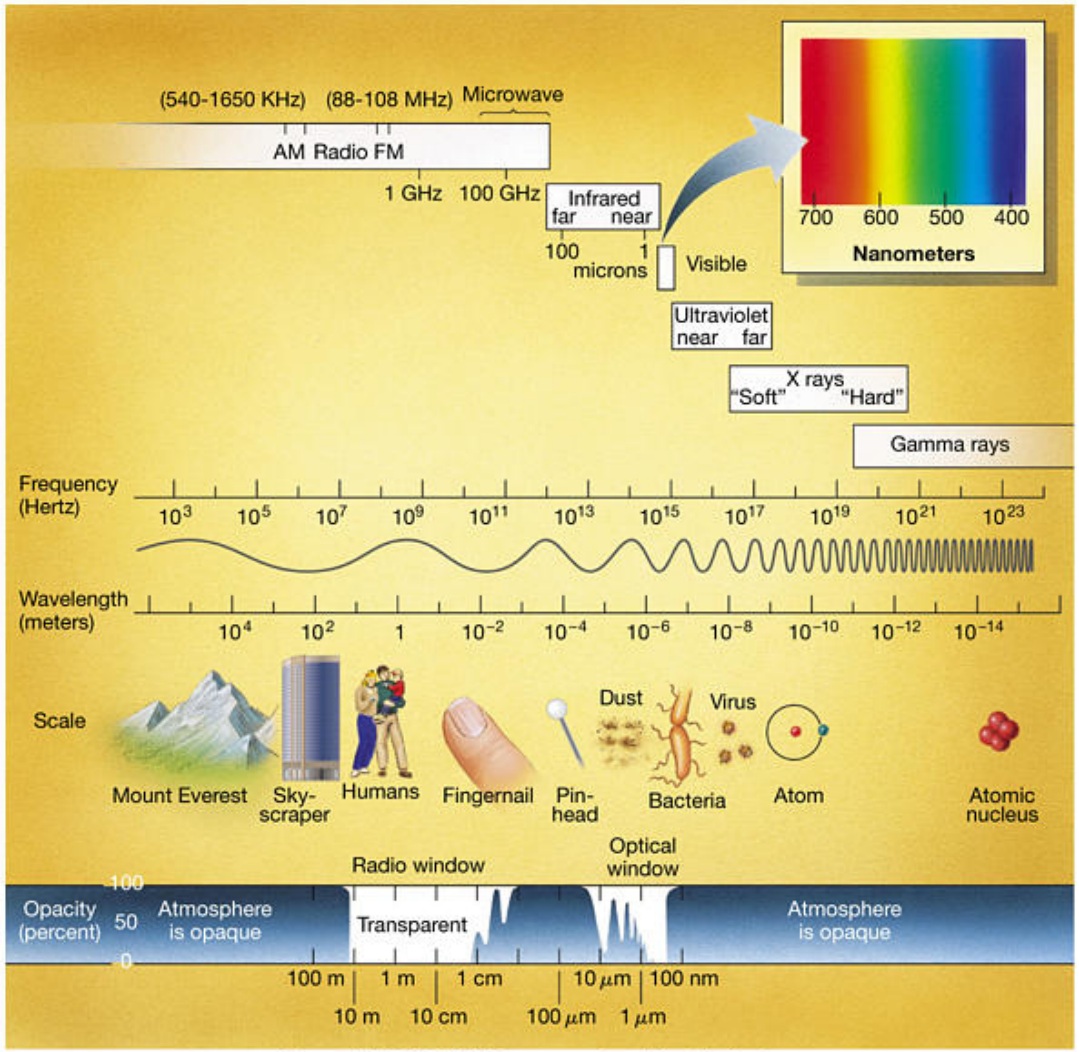
X-ray absorption spectroscopy

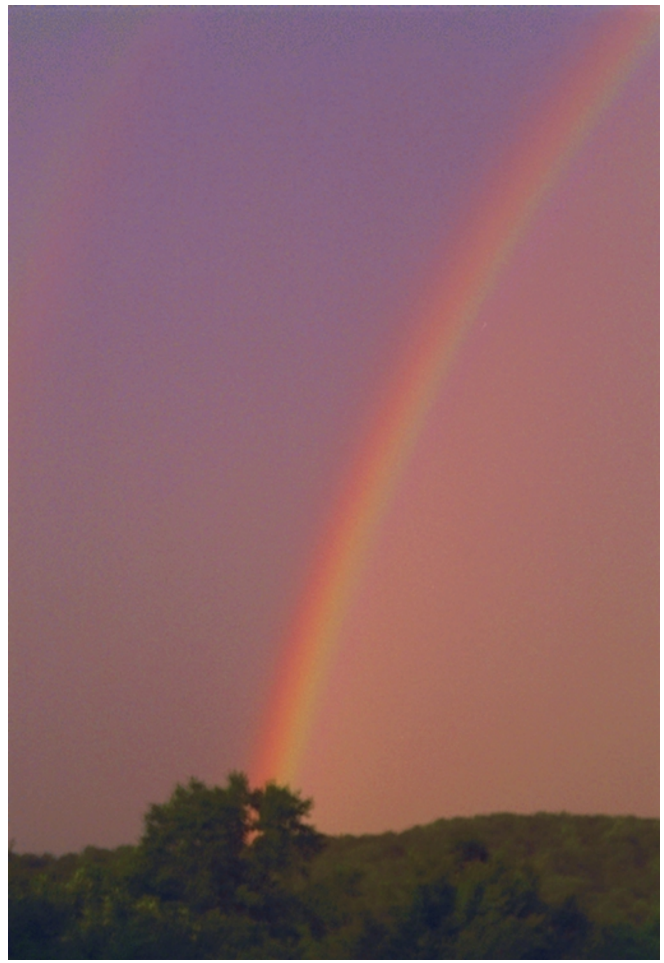
Literature recommendations

- 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

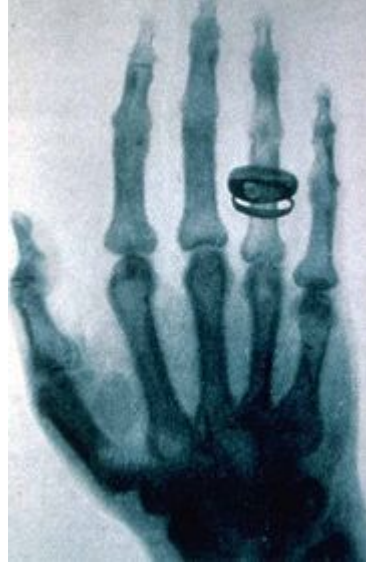

(540-1650 KHz)
(88-108 MHz)
Microwave
AM Radio FM
1 GHz
100 GHz
Infrared
far near
100
1
microns
Visible
700 600 500 400
Nanometers
Ultraviolet
near far
X rays
"Soft" "Hard"
Gamma rays
Frequency
(Hertz)
10^3 10^5 10^7 10^9 10^{11} 10^{13} 10^{15} 10^{17} 10^{19} 10^{21} 10^{23}
Wavelength
(meters)
10^4 10^2 1 10^{-2} 10^{-4} 10^{-6} 10^{-8} 10^{-10} 10^{-12} 10^{-14}
Scale
Mount Everest
Sky-
scraper
Humans
Fingernail
Pin-
head
Dust
Virus
Bacteria
Atom
Atomic
nucleus
Radio window
Optical
window
100
Opacity
(percent)
50
0
Atmosphere
is opaque
Transparent
Atmosphere
is opaque
100 m
10 m
1 m
10 cm
1 cm
100 μm
10 μm
1 μm
100 nm



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

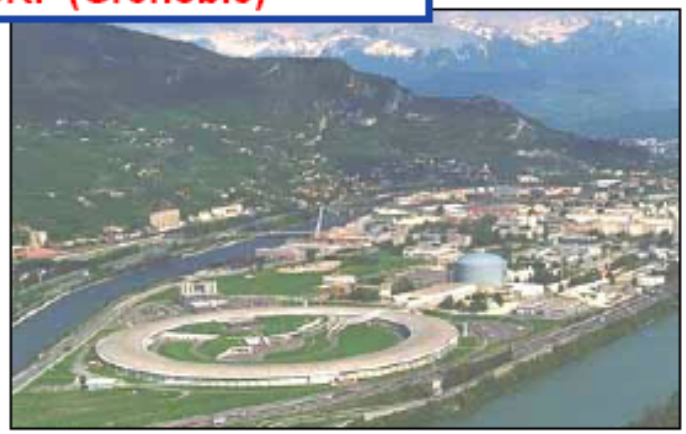
- **Wide range of applications**
- Structural information (EXAFS)
- Electronic information (XANES)
- Capable of in-situ application

Disadvantages

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

Synchrotron needed

ESRF (Grenoble)

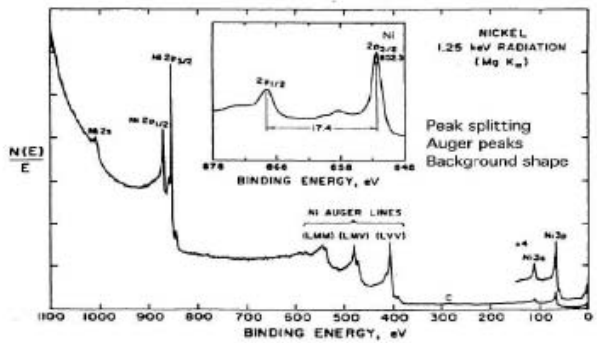


DESY (Hamburg)

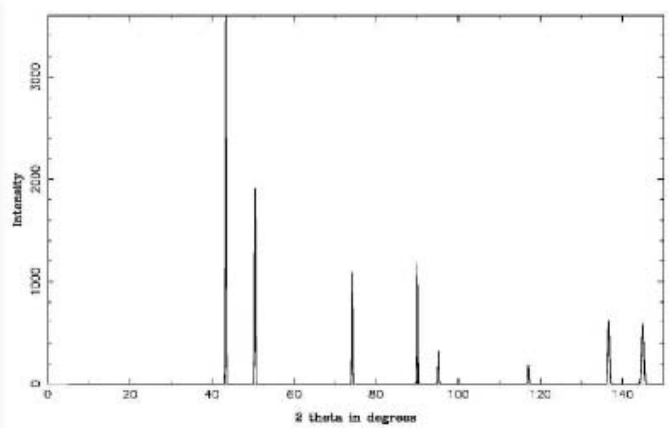
SLS (Villigen)

APS (Chicago)

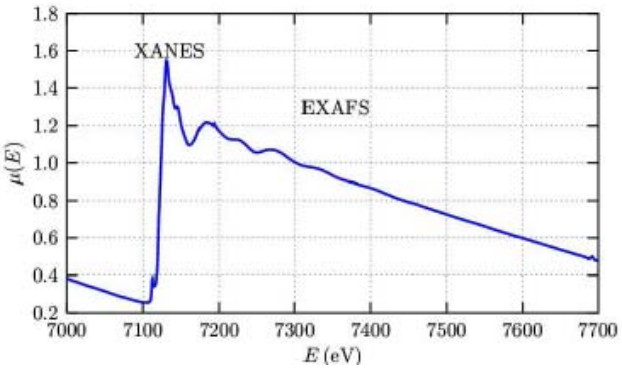
Comparison: XPS, XRD, XAS



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

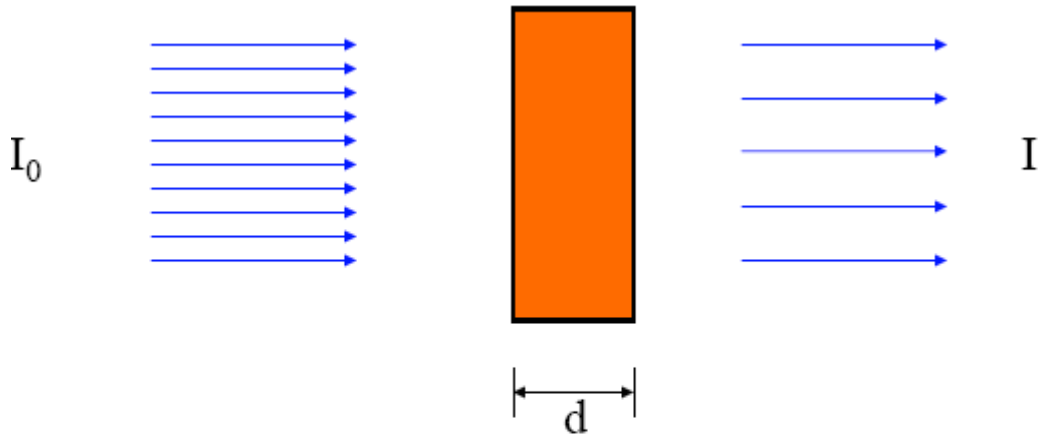


- Yields structural information
- Bulk technique
- In-situ applications realizable
- Needs long range order to work



