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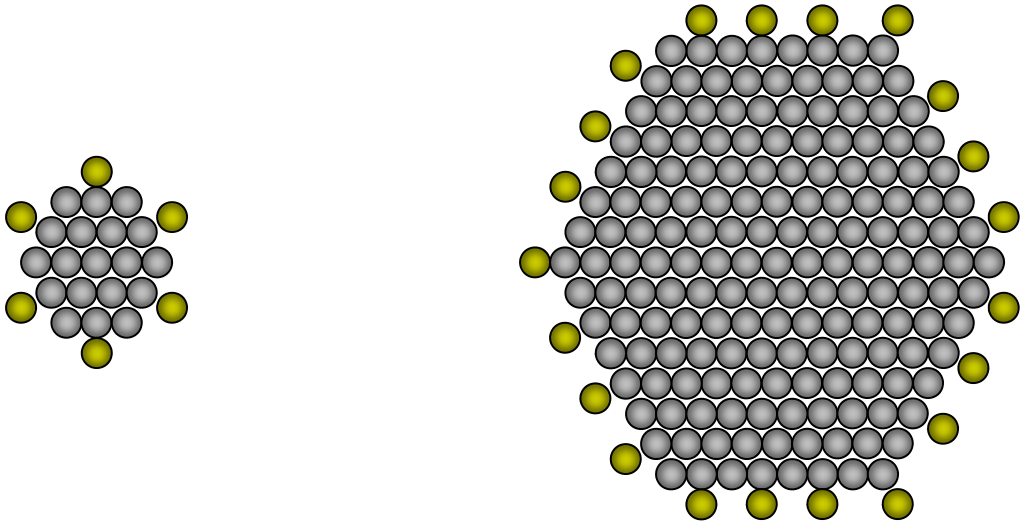
Modulated excitation X-ray absorption spectroscopy
Part I - Theory

In-situ methods of X-ray absorption spectroscopy
Brookhaven National Lab – October 2013

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

Techniques to improve sensitivity

Uncertainties in regular EXAFS:

- In coordination number: ~ 10%
- In radial distance: ~ 0.005 Å

Approaches to improve sensitivity:

- Difference XAS increases sensitivity in R to ~ 1 fm

(Pettifer et al, Nature, 2006)

- Δμ XANES requires simulations to identify adsorbates

(Ramaker & Koningsberger, PCCP, 2010)

