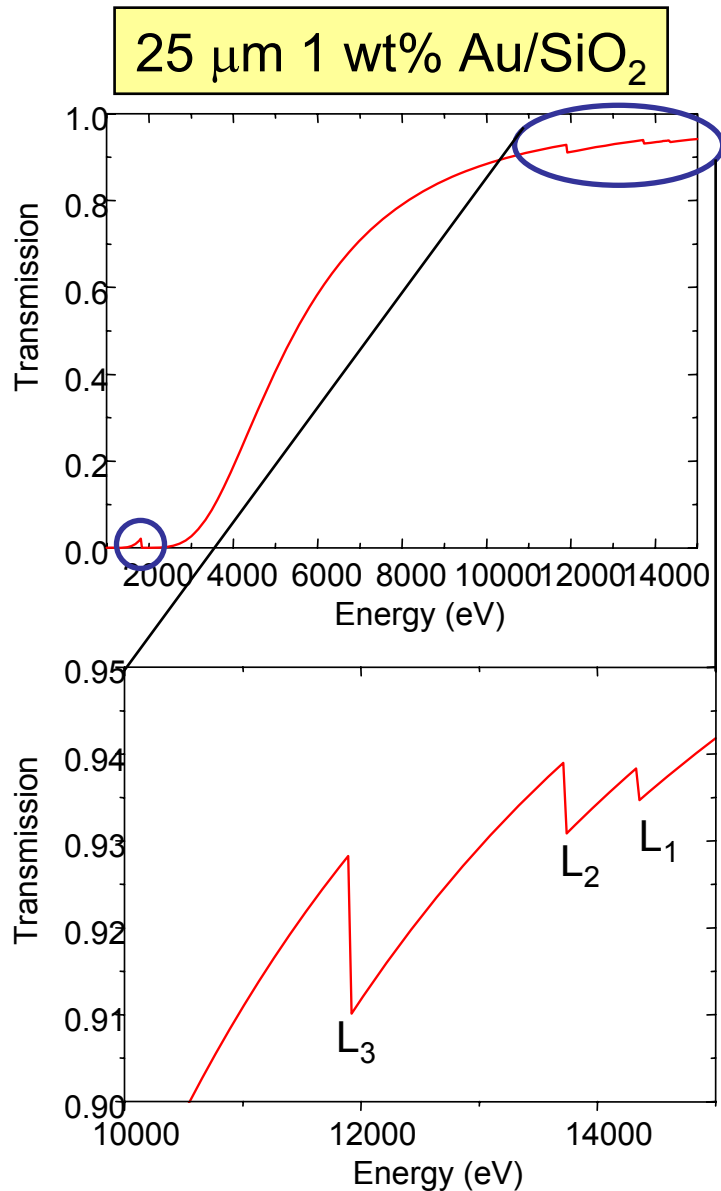
X-ray absorption through matter



Lambert Beer's law

$$dI = -\mu(E)I dx$$

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



Sample environment

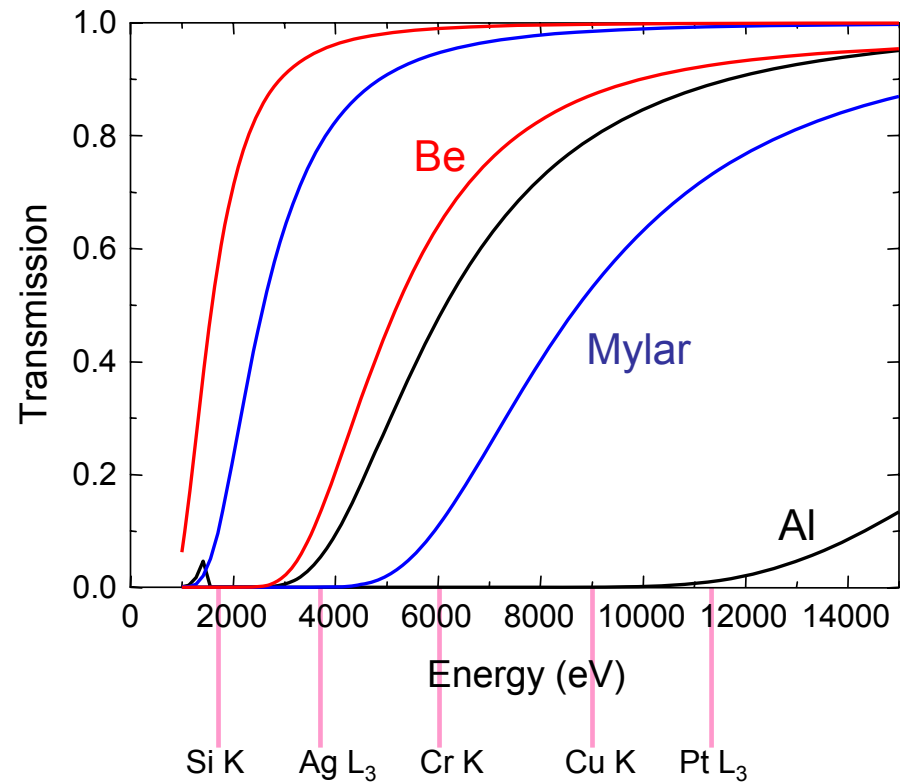
Absorption of X-rays is limiting factor

Find a good window material

- Size of window
- Thickness
- Inertness
- Temperature resistance
- Pressure
- Safety

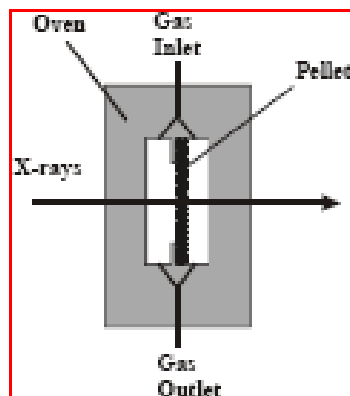
pressure
temperature
environment

Transmission through
25 μm and 1 mm



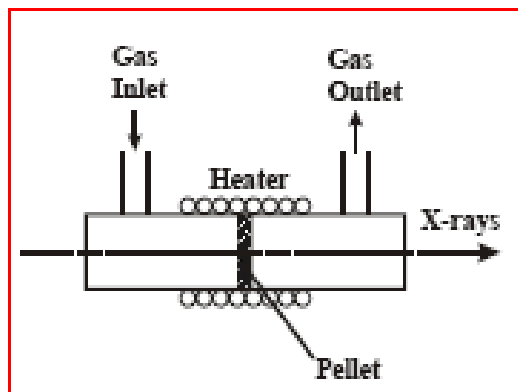
In situ EXAFS cells for gas-solid reactions

