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Wir schaffen Wissen – heute für morgen

Time-resolved X-ray absorption and emission spectroscopy for determining the dynamic geometric and electronic structure of functional materials

Maarten Nachtegaal

- In situ X-ray spectroscopy group (IXS), laboratory for bioenergy and catalysis (LBK)/ENE
- SuperXAS beamline, laboratory for catalysis and sustainable chemistry (LSK)/SYN
- Department of environmental system science ETHZ

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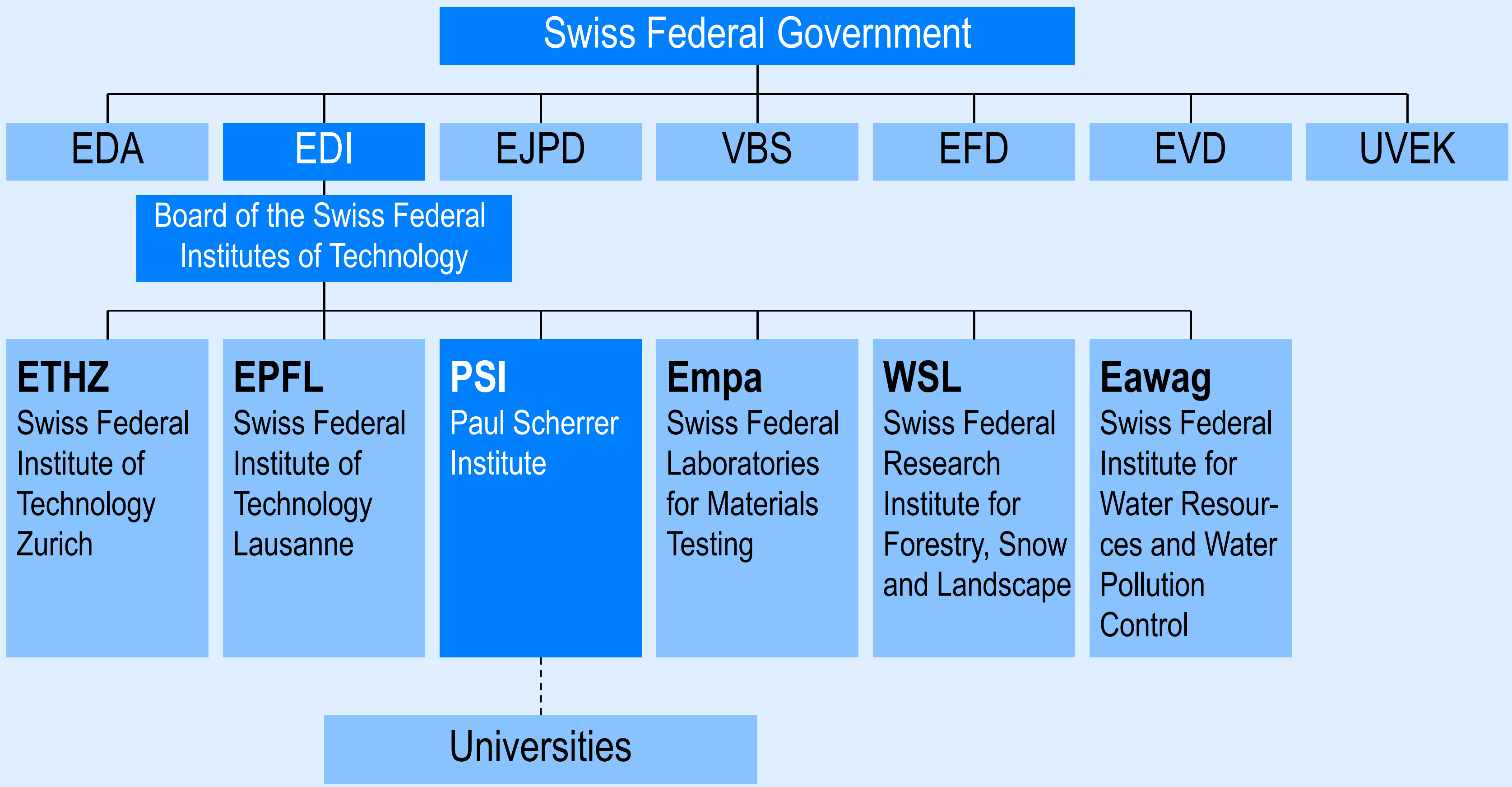
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Empa Swiss Federal Laboratories for Materials Testing
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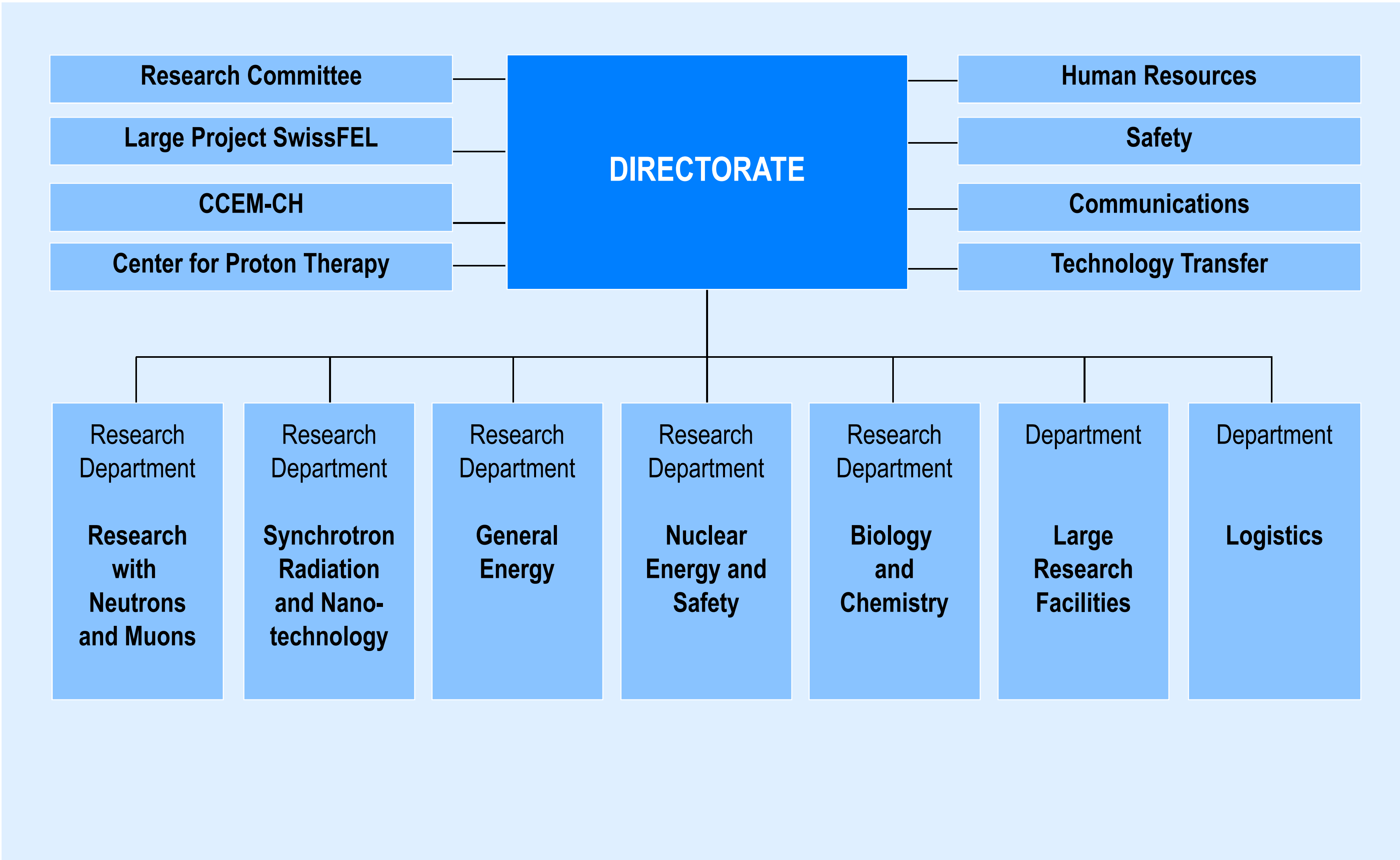
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Questions addressed today:

- Why is time resolution (Quick EXAFS) important in environmental chemistry?
- How is time resolution achieved? (technical details)
- What is x-ray emission spectroscopy? (RXES, RIXS, HEROS, valence to core XES, etc.)
- Quick XES examples
- Quick XAS examples

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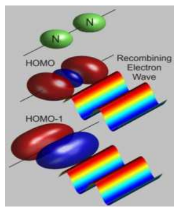
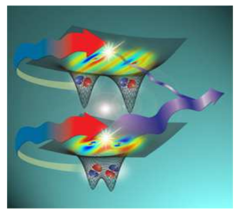
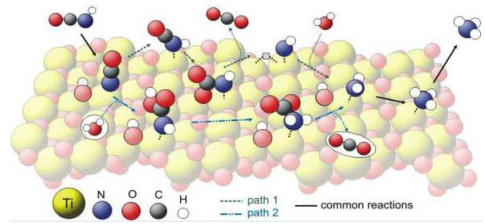
Setting the stage

Heterogeneous catalysis from atoms to particles



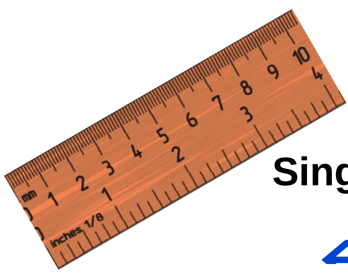




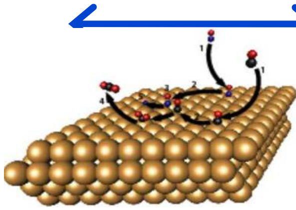
Fundamental **Applied**

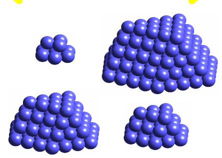
10^{-18} 10^{-15} 10^{-12} 10^{-9} 10^{-6} 10^{-3} 1 10^{3} s

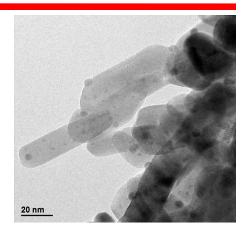
Bond breaking/ formation **Reaction kinetics** **Stability, deactivation**

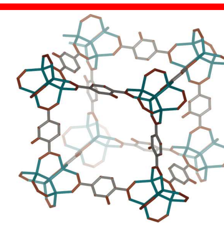


Single crystals · · · clusters · · · supported metals · · · single site catalysts · · · reactors









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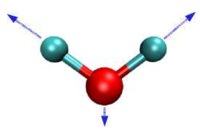
Timescales

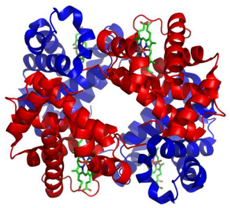
attoseconds 10^{-18} s	femtoseconds 10^{-15} s	picoseconds 10^{-12} s	nanoseconds 10^{-9} s	microseconds 10^{-6} s	milliseconds 10^{-3} s
electron motion core-hole lifetimes	motion of nuclei molecular vibrations optical phonons molecular bond formation	rotation of molecules molecular librations vibrational dephasing	electronic relaxation fluorescence thermal effects	large-scale protein motion phosphorescence	protein folding chemical kinetics

The Fe K-edge core-hole lifetime is 4 fs

period of the symmetric stretch in H_2O is 10 fs



Hemoglobin R->T transition takes microseconds

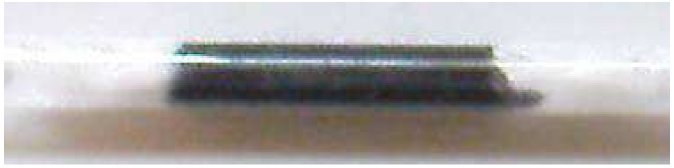


Camera shutter speeds range from ms through to seconds

Chemical kinetics

Plug flow reactor

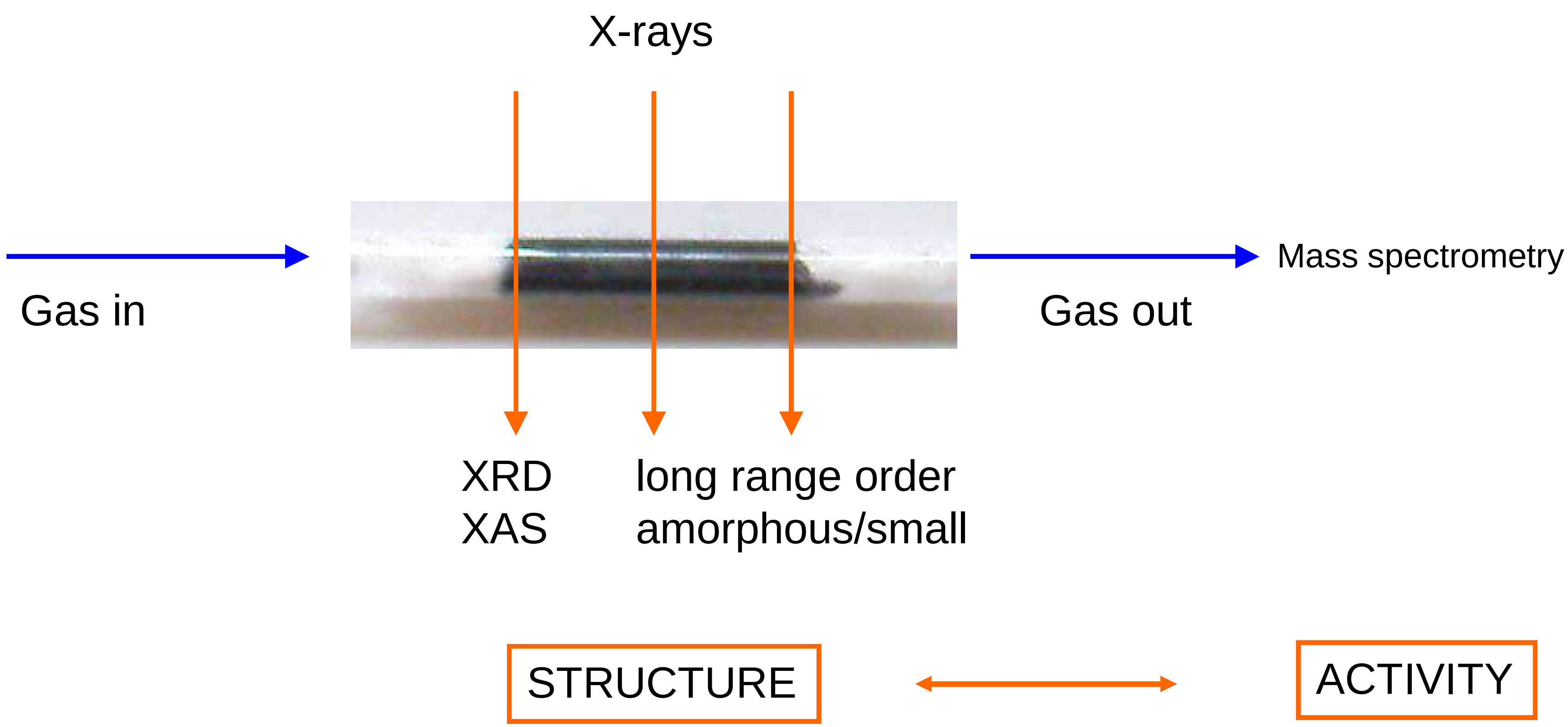
Gas in



Gas out

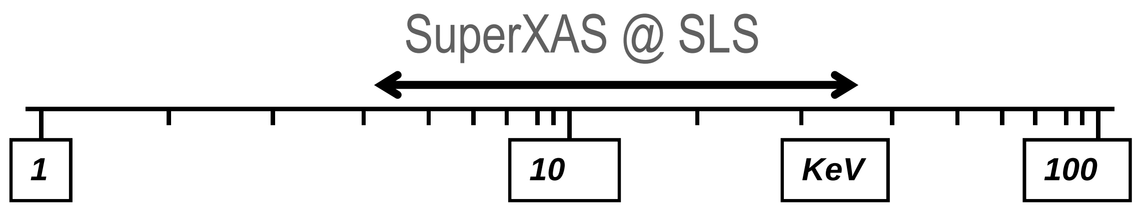
Mass spectrometry

Spatially resolved, chemical kinetics



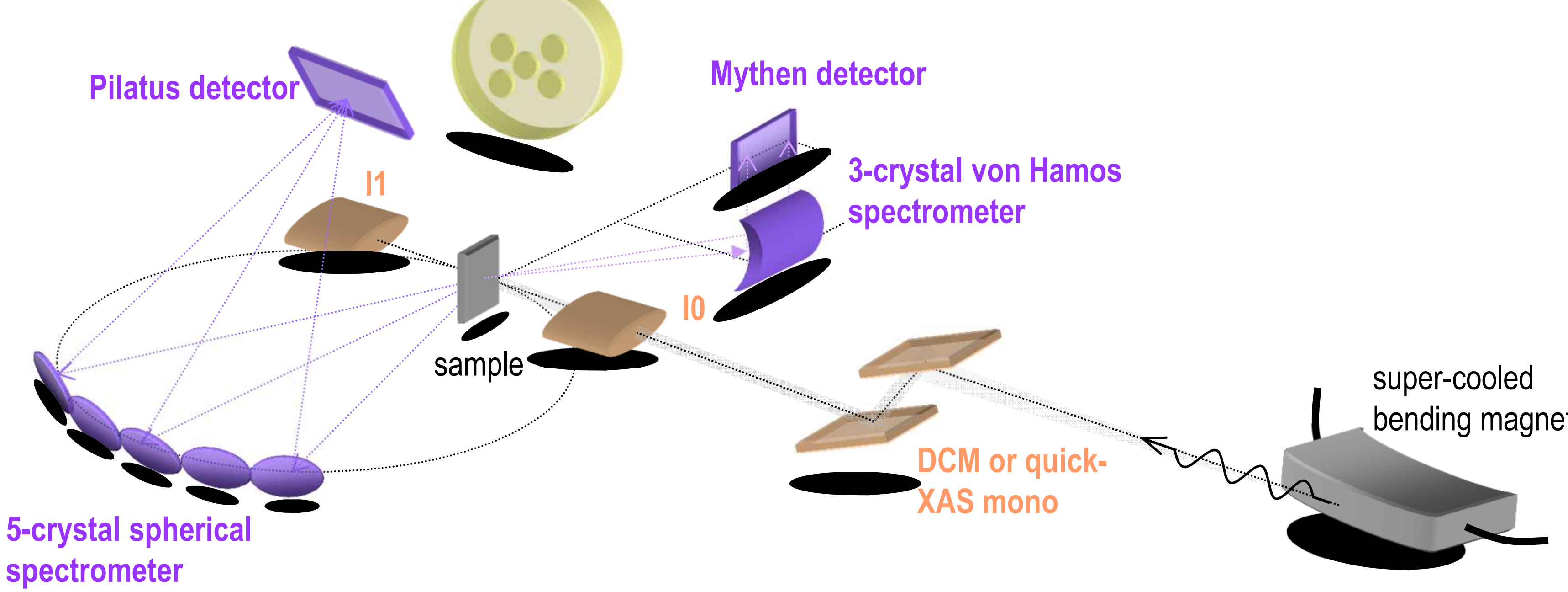
Challenges:
- Time resolution
- Space resolution
- Sensitivity (energy resolution)

In-situ X-ray absorption & X-ray emission spectroscopy



Key points:

- ✓time resolution (~msec)
- ✓sensitivity (~ppm)
- ✓high energy resolution (~eV)



State-of-the-art XAS and XES at SuperXAS

Multi-modal detection

fluorescence detected XAS/XES

5 element SDD detector

- high sensitivity
- Low detection limits

time resolved XAS

quick-XAS monochromator

- msec time resolution
- Fluo und trans. XAS

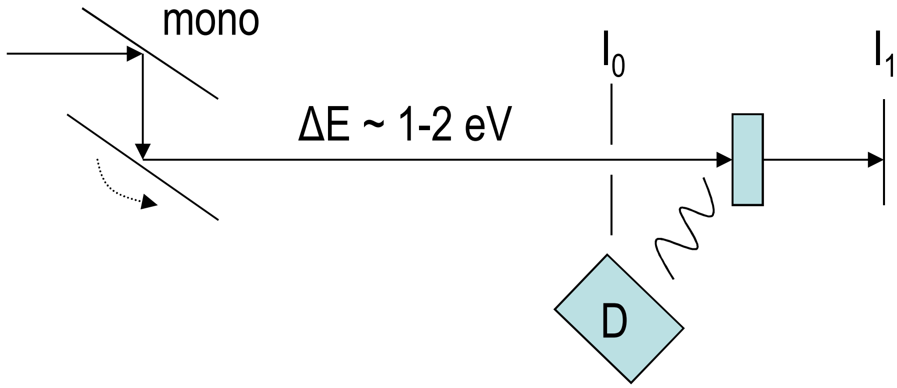
high resolution XAS/XES

5 crystal spectrometer

- sub eV energy resolution
- HERFD XAS

Time resolved XAS: below 1 second

QEXAFS

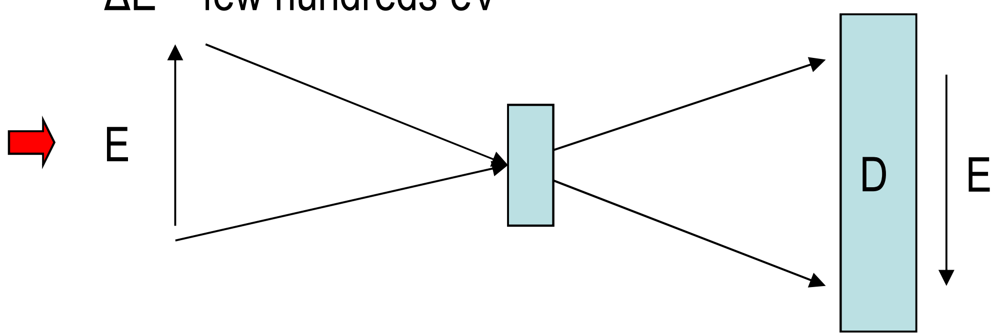


- I_0 control
- time limited to > ms (detector/flux)

stable x-ray source

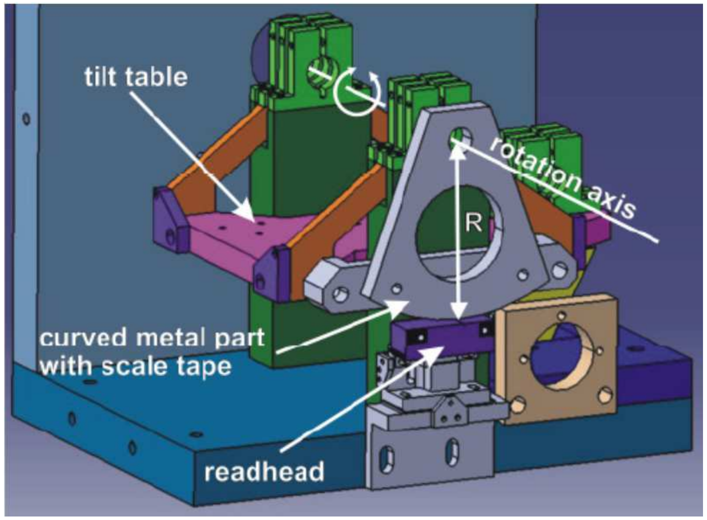
Energy dispersive-XAS

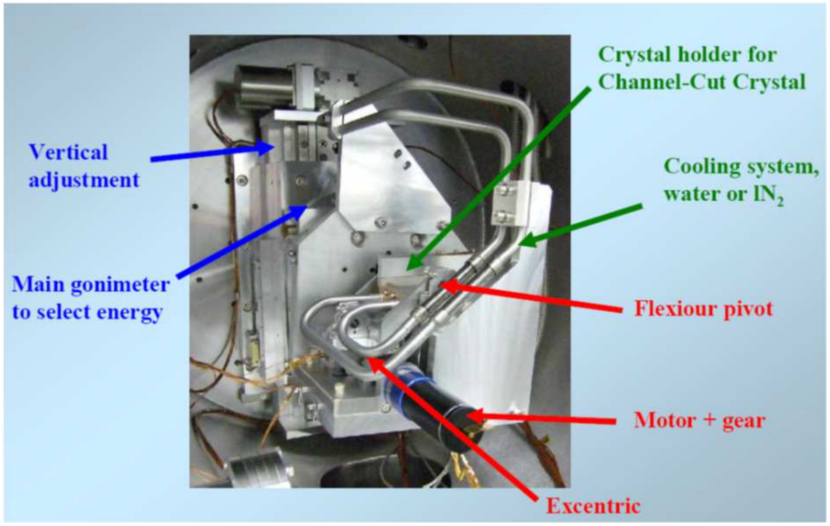
ΔE ~ few hundreds eV

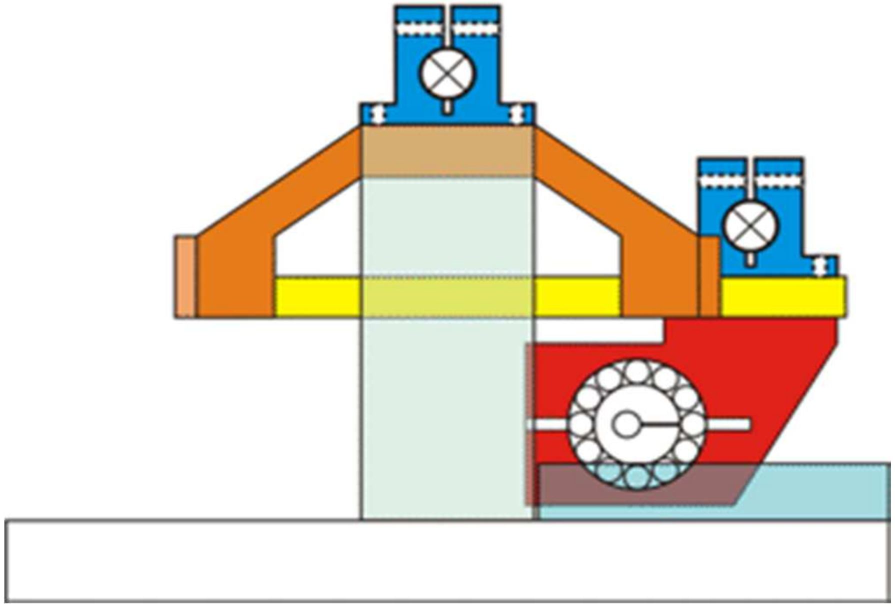


- Time limited to <ms (detector/flux)
- I_0 control impossible
- requires very stable beam
- only transmission mode possible