Goal: have method that exploits time resolution, detects intermediates

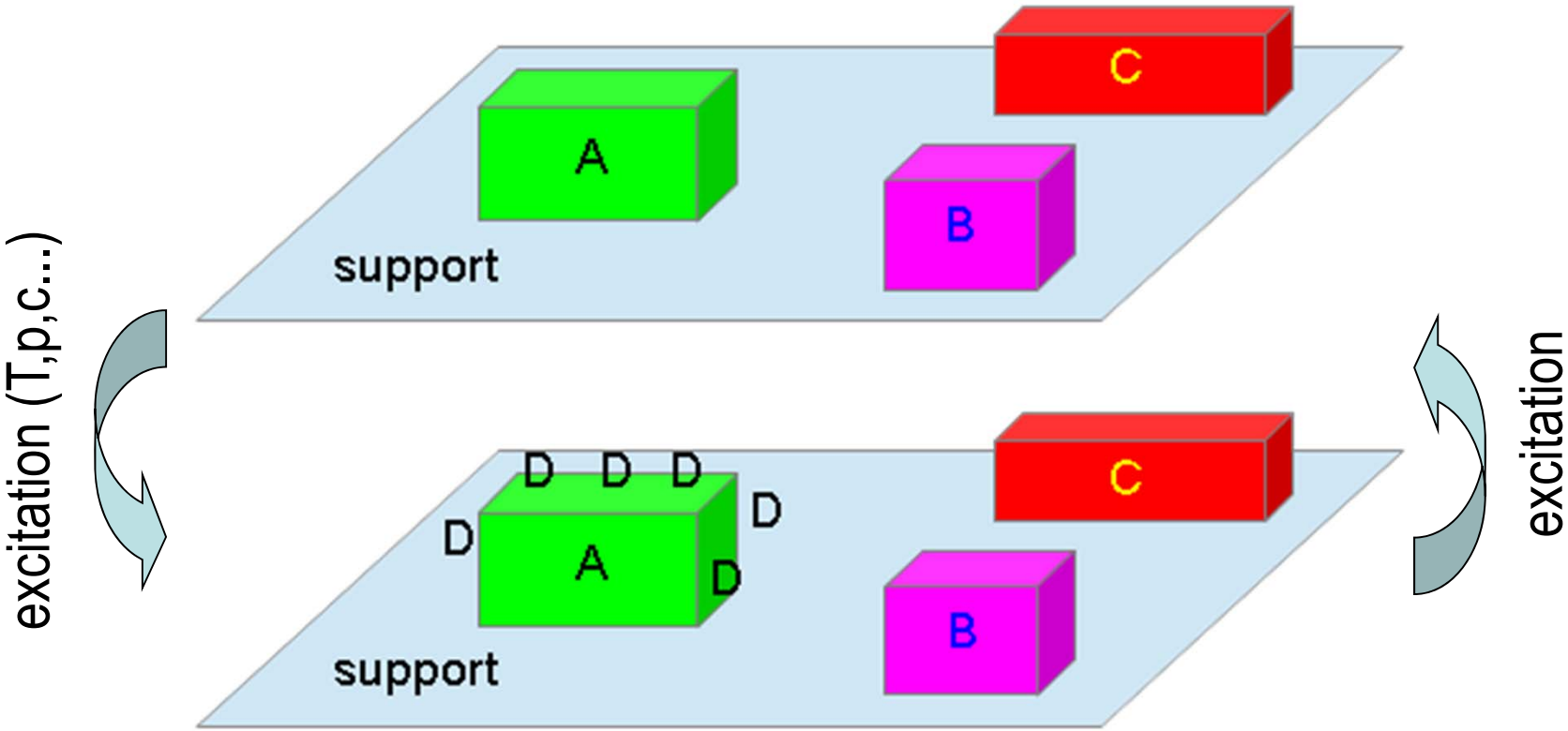
Outline

Part I – Theory / Background

1) Modulated-excitation XAS: Concept
2) Qualitative interpretation – Fingerprinting
3) Quantification – EXAFS fitting
4) Theoretical and practical considerations
5) Summary / Outlook