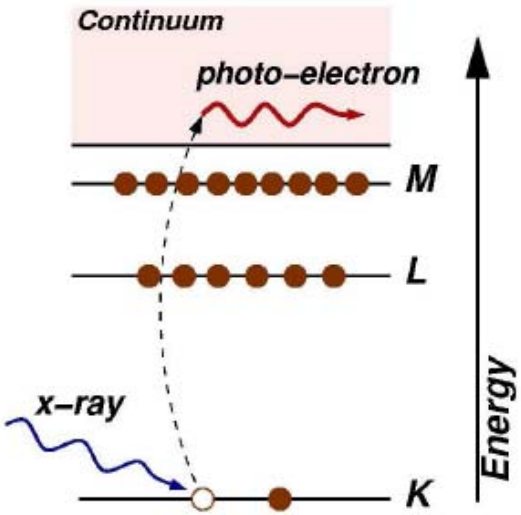
- Yields electronic and structural information
- In-situ application easy to realize
- Needs a synchrotron
- Data interpretation difficult

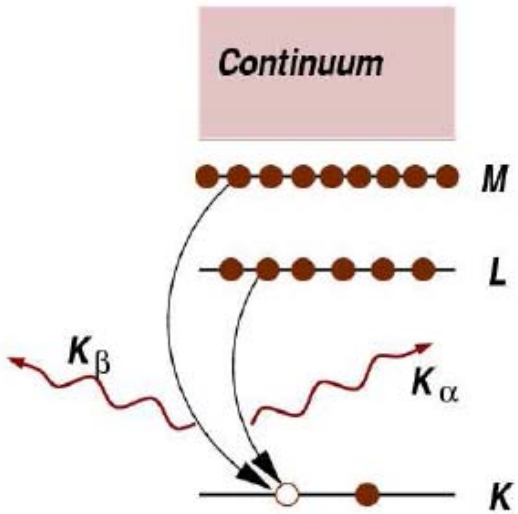
Absorption through matter

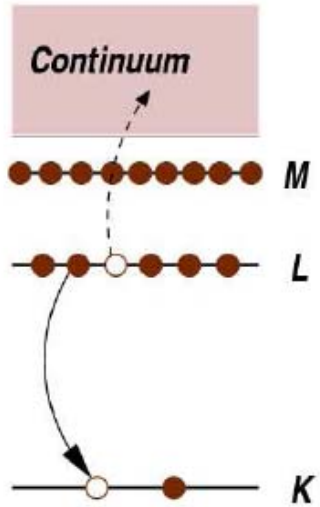


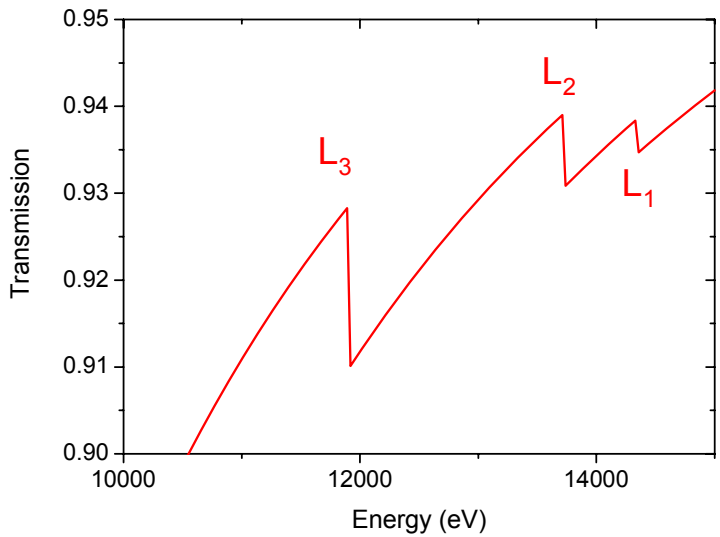
Lambert Beer's Law: $I = I_0 \cdot e^{-\mu d}$

Reminder: Photoemission, Fluorescence, Auger Emission



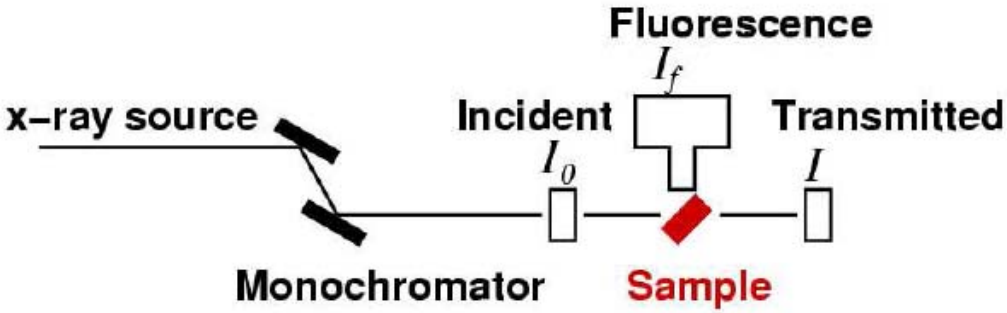


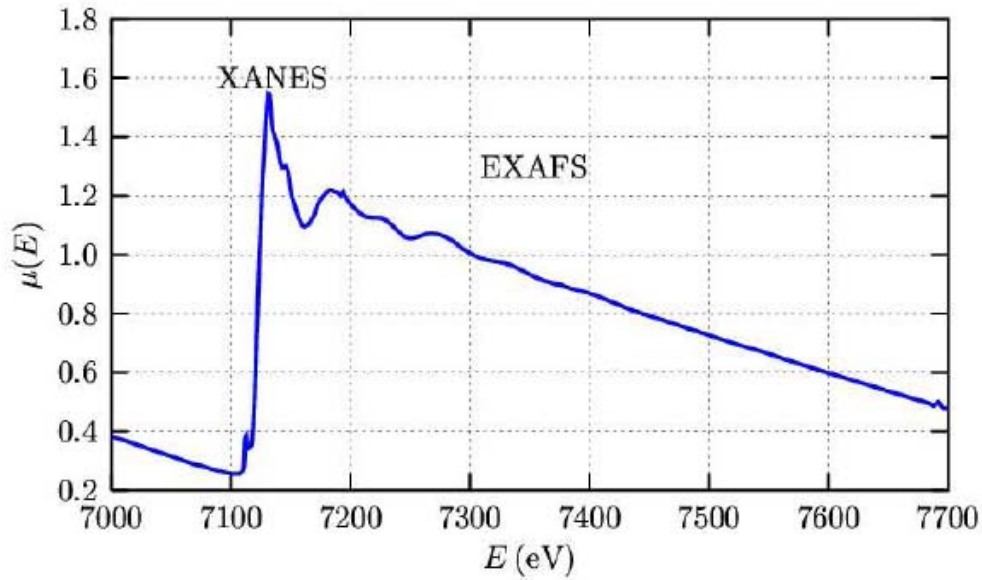




Au Foil

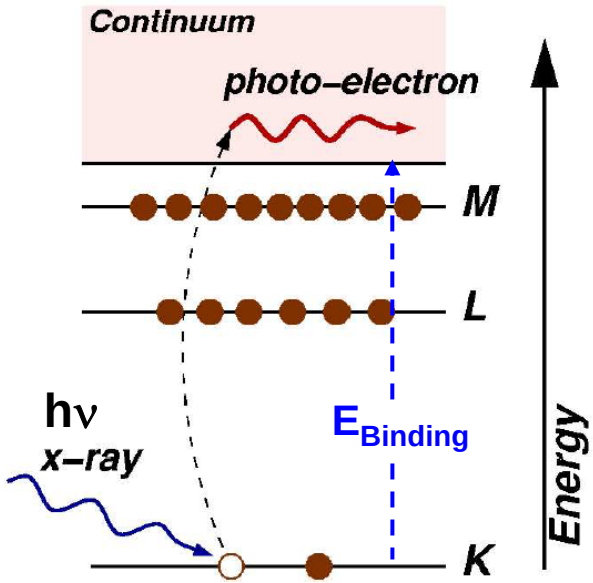
What is XAS?

