

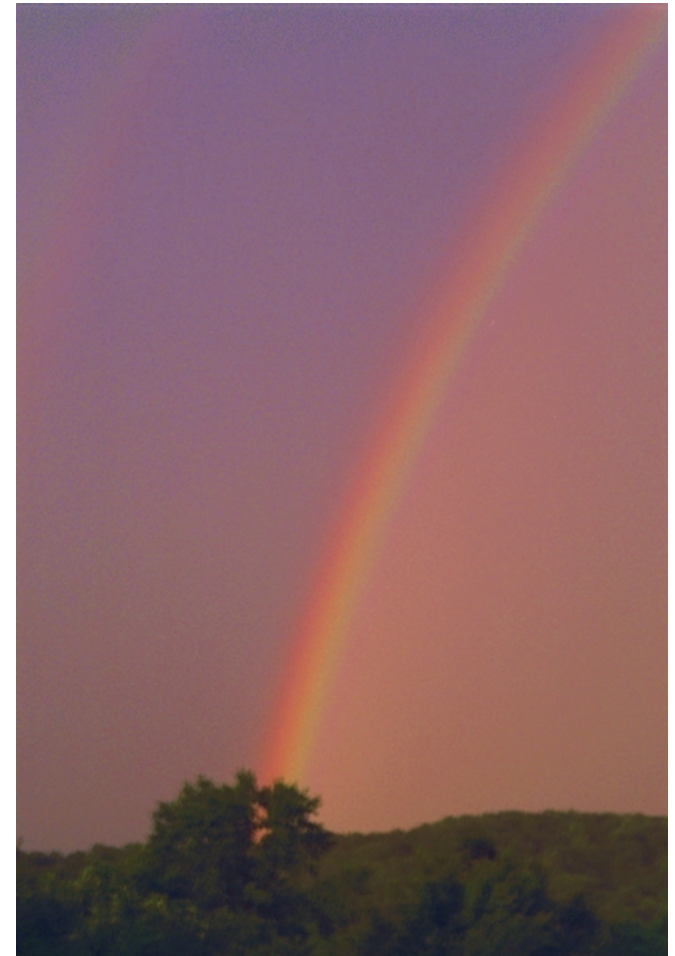
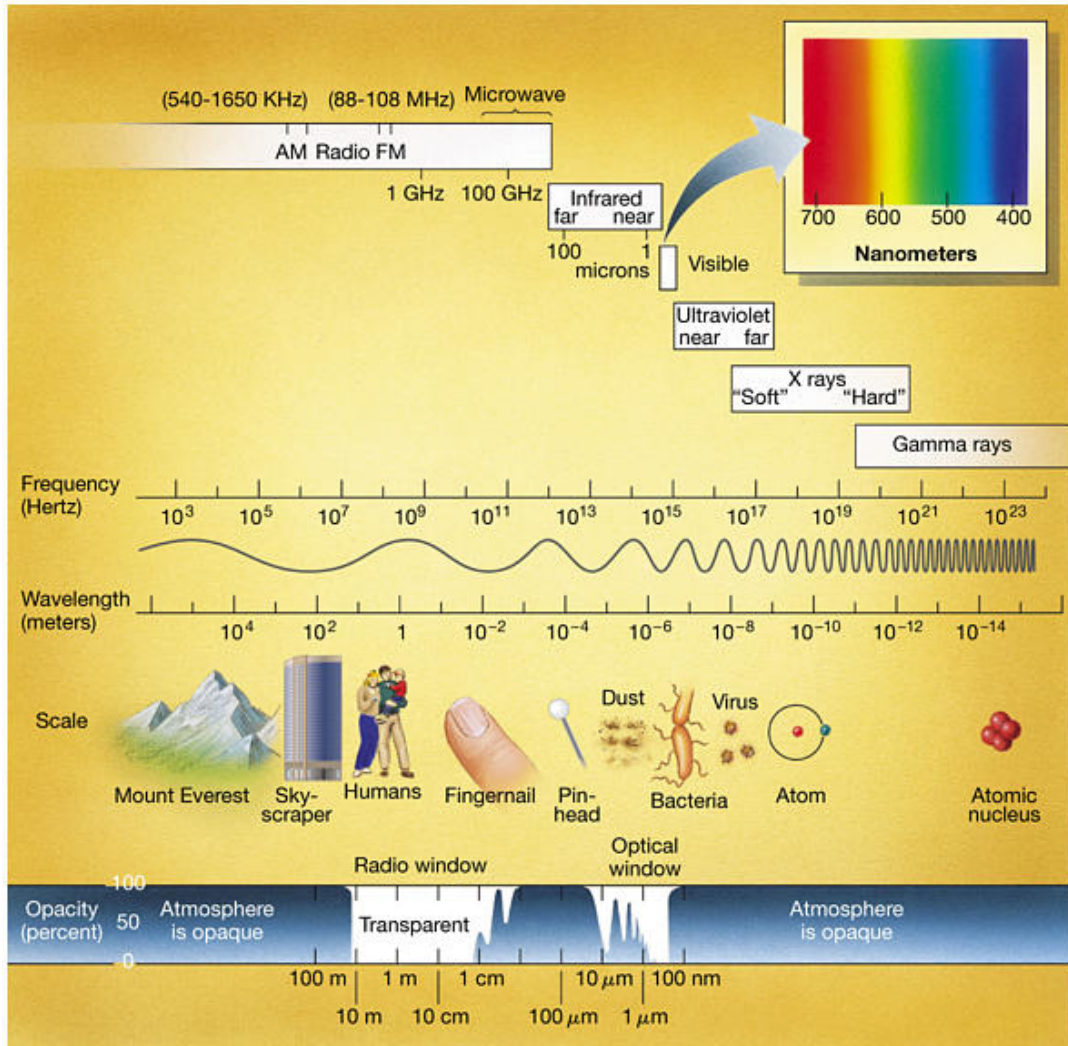
# X-ray absorption spectroscopy

## 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

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<b>XAS</b>	X-ray Absorption Spectroscopy
<b>EXAFS</b>	Extended X-ray Absorption Fine Structure
<b>XANES</b>	X-ray Absorption Near Edge Structure
<b>NEXAFS</b>	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

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### 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)**

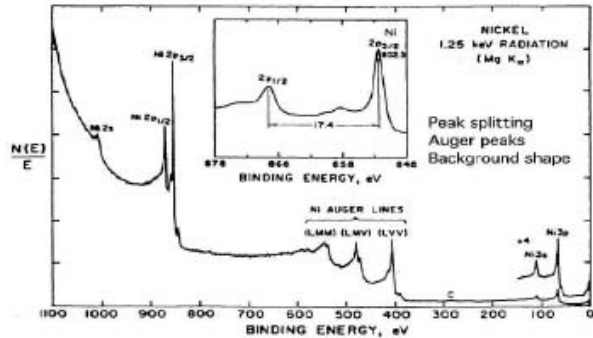


**APS (Chicago)**



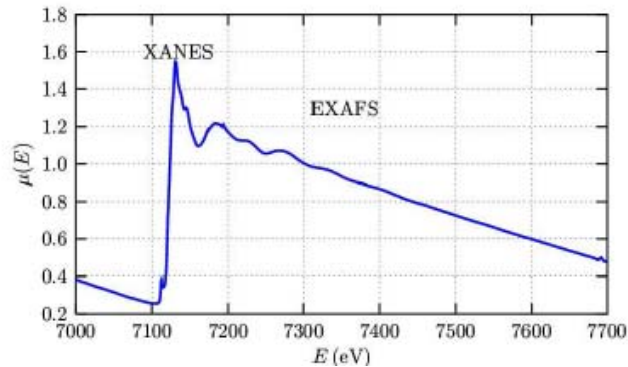
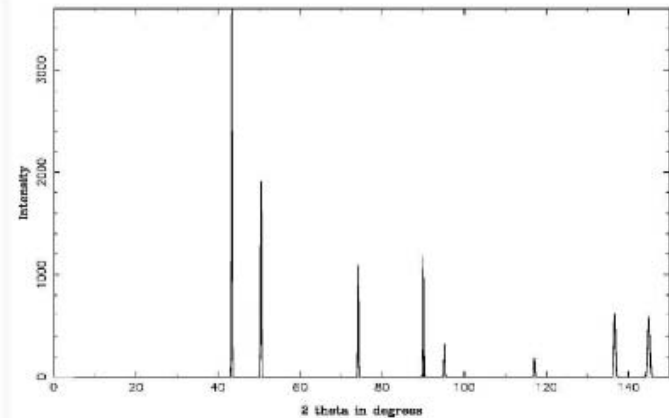


# Comparison: XPS, XRD, XAS



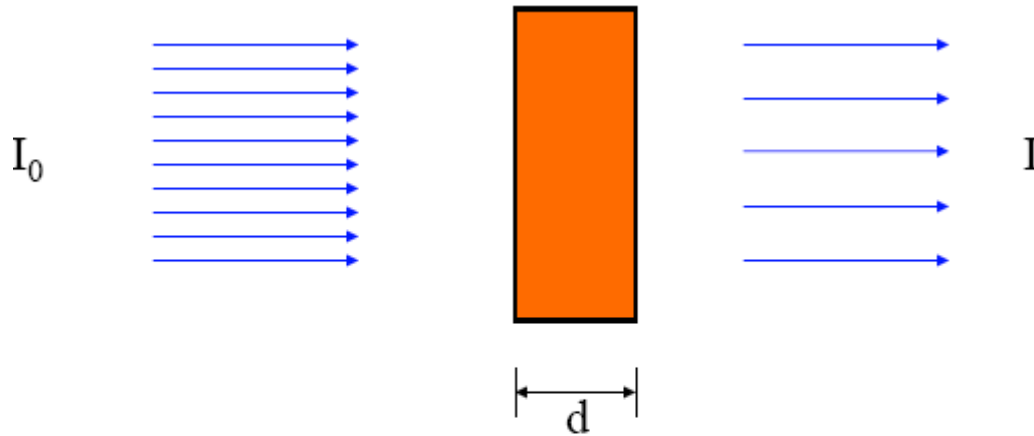
- Yields electronic information
- Surface sensitive
- In-situ application difficult
- Needs UHV

- 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

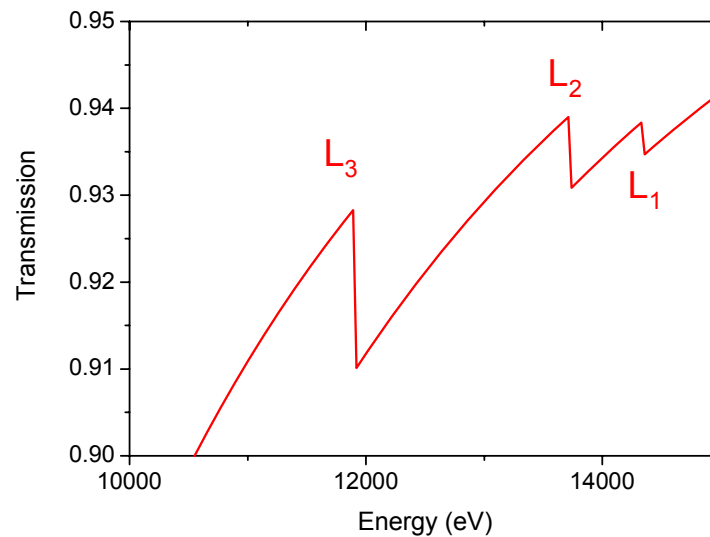
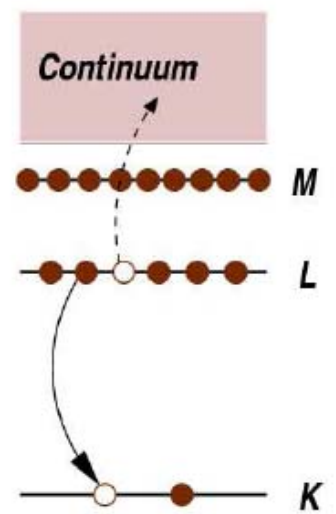
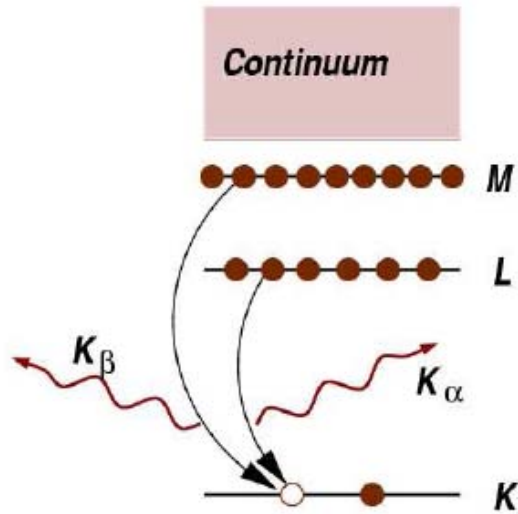
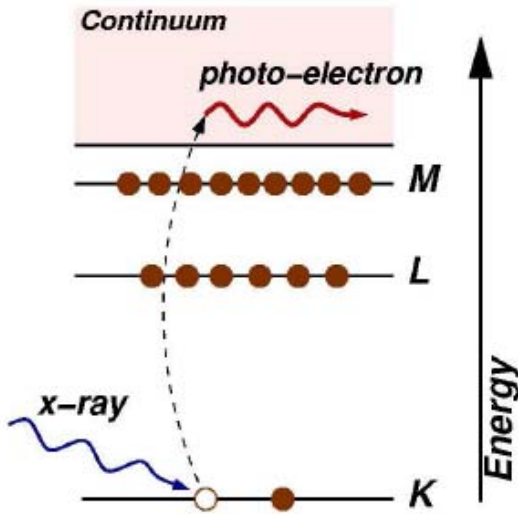
# Absorption through matter