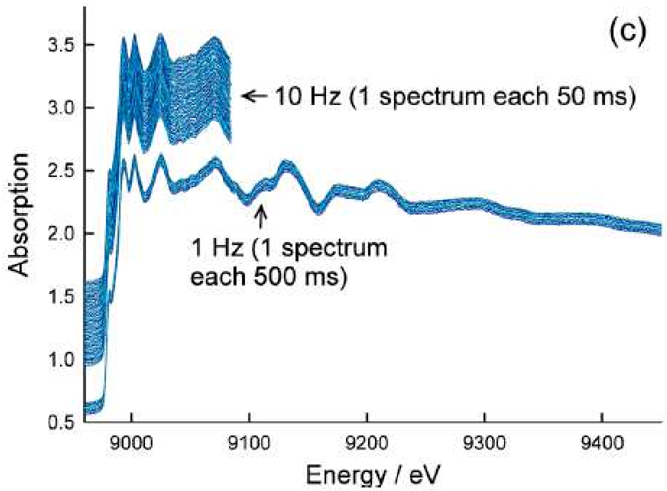
Quick EXAFS monochromator



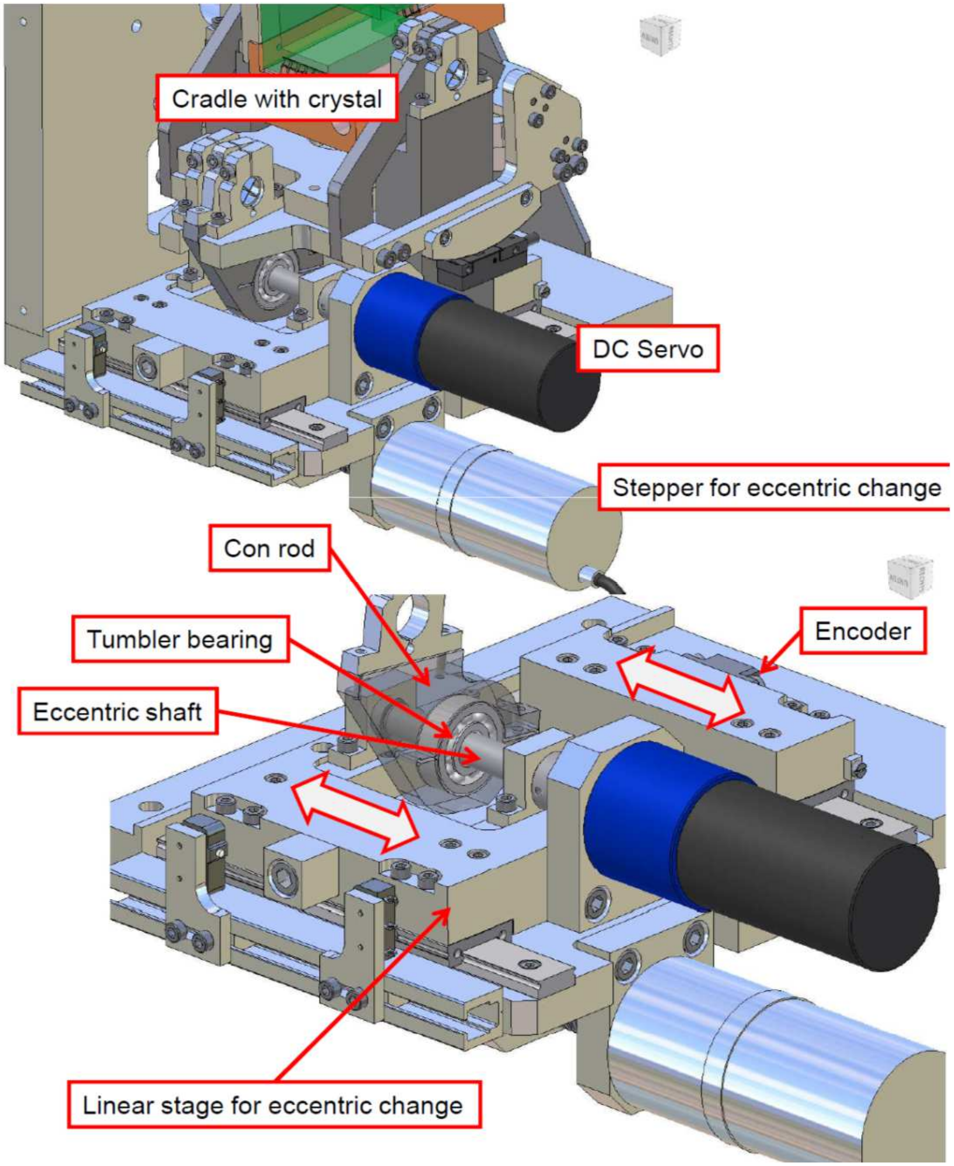


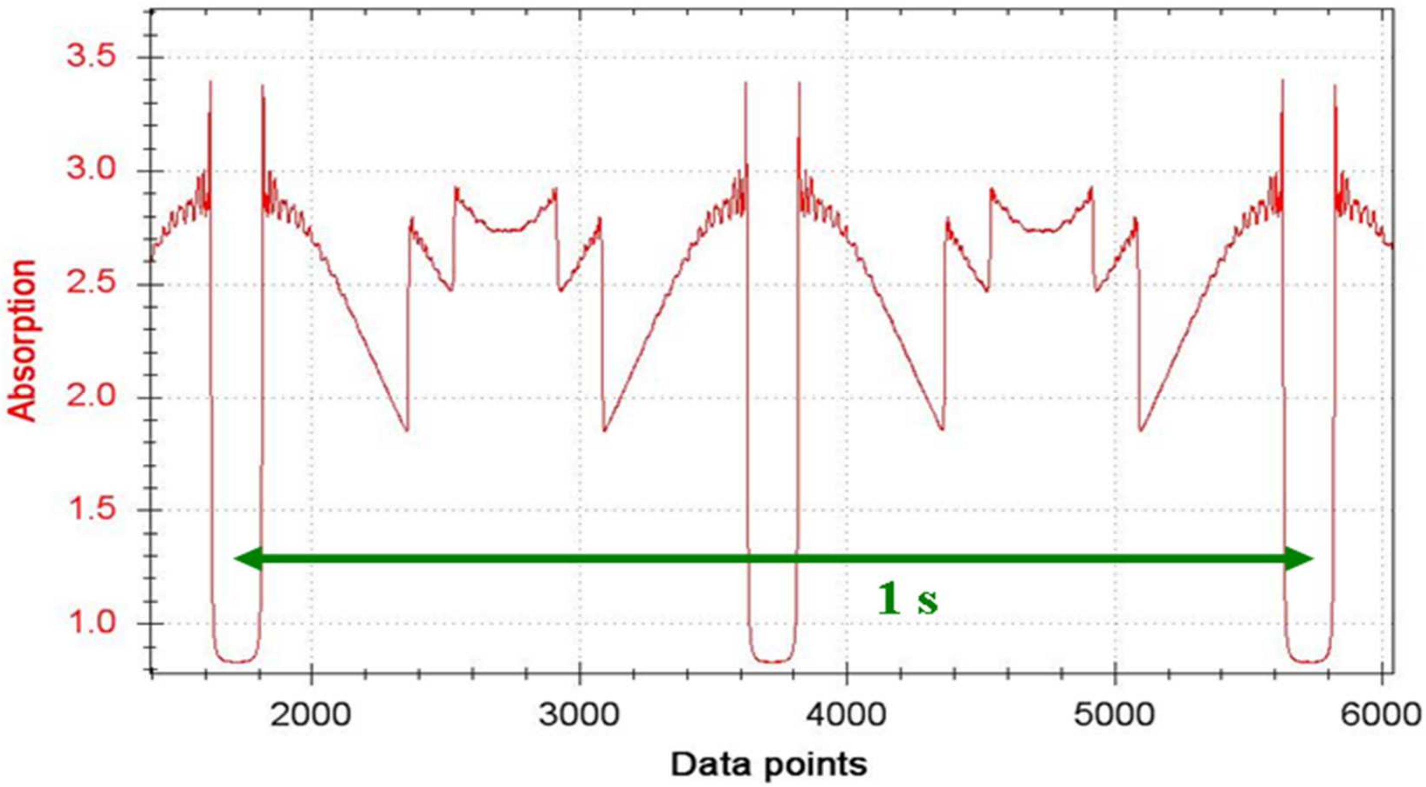


Courtesy of R. Frahm

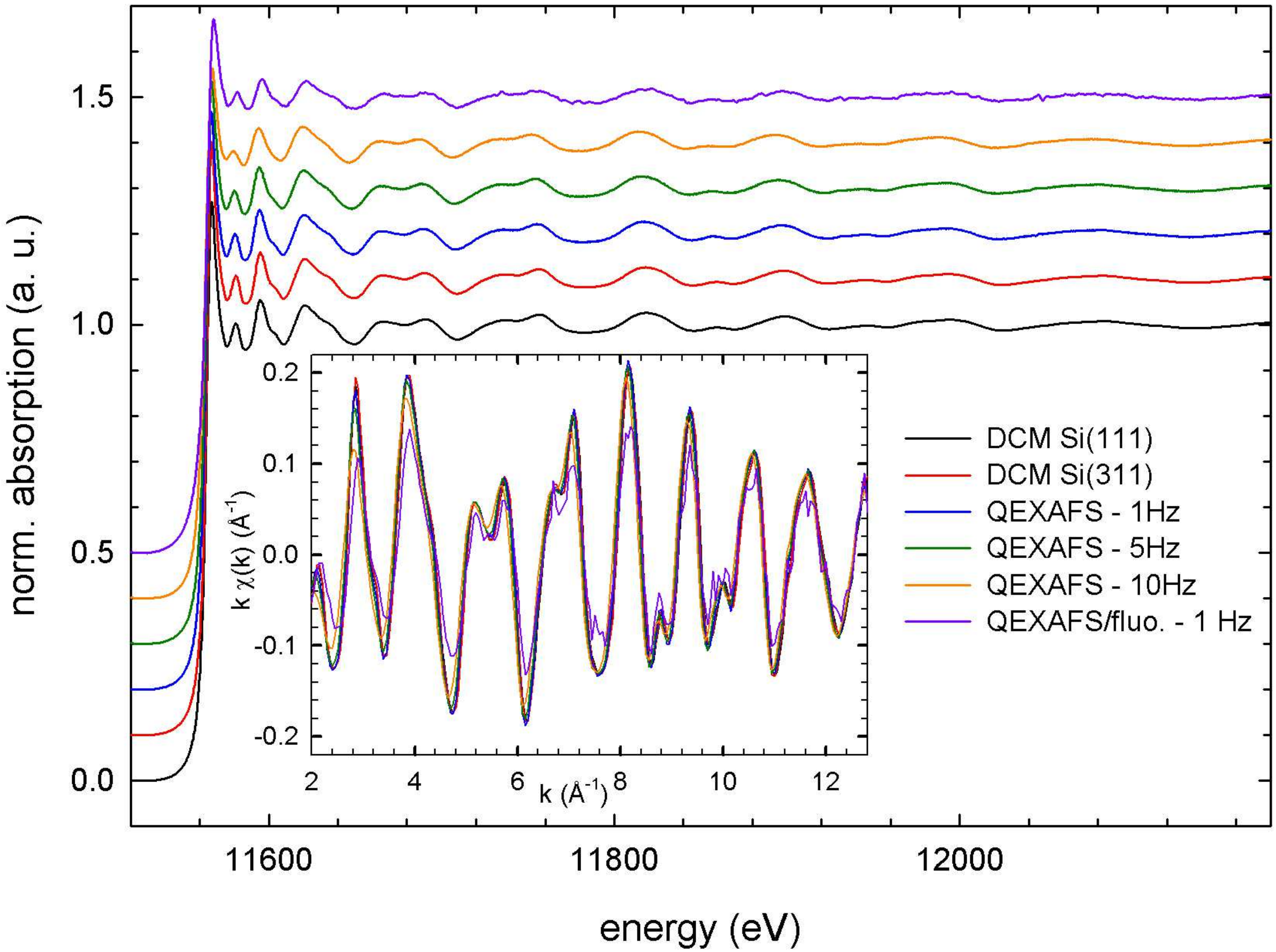


Stötzel et al, Rev. Sci. Inst, 2010

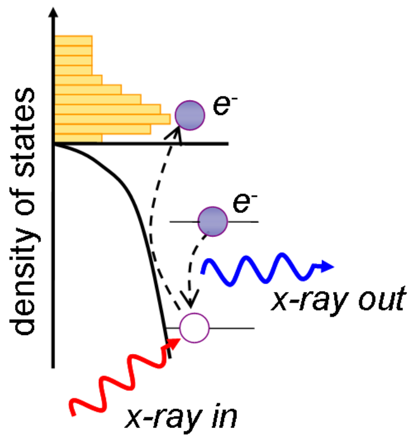


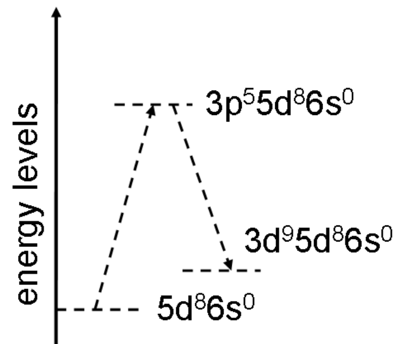


Raw absorption data of the L-edges of a platinum foil,
2 Hz oscillation frequency


norm. absorption (a. u.)
energy (eV)
11600
11800
12000
0.0
0.5
1.0
1.5
k χ(k) (Å⁻¹)
k (Å⁻¹)
DCM Si(111)
DCM Si(311)
QEXAFS - 1Hz
QEXAFS - 5Hz
QEXAFS - 10Hz
QEXAFS/fluo. - 1 Hz

RXES spectroscopy





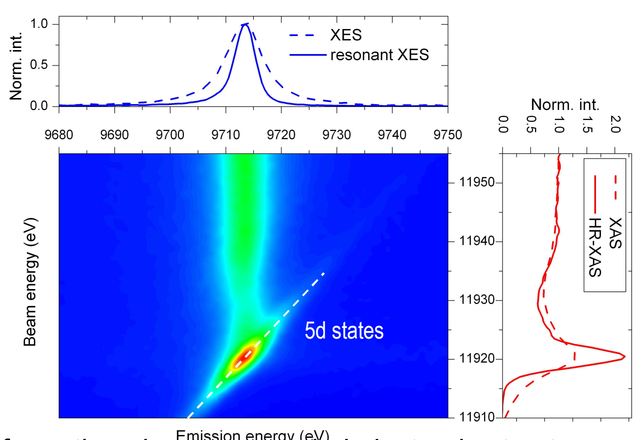
RXES/RIXS: photon-in photon-out technique, a combination of XAS and XES spectroscopy

XAS = unoccupied density of states

XES = occupied electronic states.

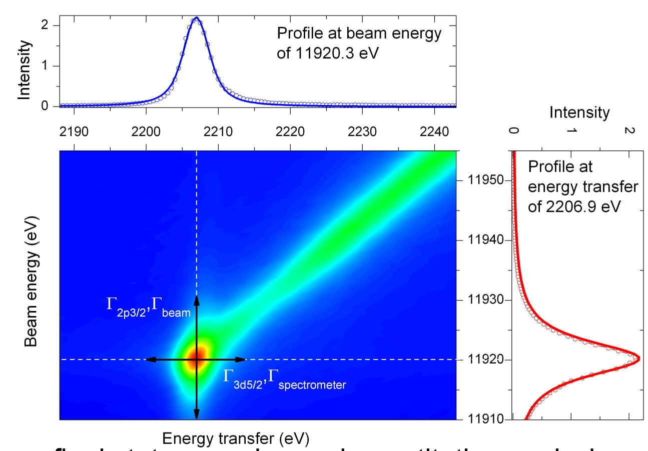
RIXS of Au_2O_3

RIXS plane



-detailed information about unoccupied electronic structure

Energy transfer (E_1-E_2) plane

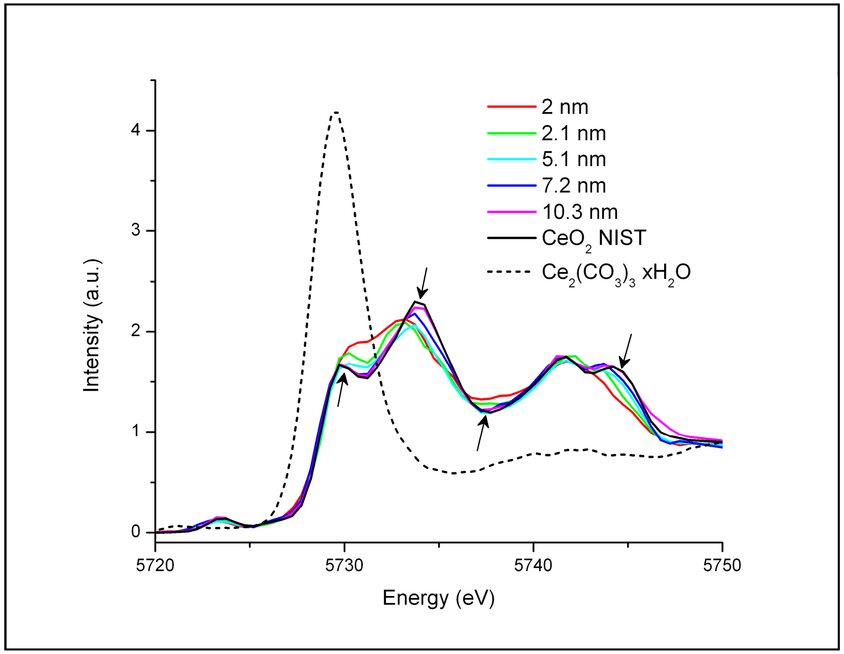


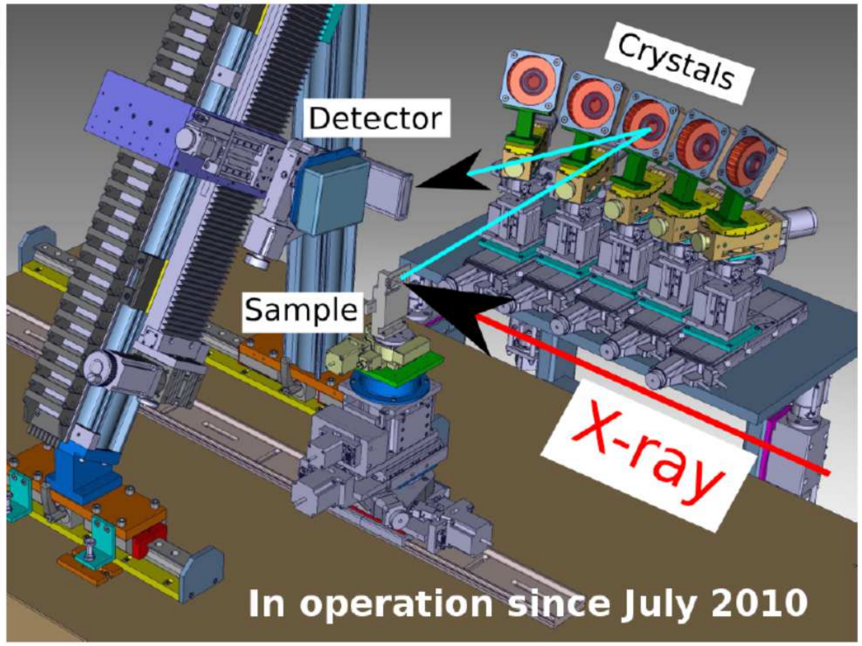
-final state energies and quantitative analysis

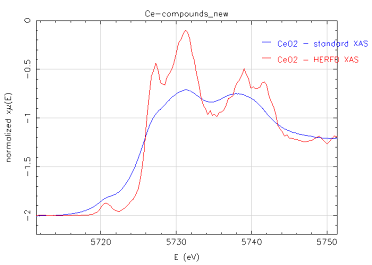
J. Szlachetko et al.,.J Elec. Spectr. And Rel. Phen., **188**, 161-165 (2013)

Johann type emission spectrometer

Ce L_3-edge HERFD XANES







CeO_2 provides reactive oxygen in the absence of O_2 in the atmosphere

$$(x/2)\ CO + CeO_2 = CeO_{2-x} + (x/2)\ CO_2$$

Applications: exhaust gas treatment, particulate burning, water gas shift reactions, PROX, …

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State-of-the-art XAS and XES at SuperXAS

Development strategy

Multi-modal detection

fluorescence detected XAS/XES

time resolved XAS

high resolution XAS/XES

5 elements SDD detector

- high sensitivity
- low detection limits

quick-XAS monochromator

- msec time resolution
- Fluo und trans. XAS

5 crystal spectrometer

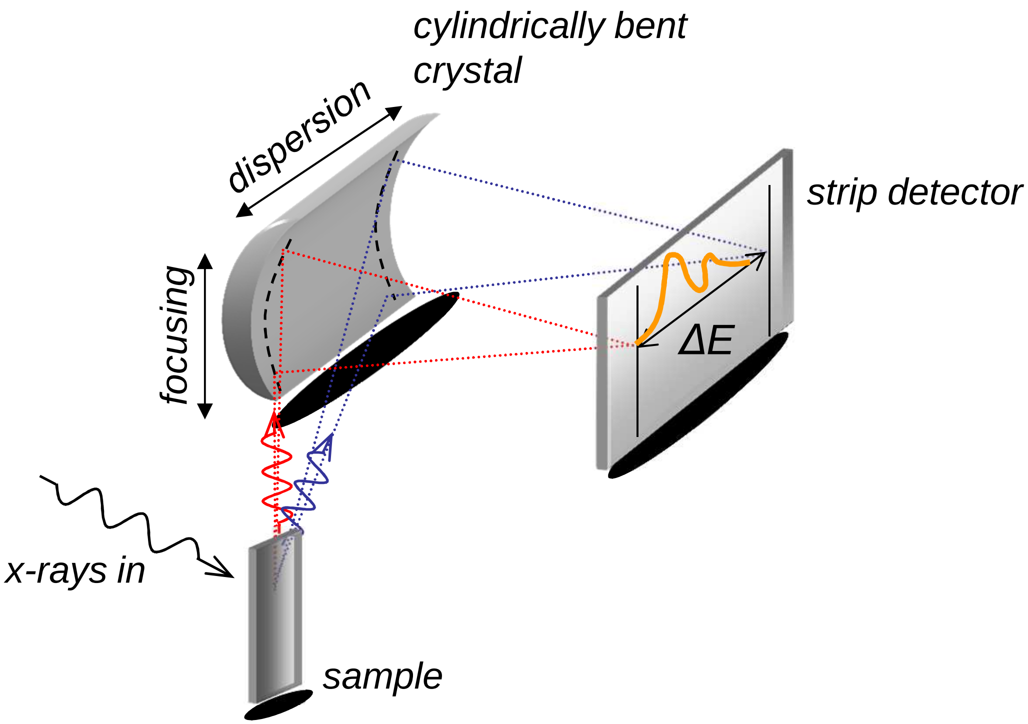
- sub eV energy resolution
- HERFD XAS

our goal

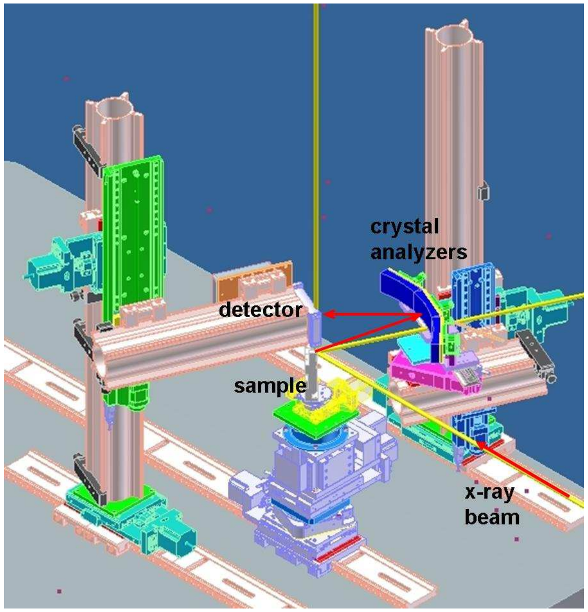
time resolution & energy resolution

Single-shot XAS & XES

X-ray spectrometer for time resolved spectroscopy



Spectrometer design @ SuperXAS

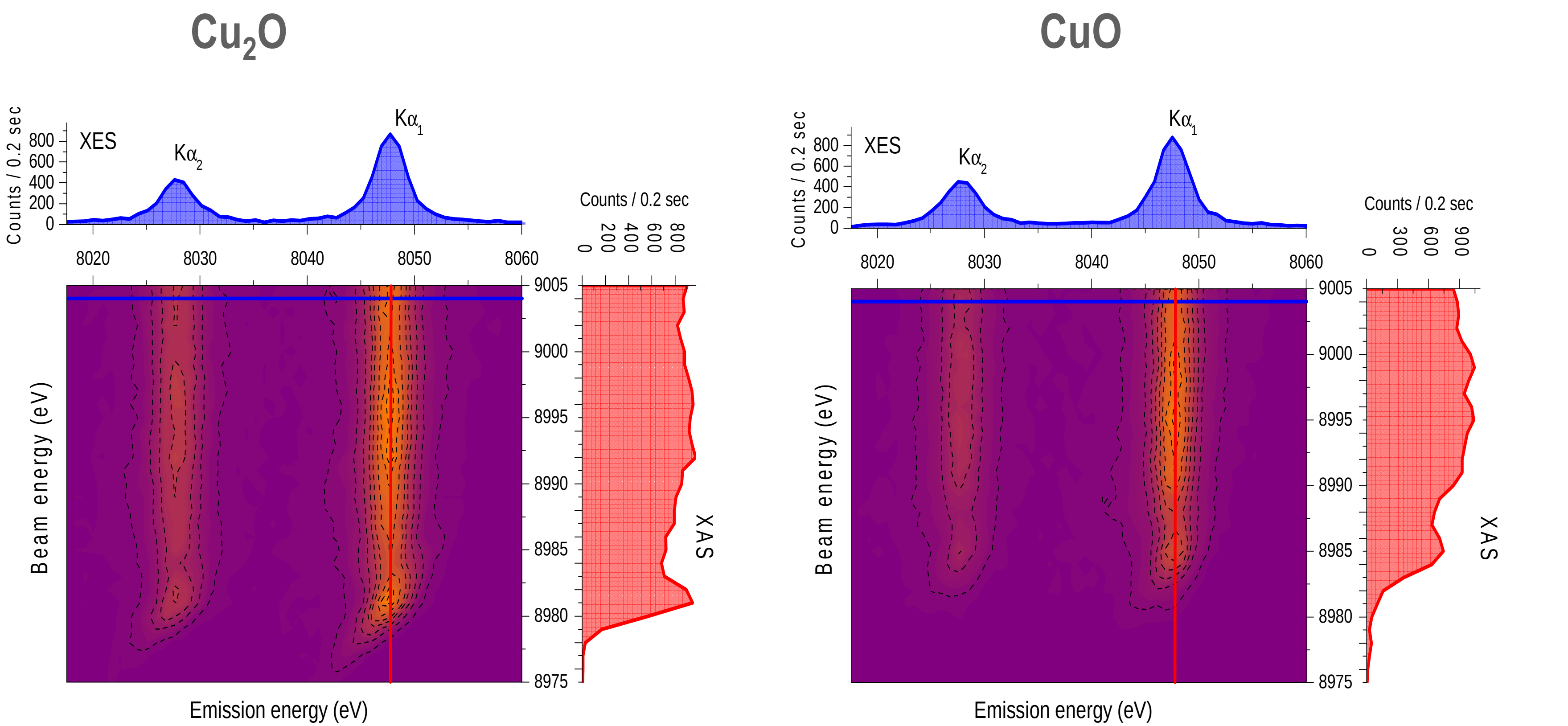


- ➢resolution ~eV
- ➢large energy bandwidth for single measurement
- ➢single-shot capability
- ➢vertical or horizontal scattering geometry
- ➢easy adaptation to shorter/longer radiuses

