X-ray absorption spectroscopy in materials science

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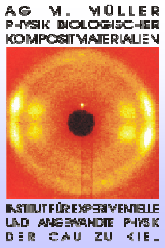
- Photoelectric absorption
- XANES
- EXAFS
- Instrumentation
- Examples



Uses of X-ray spectroscopy

XAFS: X-ray absorption fine structure

local technique:

- element-specific
- diluted or concentrated systems can be studied
- study of disordered systems possible
- wide temperature and pressure range

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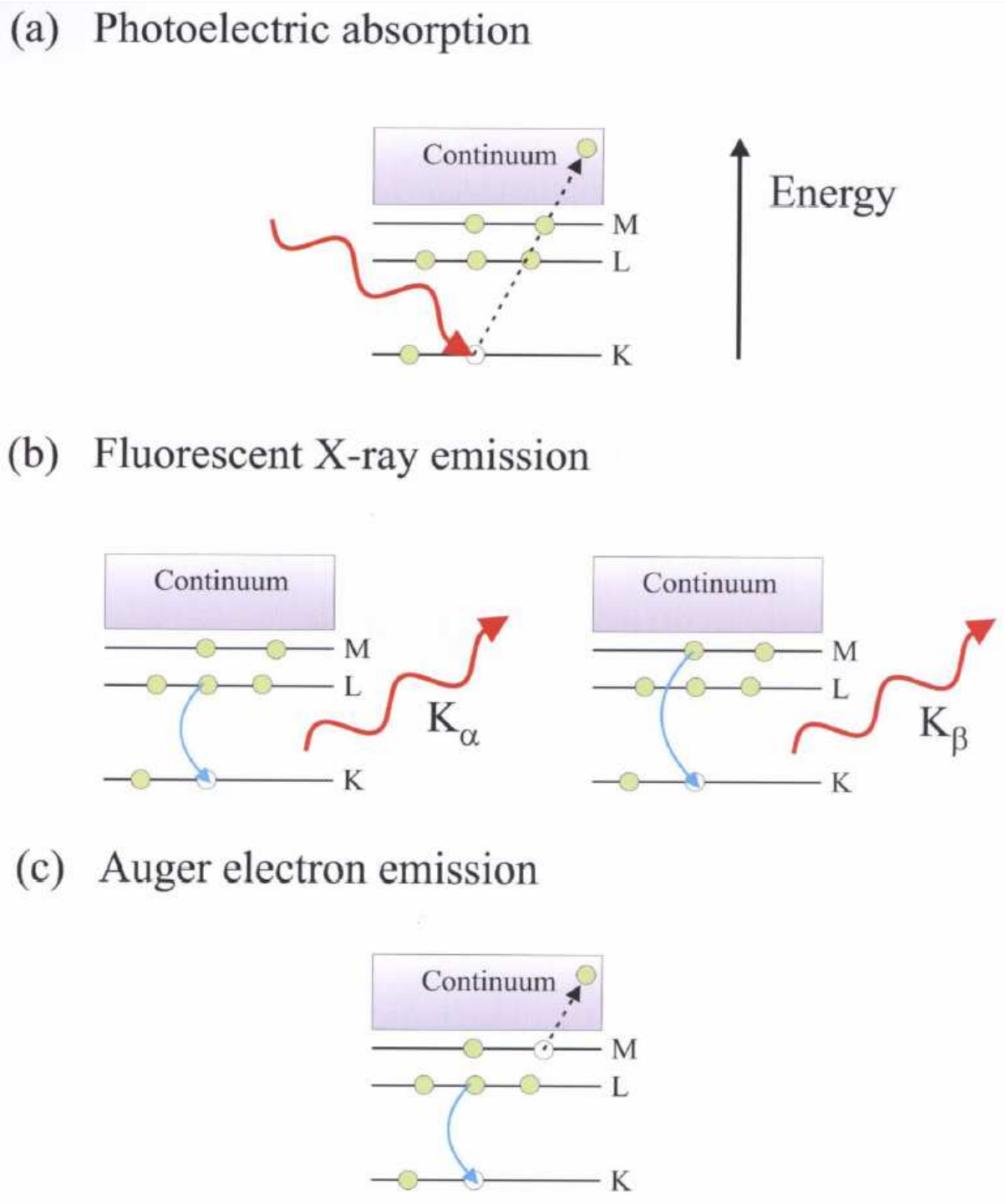
Photoelectric absorption

(a) ionisation energy of inner shell smaller than X-ray energy

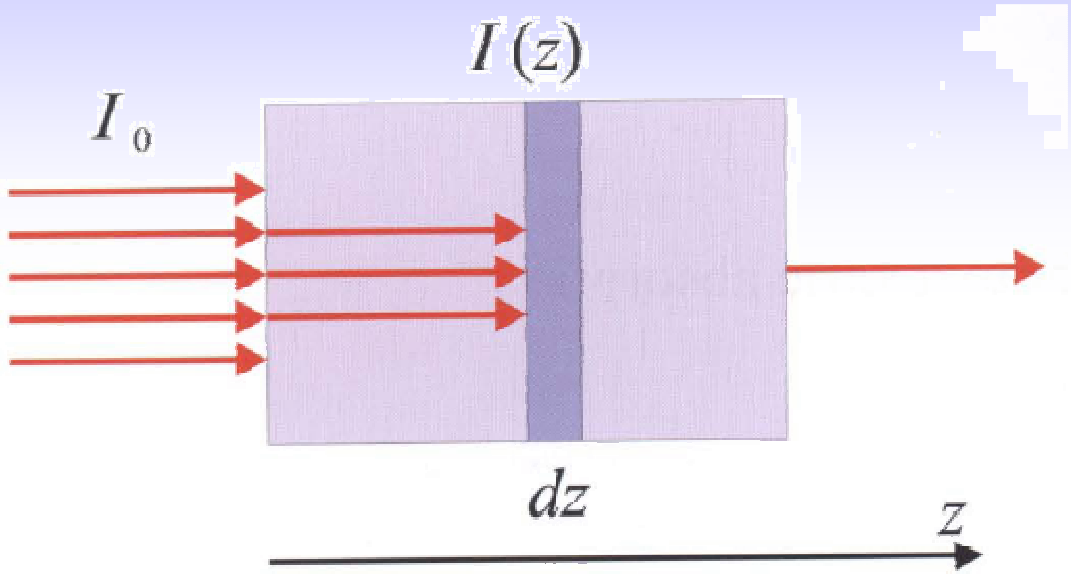
⇓

photoemission of core electron

(b,c) two possible secondary processes to fill the hole



Transmission and absorption cross section



transmitted intensity decays exponentially with thickness:

$$T = \frac{I}{I_0} = e^{-\mu z}$$

absorption coefficient

$$\mu = \left(\frac{\rho_m N_A}{A} \right) \sigma_a$$

absorption cross-section

mass density

atomic mass number

Avogadro's number

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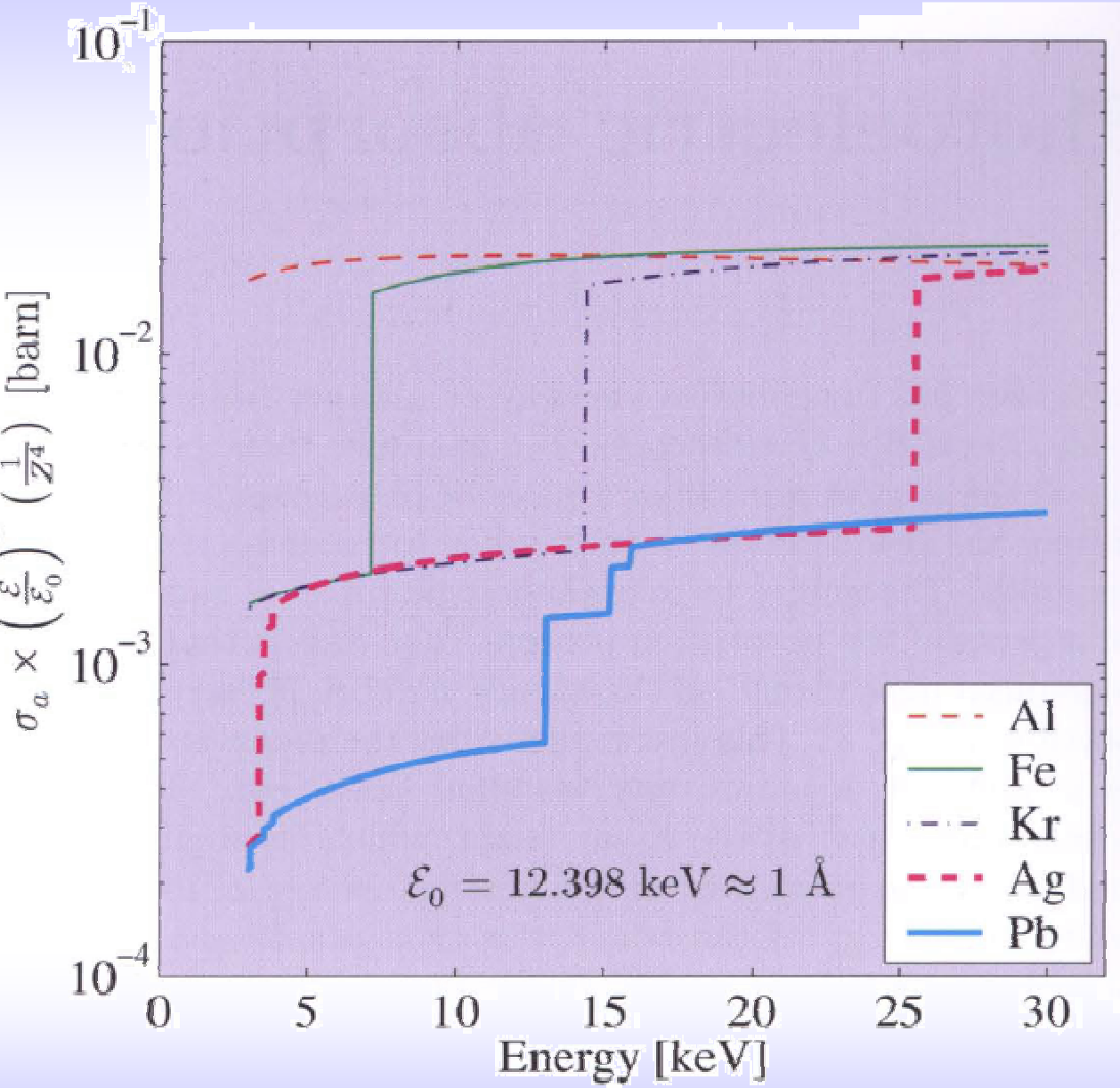
Absorption edges

