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LECTURE SERIES
HETEROGENEOUS CATALYSIS

EXAFS – Extended X-Ray Absorption Fine Structure

Lecture series:
Modern Methods in Heterogeneous Catalysis Research

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Outline

- Basics
  - Fundamentals
  - What can we learn from an EXAFS experiment?

- How to perform an EXAFS experiment?
  - Synchroton radiation
  - Experimental setup, detection

- How extract information from am EXAFS spectrum
  - The EXAFS equation
  - Data treatment

- Examples
  - Application in heterogeneous catalysis

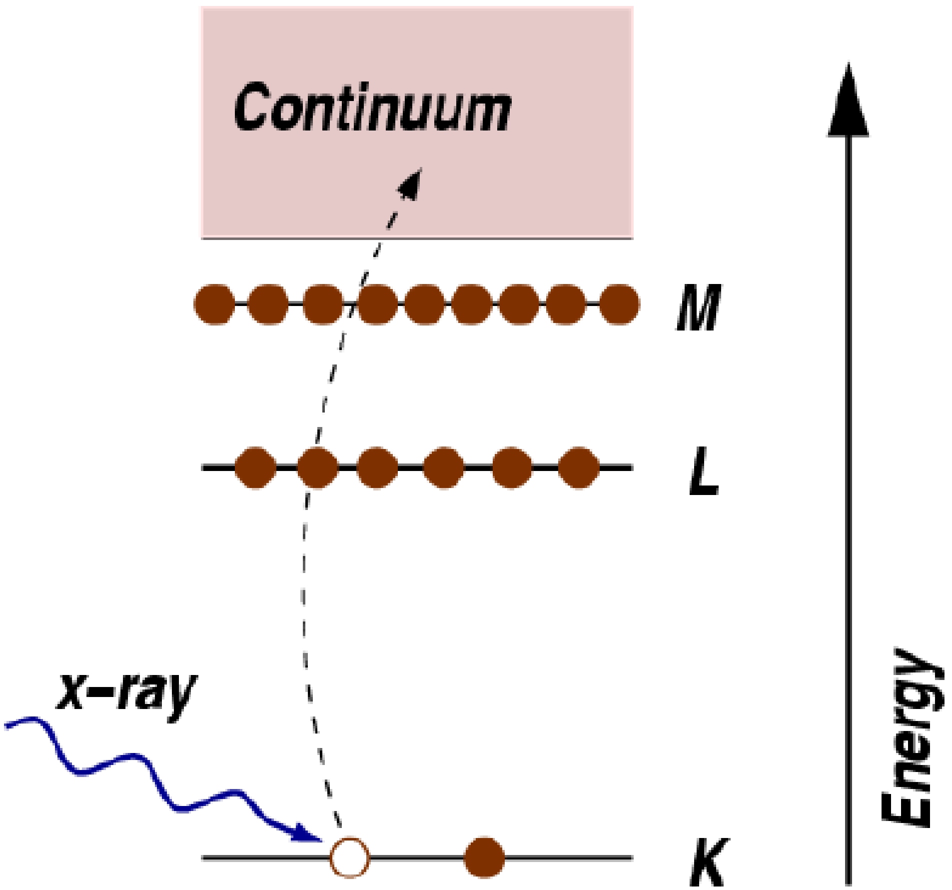
History

- *1895* Röntgen discovered X-rays
- *1913* De Broglie measured first absorption edge
- *1920* Fricke observed fine structure above X-ray absorption edges
- *1930* Kronig proposed a LRO theory based on crystal periodicity; then a SRO theory to explain EXAFS in the $GeCl_4$ molecule
- *1960* Van Nordstrand improved XAS instrumentation, used fingerprint ID and valence shift to characterize catalysts
- *1970* Sayers, Stern, and Lytle: Modern theory, FT of EXAFS
- *1974* Synchrotron X-radiation available at Stanford, CA
- *1994* Opening of ESRF (Grenoble); 3rd Generation Synchrotron Sources

Acronyms

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

Principle

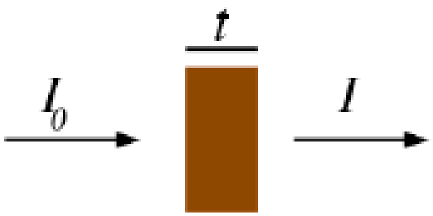


- X-ray photons from the incoming beam eject core electron beyond the ionization threshold

- The atom is in an excited state, i.e. there is a core hole. Electron ejected is called a photo-electron

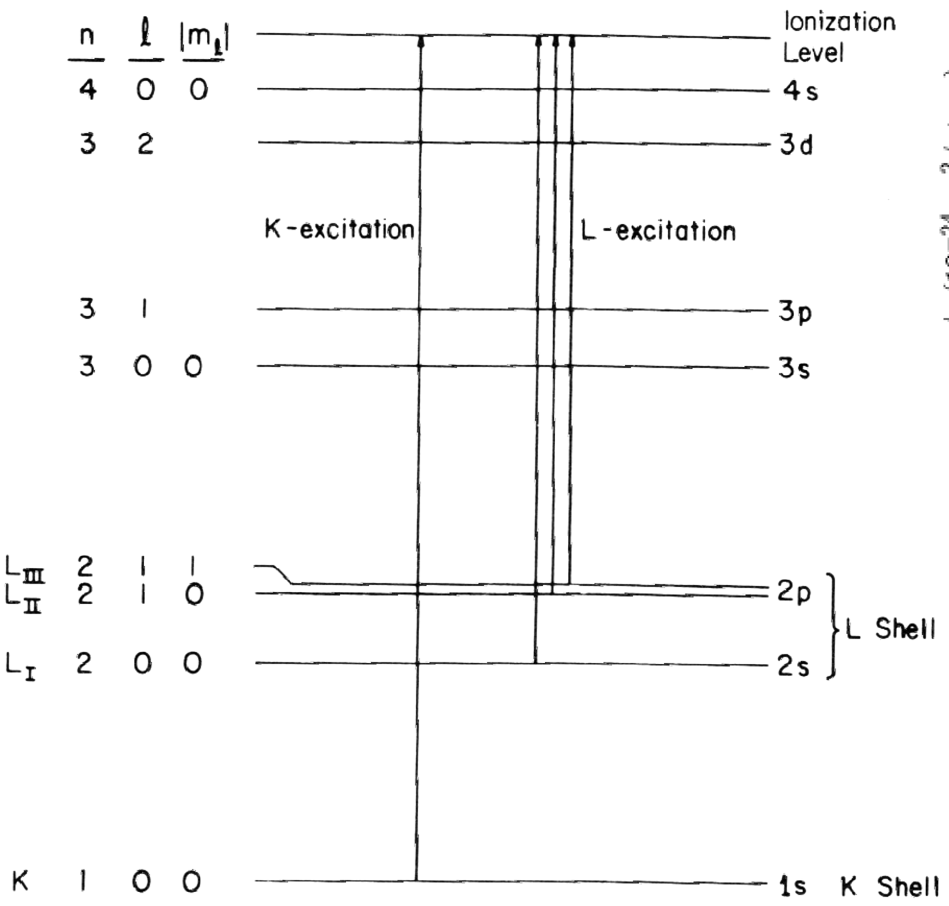
- The x-ray intensity is measured before and after the sample and the X-ray absorption coefficient μ is calculated

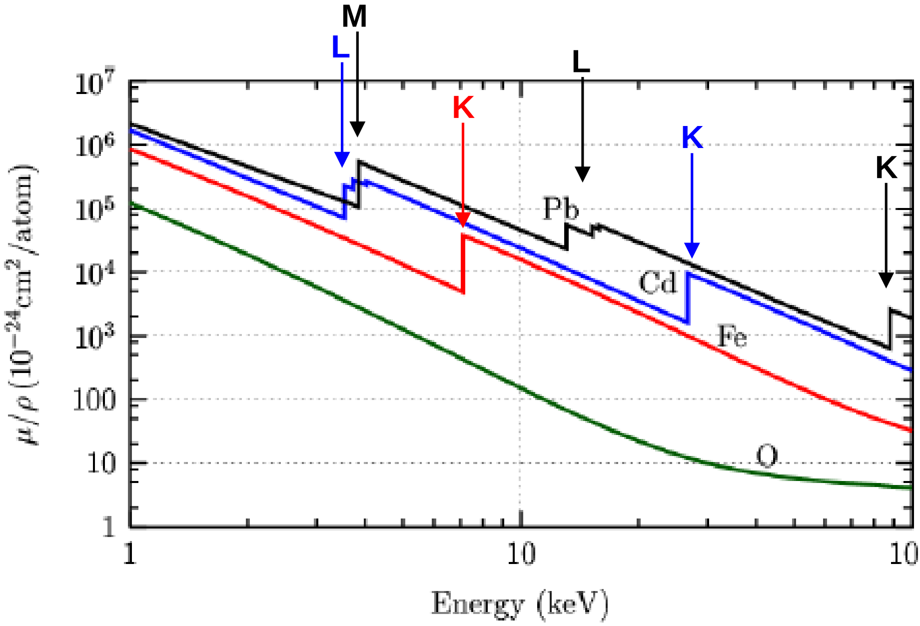
$$\boxed{I = I_0 e^{-\mu t}}$$



M. Newville

X-ray photon absorption





sharp absorption edges in μ

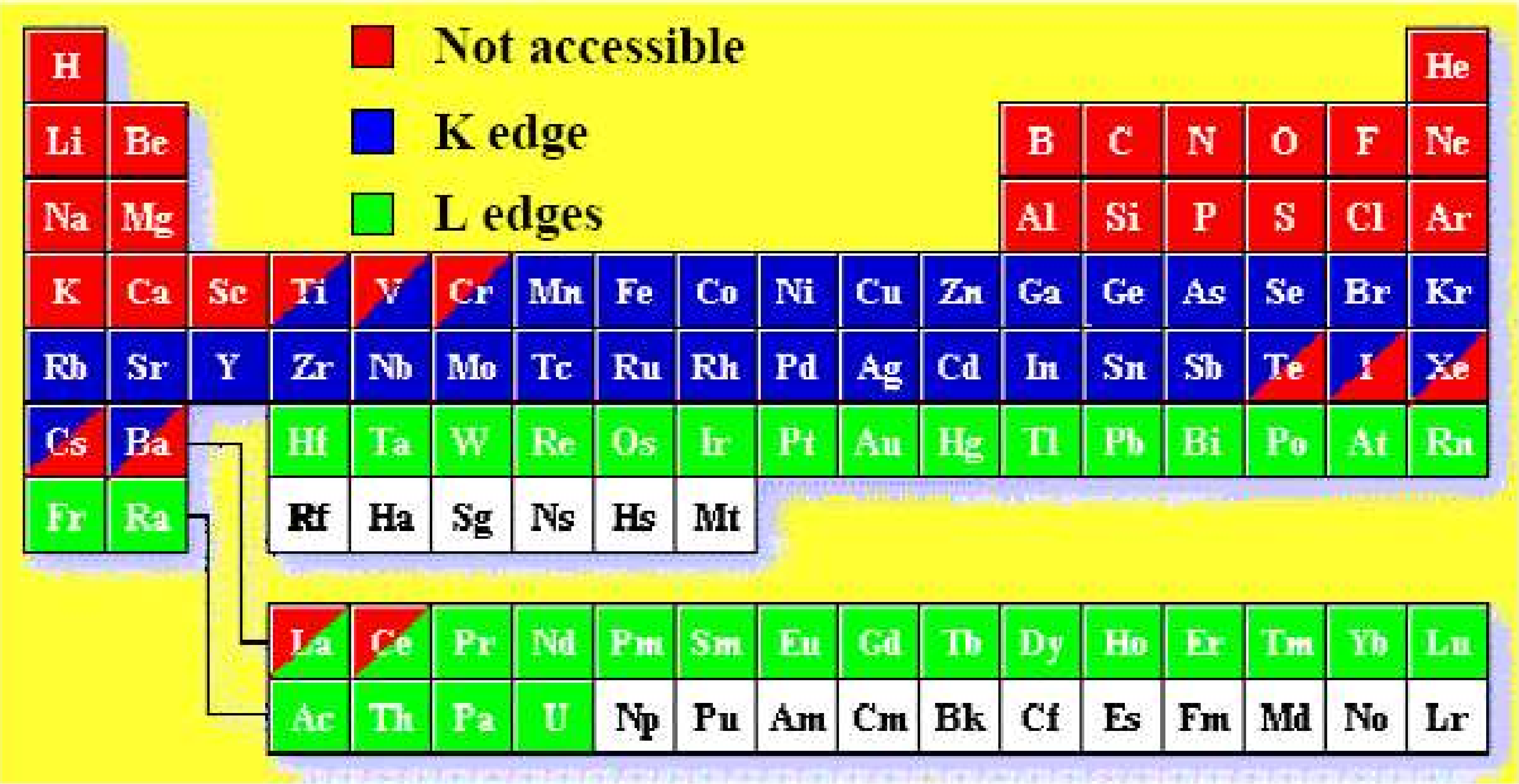
↓

characteristic core level energies

EXAFS is element-specific

L.H. Schwarz, J.B. Cohen / M. Newville

Elements for EXAFS
(hard X-rays)



🟥 Not accessible

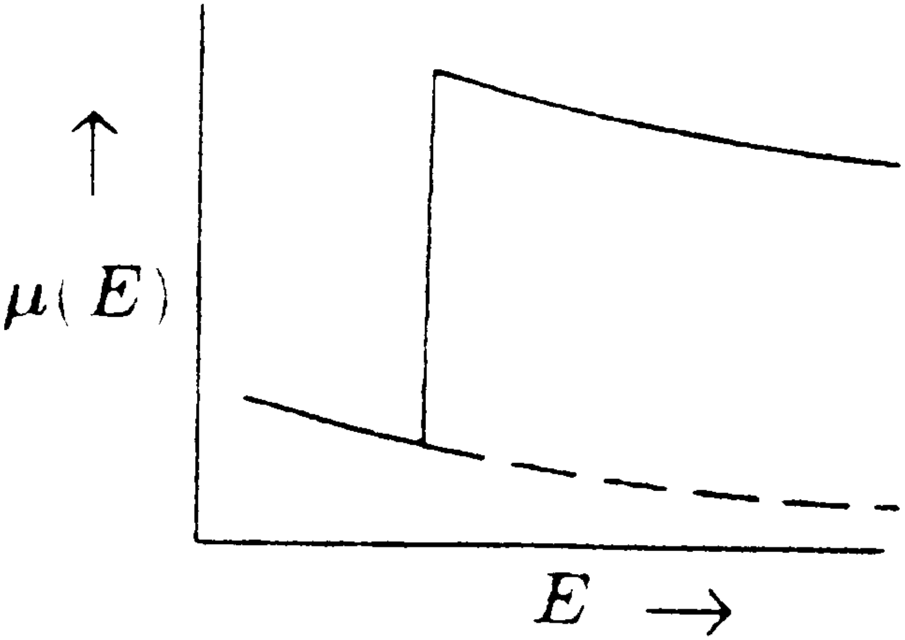
🟦 K edge

🟩 L edges

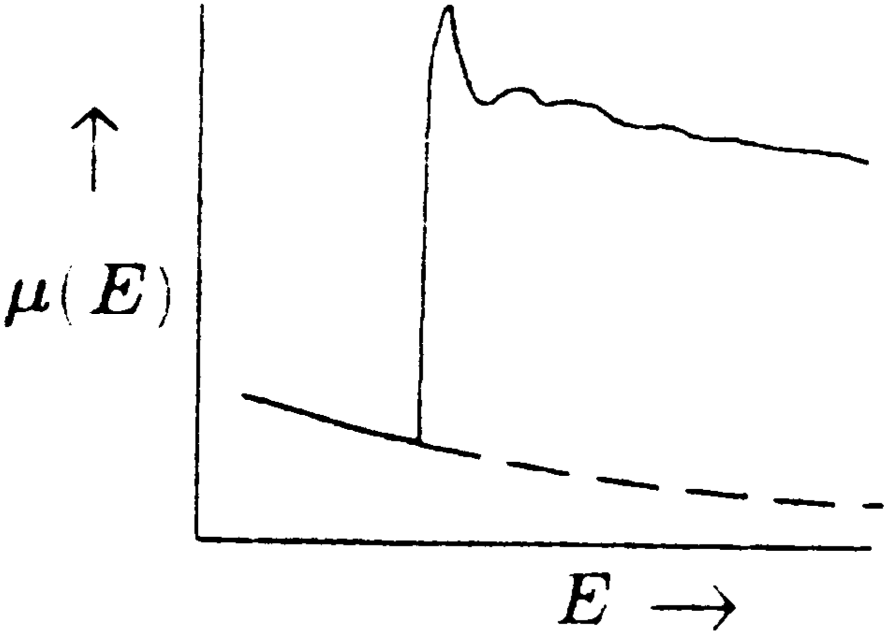
🟥 H																	🟥 He
🟥 Li	🟥 Be											🟥 B	🟥 C	🟥 N	🟥 O	🟥 F	🟥 Ne
🟥 Na	🟥 Mg											🟥 Al	🟥 Si	🟥 P	🟥 S	🟥 Cl	🟥 Ar
🟥 K	🟥 Ca	🟥 Sc	🟥🟦 Ti	🟥🟦 V	🟥🟦 Cr	🟦 Mn	🟦 Fe	🟦 Co	🟦 Ni	🟦 Cu	🟦 Zn	🟦 Ga	🟦 Ge	🟦 As	🟦 Se	🟦 Br	🟦 Kr
🟦 Rb	🟦 Sr	🟦 Y	🟦 Zr	🟦 Nb	🟦 Mo	🟦 Tc	🟦 Ru	🟦 Rh	🟦 Pd	🟦 Ag	🟦 Cd	🟦 In	🟦 Sn	🟦 Sb	🟦🟥 Te	🟦🟥 I	🟦🟥 Xe
🟦🟥 Cs	🟦🟥 Ba		🟩 Hf	🟩 Ta	🟩 W	🟩 Re	🟩 Os	🟩 Ir	🟩 Pt	🟩 Au	🟩 Hg	🟩 Tl	🟩 Pb	🟩 Bi	🟩 Po	🟩 At	🟩 Rn
🟩 Fr	🟩 Ra		⬜ Rf	⬜ Ha	⬜ Sg	⬜ Ns	⬜ Hs	⬜ Mt									
			🟥🟩 La	🟥🟩 Ce	🟩 Pr	🟩 Nd	🟩 Pm	🟩 Sm	🟩 Eu	🟩 Gd	🟩 Tb	🟩 Dy	🟩 Ho	🟩 Er	🟩 Tm	🟩 Yb	🟩 Lu
			🟩 Ac	🟩 Th	🟩 Pa	🟩 U	⬜ Np	⬜ Pu	⬜ Am	⬜ Cm	⬜ Bk	⬜ Cf	⬜ Es	⬜ Fm	⬜ Md	⬜ No	⬜ Lr