Reaction gas mixture flows around a pellet



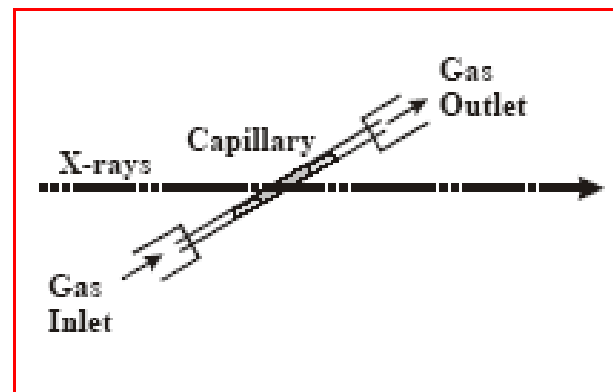
Large dead volume
Good for stationary conditions

Reaction gas flows through a catalyst pellet

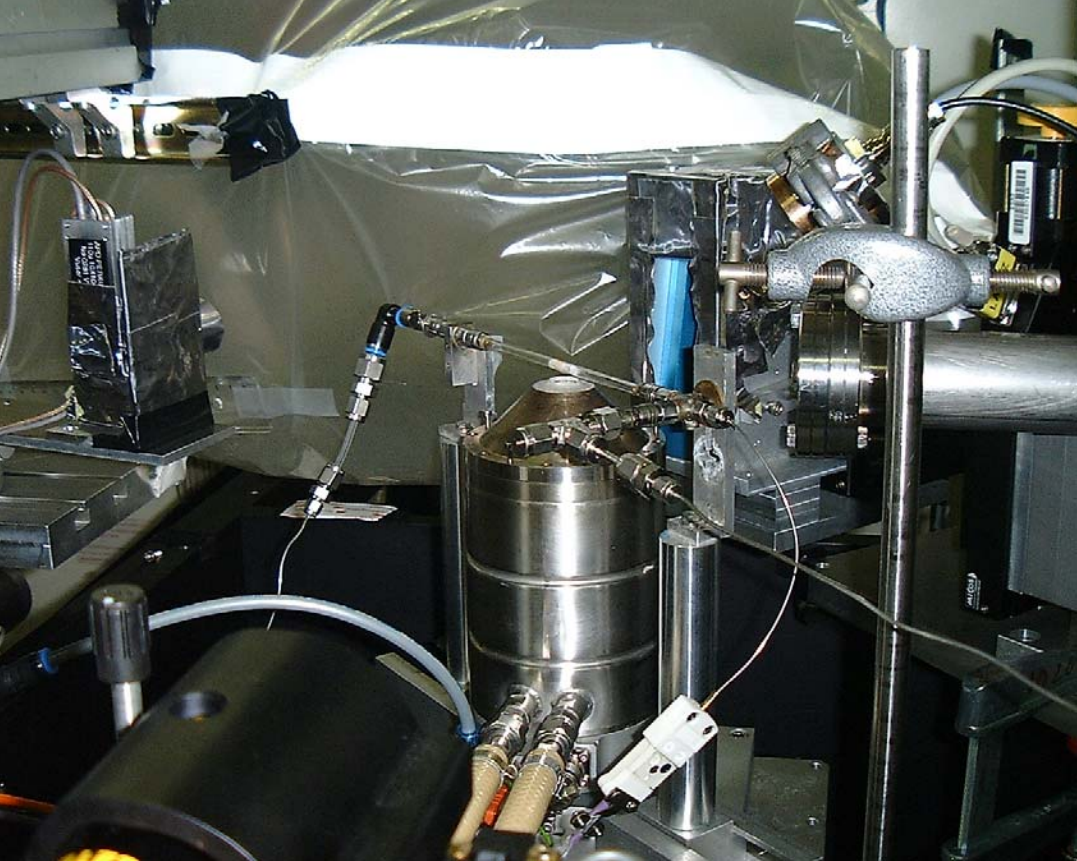


Critical d/l (smaller effectivity of the catalyst)

Small Glass Reactor with very thin windows (0.01mm)



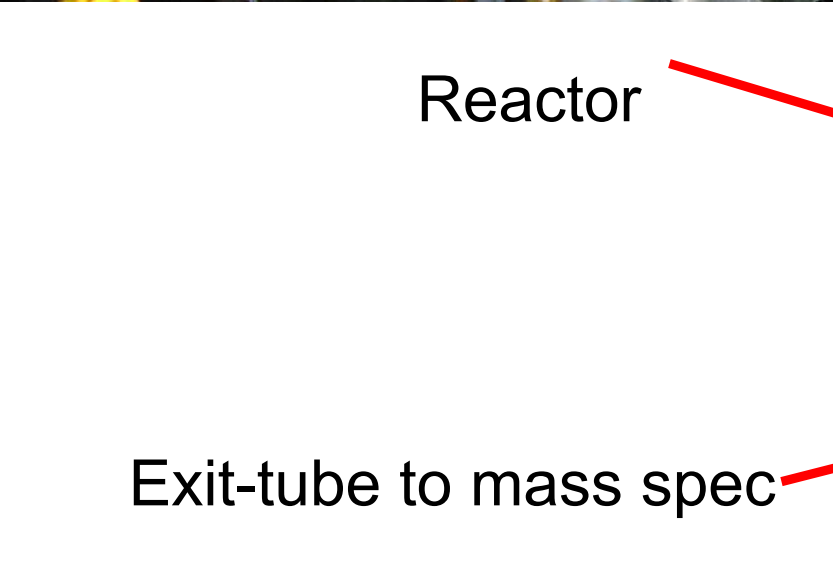
Small dead volume
Optimal d/l
Good for structural changes
Structure-activity relations