general behaviour of cross-section:

$$\sigma_a \propto Z^4$$

$$\sigma_a \propto E^{-3}$$

sudden increase in absorbance at ionisation energy of core electron = **absorption edge**



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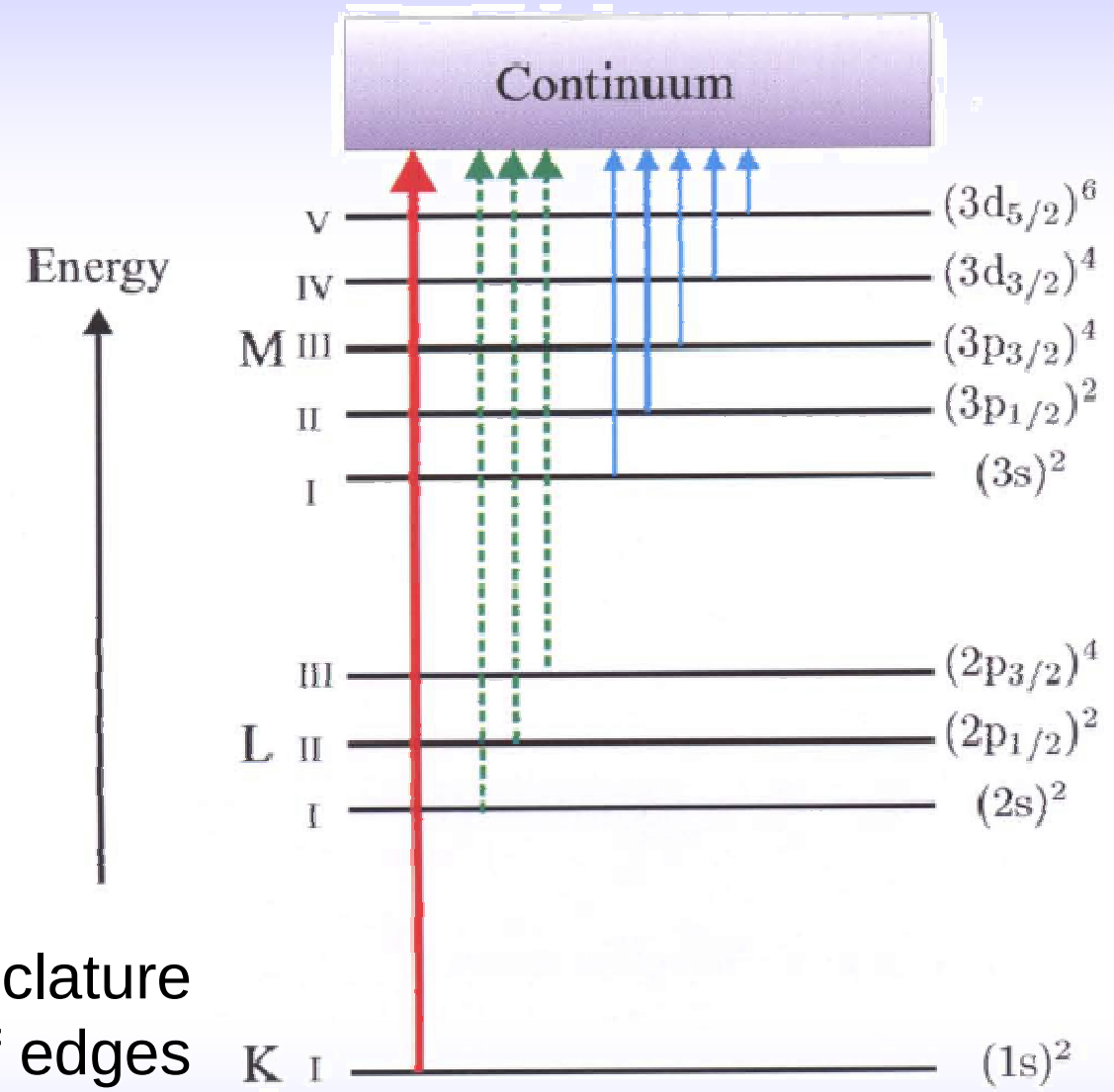
Absorption edges

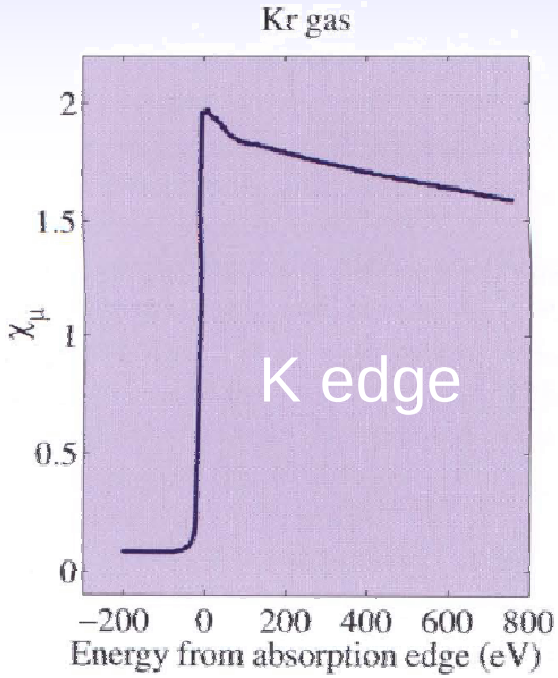


electron states

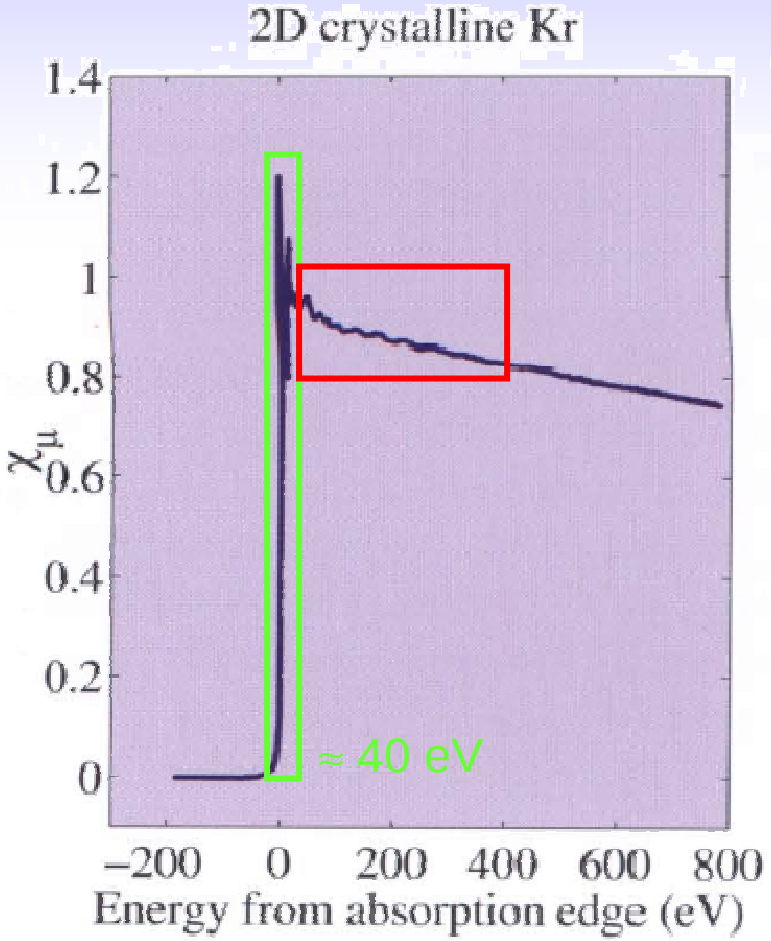
nomenclature of edges

Fine structure of absorption edges

example: krypton



gas



2D crystal

XAFS

X-ray **A**bsorption **N**ear-**E**dge **S**tructure

Extended **X**-ray **A**bsorption **F**ine **S**tructure

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XAFS accessible elements

XANES only

EXAFS difficult

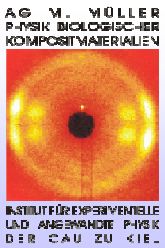
K-edge EXAFS

L3/K-edge EXAFS

L3-edge EXAFS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	*	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
		*																