L. von Hamos, Naturwiss. 20, 705 (1932).

J. Szlachetko et al., Rev. Sci. Instrum. 83, 103105 (2012).

Applications: quick RIXS



total acquisition time for full RIXS map ~7sec

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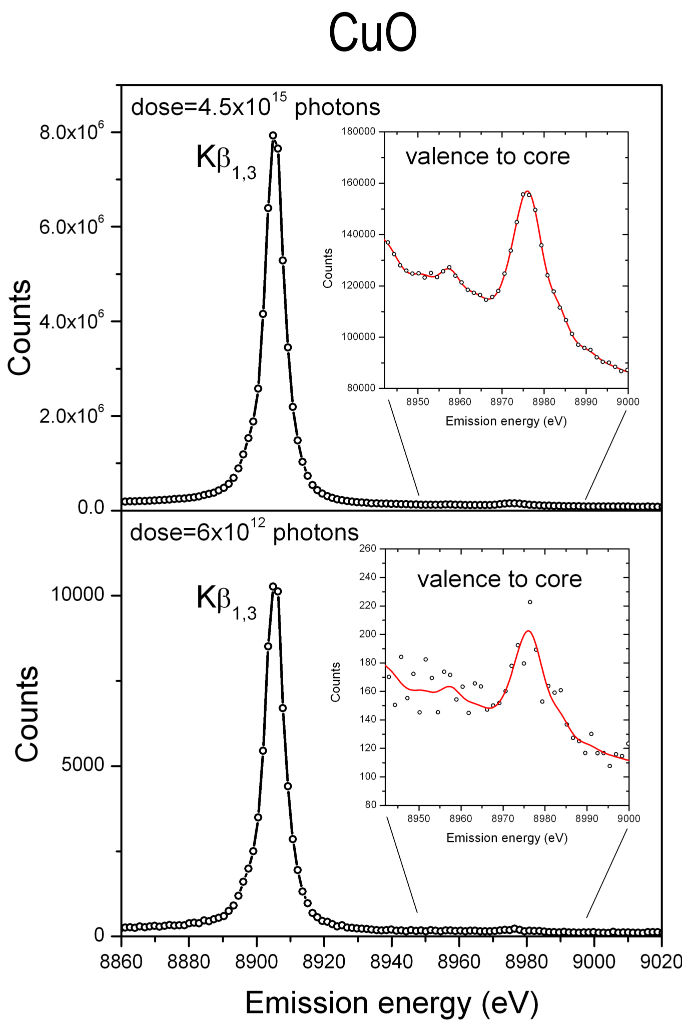
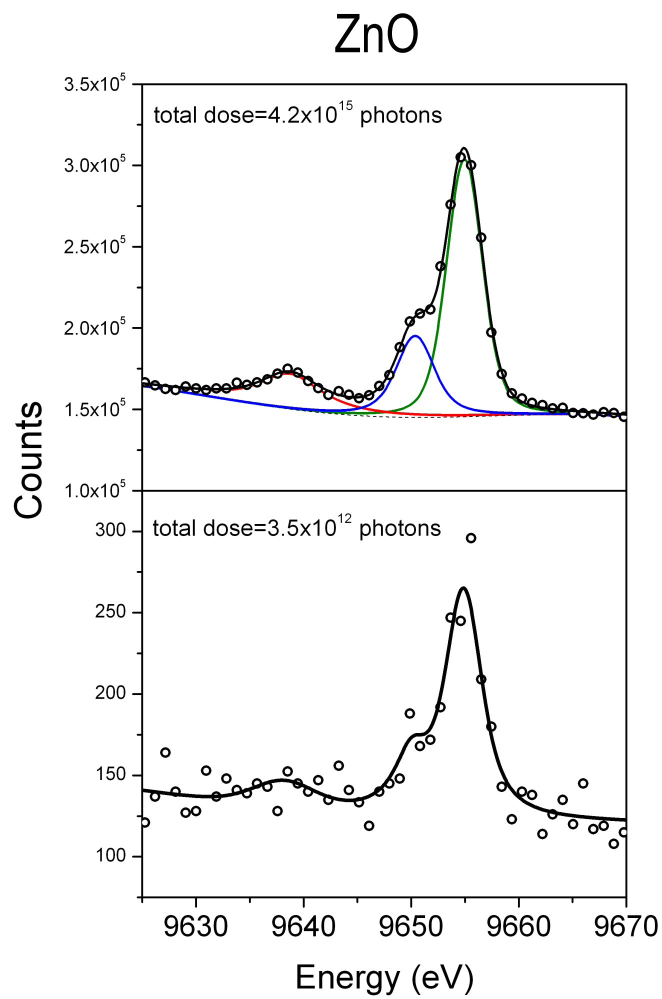
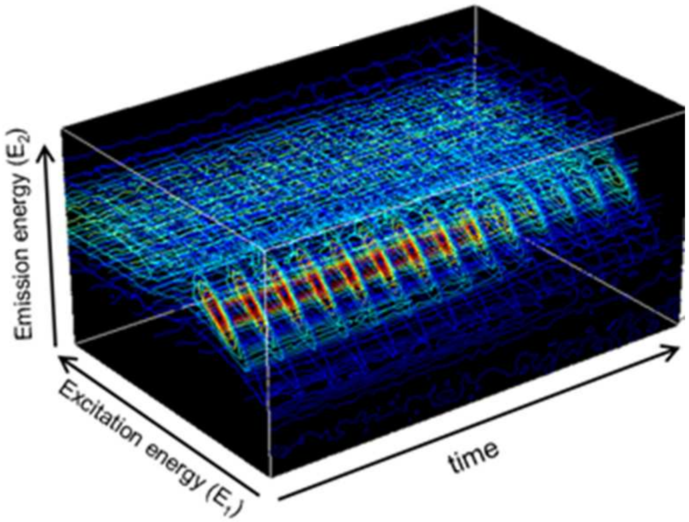
Applications: Single-shot XES

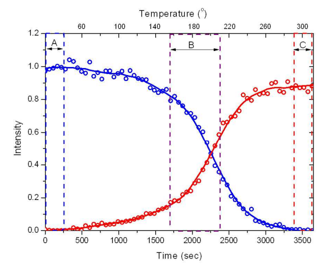


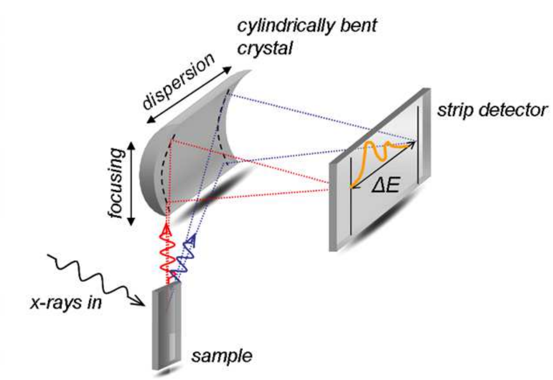


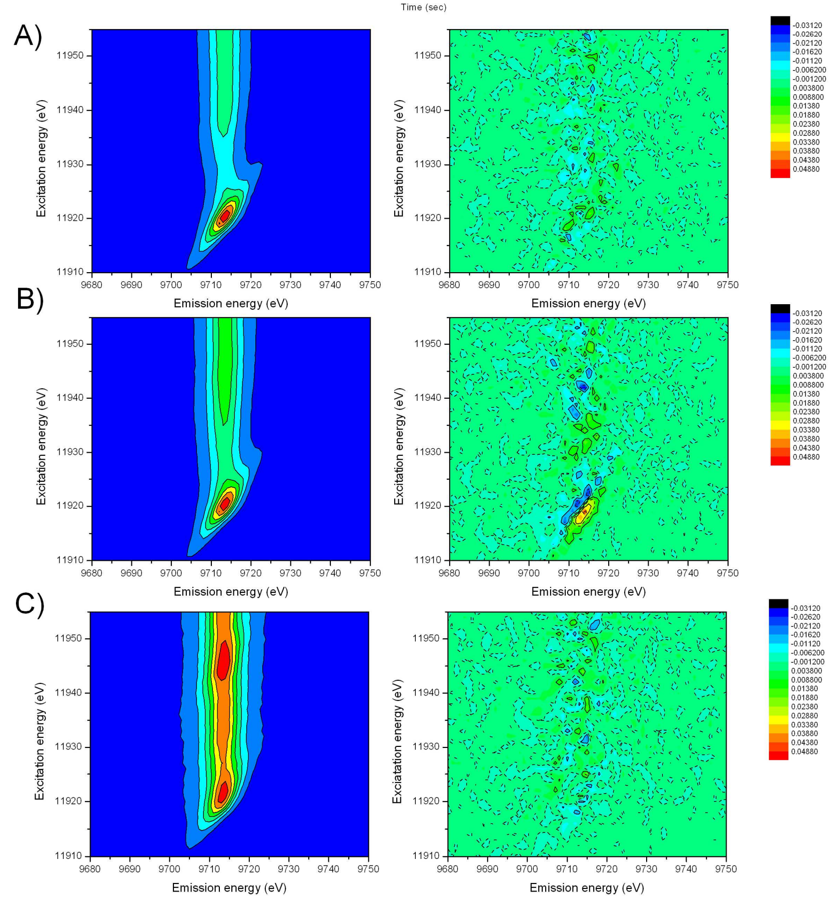
In-situ quick-RIXS spectroscopy

TPR of Au(III) – results of RIXS LCF



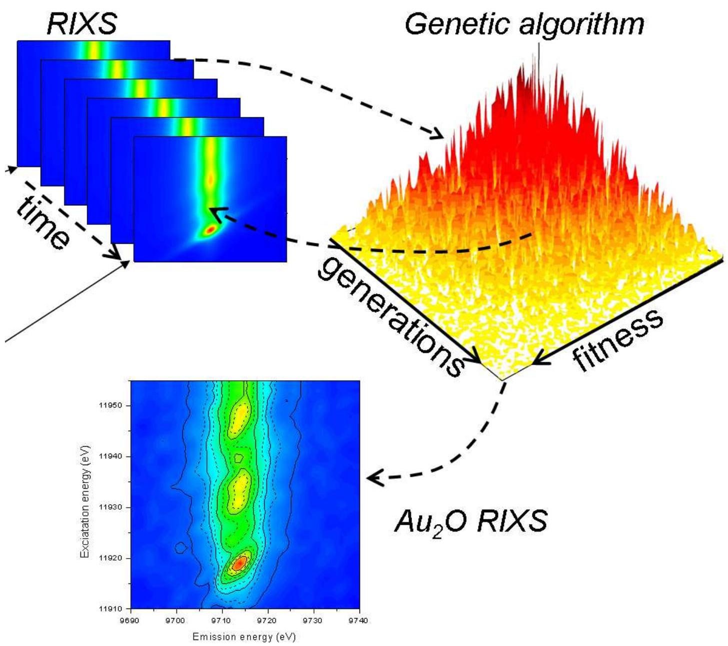


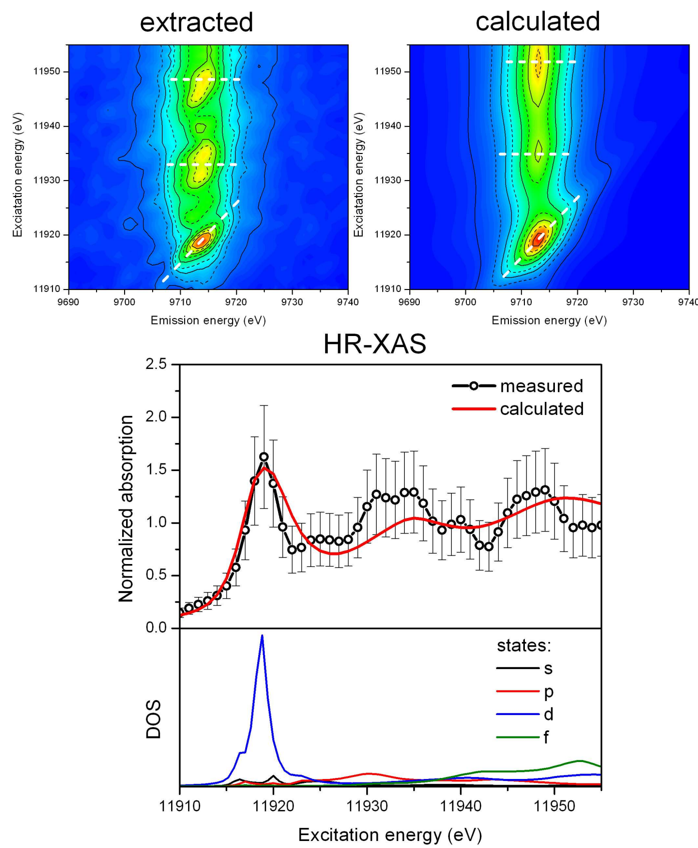




Quick-RIXS spectroscopy

TPR of Au(III) – results of Genetic Algorithm analysis



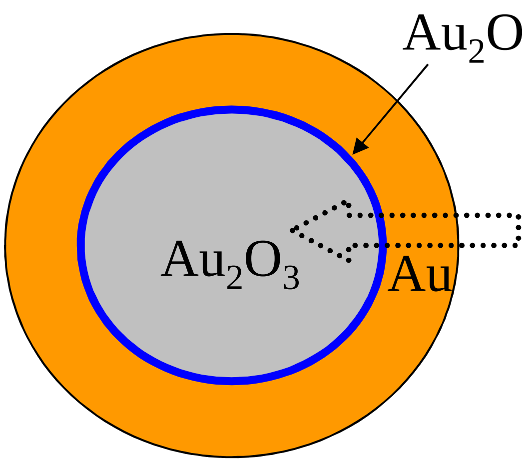


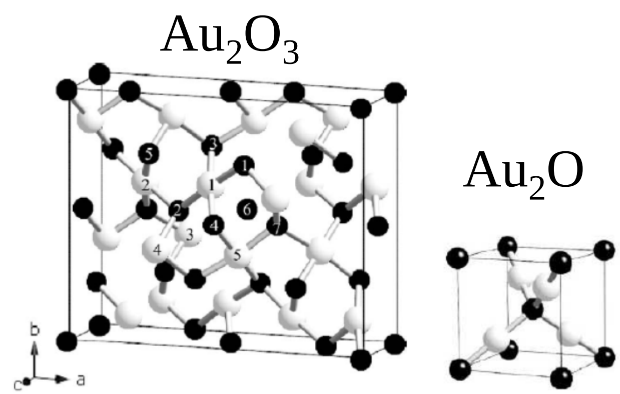
- ➢ **Calculated RIXS plane includes lattice expansion from 4.8A to 5.3A.**

Au(III) reduction: theory vs experiment

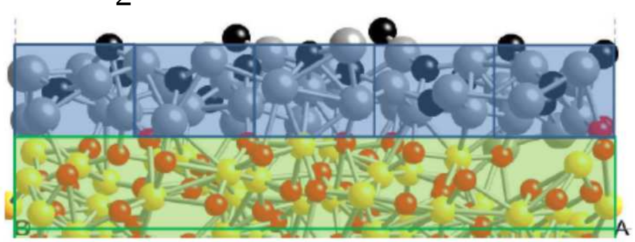
- Theory Au_2O → 4.8Å
- RIXS experiment → 5.3Å

Reaction mechanism: shell-to-core reduction





Au_2O termination on the Au_2O_3 structure:

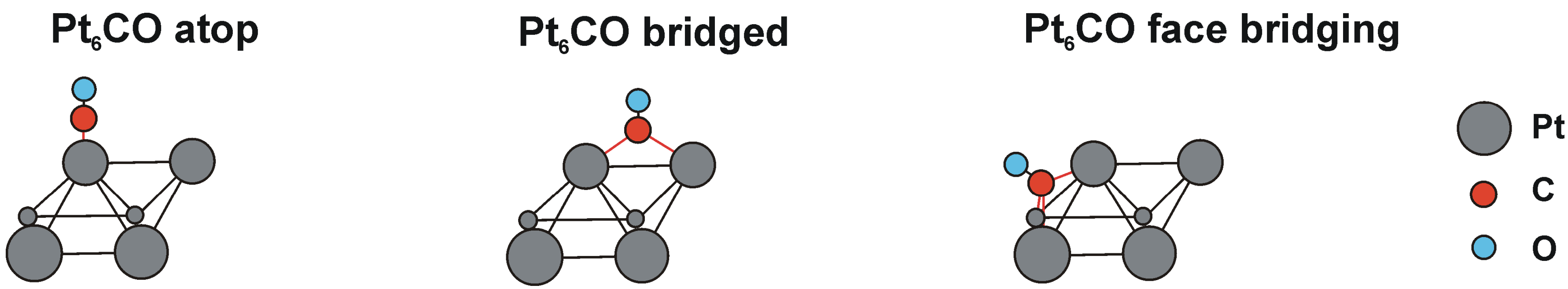


- Theory Au_2O → 5.34Å
- RIXS experiment → 5.3Å

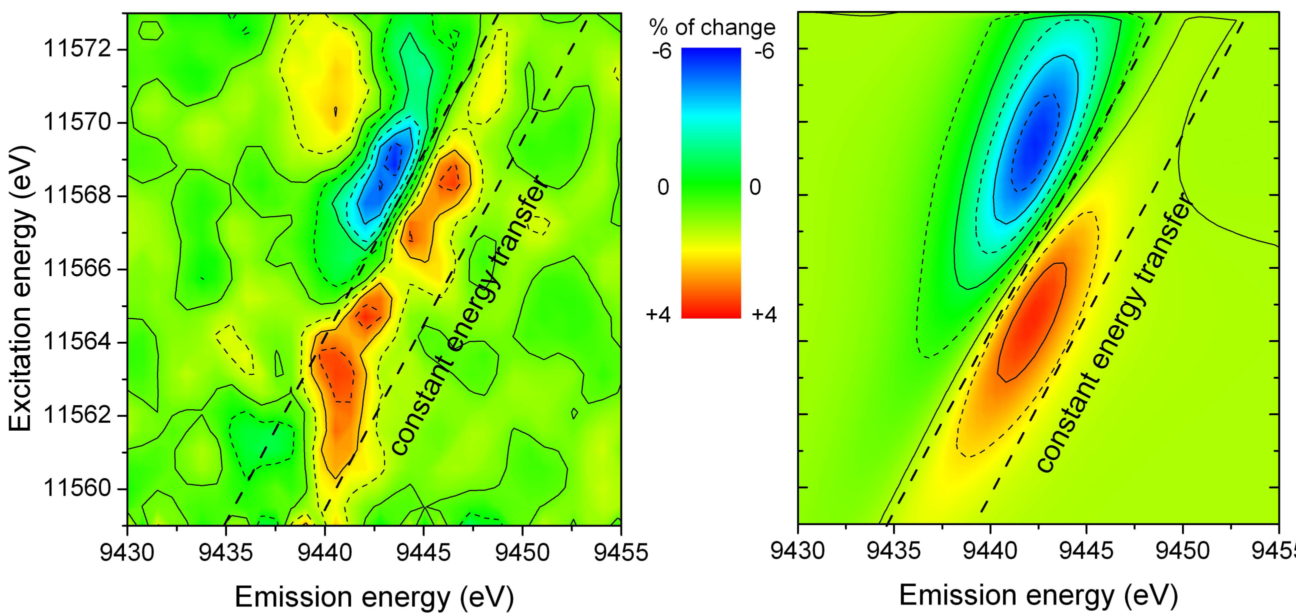
J. Szlachetko et al. J. Phys.Chem. Letters (2014)

In-situ RIXS – molecule adsorption geometries

CO adsorption on Pt-nanoparticles

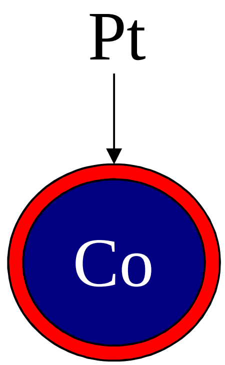


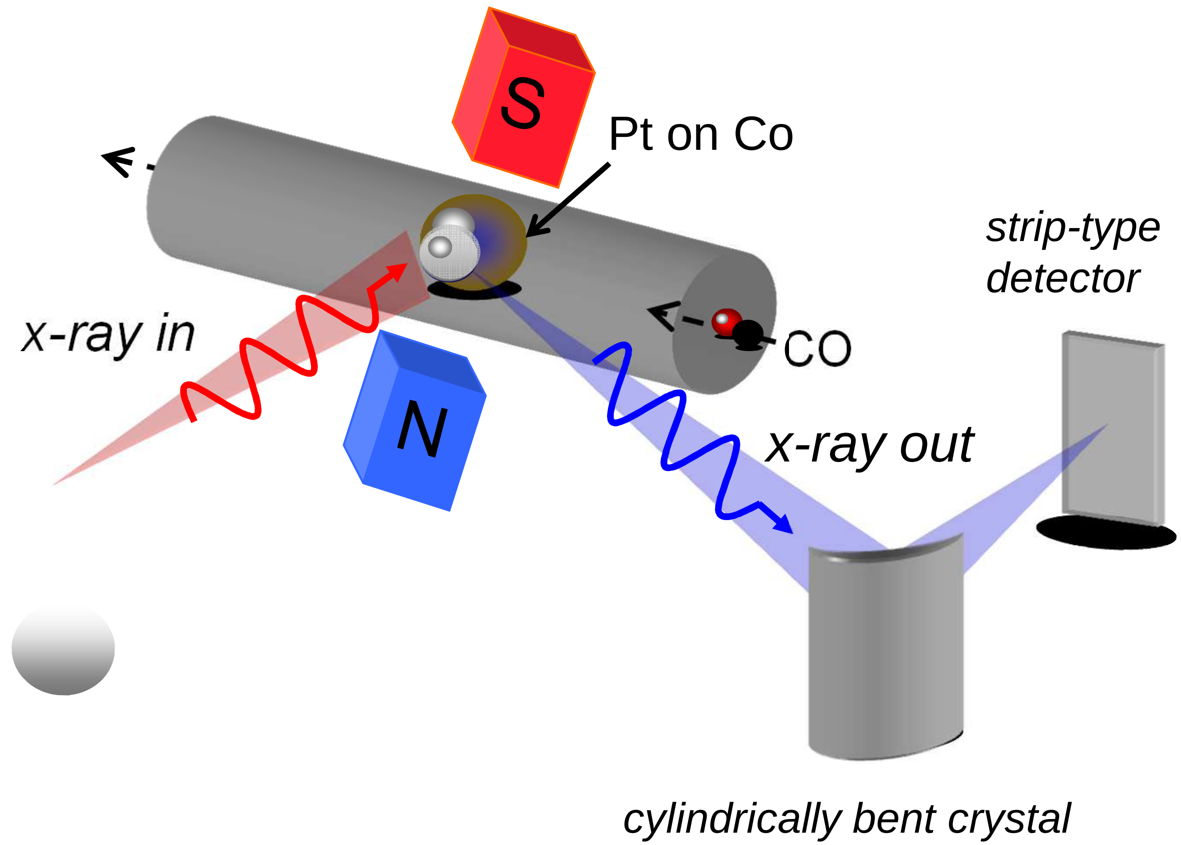
Δ-RIXS



In-situ RIXS – magnetic manipulation of adsorbed molecules

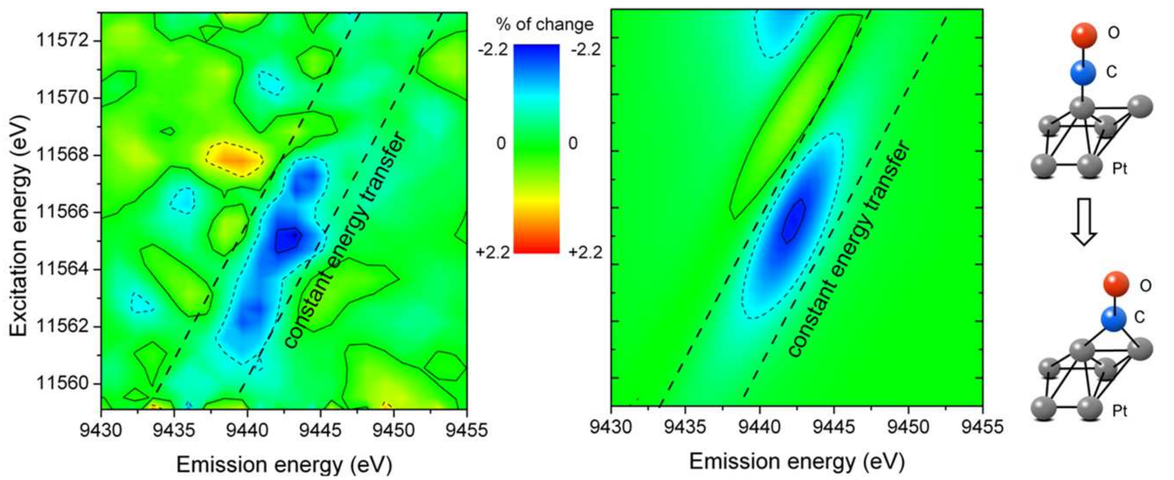
CO adsorption on Pt/Co@C

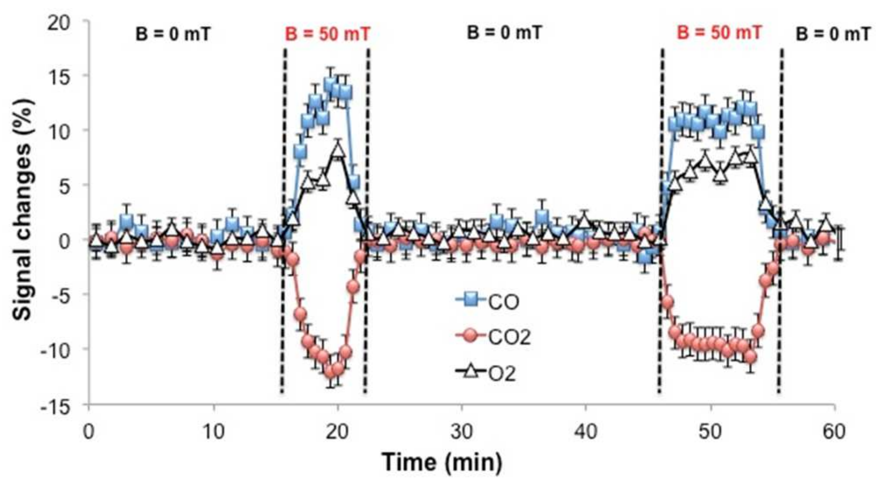




In-situ RIXS – magnetic manipulation of adsorbed molecule

CO adsorption on Pt/Co@C





~11% change in adsorption geometry

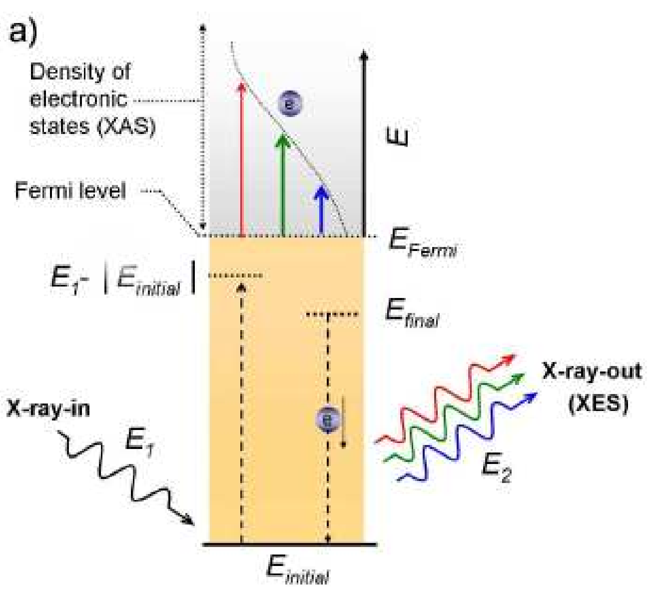
J. Sa et al., Nanoscale (2013).