ID26, ESRF

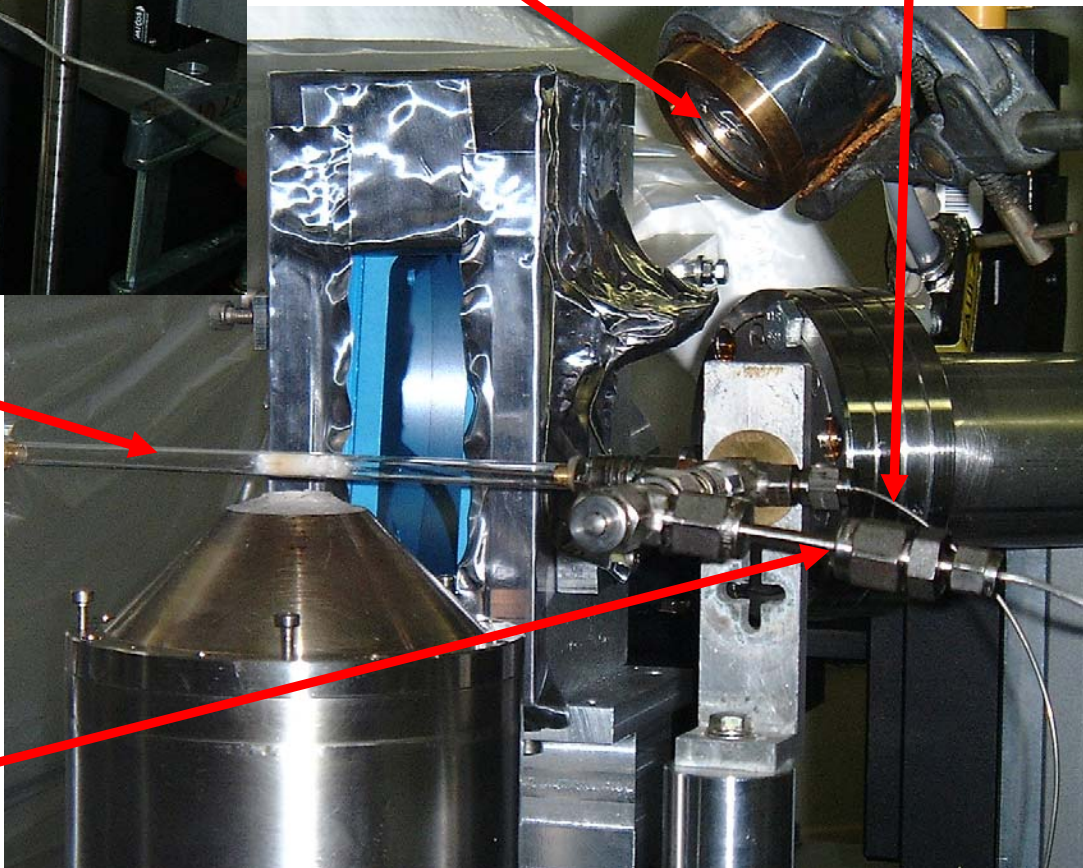
Fluorescence
detector

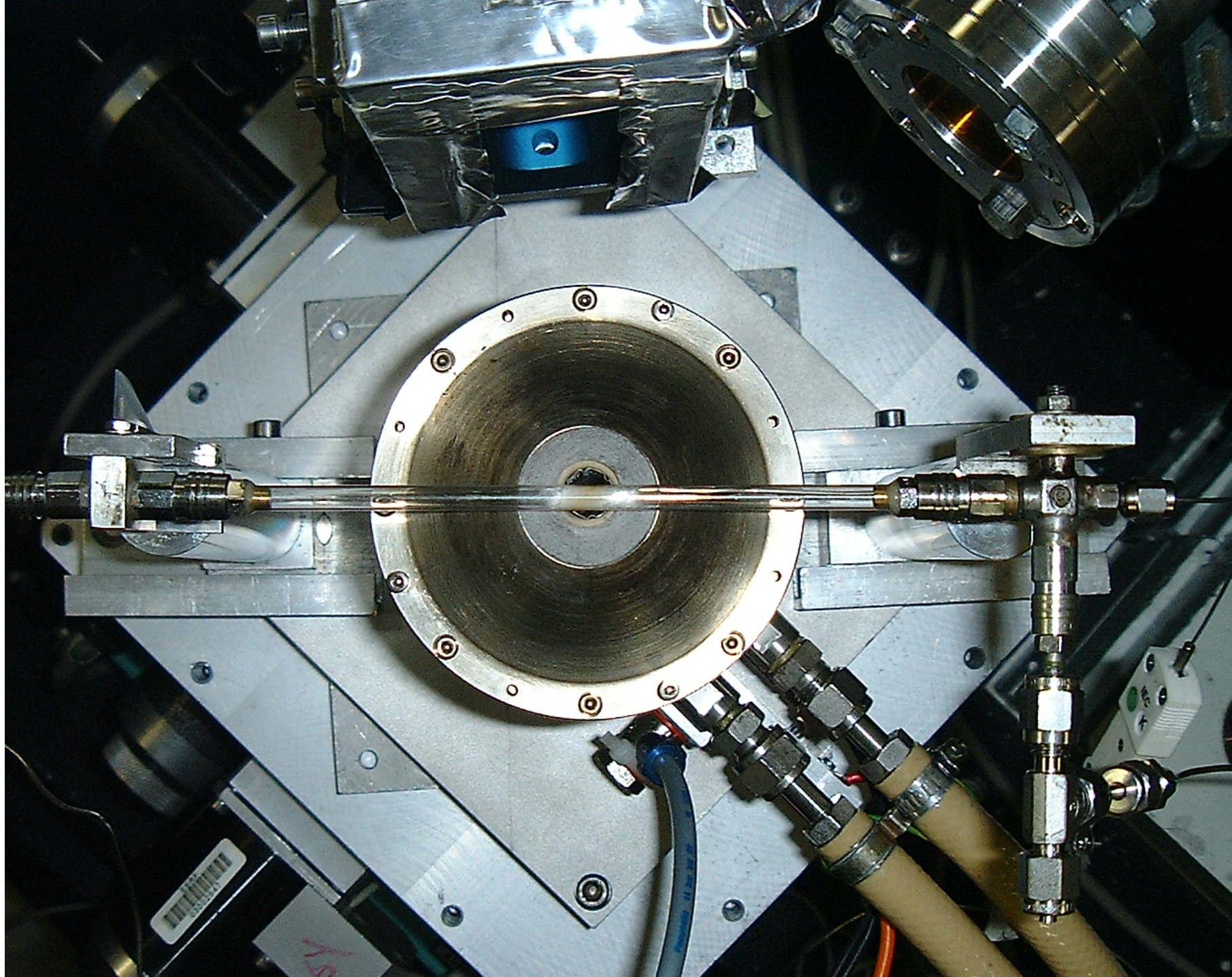
Thermo
Couple



Reactor

Exit-tube to mass spec





XANES

Fermi's Golden Rule

$$P \propto \left| \langle \Psi_i | T | \Psi_f \rangle \right|^2 \delta_{E_f - E_i - \hbar\nu}$$

Initial state

Final state

Transition operator

Dipole transition:

$$\Delta l = \pm 1$$

K edge: $1s \rightarrow p$

L edge: $2s \rightarrow p$

$2p \rightarrow s, d$

However

Quadrupole transition:

$$\Delta l = \pm 2$$

K edge $s \rightarrow d$

$p \rightarrow f$

Quad. Trans. probability is about 10^{-3} smaller, but d-DOS \gg p-DOS

Visible in the K pre-edges!!

What determines the shape of XANES spectra?