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

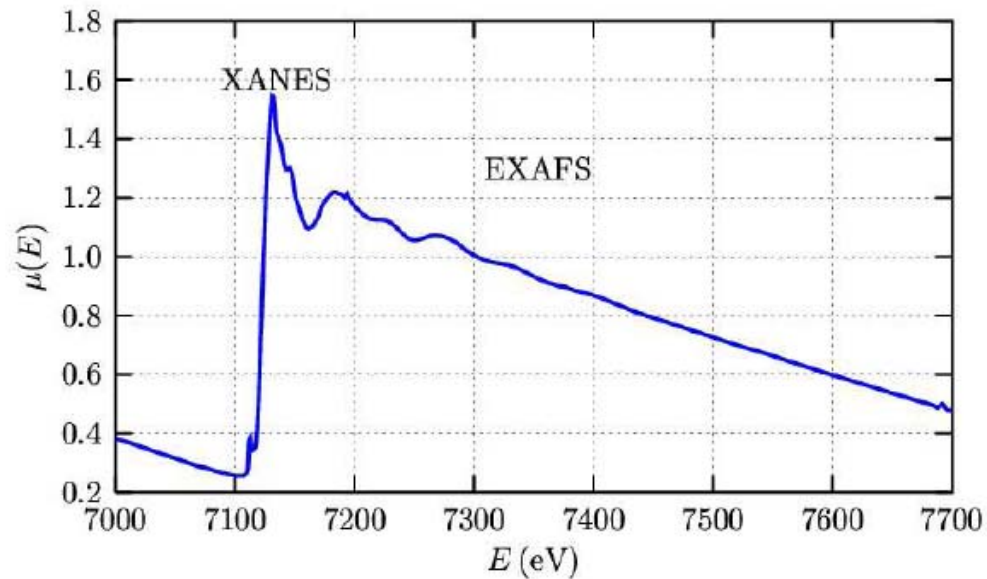
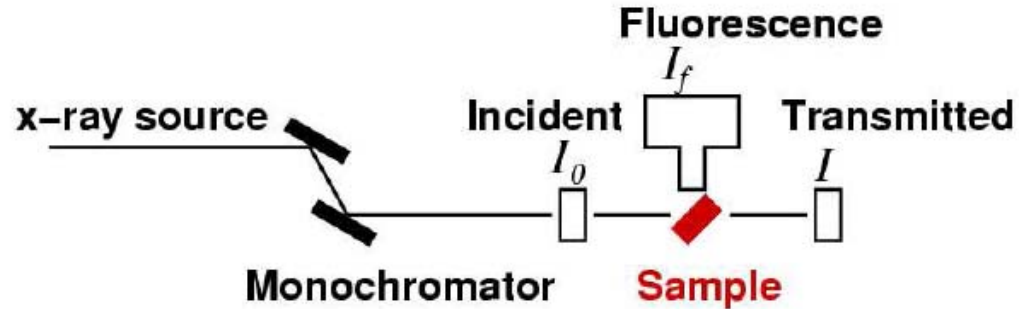


# Reminder: Photoemission, Fluorescence, Auger Emission



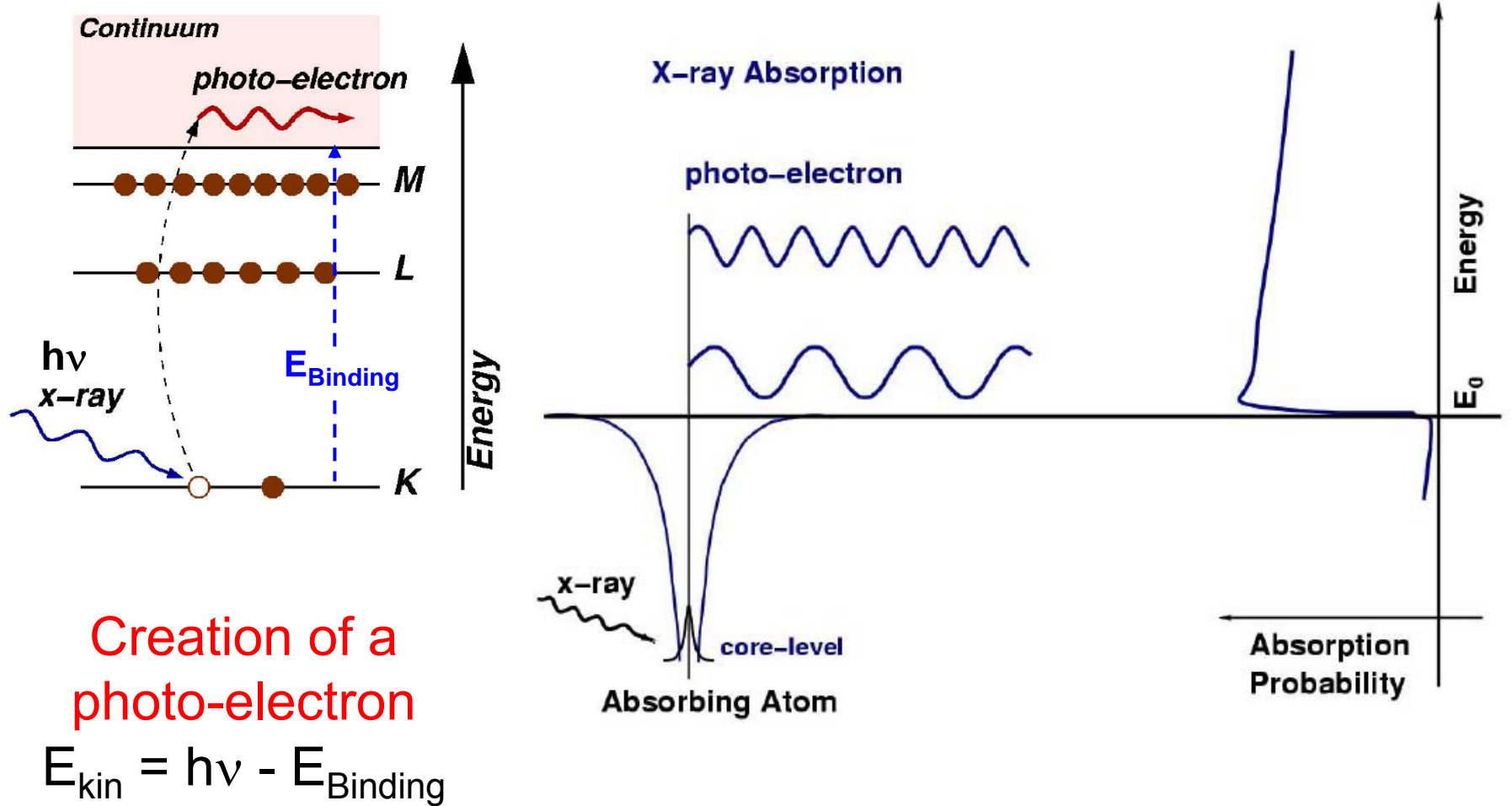
Au Foil

# What is XAS?



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

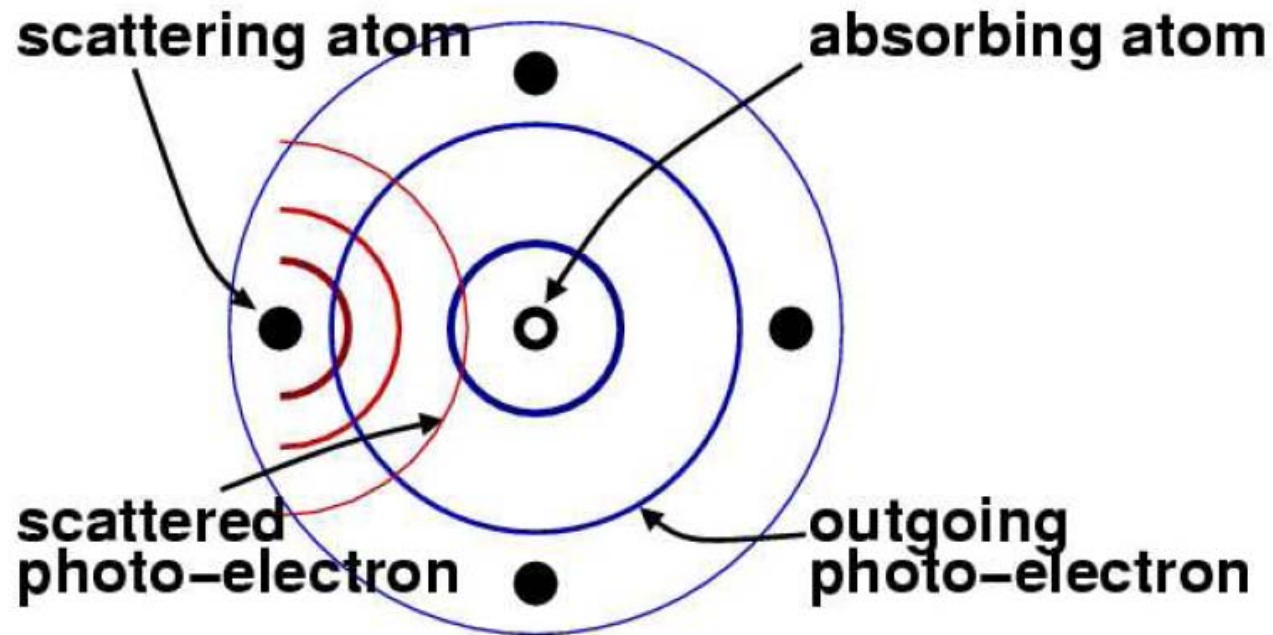
# XAFS Theory: Absorption of a monoatomic substance



*Photo-electron has kinetic energy*

## XAFS Theory: Substance with neighbor atoms present

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*Photo-electron has kinetic energy*