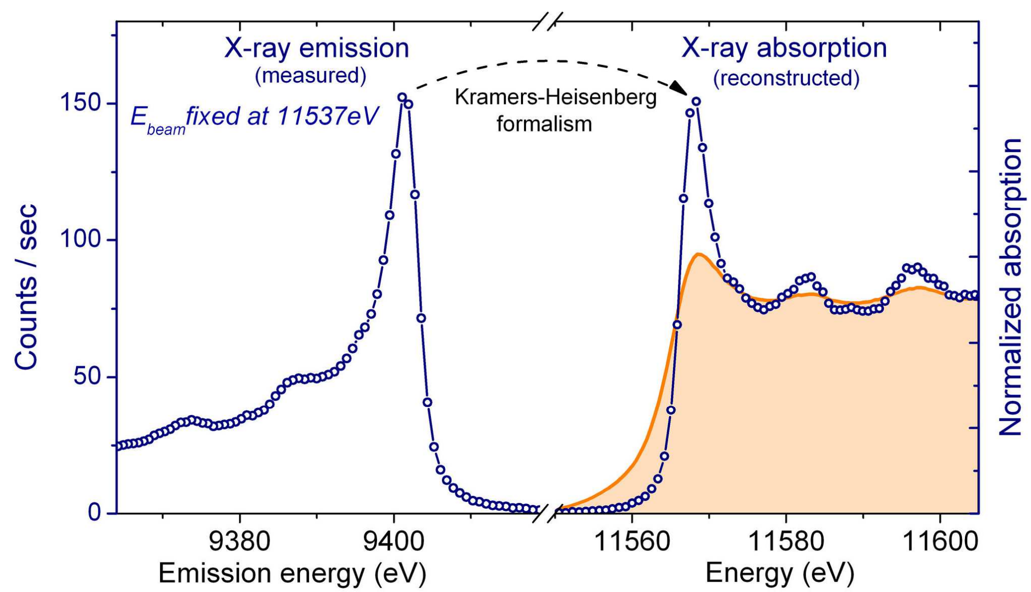
High energy resolved off resonant spectroscopy - HEROS

Re-formulate the generalized Kramers-Heisenberg formula developed by Tulkki and Åberg (1982):

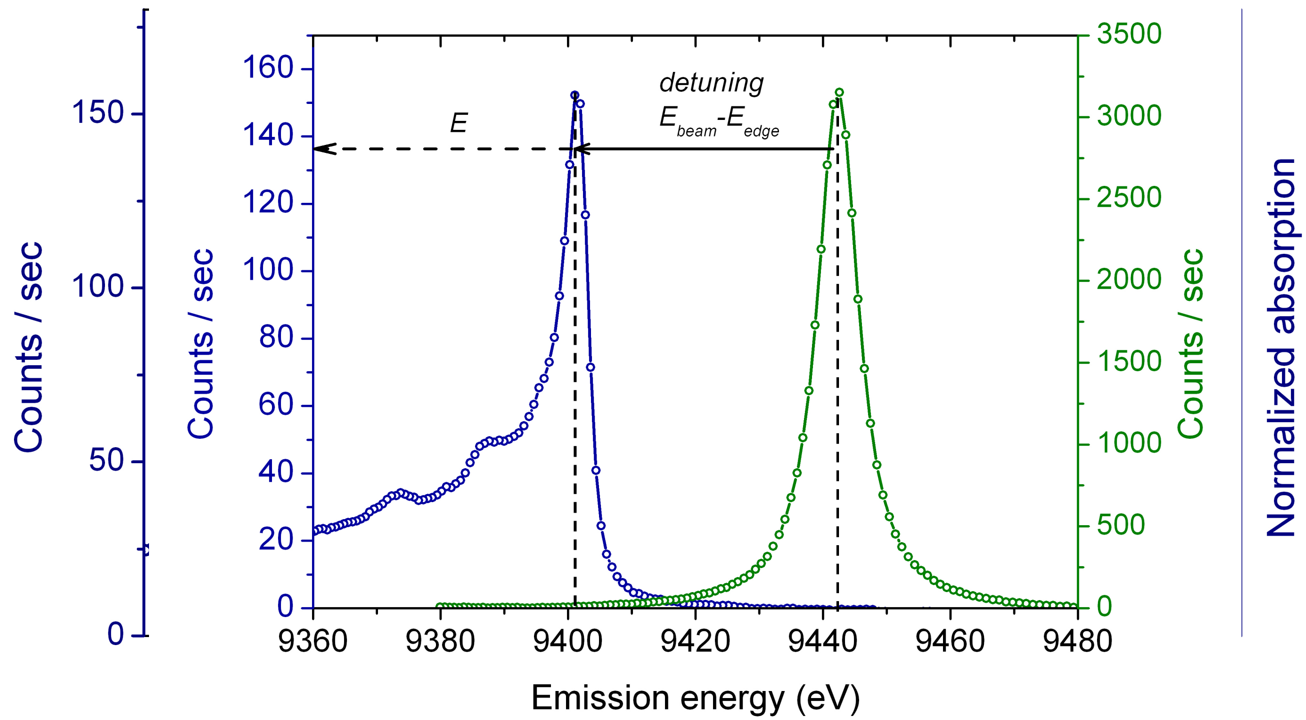
$$XES(E_2) \approx \int \frac{E_2}{E_1} \frac{(E_{initial} - E_{final})(E_{initial} + E) \cdot XAS(E)}{(E_{initial} + E - E_1)^2 + \Gamma_{initial}^2 / 4} \delta(E_1 - E_{final} - E - E_2) dE$$

Shows direct relationship between XAS and off resonant XES!





X-ray emission spectrum Pt $3d_{5/2} \rightarrow 2p_{3/2}$ ($L\alpha_1$)

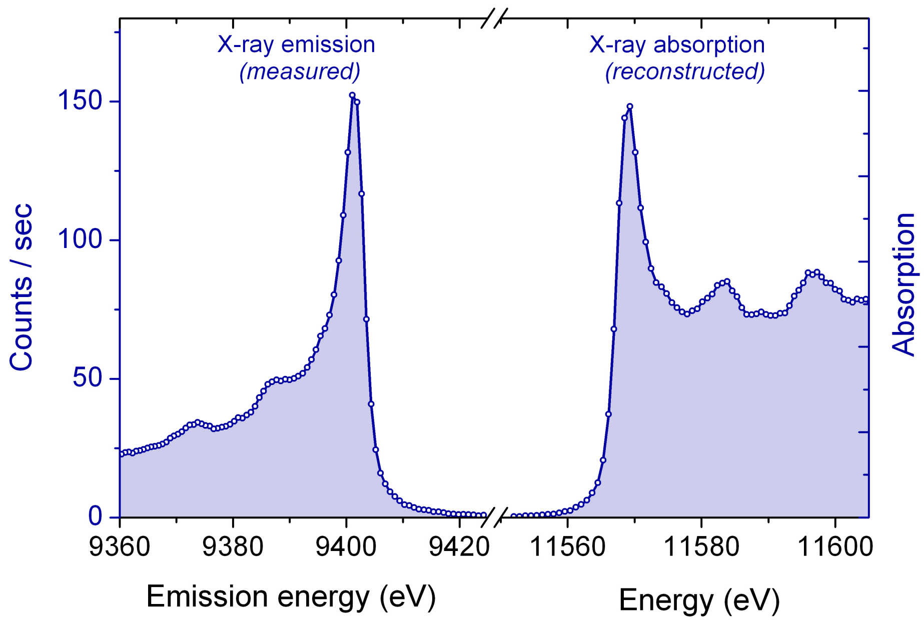


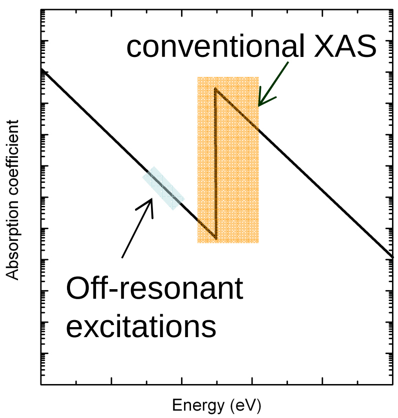
dispersive-type spectrometer: XAS can be obtained for fixed beam energy excitation without moving any optical components

high energy resolution – more detailed structure as compared to conventional XAS

High energy resolution off-resonant spectroscopy

- XAS at fixed beam energy excitation
- high energy resolution
- independent of I_0 fluctuations





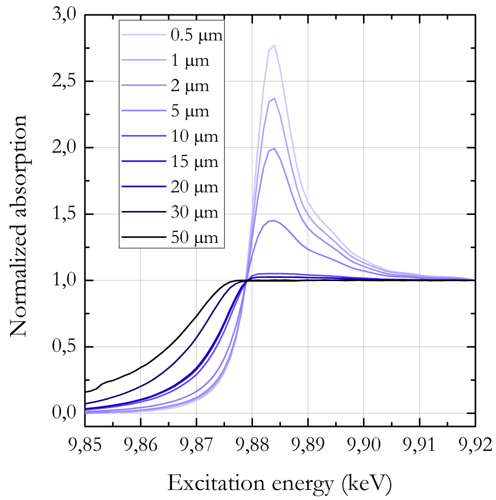
XAS shape is independent of self-absorption process.....

High energy resolution off-resonant spectroscopy

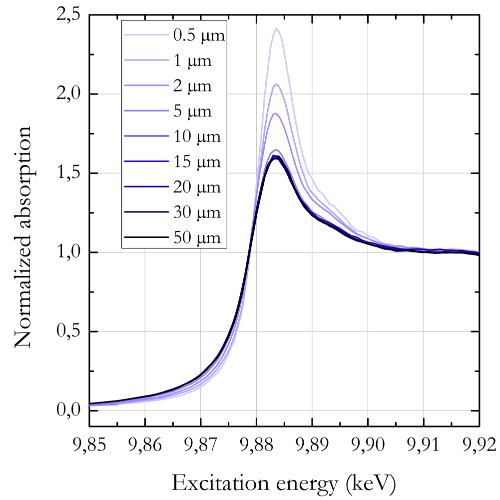
XAS shape modifications by sample concentration/thickness

Ta L_3-XAS

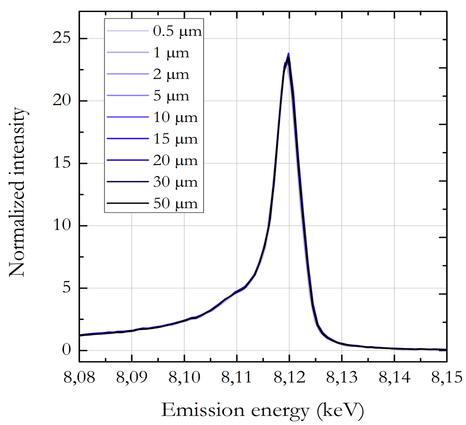
transmission XAS



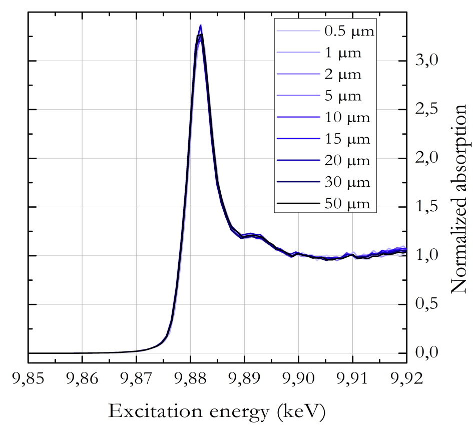
fluorescence-XAS



HEROS-XES



HEROS-XAS



W. Blachucki et al., PRL., 112, 173003 (2014)

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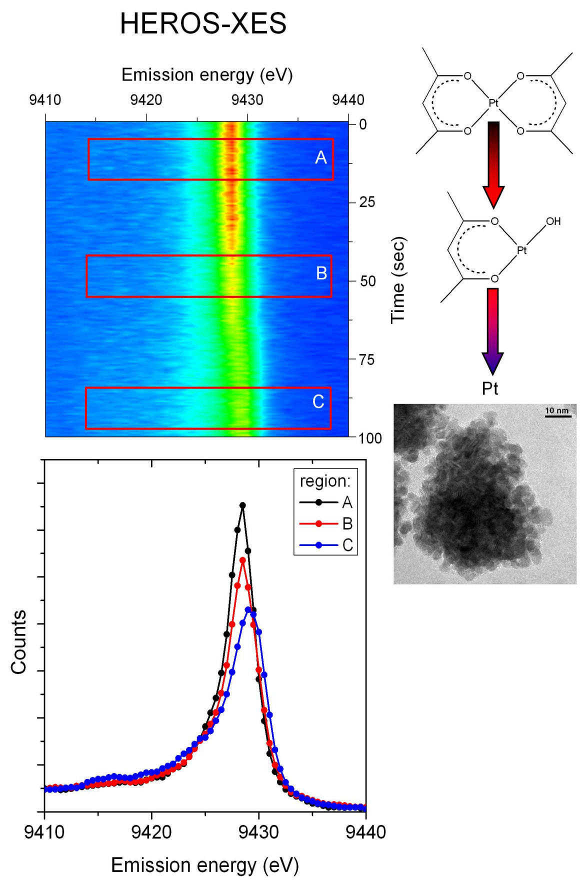
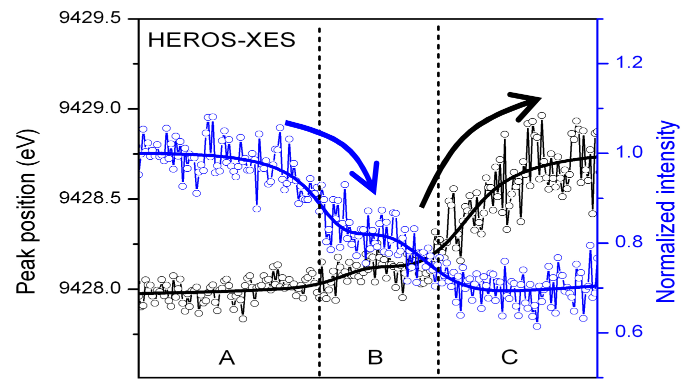
High energy resolution off-resonant spectroscopy

($Pt(acac)_2$) decomposition: 500msec time resolution

In situ decomposition of $Pt(acac)_2$ under 5% H_2 in He induced by flash heating at 150 ^oC





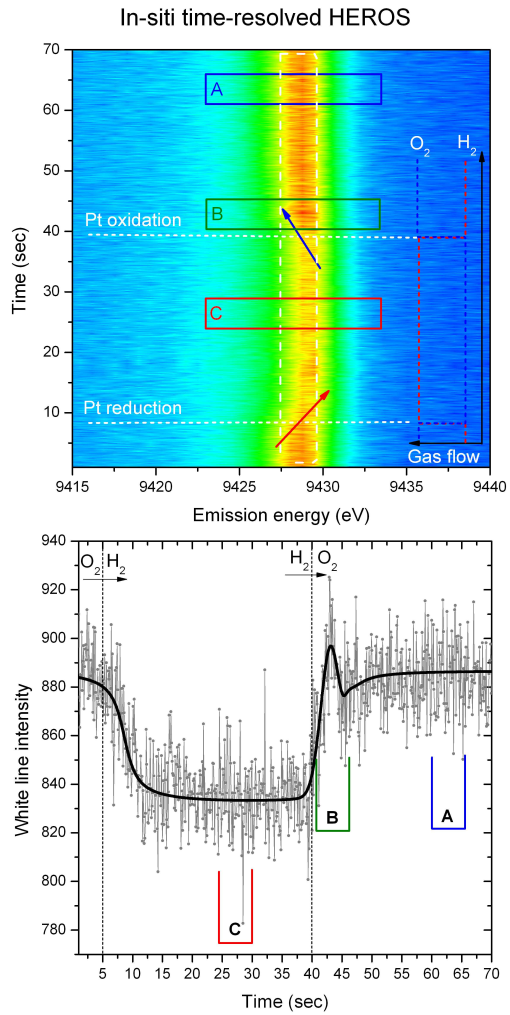
The spectral shape in intermediate zone B indicates changes in the chemical environment, such as change of the ligand of the Pt site that however do not correspond to a change in oxidation state.

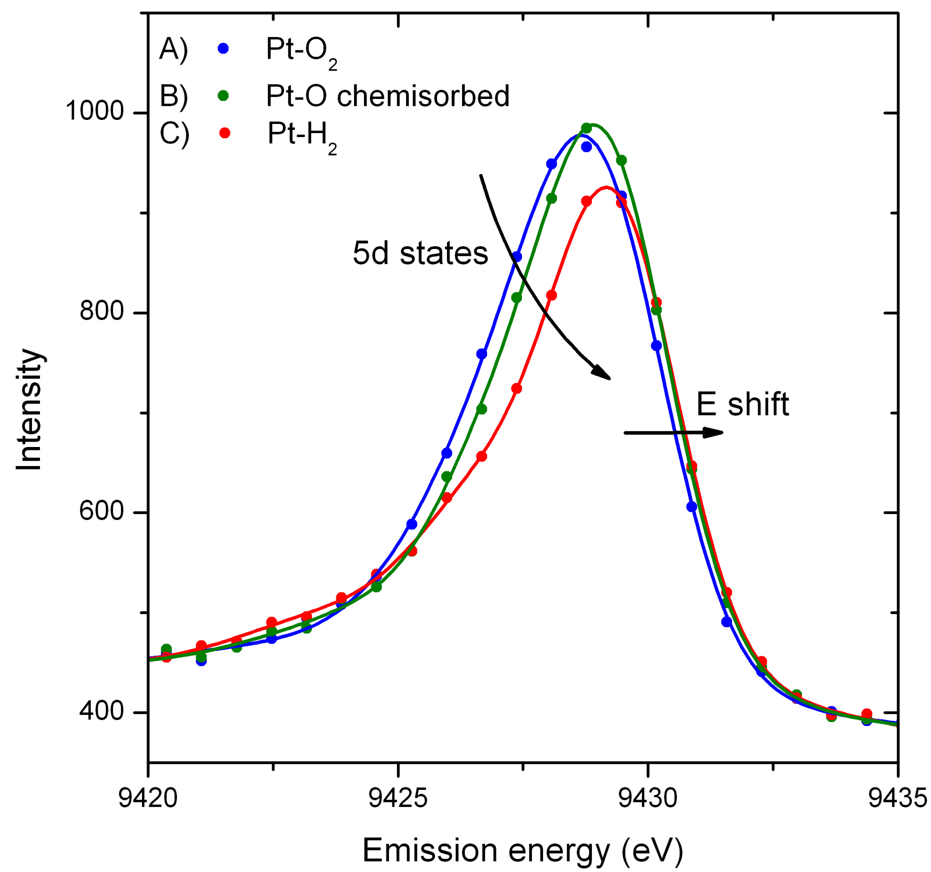
J. Szlachetko, M. Nachtegaal, J. Sa et al., Chem. Comm., 48, 10898 (2012).

High energy resolution off-resonant spectroscopy

Pt reduction/oxidation: 100msec time resolution

In situ reduction/oxidation of Pt by gas switching at 200 ^{o}C





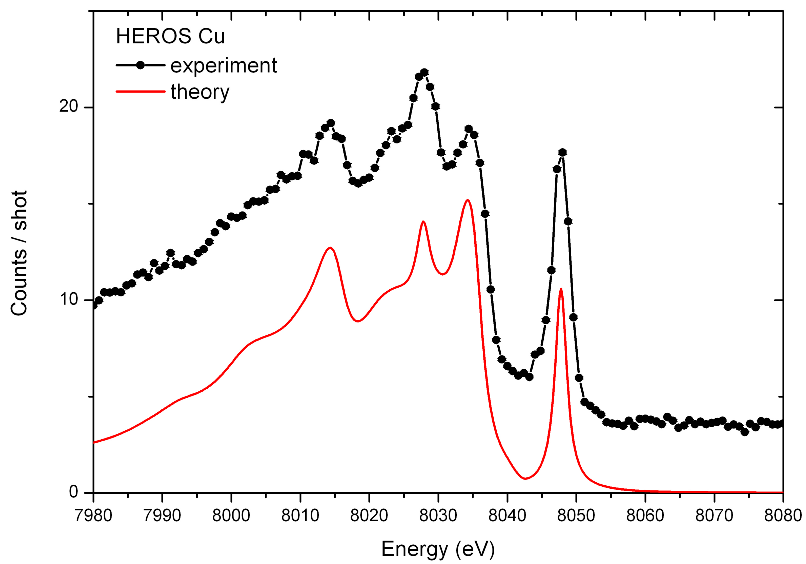
J. Szlachetko et al. JACS (2013)

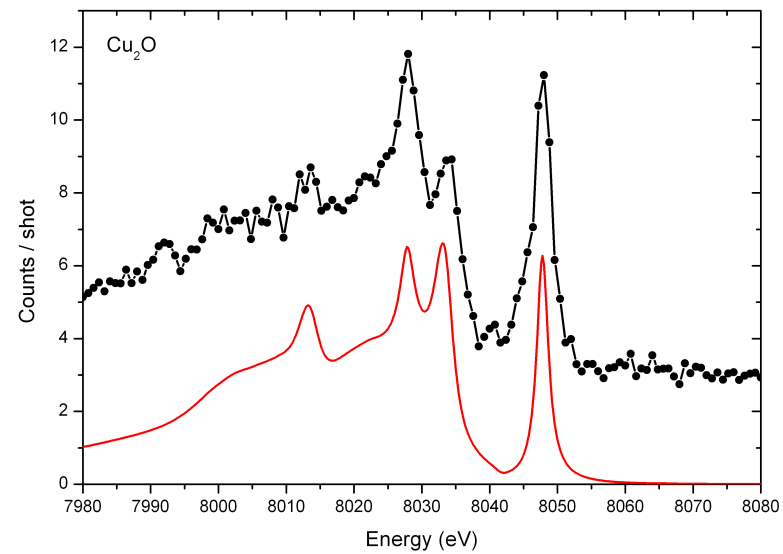
XFEL experiment

High energy resolution off-resonant spectroscopy (HEROS): Chemical speciation at femtosecond time scales.

HEROS provide information about unoccupied electronic states. Experimental approach allows for XAS-like studies on a shot-to-shot basis.

HEROS XFEL spectra, 50fsec pulses





First time demonstration of HEROS applicability to XFEL sources

J. Szlachetko et al structural dynamics (2014)

Application QEXAFS: Biomass to synthetic natural gas

Today's supply for fuels, heat, chemicals and electricity is largely based on fossil fuels

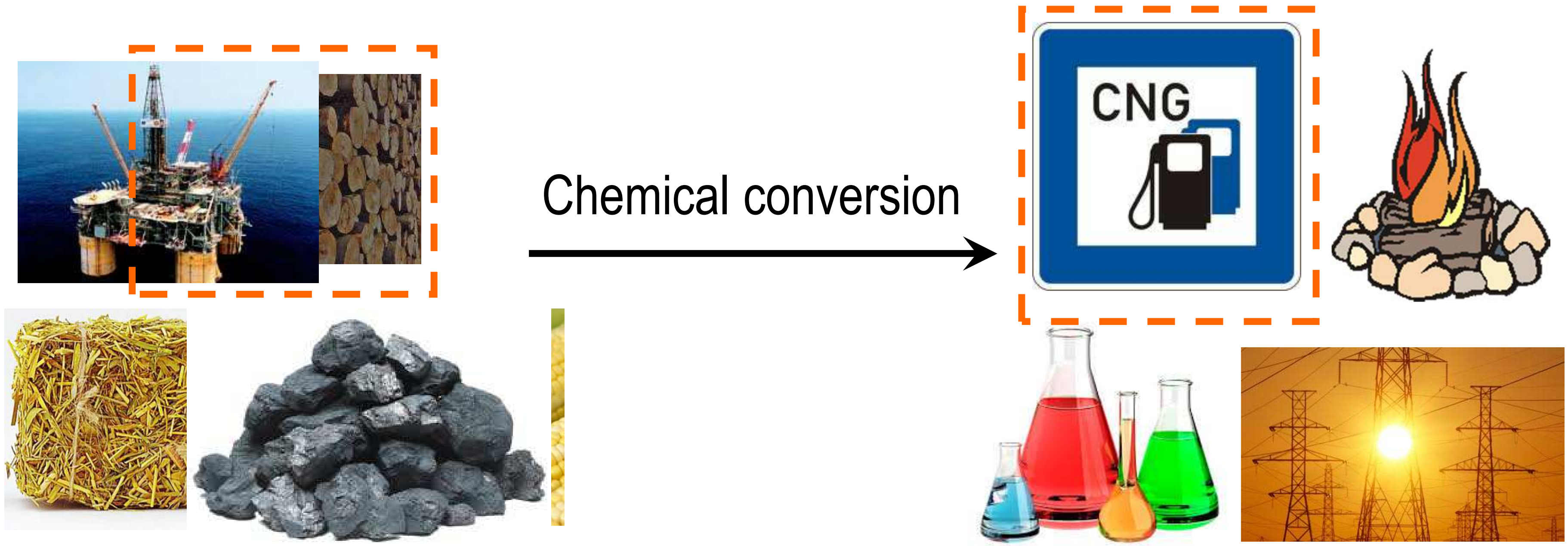


Image sources: liberstilo.com, businessweek.com, bestensee.de baricada.ro afamily.vn, erneuerbareenergiequellen.com, vebidoo.de, asg.de, worldofstock.com

Wood to SNG

Why wood to Synthetic Natural Gas (SNG)?