Part II – Practical walk-through

Concept of modulated excitation spectroscopy

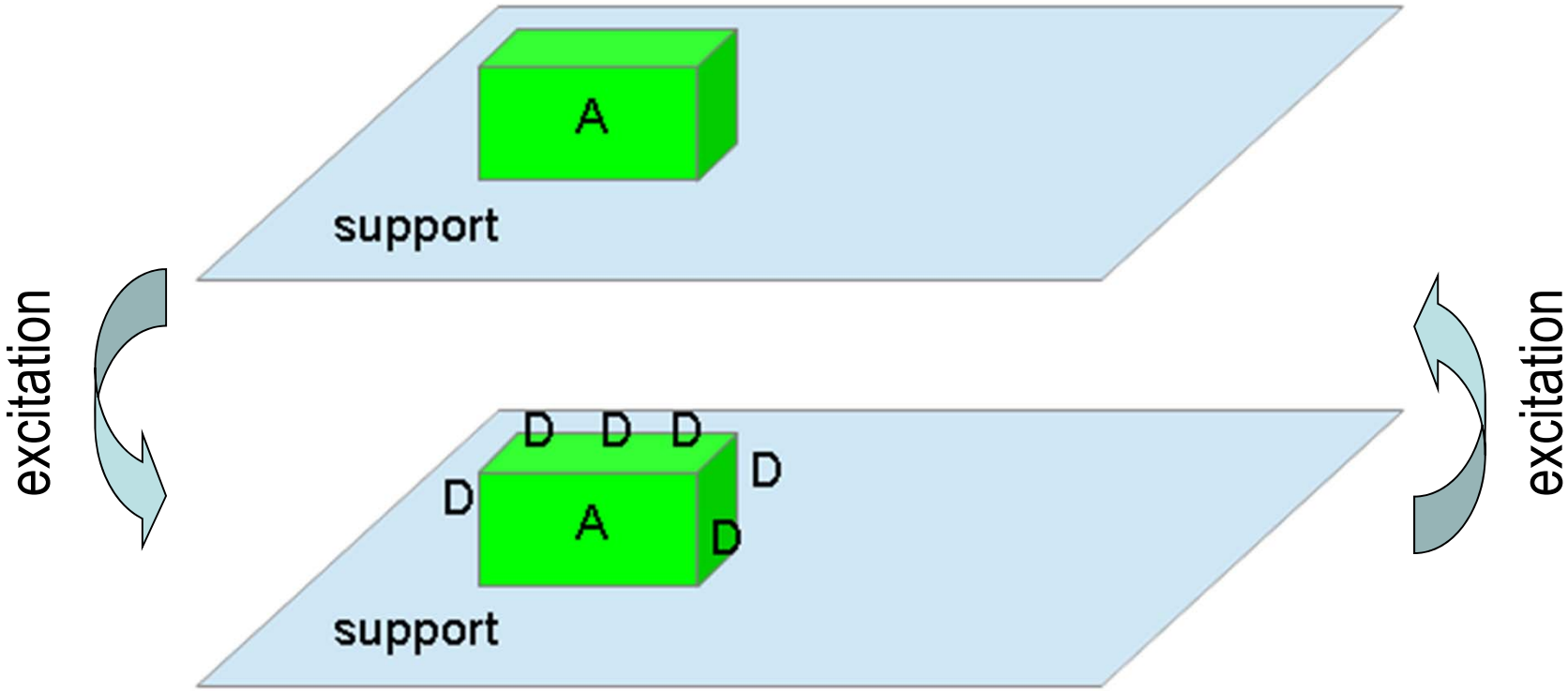


Many species on surface

→ 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

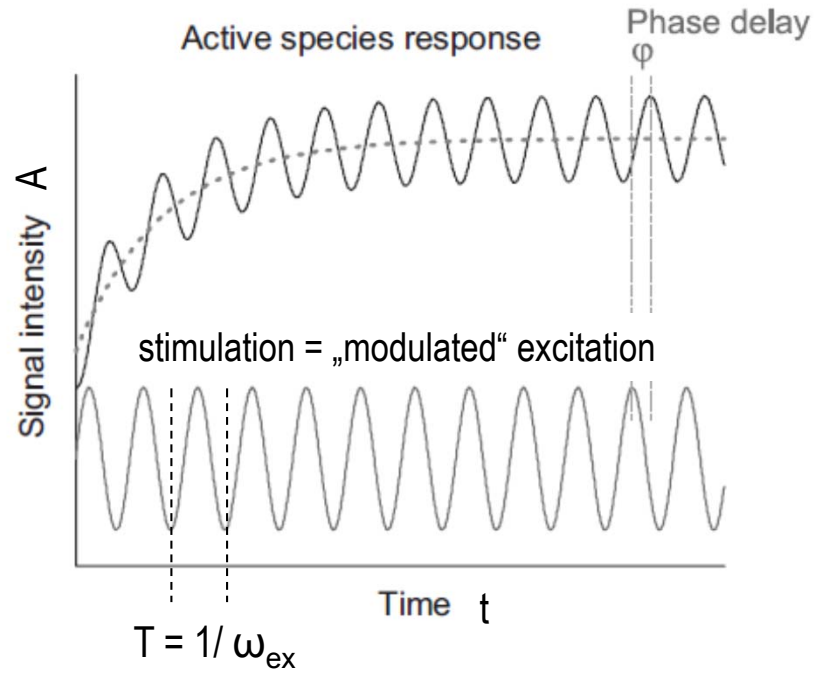
Concept of modulated excitation spectroscopy

Contains only changes due to excitation with ω_{ex}

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

XAS dataset

PSD: phase sensitive detection



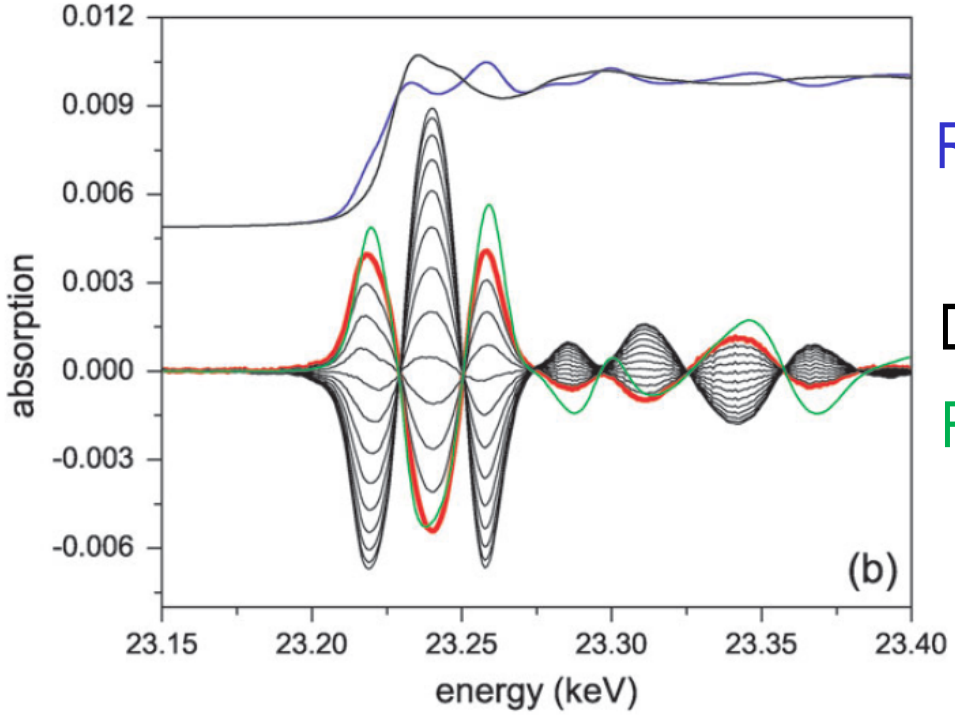
Urakawa, Chem. Eng. Sci. 2008

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
- Demodulation is essentially a frequency filtering

Qualitative interpretation of ME-XAS

Rh catalyst, periodic switches of CO → NO → CO...