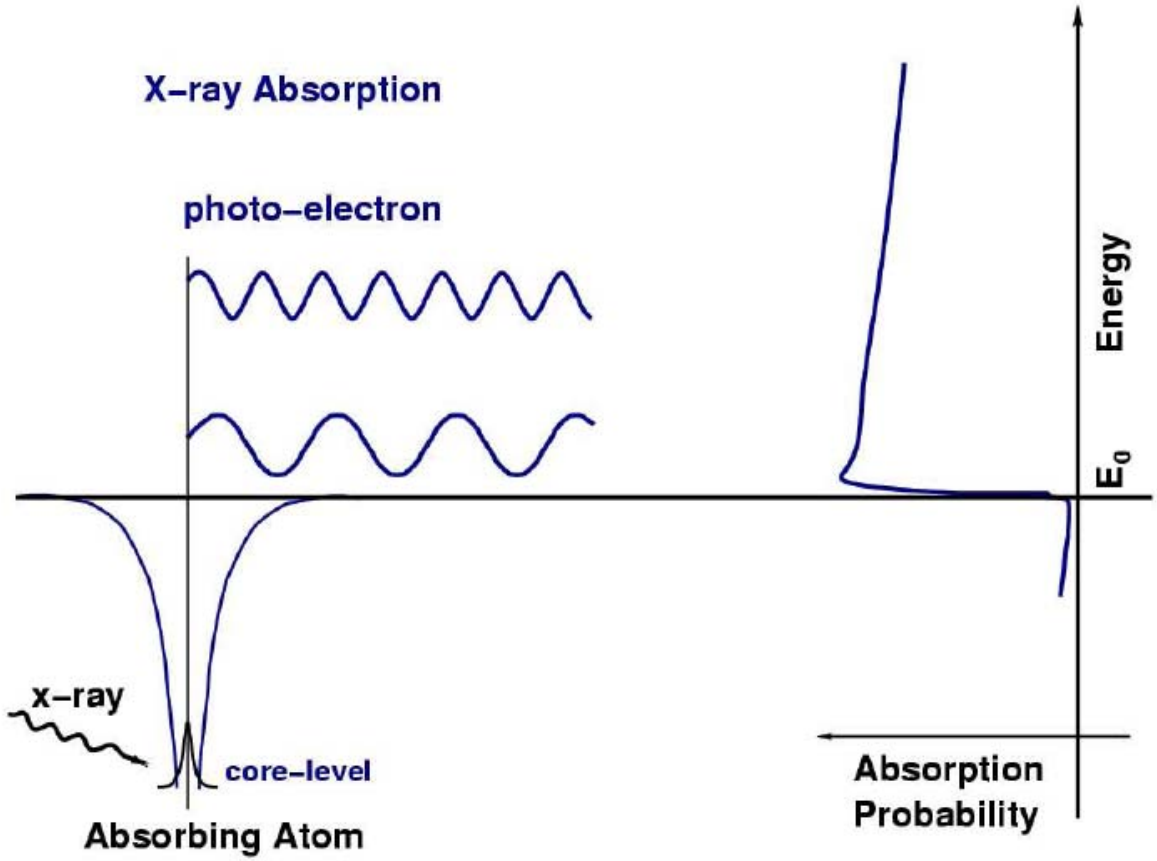




Absorption as function of energy of the x-ray
Shape is structure dependent

XAFS Theory: Absorption of a monoatomic substance





Creation of a photo-electron

$E_{kin} = h\nu - E_{Binding}$

Photo-electron has kinetic energy

XAFS Theory: Substance with neighbor atoms present

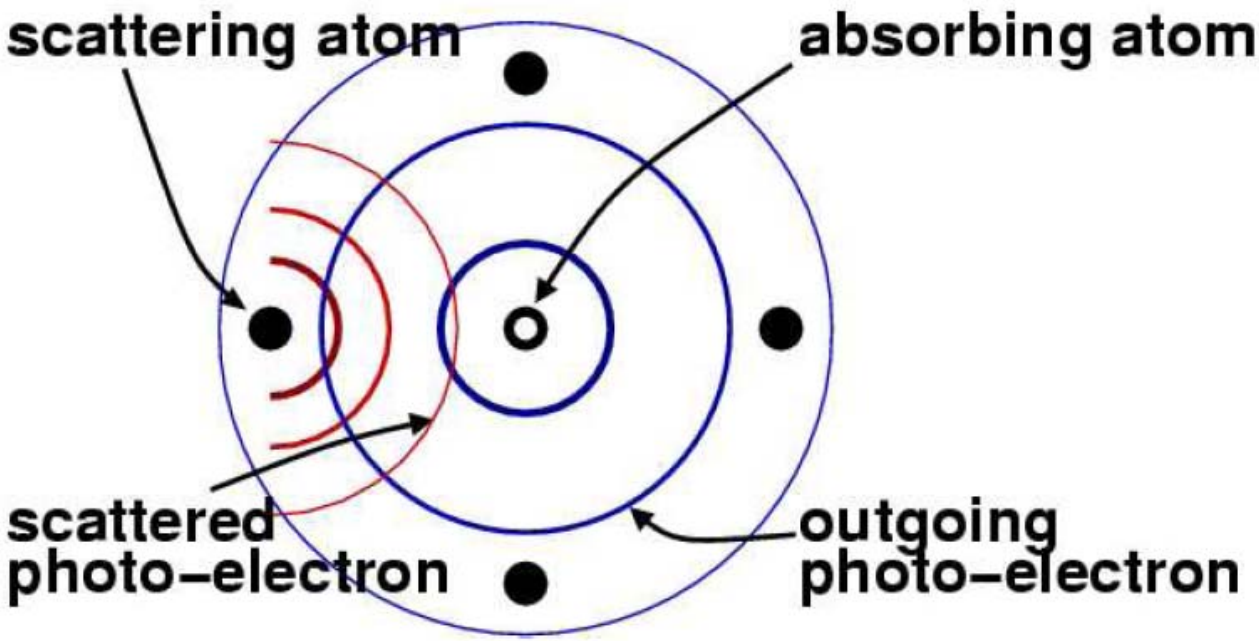


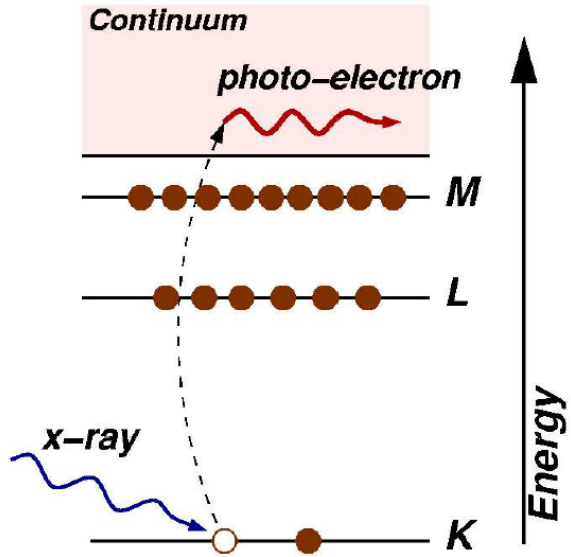
Photo-electron has kinetic energy

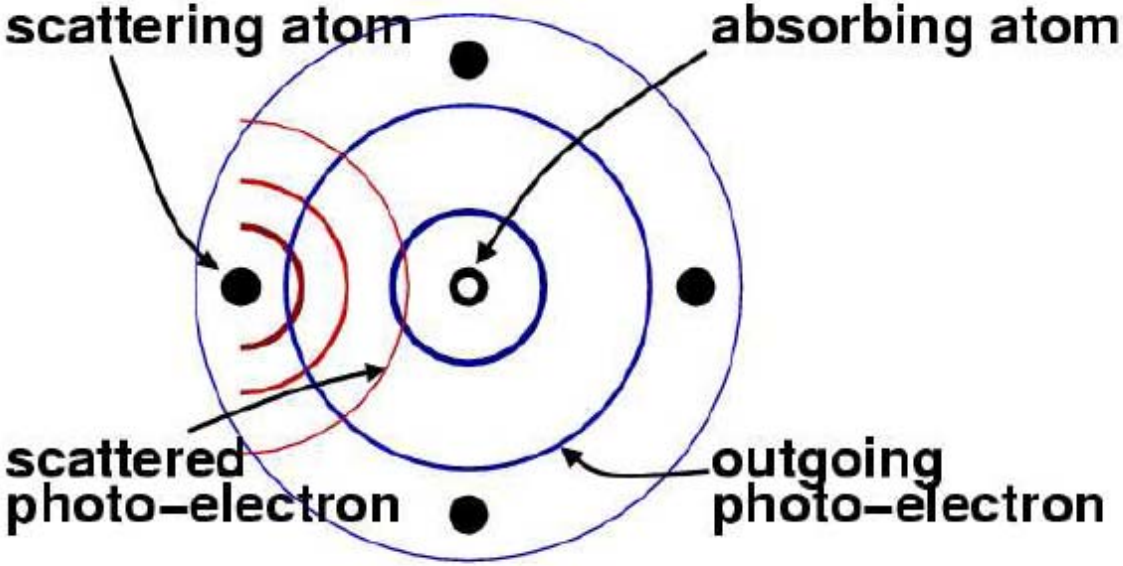
XANES

Fermi's Golden Rule

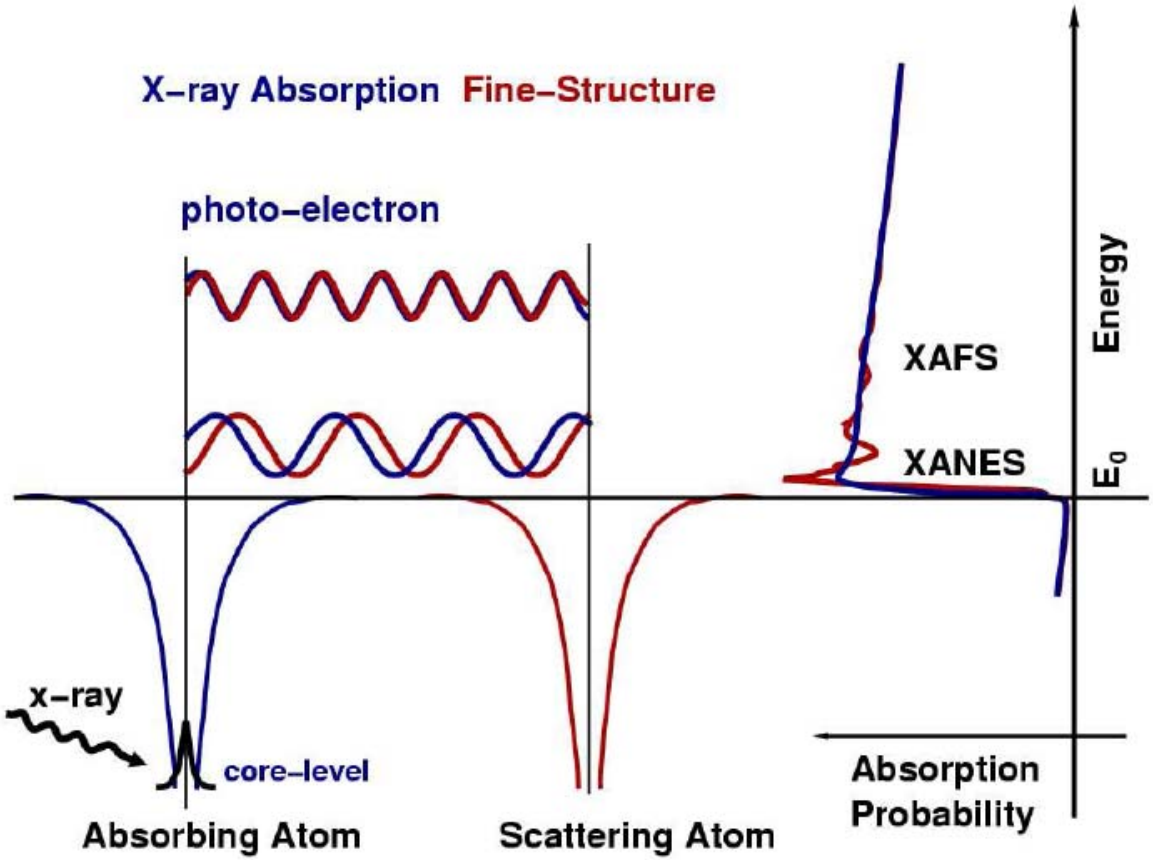
$$P \propto \left| \langle \Psi_i | T | \Psi_f \rangle \right|^2 \delta_{E_f - E_i - \hbar\nu}$$

Initial state — Transition operator — Final state





XAFS Theory: Substance with neighbor atoms present



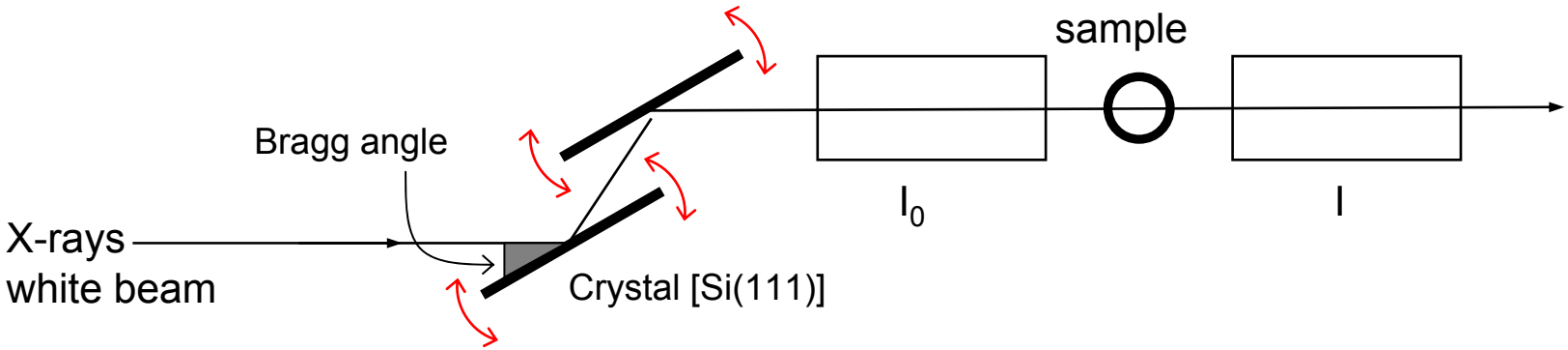
„wiggling in absorption“

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

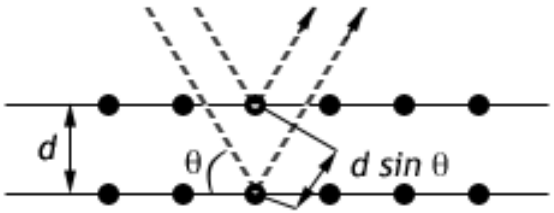
Outgoing wave === backscattering === interference pattern
Constructive / destructive interference

