



Ecole Polytechnique
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Paul Scherrer Institut

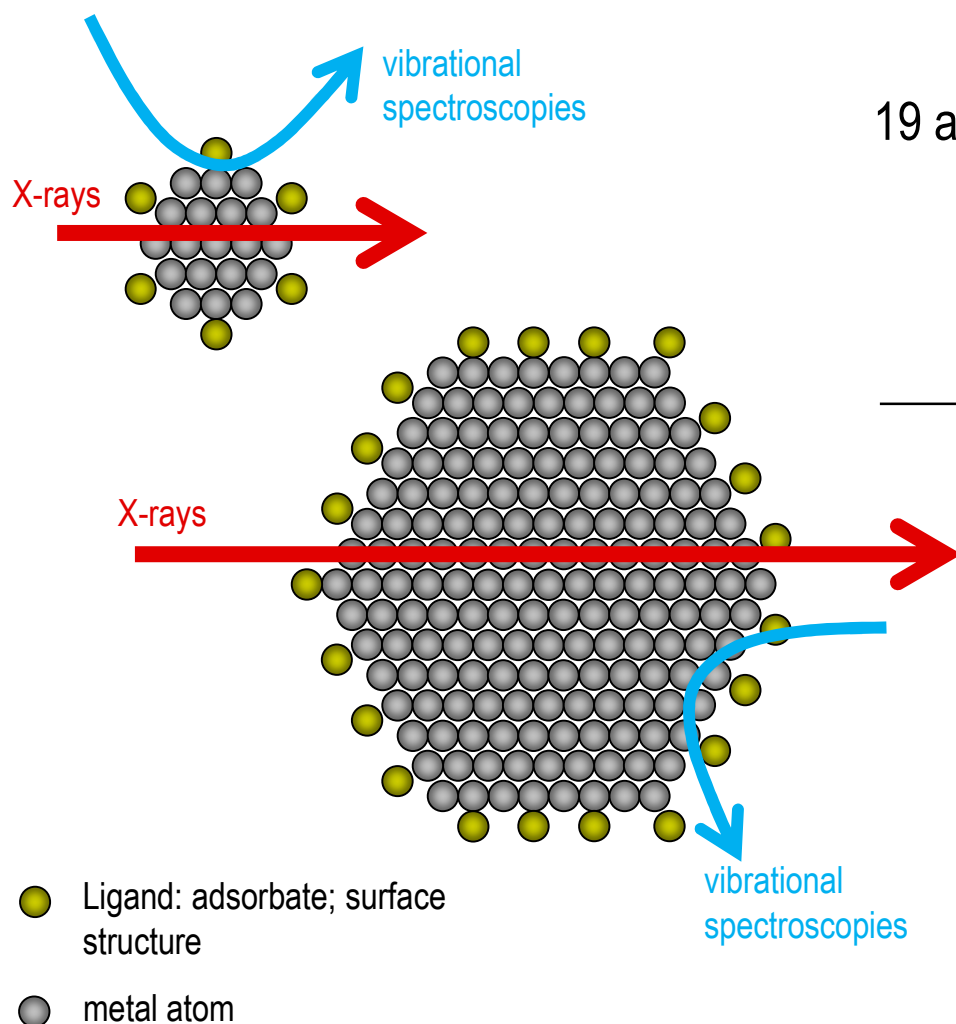


**Catalysis for Emission
Control and Energy
Processes - ChE-410**

Prof. Dr. Oliver Kröcher, Dr. Davide Ferri, **Dr. Emanuele Moioli**
davide.ferri@psi.ch

Surface vs. bulk information

Catalysis is a surface phenomenon – XRD and XAS probe the bulk



19 atoms (Ø 1.4 nm)

169 atoms (Ø 4.3 nm)

Surface coverage 50%

ligands : # catalyst

31%

12%

Advantages of X-rays

very good penetration through a number of materials

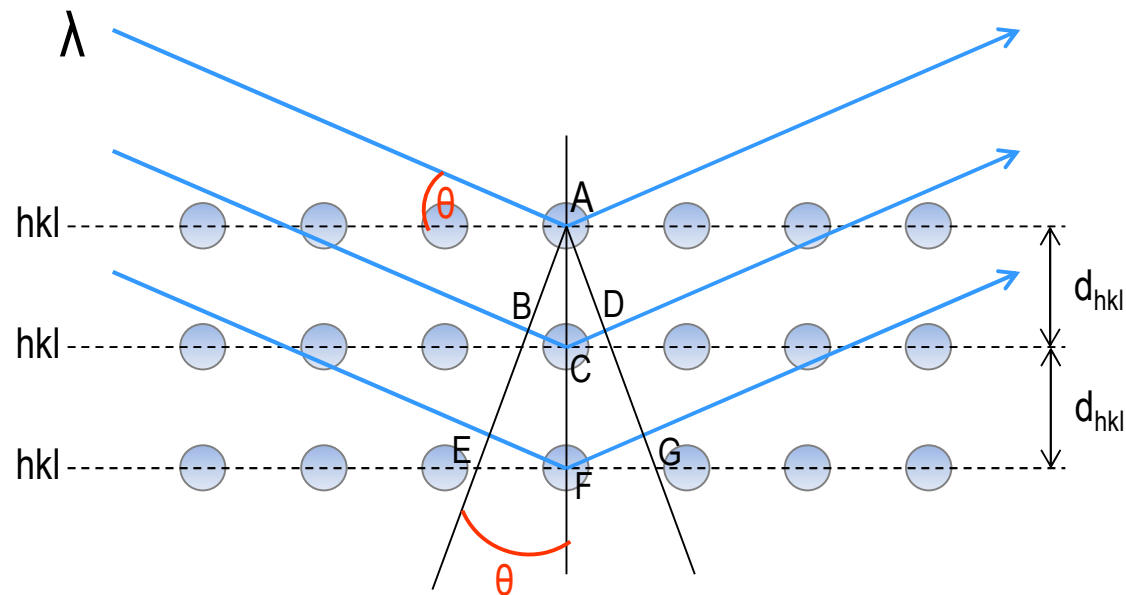
- *in situ* cells similar to catalytic reactors or synthesis vessels can be built up
- well suited for following *in situ* formation of active catalyst phases

X-ray diffraction

Bragg's condition

Distance between the lattice planes about the same as the wavelength of the X-rays

constructive interference between scattered X-rays



$$BC = d_{hkl} \sin \theta$$

but $BCD = \lambda$

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

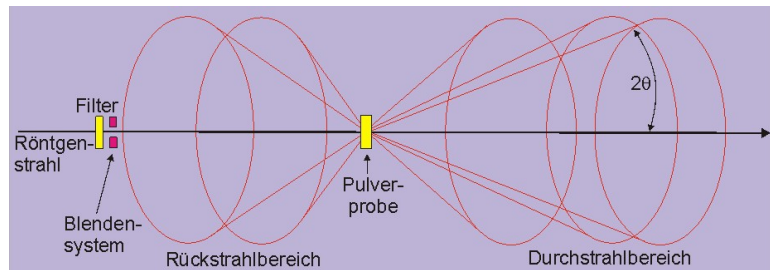
or

$$\lambda = 2d_{hkl} \sin \theta$$

Powder diffraction

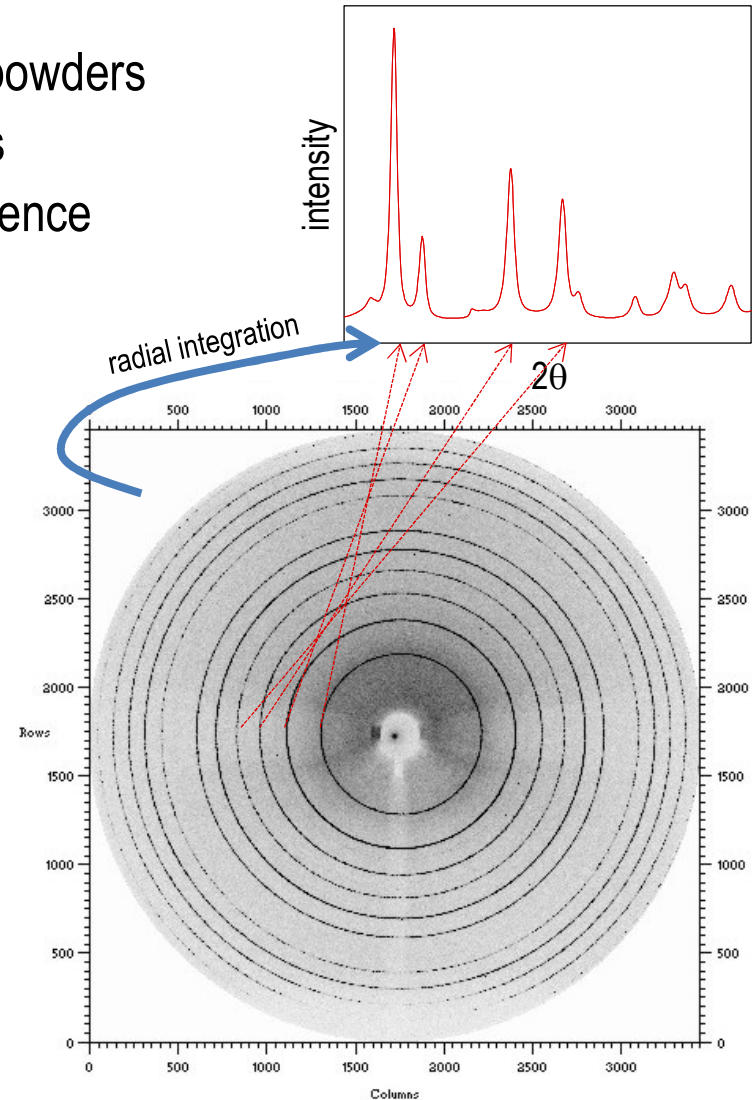
Heterogeneous catalysts: no single crystals but powders

- hundreds of single crystals in all directions
- diffraction lines, just if constructive interference
- cone with half opening angle 2θ



What is needed?

- fine powders
- or, rotation of the sample



Information contained in the XRD pattern

Peak positions

- Crystal system
- Space group symmetry
- Unit cell dimensions
- Qualitative phase identification

Peak intensities

- Unit cell contents
- Quantitative phase fractions

Peak shapes and widths

- Crystallite size (3-200 nm)
- Non uniform micro-strain
- Extended defects

Disadvantages

- amorphous phases cannot be detected
- sufficient concentration
- small particles (2-3 nm) with high dispersion and low concentration not be detected
- bulk, not surface sensitive

Line broadening

- SIZE effect: imperfection in size (i.e. no infinite crystal)
- GRAIN effect: imperfection in periodicity
- Small crystal → small nr. periods → larger imperfection → larger line
- Evident for size < 100 nm
- Lower limit: < ca. 3 nm
- Dislocations, vacancies, substitutional defects, interstitial defects