# XANES

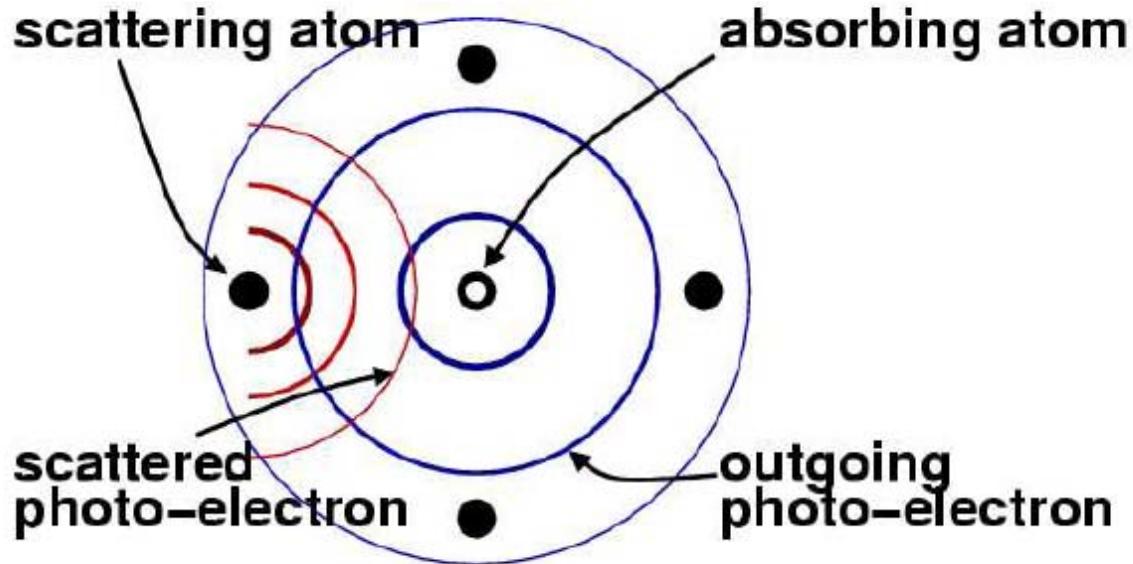
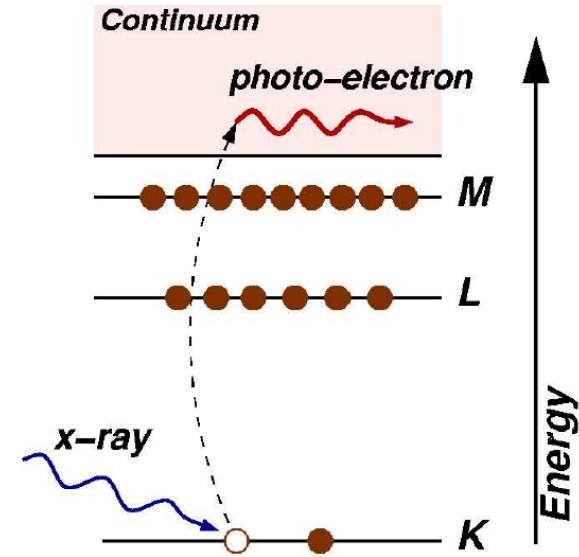
Fermi's Golden Rule

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

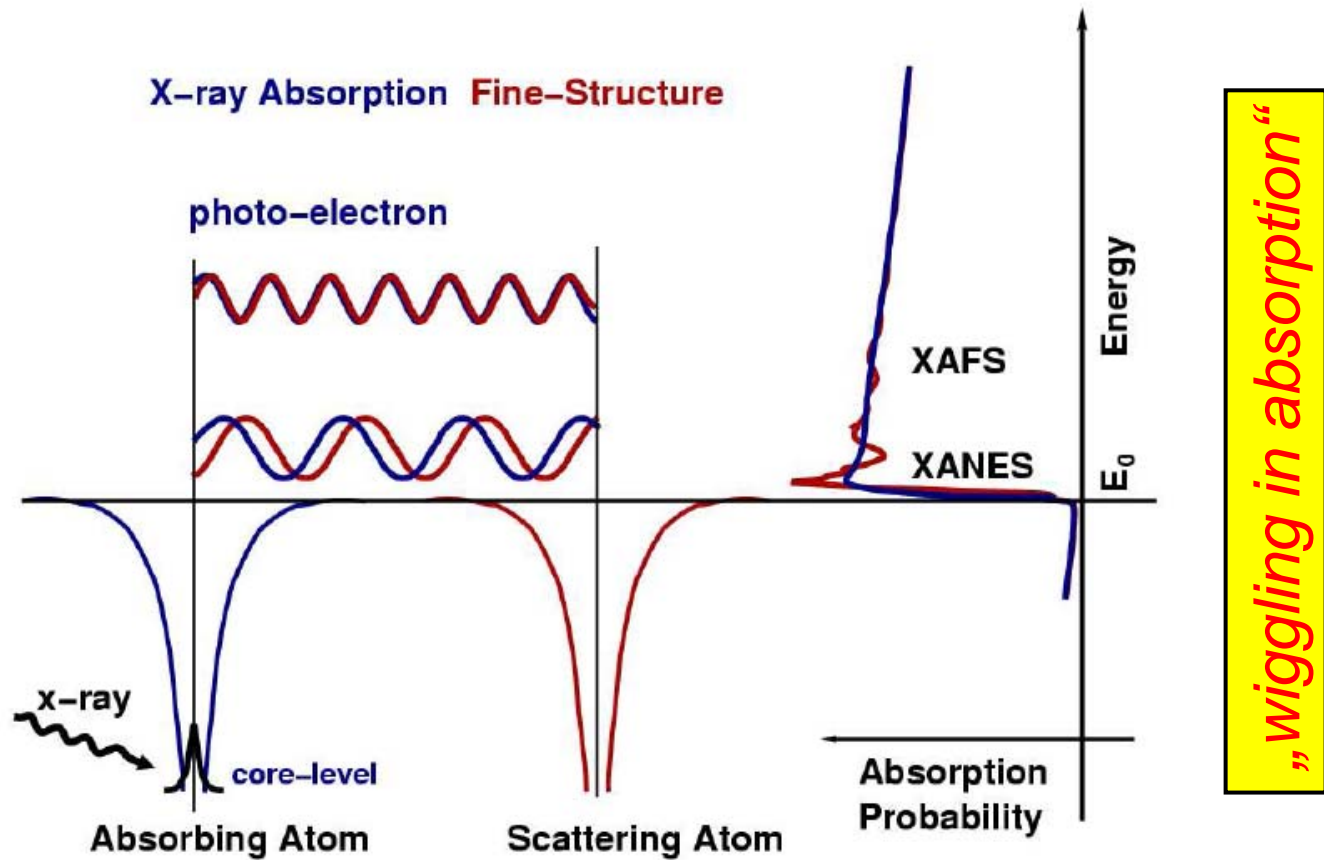
Initial state

Final state

Transition operator



# XAFS Theory: Substance with neighbor atoms present



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

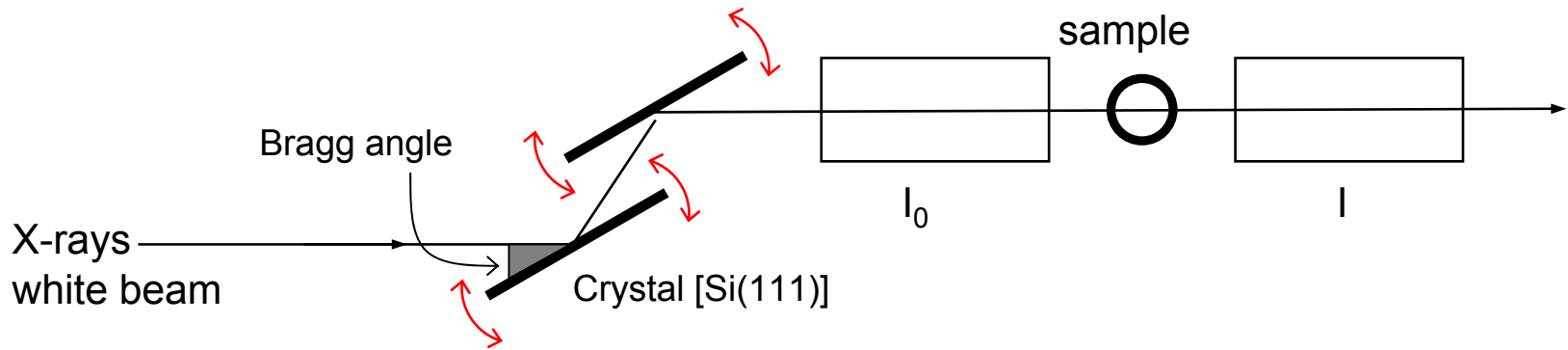
*Outgoing wave == backscattering == interference pattern  
Constructive / destructive interference*



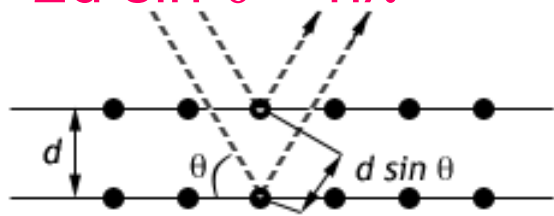
EXAFS is the wiggling part of the absorption