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
*	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
*														



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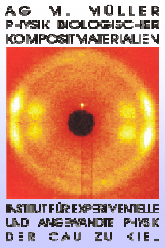
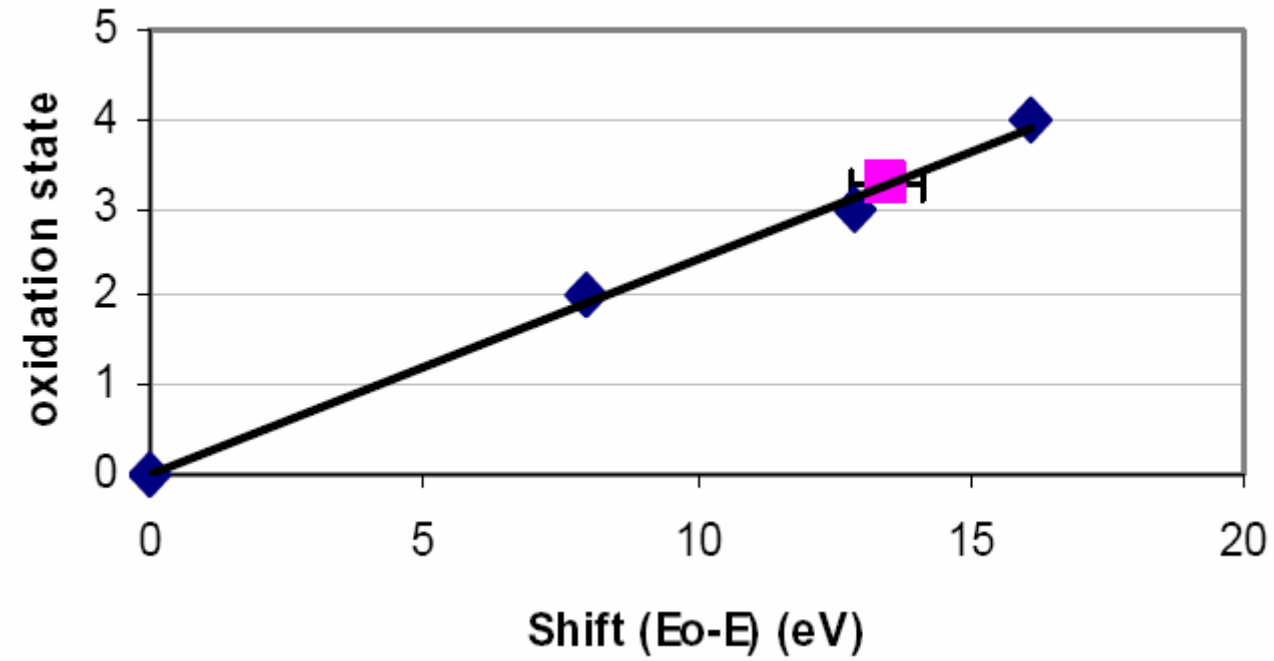


Energy shift of edge position

energy to eject core electron depends on charge it experiences:
edge energy depends on **oxidation state**

Mn compound: shift of edge position



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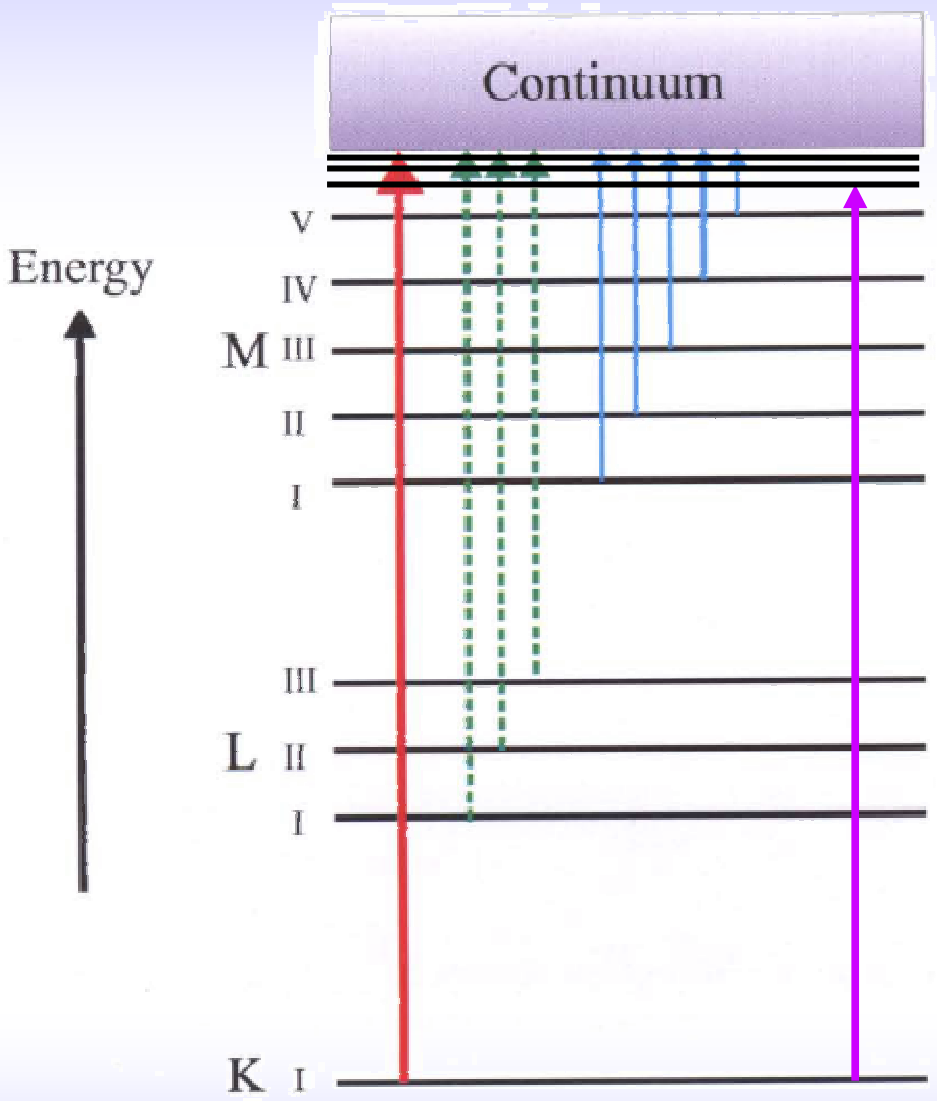
Pre-edge peaks