EXAFS is the wiggling part of the absorption

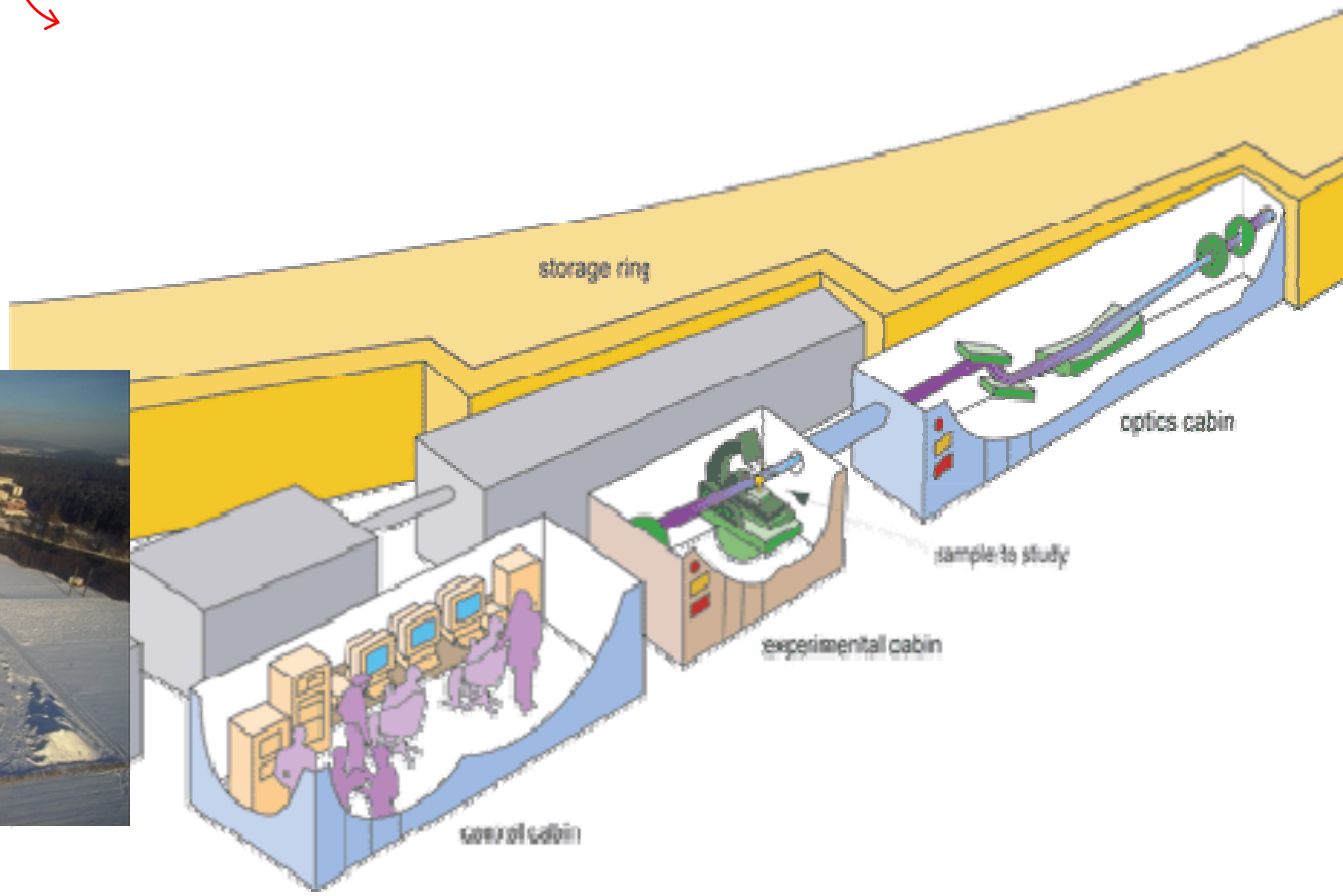
Tuning the energy
Double crystal monochromator