T. Ressler

Fine structure



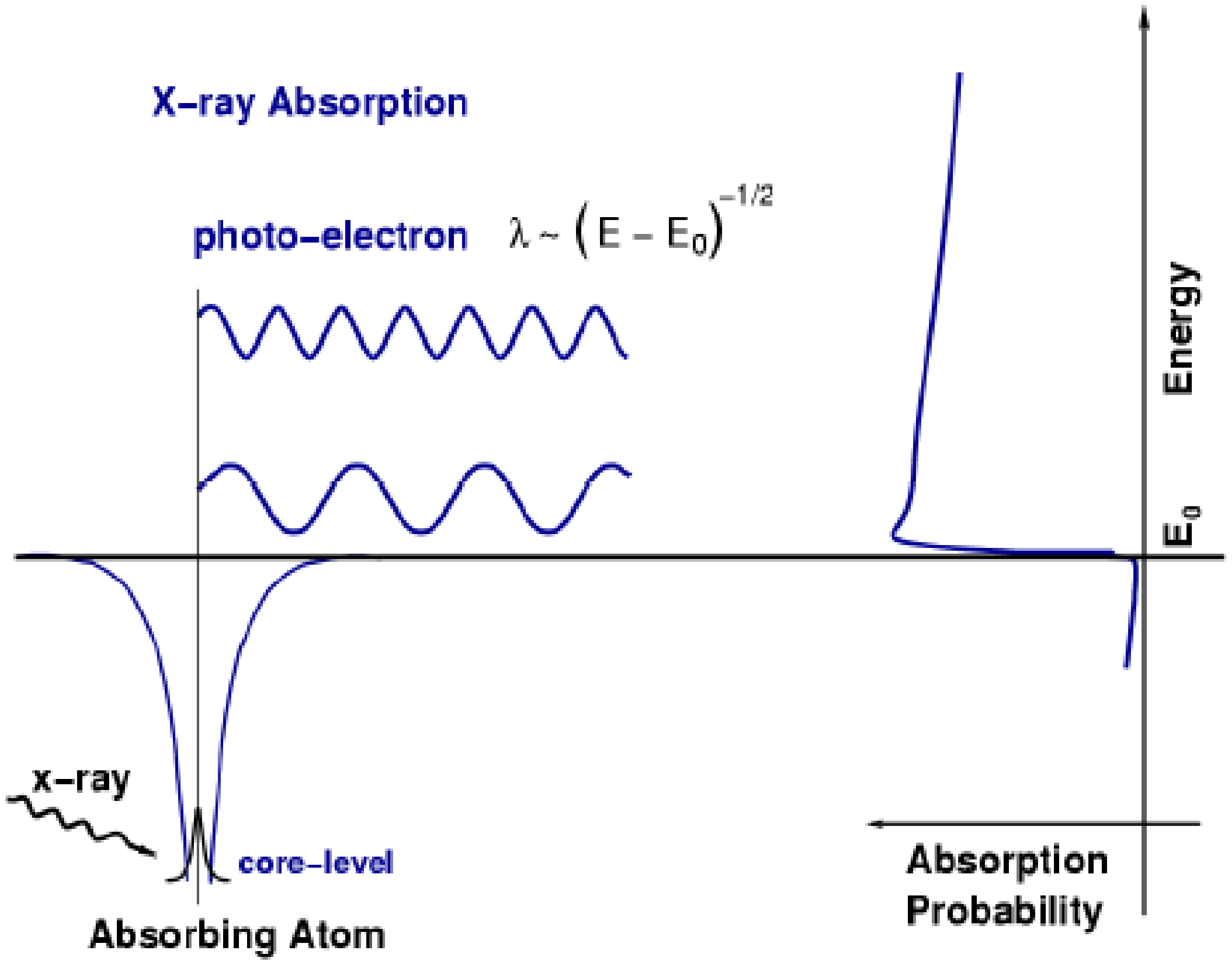
Isolated atom



Atom with neighbors

EXAFS contains information about the local environment of the absorber

Isolated atom



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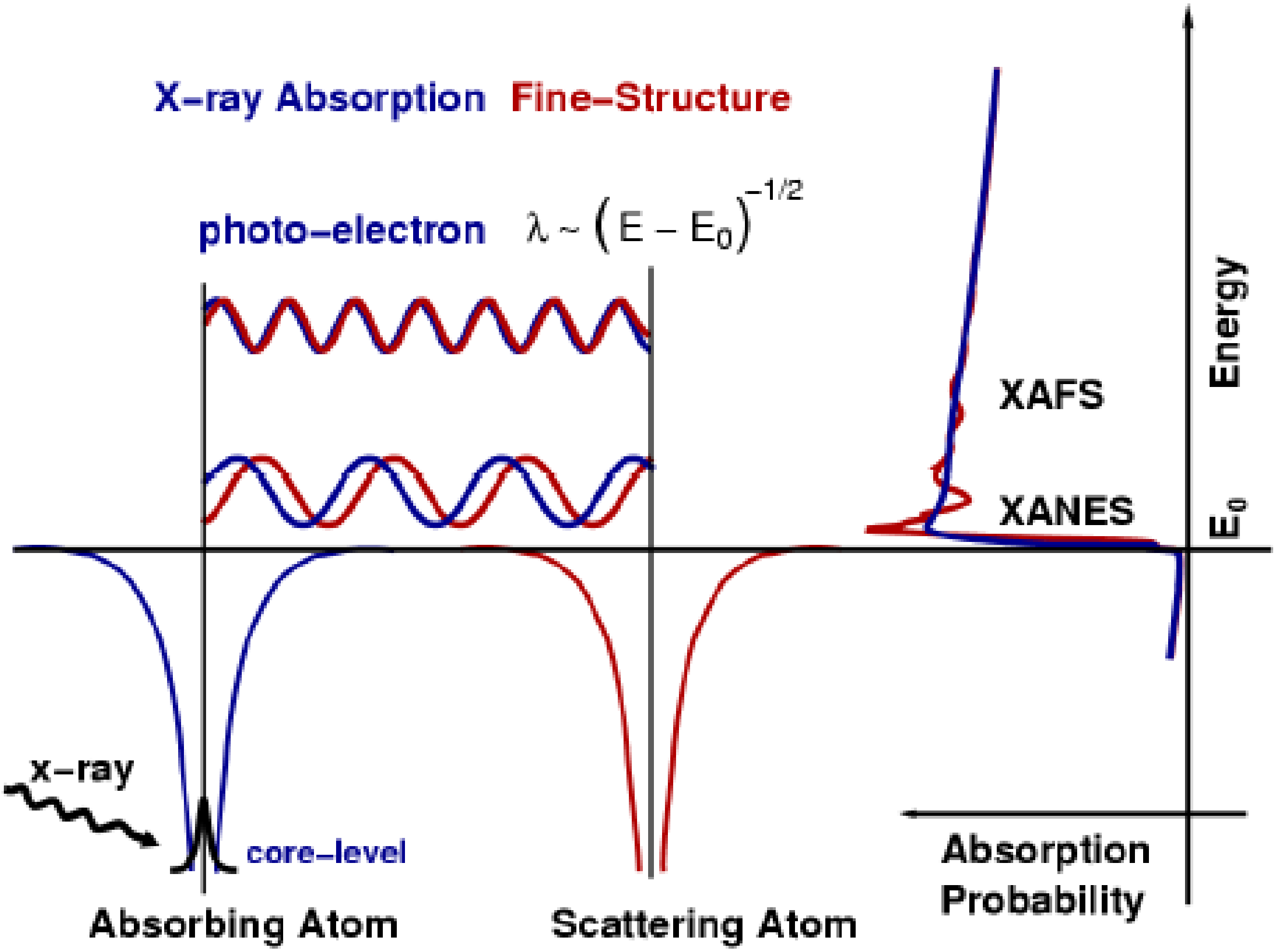
The origin of fine structure



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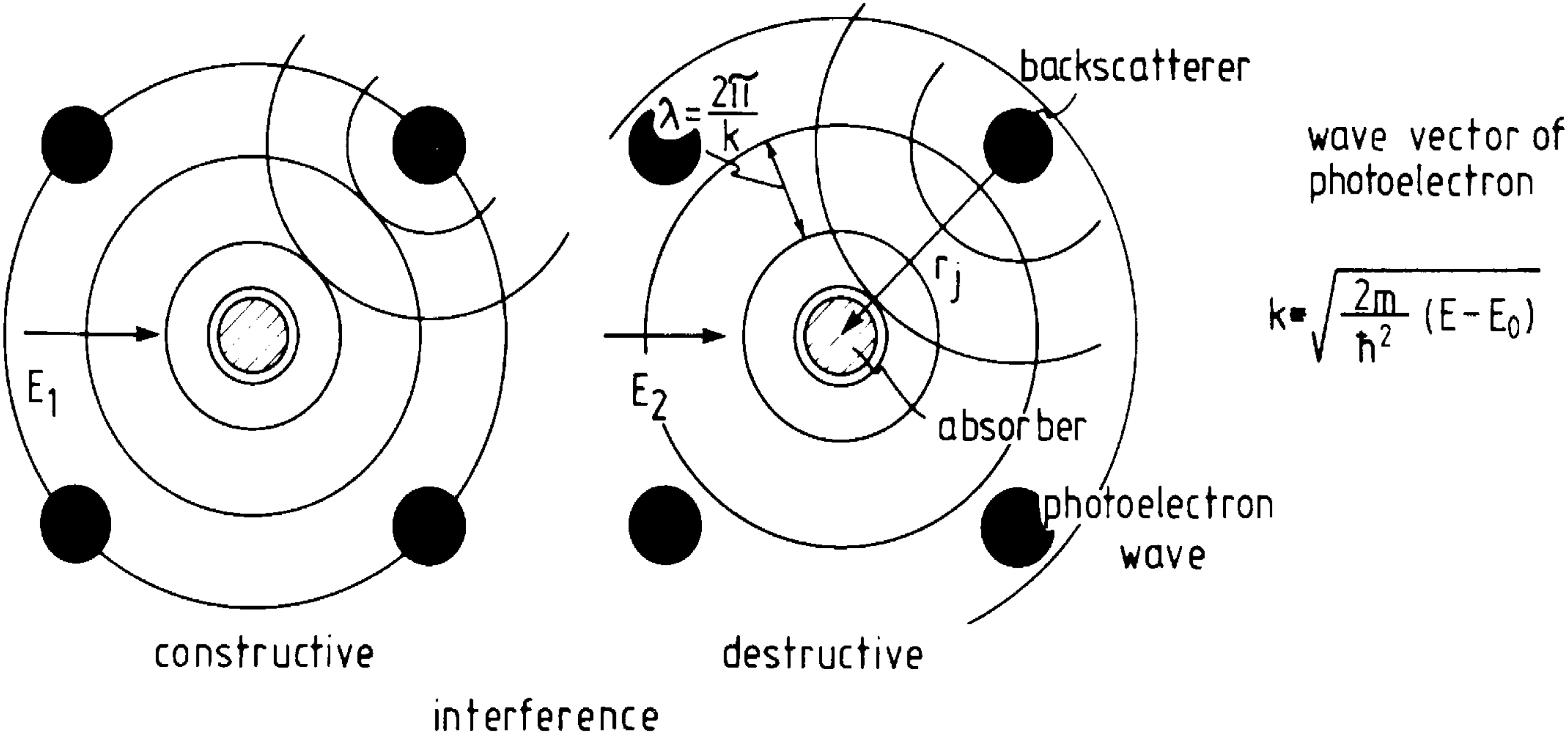
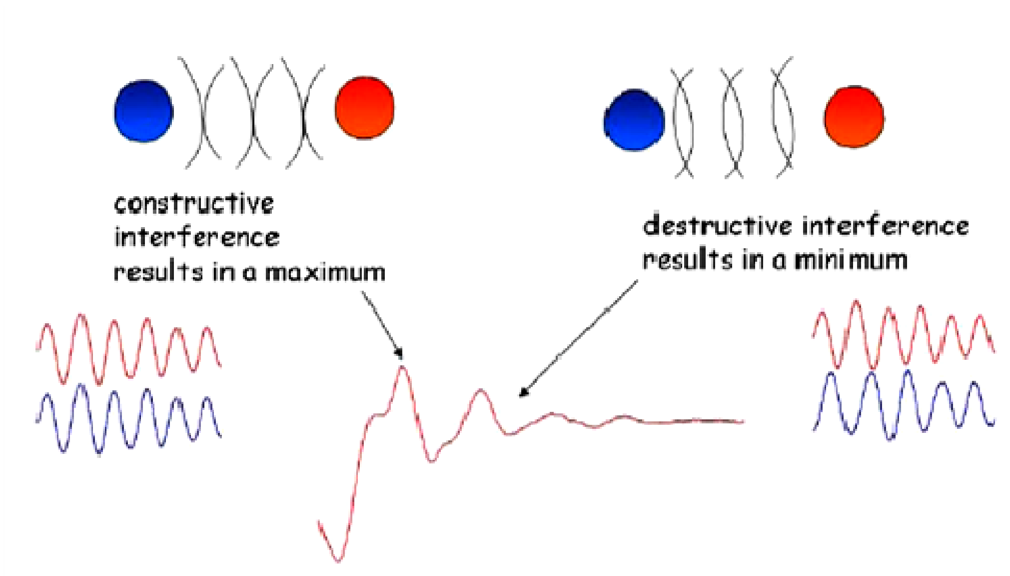
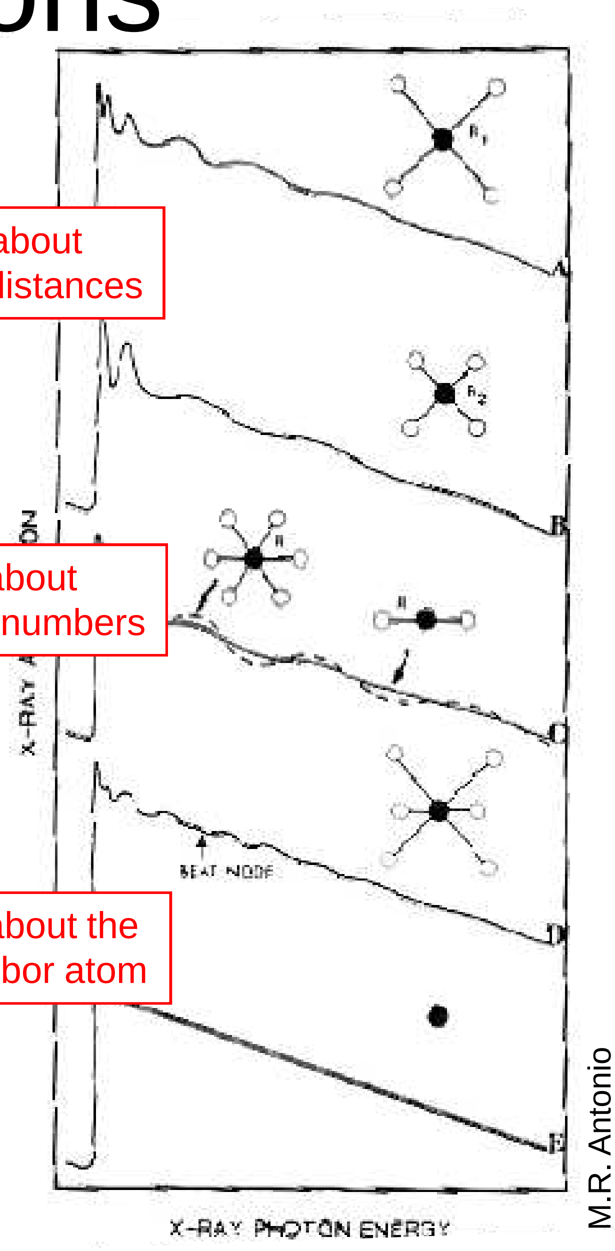
Interference effects



EXAFS: Interference phenomenon between outgoing photo-electron wave and backscattered wave

EXAFS oscillations





Information about interatomic distances

Information about coordination numbers

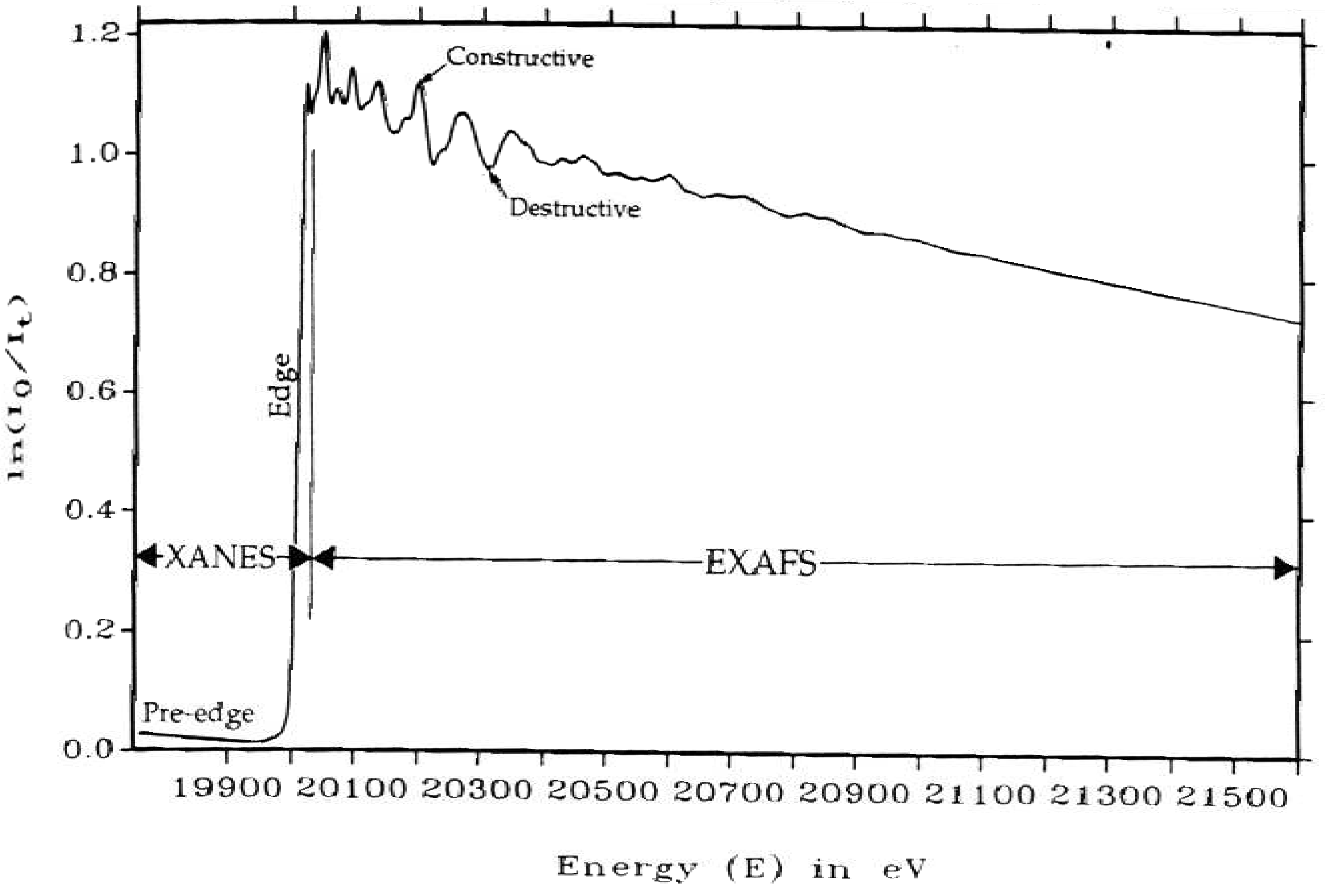
Information about the type of neighbor atom

EXAFS spectrum comprised of a series of sine waves of different amplitude representative of the different scattering paths undertaken by the photoelectron wave.