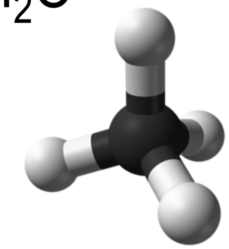
- No competition with food / agricultural areas
- Climate neutral process → CO_2 sequestration possible
- Wood widely available in many countries

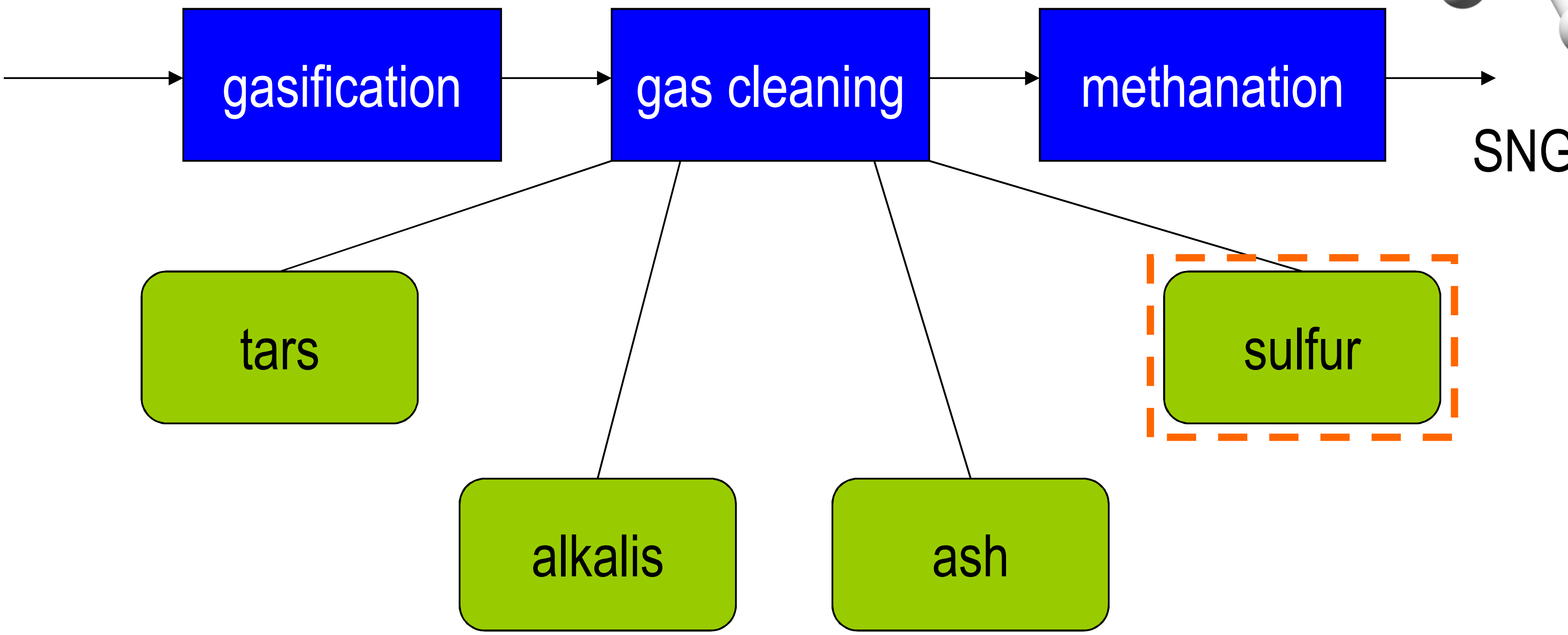
GoBiGas (Gothenburg, Sweden) 20 MW (+80 MW)

http://gobigas.goteborgenergi.se

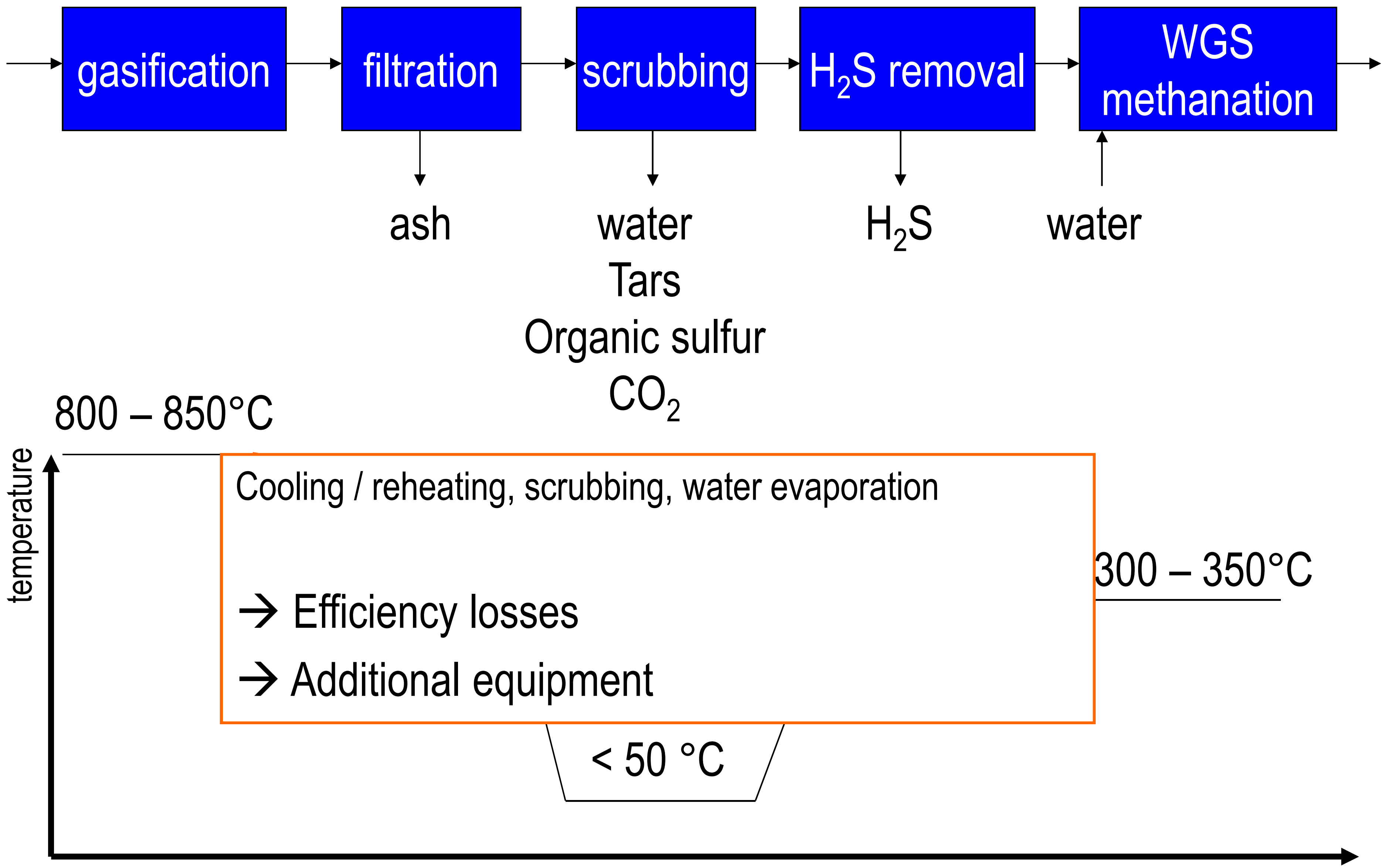
Wood to SNG – simplified process scheme

$$3\,H_2 + CO \rightarrow CH_4 + H_2O$$





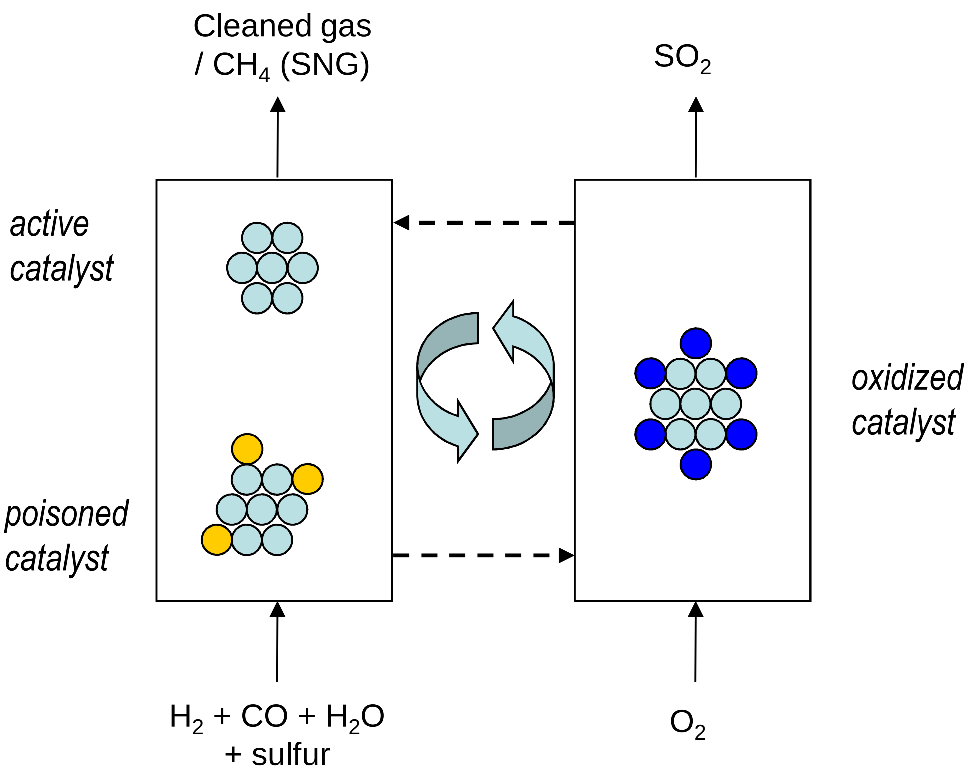
Wood to SNG – simplified process scheme



Approach for continuous removal of sulfur

Chemical looping desulfurization

Transport of material between „fuel reactor“ and „oxidizing reactor“



Advantages:

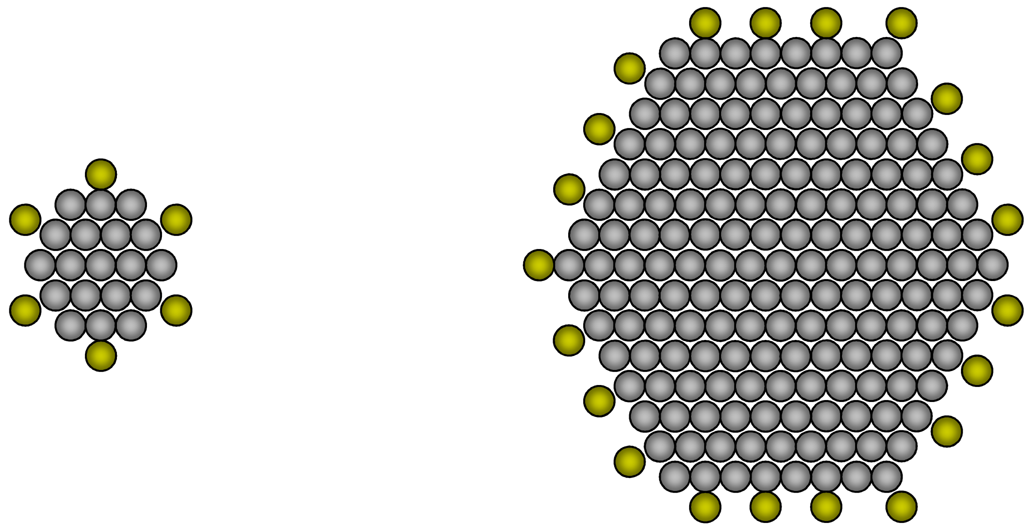
- Sulfur is continuously removed
- High temperature process
- Combination with tar reforming / methanation

Challenges:

- Attrition
- Hydrodynamics
- Transient reactions

XAS – sensitivity to changes at the surface

Catalysis takes place at the surface – XAS probes the bulk



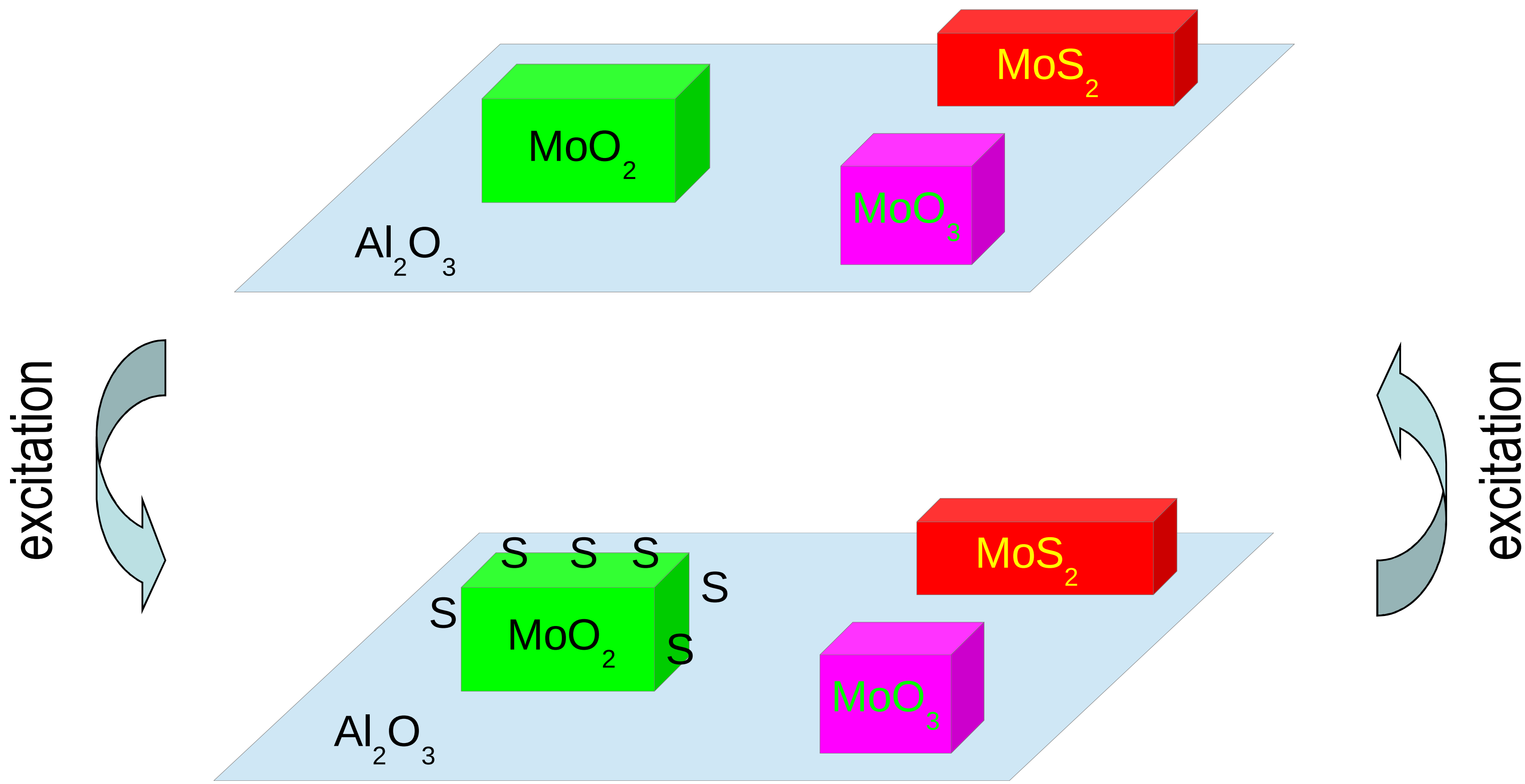
19 atoms (Ø 1.4 nm)	169 atoms (Ø 4.3 nm)

Surface coverage 50%

# ligands : # catalyst	
31%	12%

→ Increasing the sensitivity to changes at the surface is desired for catalysis

Concept of modulated excitation spectroscopy

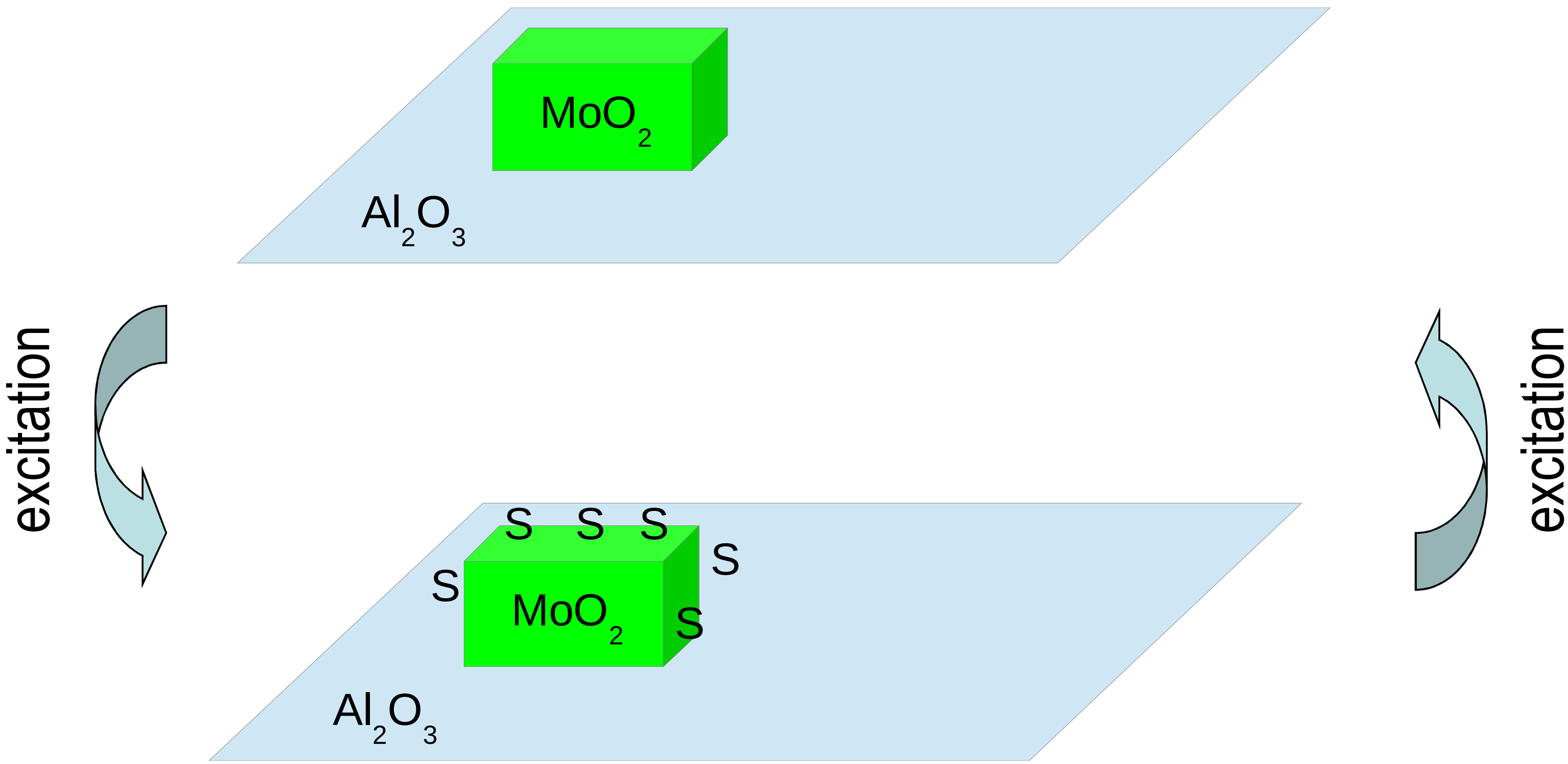


Many species on surface

→ XAS probes all species of selected element

→ We want to filter out the one that changes

Concept of modulated excitation spectroscopy



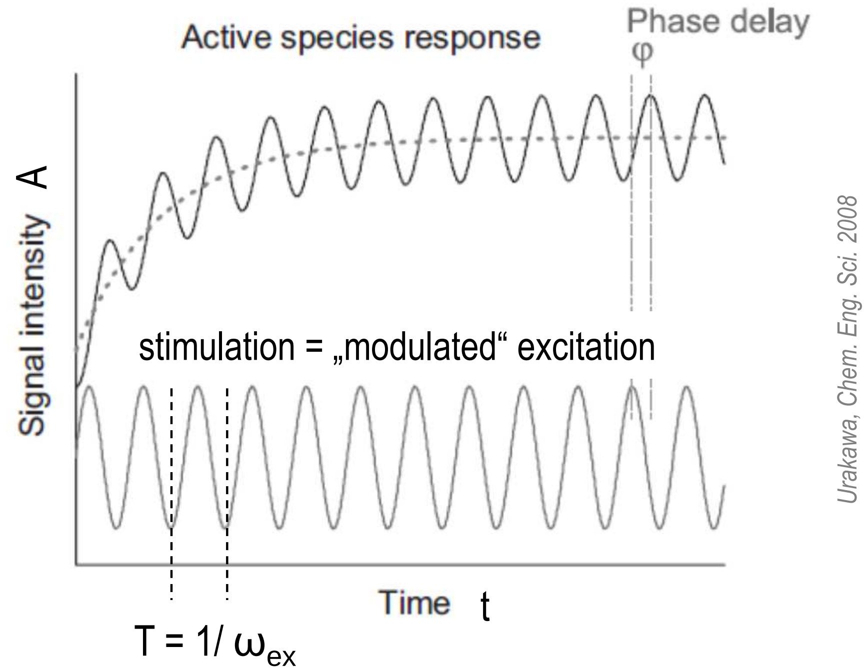
→ Isolate only that species that changes upon excitation

Concept of modulated excitation spectroscopy

Contains only changes due to excitation with ω_{ex}

$$A_k^{\phi^{PSD}}(e) = \frac{2}{T}\int_0^T A(e,t)\sin(k\omega t + \phi_k^{PSD})\,dt$$

XAS dataset



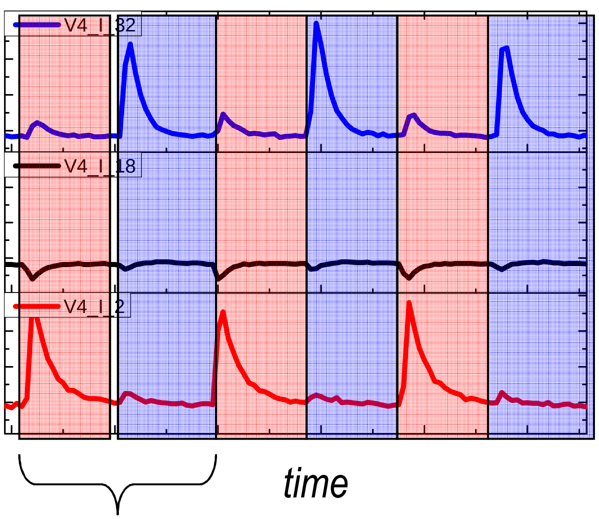
Differentiate between **active species** ($\omega = \omega_{ex}$), spectator species ($\omega = 0$) and noise ($\omega > \omega_{ex}$)

- Applied to IR for > 10 years, recently to XRD
- So far: qualitative interpretation of ME-XAS
- *Is a quantitative analysis of demodulated spectra possible?*

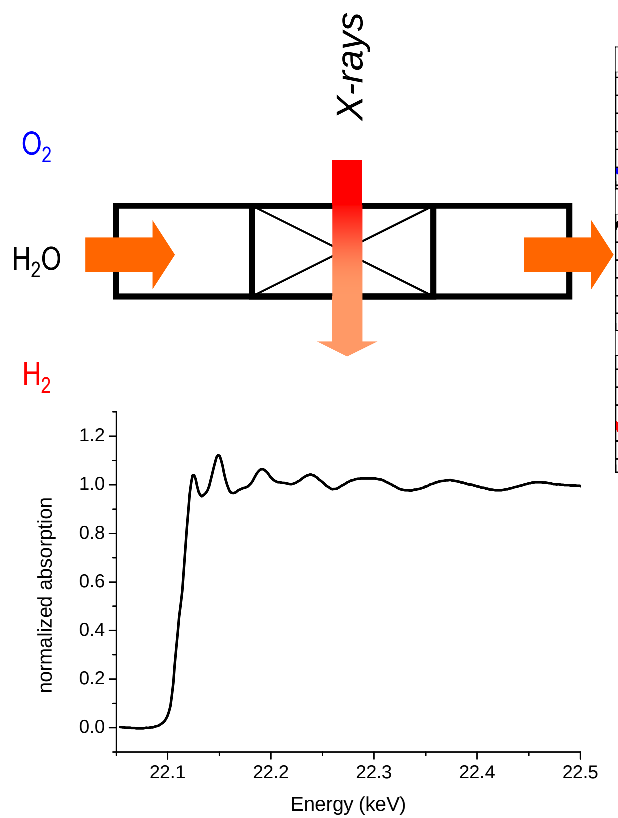
ME-XAS – Experimental setup

- 2 wt-% Ru / Al_2O_3 catalyst
- test reaction: reduction / oxidation
- Quick XAS Monochromator (SuperXAS beamline, SLS)
  → 1 spectrum / second @ Ru K-edge