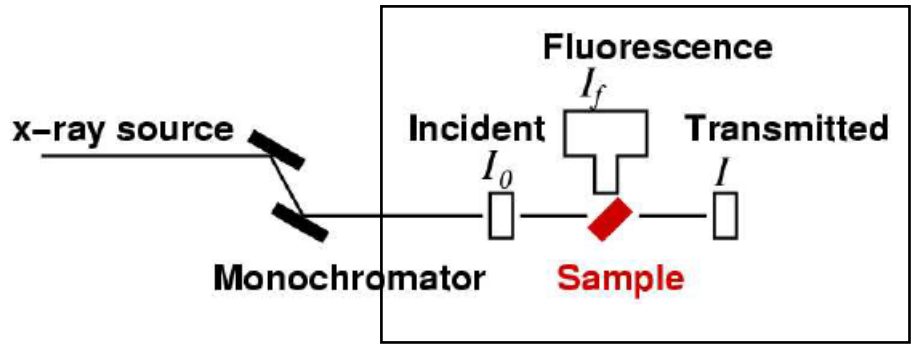
$2d \sin\theta = n\lambda$

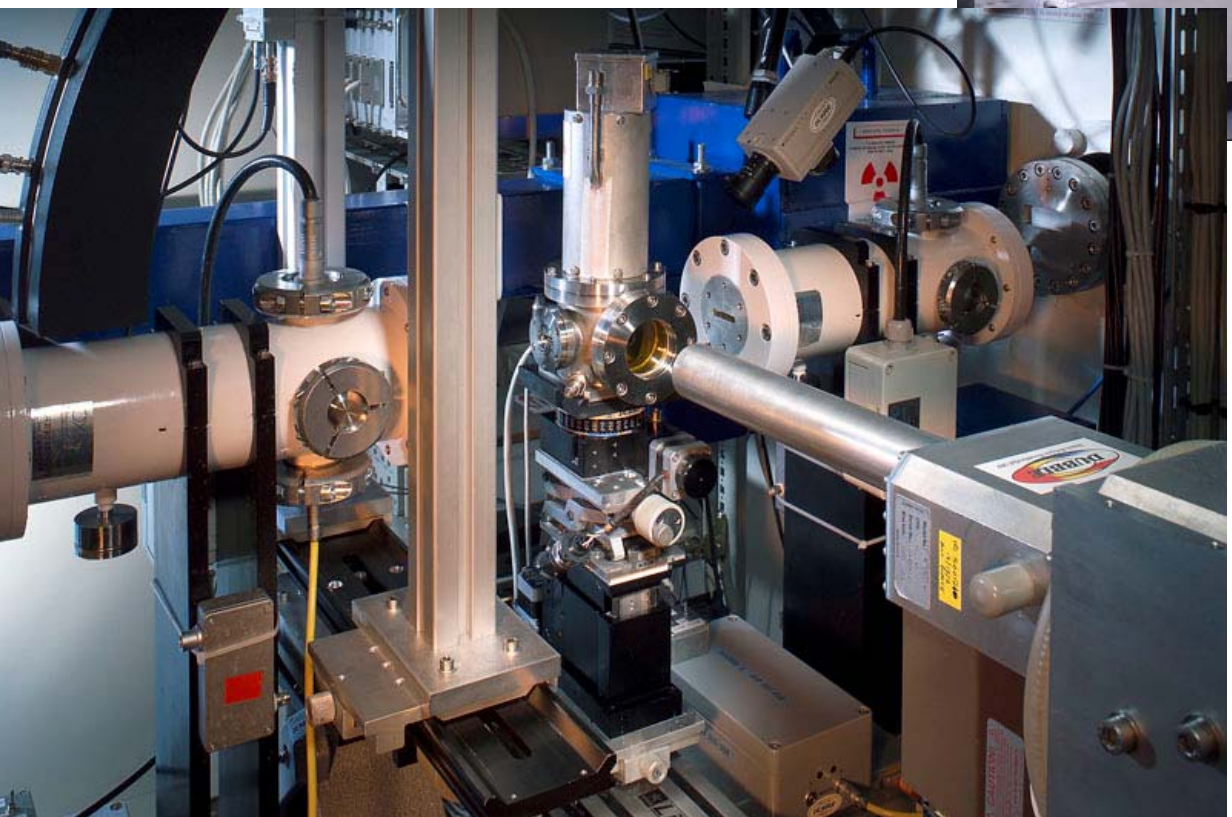


SLS, Villigen



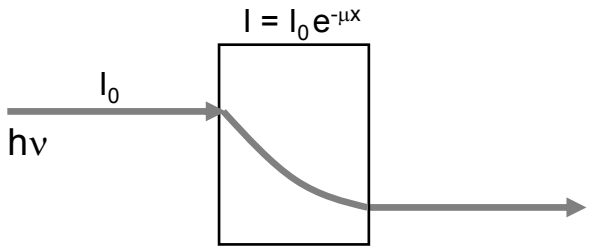
Experimental Hutch

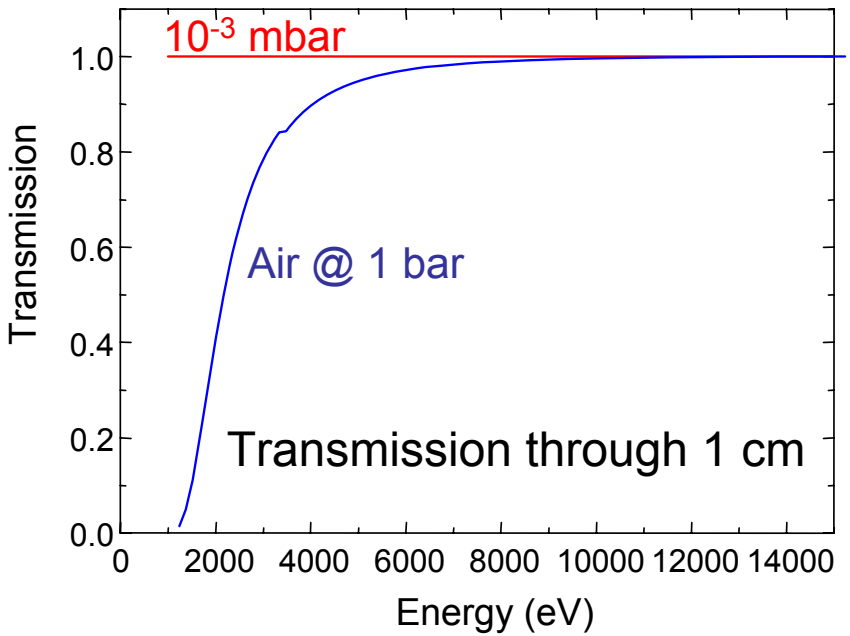




BM26 (DUBBLE), ESRF Grenoble

X-ray absorption through matter



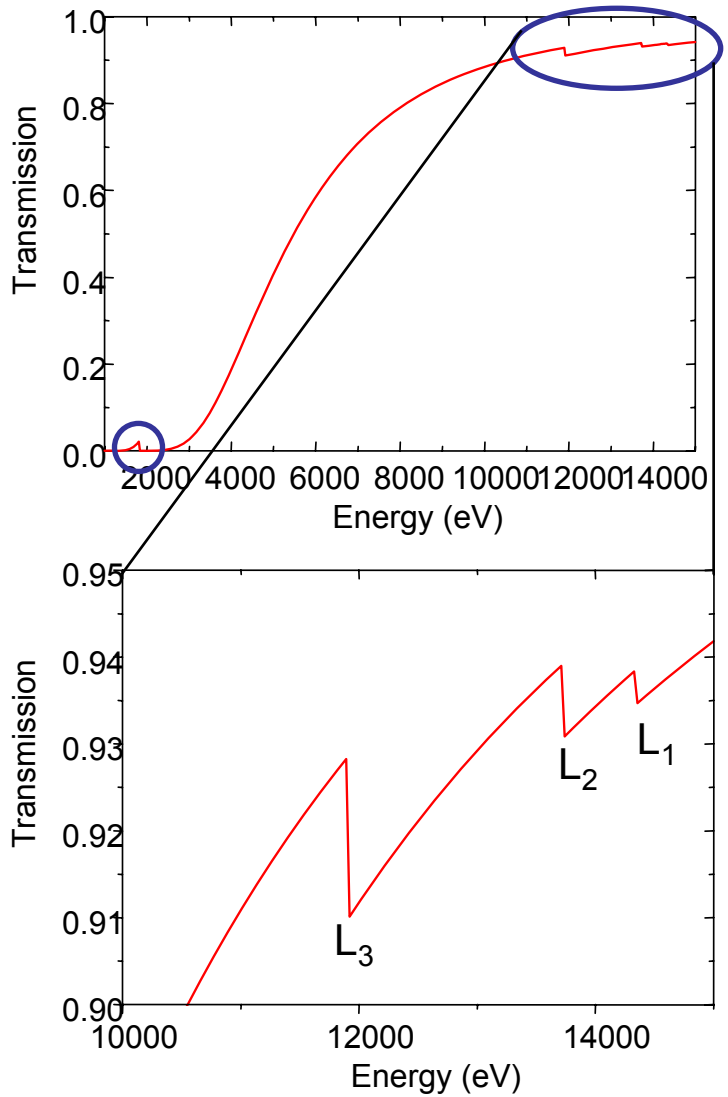


Lambert Beer's law

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

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

25 μm 1 wt% Au/SiO_2



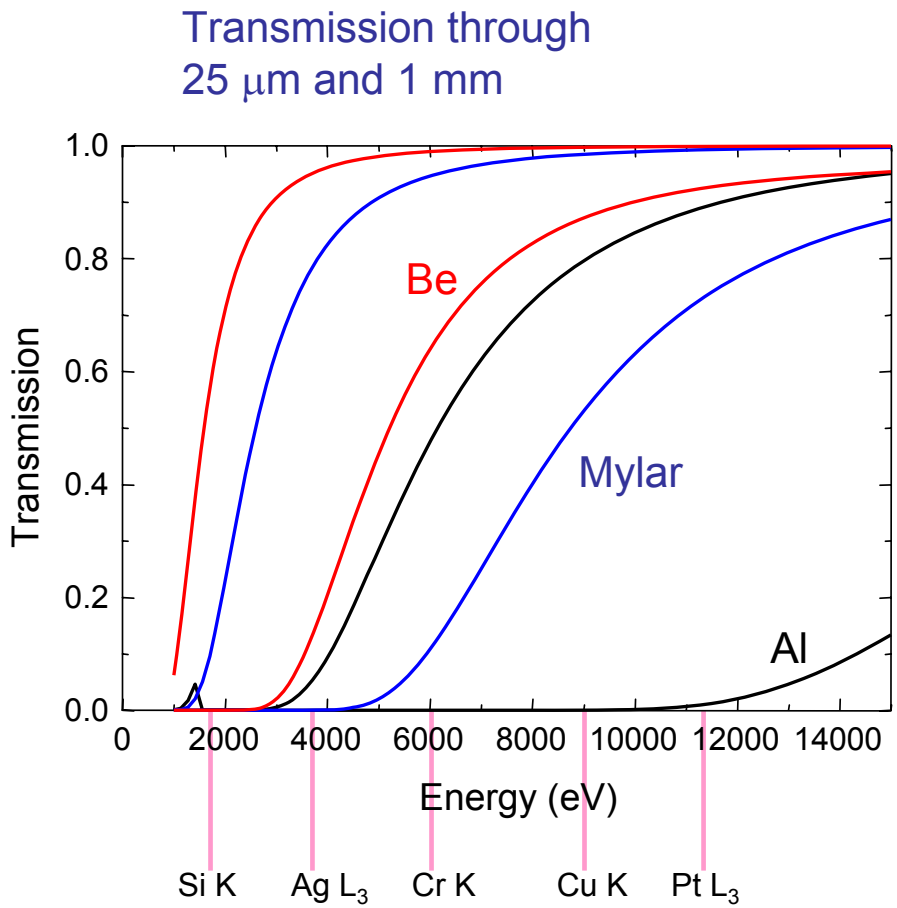
Sample environment

Absorption of X-rays is limiting factor

Find a good window material

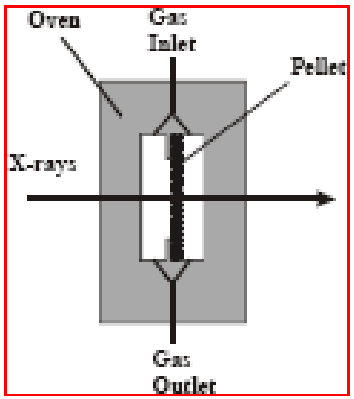
- Size of window
- Thickness
- Inertness
- Temperature resistance
- Pressure
- Safety

pressure
temperature
environment



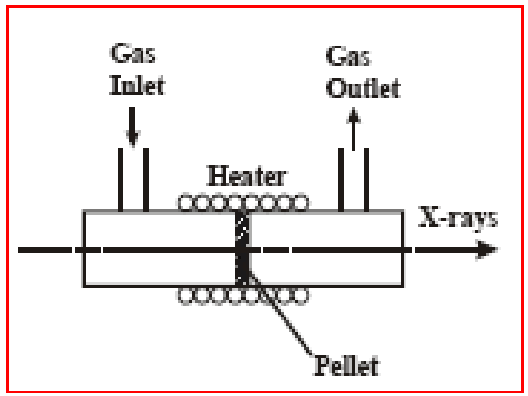
In situ EXAFS cells for gas-solid reactions

Reaction gas mixture flows around a pellet



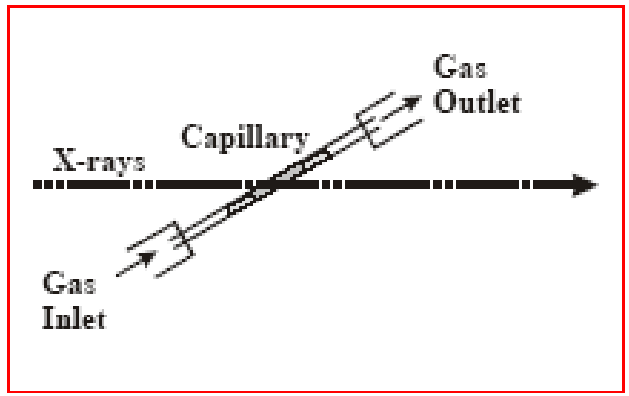
Large dead volume
Good for stationary conditions

Reaction gas flows through a catalyst pellet



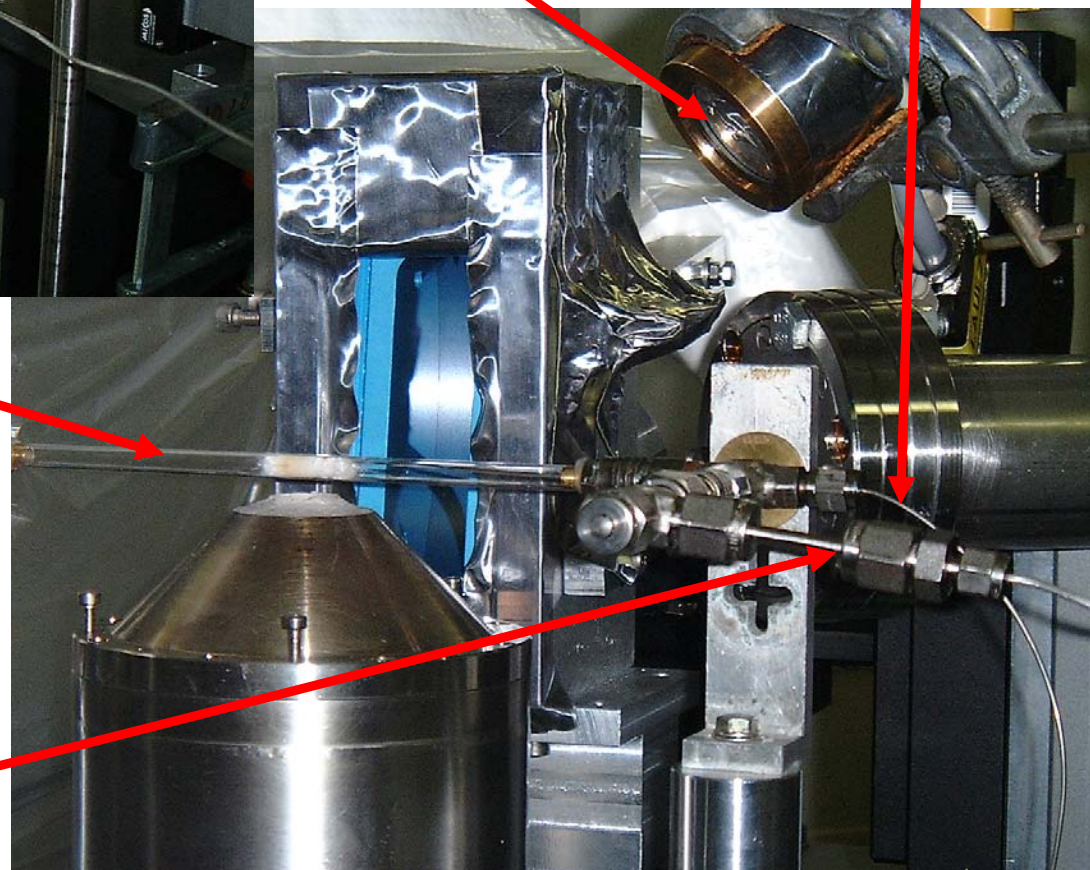
Critical d/l (smaller effectivity of the catalyst)