# Tuning the energy

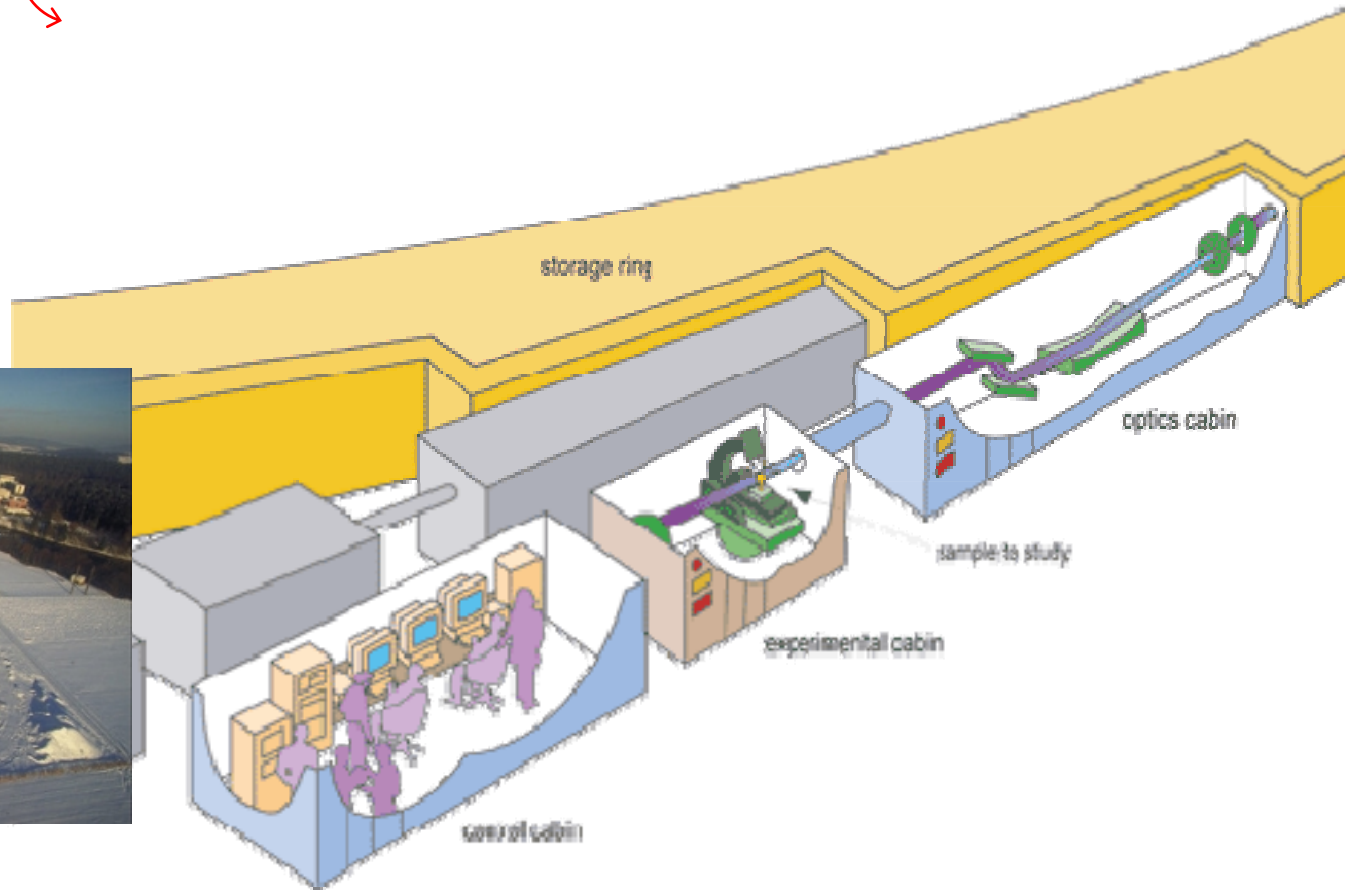
## Double crystal monochromator



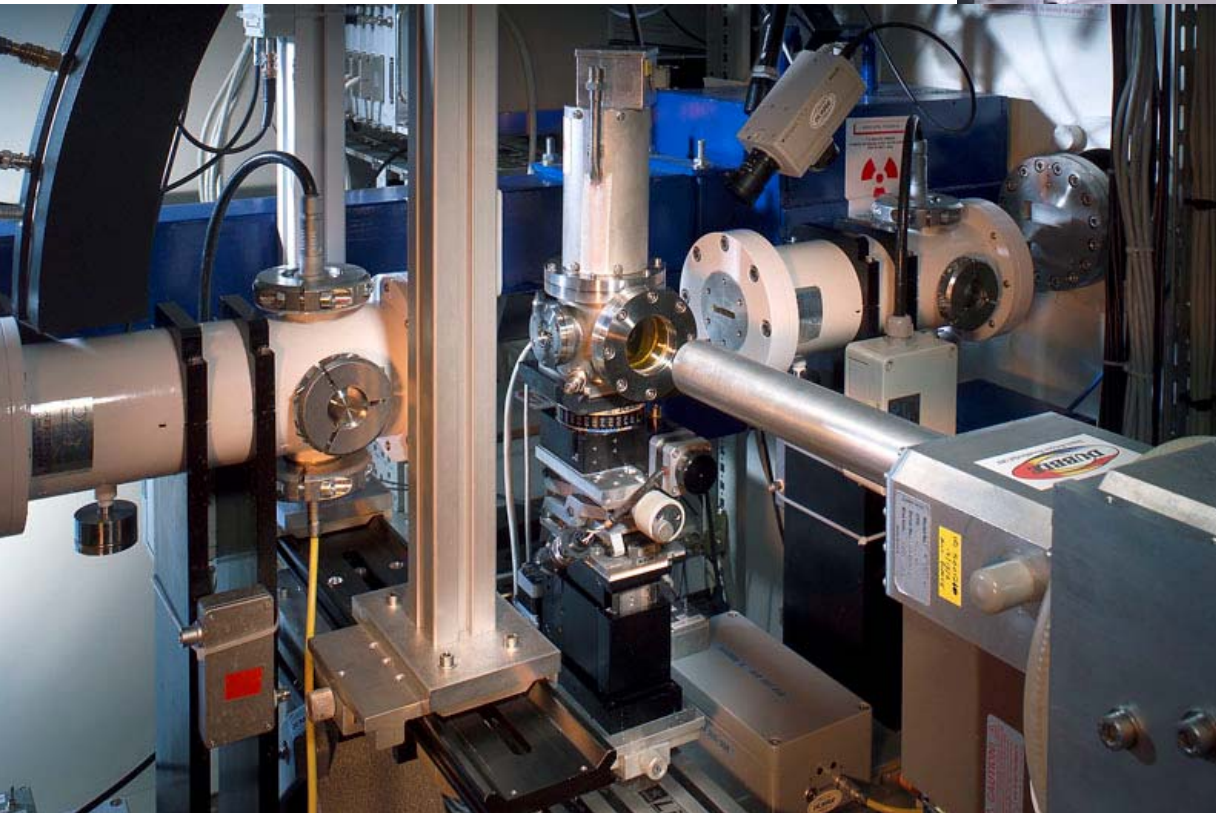
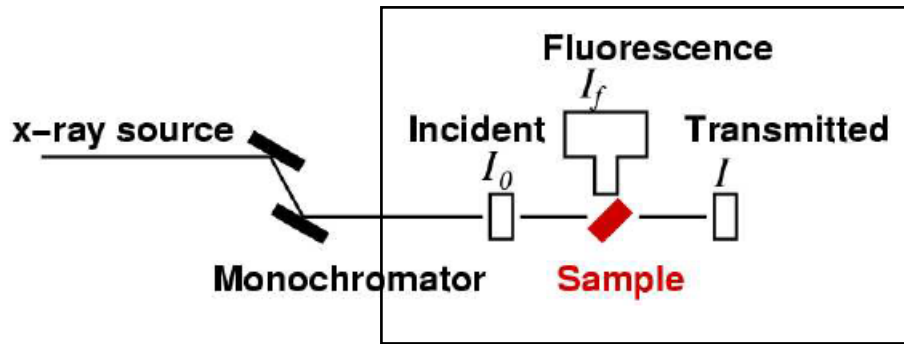
$$2d \sin \theta = n\lambda$$



SLS, Villigen

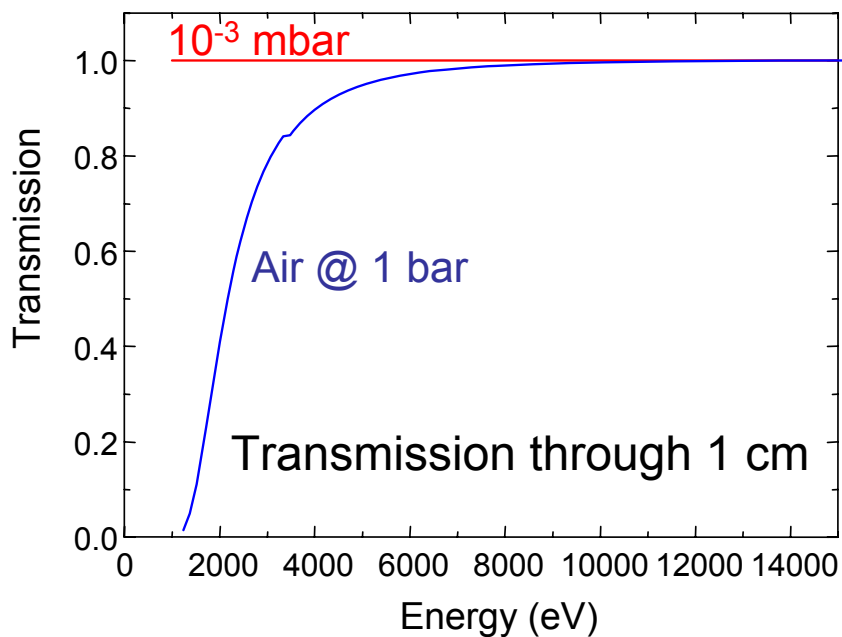
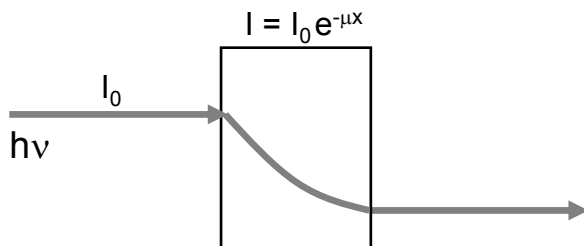


# Experimental Hutch

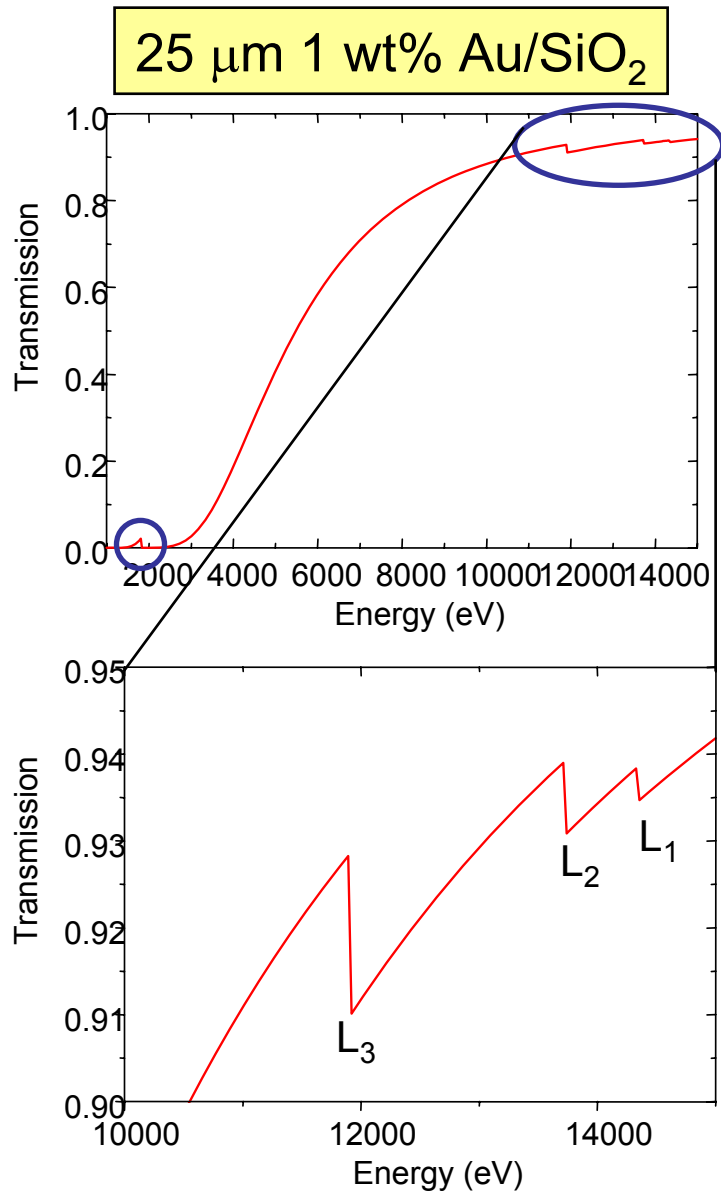


BM26 (DUBBLE), ESRF Grenoble

# X-ray absorption through matter



**Lambert Beer's law**  
 $dl = -\mu(E)l dx$   
 $I = I_0 \exp(-\mu(E)x)$



# Sample environment

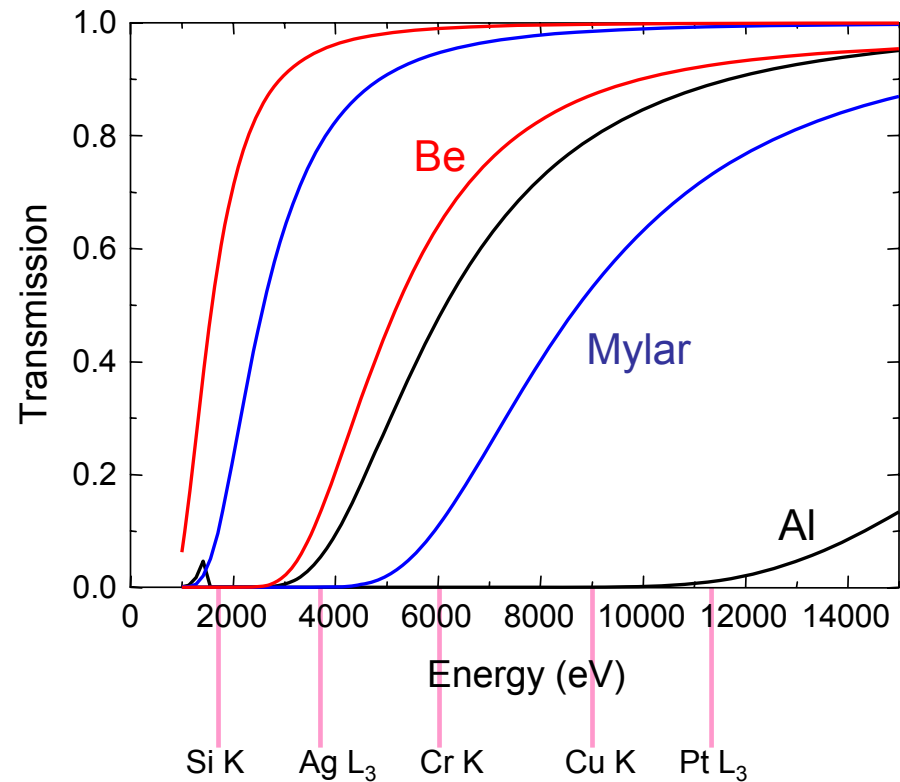
*Absorption of X-rays is limiting factor*