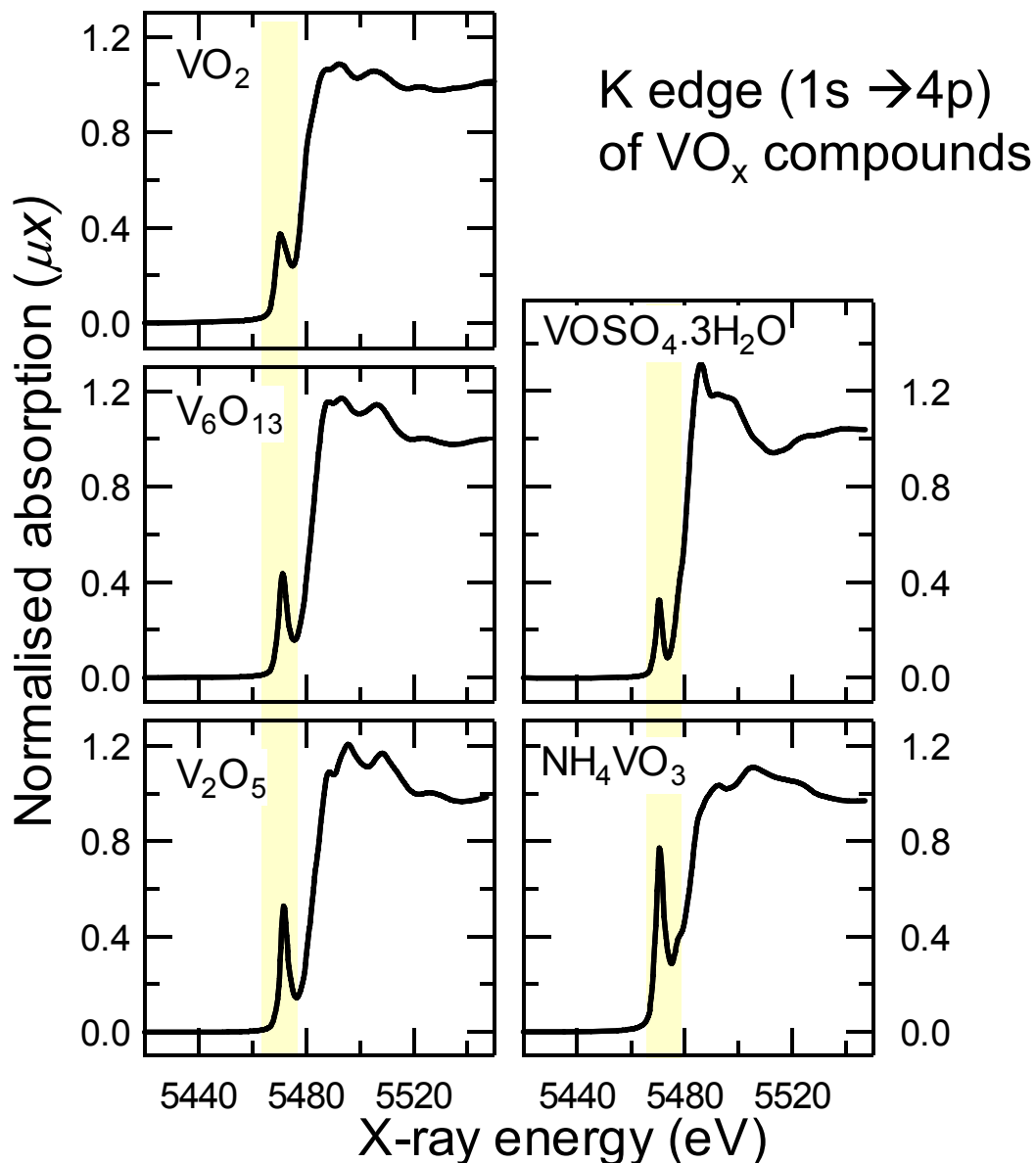
- Pre-edge
- Edge-energy
- Shape over the edge

Pre-edge

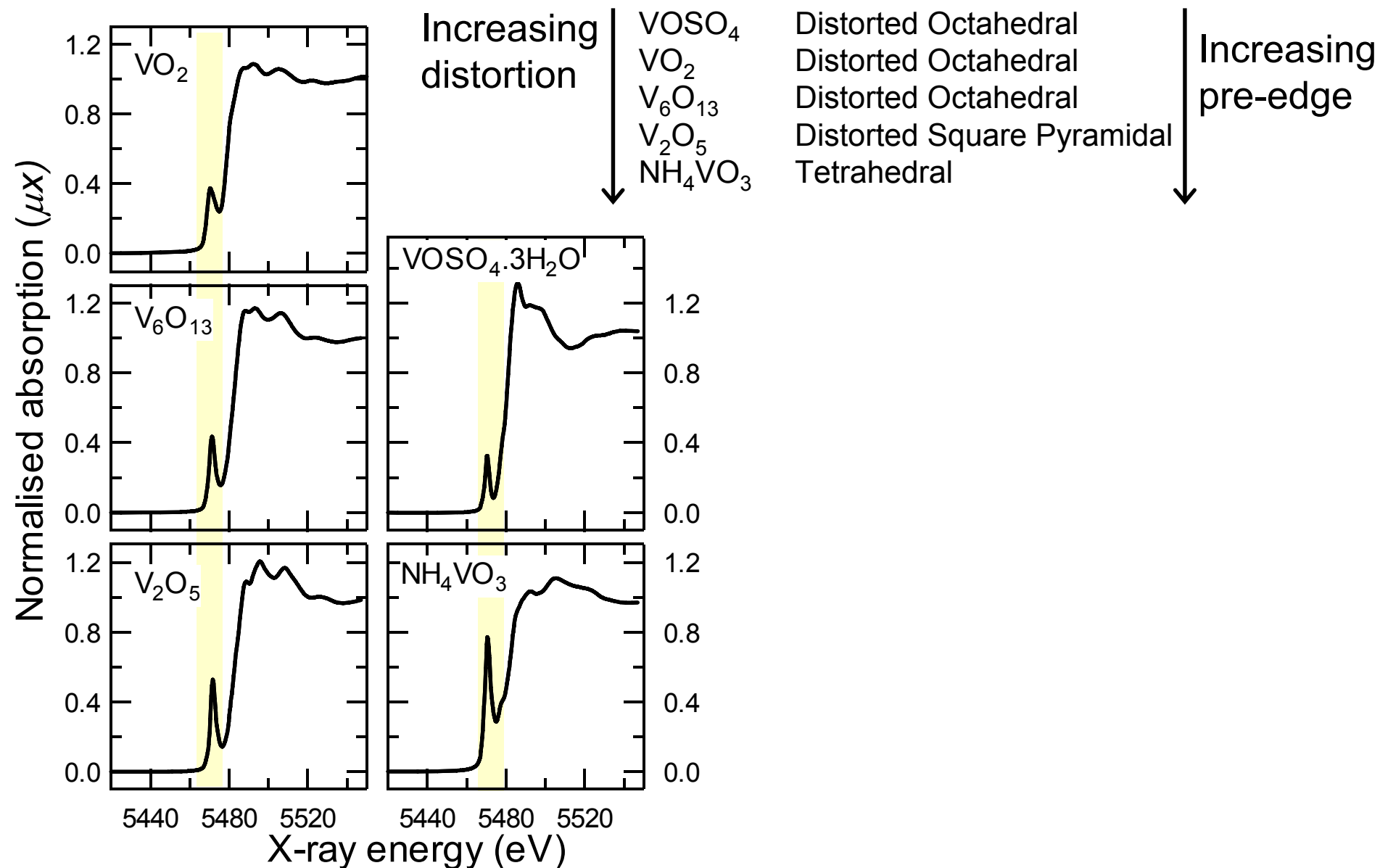
- intensity
- energy

BUT.....