Crystallite size

Crystallite size can be estimated from line width

$$D = \frac{K \cdot \lambda}{B \cdot \cos \theta}$$

Scherrer equation

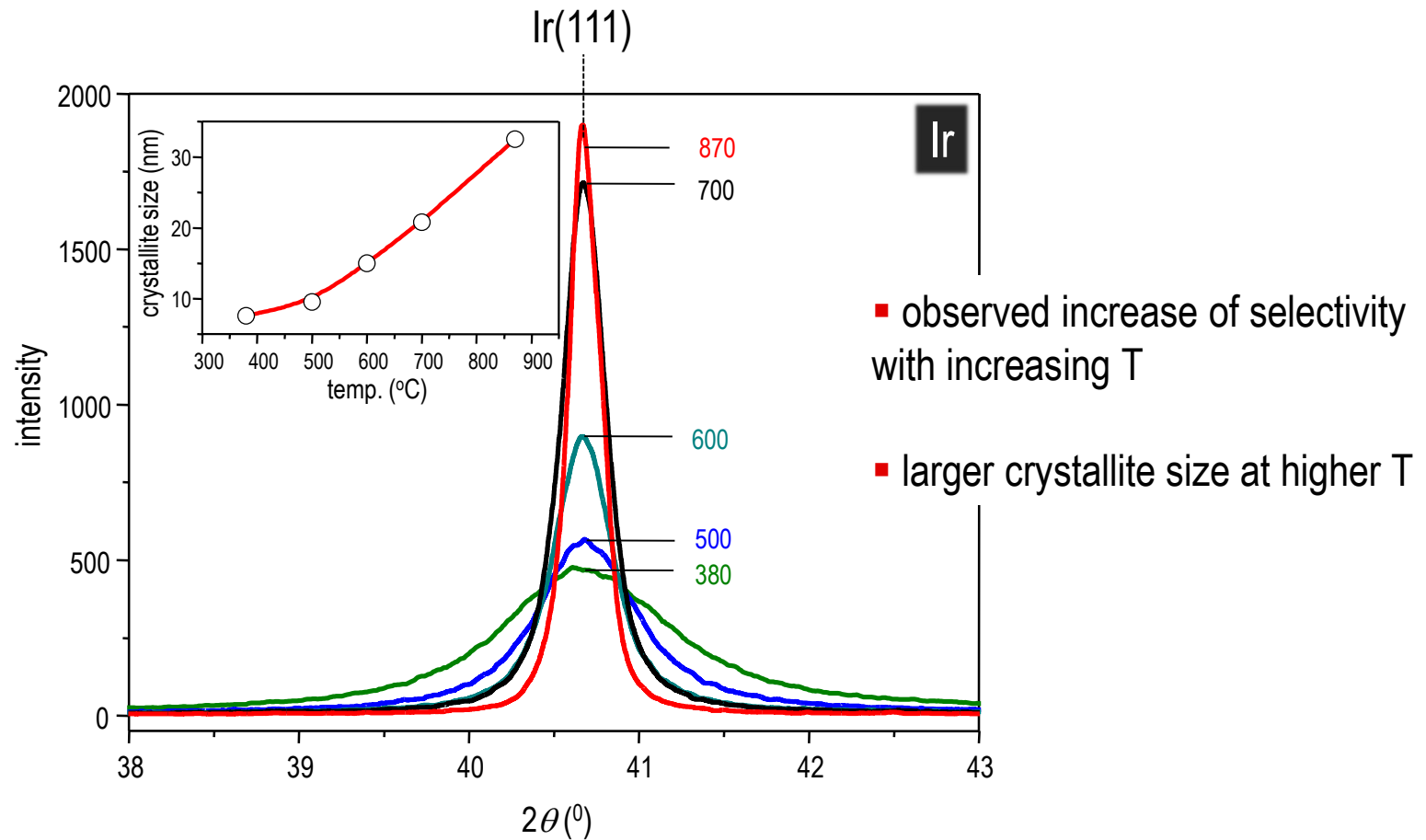
$$B = (B_{\text{measured}}^2 - B_{\text{instrument}}^2)^{1/2}$$

- K often taken as 0.9
- Wavelength, λ
- Diffraction angle, θ (rad)
- Instrumental half-width, $B_{\text{instrument}}$

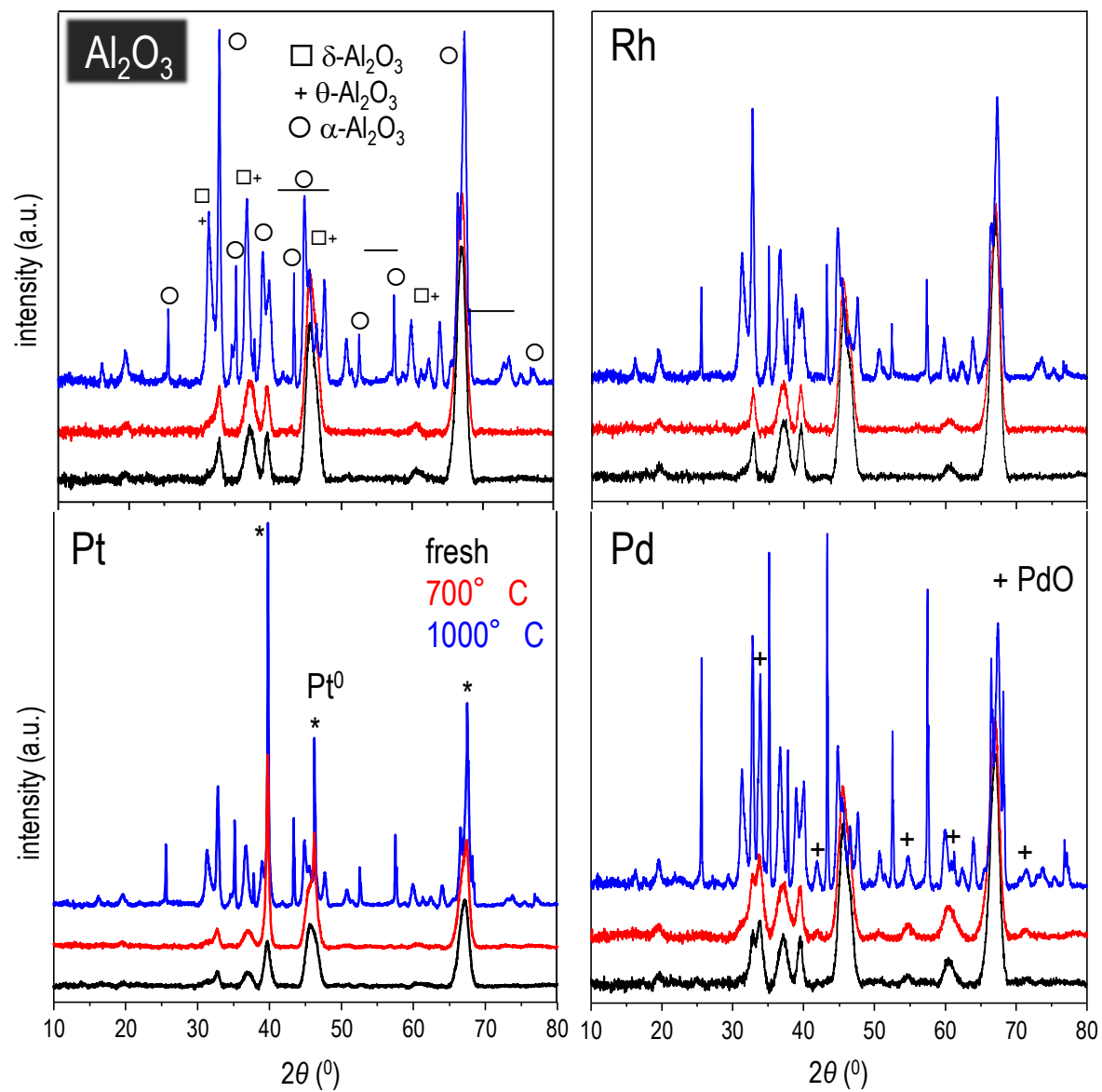
Q Calculate the copper particle size in two different Cu-catalysts (at $2\theta=40^\circ$), that show a FWHM of 0.12° and 2.50° . The instrumental resolution is 0.10° . The widely applied X-ray source with a Cu-anode and Ni-filter has been used.

Crystallite size

- Dispersed metal nano-particles

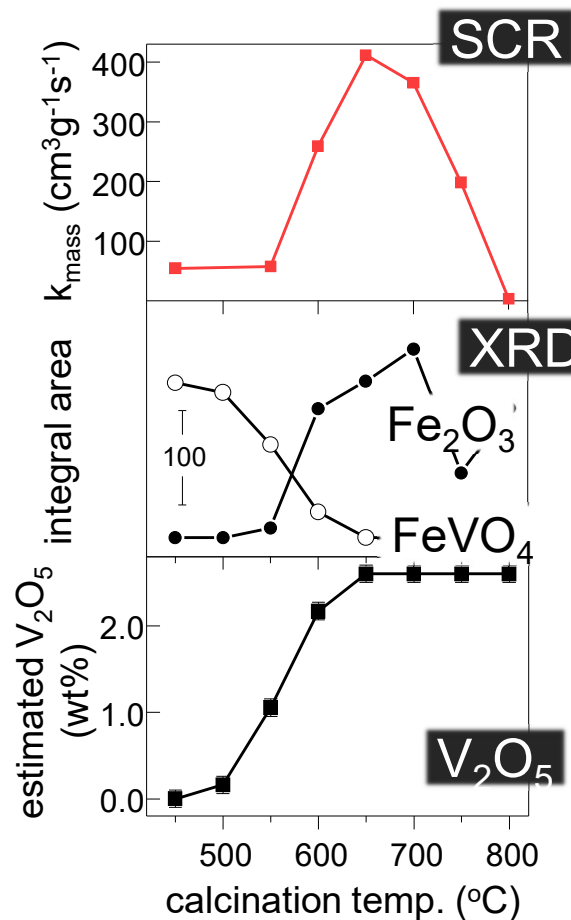
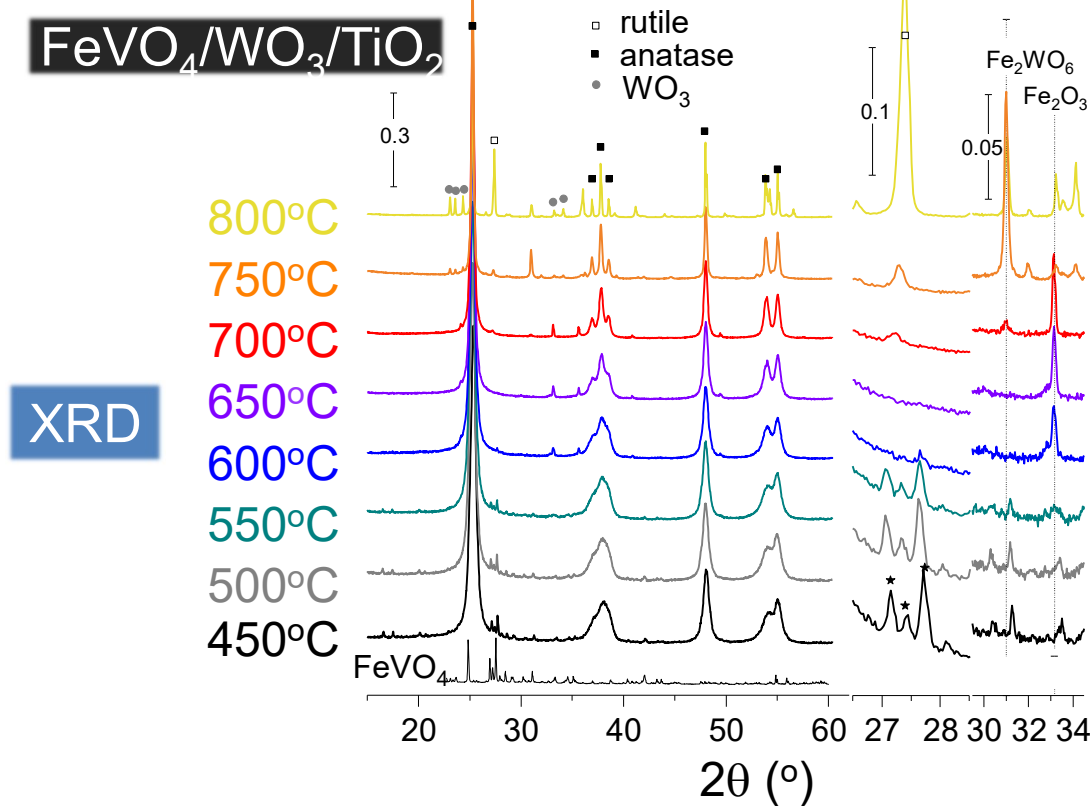


Phase composition



Phase composition

- Unsupported FeVO_4 stable up to 700°C
- The catalyst is obtained only after FeVO_4 decomposition