## Find a good window material

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

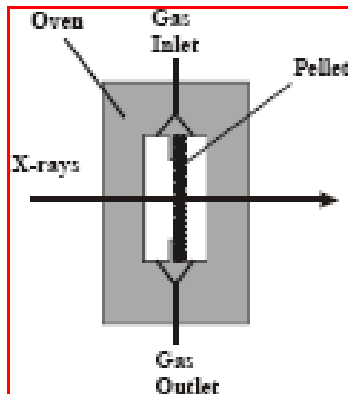
*pressure*  
*temperature*  
*environment*

Transmission through  
25  $\mu\text{m}$  and 1 mm



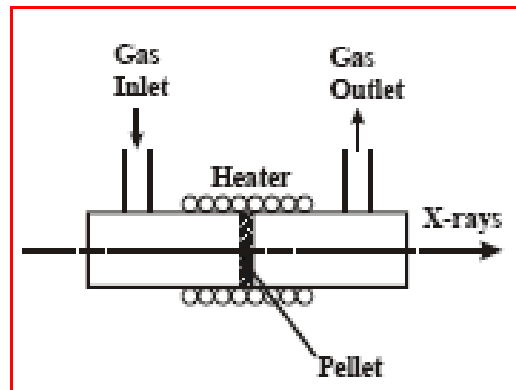
# *In situ* EXAFS cells for gas-solid reactions

Reaction gas mixture flows around a pellet



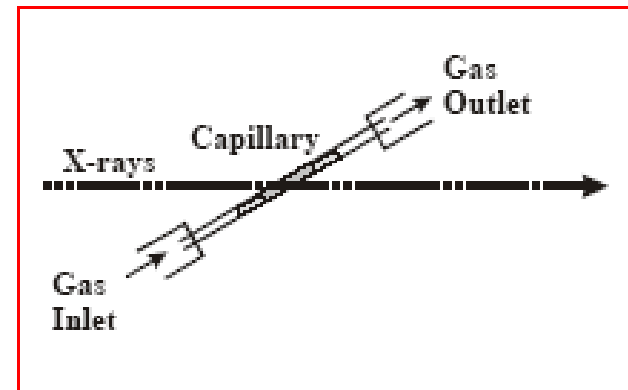
Large dead volume  
Good for stationary conditions

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



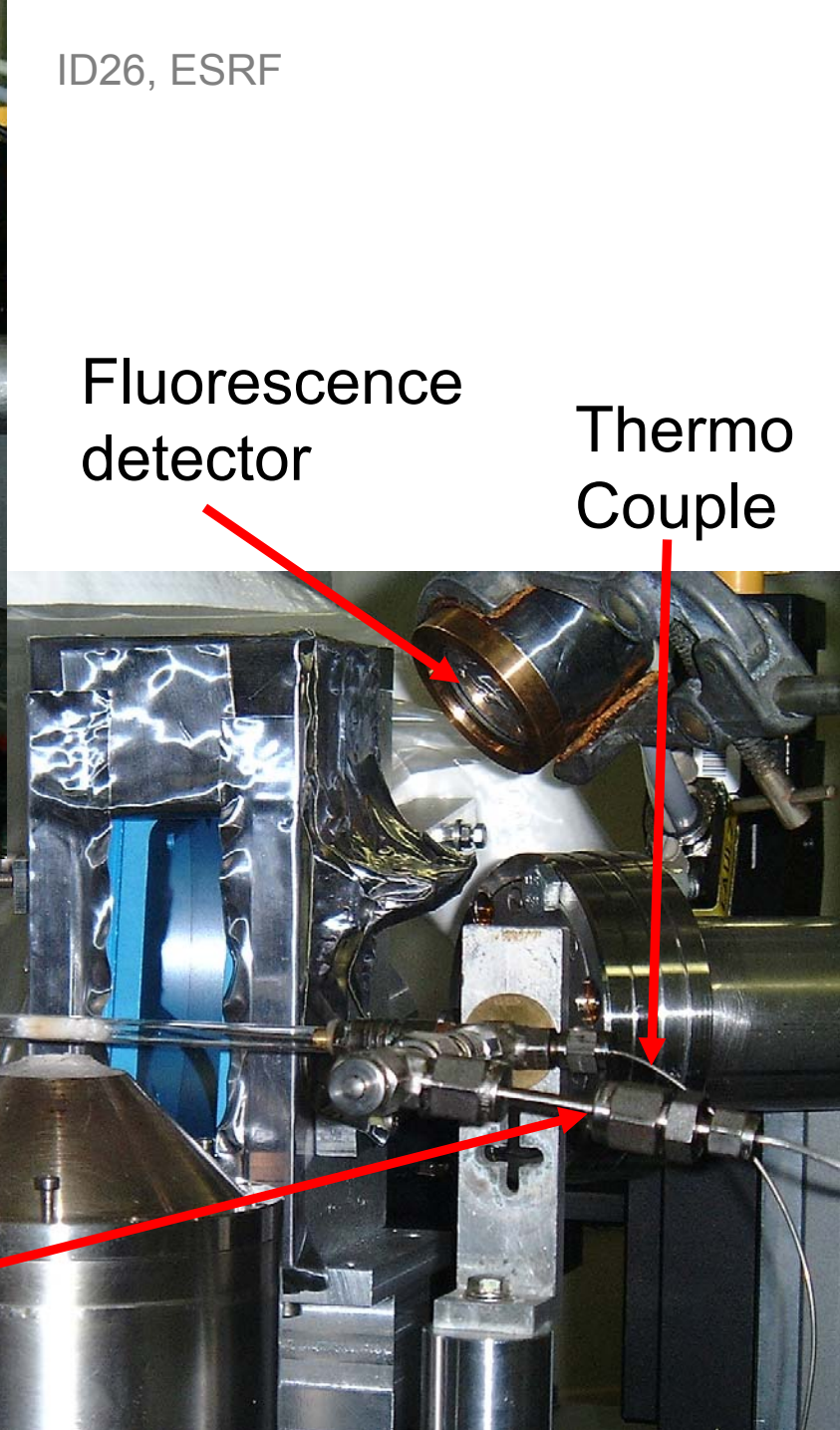
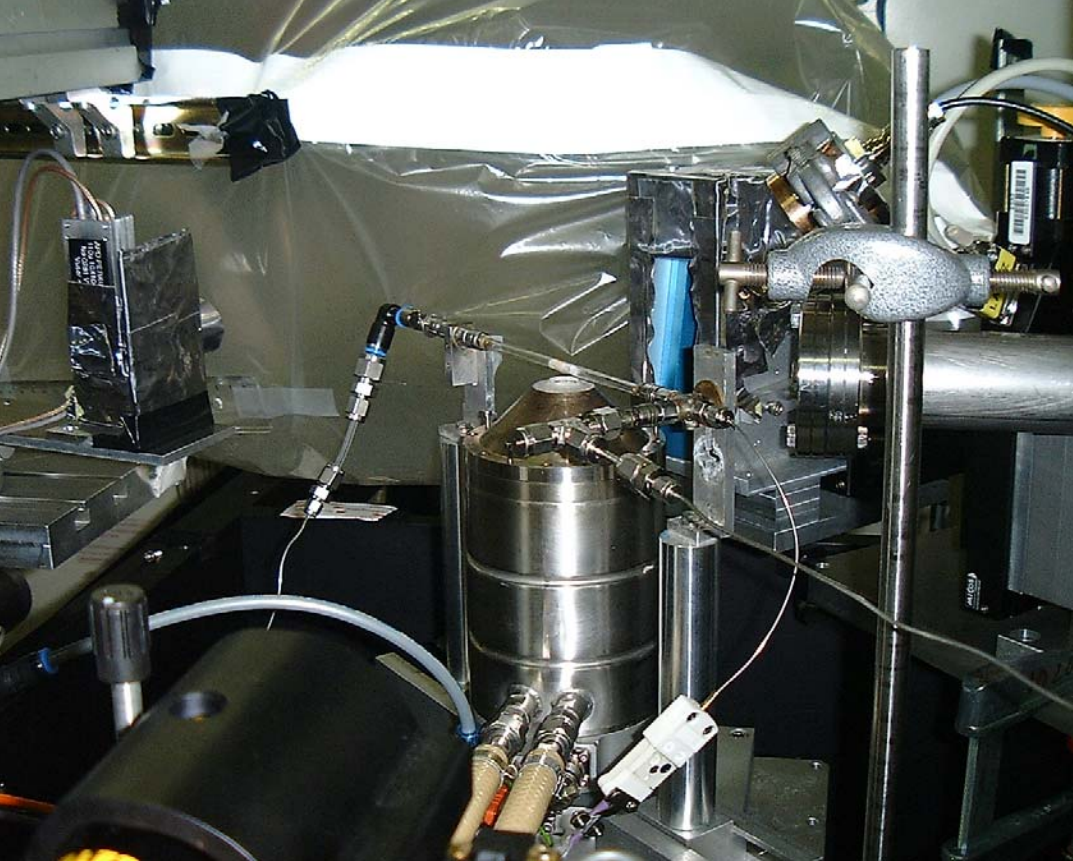
ID26, ESRF

Fluorescence  
detector

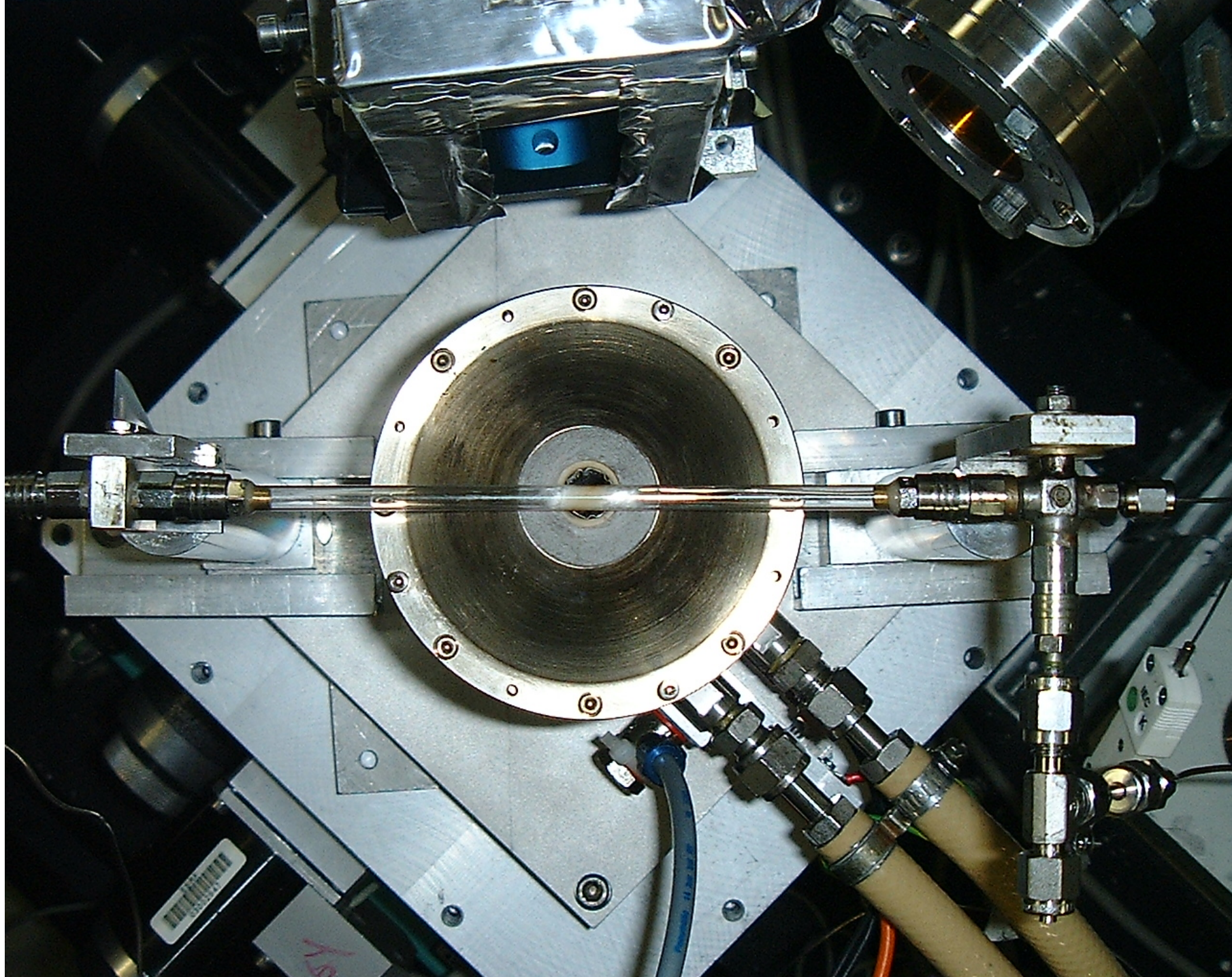
Thermo  
Couple

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?