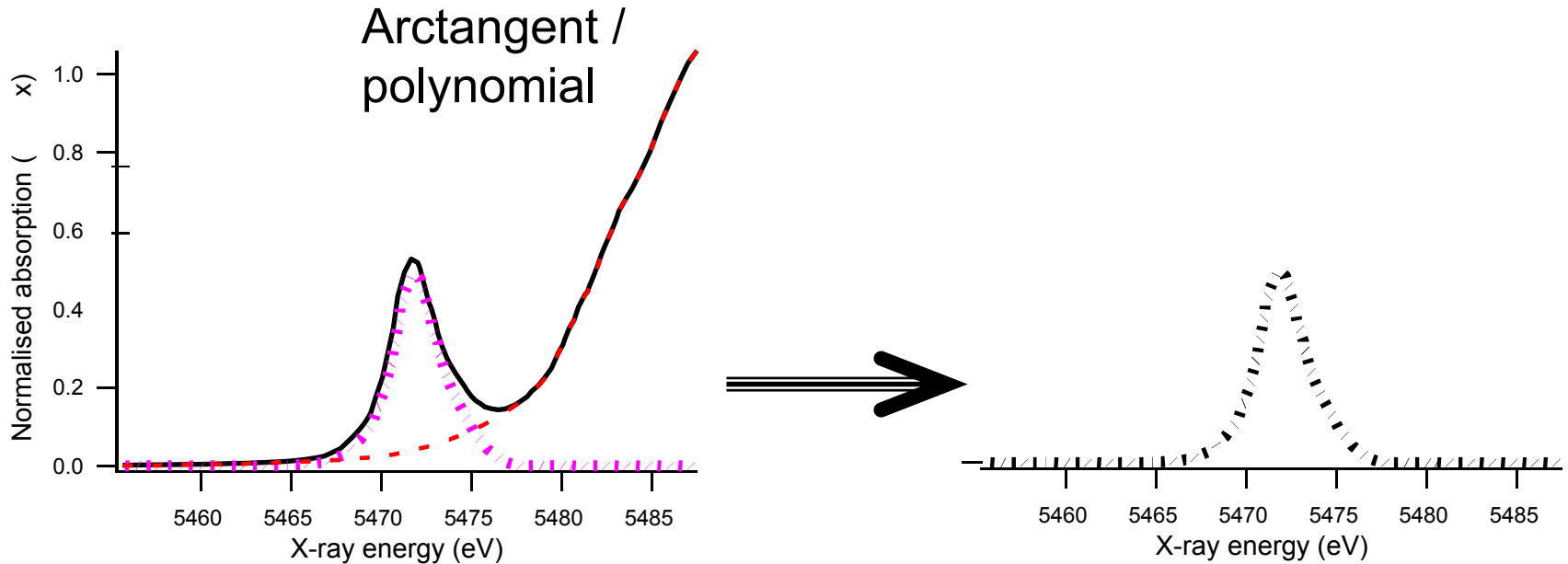
..... there is not always a pre-edge



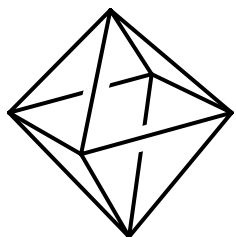
In order of increasing distortion from octahedral



Isolation of the pre edge *by edge subtraction*



Pre-edges intensity & energy varies (K edge)



Pure octahedral case

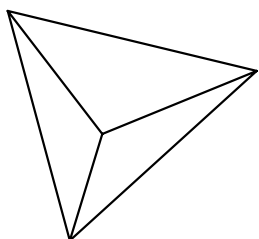
Centro-symmetry: no p-d mixing allowed: only quadrupole transition

→ very low intensity

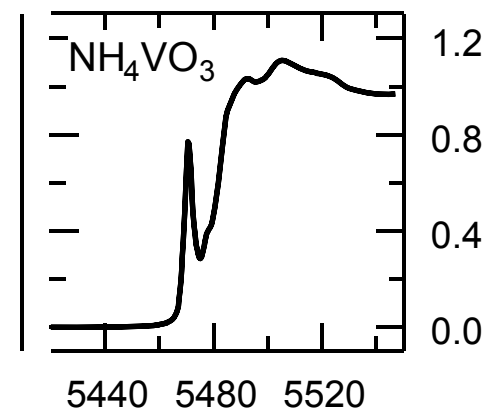
Distortion from octahedral

P-d mixing allowed: dipole transition in pre-edge + quadrupolar trans.