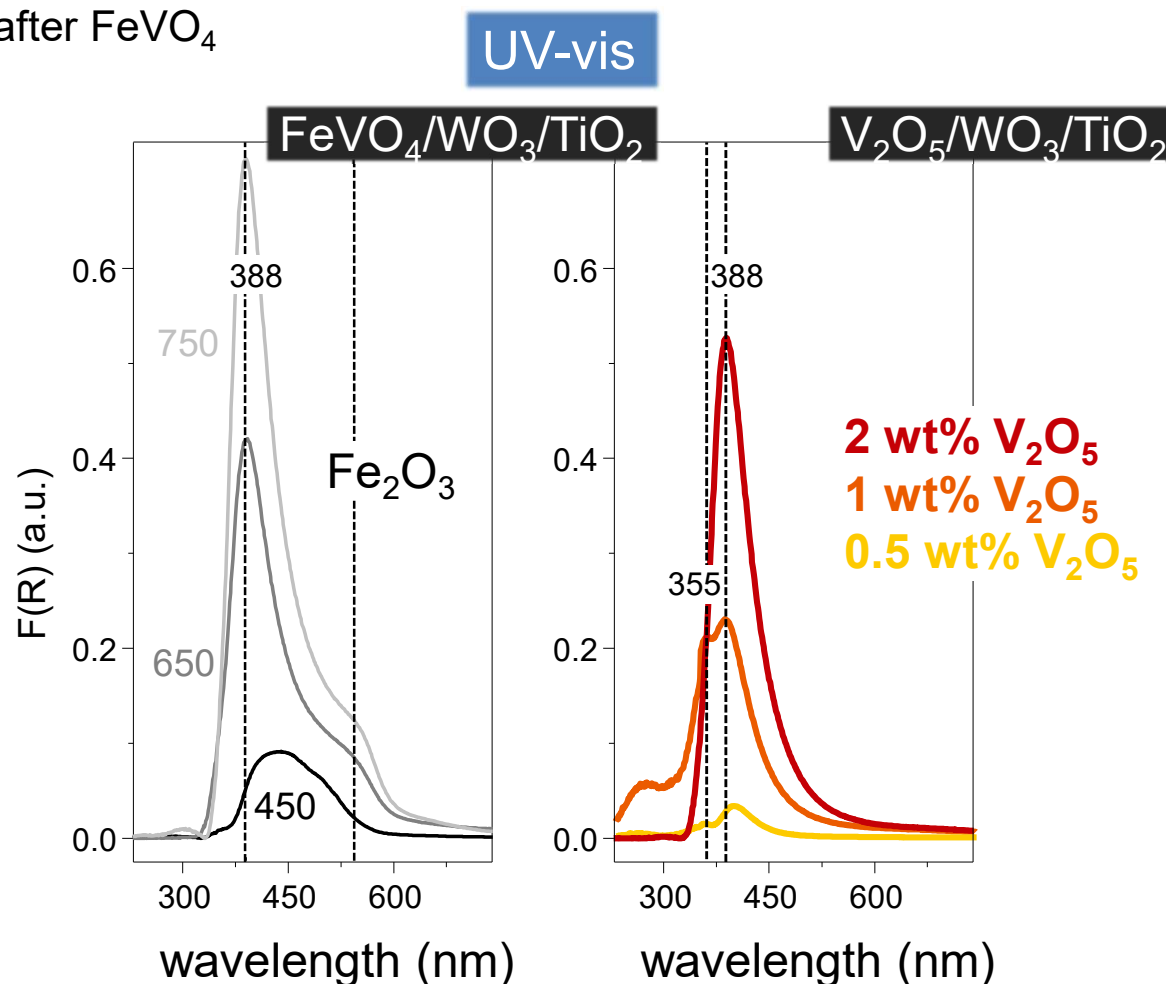


- What about Vanadium species?

Phase composition

- Unsupported FeVO_4 stable up to 700°C
- The catalyst is obtained only after FeVO_4 decomposition

- Fresh supported FeVO_4 :
no V_2O_5 species
- After heat treatment:
 V_2O_5 formation – 388 nm



similar VO_x species to ref. catalyst

XRD and TEM

XRD

- averaging over the whole sample
- limited to larger crystallites (> 3 nm)
- amorphous material invisible
- 3D distribution of d-spacings (but collapsed into 1D)
- usually no beam damage

TEM

- local
- limited to smaller crystallites (beam transparency required)
- amorphous material visible
- 2D projection of d-spacing
- beam damage possible

Synchrotron radiation

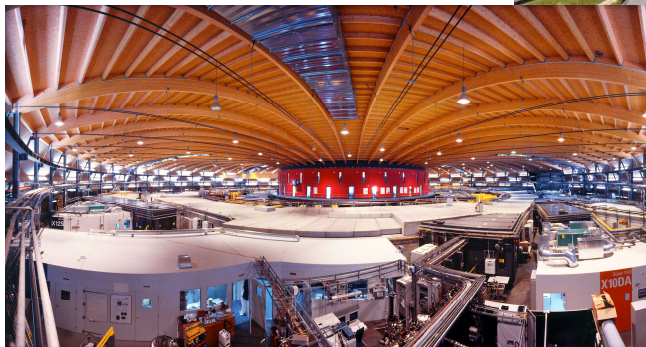
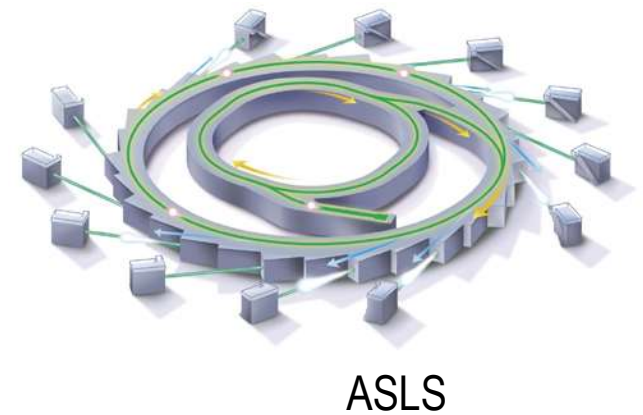
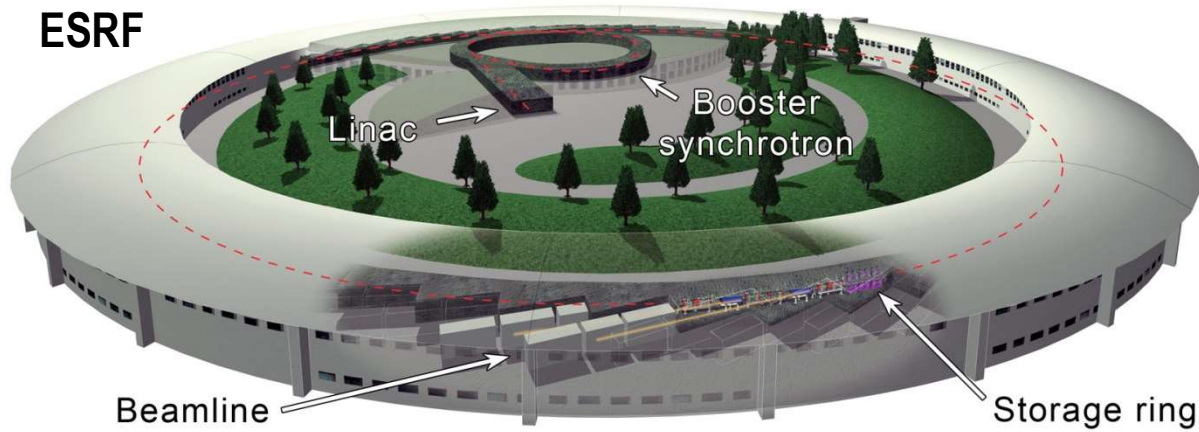
Synchrotron light is the electromagnetic radiation emitted when electrons, moving at velocities close to the speed of light, are forced to change direction under the action of a magnetic field.

The electromagnetic radiation is emitted in a narrow cone in the forward direction, at a tangent to the electron's orbit.

Properties

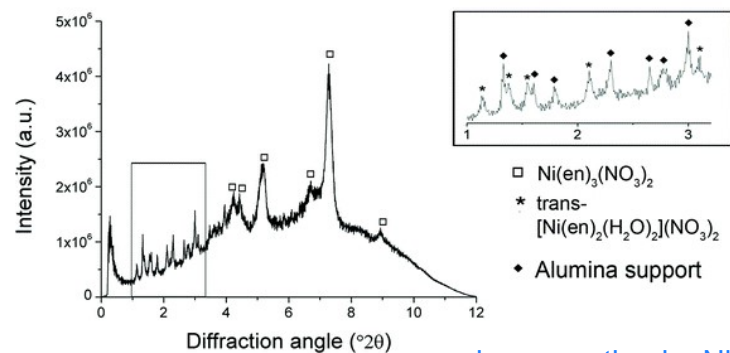
- **High brightness:** synchrotron light is extremely intense (hundreds of thousands of times more intense than that from conventional x-ray tubes) and highly collimated
- **Wide energy spectrum:** synchrotron light is emitted with energies ranging from infrared light to hard x-rays
- **Tunable:** it is possible to obtain an intense beam of any selected wavelength
- **Highly polarized:** the synchrotron emits highly polarized radiation, which can be linear, circular or elliptical
- **Emitted in very short pulses:** pulses emitted are typically less than a nano-second (a billionth of a second), enabling time-resolved studies

Synchrotron radiation

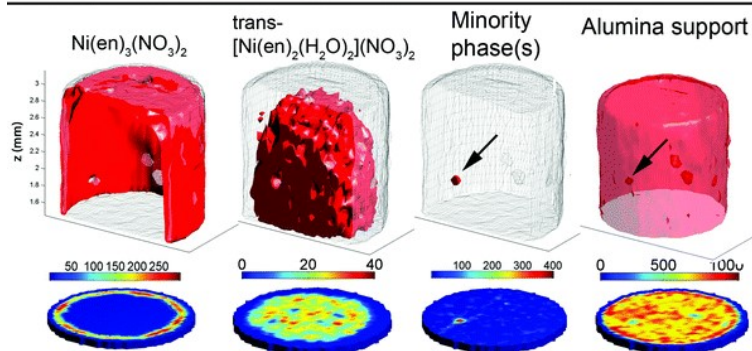


XRD | μ -Tomography of catalyst bodies

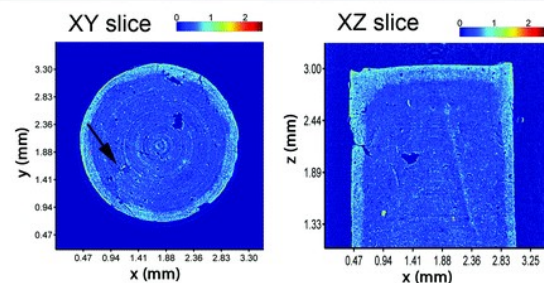
Summed 1D XRD



2D/3D μ -XRD-CT phase maps



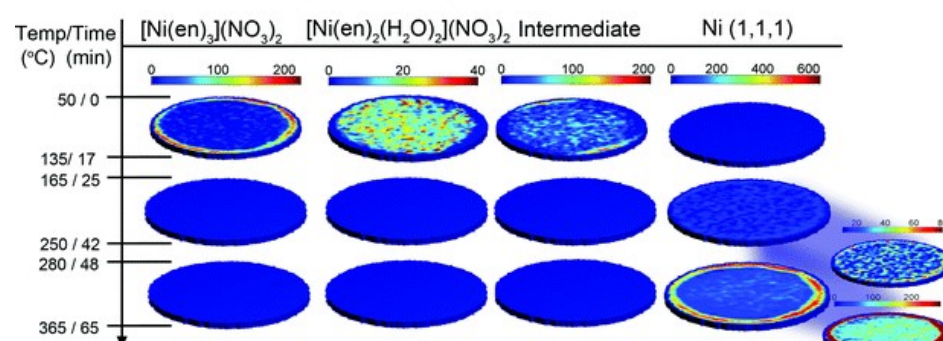
Absorption-CT



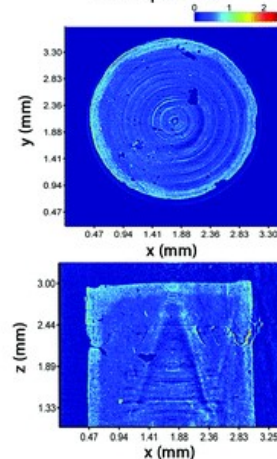
beam size: $50 \times 100 \mu\text{m}$
 pixel res.: $50 \mu\text{m}$
 Al_2O_3 pellet: $3 \times 3 \text{ mm}$

activation in N_2 flow

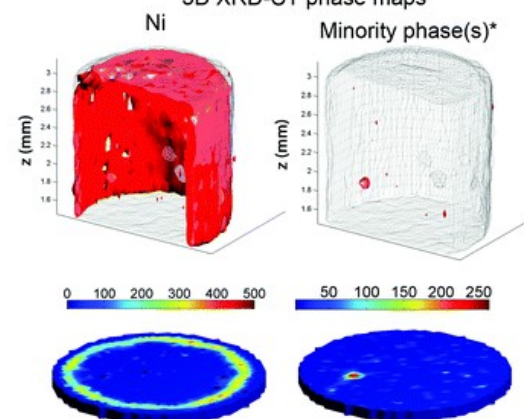
Time-resolved operando 2D XRD-CT phase maps