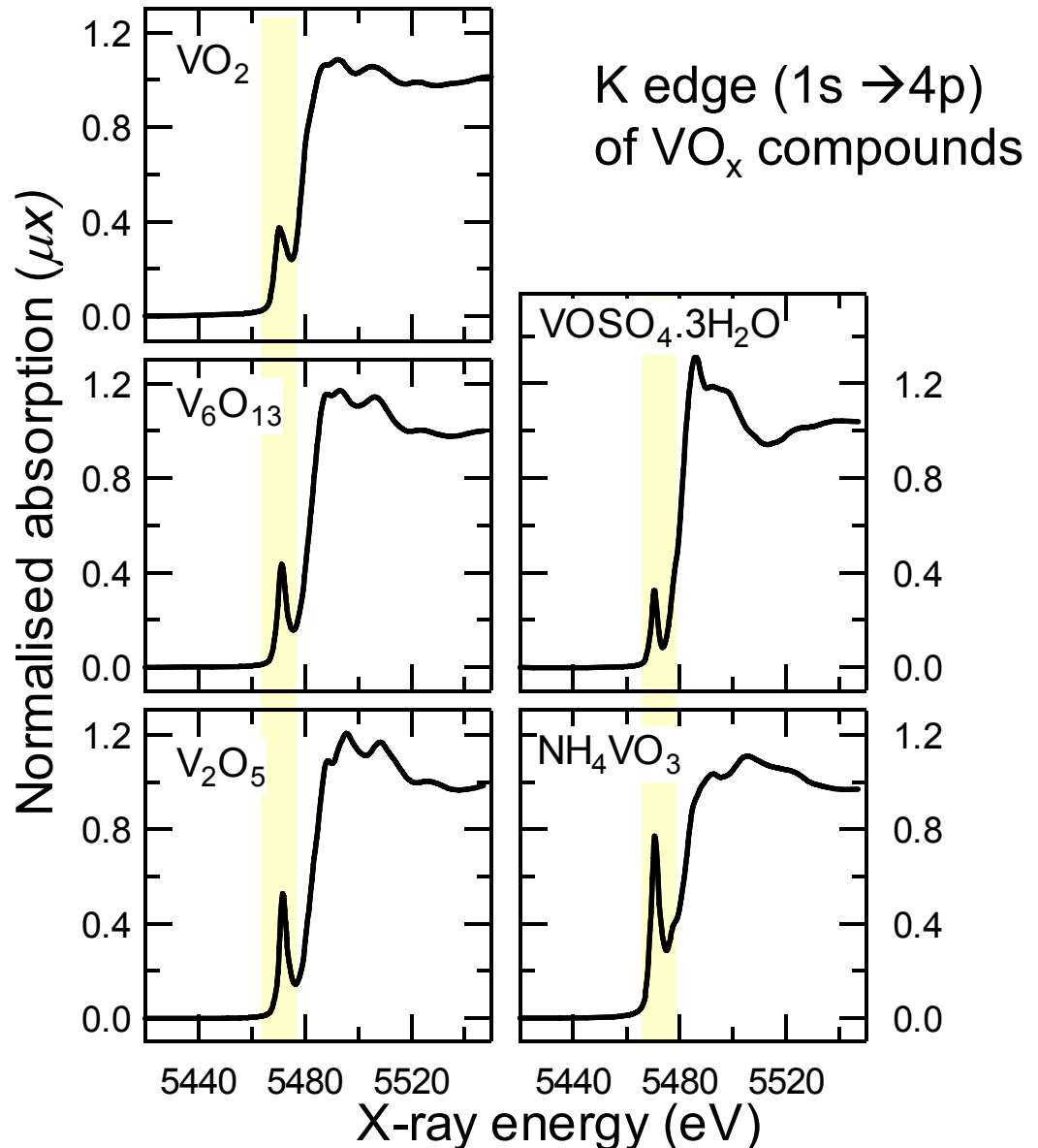
- Pre-edge
- Edge-energy
- Shape over the edge

## Pre-edge

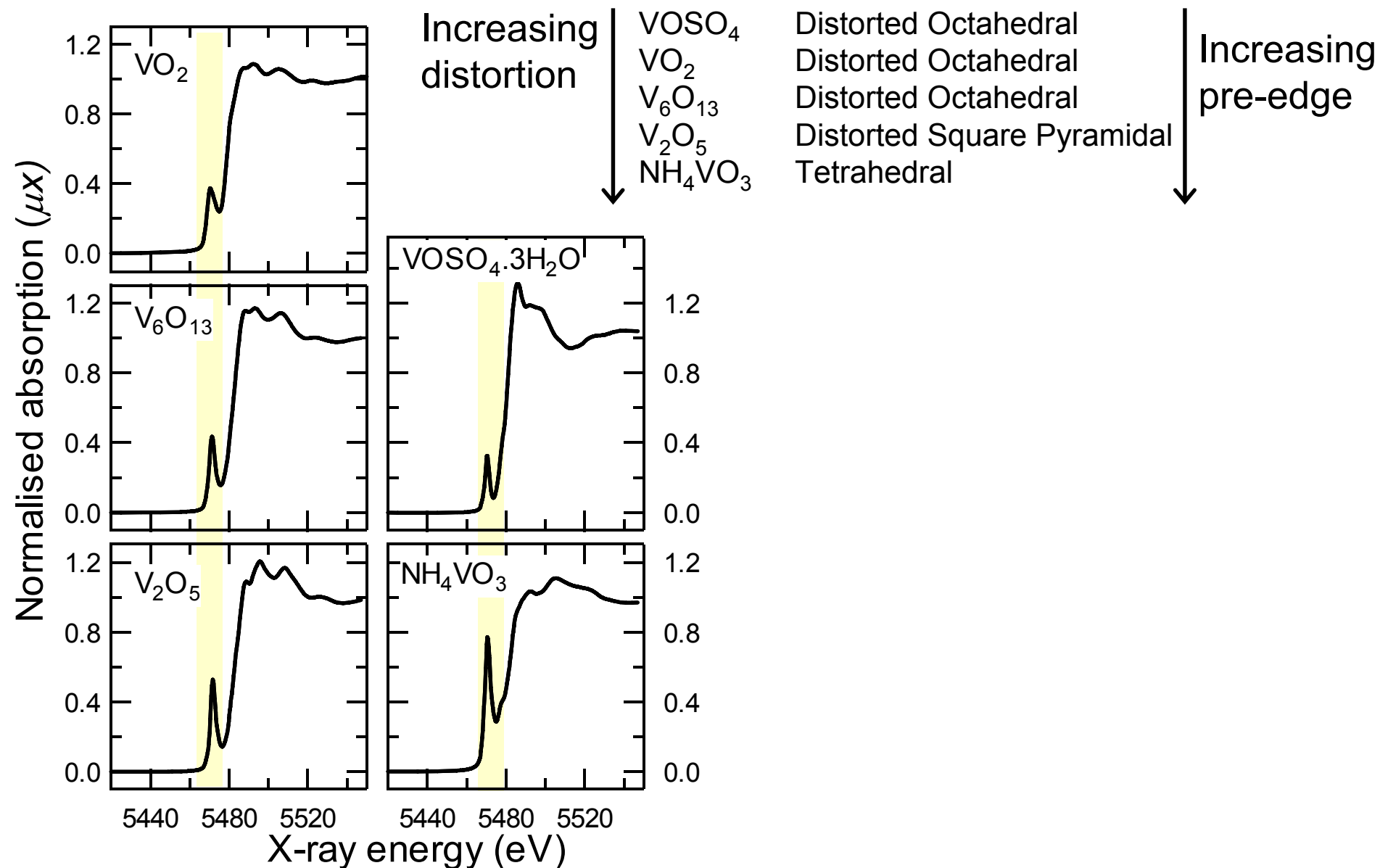
- intensity
- energy

**BUT.....**

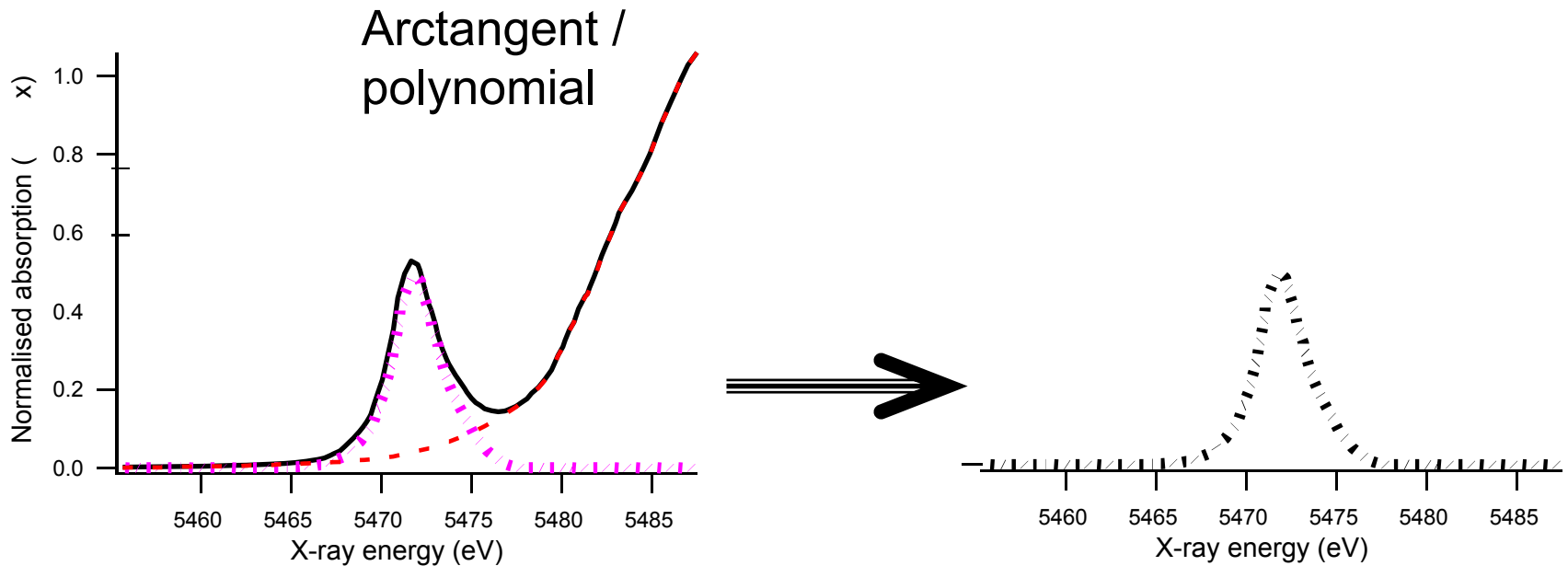
*..... there is not always a pre-edge*



# In order of increasing distortion from octahedral

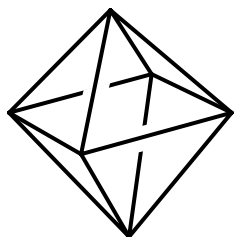


# Isolation of the pre edge *by edge subtraction*





# Pre-edges intensity & energy varies (K edge)



## Pure octahedral case

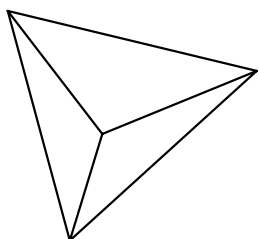
Centro-symmetry: no p-d mixing allowed: only quadrupole transition