M.R. Antonio

S. Bare

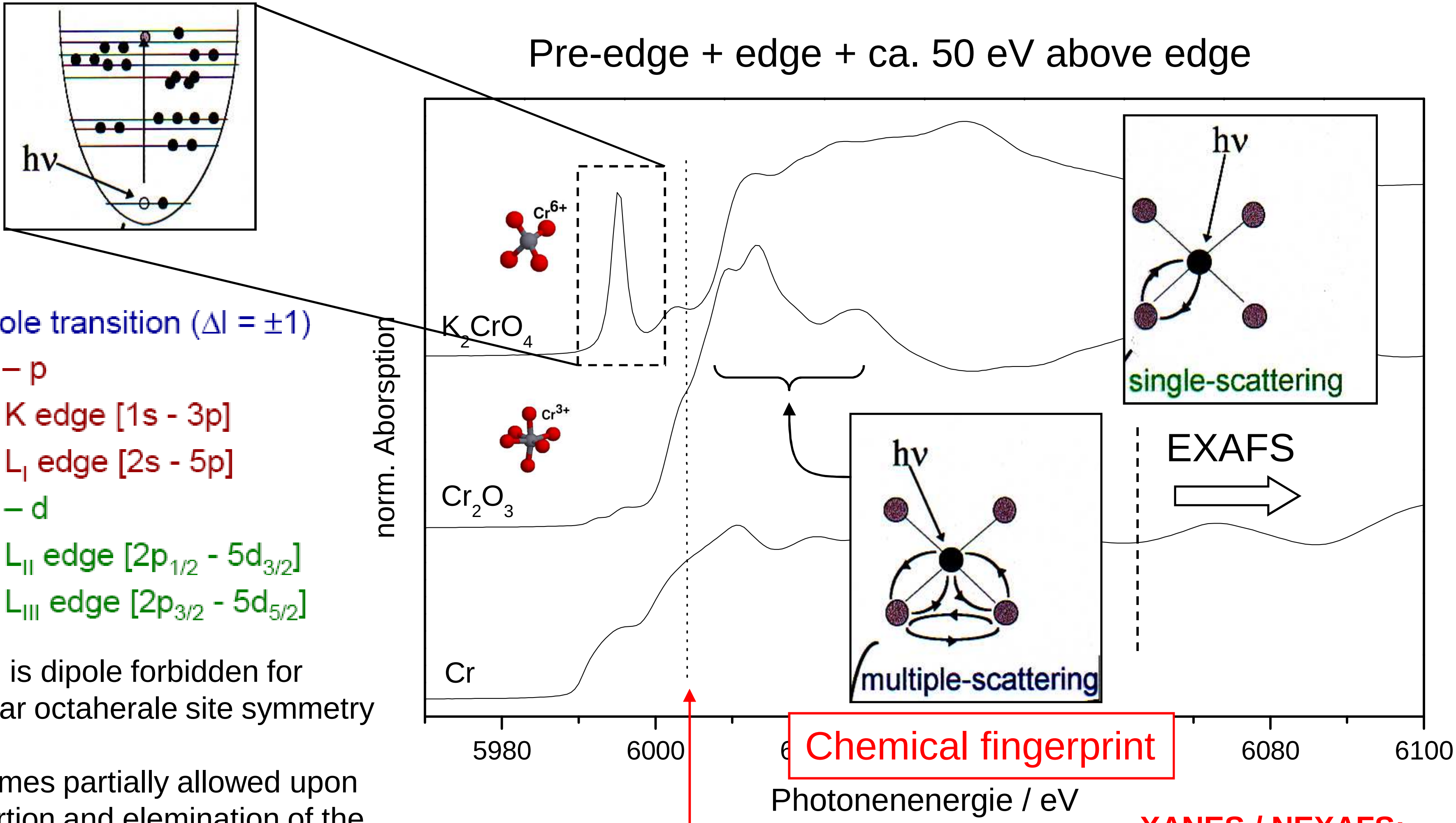
XAFS spectrum (Mo-K)



Information about local geometry

XANES region

Pre-edge + edge + ca. 50 eV above edge



Chemical fingerprint

Information about oxidation state

Dipole transition (Δl = ±1)

- s – p
  - K edge [1s - 3p]
  - L_I edge [2s - 5p]
- p – d
  - L_{II} edge [$2p_{1/2}$ - $5d_{3/2}$]
  - L_{III} edge [$2p_{3/2}$ - $5d_{5/2}$]

s→ d is dipole forbidden for regular octaherale site symmetry

becomes partially allowed upon distortion and elemination of the center of inversion (p-d hydbridization - open d shell)

T. Ressler

XANES / NEXAFS:
Lectures by
A. Knop-Gericke,
K. Hermann

What do we learn from EXAFS?

- EXAFS gives information about the local environment (up to ca. 6 Å) around a specific type of absorber atom
  - Distance to neighboring atoms
  - Type of neighboring atoms
  - Number of neighboring atoms

- XANES gives information about the
  - oxidation state of the absorber
  - local geometry around the absorber

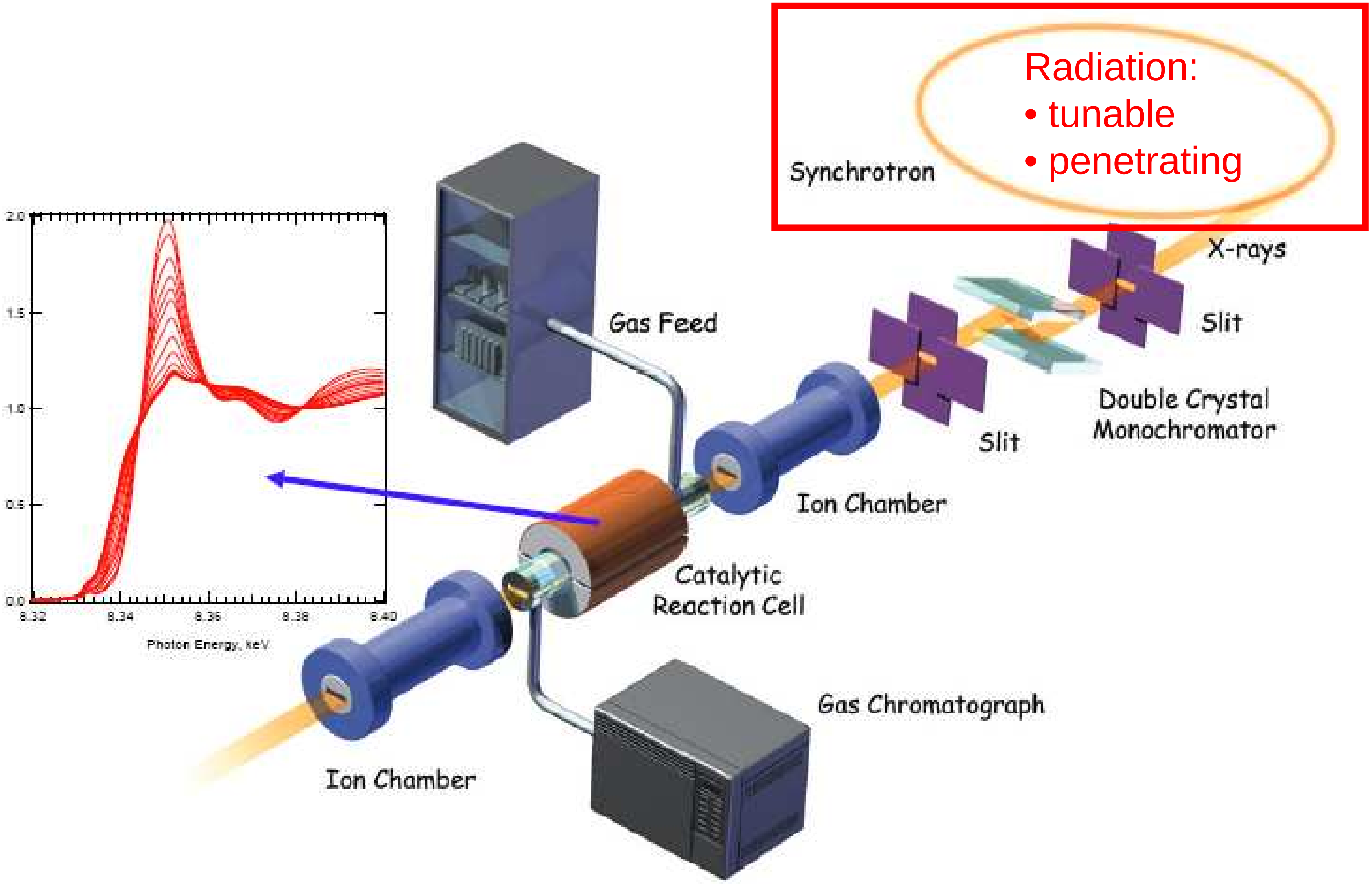
EXAFS is

- independent of long range order
  - complementary to diffraction
  - gases, liquids, amorphous and crystalline solids
  - highly dispersed phases (catalysis!)

- in general a bulk technique, but has a detection limit in the ppm range
  - Nanoparticles, diluted systems, promoters (catalysis!)

- applicable in-situ (catalysis!)

EXAFS (in-situ) experiment



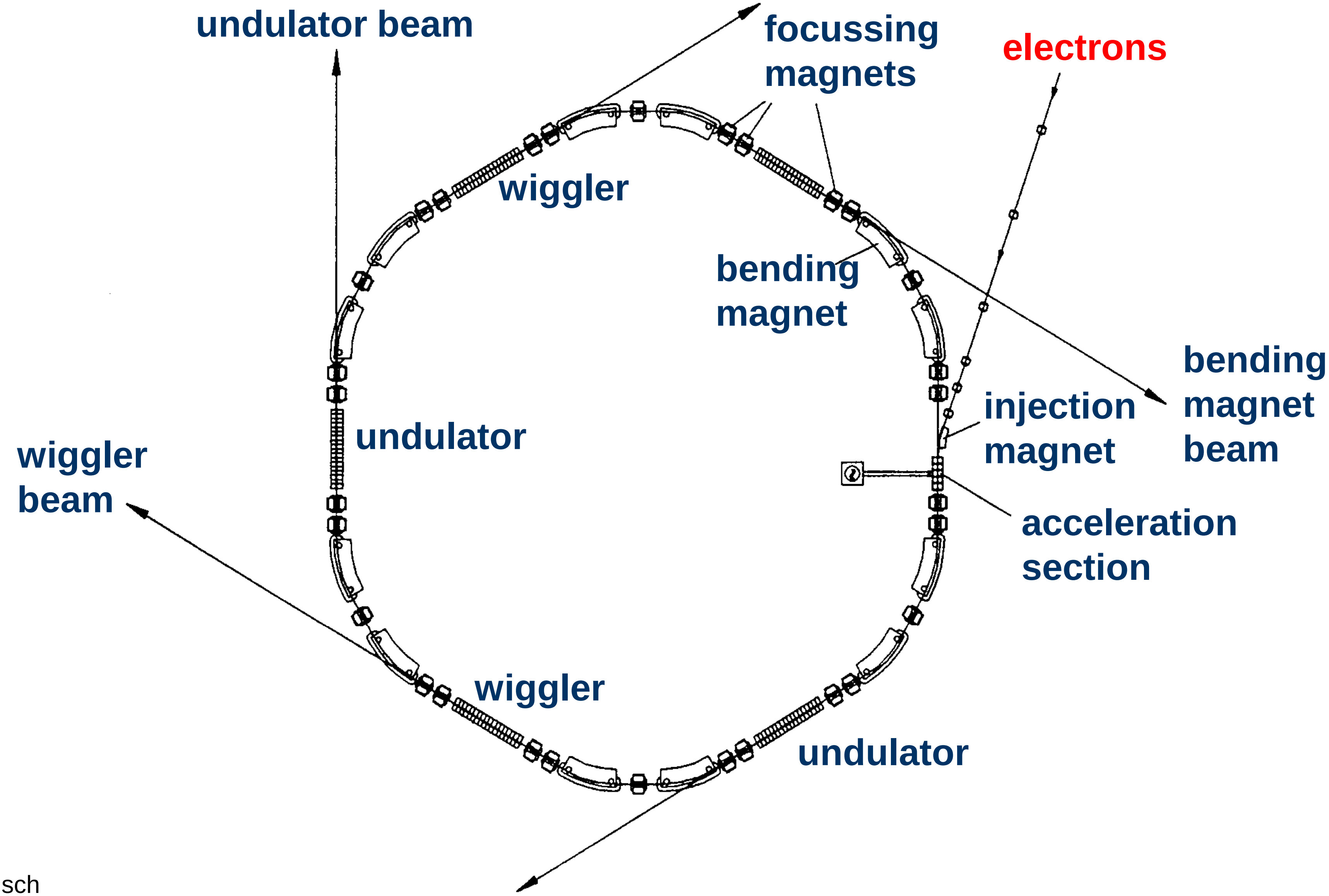
Radiation:
- tunable
- penetrating

S. Bare

X-ray source: Synchroton

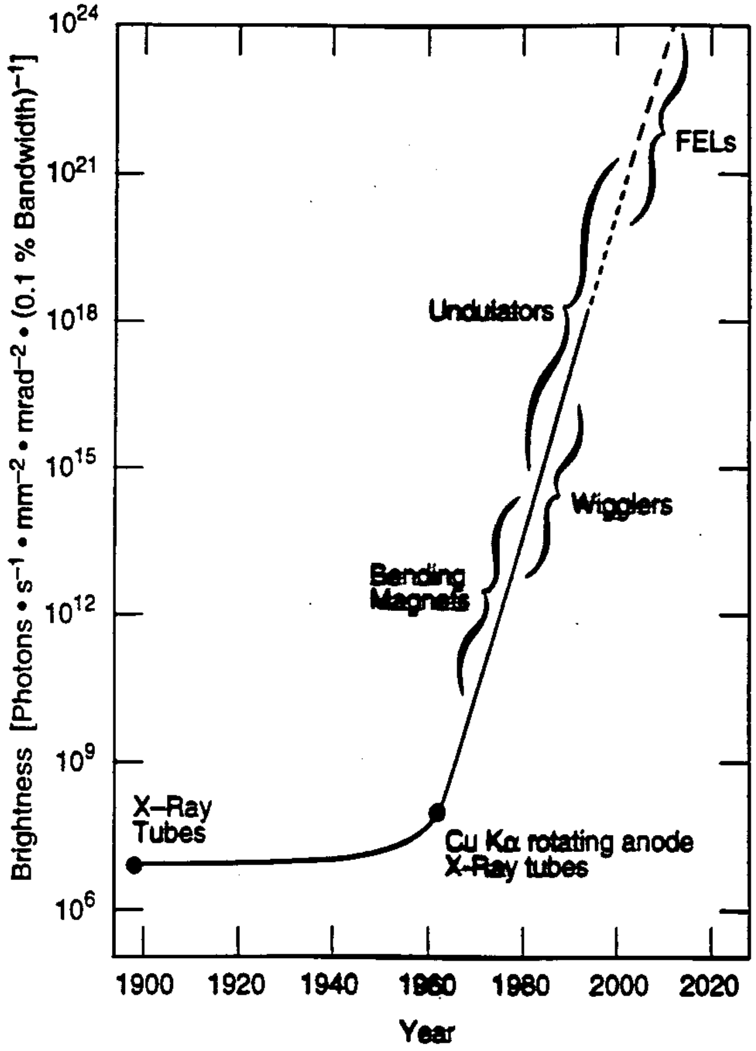
- Electrons near relativistic energies are confined to a circular orbit
- They give off energy as they are deflected
- Synchroton radiation
  - tunable: IR (0.1 mm) to hard X-rays (0.01 nm)
  - high intensity: 10^6 x higher than lab X-ray tubes
  - high collimation
  - plane polarization
  - time structure