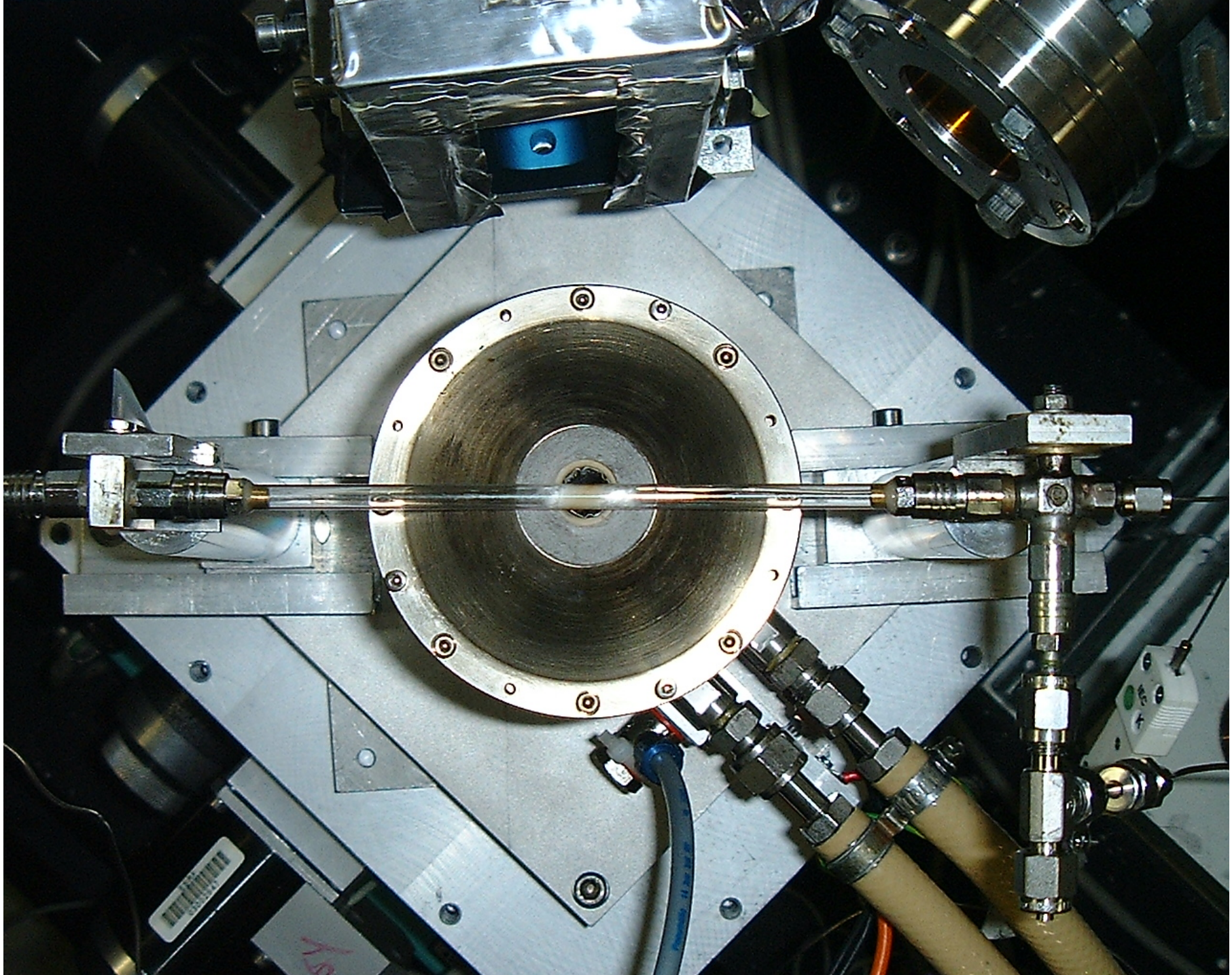
Small Glass Reactor with very thin windows (0.01mm)



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 — Transition operator — Final state

Dipole transition: $\Delta l = \pm 1$

K edge: 1s → p

L edge: 2s → p

2p → s,d

However

Quadrupole transition: $\Delta l = \pm 2$

K edge s → d

p → f

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

Visible in the K pre-edges!!

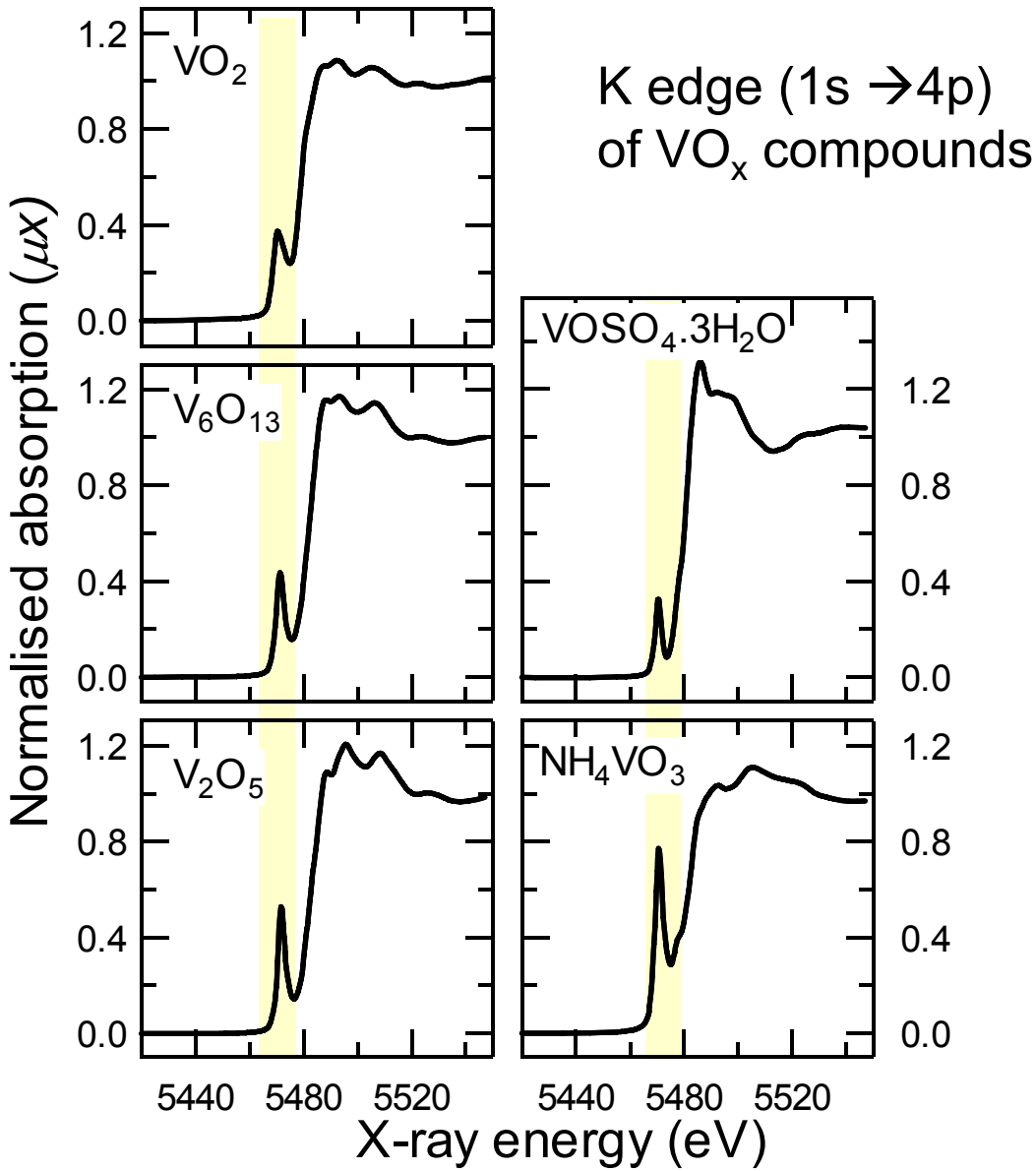
What determines the shape of XANES spectra?

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

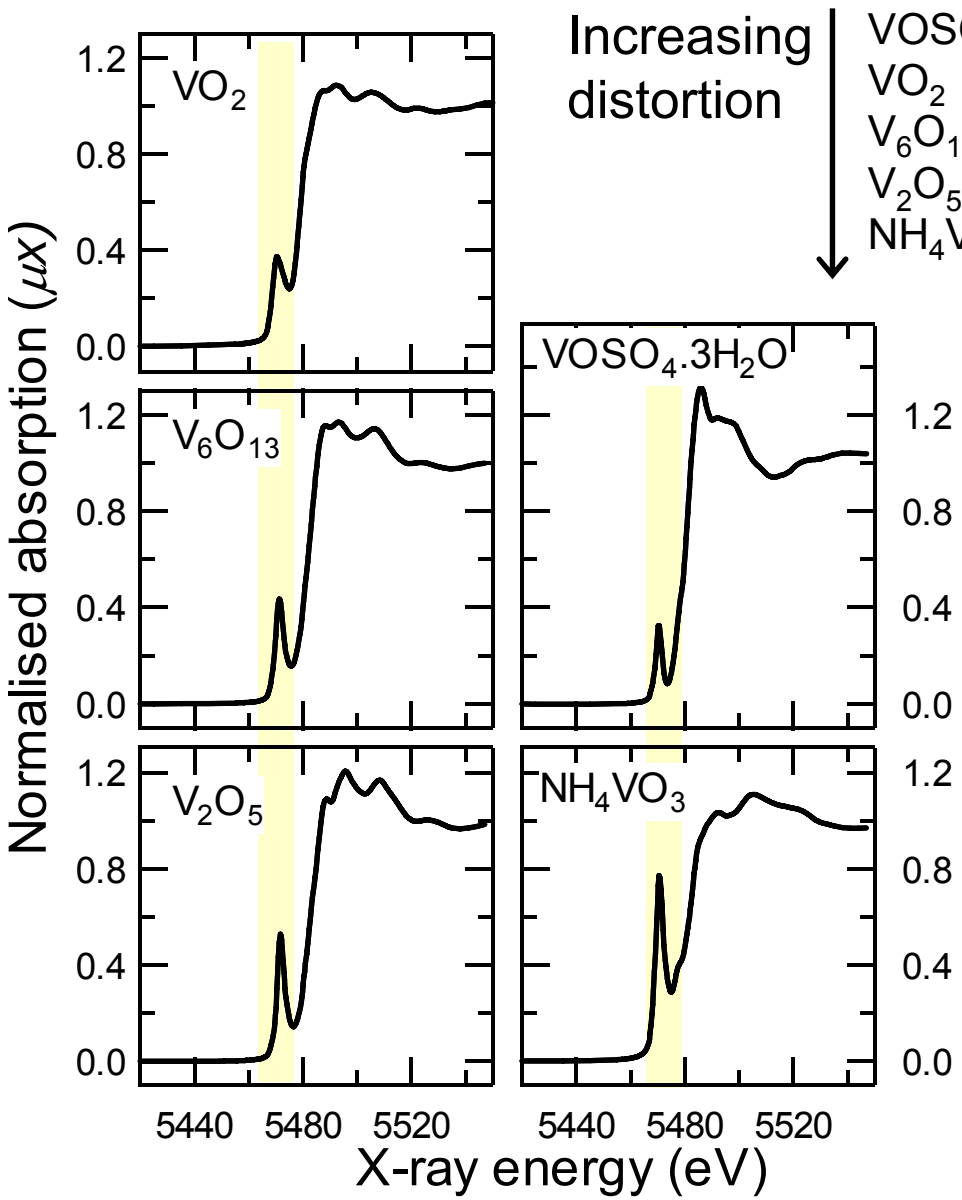
Pre-edge
- intensity
- energy

BUT…..

…… there is not always a pre-edge



In order of increasing distortion from octahedral



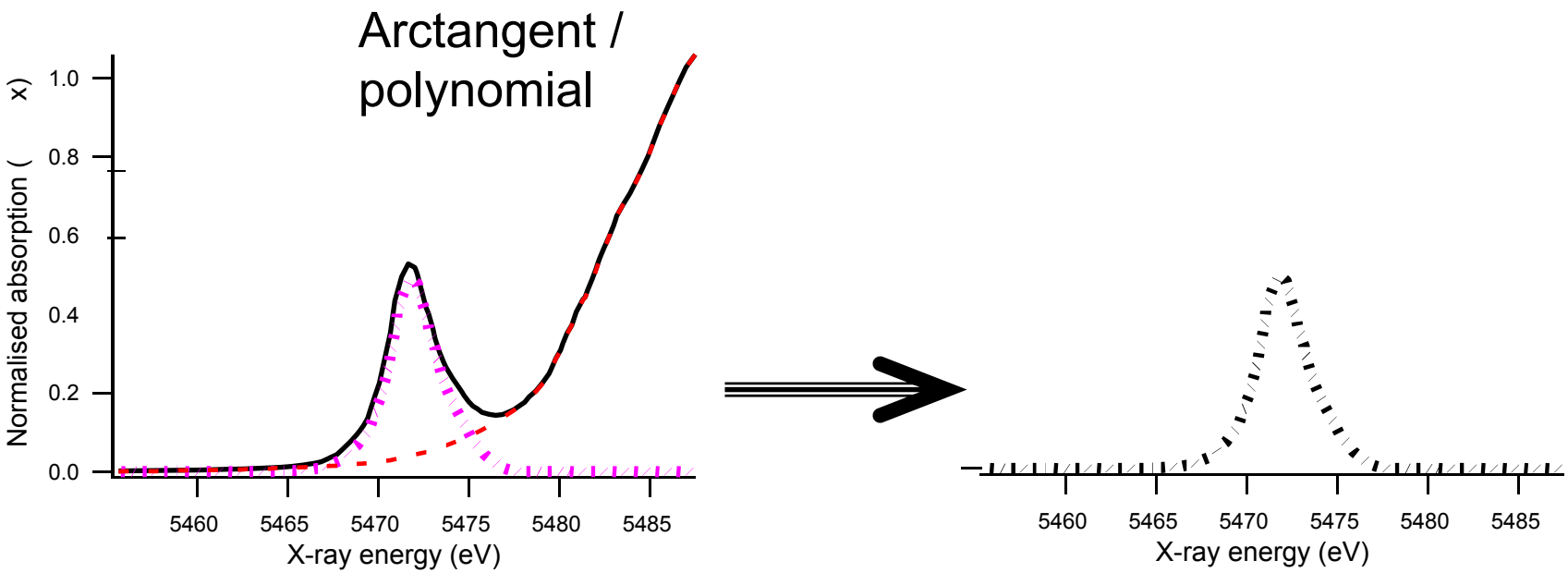
Increasing distortion

$VOSO_4$	Distorted Octahedral
VO_2	Distorted Octahedral
V_6O_{13}	Distorted Octahedral
V_2O_5	Distorted Square Pyramidal
NH_4VO_3	Tetrahedral