Rh, Rh_2O_3 (references)

Demodulated spectra (various φ)

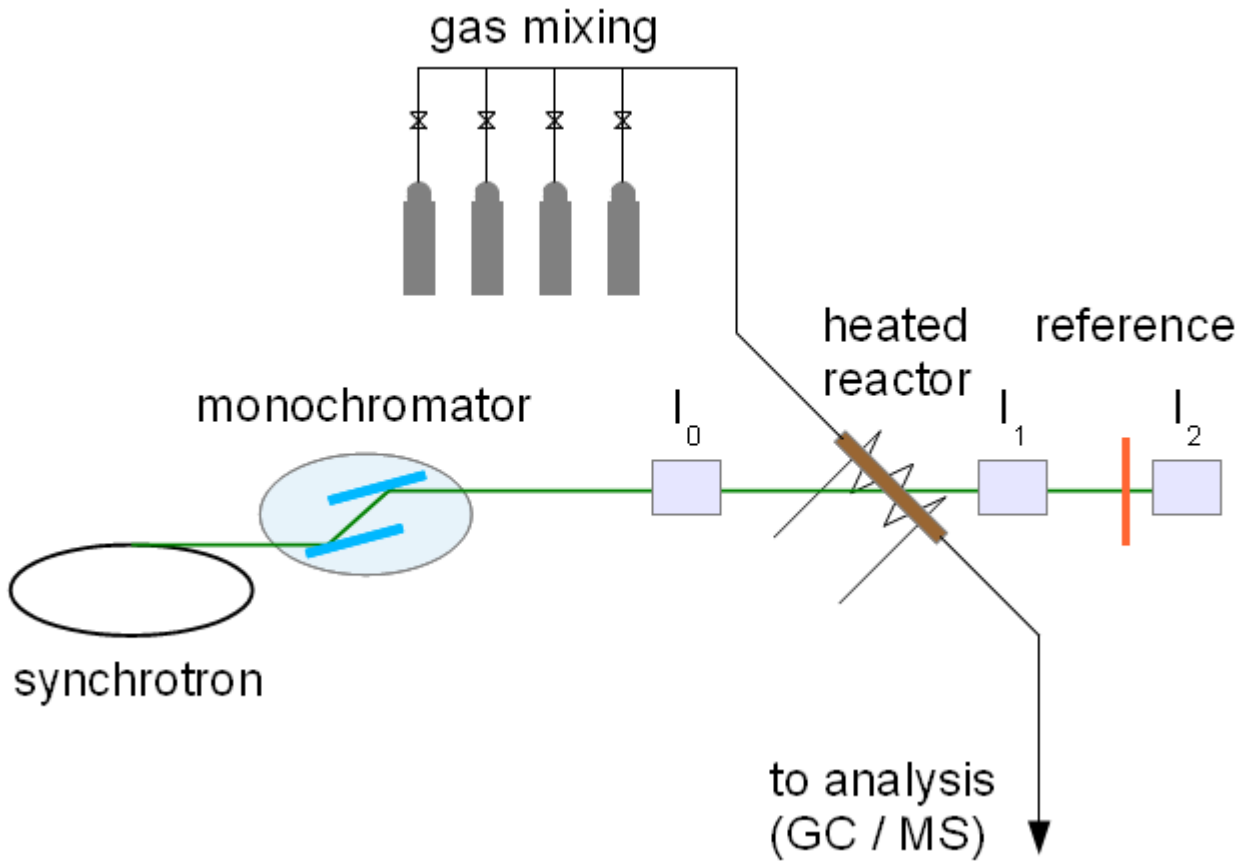
Rh - Rh_2O_3

Demodulated spectra similar to Rh – Rh_2O_3
→Most likely simple reduction / oxidation

What about quantification?

Ferri et al, Phys Chem Chem Phys (2010)