→ very low intensity

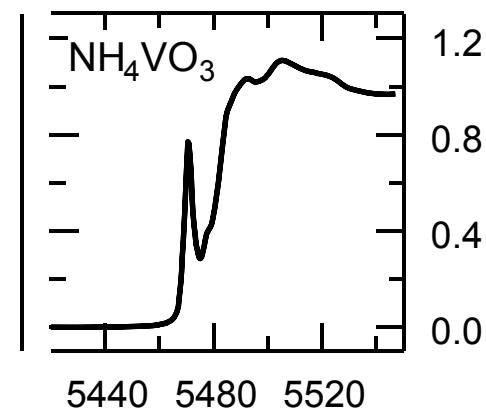
## Distortion from octahedral

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

→ increasingly large intensity



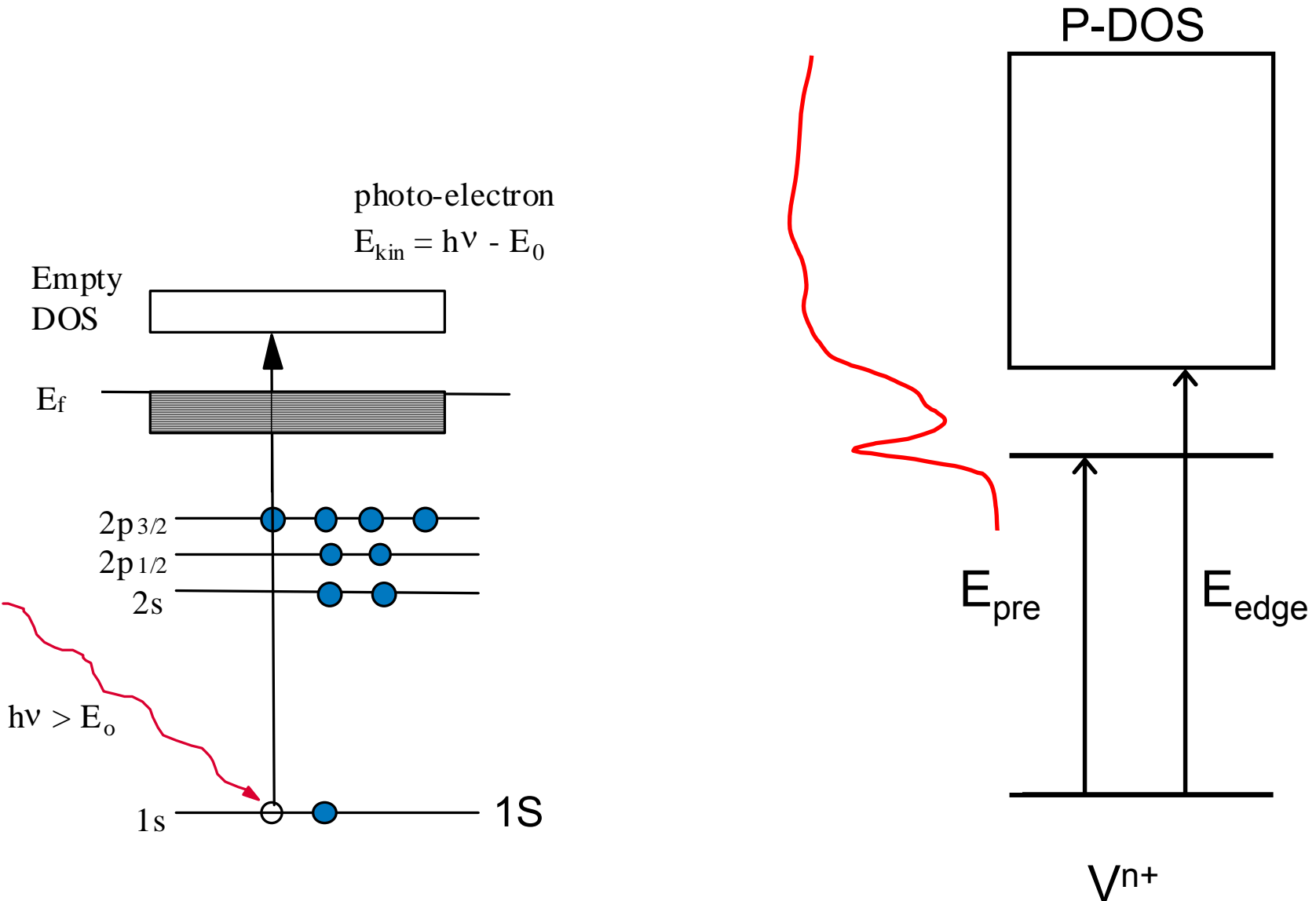
Pure tetrahedral => largest pre-edge



*Intensity pre-edge indicative of geometry*

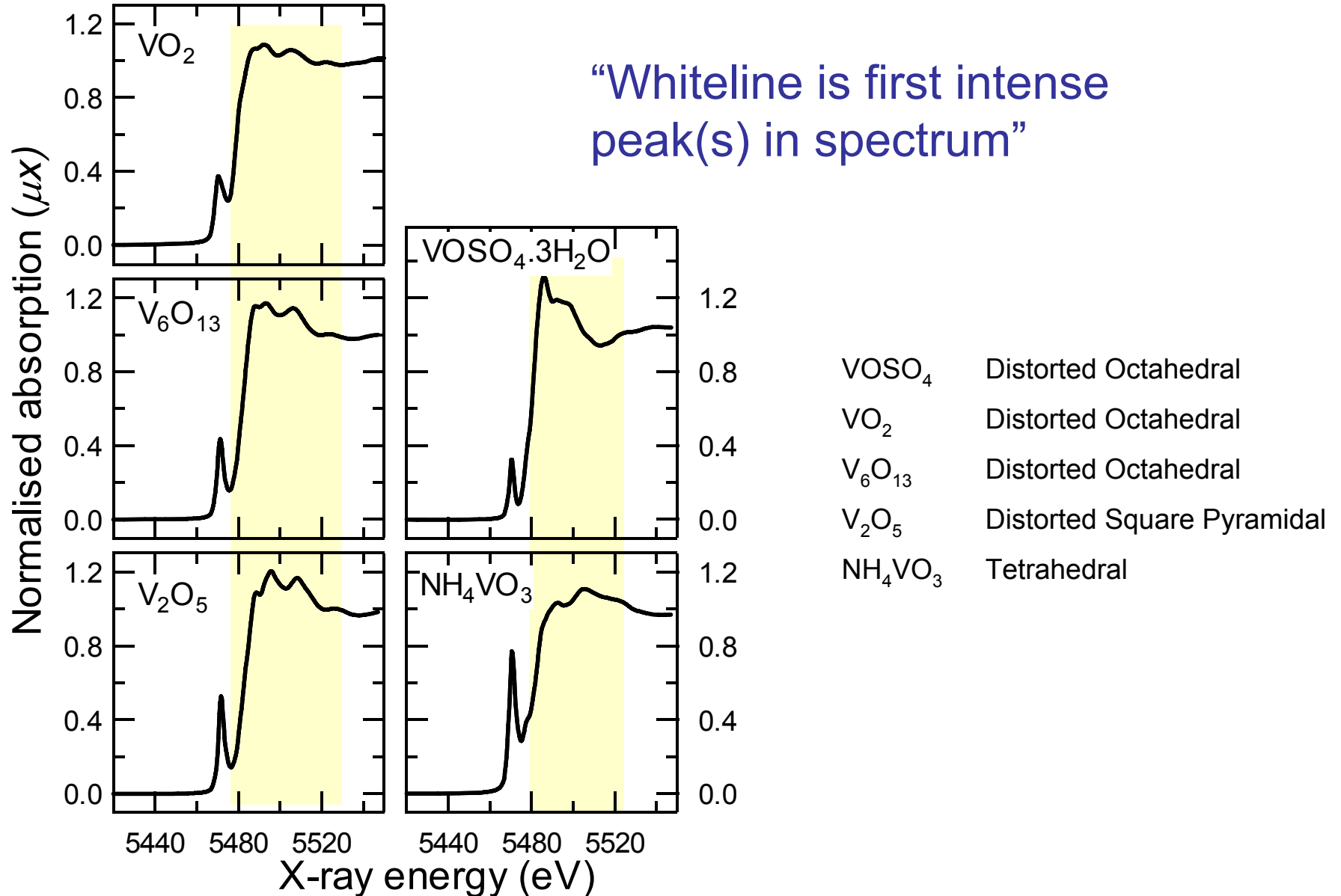
# (Pre-)edge Energy and Valence

*Edge position is measure of oxidation state*



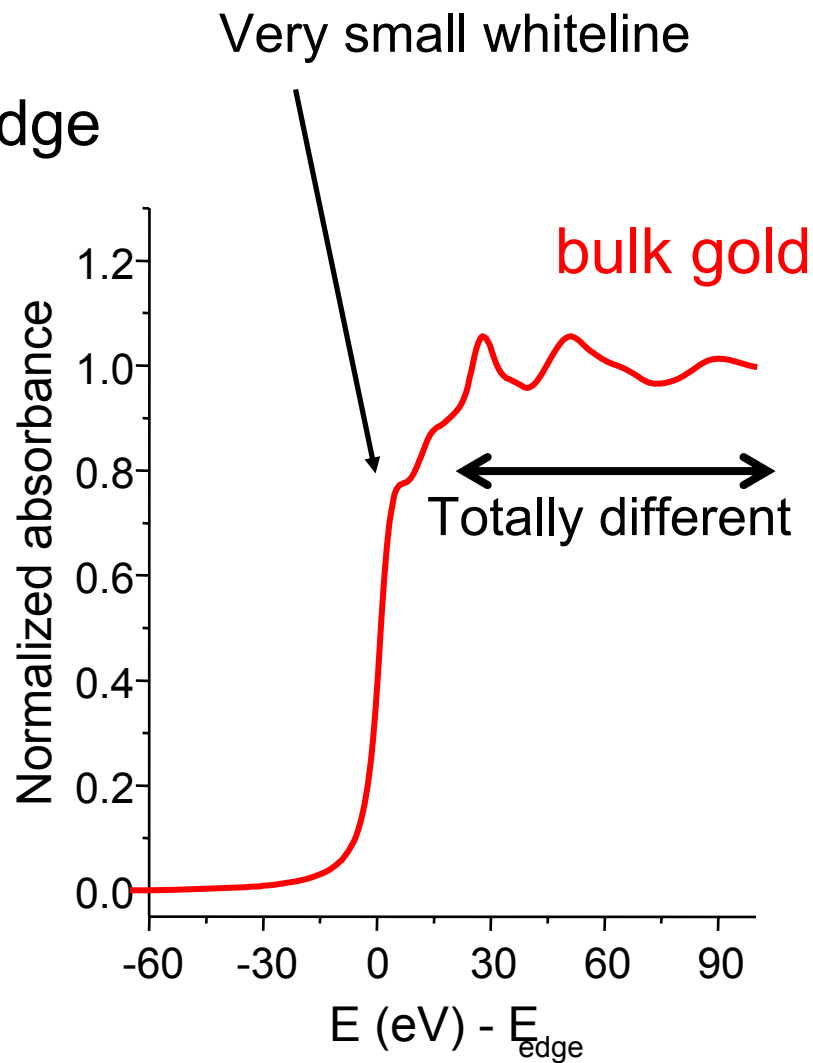
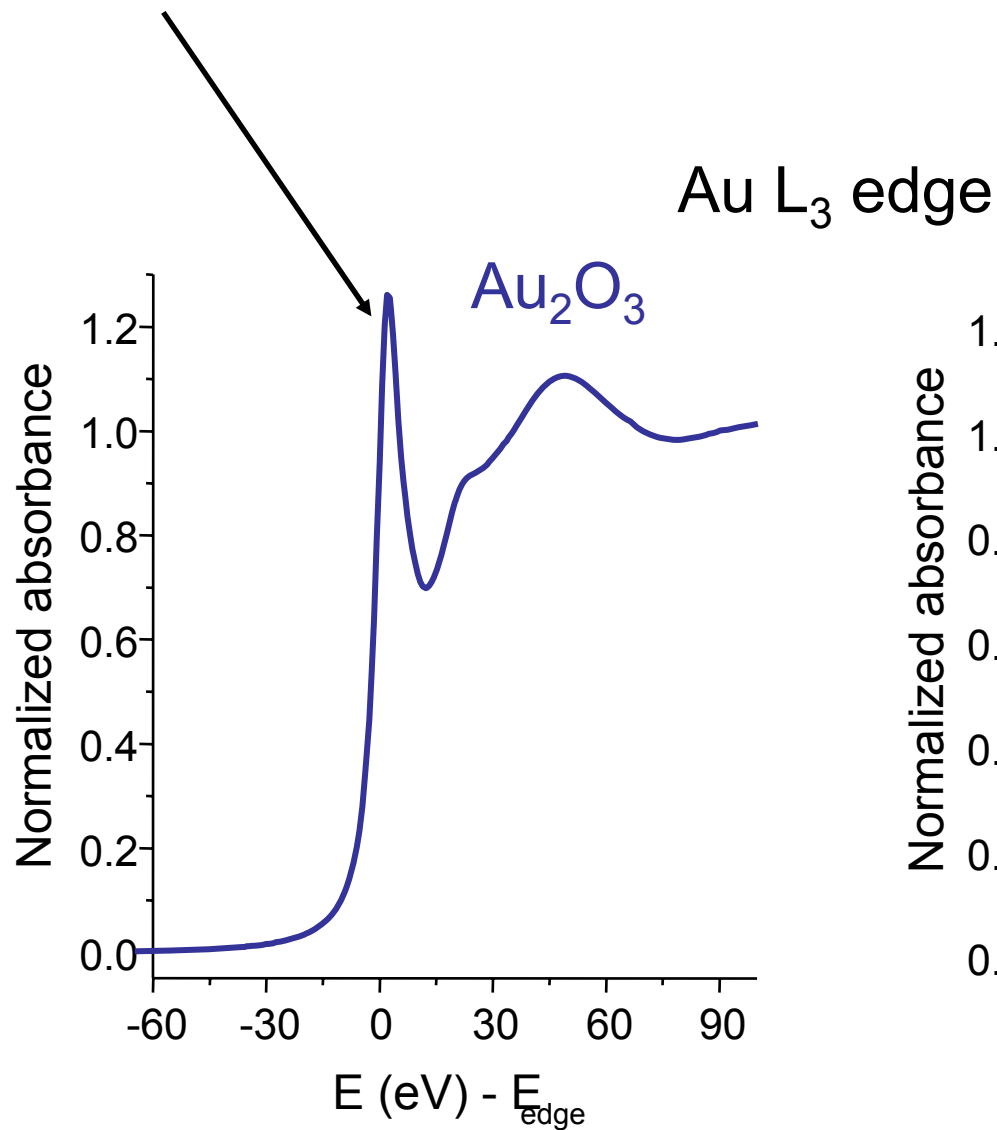
# Shape of the whiteline