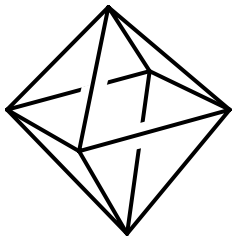
Increasing pre-edge

Isolation of the pre edge

by edge subtraction



Pre-edges intensity & energy varies (K edge)



Pure octahedral case

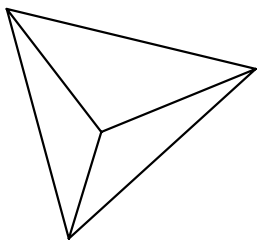
Centro-symmetry: no p-d mixing allowed: only quadrupole transition

➔ very low intensity

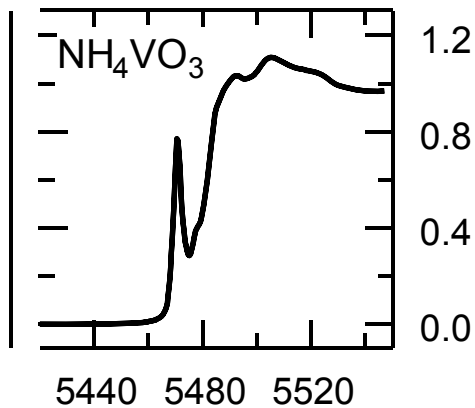
Distortion from octahedral

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

➔ increasingly large intensity



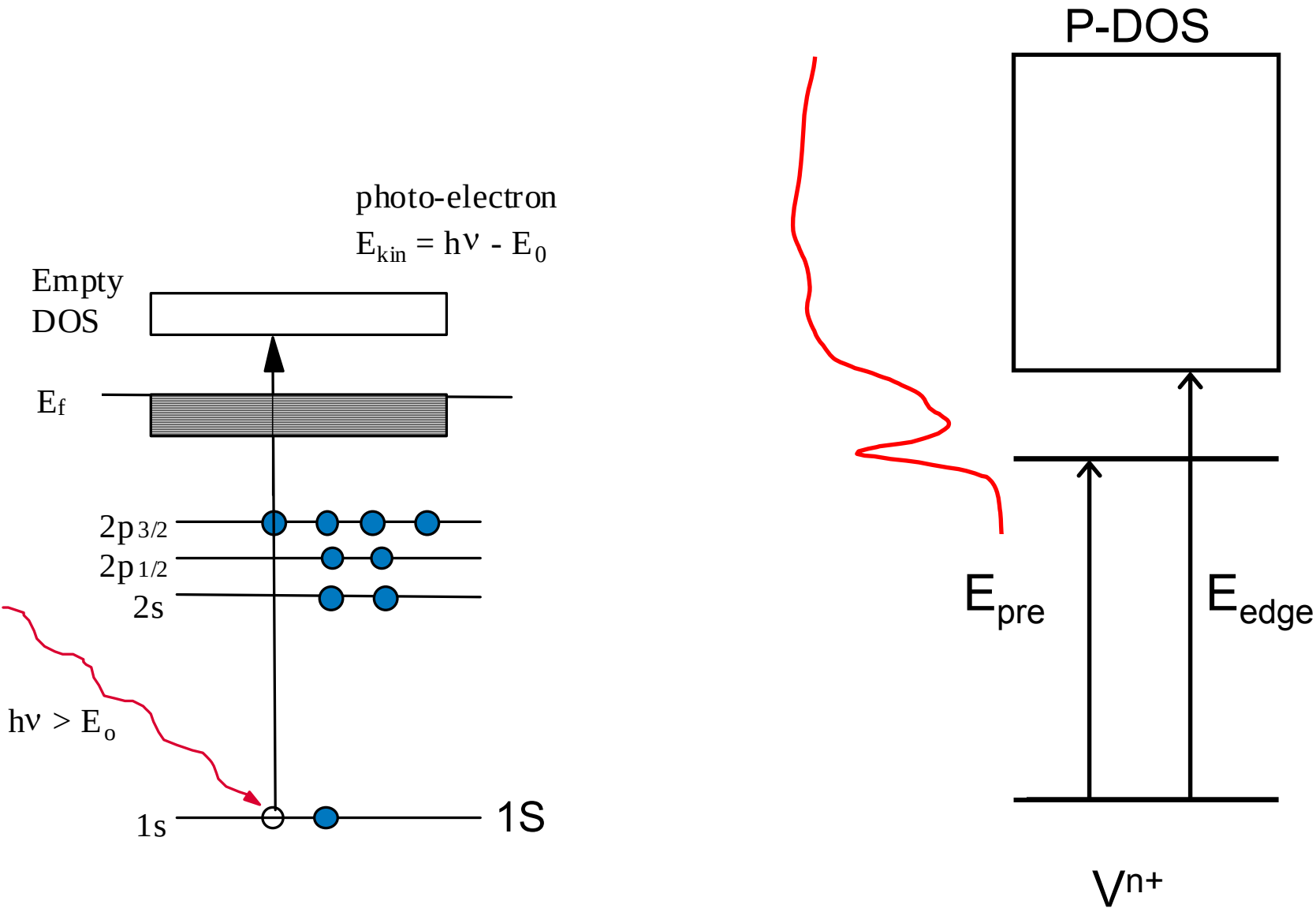
Pure tetrahedral => largest pre-edge



Intensity pre-edge indicative of geometry

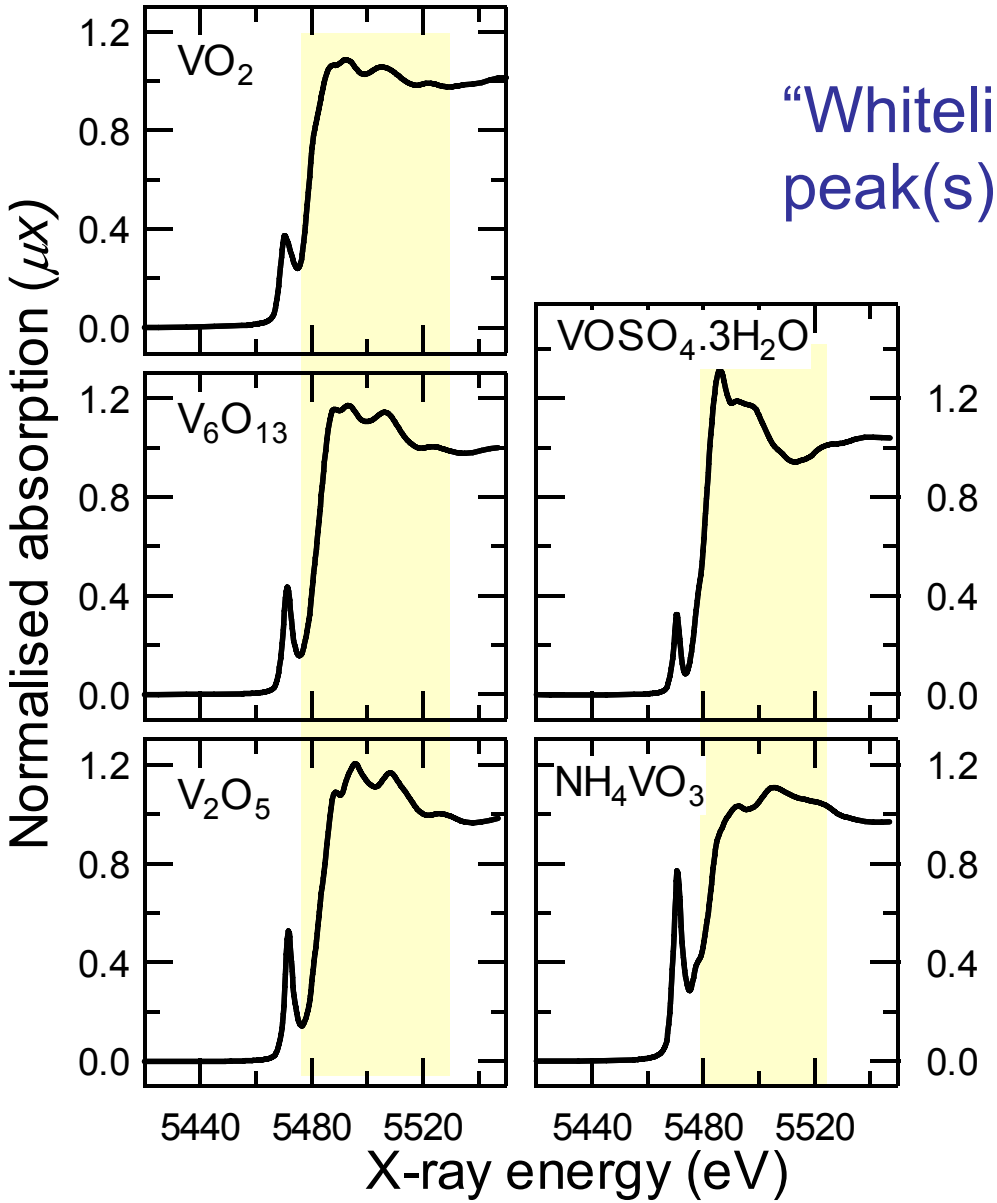
(Pre-)edge Energy and Valence

Edge position is measure of oxidation state