XAS – experimental layout

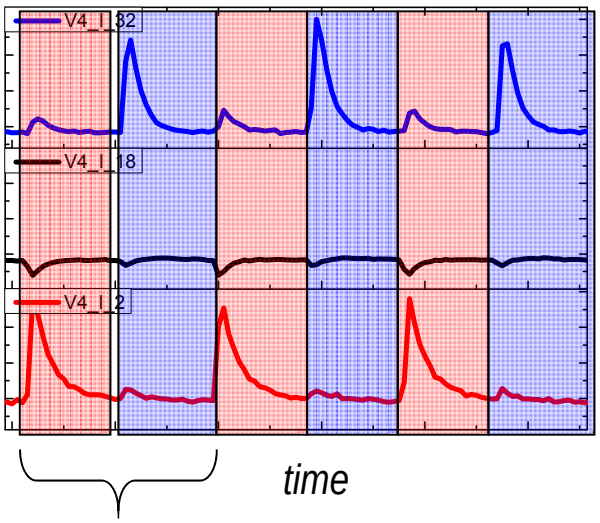


SuperXAS beamline @ Swiss Light Source

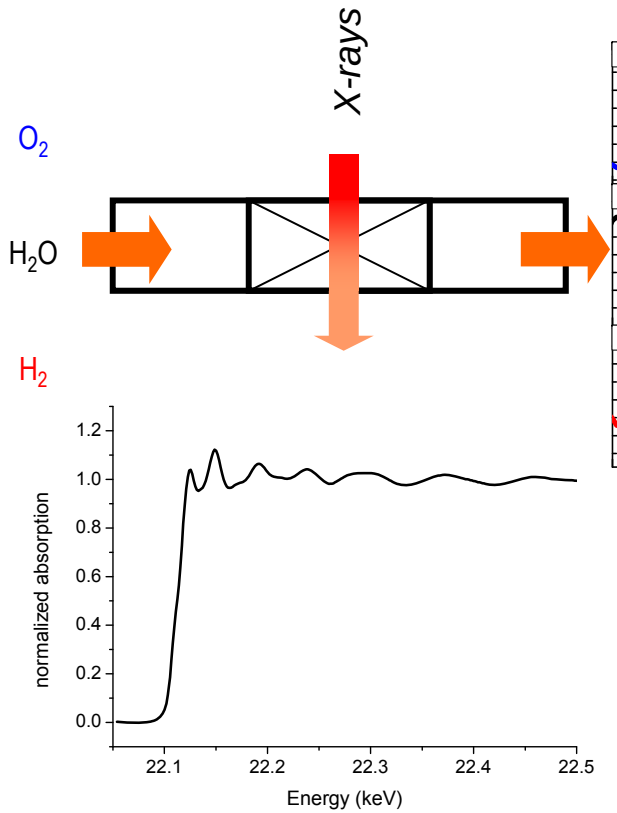
ME-XAS – Experimental setup

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

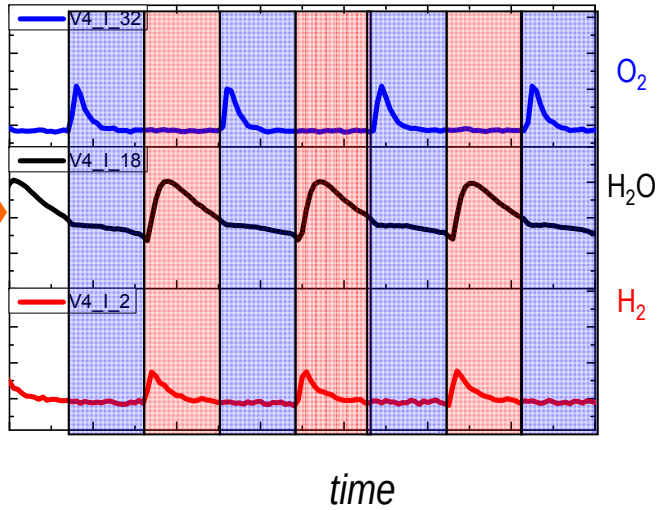
MS data: reactor inlet



T = 1/ω

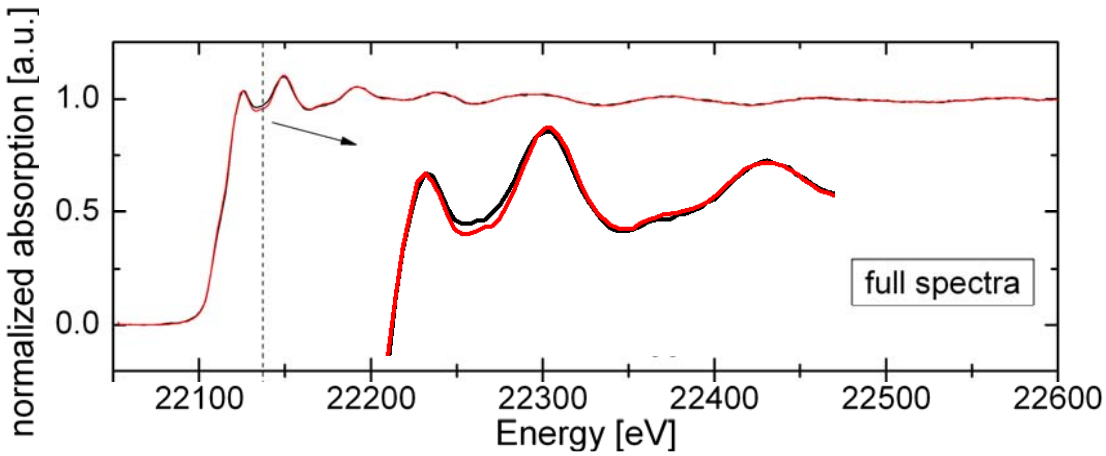


MS data: reactor outlet



- ➢ 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

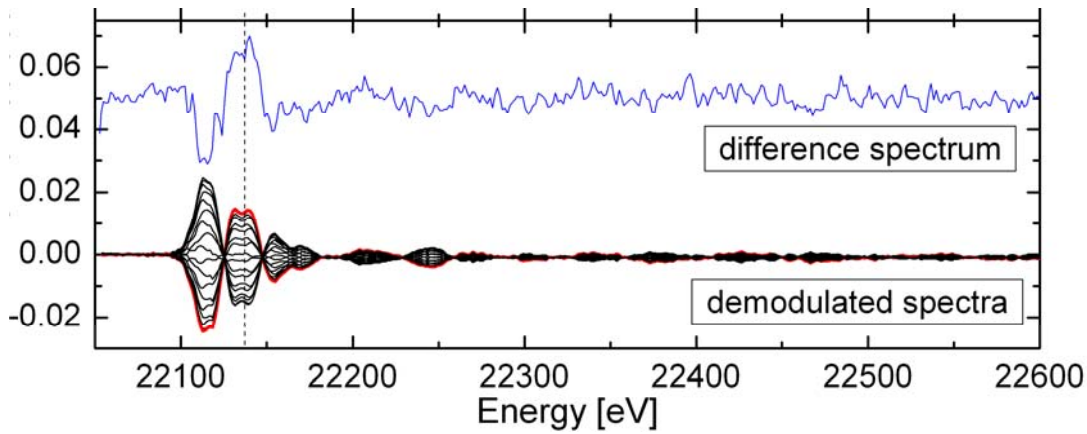
Contains only changes due to excitation with ω_{ex}