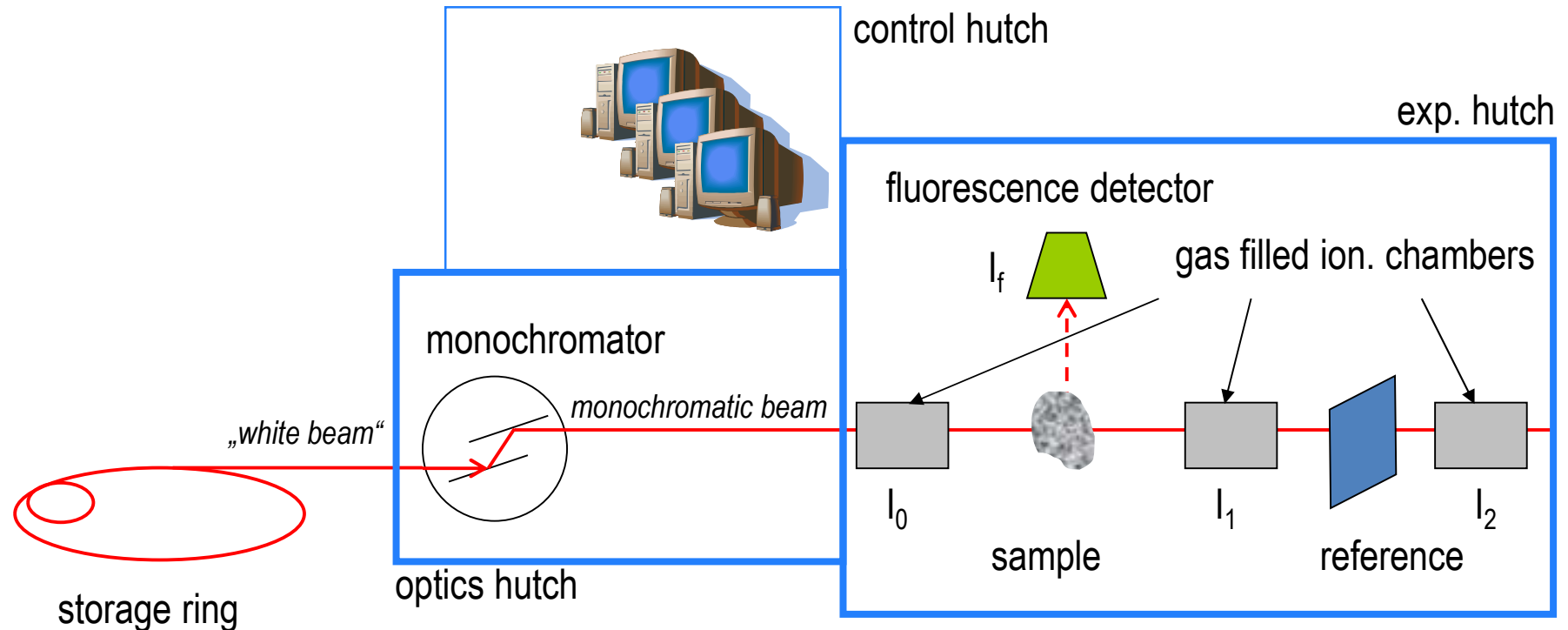
Absorption-CT



3D XRD-CT phase maps



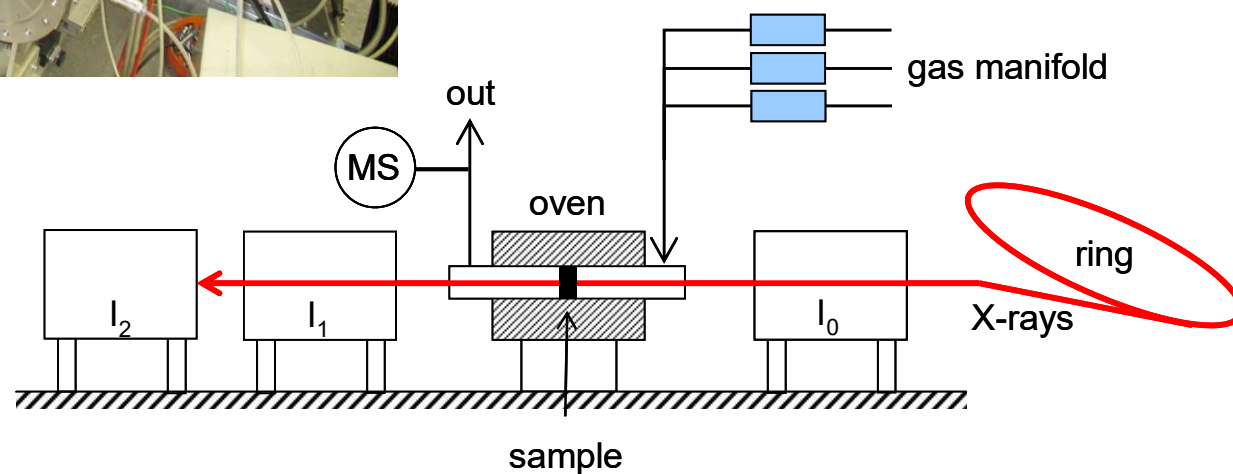
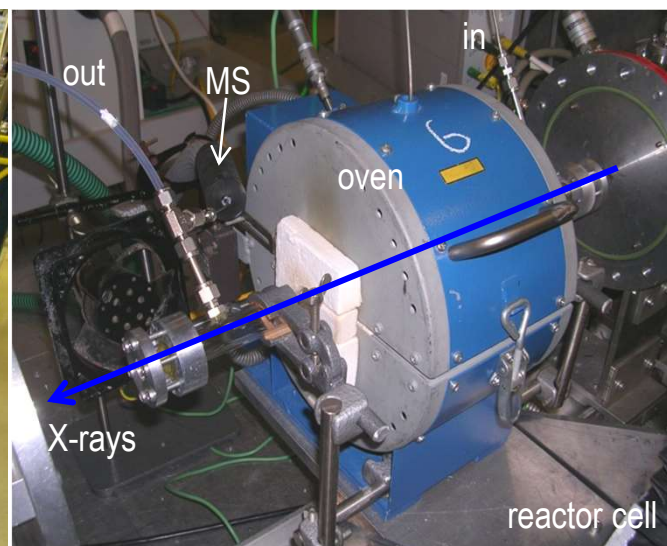
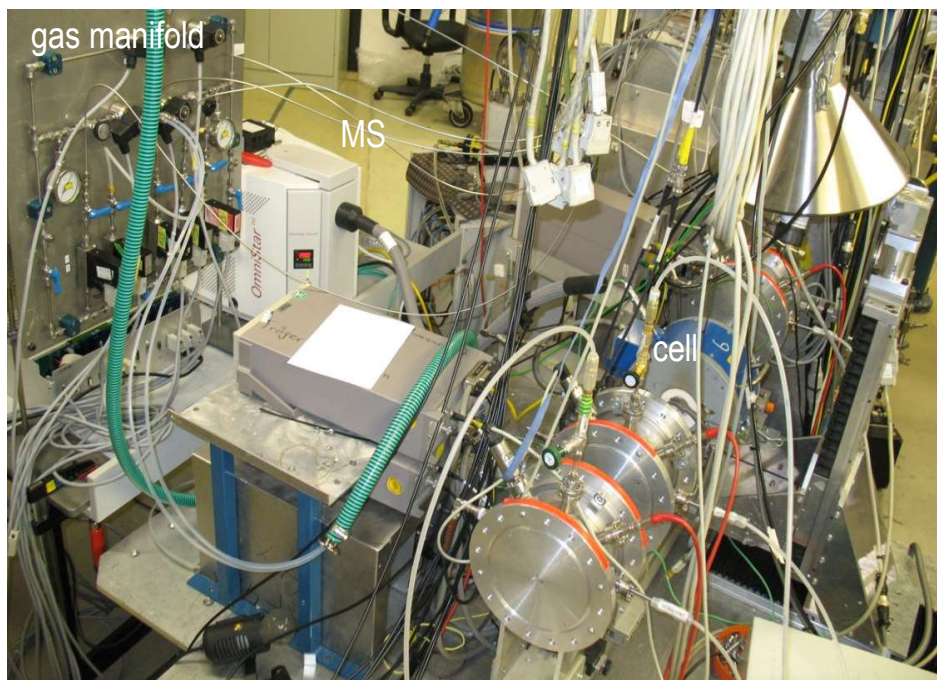
Simplified beamline layout



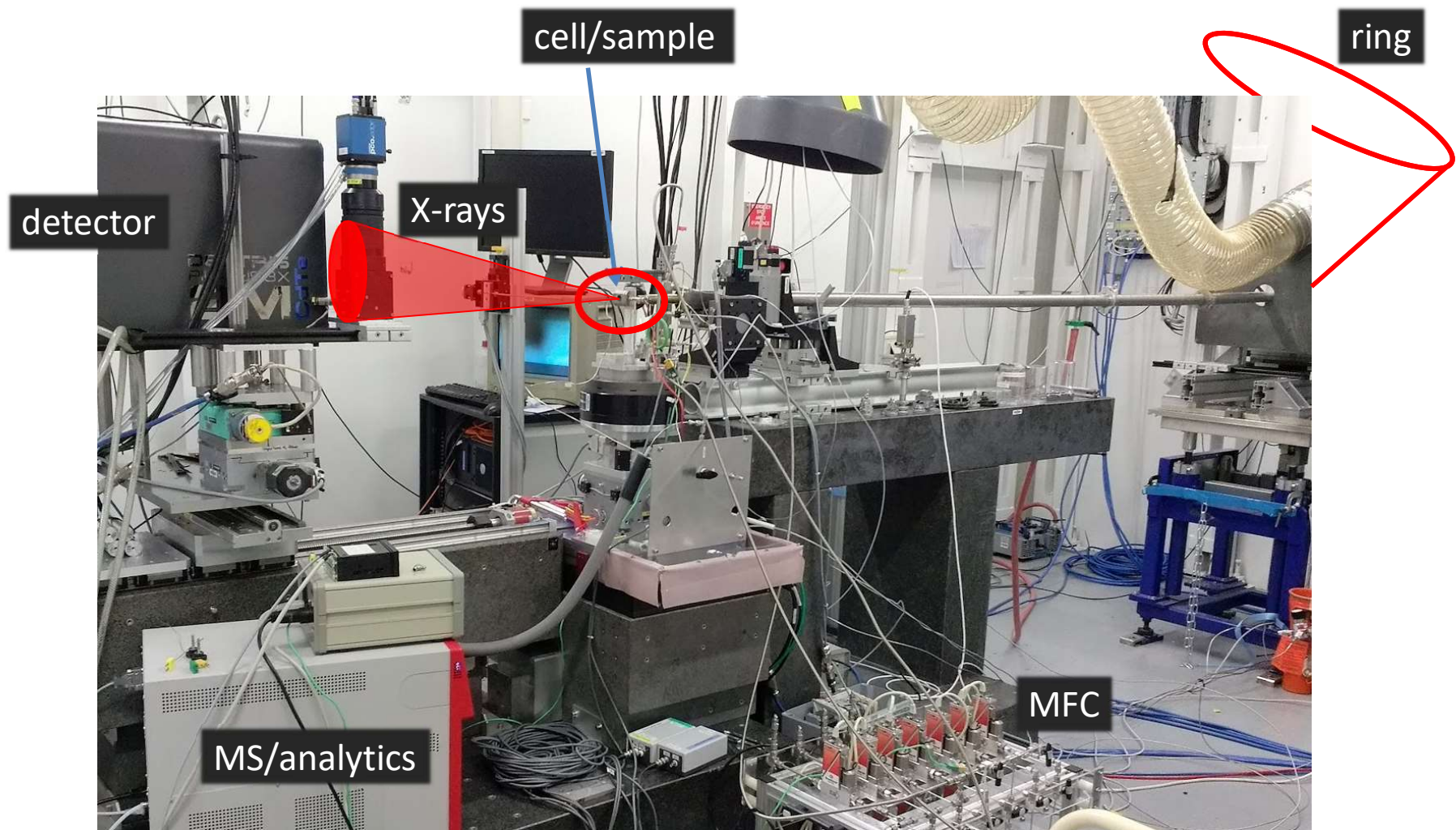
Some things to consider:

- which elements/edges → *energy range*
- absorption too high/low → *element concentration*
- kinetics of process → *time resolution*
- absorption of environment (reactor, gases)
- fluorescence detector is needed if the sample absorbs too much/too little
- measuring the reference (e.g. a metal foil) simultaneously allows for a precise energy calibration
- typically enough space around sample

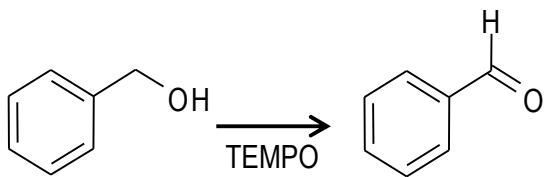
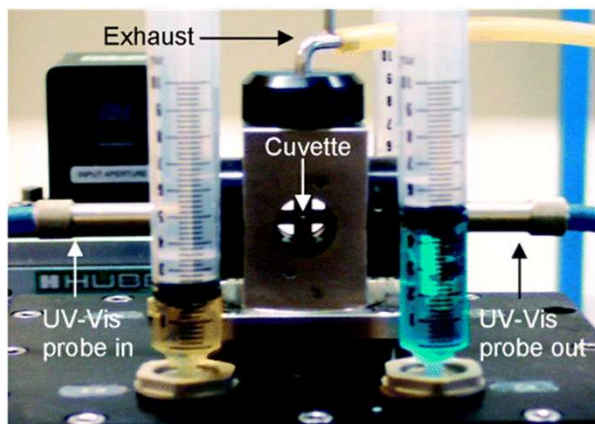
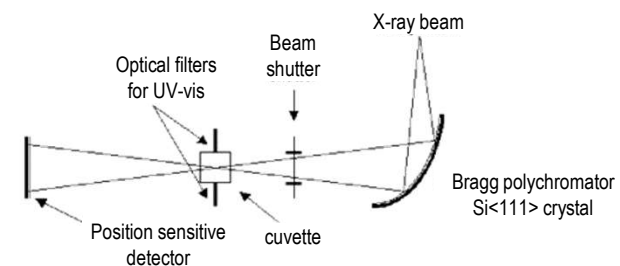
X-ray absorption spectroscopy



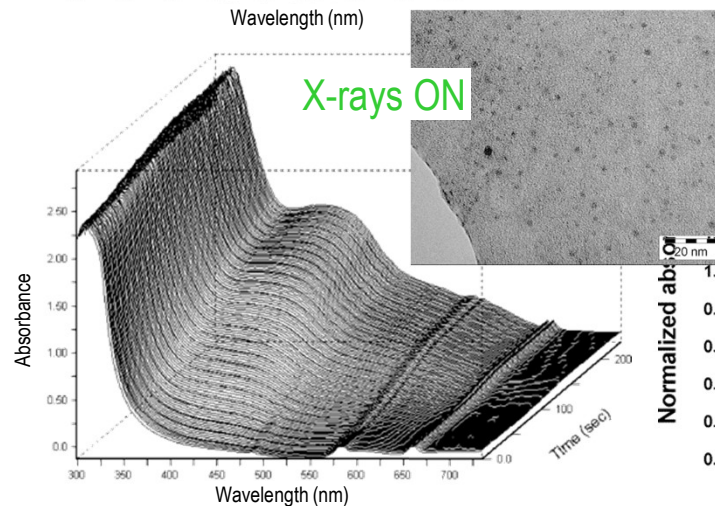
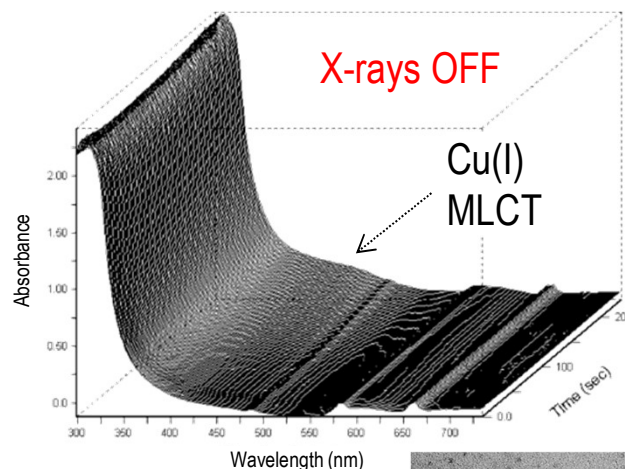
Time-resolved X-ray diffraction



Sample damage by X-rays

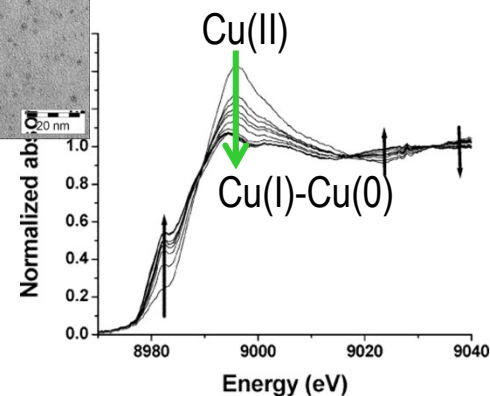


UV-vis



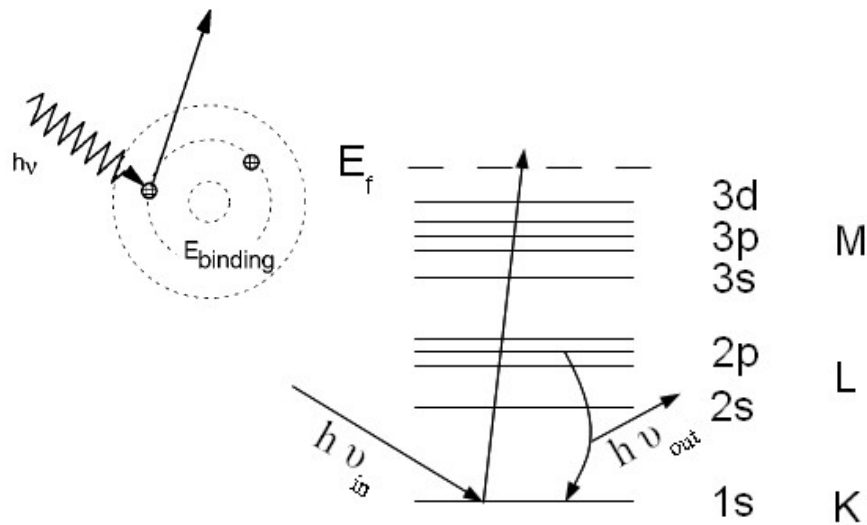
XANES

- CuBr₂/bipyridine, stable w/o X-rays
- **Cu(0) formed with X-rays**
- CuBr₂ and CuCl₂ sensitive to X-rays
- reducing effect of X-rays