electron might also be excited into **bound states**



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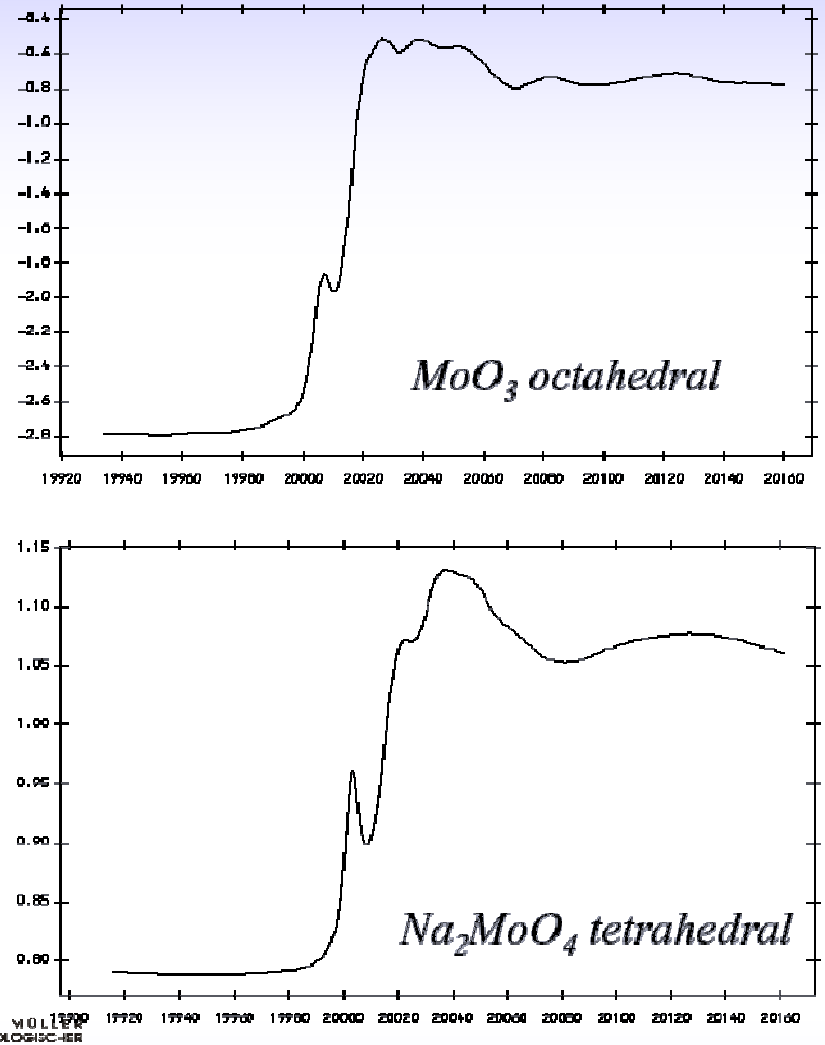
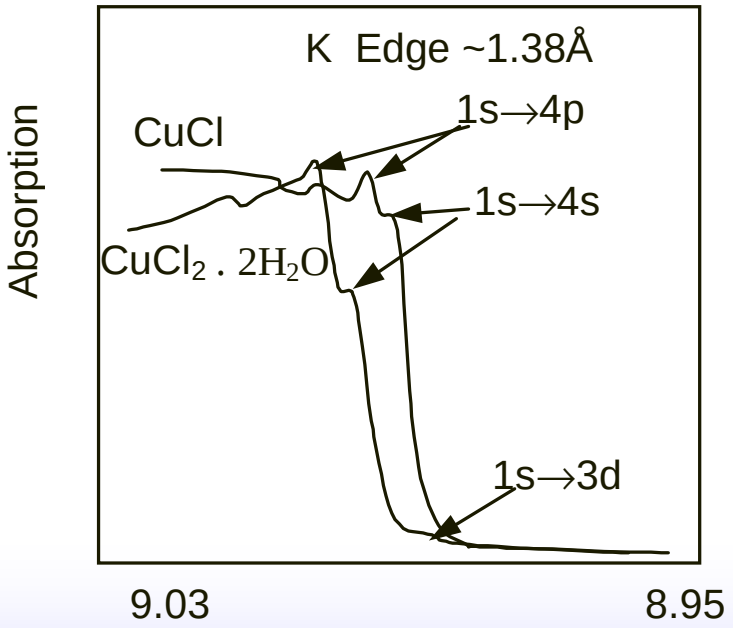
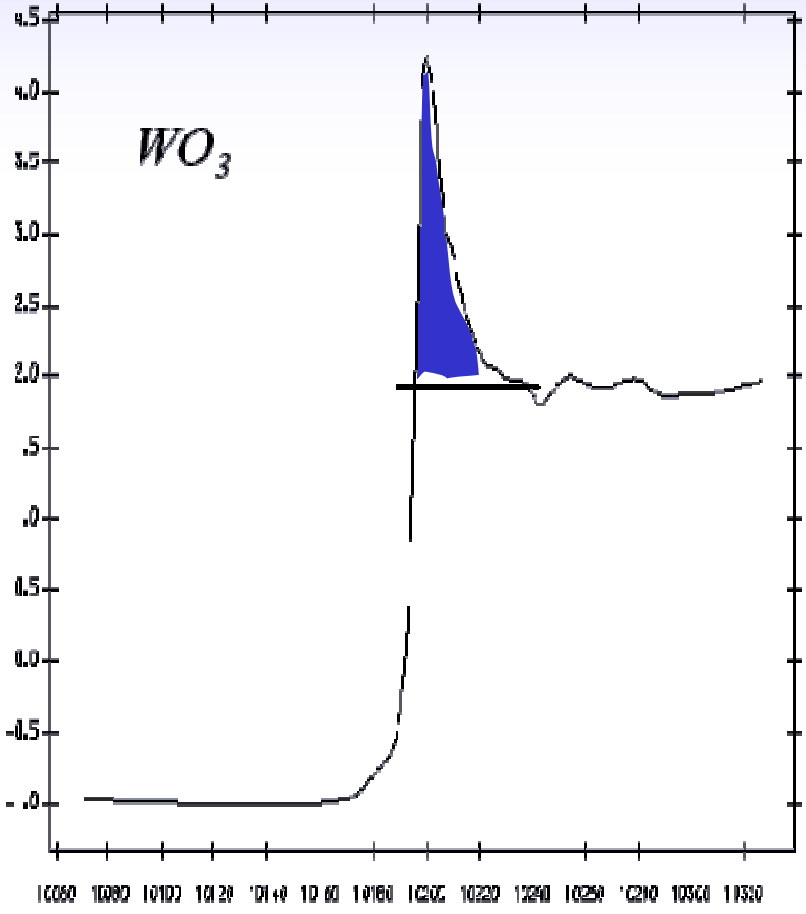


depend on **geometry**:

- oxidation state
- site symmetry
- surrounding ligands
- nature of bonding



XANES white lines



in transition metals:
area of white line
indicates number of empty d-states

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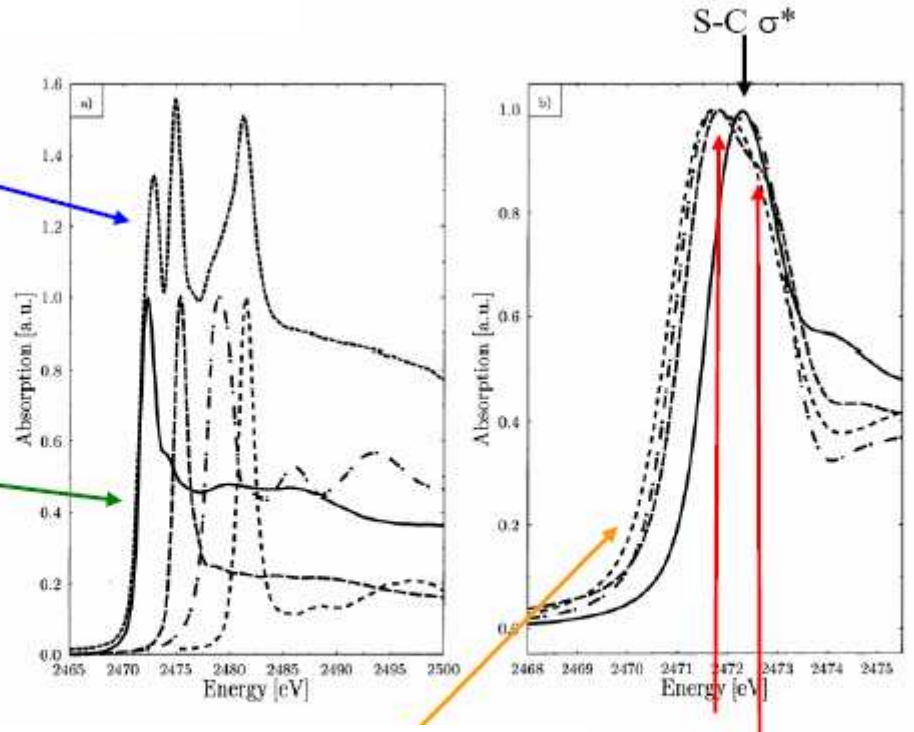
XANES fingerprinting

XANES characteristic of *chemical environment* and *valence state*:

- fingerprinting
- phase analysis by **linear combination** of known species

unknown
S spectrum

known references
(oxidation numbers
0, 2, 4, 6)



high sensitivity
to electronic states!