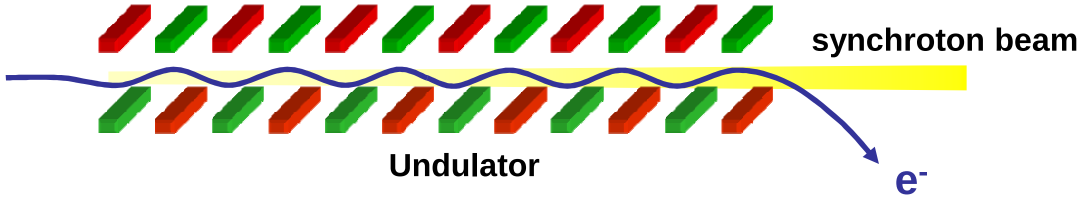
Synchroton radiation

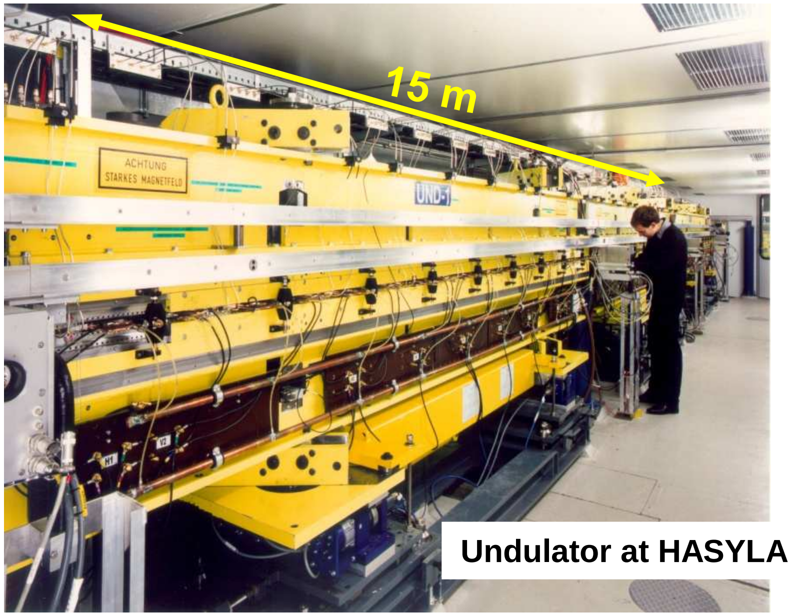


W. Bensch

Synchroton beamlines



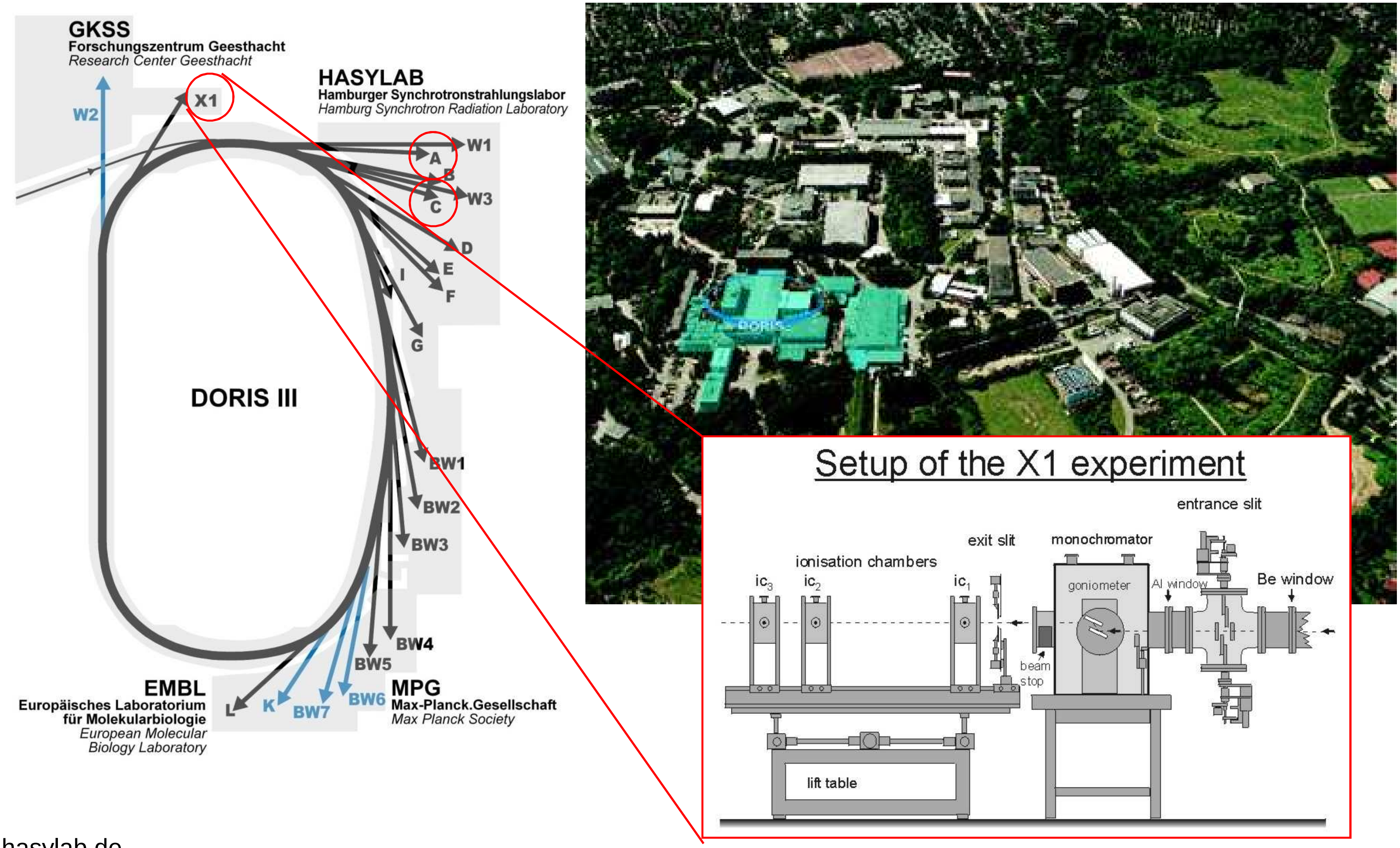




Undulator at HASYLAB, Hamburg

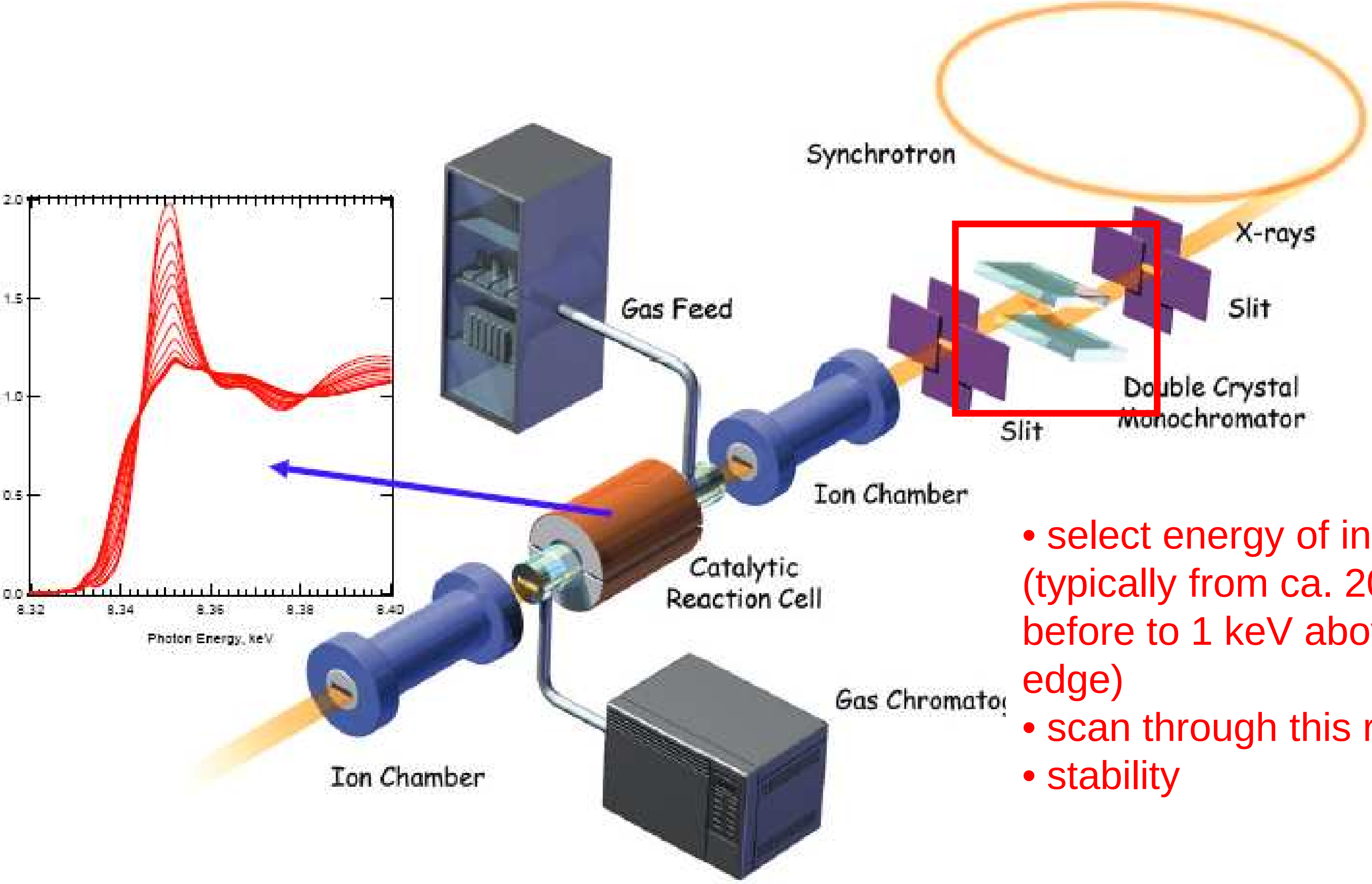
T. Tschentscher

EXAFS at HASYLAB



www.hasylab.de

Monochromators



- select energy of interest (typically from ca. 200eV before to 1 keV above the edge)
- scan through this regime
- stability

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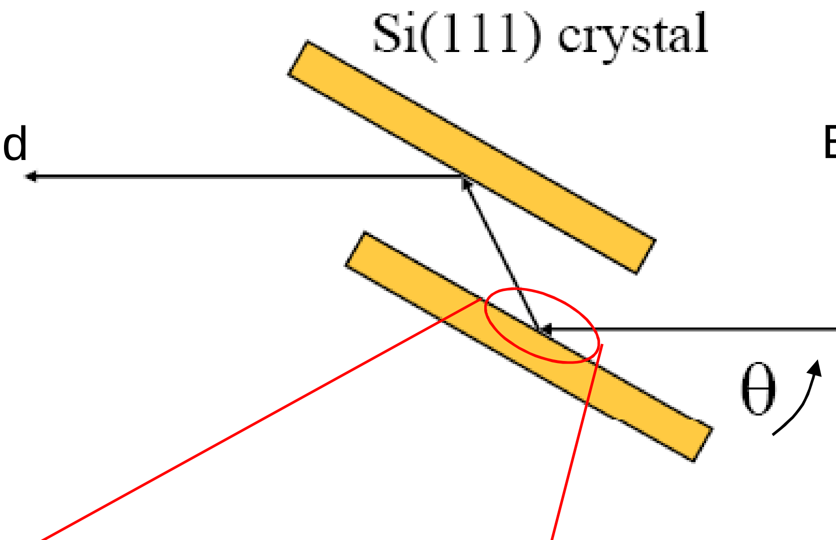
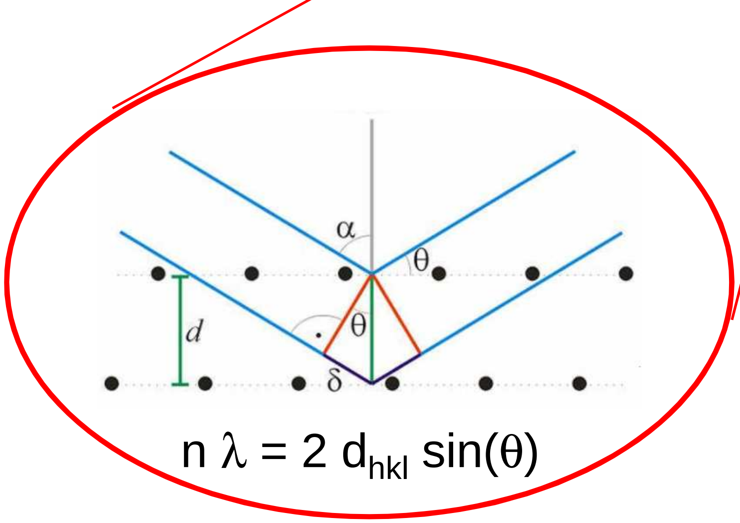
Double single crystal monochromator



monochromized
X-ray beam

Energy scanning by rotating θ

“white” X-ray beam

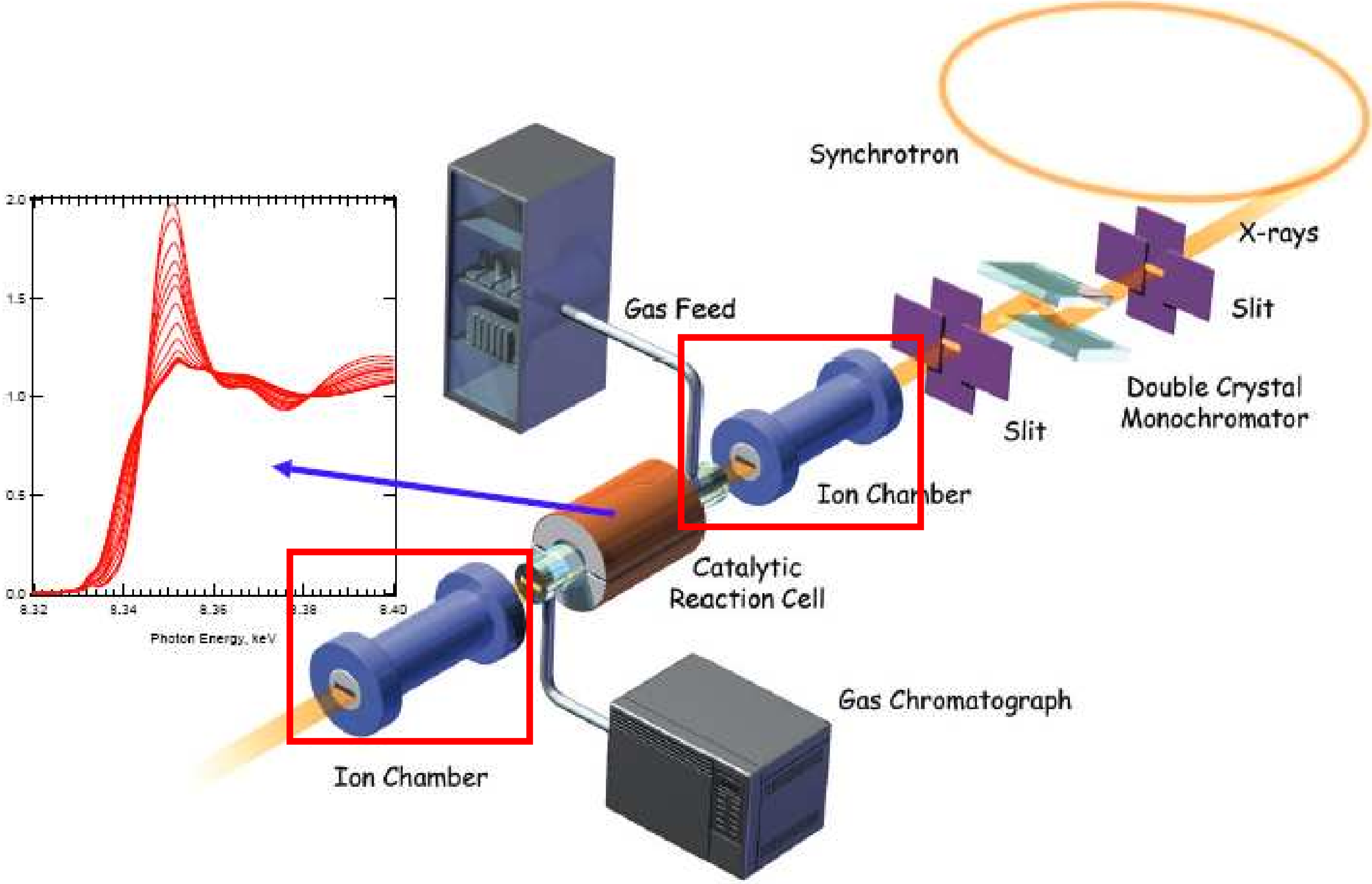


$n\,\lambda = 2\,d_{hkl}\sin(\theta)$

X1 at HASYLAB

Available crystals:
Si 111: Energy range 7 - 20 keV
Si 311: Energy range 9 - 40 keV
Si 511: Energy range 11 - 100 KeV