CuBr₂/bipyridine, benzyl alcohol, TEMPO, TEAOH 1:1:1:1
NMP/H₂O 1:1; rt

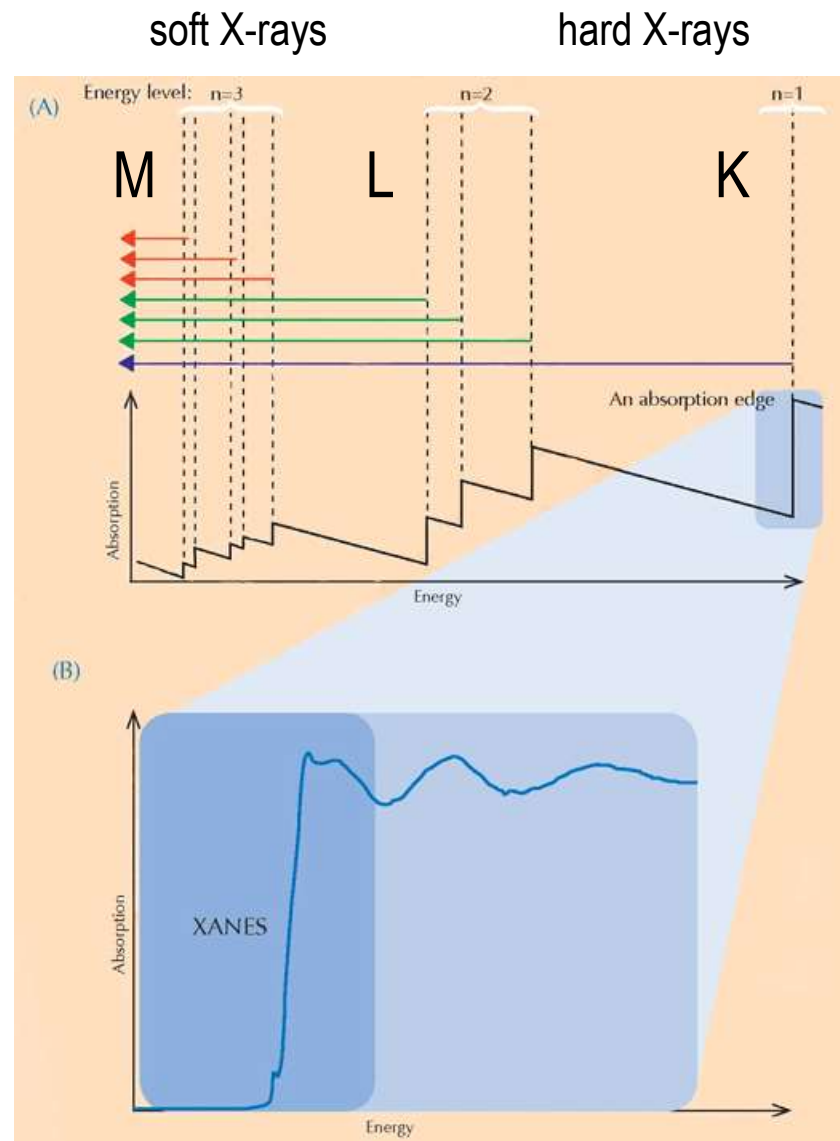
X-ray absorption spectroscopy



if energy of incoming photon matches binding energy of electron

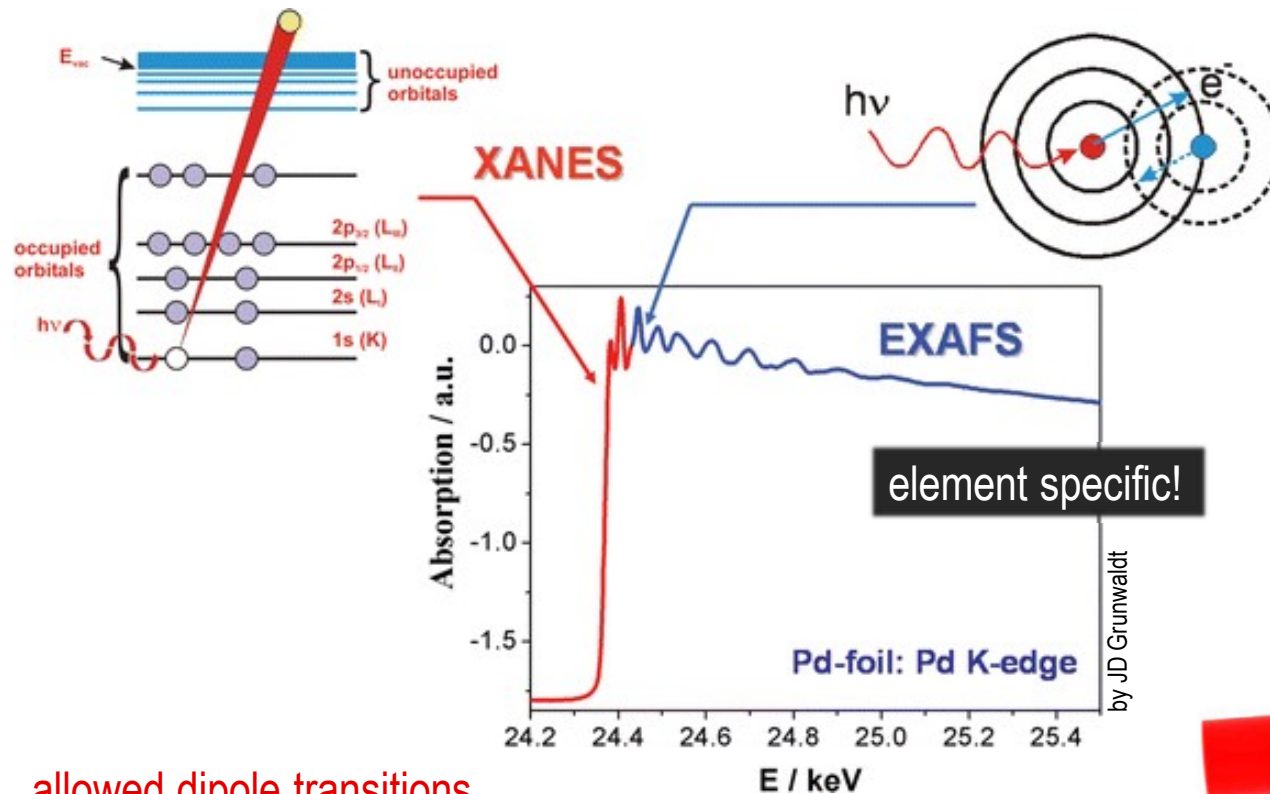
- photon is absorbed
- photoelectron is created
- photoelectron probes the environment

$$E_{kinetic} = E_{photon,in} - E_{binding}$$

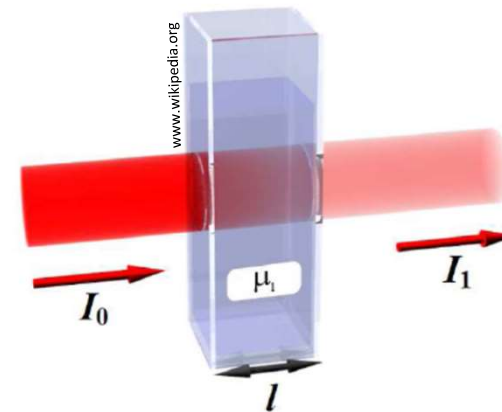


<http://www.scienceinschool.org/2011/issue19/vangogh/german/>; M Blank: Bildquelle; Wikimedia Commons;

X-ray absorption spectroscopy



Quantification possible:
Lambert-Beer law



allowed dipole transitions

K-edge $1s \rightarrow p$

L-edge $2s \rightarrow p$ and $2p \rightarrow s, d$

EXAFS single (+multiple) scattering

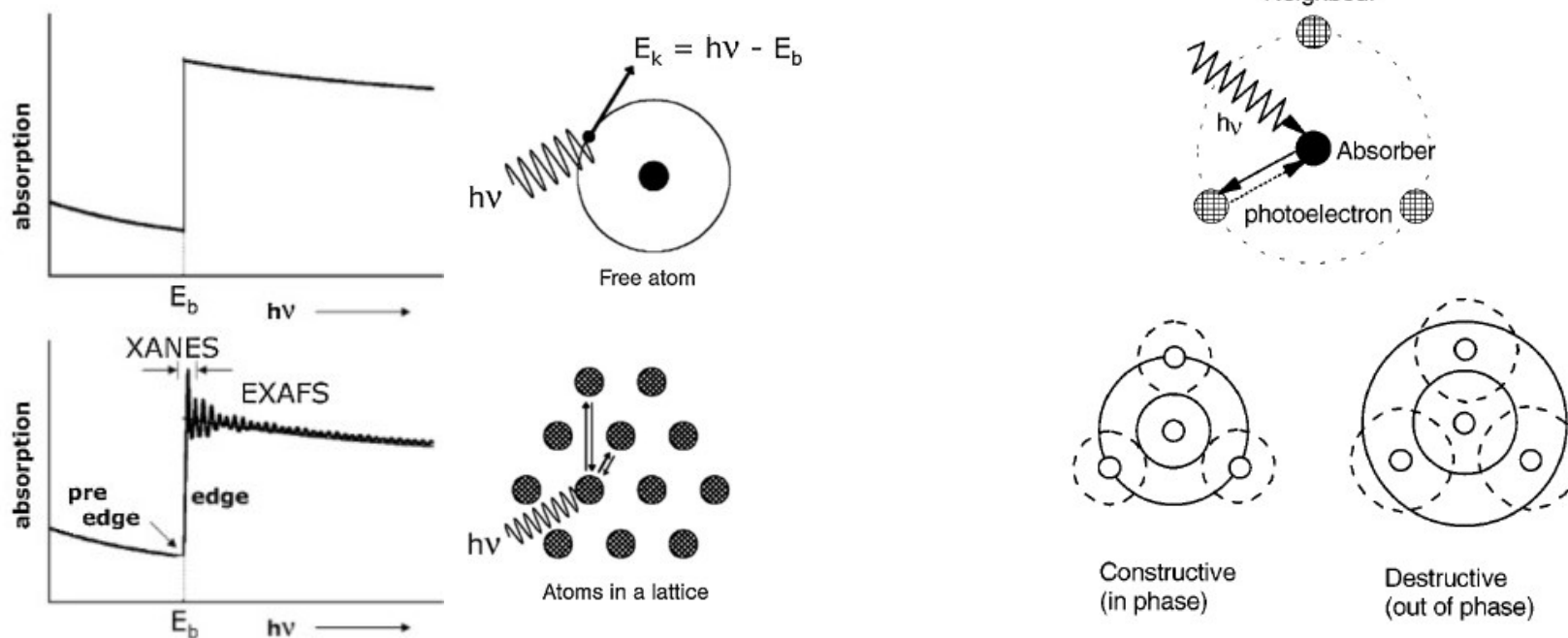
XANES multiple scattering+electronic transitions

$$I(l) = I_0 e^{-\mu_l l} \quad \mu: \text{absorption coefficient}$$

X-ray absorption spectroscopy

There is a difference in the absorption spectrum between a gas and a solid/liquid sample

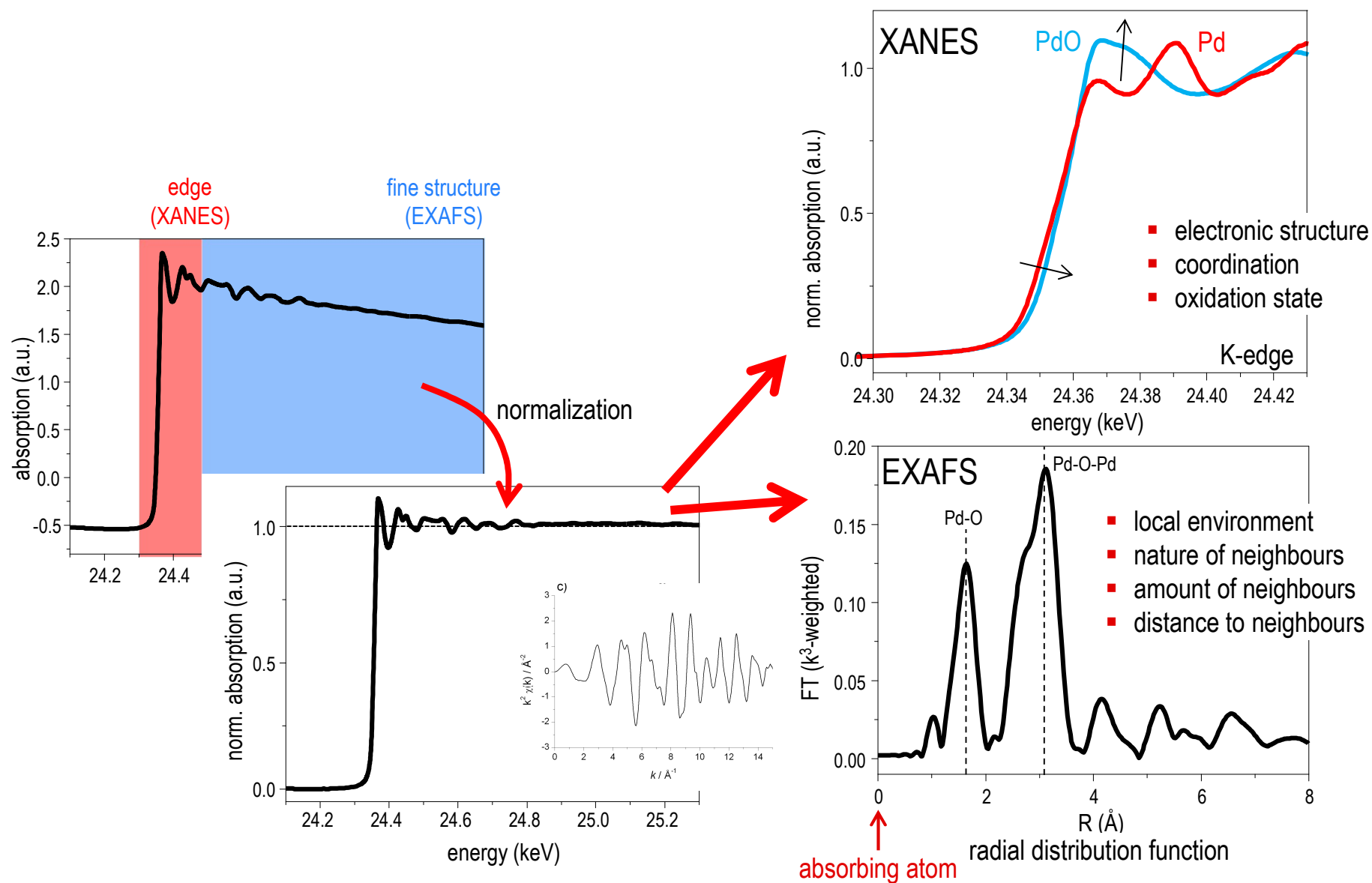
- gas: photon hits sample, photoelectron is emitted, no interference
- solid matter (not necessarily crystalline): photoelectron is scattered back on neighbouring atoms, it interferes with absorbing atom