→ increasingly large intensity



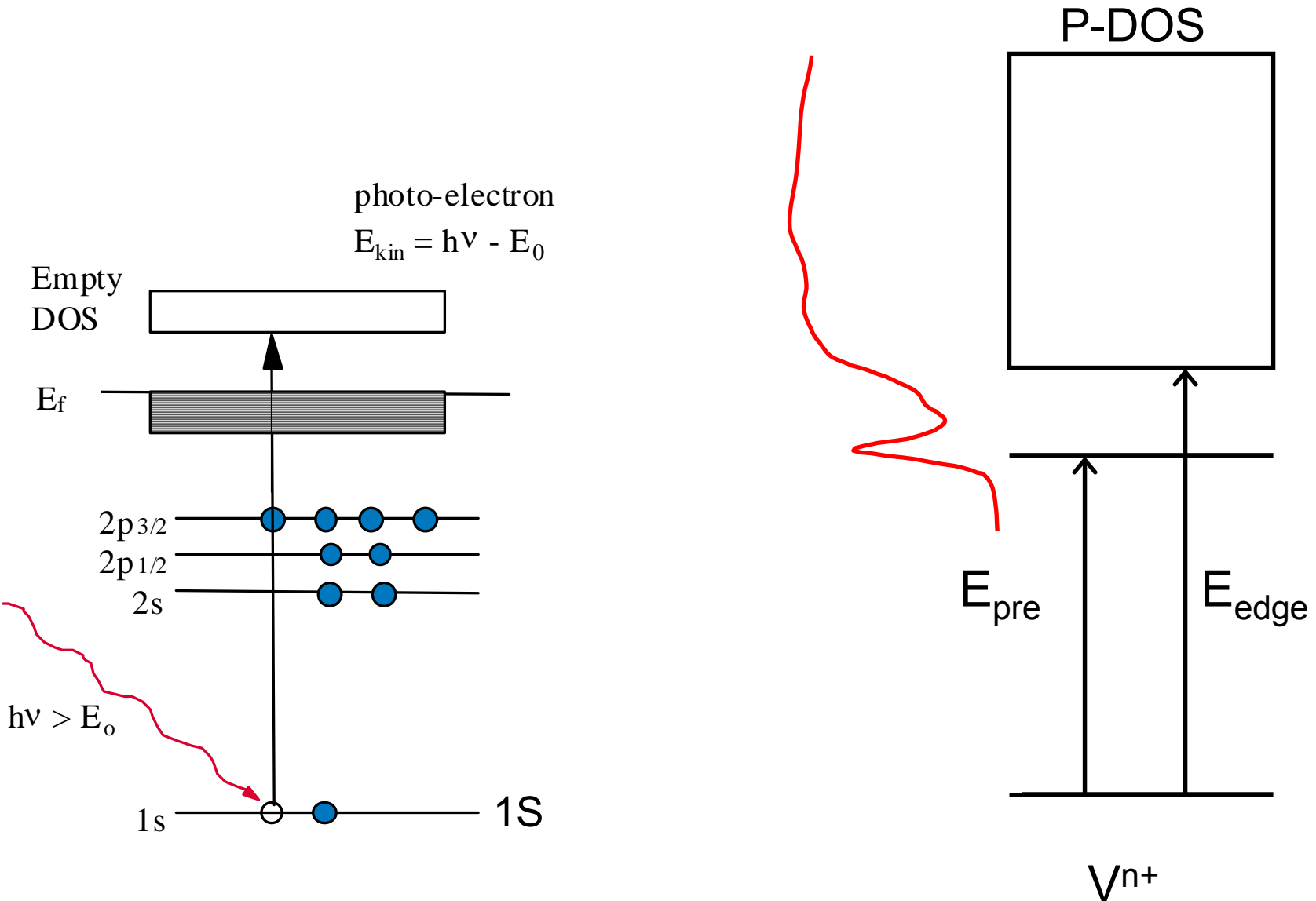
Pure tetrahedral => largest pre-edge



Intensity pre-edge indicative of geometry

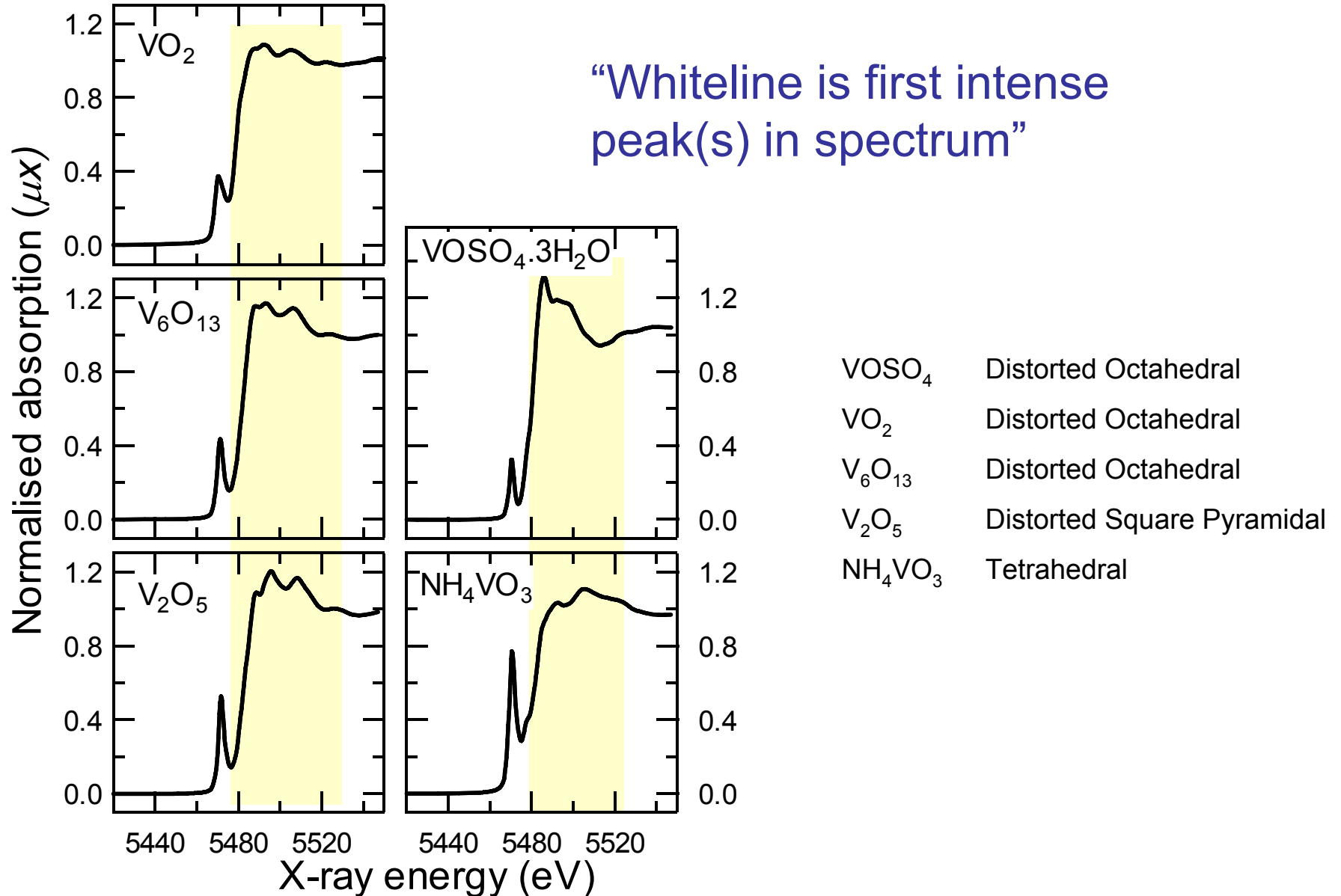
(Pre-)edge Energy and Valence