Detection: Transmission geometry



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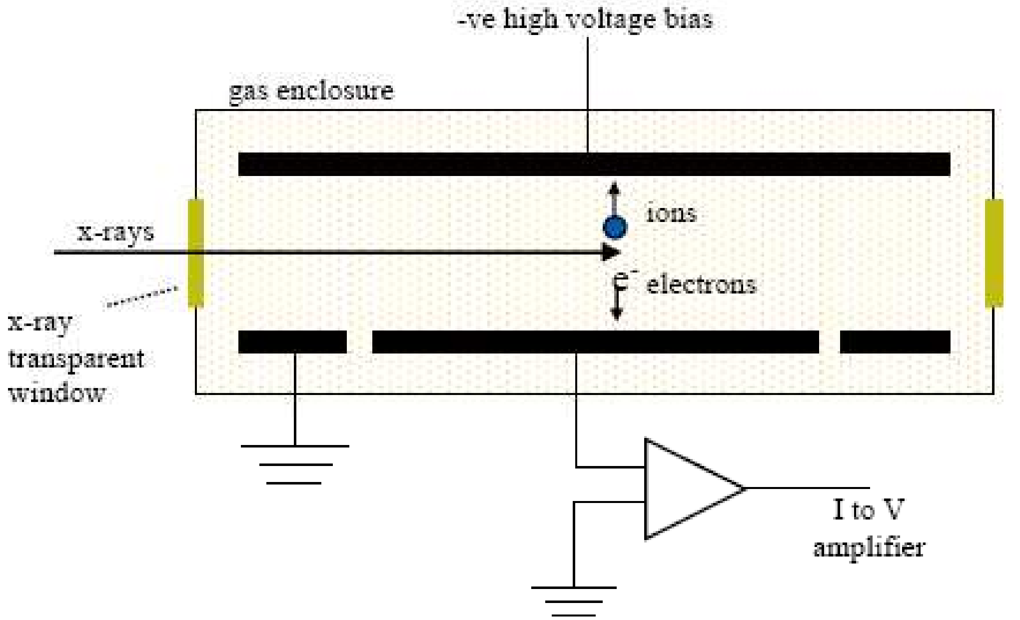
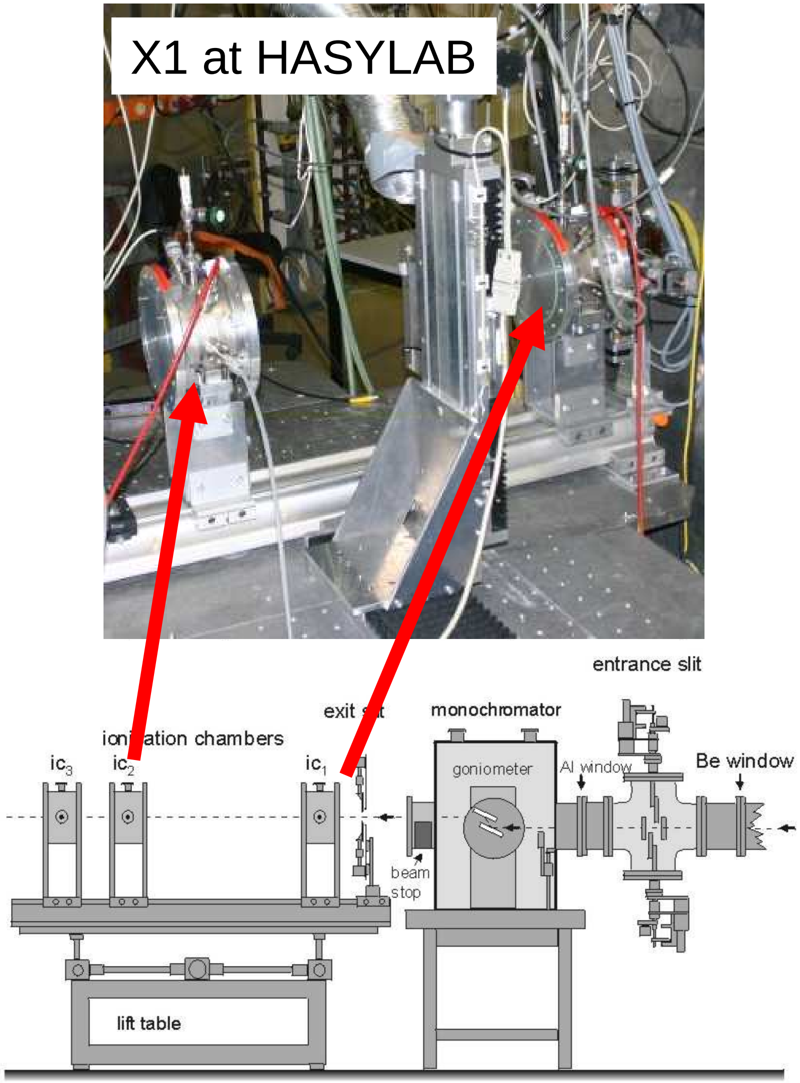
Ionization chambers





- Photon is absorbed by gas atom (He, N_2, Ar)
- Photoelectrons emitted (ionization)
- These electron initiate more ionization
- High voltage bias across plates causes electron and ions to drift in opposite directions.
- Charges collected result in current flow which is proportional to the incident x-ray intensity

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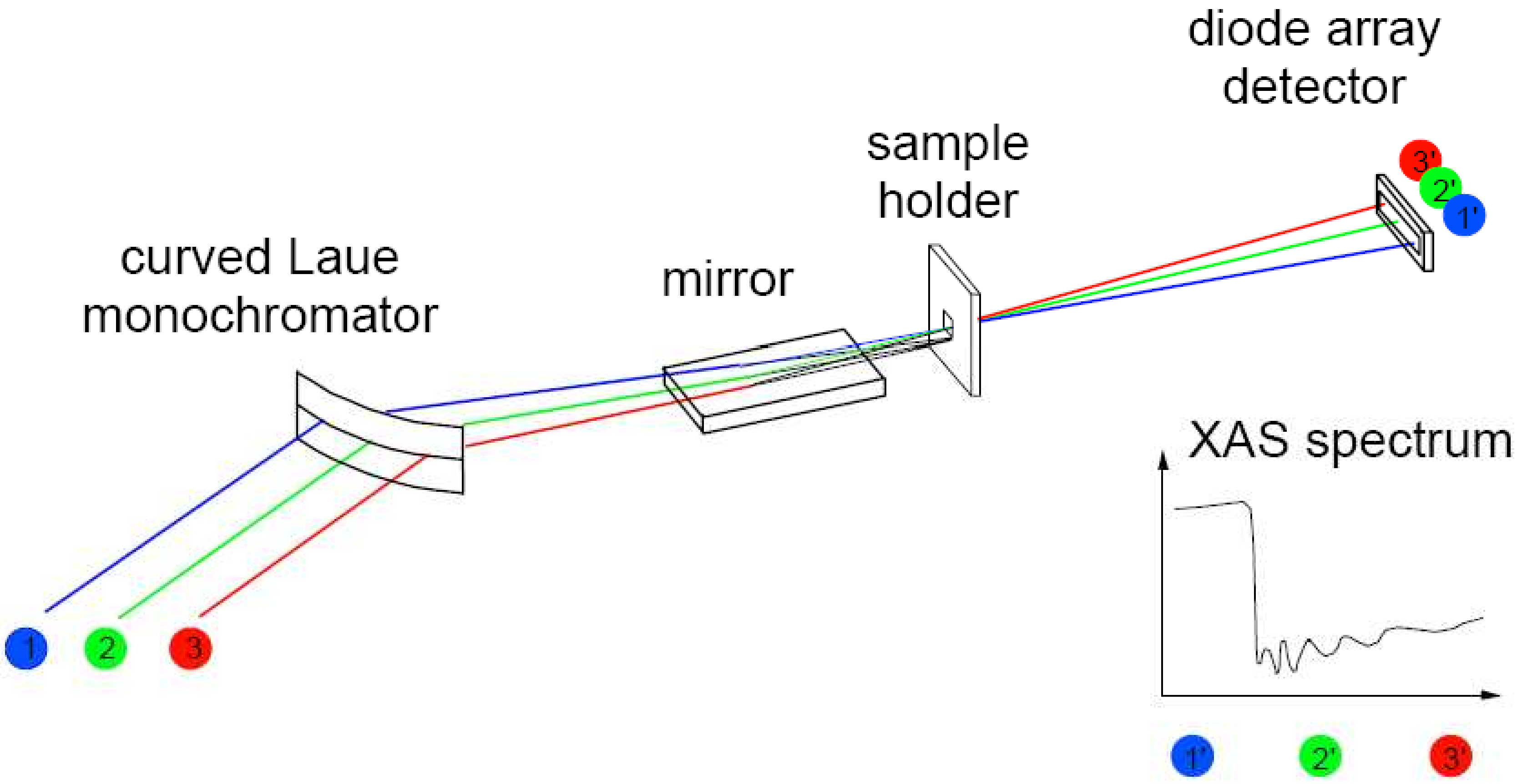
DXAFS



curved Laue monochromator

mirror

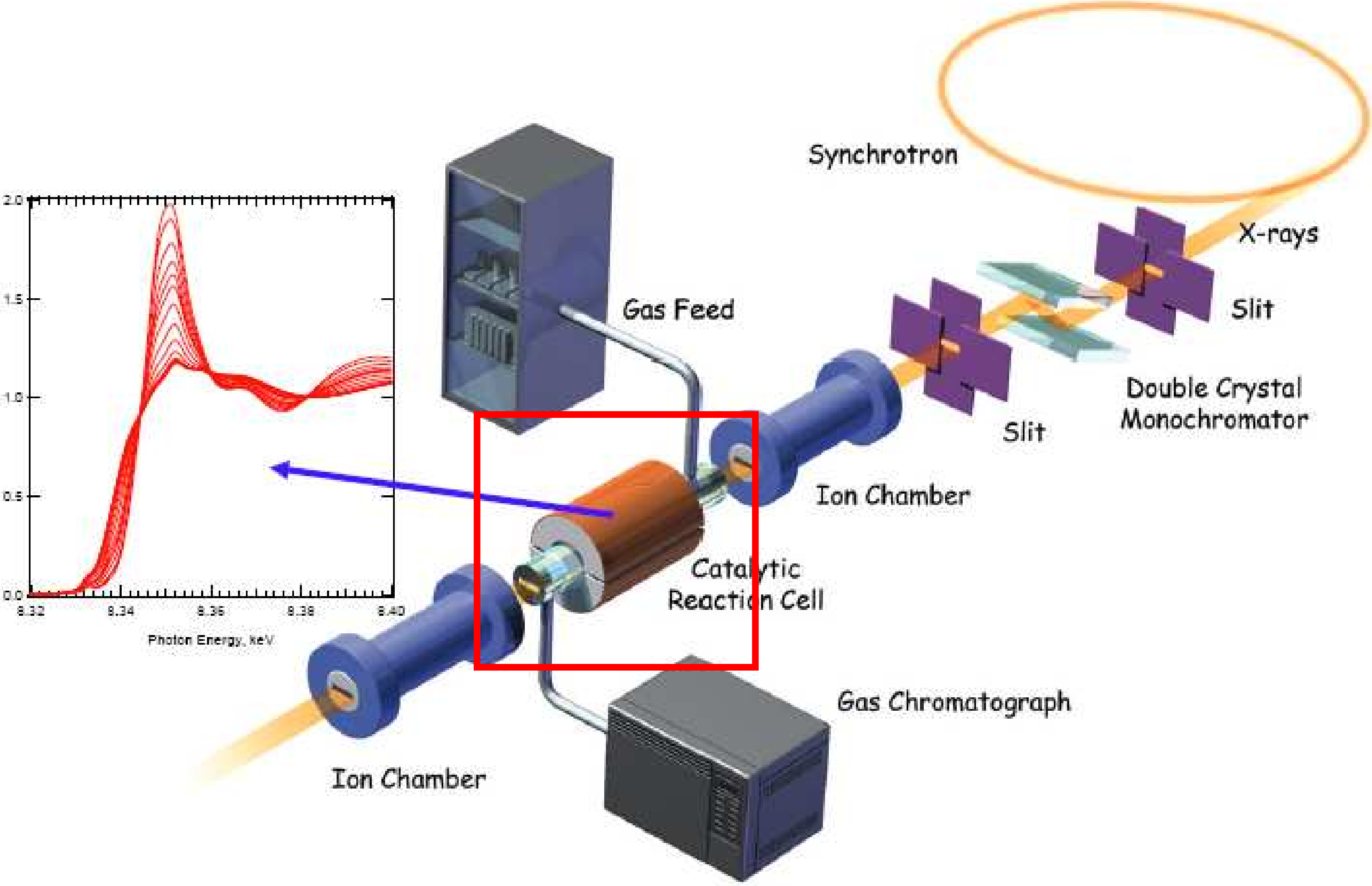
sample holder

diode array detector

XAS spectrum

Energy-dispersive XAS (DXAFS), (ESRF, ID24), ~ s/spec

Sample environment



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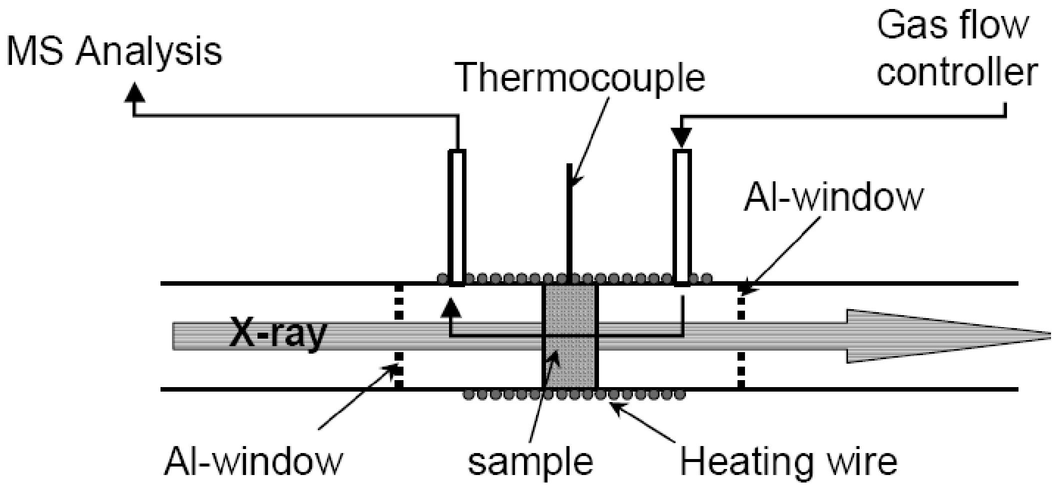
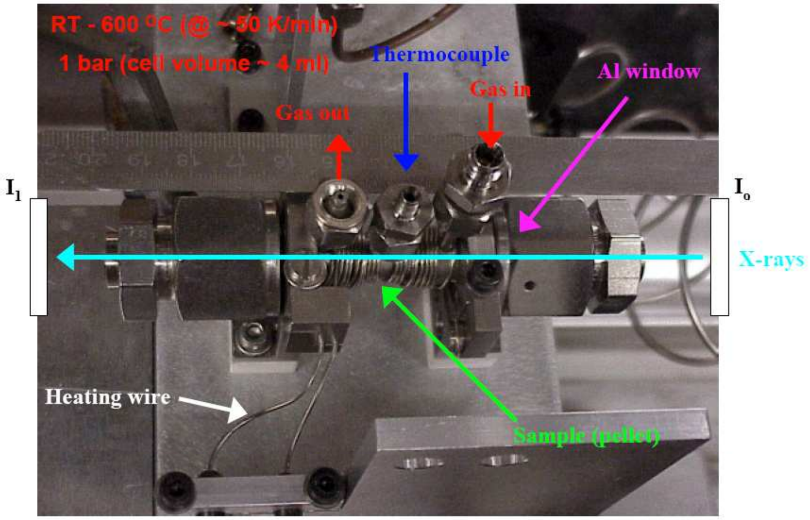
Catalytic in-situ cells





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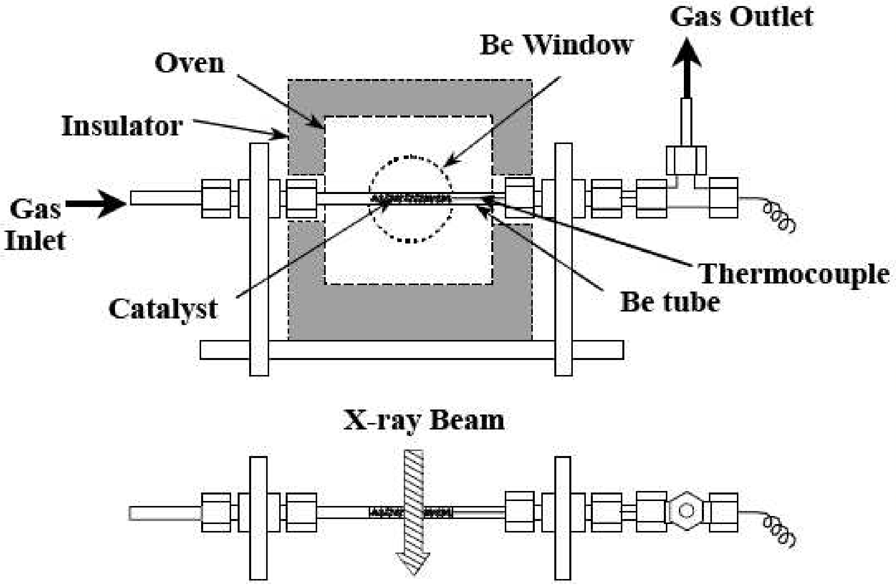

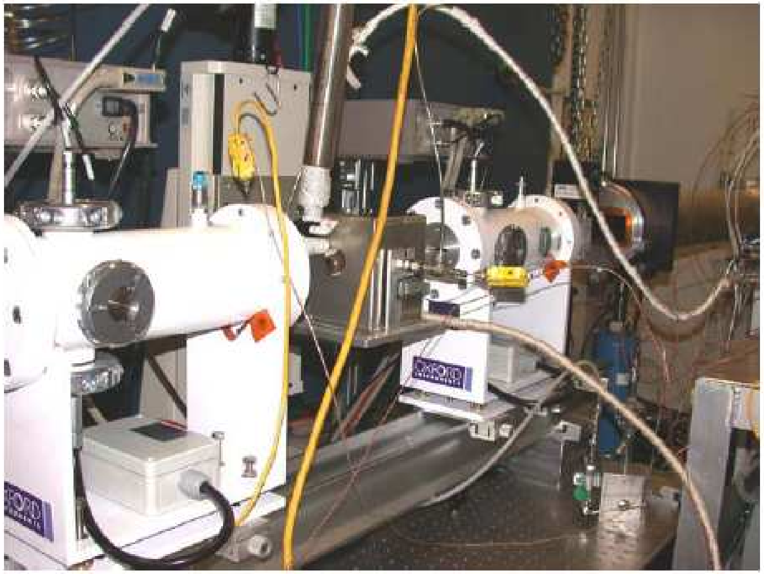

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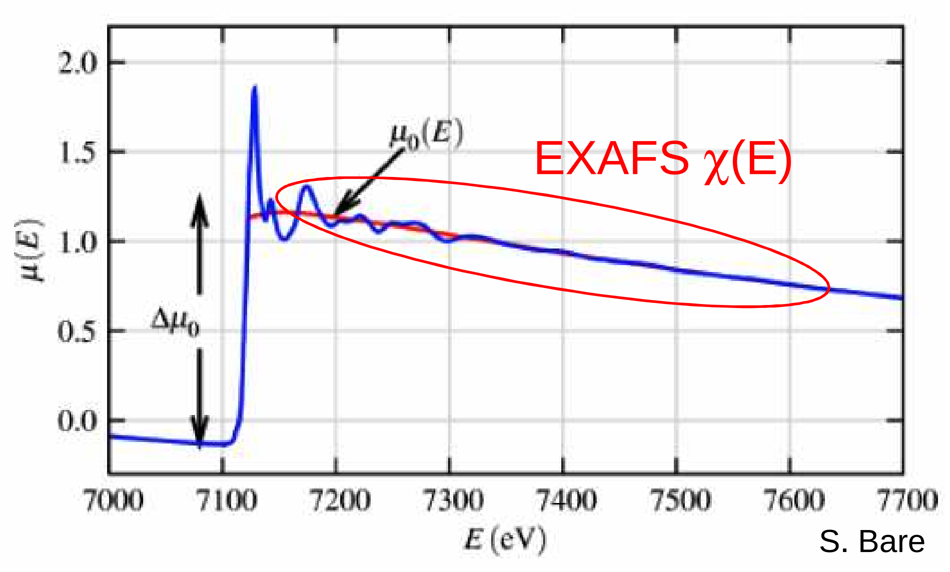
Raw data treatment

- The spectrum $\mu(E)$ contains the EXAFS oscillations $\chi(E)$, which contain the structural information we are interested in.