Koningsberger, *Top. Catal.* 2000

courtesy Dr. König

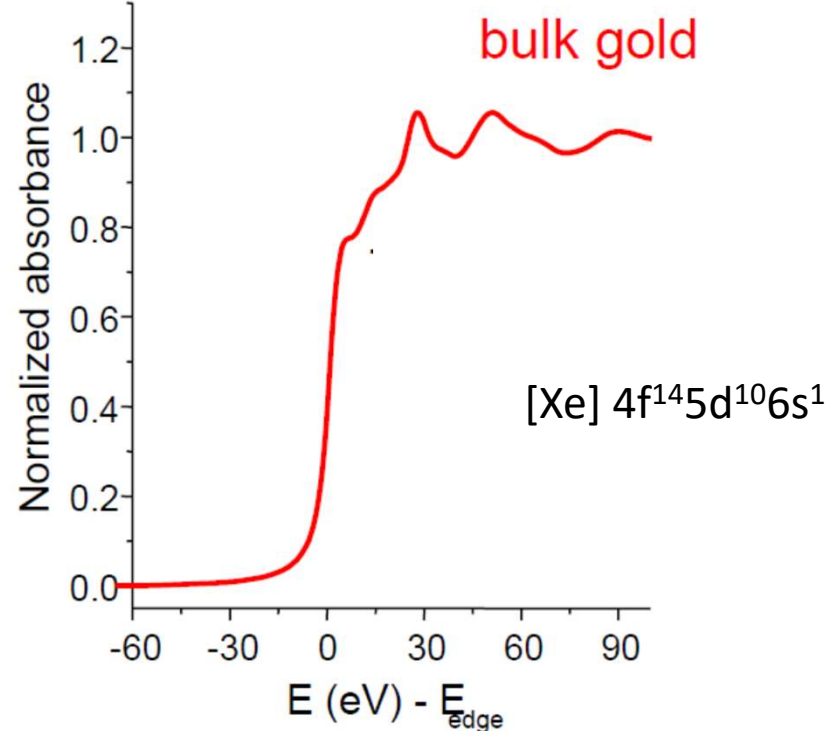
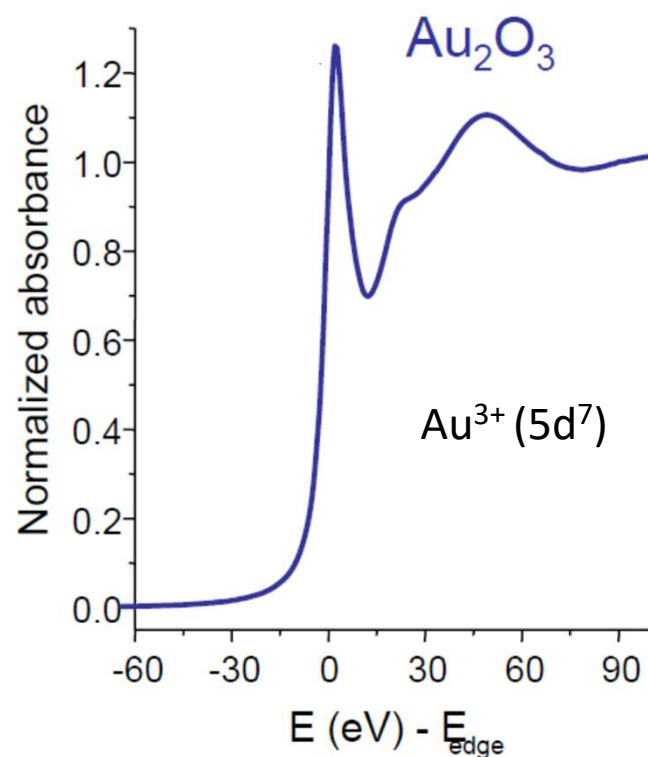
X-ray absorption spectroscopy



X-ray absorption spectroscopy

- Shape of XANES spectra: intensity of whiteline (L-edge)

Au L₃-edge (11.919 keV)



whiteline reflects holes in d-band → unoccupied d orbitals

X-ray absorption spectroscopy

EXAFS equation

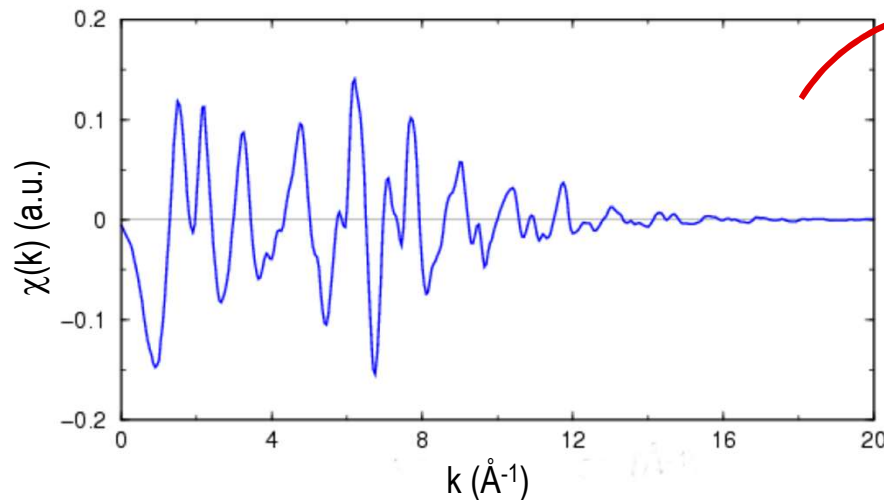
$$\chi(k) = \mu(E) - \mu_0(E) / \mu_0(E_0)$$

$$\chi(k) = \sum N_i F_i(k) S_0^2 / R_i^2 \exp(-2R_i/\lambda) \exp(-2\sigma_i^2 k^2) \sin(2kR_i + \phi(k))$$

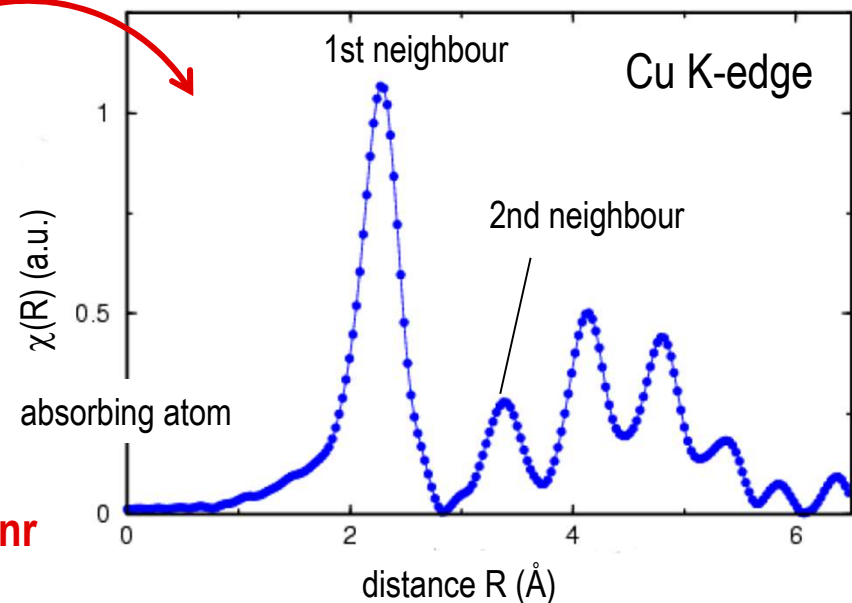
scatter power damping disorder

- EXAFS signal $\chi(k)$ is sum of sin functions
- FT changes $\chi(k)$ into the space domain (**bond distances**)

- μ , absorption coefficient
- μ_0 , atomic absorption coefficient
- E_0 , edge energy
- N , number of scattering atoms
- F , scattering amplitude
- S_0 , passive electron reduction factor
- R , interatomic distance
- λ , mean free path
- σ^2 , Debye-Waller factor
- ϕ , phase shift
- k , photo-electron wave function



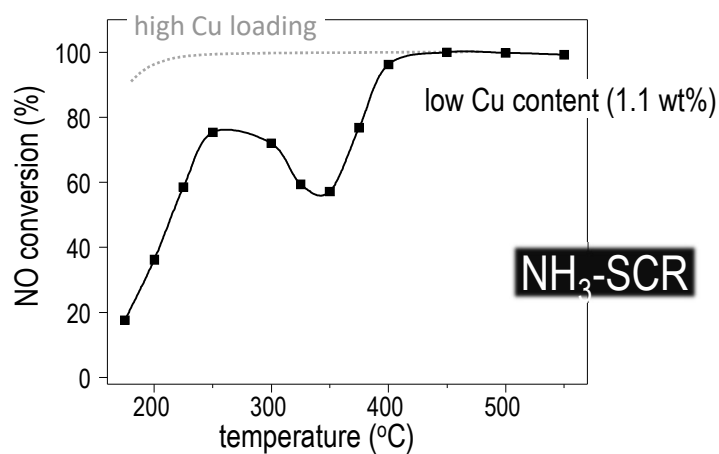
FT



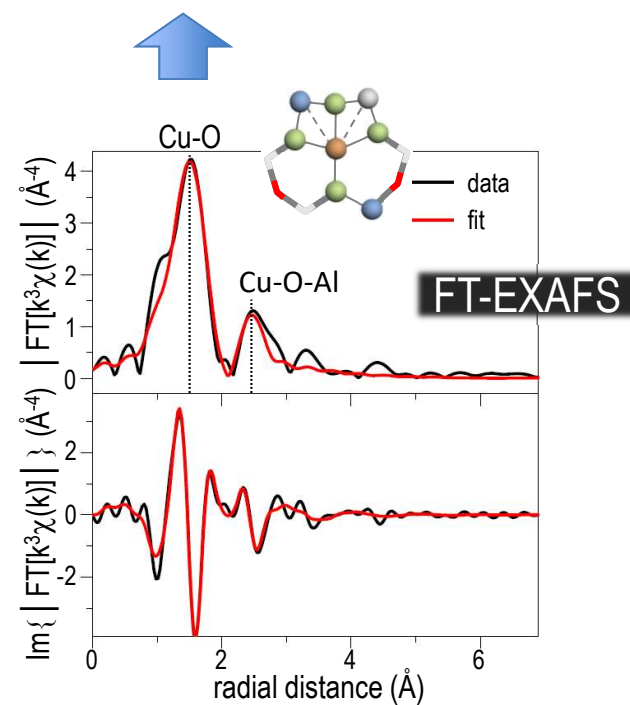
- Quantification: **bond distances/coordination nr**

Example

- NH_3 -SCR on Cu-SSZ13
- Low Cu content, Si/Al= 14 and Cu/Al= 0.17
- Well dispersed Cu ions



compare with spectra of references
e.g. CuO, Cu₂O, supported CuO and inorganic compounds

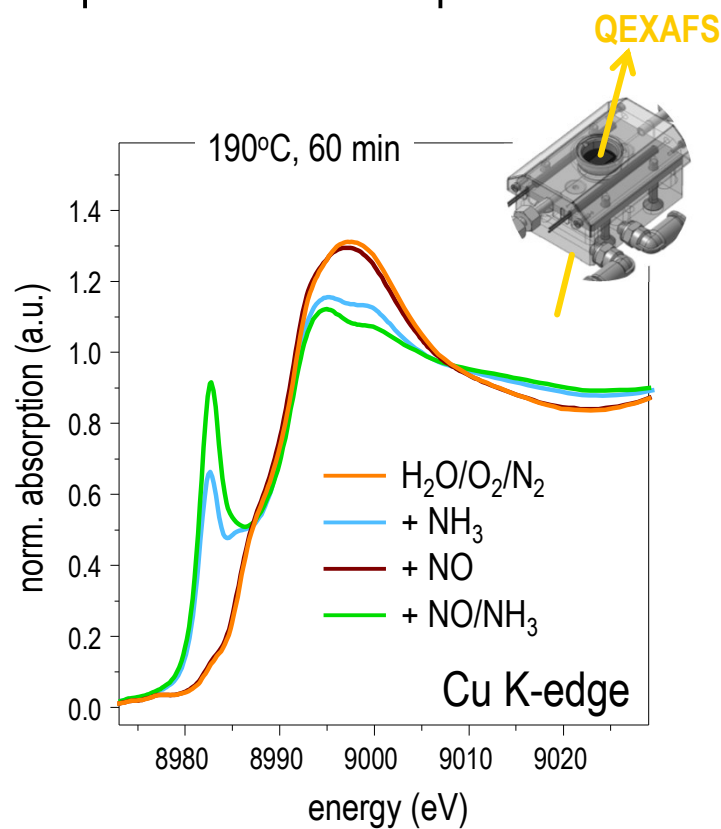


500 ppm NH_3 + 500 ppm NO , 10 vol% O_2 , 6 vol% H_2O , bal. N_2 ; 50,000 h^{-1}
Marberger et al., *Nat. Catal.* 1 (2018) 221