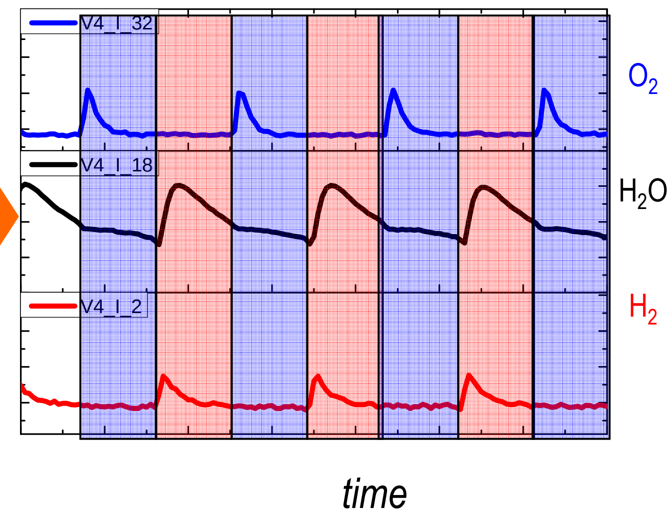
MS data: reactor inlet



T = 1/ω

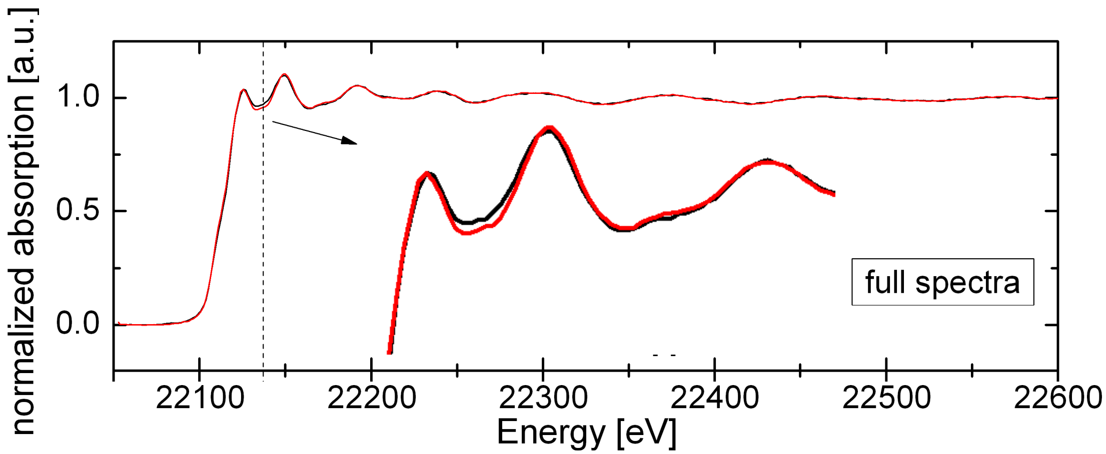


MS data: reactor outlet



- H_2 and O_2 consumed
- H_2O produced

ME-XAS – schematic procedure



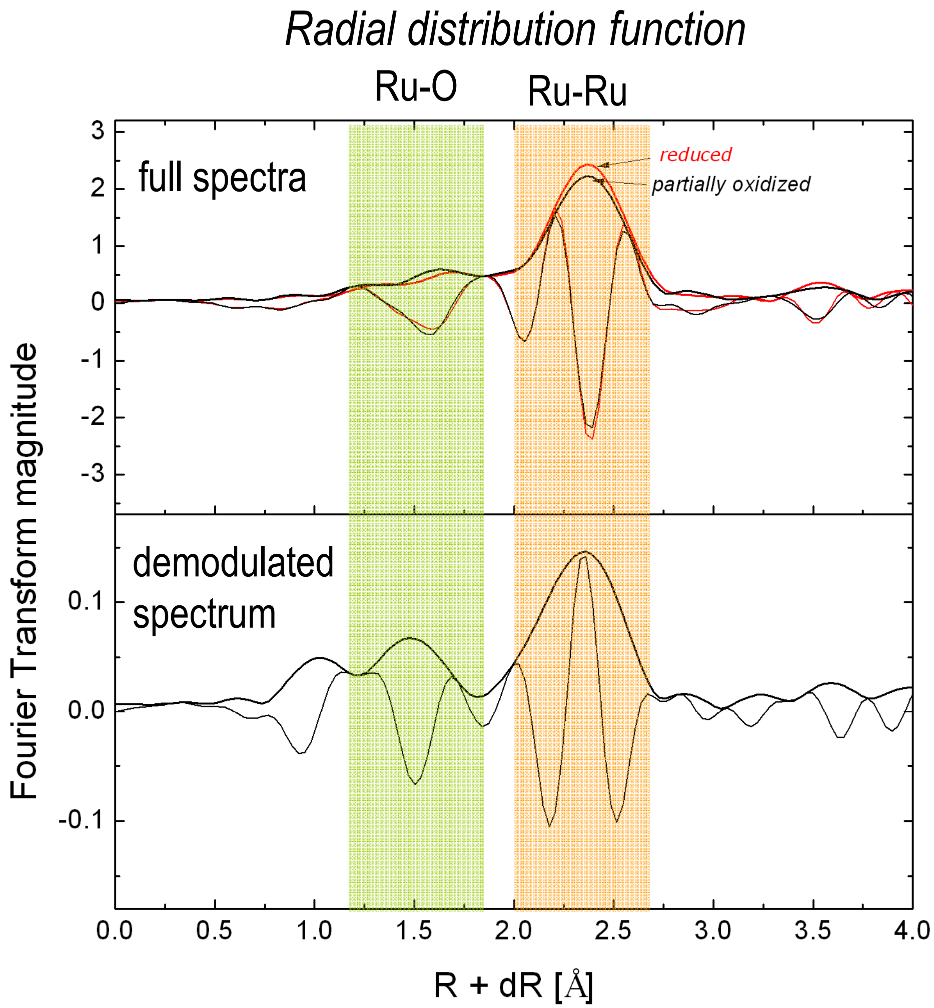
Full spectra
→ reproducible, small changes

Δ-spectrum
→ little structural data

Demodulated spectra
→ same information, but better S/N

König, van Bokhoven, Schildhauer, Nachtegaal *J. Phys. Chem C* (2012)

Full spectra vs. demodulated spectra

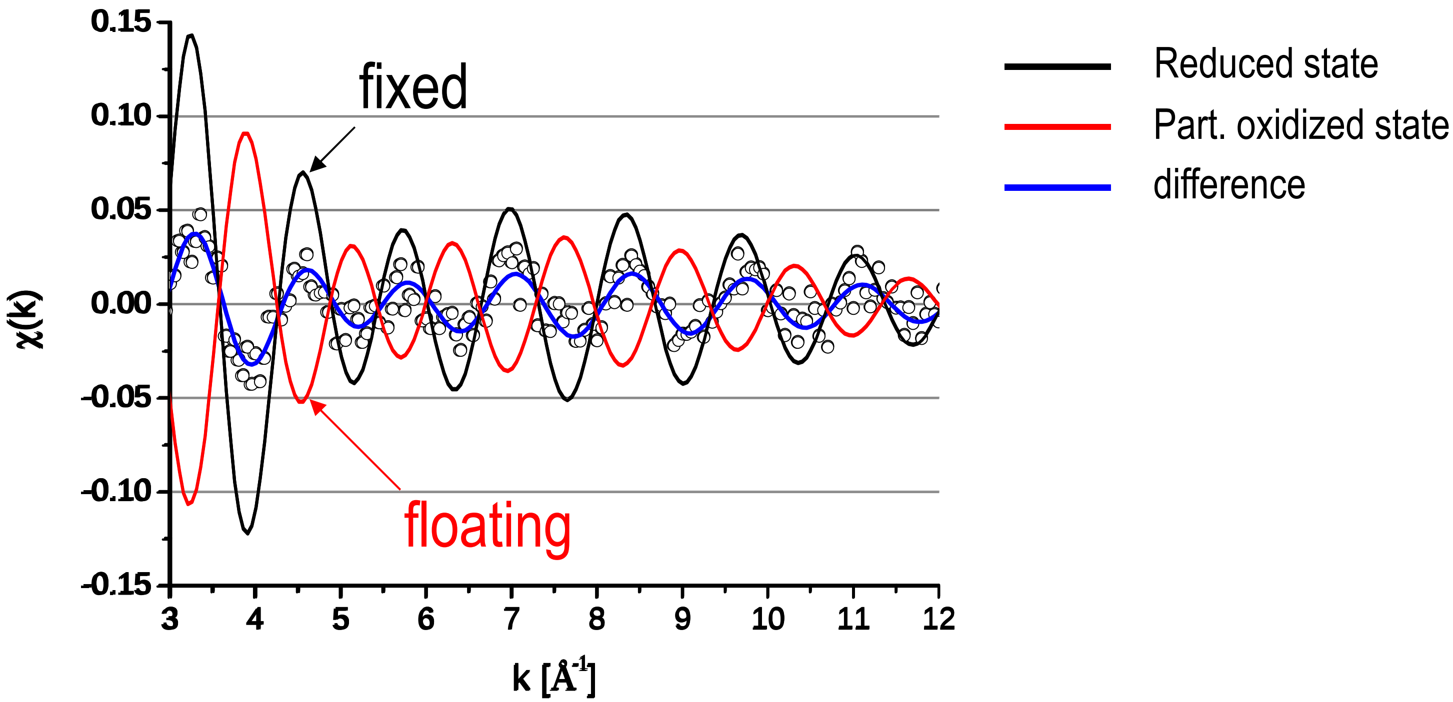


The **full spectra** show little difference

The **demodulated** spectra show only structural *changes*

→ How can we extract structural information?

ME-XAS – Fitting approach



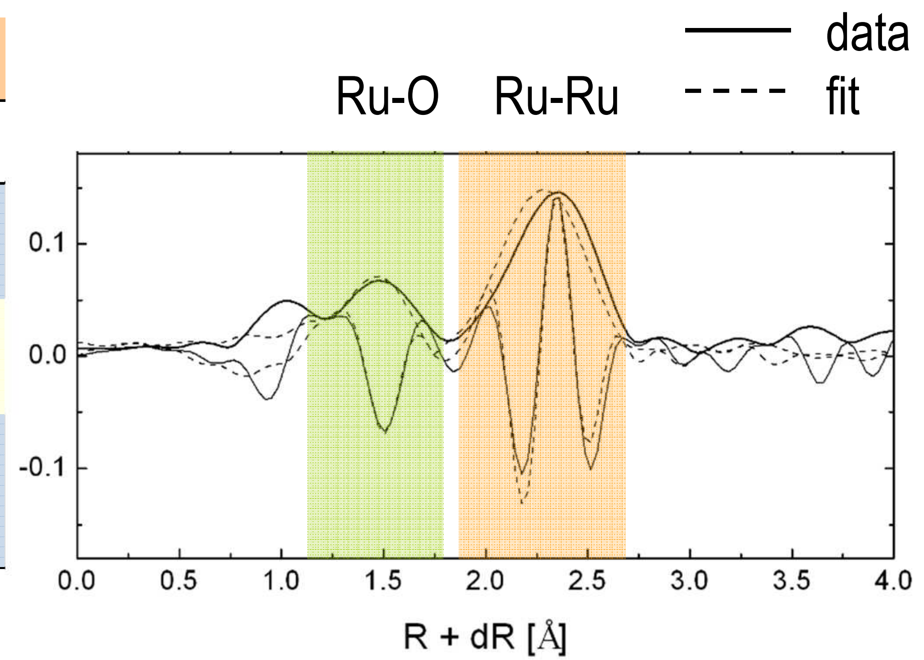
Demodulated spectrum = reduced spectrum – oxidized spectrum

→ Use two fitting functions (shells, paths), subtract one from the other
→ Fix one function of a known state (e.g. reduced state)

Differences are well fitted, even if absolute numbers have errors

ME-XAS - fit results

	Ru-Ru shell	
	Coordination number	Distance [Å]
reduced (full spectrum)	**10.0 ± 1.2**	**2.683 ± 0.005**
partially oxidized (full spectrum)	**9.3 ± 1.1**	**2.681 ± 0.005**
partially oxidized (demodulated spectrum)	**Δ - 0.8 ± 0.2**	**Δ 0.0022 ± 0.0006**



Fitting of demodulated spectra

- Same differences as full spectra
- Increased precision → higher sensitivity
- Ru-oxide shell at 1.945 Å with CN 0.25 (± 0.09)
  → not detectable with analysis of full EXAFS spectra

ME-XAS - conclusion

Quantitative analysis (i.e. fitting) of demodulated spectra

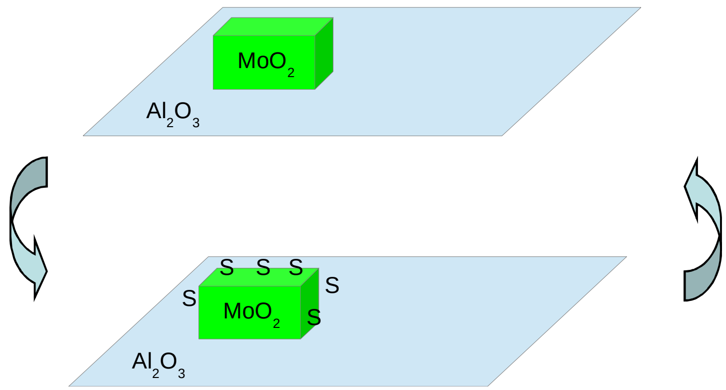
→ robust fitting

→ results comparable to „regular“ EXAFS analysis

→ improved precision (~ 5 - 10x)

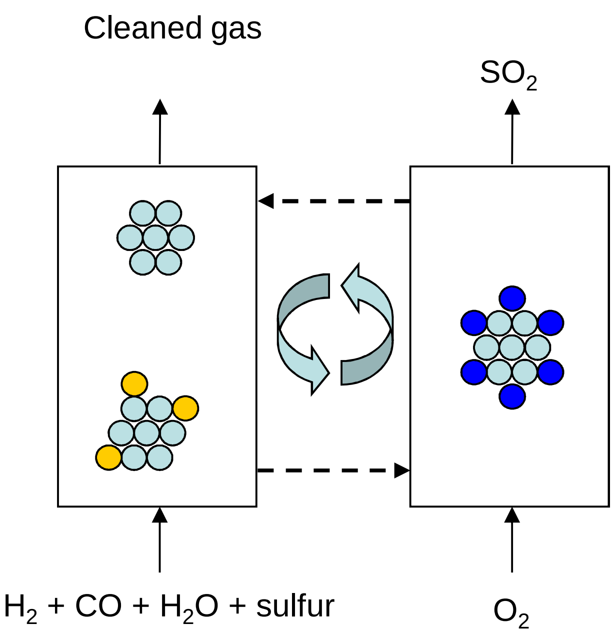
→ detection of minority oxide species

→ **ME-XAS enhances the sensitivity of XAS to small reproducible structural changes of the active site**



Requirements for materials

Now we have the tool to study periodic processes with high sensitivity



Requirements for materials:

- No formation of stable sulfate phase
- Reactive towards H_2S and organic sulfur species
- Stable under reducing / oxidizing conditions
- High temperature stable
- (Catalyze methanation)

Molybdenum or Ruthenium are viable options

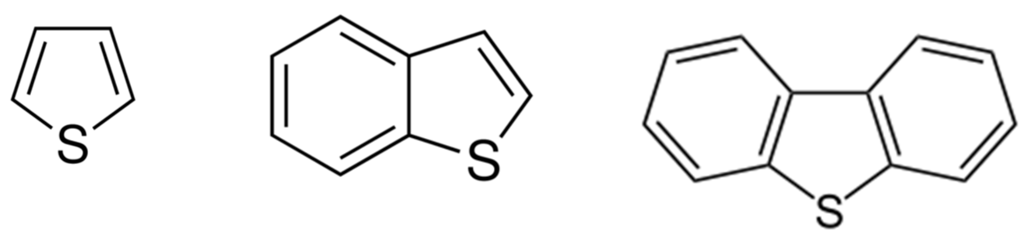
Stand-alone desulfurization over Mo

Goal: Complete removal of inorganic and organic sulfur

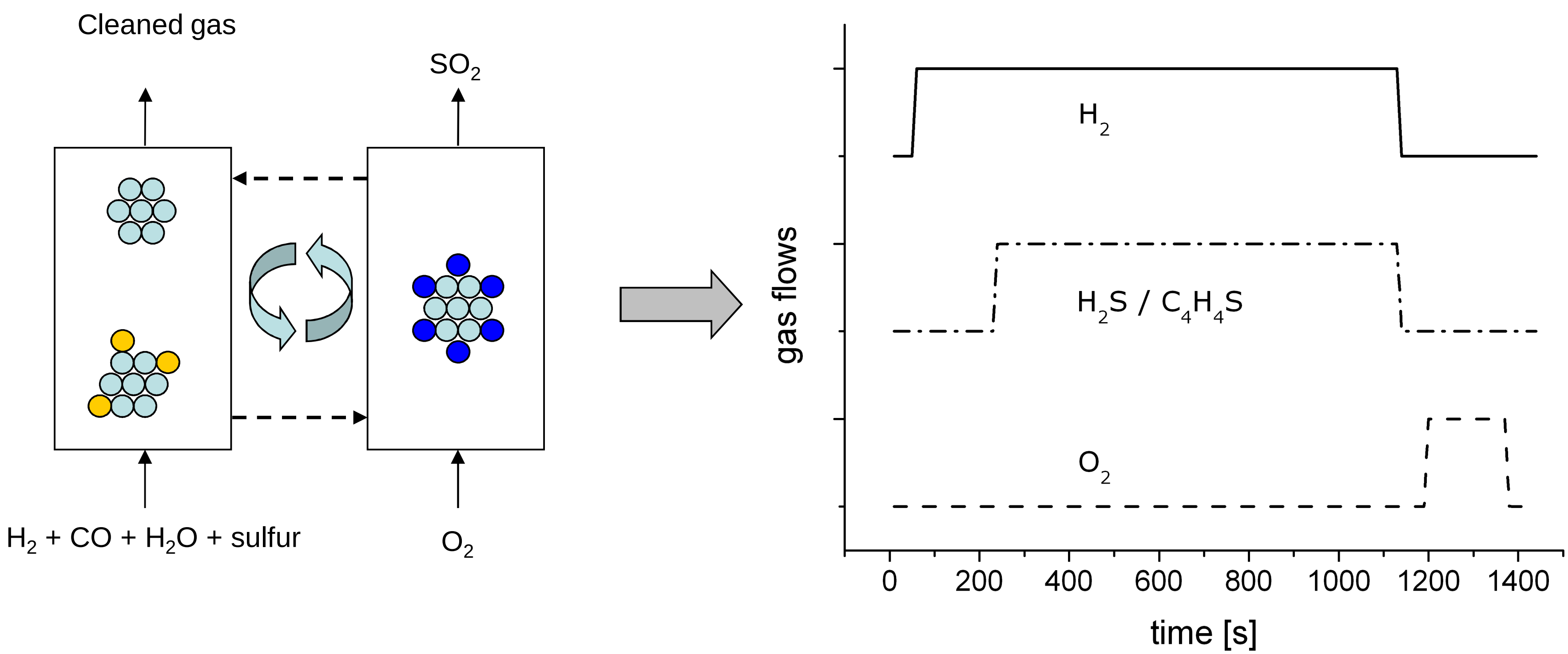
Background:

- Gasified biomass contains organic and inorganic sulfur
- Mo is used in petrochemical refining (HDS)

- *Is removal of inorganic and organic sulfur possible over Mo?*

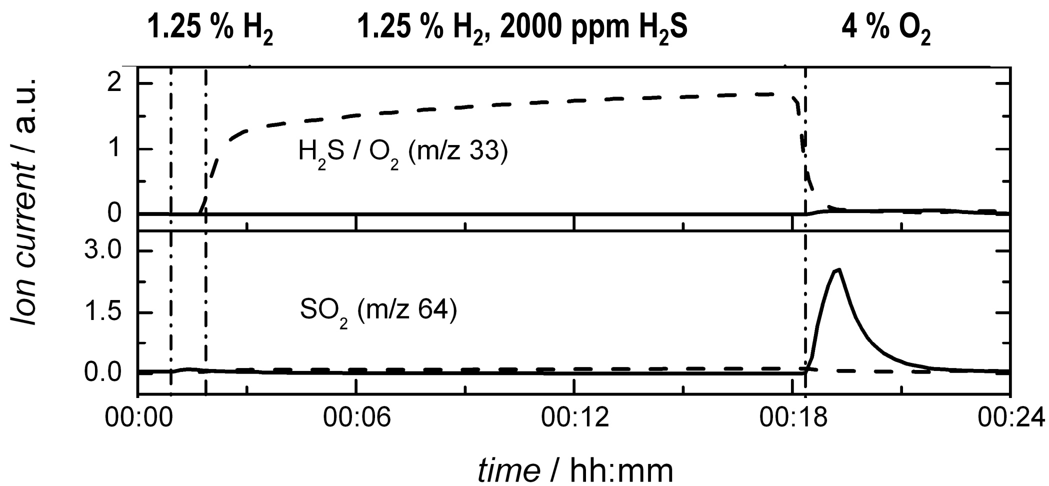


Mo – experiment

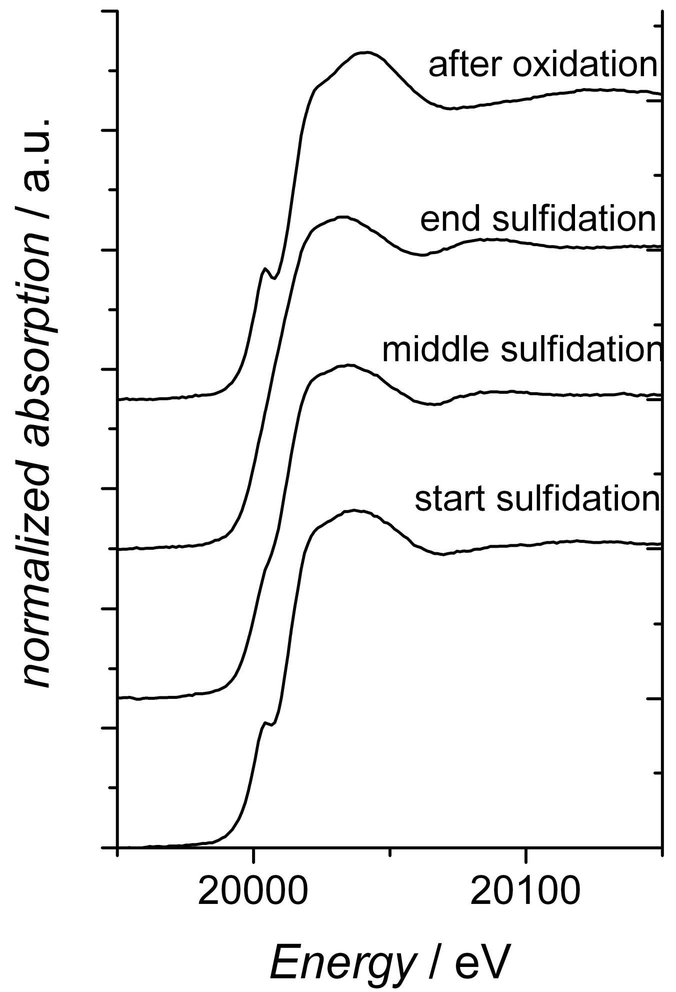


Instead of moving the particle, gas atmosphere is changed

Mo – removal of H_2S



Fitting with reference spectra

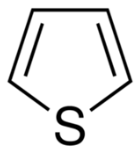


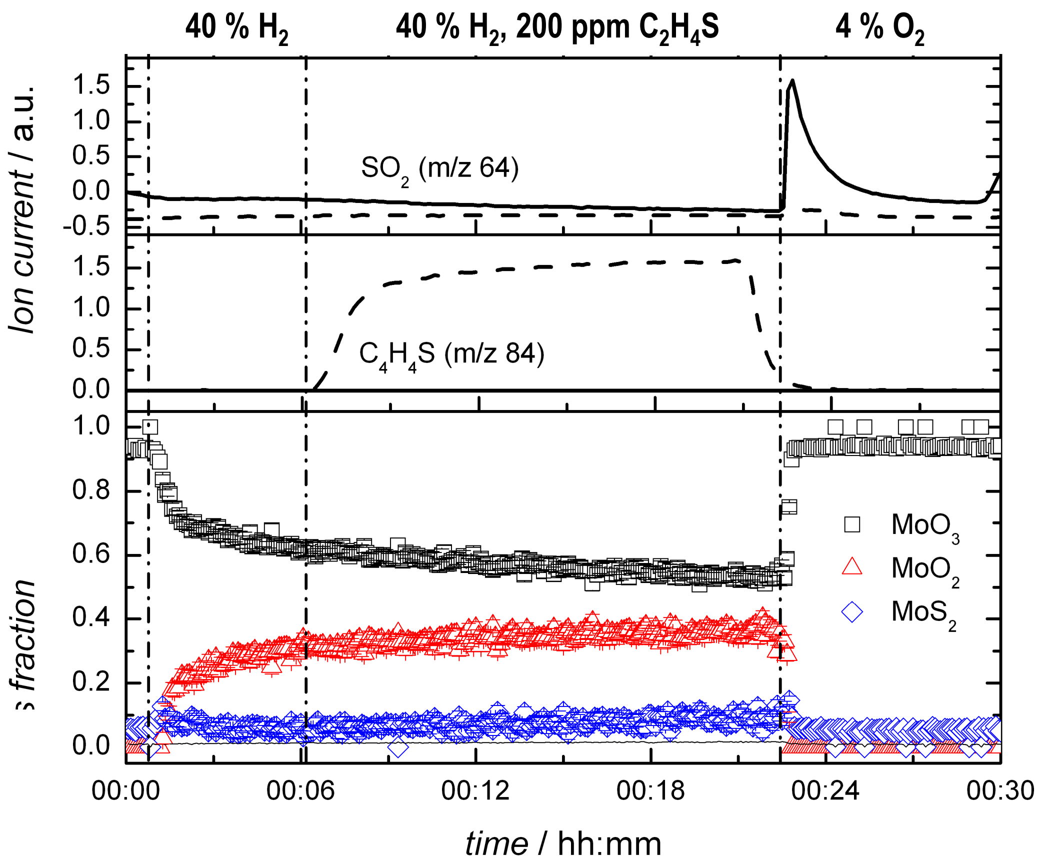
$$MoO_3 + H_2S \rightarrow MoO_2 + MoS_2$$

T = 600 °C, p = 1.5 bar

König, Schuh, Schildhauer, Nachtegaal *ChemCatChem* 5, 3700-3711 (2013)

Mo – removal of thiophene

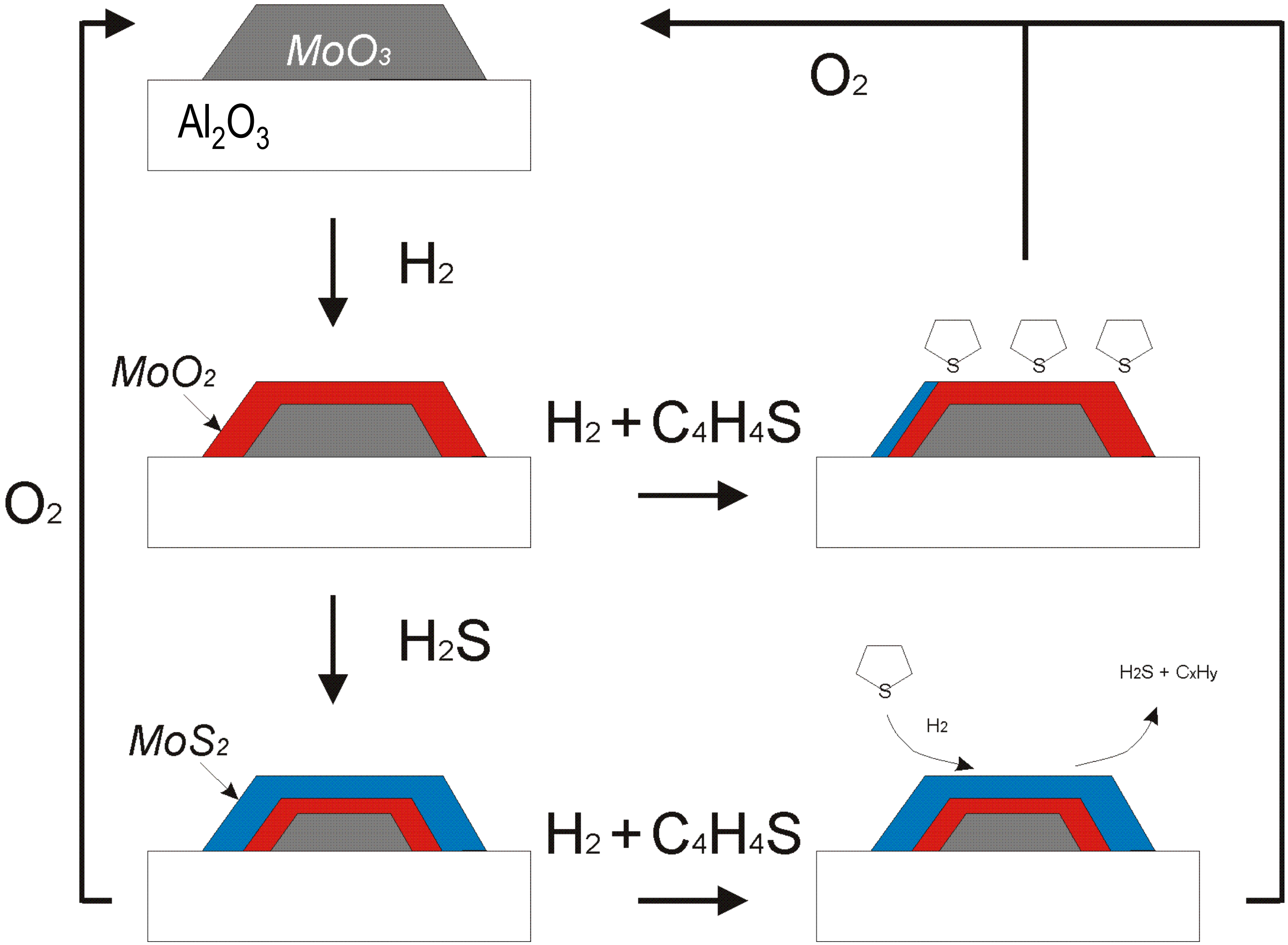




- SO_2 is generated
- Thiophene is removed
- Conversion over MoO_2 / MoO_3
- What happens to sulfur?