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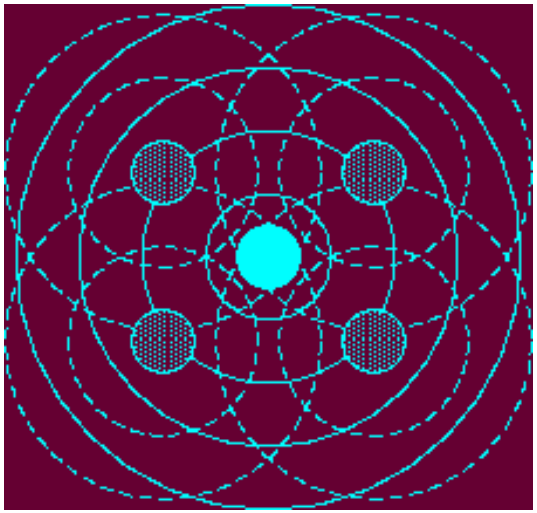
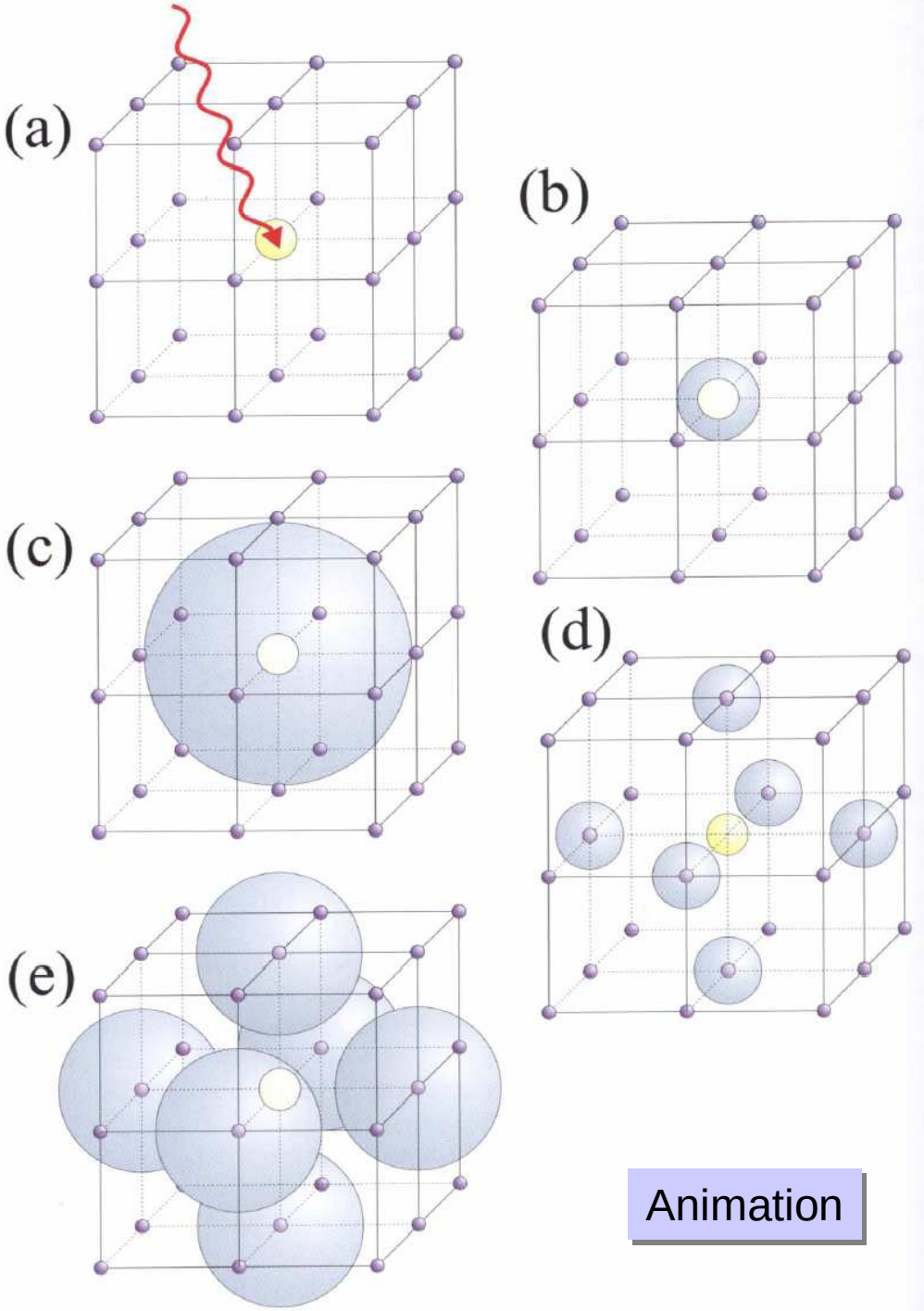
Principle of EXAFS oscillations

Interference of wavefunctions of photoelectron and of **backscattered** electrons (from neighbouring atoms)





Animation

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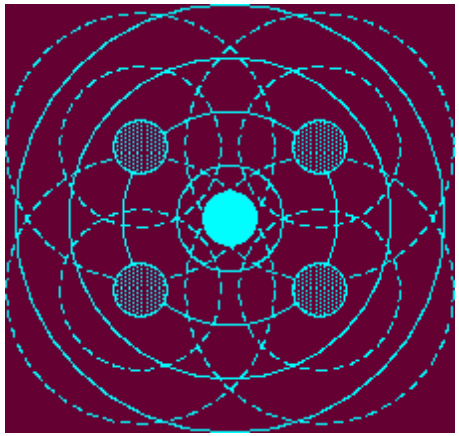
Parameters accessible with EXAFS

- **type** of atoms surrounding central absorber ($Z \pm 3$)
- **number** of atoms surrounding absorber ($\pm$ 20%)
- **distances** absorber – scatterer (accuracy 0.1 Å)



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EXAFS data analysis

EXAFS signal:

isolated atom

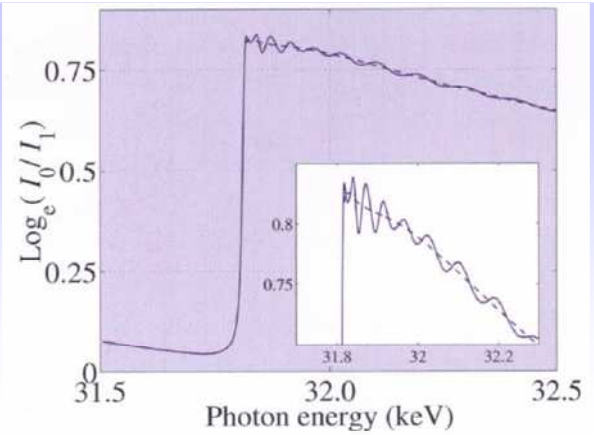
$$\chi(q(E)) = \frac{\mu_\chi(E) - \mu_0(E)}{\mu_0(E)}$$

in material of interest

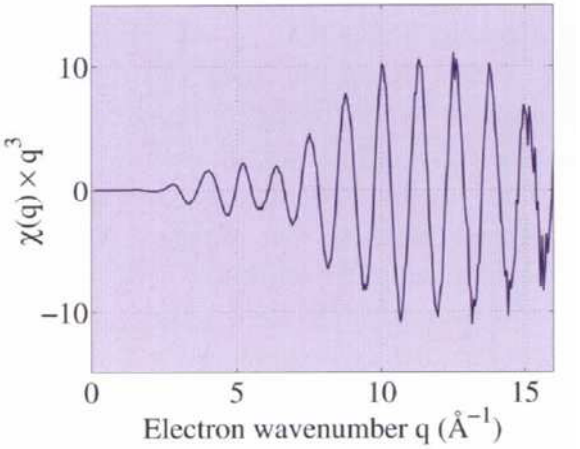
electron wave vector

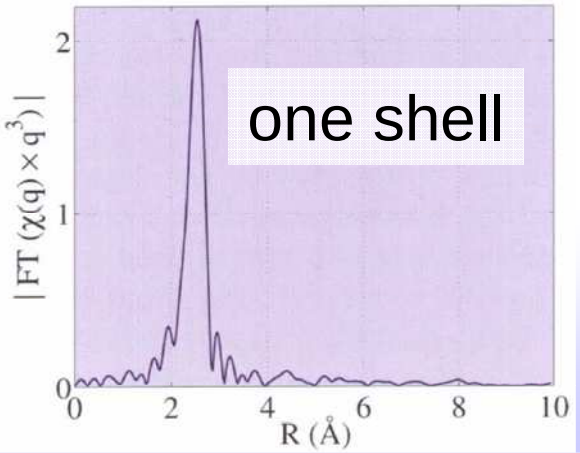
$$\frac{\hbar^2 q^2}{2m} = E - \hbar\omega_K$$

Fourier transform:
radial distribution function



CdTe nanocrystals





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The EXAFS formula …

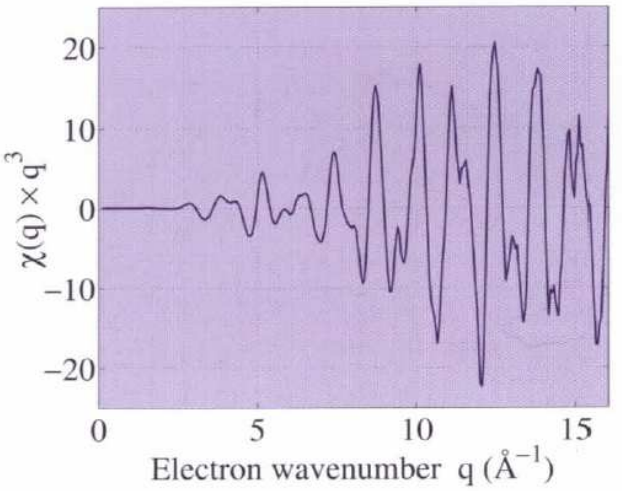
$$q\chi(q) \propto \sum_j N_j \frac{t_j(q)\sin(2qR_j + \delta_j(q))}{R_j^2} e^{-2(q\sigma_j)^2} e^{-2R_j/\Lambda}$$

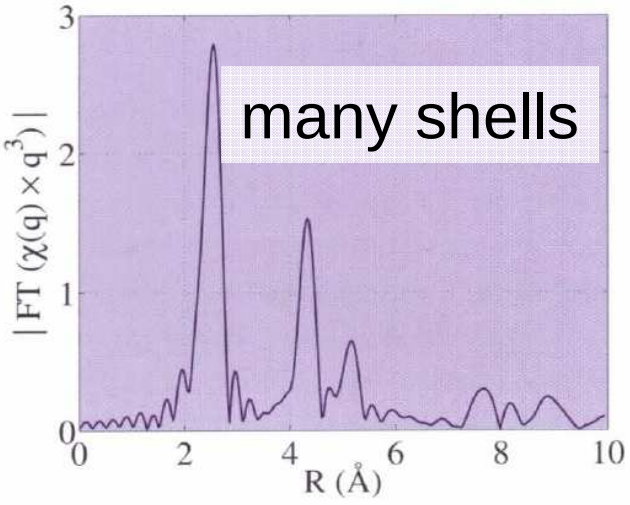
- sum over *j* **neighbouring** shells
- **goal**: extract radii R_j and occupation numbers N_j
- **damping** due to loss (mean free path Λ) and disorder (Debye-Waller factor)