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

XAS dataset

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

Quantification



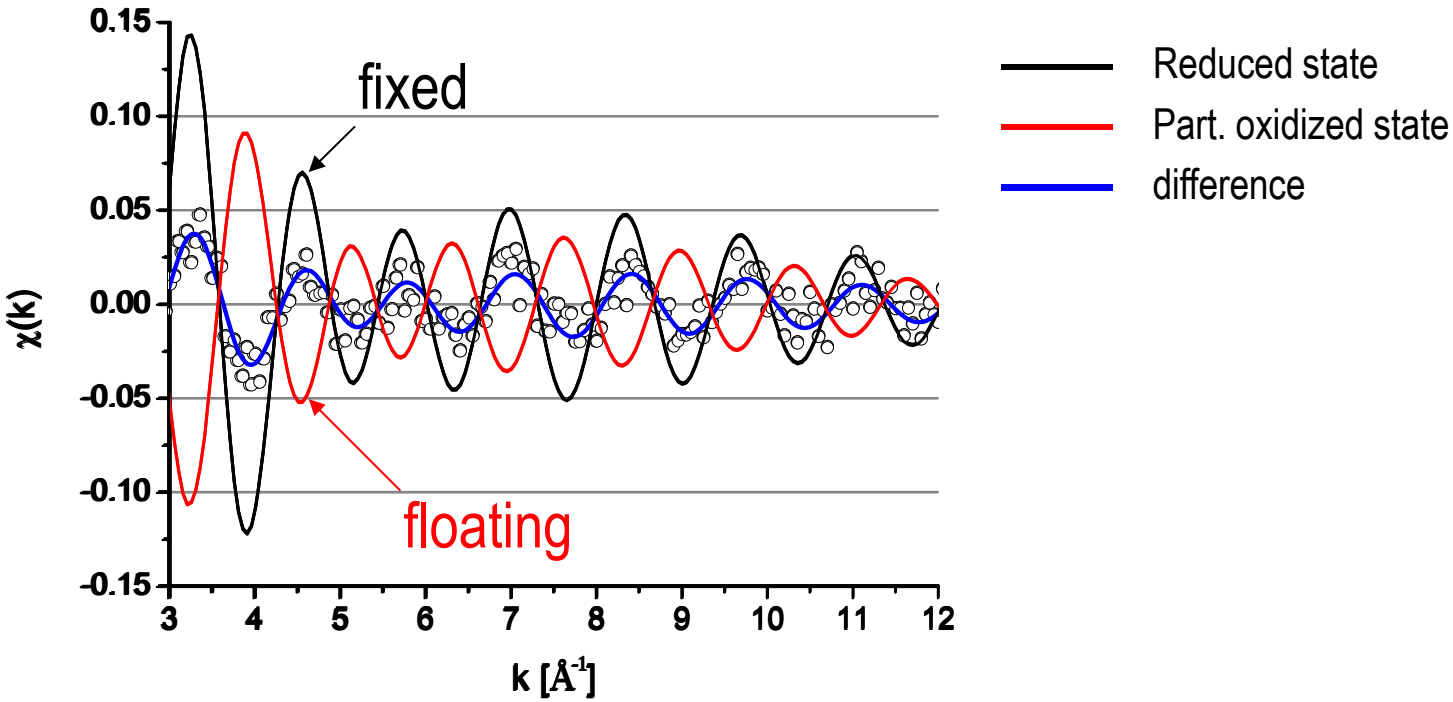
- What is the relation between demodulated spectra and difference spectra?

  We know: for square wave excitation: $A_{demod} = 2/\pi\ A_{diff}$ (Urukawa, Chem. Phys. 2006)

- Which phase angle to choose?

- How to use the demodulated spectra for quantification?