Edge position is measure of oxidation state



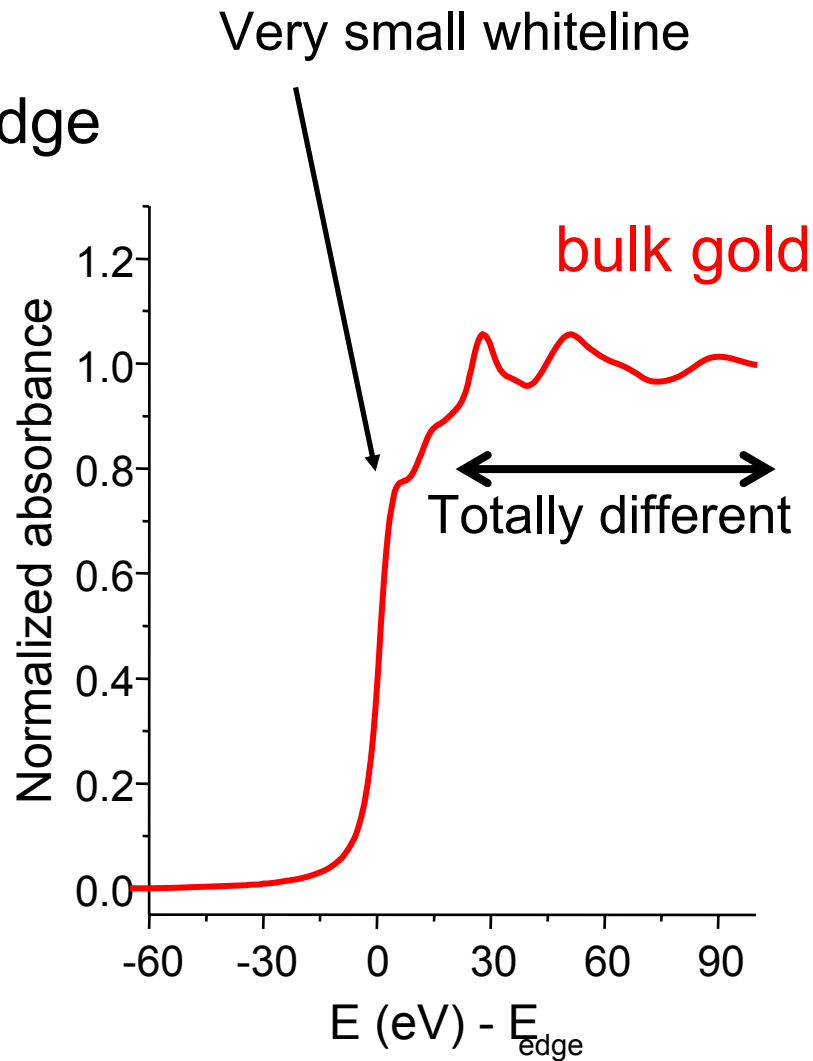
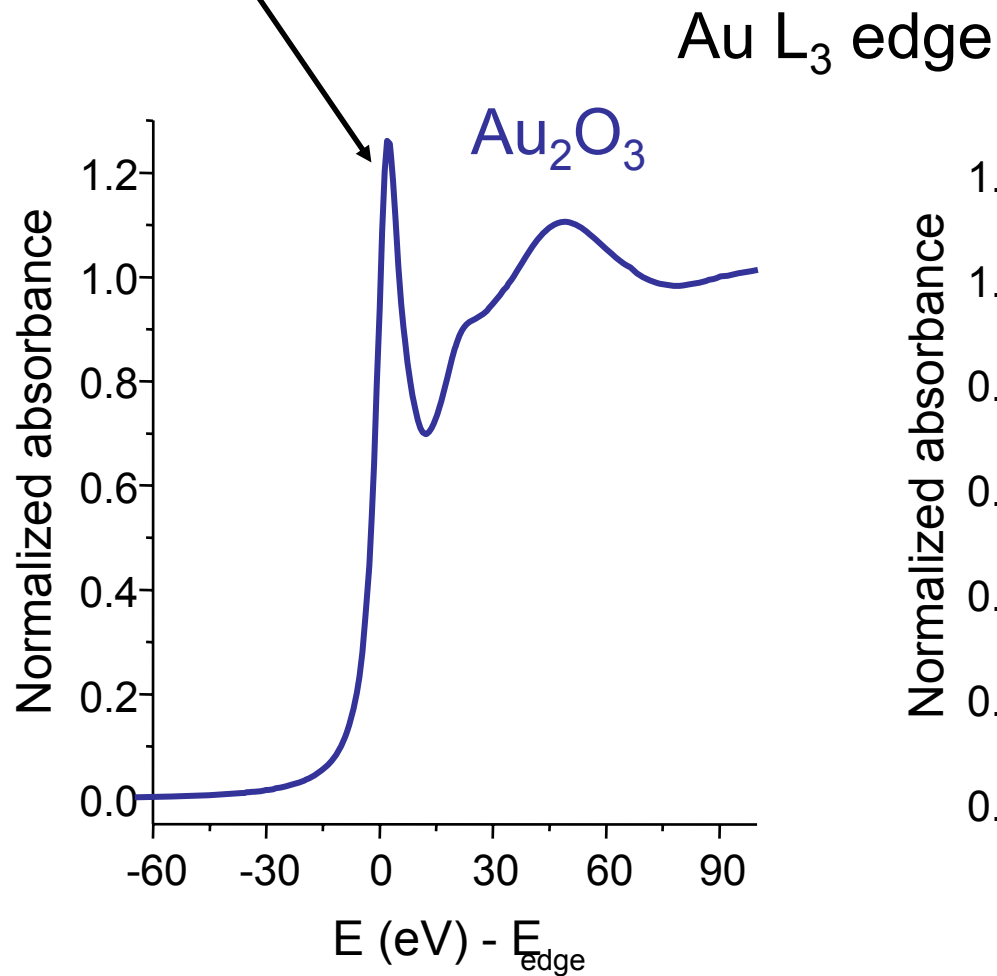
Shape of the whiteline

For L edges > 3 keV and all K edges

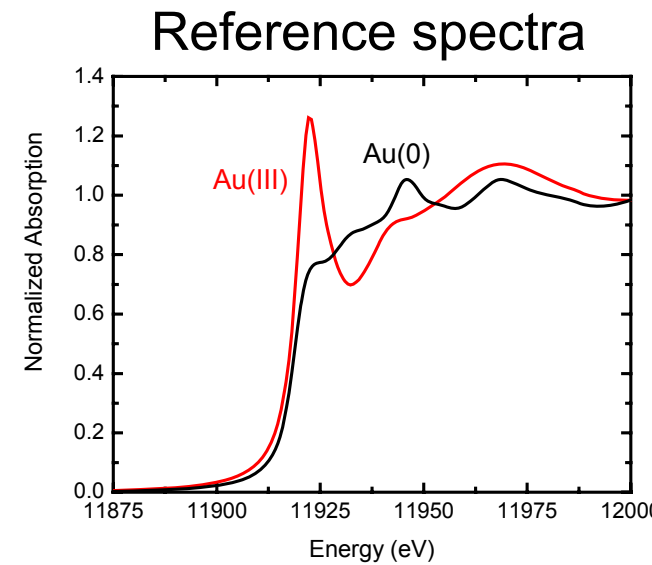
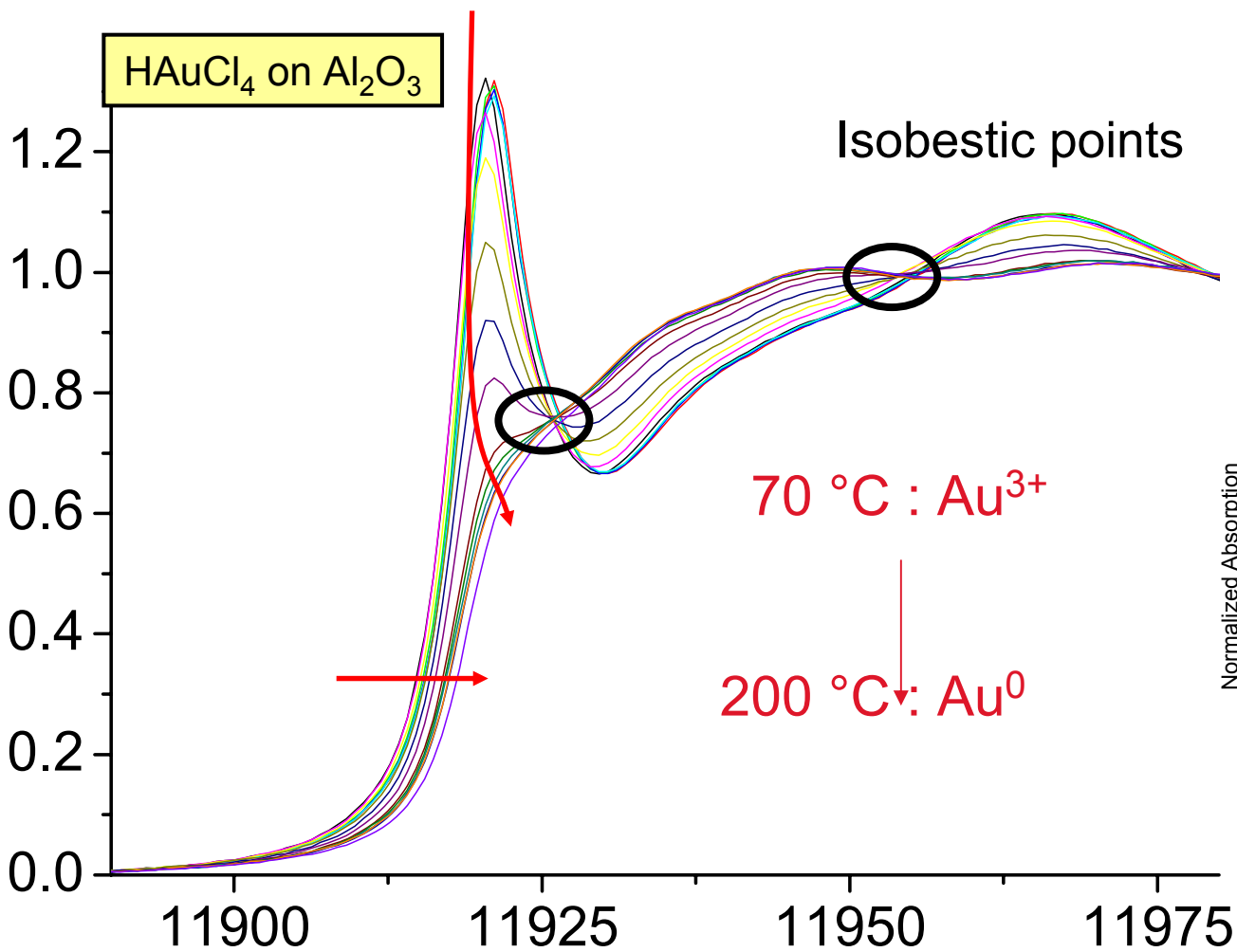