- How to extract this information from the spectrum?

Subtraction of the “bare atom” background $\mu_0(E)$

Division by the “edge step” $\Delta\mu_0(E)$



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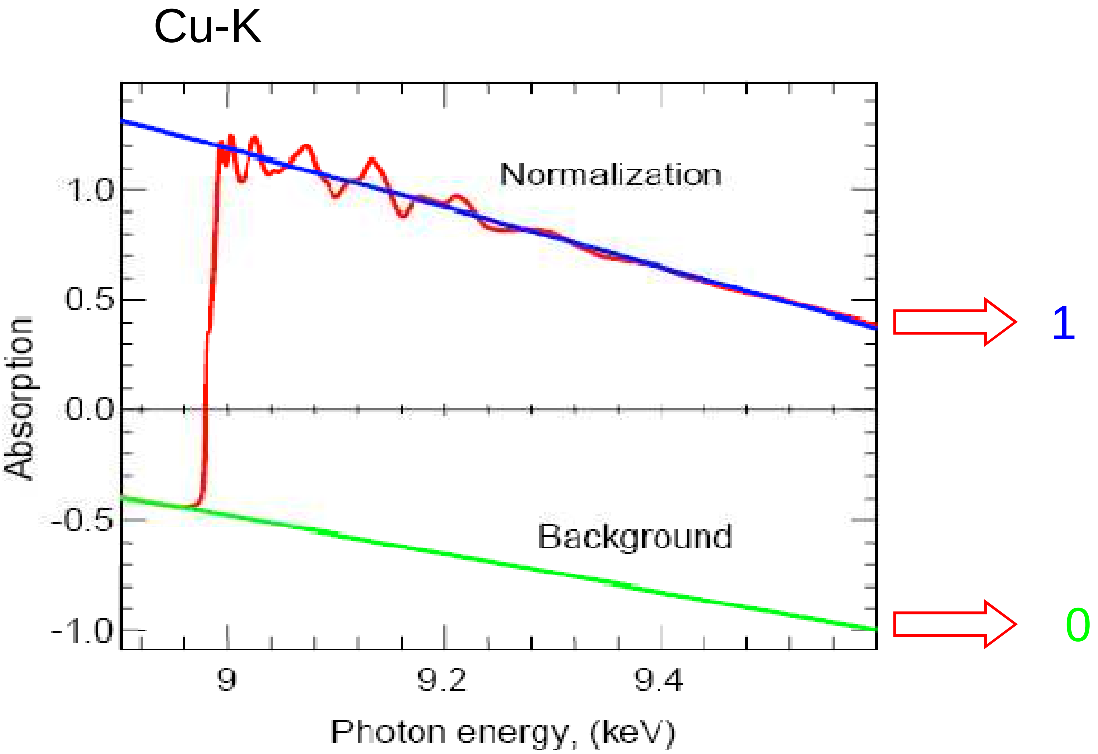
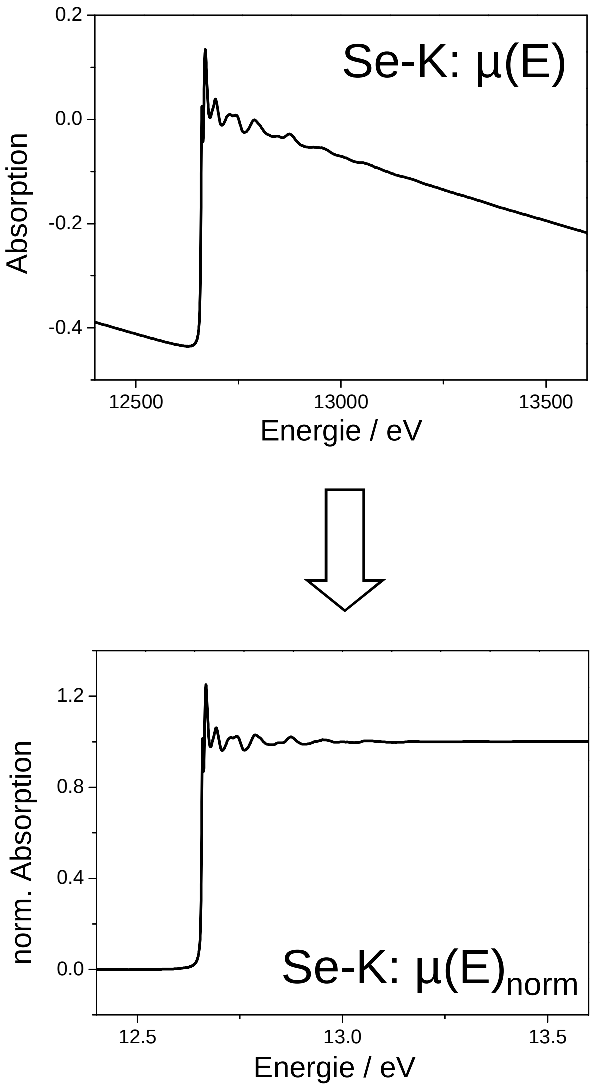
Normalization





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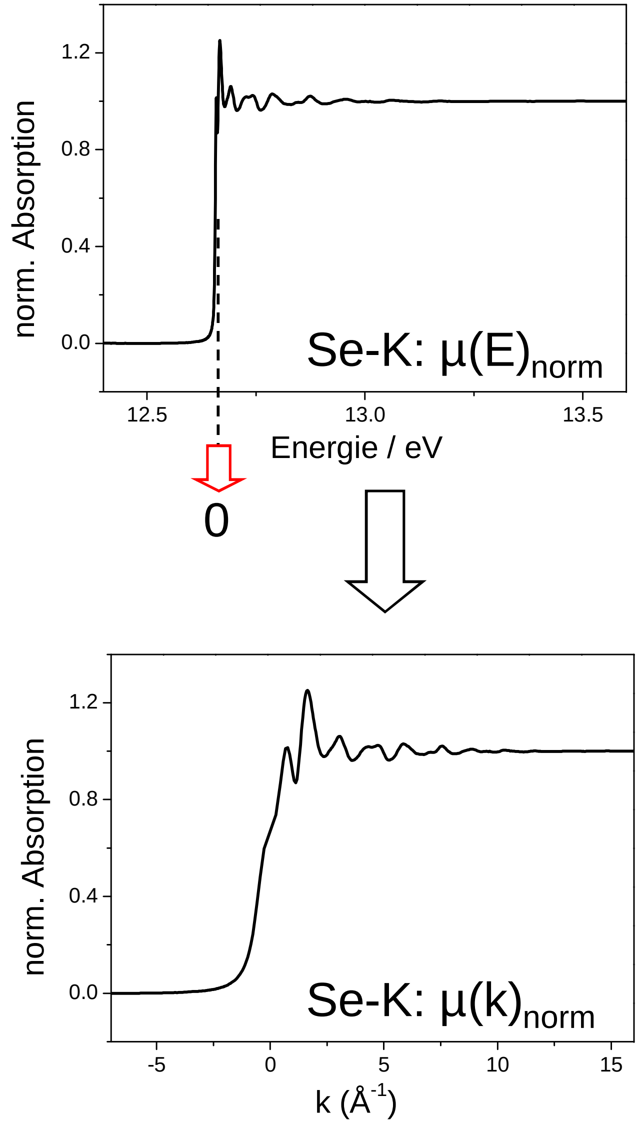
Transformation $\mu(E)_{norm} \rightarrow \mu(k)_{norm}$

EXAFS is an interference effect that depends on the wave nature of the photoelectron. It is therefore convenient to think of EXAFS in terms of the photoelectron wavenumber, *k*, rather than x-ray energy



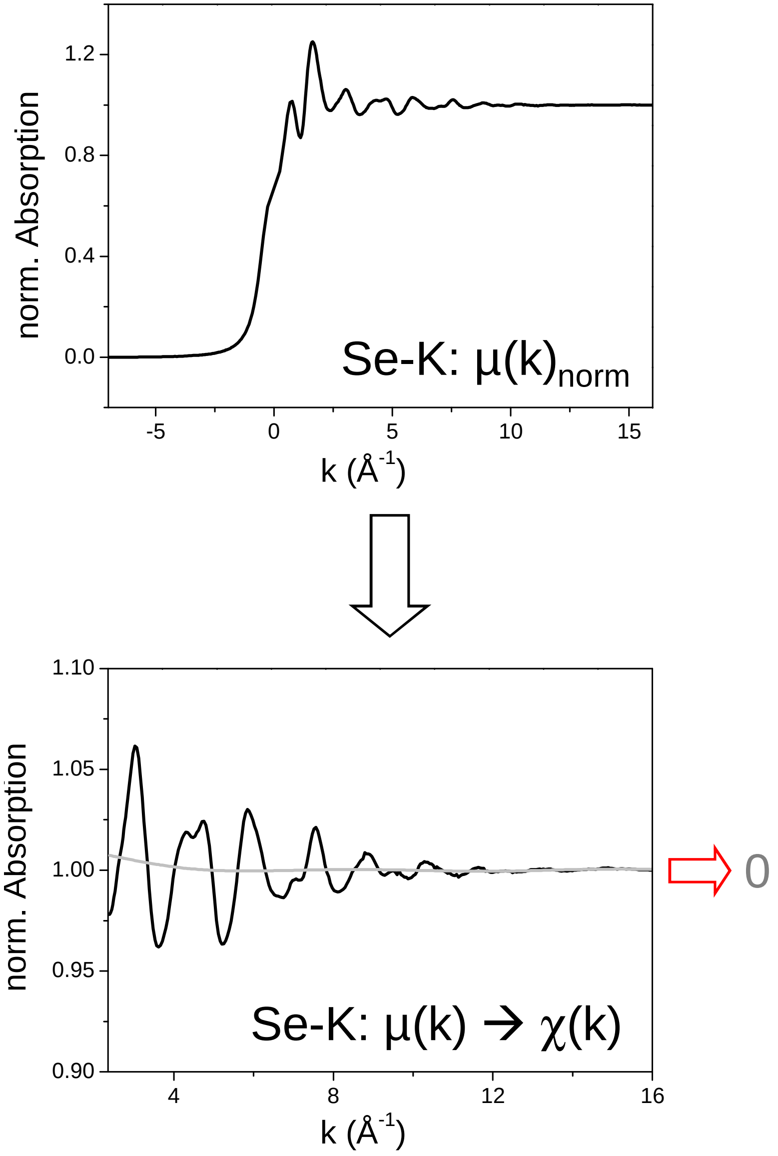
$$k = \sqrt{\frac{8\pi^2 m_e}{h}(E - E_0)}$$

m_e: mass of electron
E: Energy of incoming photon
E_0: Threshold energy at absorption edge

$\mu_0(k)$ Fit

EXAFS oscillations are extracted from $\mu(k)_{norm}$ by subtraction of the "bare atom" background $\mu_0(k)$ and normalizing

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$$

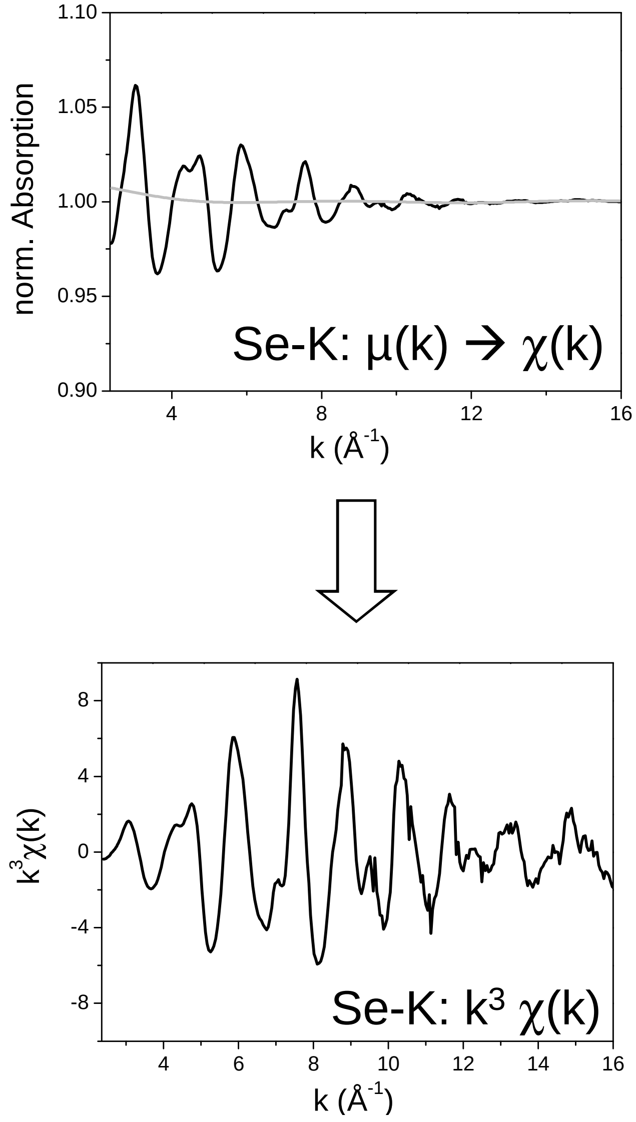


k-Weighting

χ(k) is typically weighted be k^2 or k^3 to amplify the oscillations at high k.

One way to separate the sine waves (scattering paths) from one another is to perform a Fourier transform.

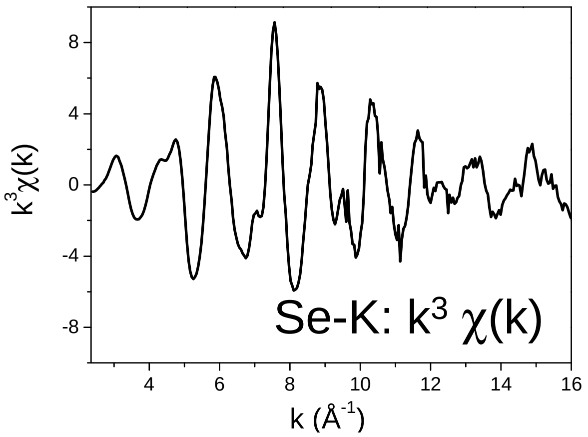
For the Fourier transformation it is best when the amplitudes of c(k) are similar thourght χ(k)

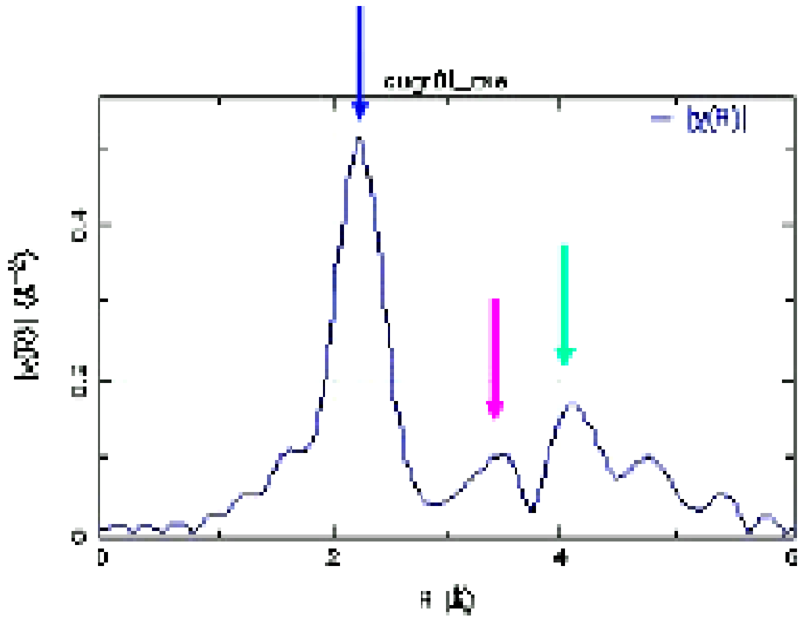


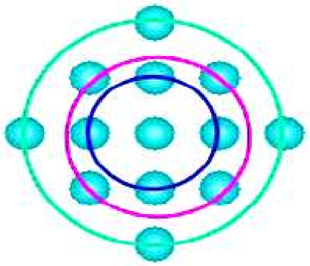
Fourier transformation

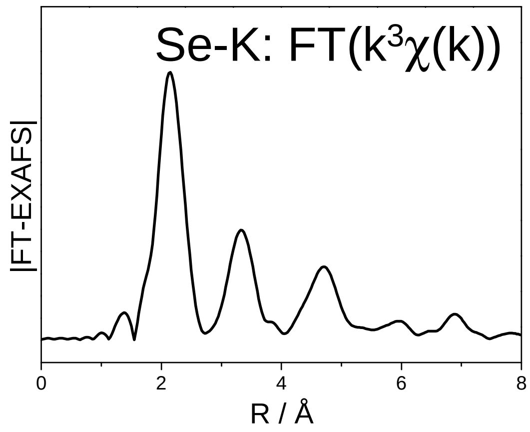
The resulting magnitude of the transform now has peaks representative of the different scattering paths of the photoelectron

→ Radial distribution function FT(χ(k))