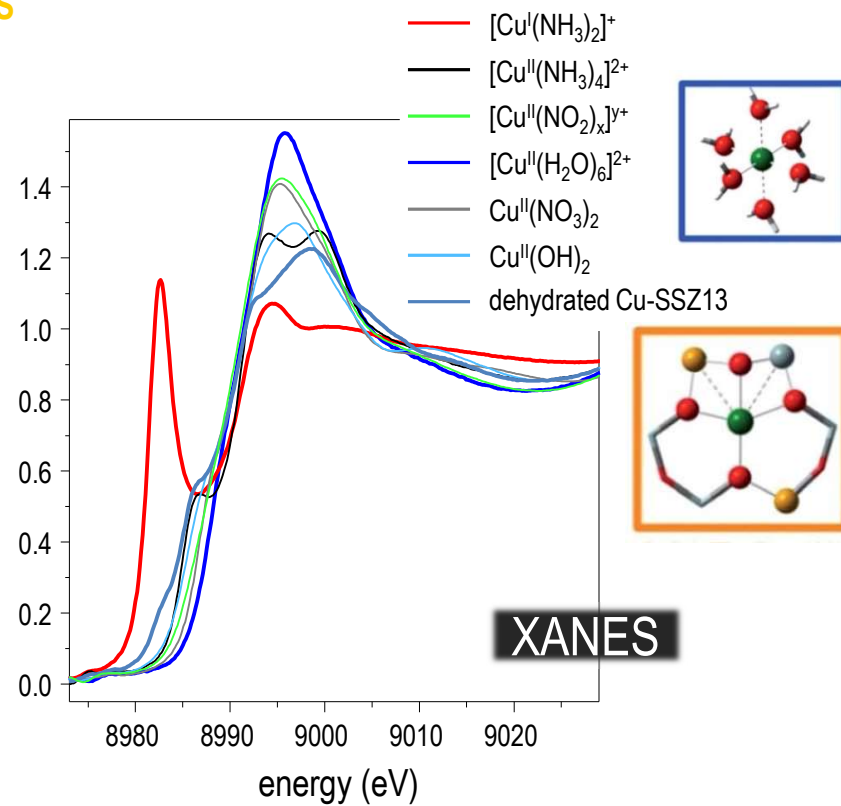
Example

- NH_3 -SCR on Cu-SSZ13
- Choice of reference compounds

operando XANES spectra

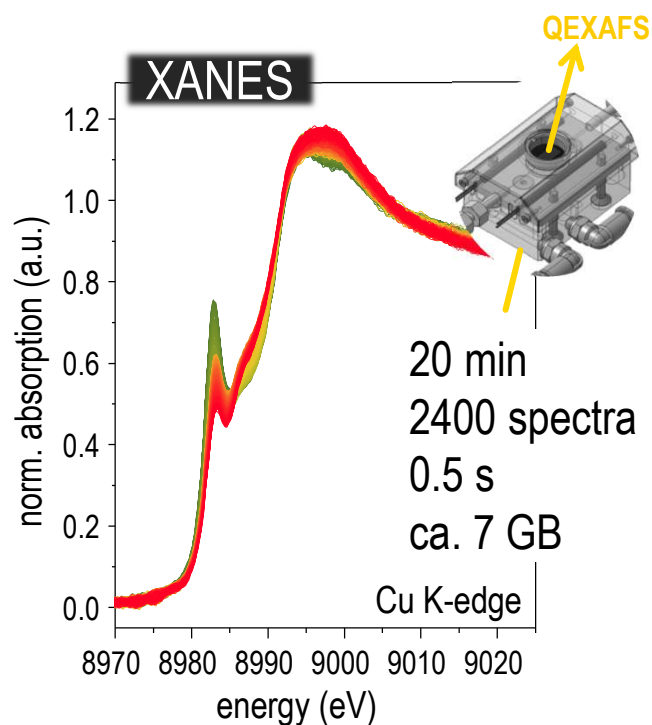


spectra of tentative references



Example

- NH_3 -SCR on Cu-SSZ13
- Operando experiment, single transient

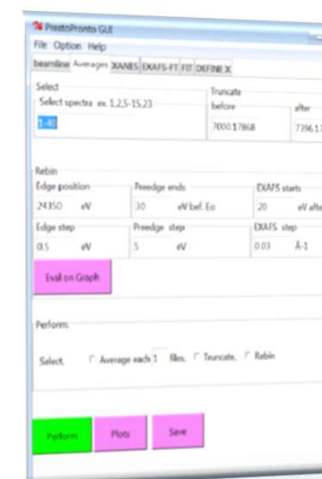


linear
combination
fit (LCF)
subject to
intuition

SuperX^{OS}



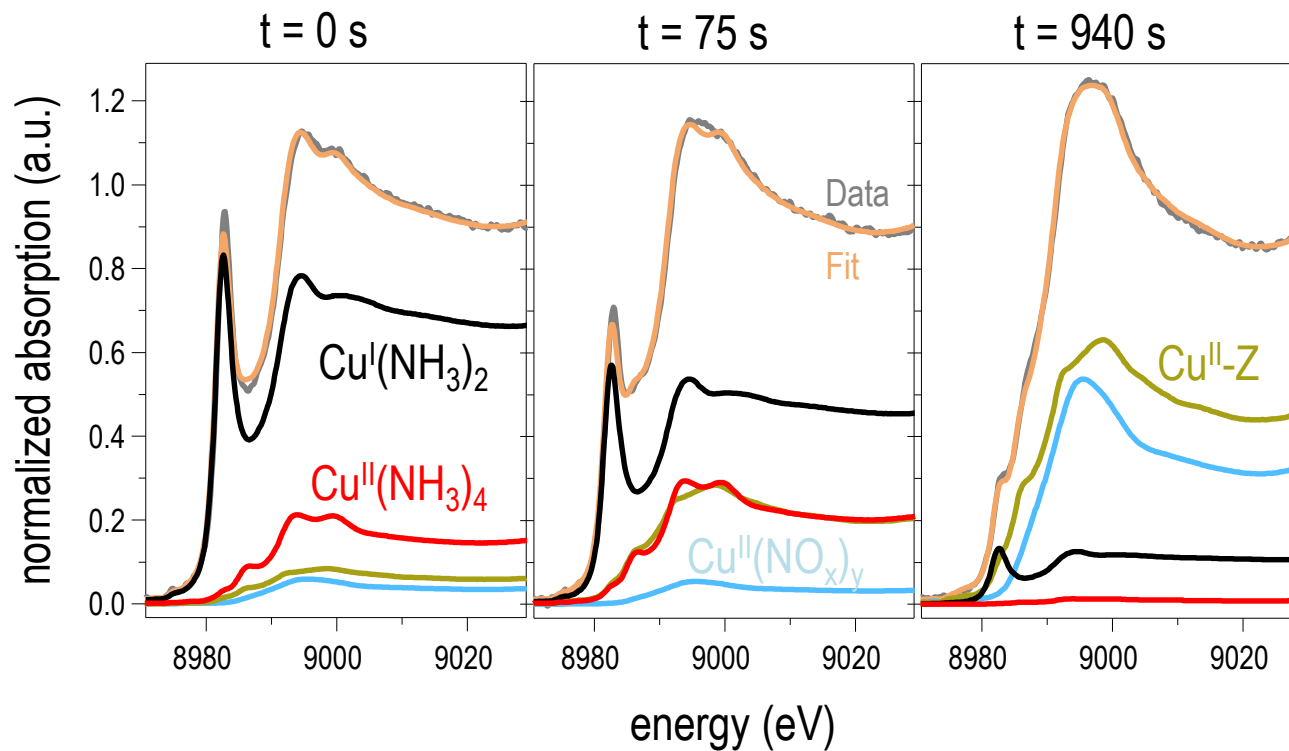
Athena XAS
data processing...



500 ppm NH_3 + 500 ppm NO, 10 vol% O_2 , 6 vol% H_2O , bal. N_2 ; 50,000 h^{-1}
Marberger et al., *Nat. Catal.* 1 (2018) 221

Example

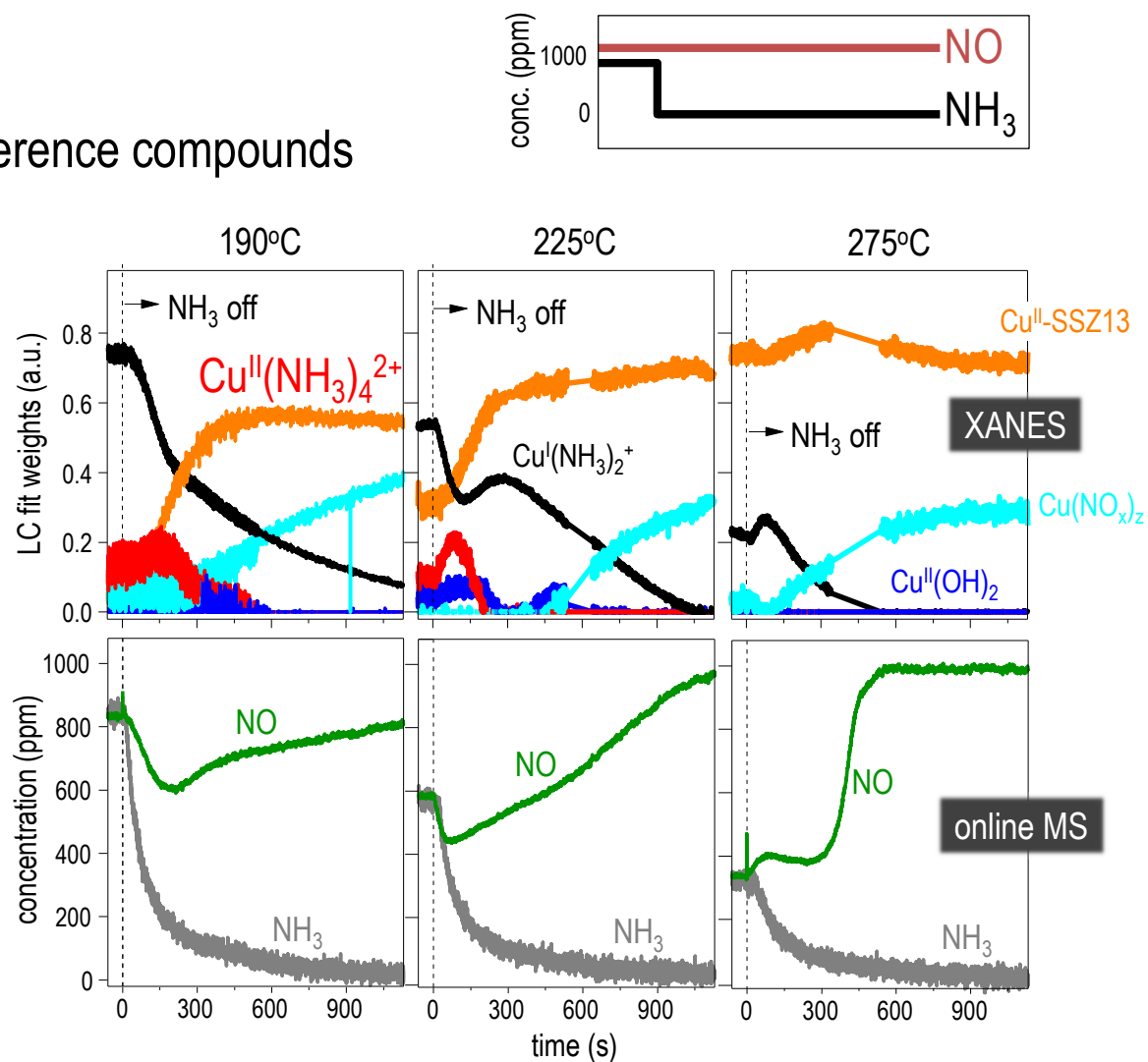
- NH_3 -SCR on Cu-SSZ13
- Linear combination fit of spectra of predefined reference compounds



Example

- NH_3 -SCR on Cu-SSZ13
- LCF of spectra of selected reference compounds

- time resolution enables following precisely evolution of species
- transient exp enables seeing behaviours not visible in steady state



XRD and XAS

XRD

- analysis of **long range** order
- limited to crystalline material
- not element specific
- distinguishes different crystallographic sites
- averages over different elements on the same crystallographic site
- distinguishes different (crystalline) phases
- BOTH: carefully planning of experiments necessary for synchrotron use

EXAFS

- analysis of **short range** order
- both crystalline and amorphous material
- element specific
- averages over different sites (for the same element)
- distinguishes different elements on the same crystallographic site
- averages over different phases (containing the same element)