Shape of the whitenline: L-edges

Whiteline reflects holes in d-band

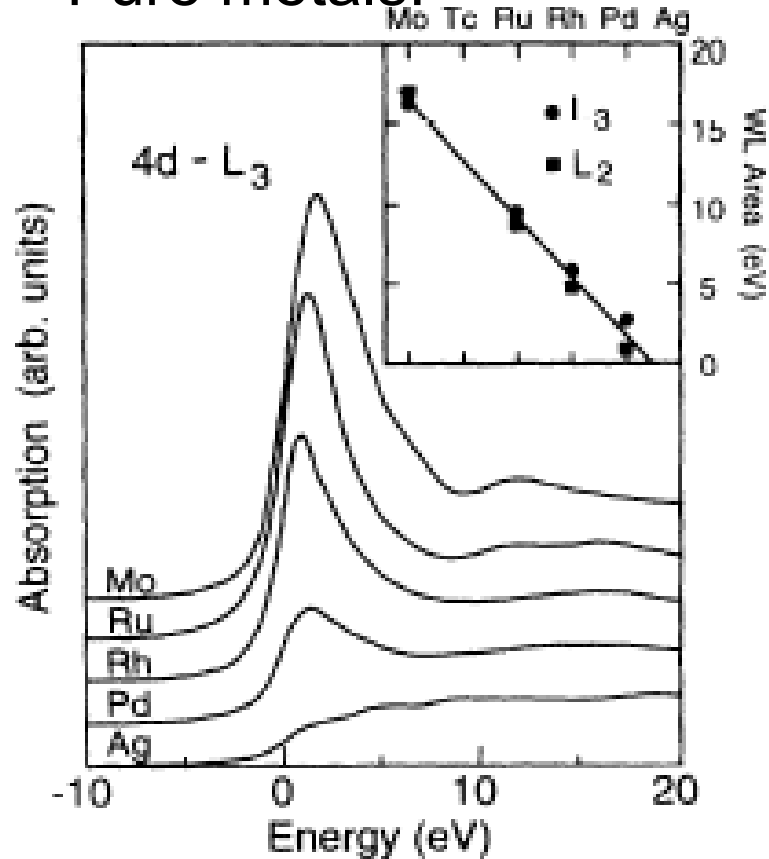


In situ Au^{3+} reduction in He/H_2



Shape of the whiteline: L-edges

Pure metals:

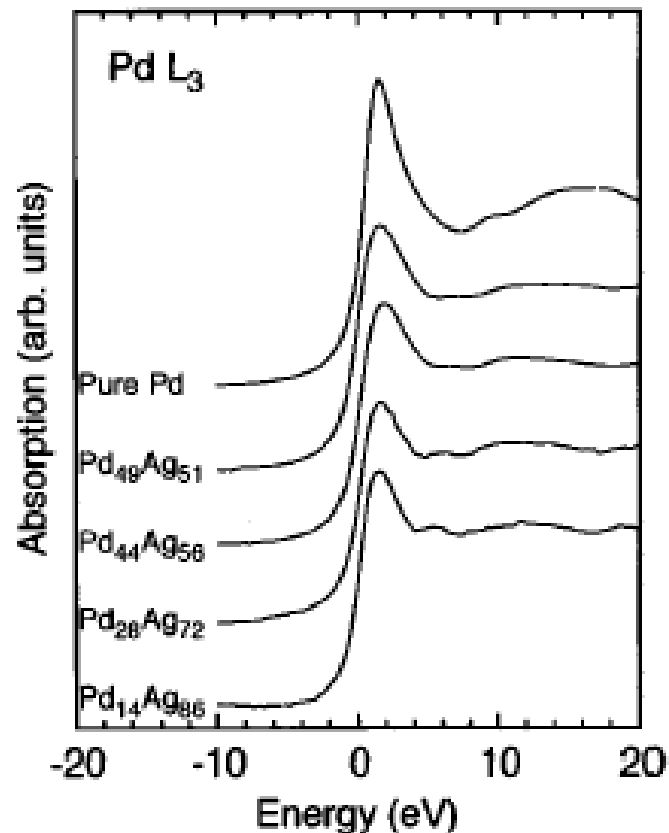


Whiteline reflects holes in d-band

Mo	Tc	Ru	Rh	Pd	Ag
0.5	0.6	0.7	0.8	0.9	1.0

Ideal d-band filling

Alloying:



Whiteline reflects charge transfer

Abstract (I)

Pre-edge

- Valence
- Geometry

Edge

- Valence

Shape over the edge

- Geometry
- D-band filling (L_{III} -edge)
- (Non- / Anti-bonding) DOS states
(- Adsorbates)

For many (many!) compounds structures and spectra are available in literature

Note

Variations in XANES may be very subtle and hardly visible in the data:
take (negative) second derivative

L edges

Whiteline intensity reflects number of holes in the d band (valence)

K edges

(Pre) edge position reflects valence

Shape of XANES indicative of geometry

Typical XANES Experiment

- Catalyst samples, measured in desired conditions
temperature, pressure, aggregation state
- Reference samples that likely resemble the state of the catalyst
 - Various oxidation states
 - Various coordinations
- Identification of trends, similarities in reference samples
- Comparison of trends, similarities to 'unknowns'
- Application of theory to obtain ultimate information (expert option).