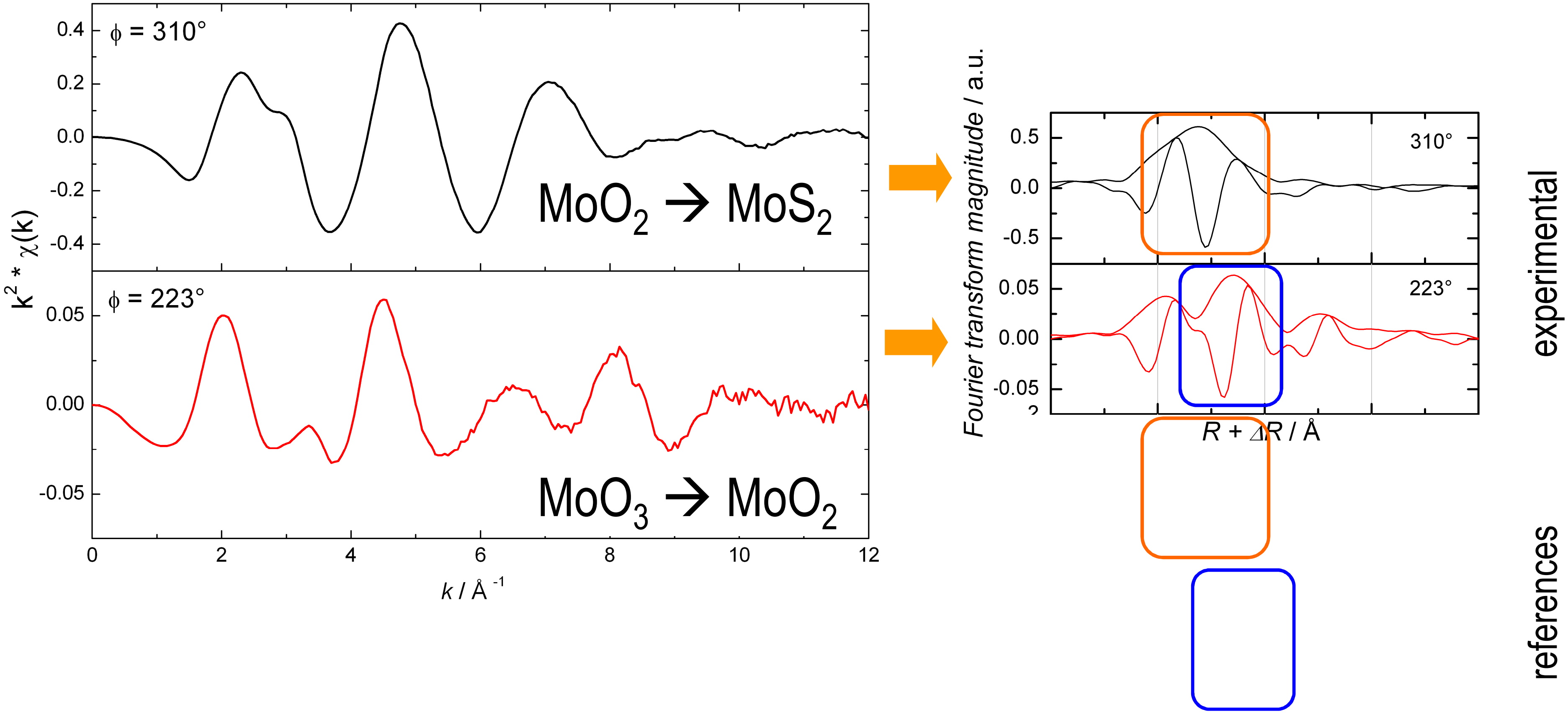
T = 600 °C, p = 1.5 bar

Mo - conclusion



- H_2S and C_4H_4S removed

Mo – thiophene removal – demodulated spectra



Two distinctively different spectra → at least three Mo species

$MoO_3 \rightarrow MoO_2 \rightarrow MoS_2$

Integrated methanation / desulfurization over Ru

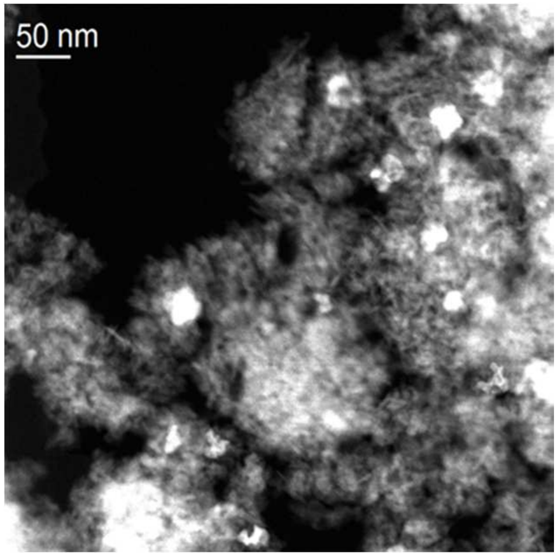
Goal: Integrated methanation and sulfur removal

Background:

- Ruthenium / Nickel catalyze methanation
- Catalysts sensitive to sulfur poisoning
- Ni is very difficult to regenerate
- Periodic regeneration can allow process integration

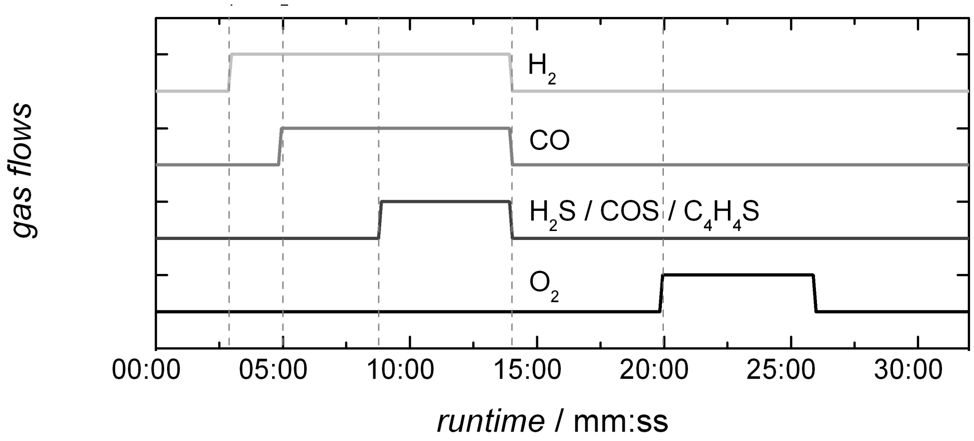
- *Is periodic regeneration possible over Ru catalysts?*

Ru – material and experimental conditions



Ru / Al_2O_3

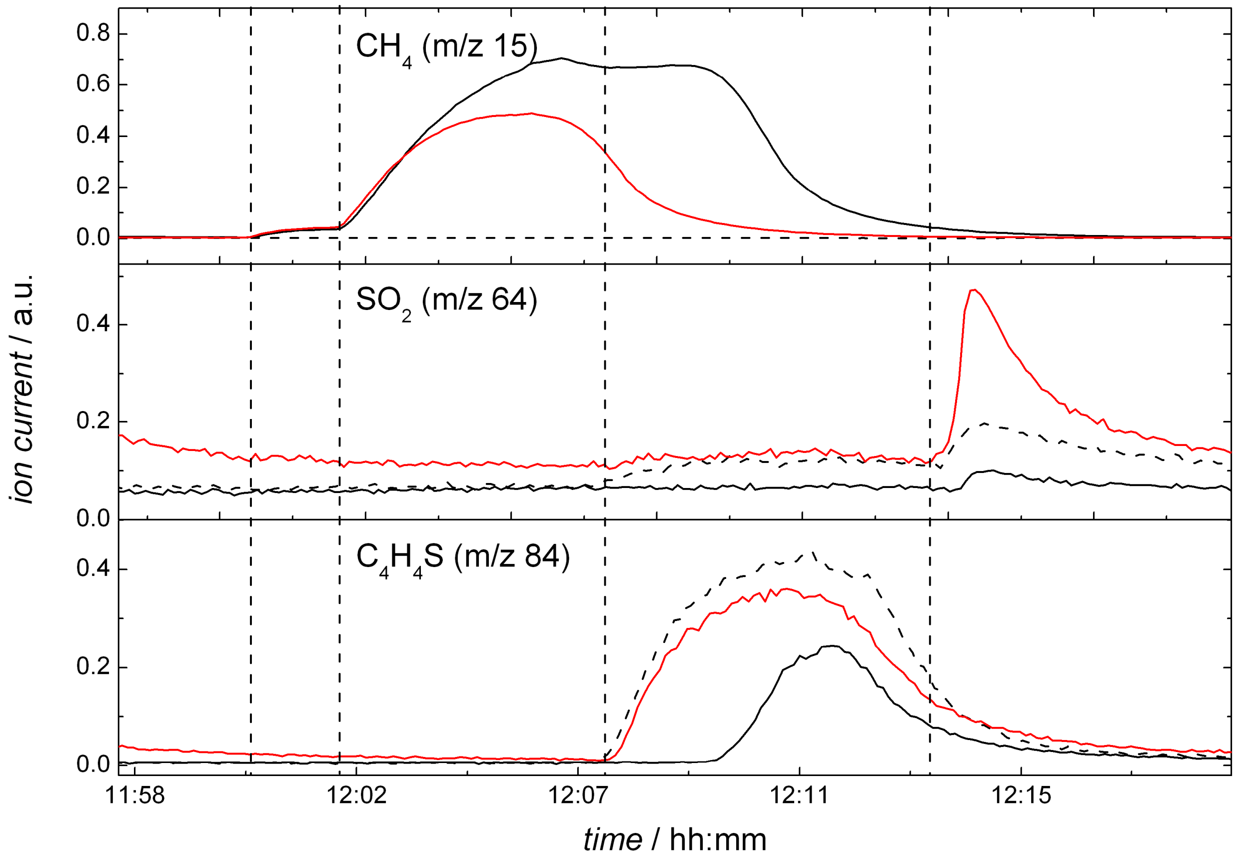
Particle size 10-40 nm



Ru - reactivity

2.5 % H_2 | 2.5 % H_2, 0.25 % CO | 12 ppm C_4H_4S, 6 ppm COS, 60 ppm H_2S | 0.25 % O_2

- - - - inlet
—— outlet (1st cycle)
—— outlet (20th cycle)



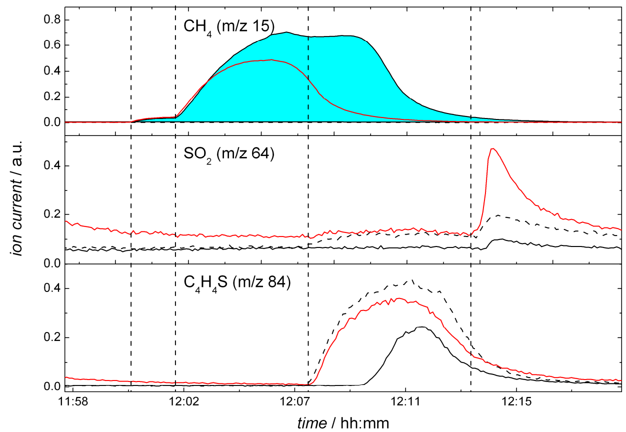
T = 430 °C, p = 1.5 bar

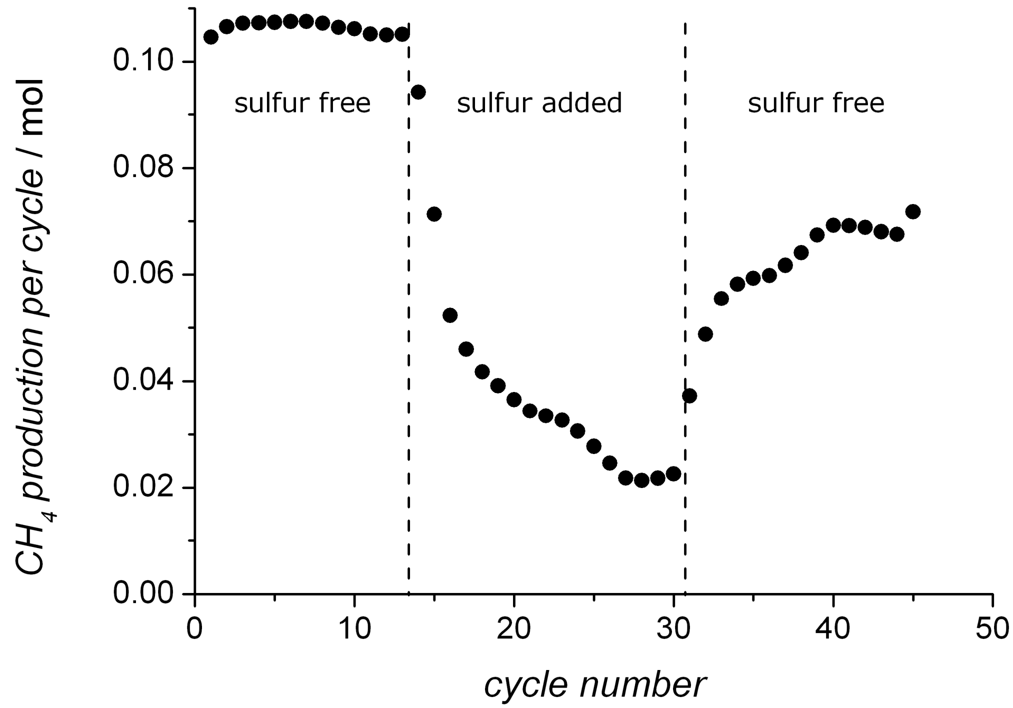
- Ru synthesizes methane
- Oxidation releases SO_2, regenerates CH_4
- When C_4H_4S breaks through, CH_4 drops

König, Schildhauer, Nachtegaal *J. Catal.* 305, 92-100 (2013)

König, Schildhauer, Nachtegaal et al, Patent application (2012) 2012P16103EP

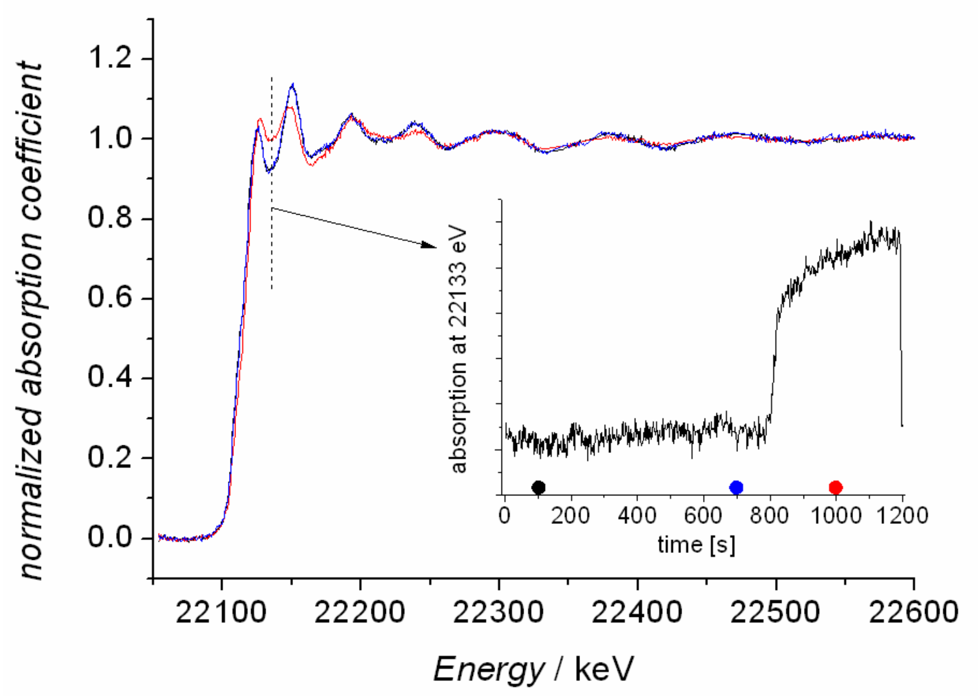
Ru - reactivity





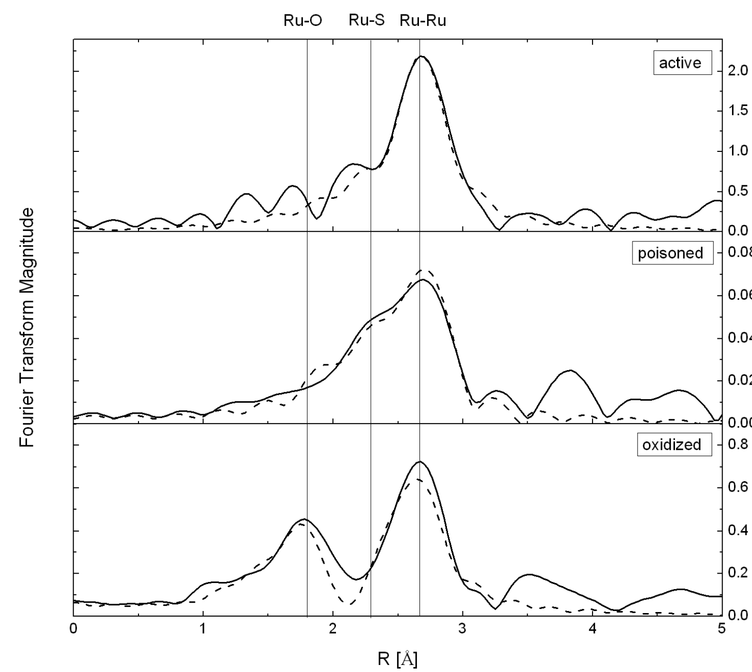
- ➢ Regeneration possible over several cycles
- ➢ Steady state operation seems feasible
- ➢ Activity not recovered to 100 %

Ru – structure



Ru K-edge XAS

- Change from Ru metal to Ru oxide
- No bulk Ru-sulfide detected

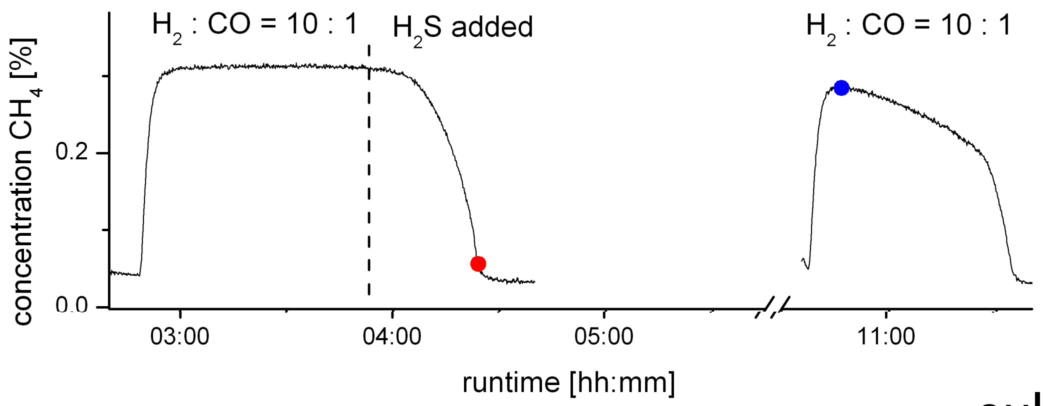


Demodulated spectra

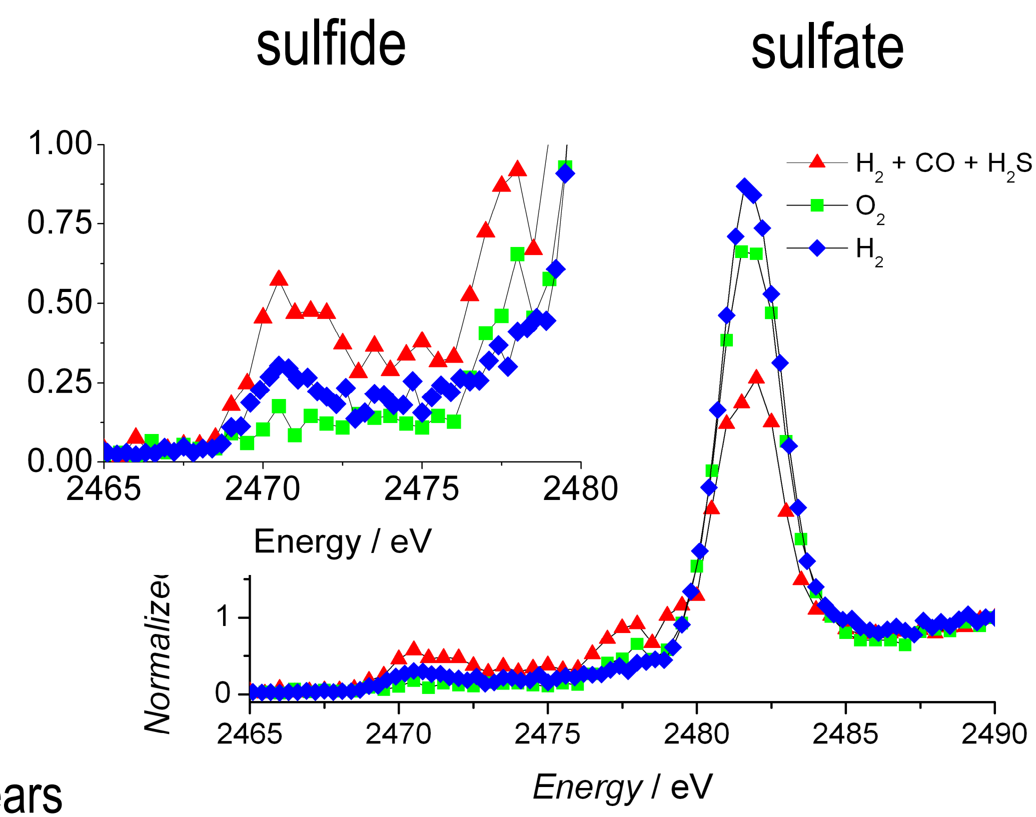
- Detection and quantification of Ru-S
- Ru-S is formed and removed
- Coordination number 0.07 ± 0.02

State of sulfur?