- phase shifts
- backscattering amplitude

} difficult…

CdTe bulk





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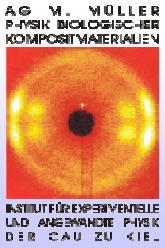
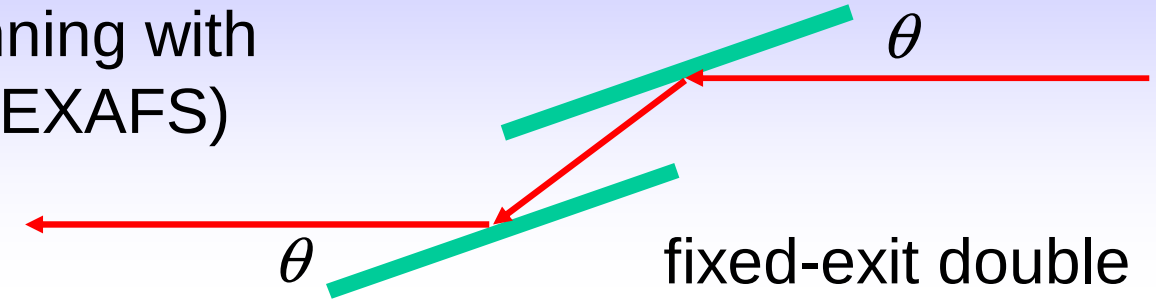
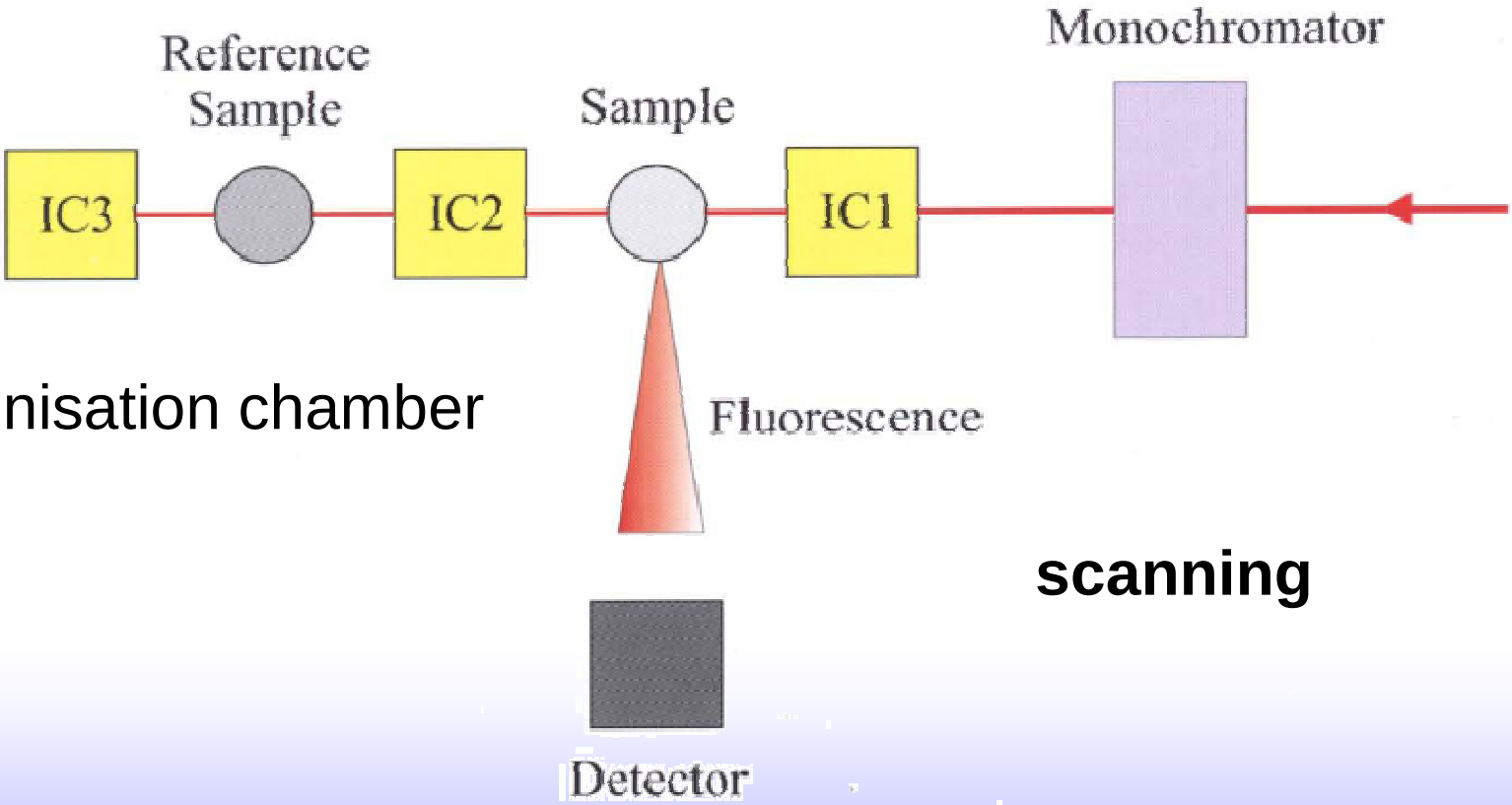


Absorption spectrometer

(fast scanning with
piezos: QEXAFS)



fixed-exit double
crystal monochromator



IC: ionisation chamber

scanning

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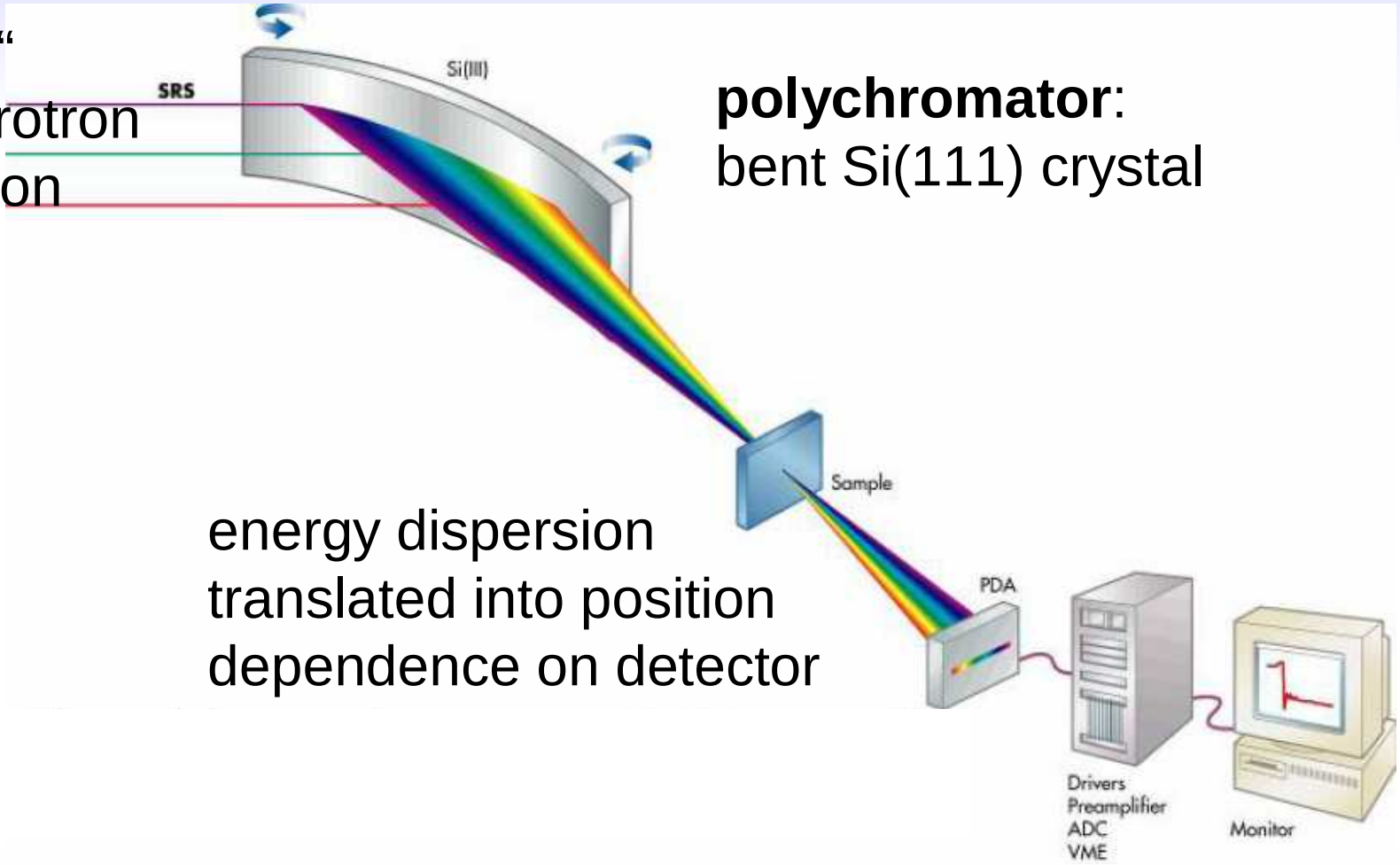
EXAFS / XANES in one shot: DEXAFS