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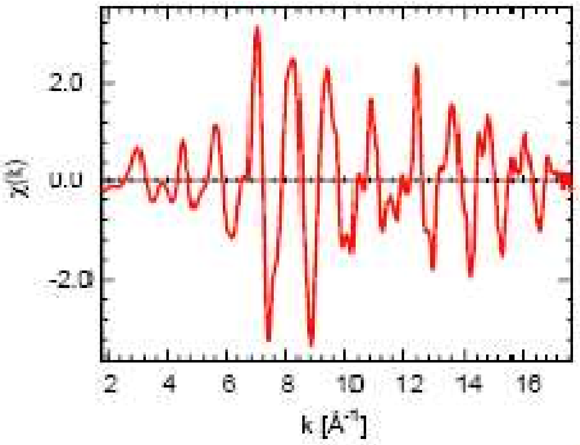
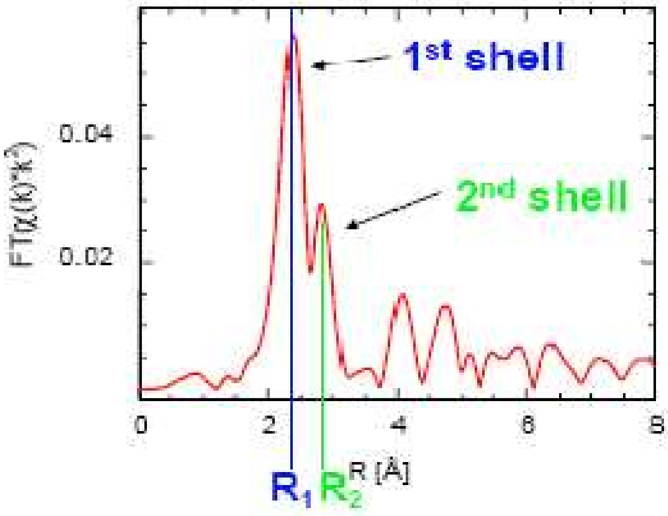
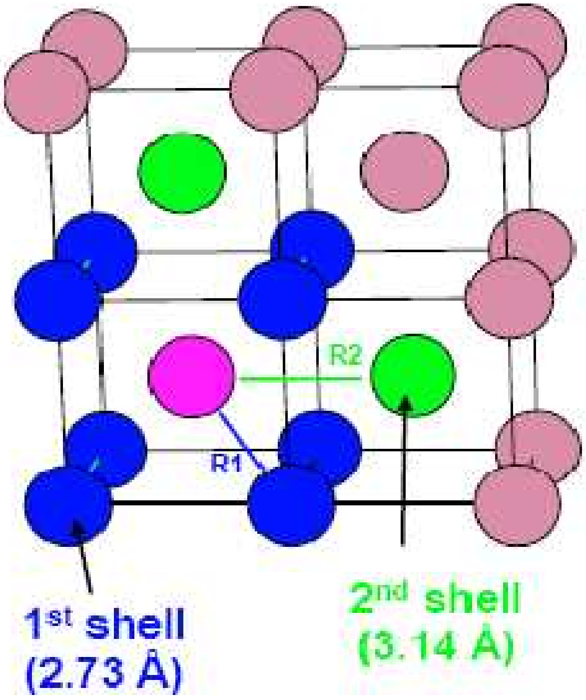
Scattering paths



FT →



Mo Metal (bcc)



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The EXAFS equation

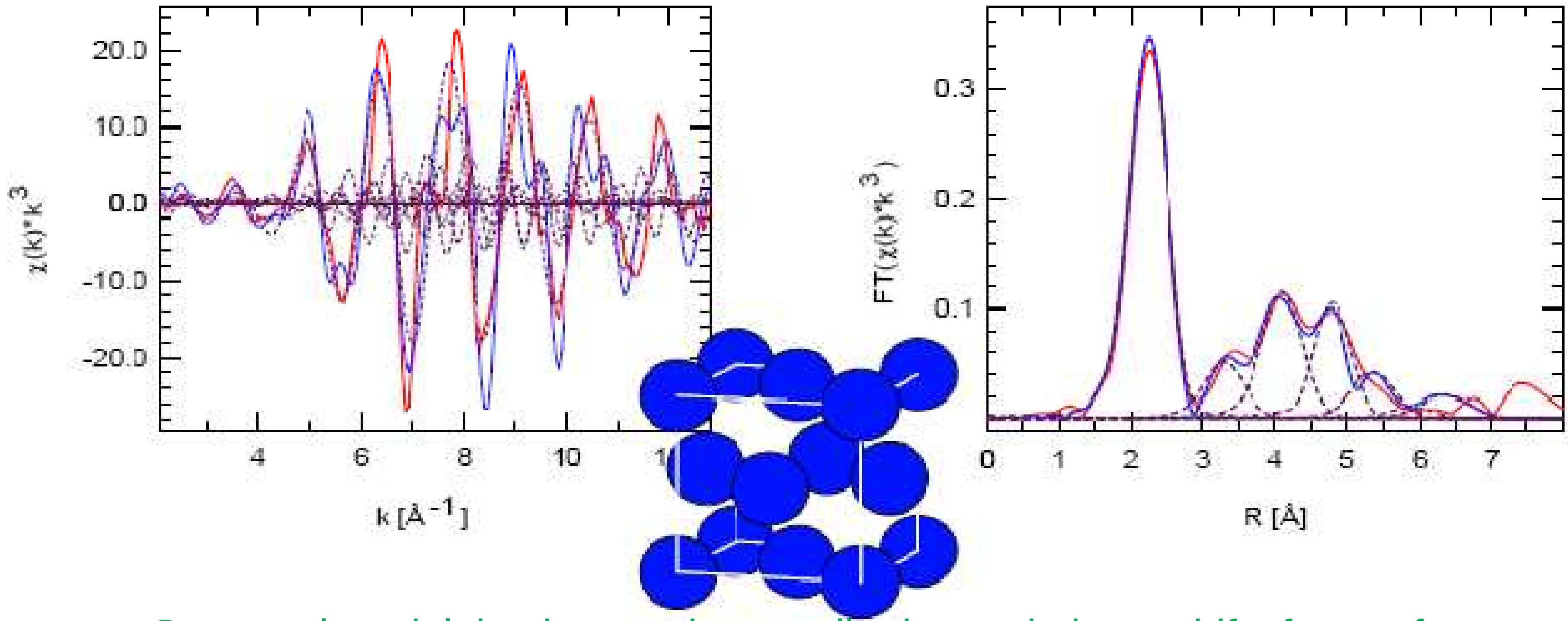
$$\chi(k) = S_0^2 \sum_i N_i \frac{|f_i(k)|}{kR_i^2} e^{(-2\sigma_i^2 k^2)} e^{(-2R_i/\lambda(k))} \sin(2kR_i + 2\delta_i + \varphi_i)$$

$\mathbf{N_i}$	is the number of scattering atoms of type *i*
$\mathbf{R_i}$	is the distance from the central atom to the scattering atom
S_0^2	is the amplitude reduction factor (due to multielectron processes).
$e^{(-2\sigma_i^2 k^2)}$	is a term to account for the disorder in the position of the atoms.
$e^{(-2R_i/\lambda(k))}$	is a damping factor to account for the fact that the photoelectron wave is only scattered elastically over a short distance.
$f_i(k)$	is the scattering amplitude at atom *i*
δ_i	is the phase shift undergone by the photoelectron at the central atom
φ_i	is the phase shift undergone by the photoelectron when it bounces off the scattering atom

S. Bare

Fitting of EXAFS data

$$\chi(k) = \sum_j \frac{N_j S_0^2 F_j(k)}{kR_j^2} \cdot e^{\left(-2k^2\sigma_j^2\right)} \cdot e^{\left(\frac{-2R_j}{\lambda}\right)} \cdot e^{\left(\frac{2}{3}\sigma_j^{(4)} k^4\right)} \cdot \sin\left[2kR_j + \delta_j(k) - \tfrac{4}{3}\sigma_j' k^3\right]$$



Structural model: backscattering amplitudes and phase shifts from reference spectra or calculated *ab initio* (e.g. FEFF code) and starting parameters

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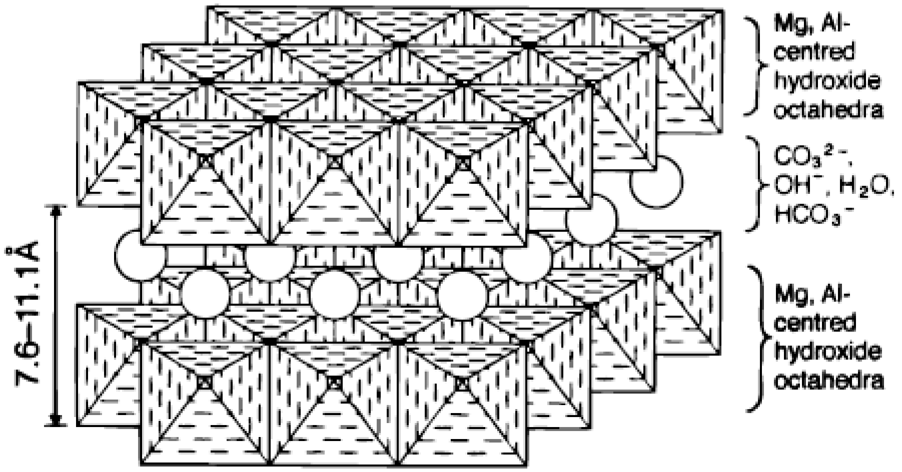
Fitted parameters: Least squares fitting (e.g. WinXAS package)

EXAFS Fitting: Cu LDH

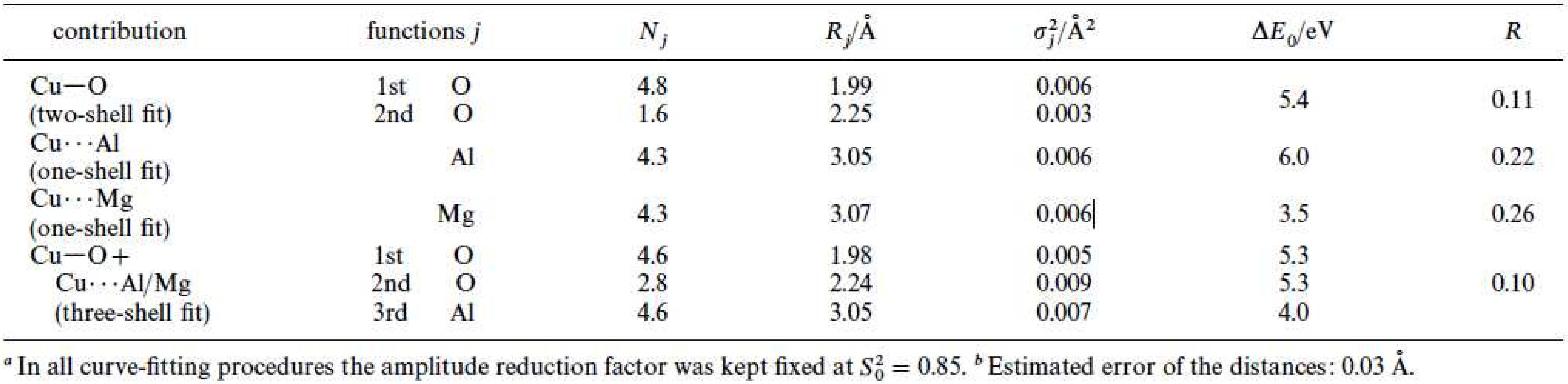


Layered double hydroxide:

$(Mg,Cu)_{1-x}(OH)_2Al_x(CO3)_{2/x} \cdot m\ H_2O$

10 % Cu: Is it in or between the layers?

Cu-K EXAFS fitting



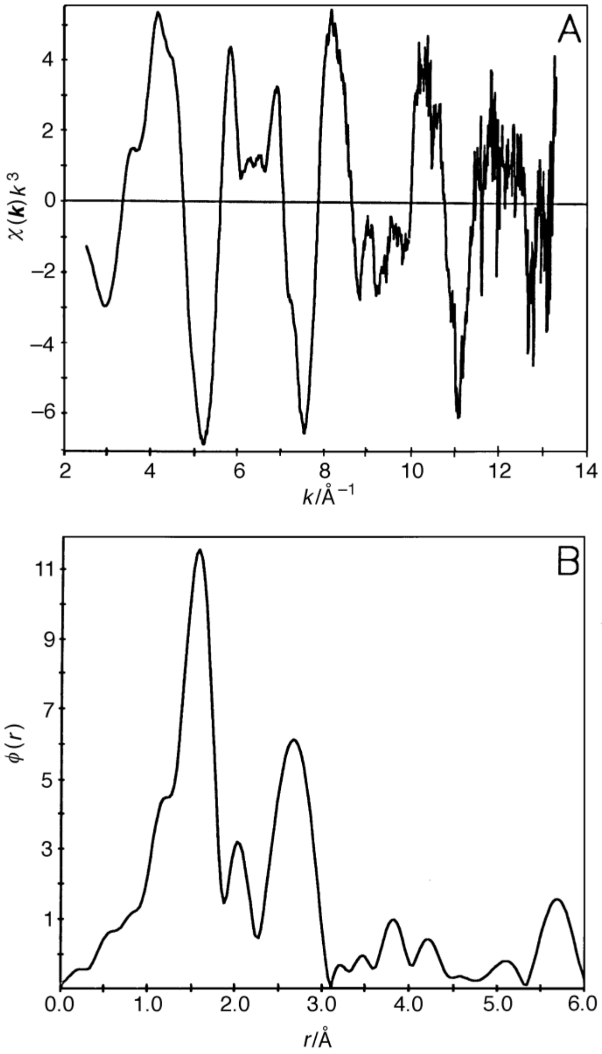
contribution	functions j		N_j	R_j/Å	σ_j^2/Å^2	ΔE_0/eV	R
Cu—O	1st	O	4.8	1.99	0.006	5.4	0.11
(two-shell fit)	2nd	O	1.6	2.25	0.003		
Cu···Al (one-shell fit)		Al	4.3	3.05	0.006	6.0	0.22
Cu···Mg (one-shell fit)		Mg	4.3	3.07	0.006	3.5	0.26
Cu—O +	1st	O	4.6	1.98	0.005	5.3	0.10
Cu···Al/Mg	2nd	O	2.8	2.24	0.009	5.3	
(three-shell fit)	3rd	Al	4.6	3.05	0.007	4.0	

[a] In all curve-fitting procedures the amplitude reduction factor was kept fixed at $S_0^2 = 0.85$. [b] Estimated error of the distances: 0.03 Å.

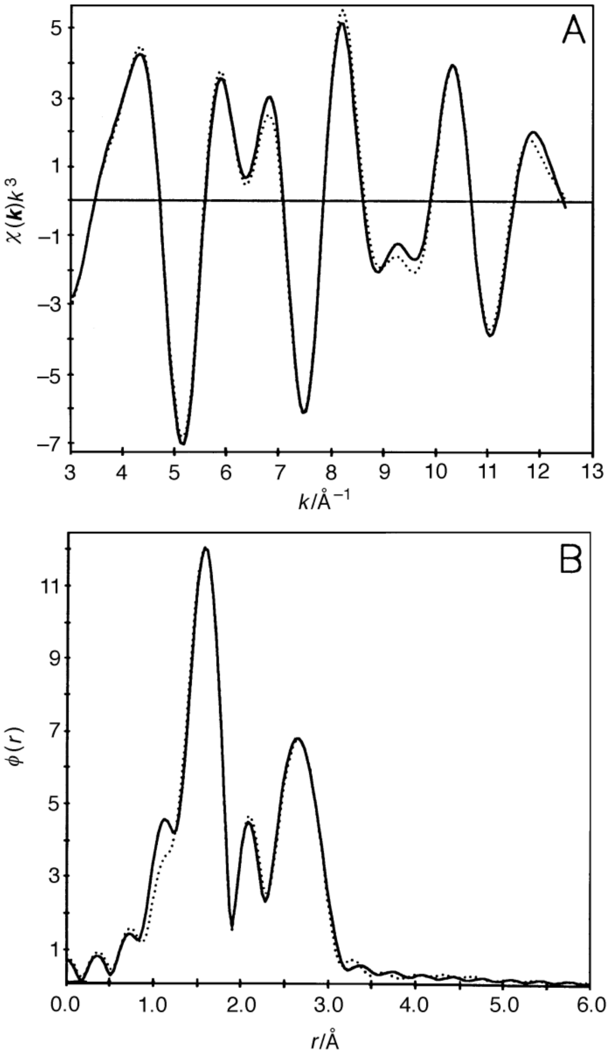
Cu^{2+} is incorporated in the LDH layers

Köckerling, Geismar, Henkel Nolting,
J. Chem. Soc., Faraday Trans., 1997,
93(3), 481.