ME-XAS – Fitting approach



Demodulated spectrum = reduced spectrum – oxidized spectrum

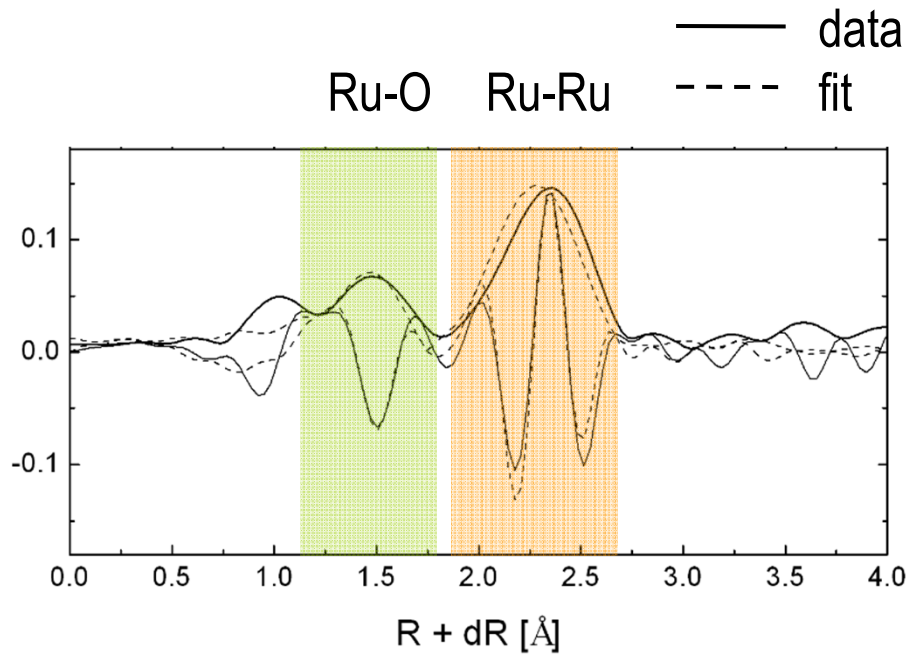
→ Use two fitting functions (shells, paths), subtract one from the other

→ Treat demodulated spectra like difference spectra

→ Fix one function of a known state (e.g. reduced state)

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

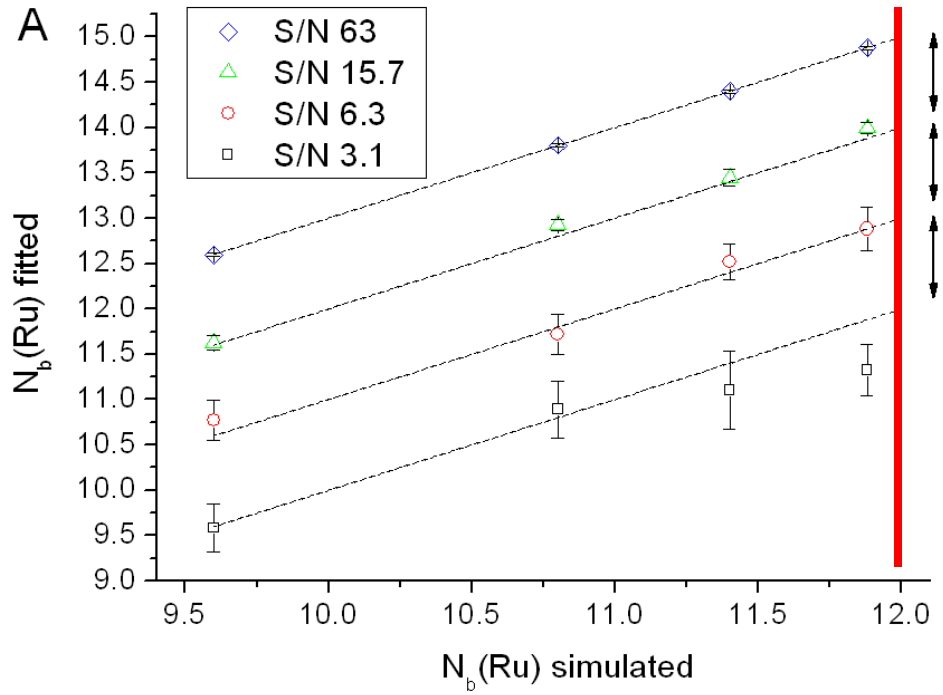


Fitting of demodulated spectra

- 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

Theoretical considerations



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

What are the theoretical limits of sensitivity?

→ Depends on signal to noise ratio

What happens if the initial „guess“ is not good?

→ Absolute values are wrong, but differences are correct

Intermediate summary

ME-XAS is providing improved spectra quality

→ small changes can be resolved

→ minority species can be detected

Quantification (=EXAFS fitting) is possible

→ Differences are the same as with „regular“ EXAFS fitting

→ Error bars are much smaller

More complex excitation - Generalization

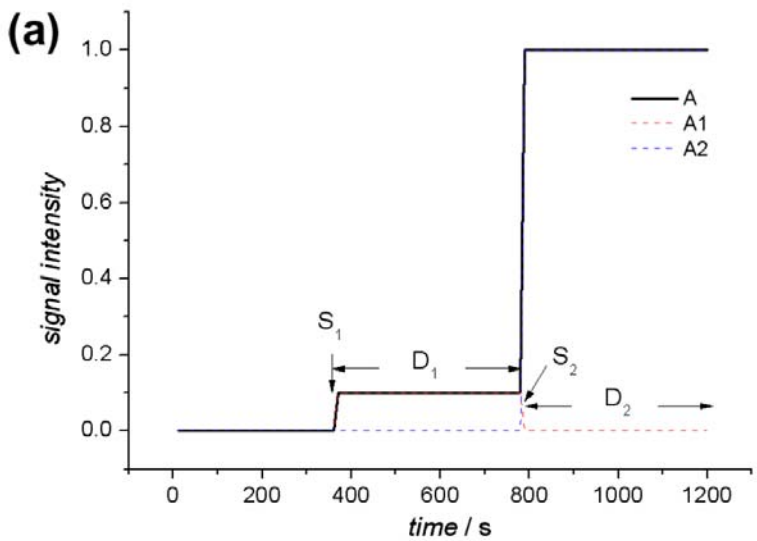
Until now, we considered a reaction: A → B → A → B ...