„white“ synchrotron radiation



polychromator:
bent Si(111) crystal

energy dispersion
translated into position
dependence on detector

energy-dispersive

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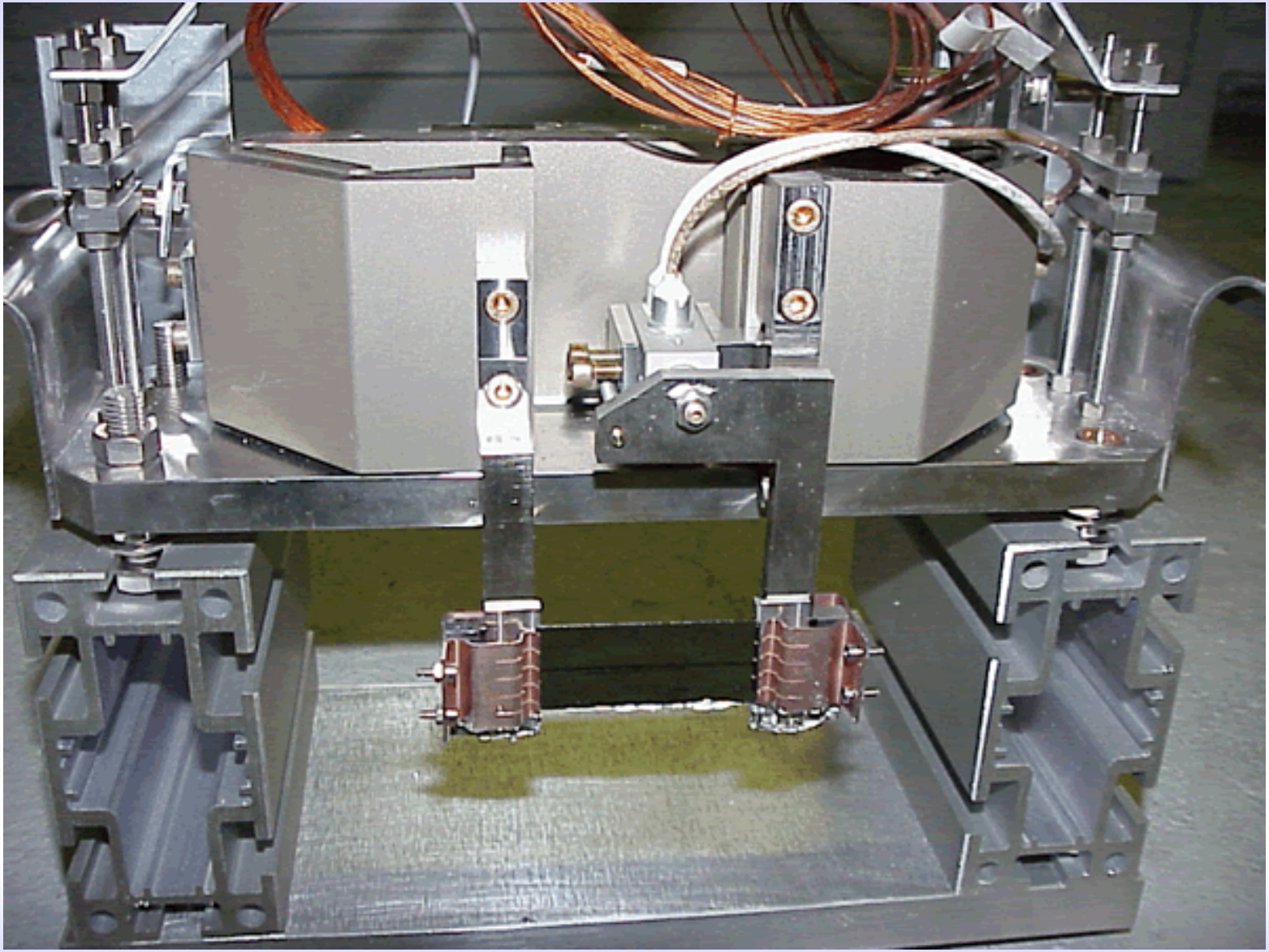
Bent crystal polychromator @ ID24 (ESRF)



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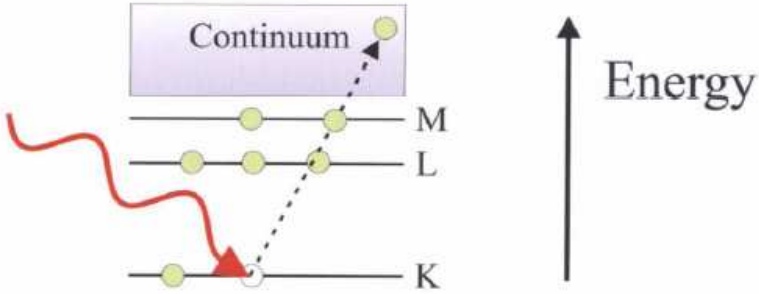
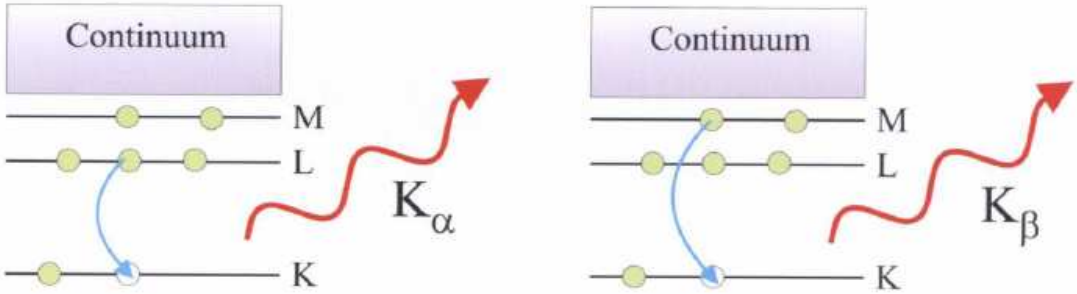
Alternatives to transmission measurements

(a) Photoelectric absorption



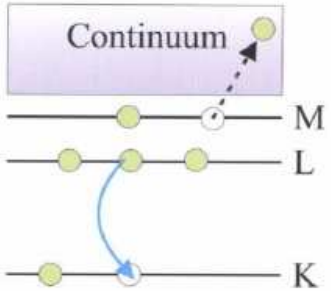
(b) Fluorescent X-ray emission

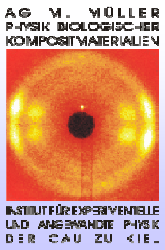
fluorescence
(high sensitivity)



(c) Auger electron emission

Auger yield
(if fluorescence yield low)