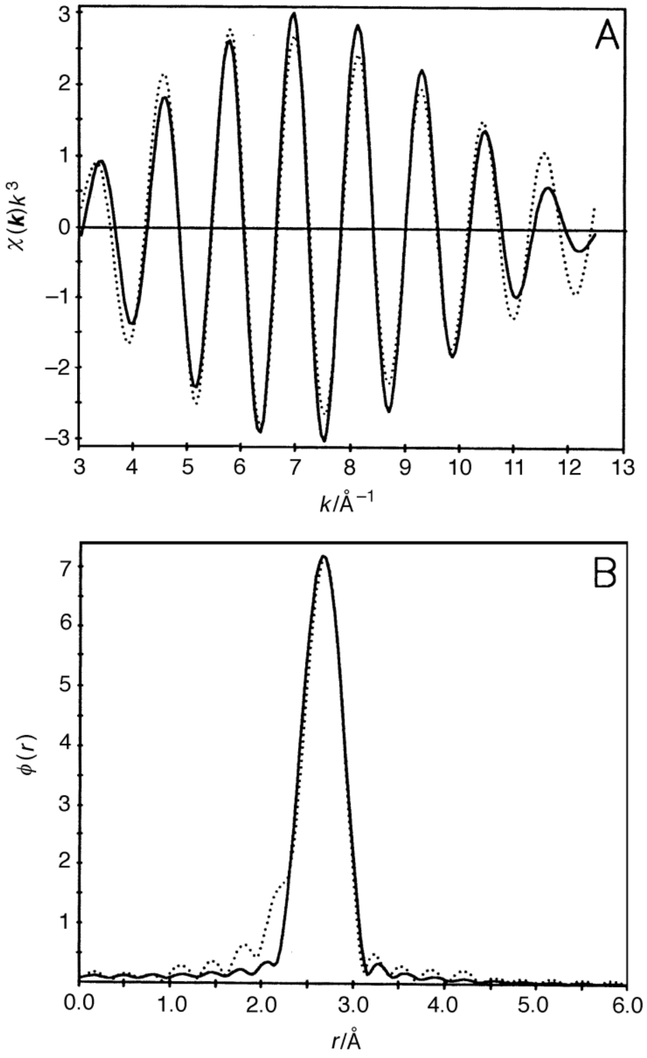
Cu LDH: Spectra



Experimental



Fourier filtered: first three shells



Fourier filtered: third shell

EXAFS fitting: metal ordering in aurichalite

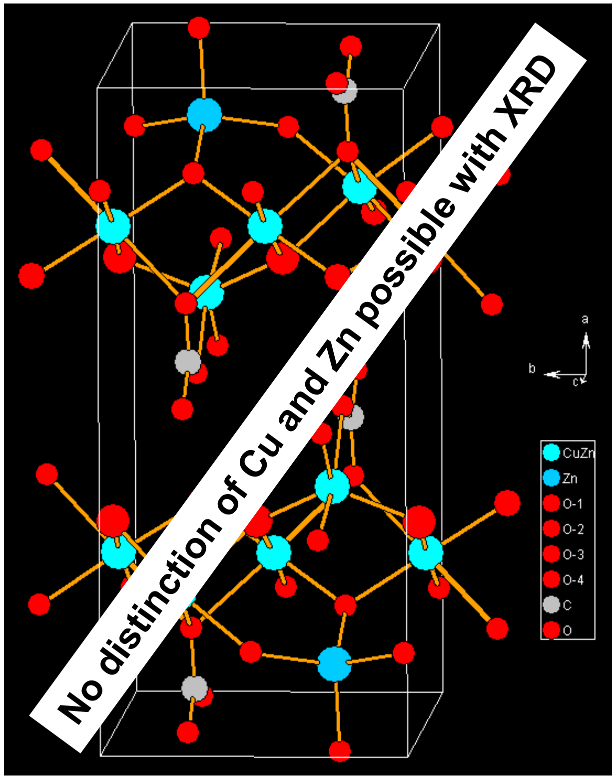
Problem: Cu/Zn ordering in aurichalcite (a possible precursor for Cu/ZnO catalysts)

Aurichalcite: $(Cu,Zn)_5(CO_3)_2(OH)_6$

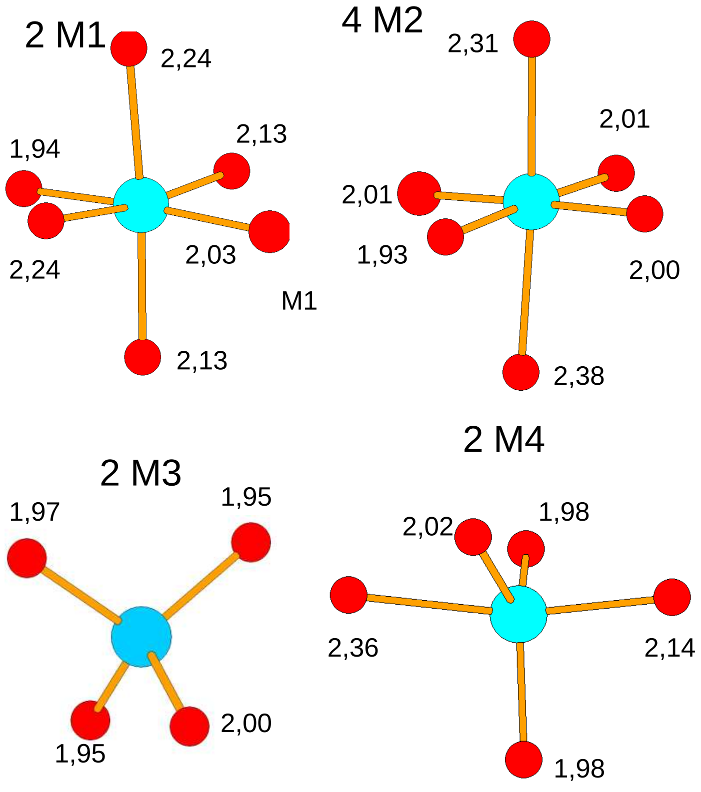
XRD crystal structure:

P 2_1/m, monoclinic

a=13.8200 Å; b=6.4190 Å
c=5.2900 Å; β=101.04°
(40% Cu)


No distinction of Cu and Zn possible with XRD

Harding, M.M.;Kariuki, B.M.;Cernik, R.;Cressey, G., Acta Cryst. B **50,** 1994, 673.



Structural model: Starting parameters for EXAFS fit

Cu/Zn ordering

Cu-K EXAFS

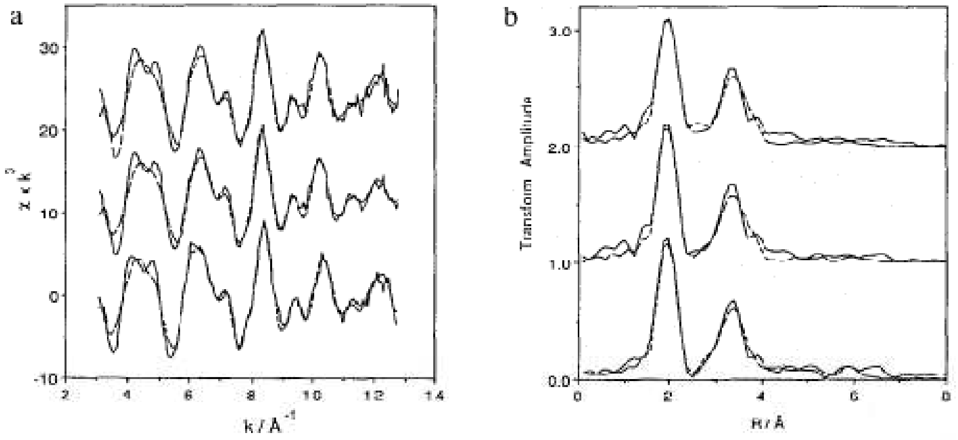


Fig. 4. (*a*) 80K Cu EXAFS (solid lines) and the corresponding best fits (broken lines) of aurichalcite. BM 1964,702 (top), BM 1983,97 (middle) and BM 1937,1355 (bottom). (*b*) Fourier transforms of the 80K Cu EXAFS (solid lines) and the corresponding best fits (broken lines) of aurichalcite. BM 1964,702 (top), BM 1983,97 (middle) and BM 1937,1355 (bottom).

Zn-K EXAFS

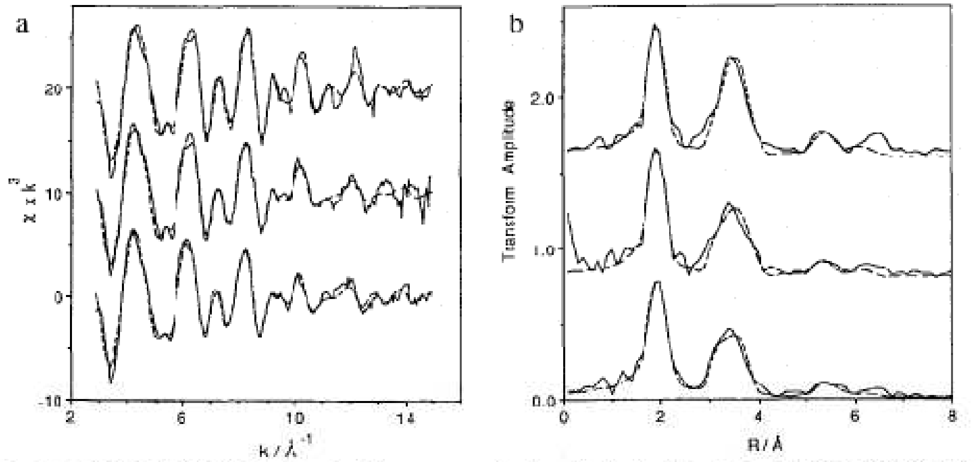
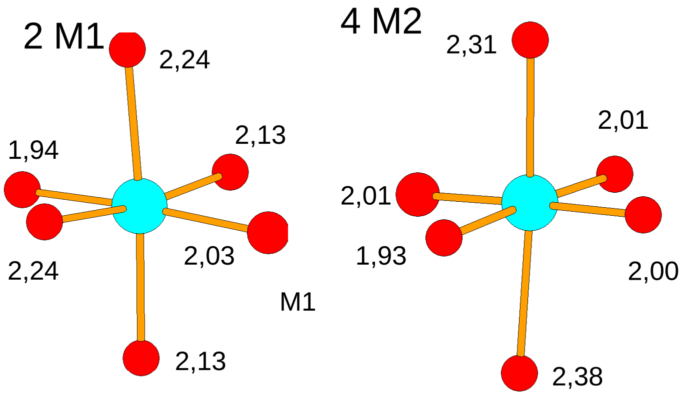
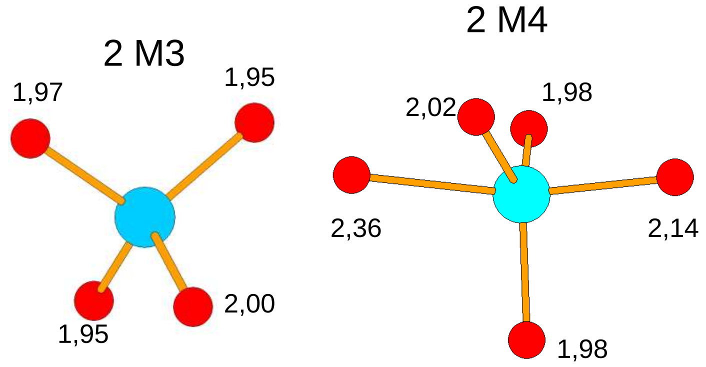


Fig. 5. (*a*) 80K Zn EXAFS (solid lines) and the corresponding best fits (broken lines) of aurichalcite. BM 1964,702 (top), BM 1983,97 (middle) and BM 1937,1355 (bottom). (*b*) Fourier transforms of the 80K Zn EXAFS (solid lines) and the corresponding best fits (broken lines) of aurichalcite. BM 1964,702 (top), BM 1983,97 (middle) and BM 1937,1355 (bottom).

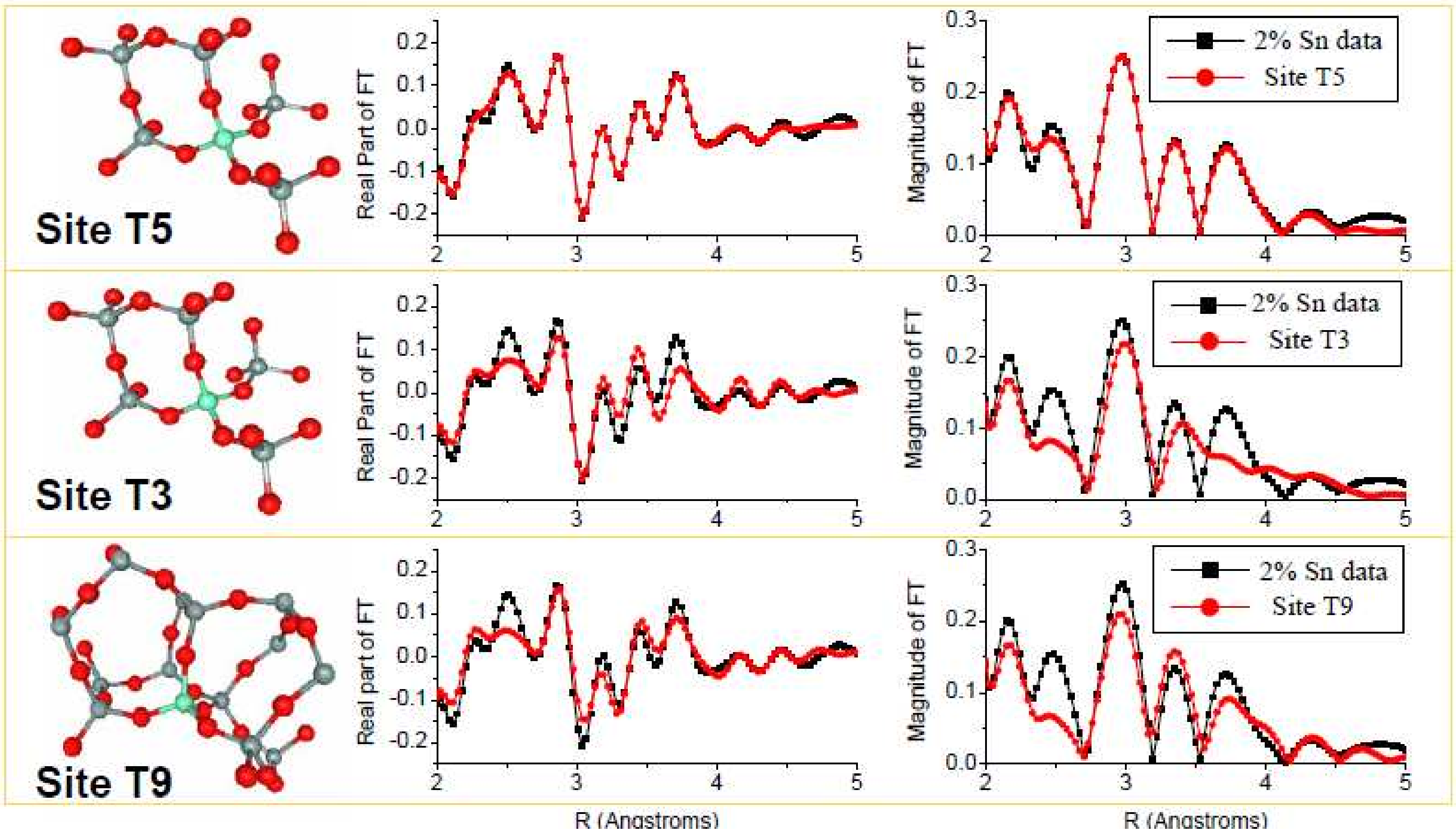


Cu on M2 (80%) & M4
Zn on M1 & M3



J.M. Charnock, P.F. Schofield, C.M.B. Henderson, G. Cressey, B.A. Cressey, Mineral. Mag. 1996, 60, 887

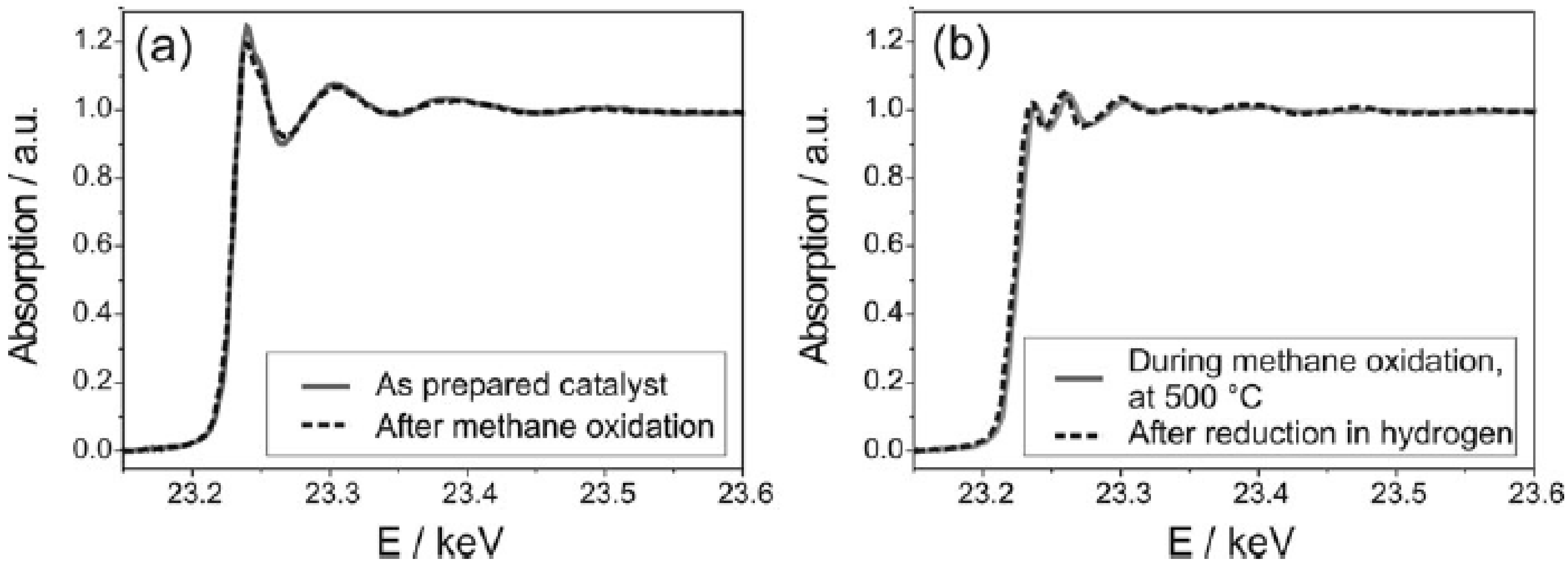
EXAFS in catalysis



Sn resides on the T5 site of beta-zeolite !

S. Bare

In-situ XAFS



Paritally oxidized

metallic Rh

Rh-Pt/Al_2O_3 catalyst in partial oxidation of methane

Grunwaldt, Baiker, Phys . Chem. Chem. Phys., 2005, 7, 3526.

EXAFS Summary

- EXAFS oscillations $\chi(k)$ are due to interference of the photoelectron wave coming from the absorber atom and backscattered waves from the neighboring atoms, various scattering paths contribute
- The shape of $\chi(k)$ is determined by the local environment around a specific element
- $\chi(k)$ contains information on the neighboring atom type, the inter-atomic distances and the coordination number
- A well develped theory is available to extract this information from experimental data by least-squares fitting (careful data reduction necessary)
- EXAFS works on all kinds of material, most elements and can be applied in-situ
- Synchroton radiation is required

Literature / references

- D.C. Koningsberger, R. Prins (ed.): “X-Ray Absorption” John Wiley & Sons, New York 1982

- D. Koningsberger, D. E. Ramaker: “Application of X-Ray Absorptions Spectroscopy in Heterogeneous Catalysis: EXAFS, Atomic XAFS and Delta XANES” in Handbook of Heterogeneous Catalyis (Ertl, Knözinger, Schüth, Weitkamp), Wiley

- Lecture scripts of Simon Bare (UOP), Thorsten Ressler (TU Berlin), Wolfgang Bensch (Uni Kiel)