Sulfur K-edge XAS

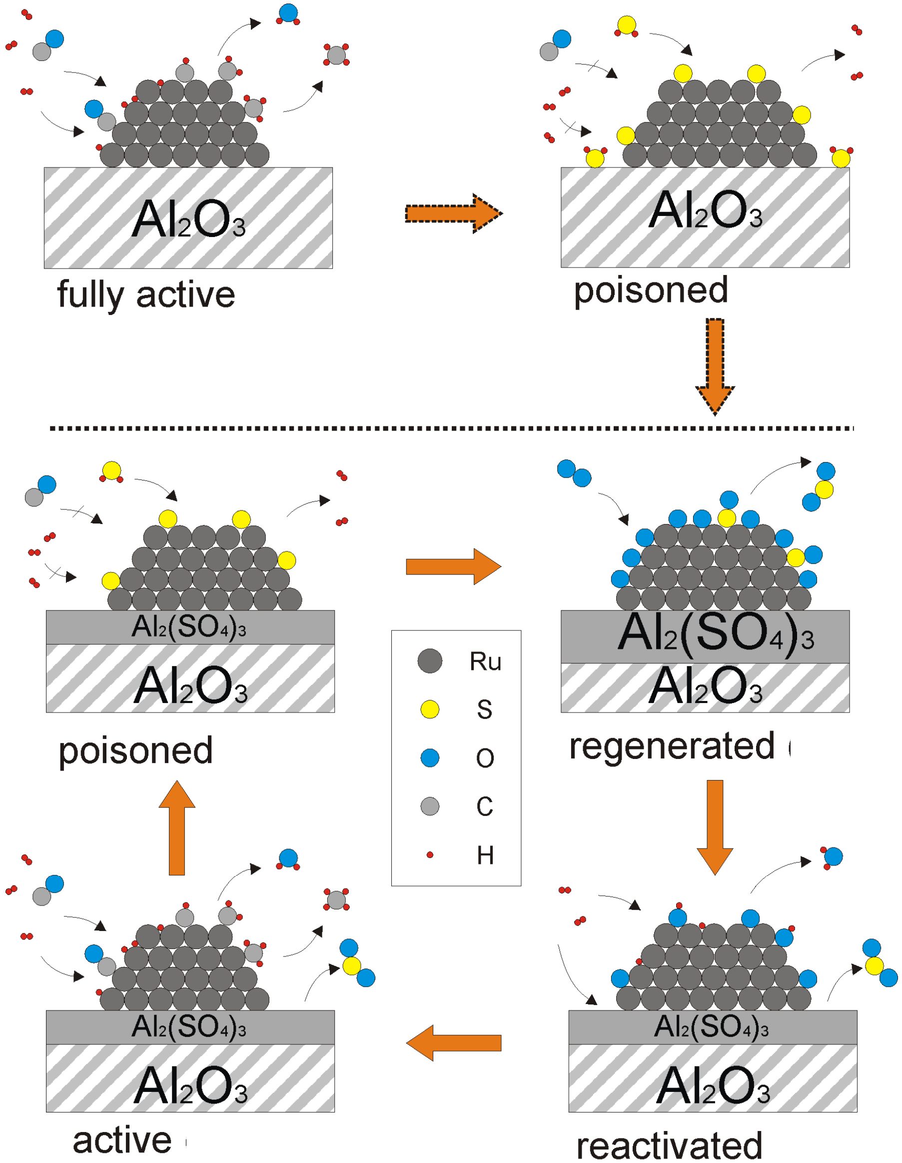


- Oxidation regenerates methanation
- After regeneration, methanation drops over time, even in sulfur-free feed



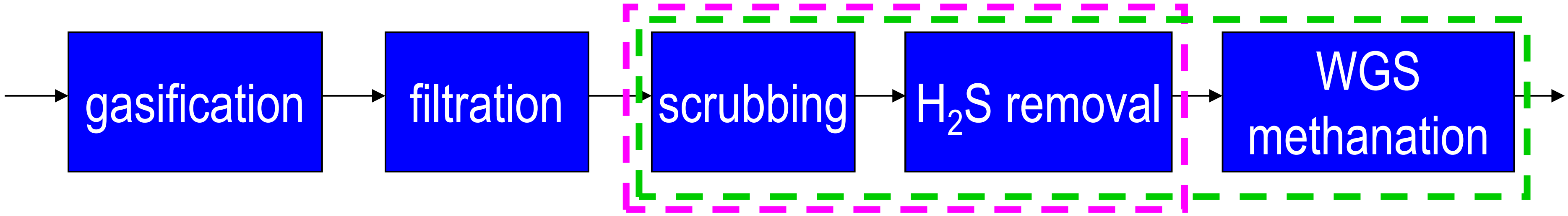
- H_2S poisoning generates sulfide and sulfate species
- Regeneration removes sulfides
- After reactivation, sulfide re-appears

Ru methanation / poisoning – proposed mechanism



→ Transport of sulfur from support to catalyst and back

Wood to SNG – simplified process scheme



High temperature desulfurization options:

Molybdenum:

- Complete H_2S removal
- Thiophene conversion

Ruthenium:

- Complete H_2S removal
- Thiophene conversion
- Methane synthesis

Questions addressed today:

Why is time resolution (Quick EXAFS) important in environmental chemistry?

Time resolution essential to study kinetics

How is time resolution achieved? (technical details)

QEXAFS monochromator OR dispersive XES spectrometer

What is x-ray emission spectroscopy? (RXES, RIXS, HEROS, valence to core XES, etc.)

Second order process: provides information on electronic structure (density of states)

Quick XES examples

Time resolved HEROS (high resolution, no self-absorption

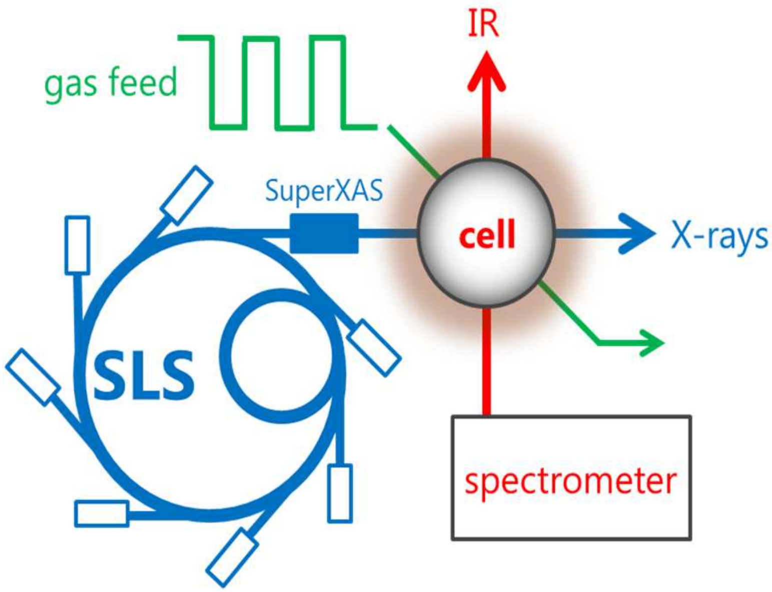
Quick XAS examples

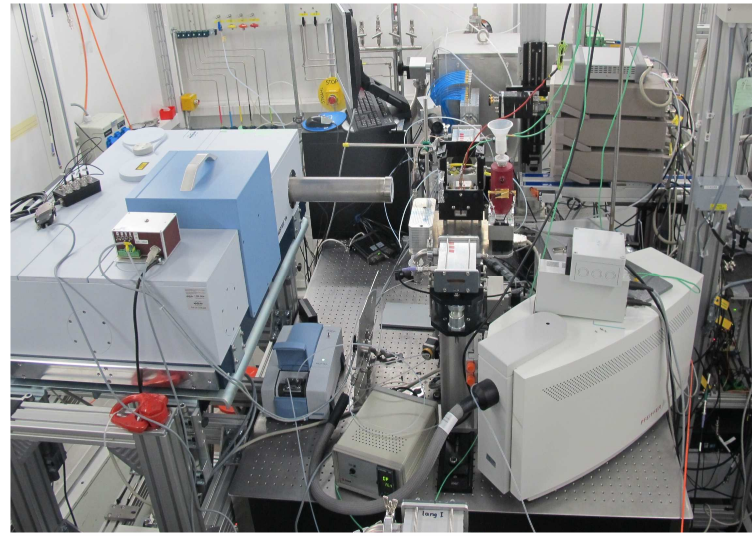
Modulation excitation spectroscopy to enhance surface sensitivity, optimizing wood to SNG process

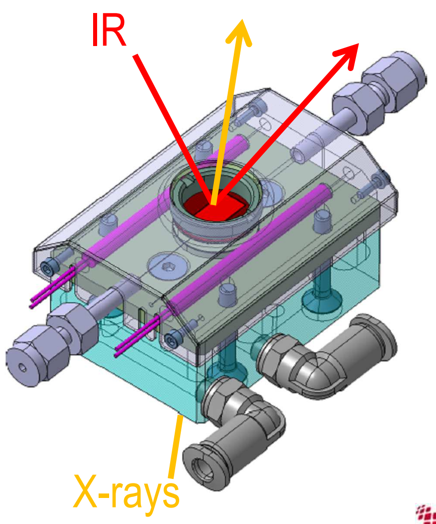
Questions?

PAUL SCHERRER INSTITUT PSI

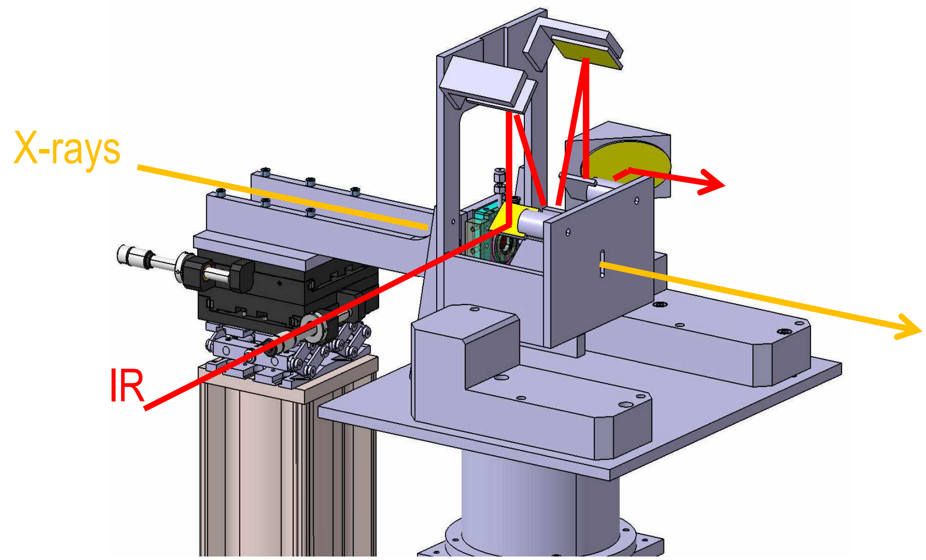
Combined synchronous XAS-IR-MES at SuperXAS







- installed at SLS for user operation
- *in situ* investigation of functional materials



Chiarello et al., *in preparation*

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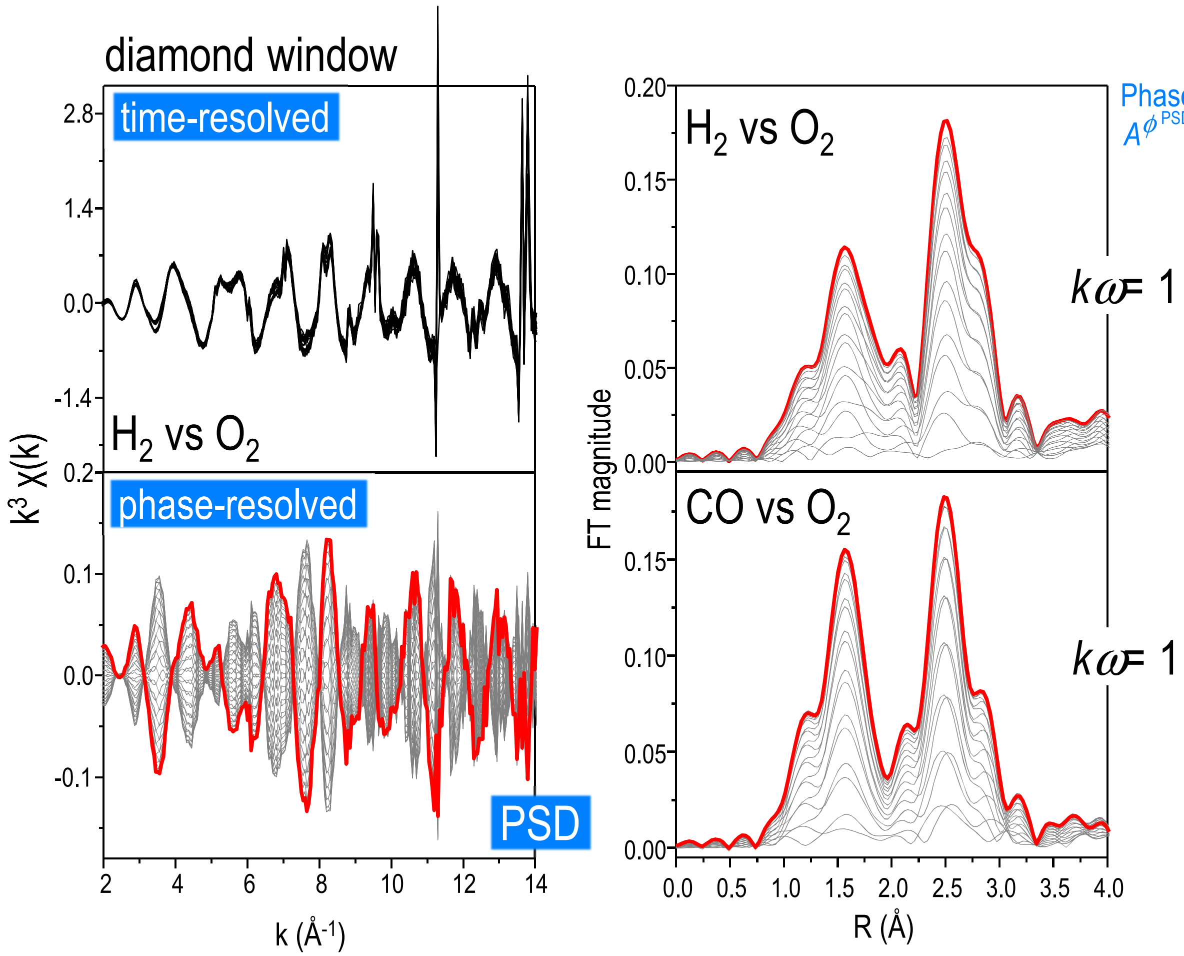
Combined synchronous XAS-IR-MES



Phase Sensitive Detection (PSD)

$A^{\phi^{PSD}}(e) = 2/T \int A(e,t)\sin(\boldsymbol{k\omega}t+\phi^{PSD})dt$

- diamond: far less diffraction peaks, but not suitable for DRIFTS…

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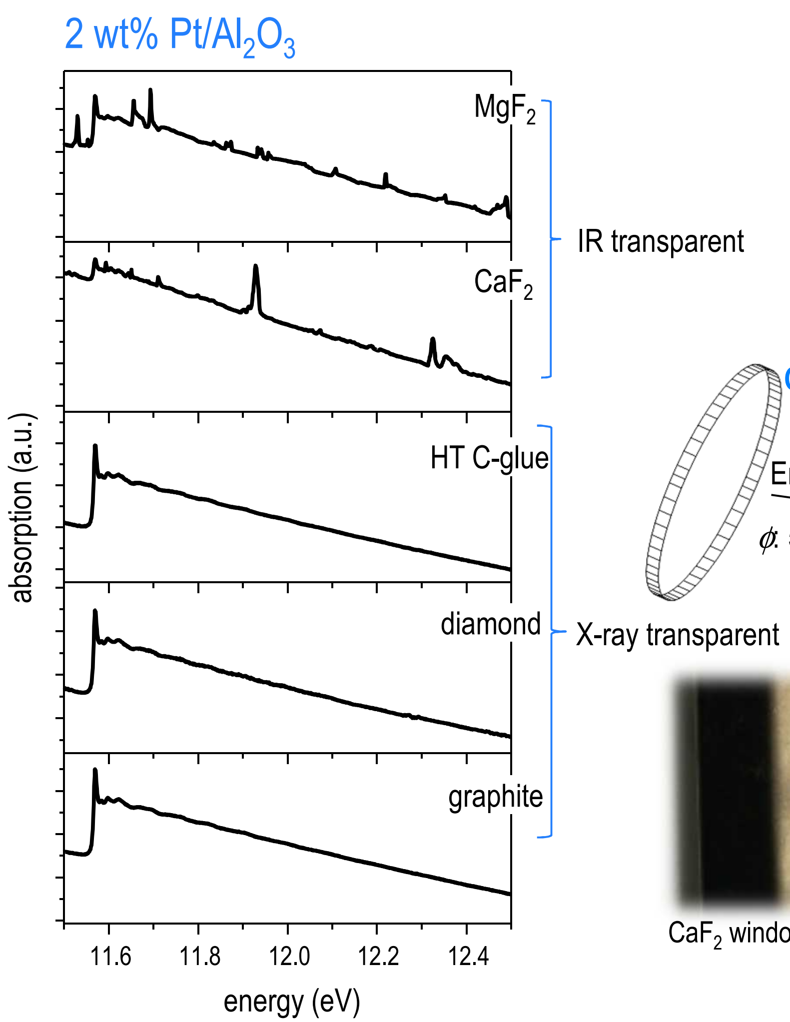
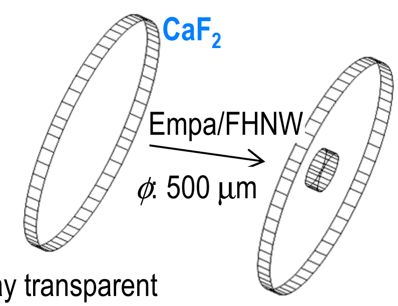
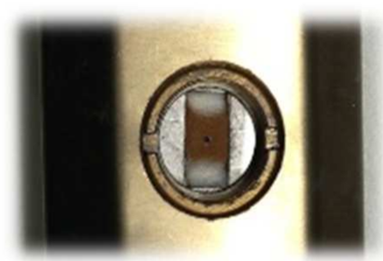
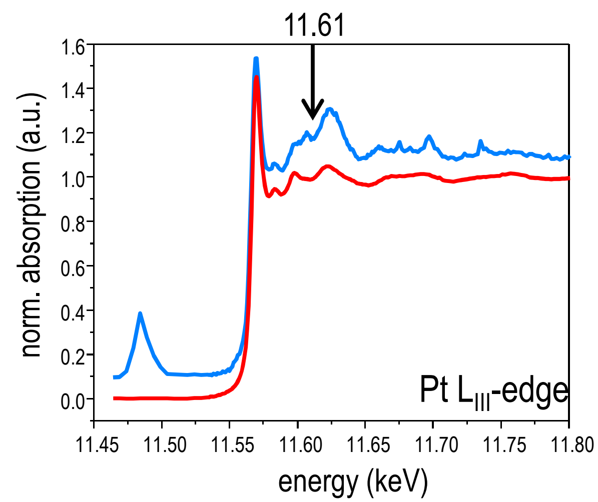
Which window for XAS-IR combination?

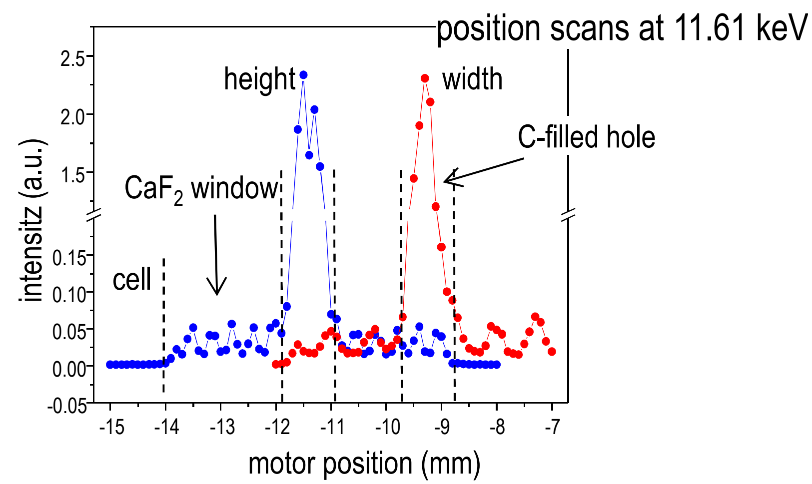






CaF$_2$ window with C-filled hole





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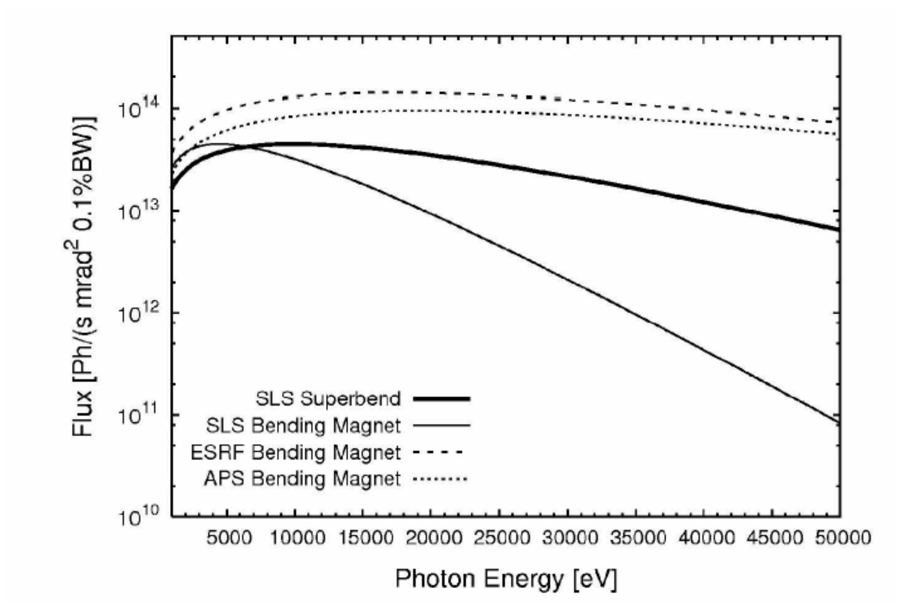
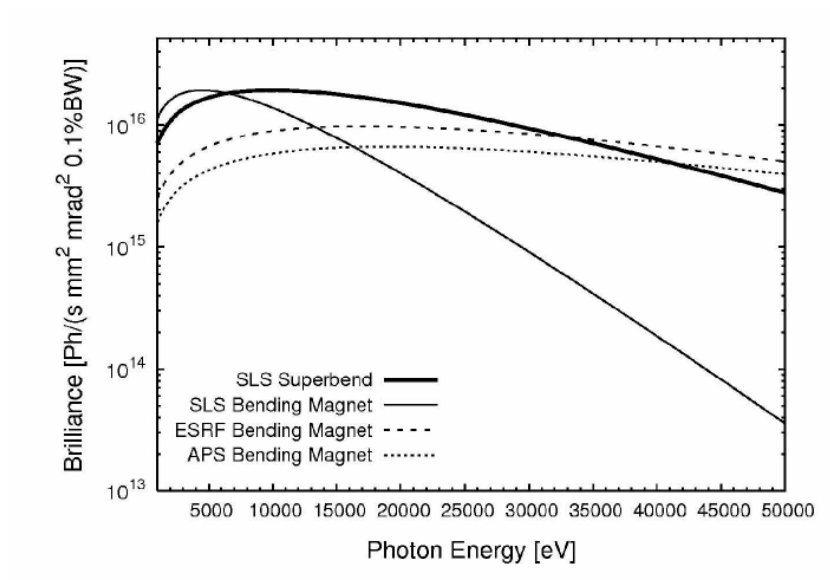
XAS at a ´superbend´

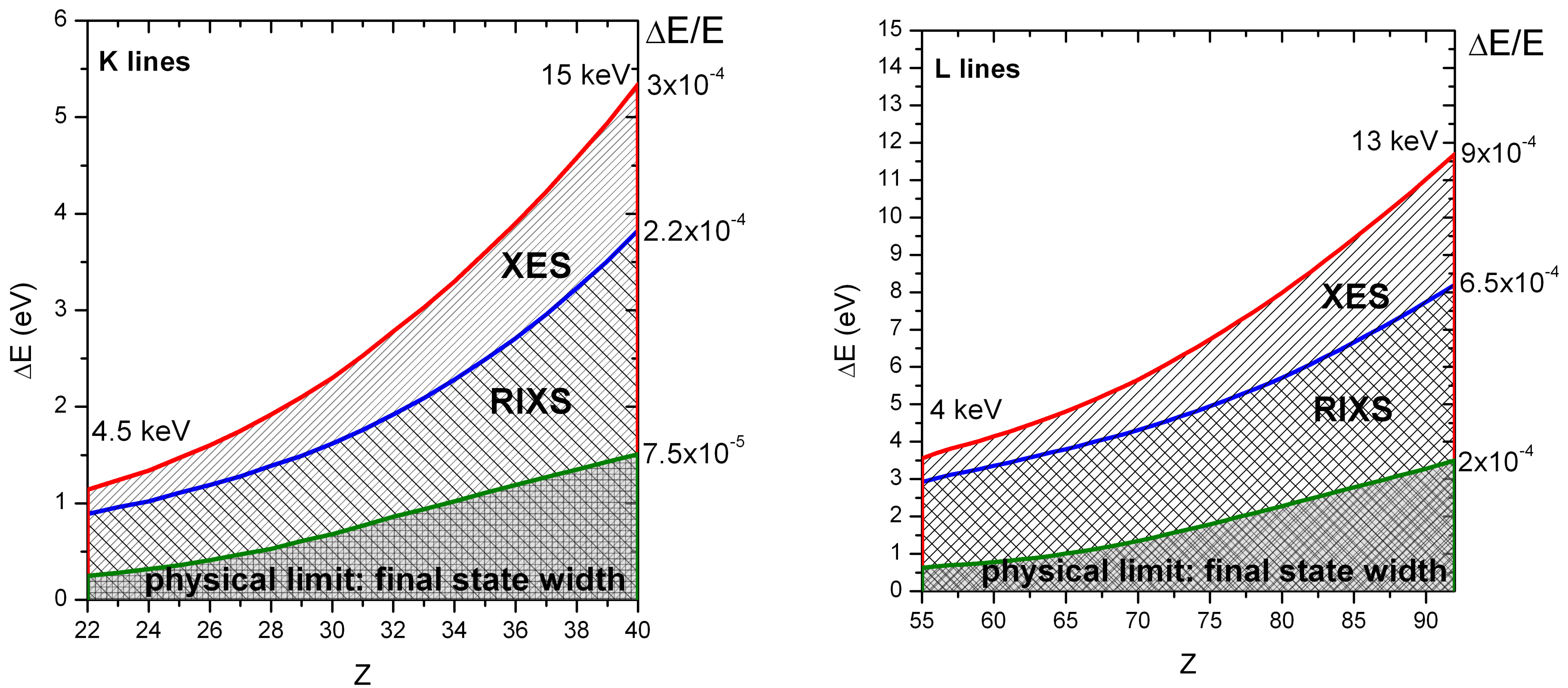


Flux at SLS Super
bend source (2.9 Tesla)

Brilliance at SLS Super
bend source (2.9 Tesla)



High resolution spectroscopy



XES resolution -> only x-ray detection

RIXS resolution -> x-ray detection & incident beam

Von Hamos spectrometer

Segmented crystals