For L edges  $> 3$  keV and all K edges

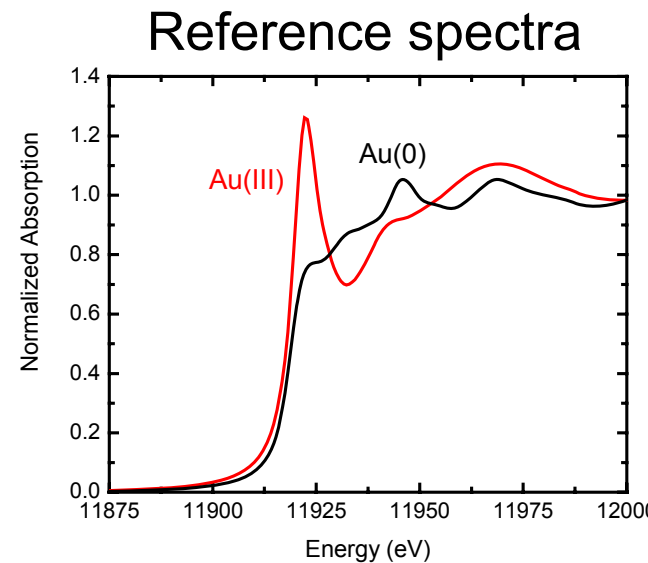
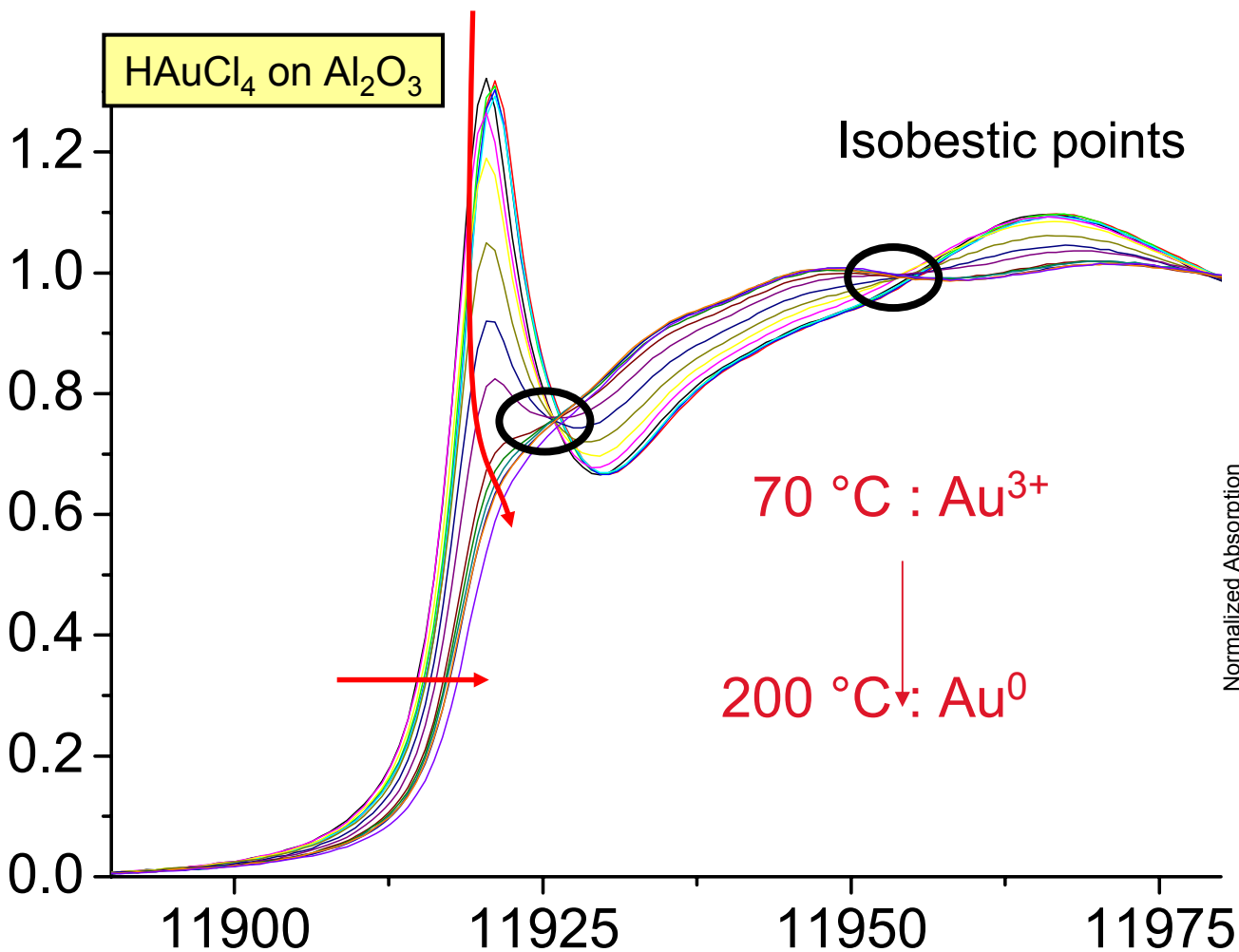


# Shape of the whitenline: L-edges

Whiteline reflects holes in d-band

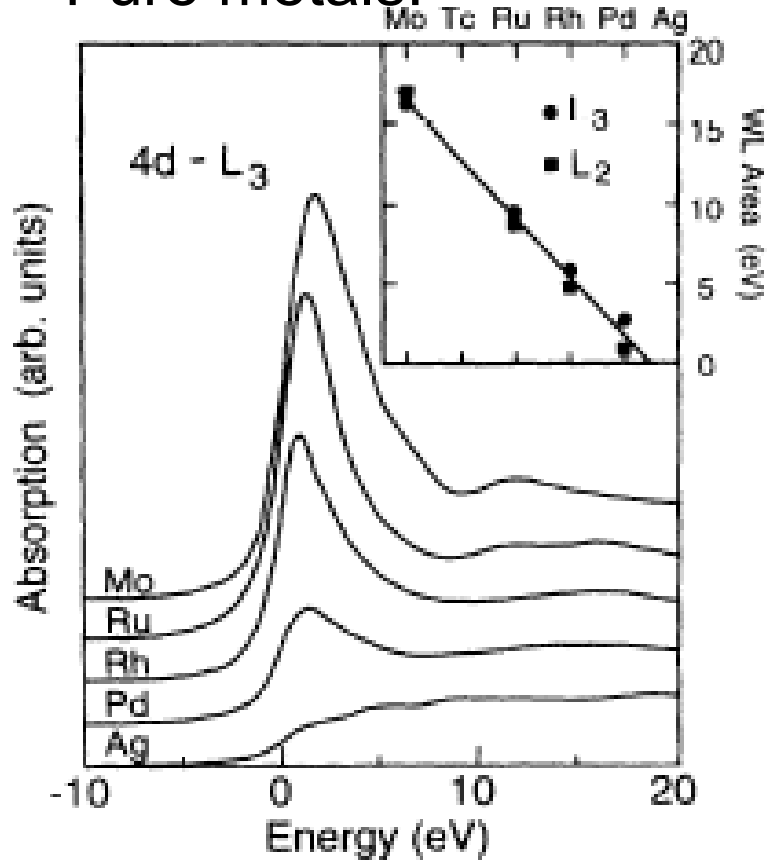


# In situ $\text{Au}^{3+}$ reduction in $\text{He}/\text{H}_2$



# Shape of the whiteline: L-edges

Pure metals:

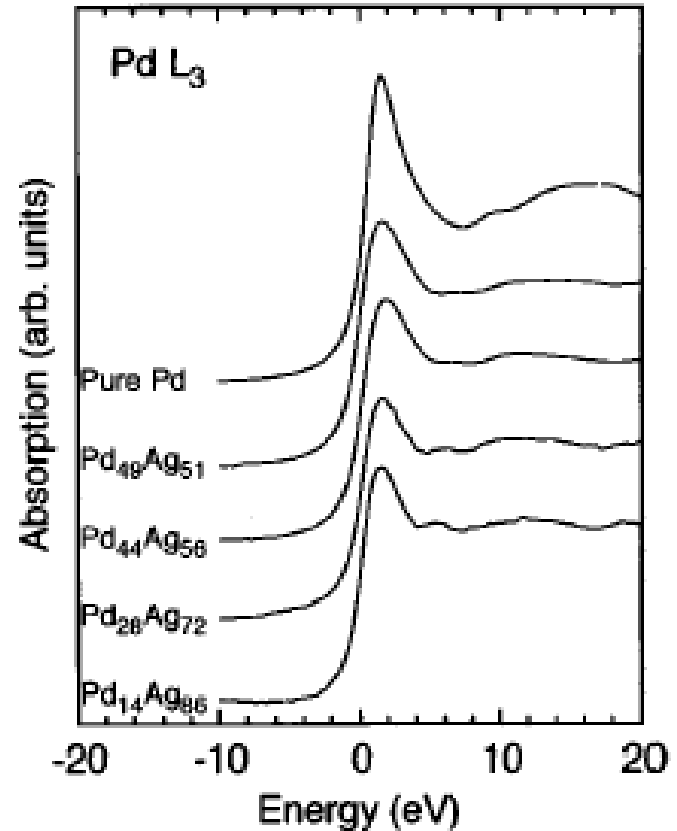


*Whiteline reflects holes in d-band*

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).