Shape of the whiteline

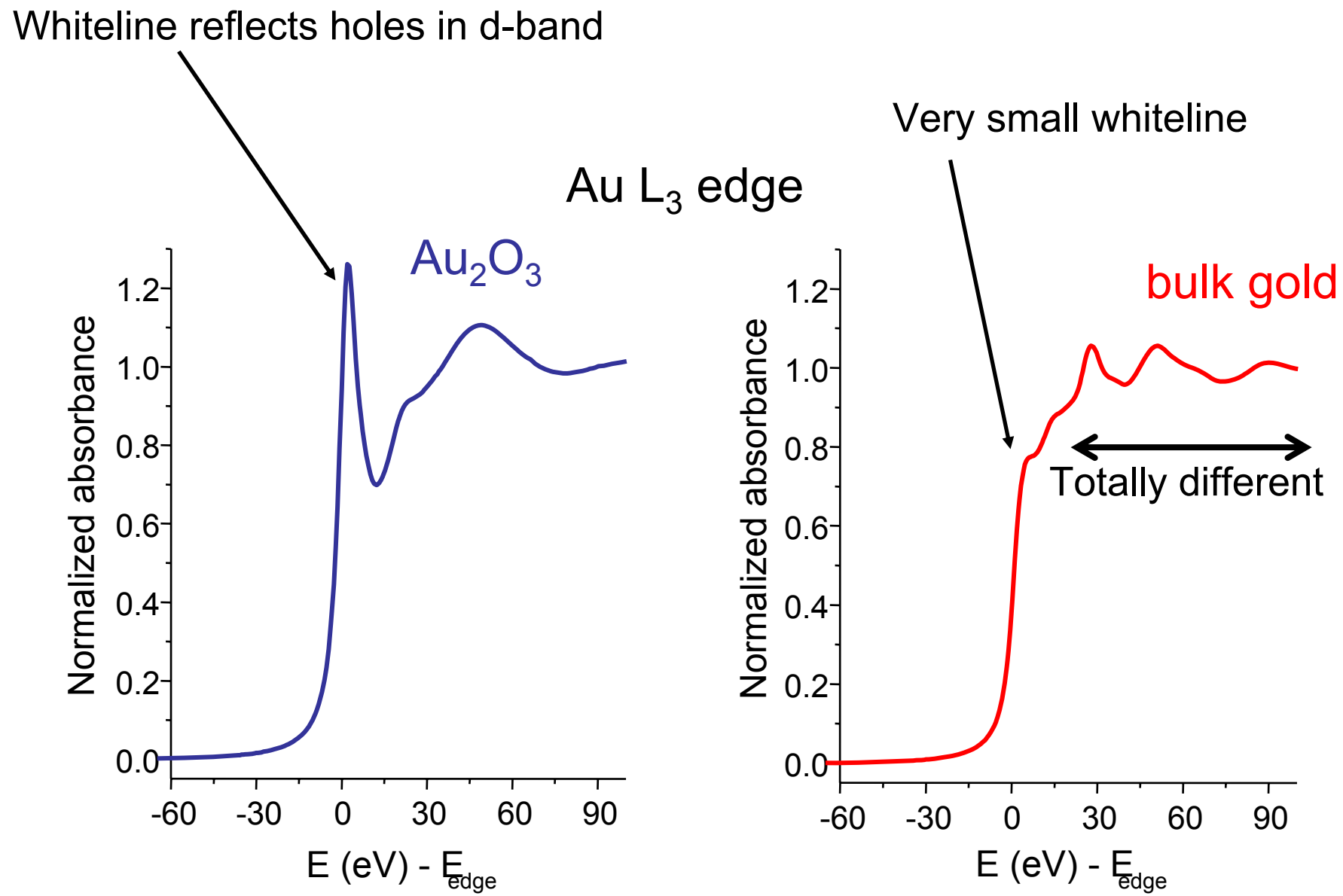
For L edges > 3 keV and all K edges



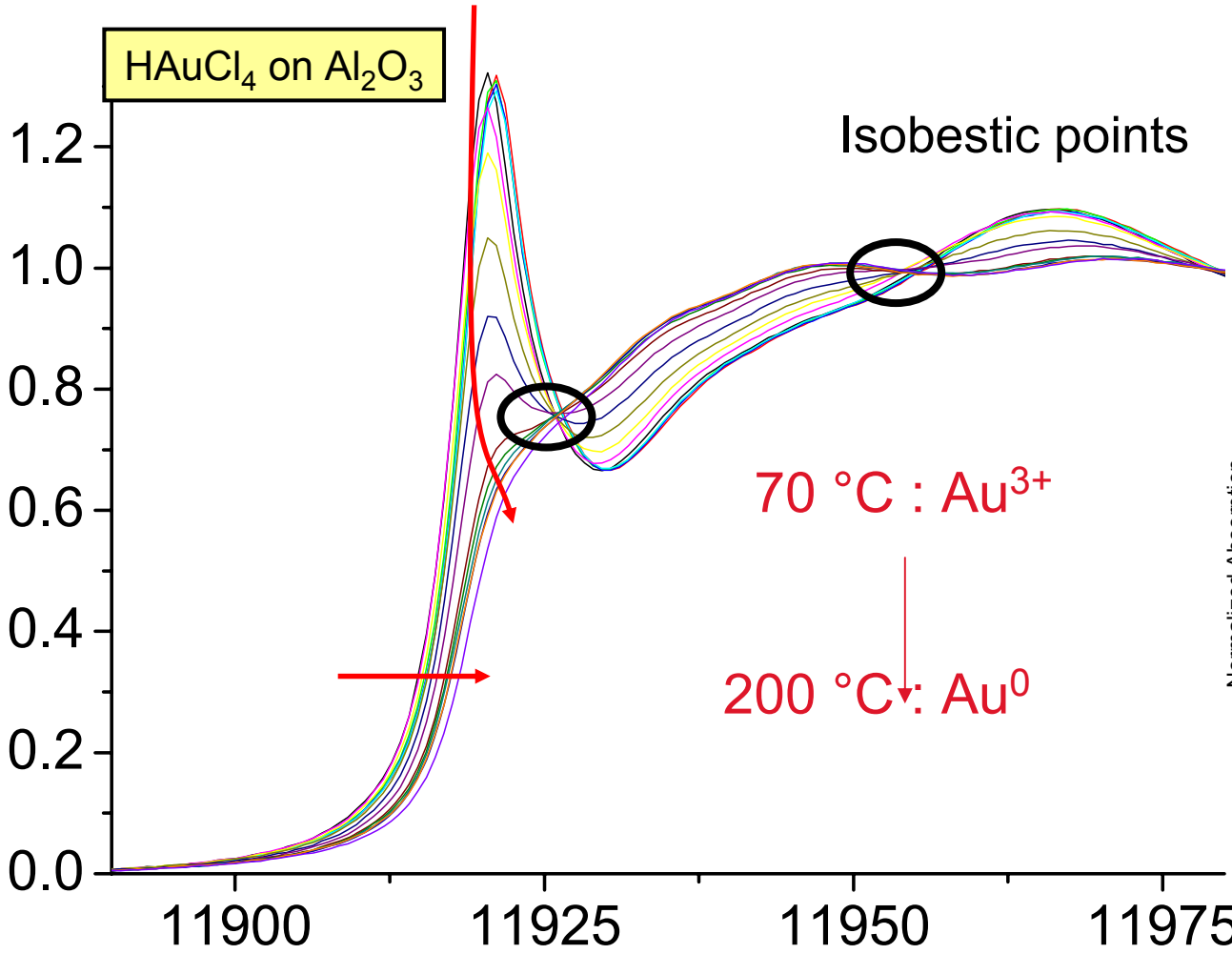
"Whiteline is first intense peak(s) in spectrum"

$VOSO_4$	Distorted Octahedral
VO_2	Distorted Octahedral
V_6O_{13}	Distorted Octahedral
V_2O_5	Distorted Square Pyramidal
NH_4VO_3	Tetrahedral

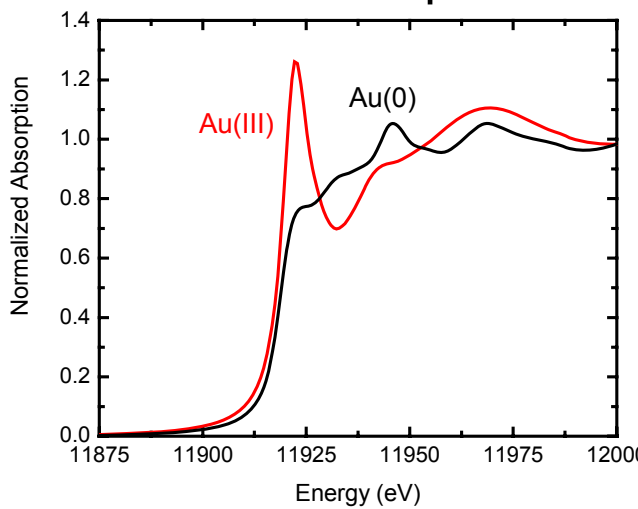
Shape of the whiteline: L-edges



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

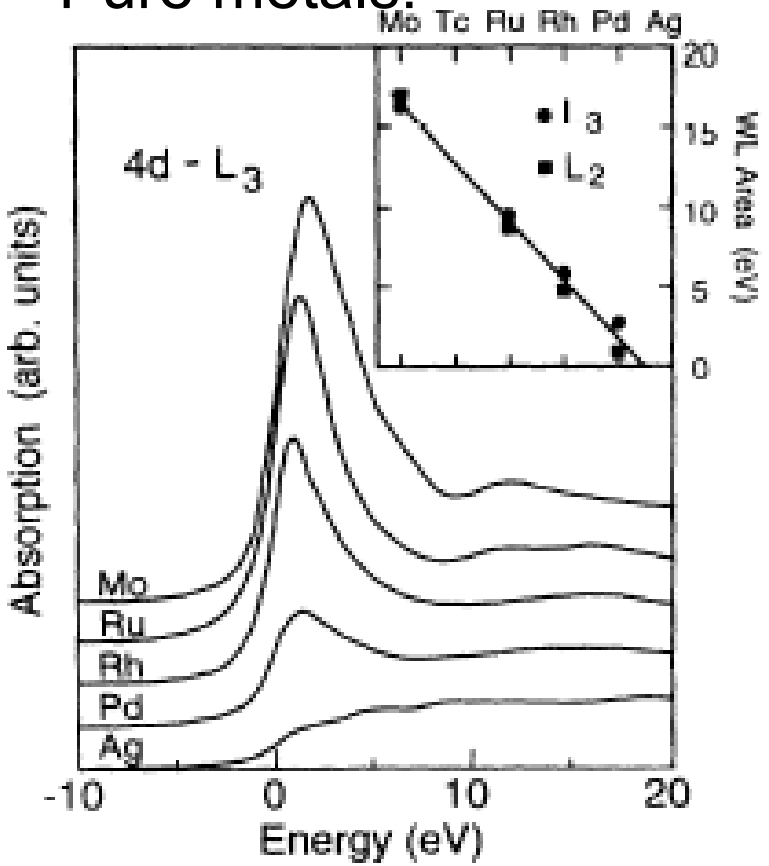


Reference spectra



Shape of the whiteline: L-edges

Pure metals:

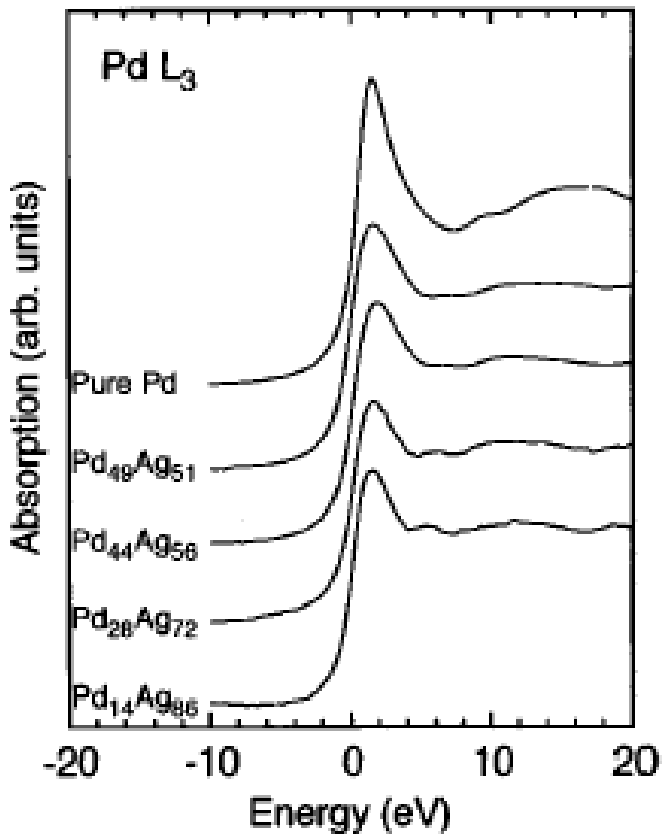


Whiteline reflects holes in d-band

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).