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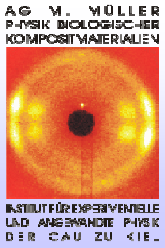
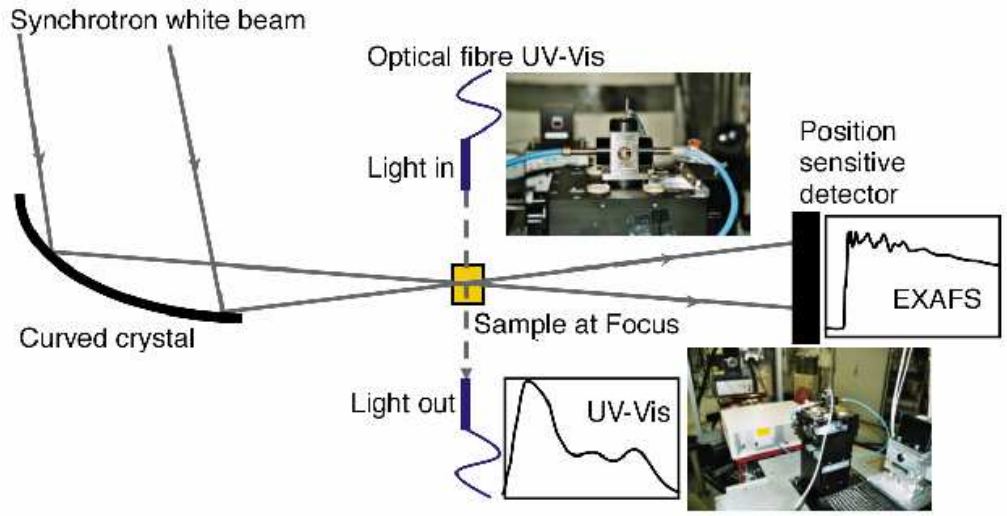
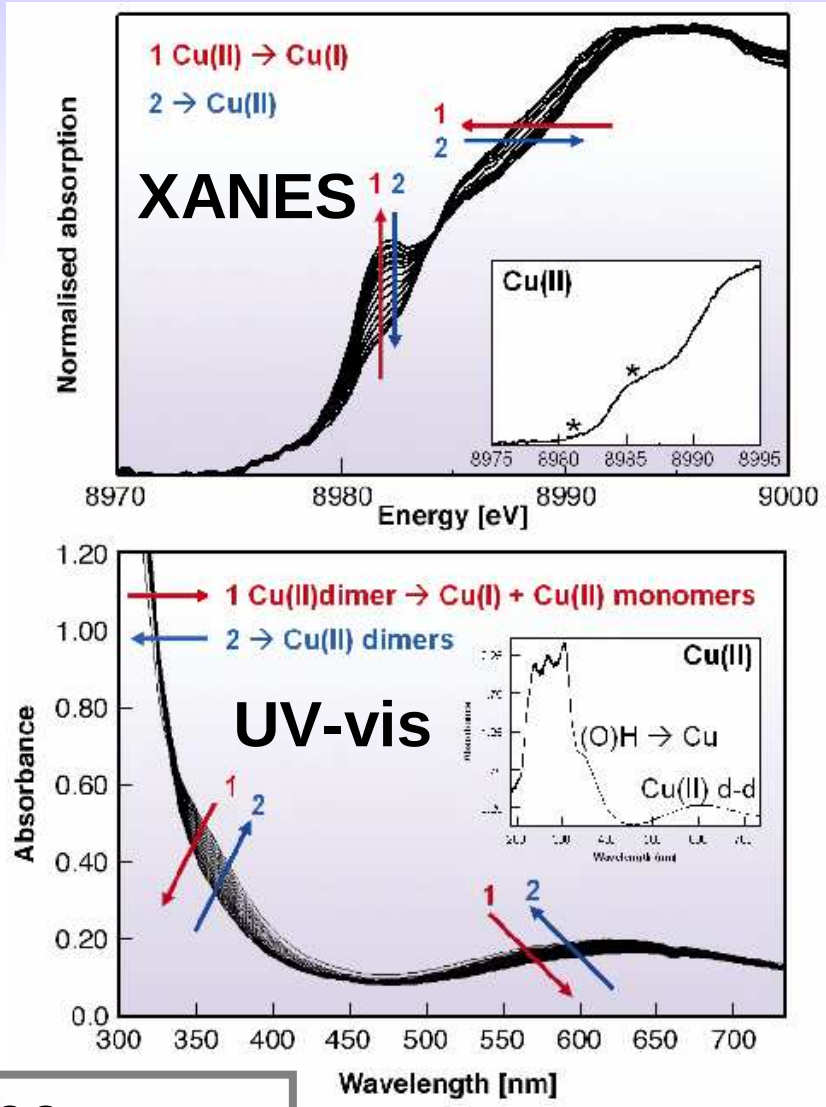


Homogeneous catalytic reaction mechanisms

Cu(II) catalyst (arylation)



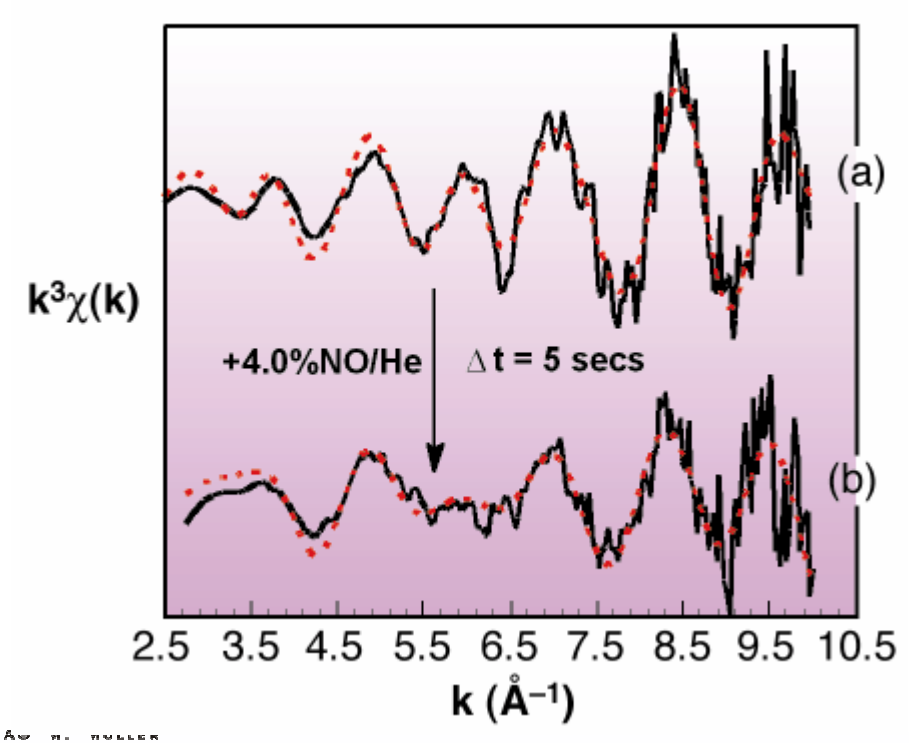


- **XANES** time resolution: 10-200 ms
- combination with UV-vis spectroscopy

Adsorbate-induced phase change in Rh catalysts

car exhaust **catalytic converters:**
NO converted to N_2

time-resolved **EXAFS** study



Rh **metal**

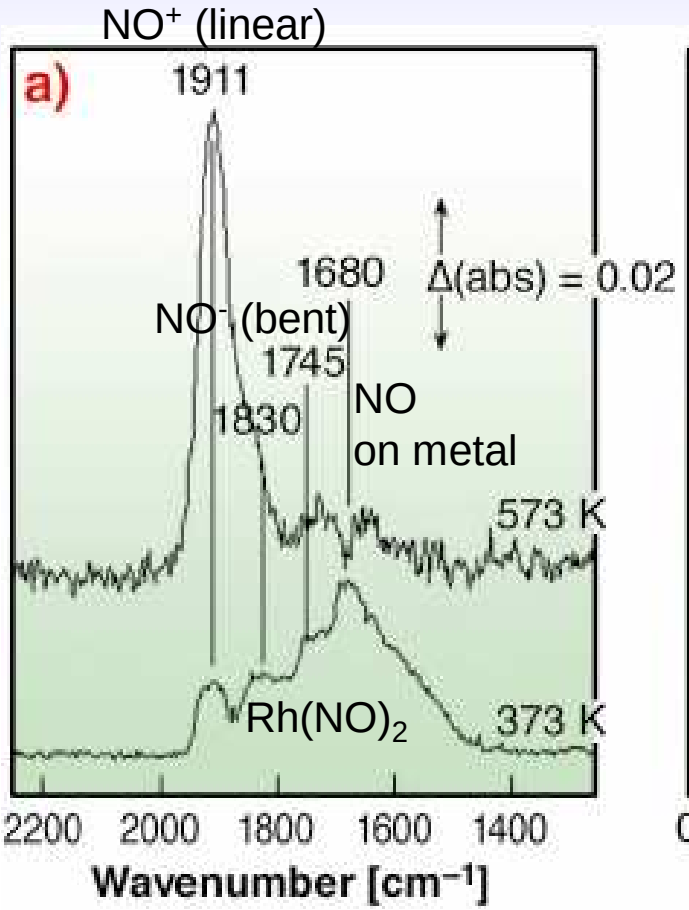
↓ Rh nanoparticles rapidly change upon exposure to NO

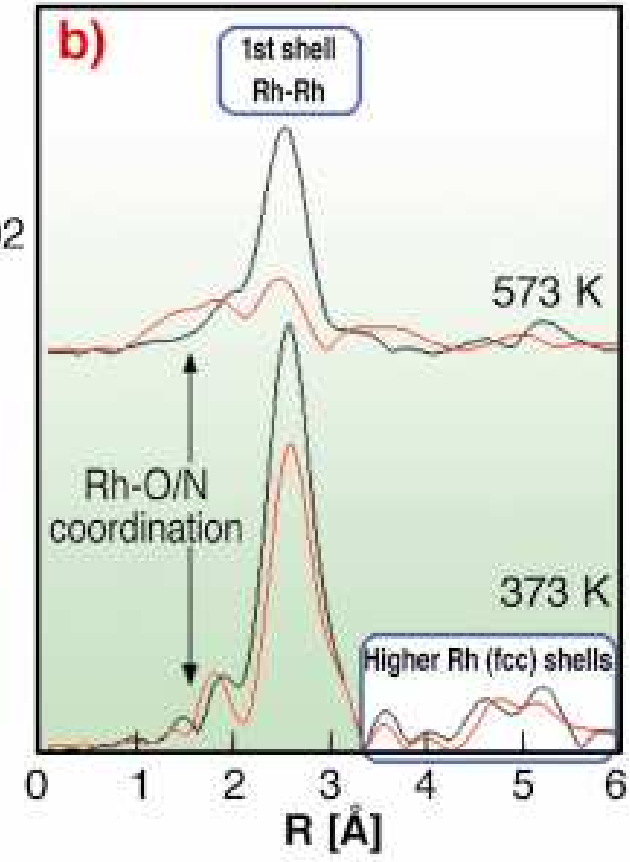
Rh_2O_3 **oxide**

Synchronizing IR spectroscopy and XAFS

again de-NOx Rh catalyst: many different components

IR





EXAFS

Rh_2O_3 **oxide**

Rh **metal**

sub-second **EXAFS** and IR time resolution