What about intermediates? A → B → C → A → B → C ...

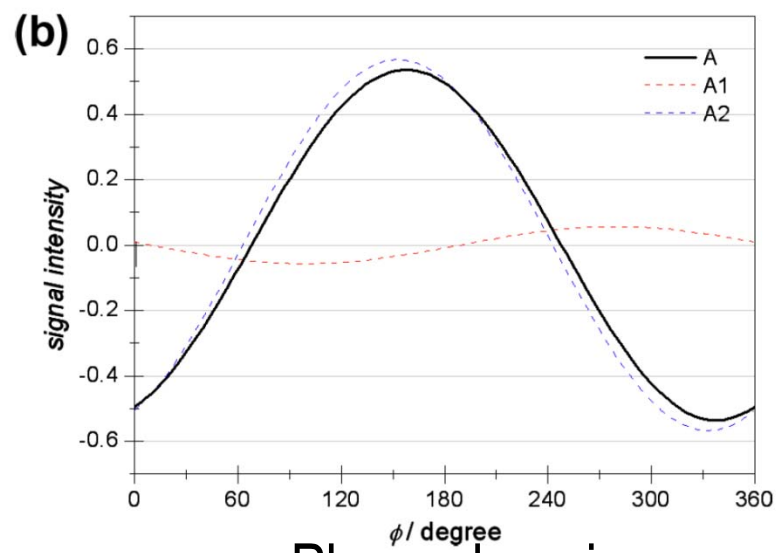
How can we detect multiple changes? How can we quantify them?

Consider a two-step function:

- Every periodic function in time-domain can be Fourier analyzed
- Fourier Components can be used as input for demodulation



Time domain



Phase domain

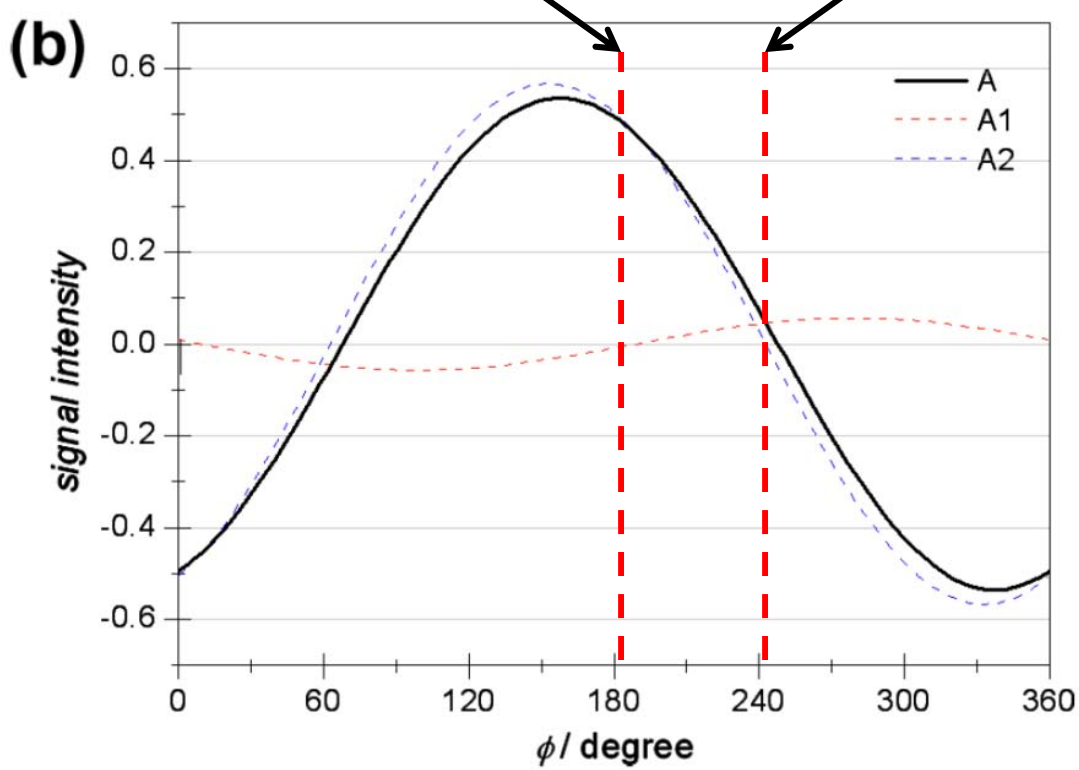
König, Schildhauer, Nachtegaal *J. Catal.* (2013) doi: 10.1016/j.jcat.2013.05.002

More complex excitation

How to isolate the different contributions from experimental data?

Φ_2: Minor contribution (A1) is zero

Φ_1: Major contribution (A2) is zero

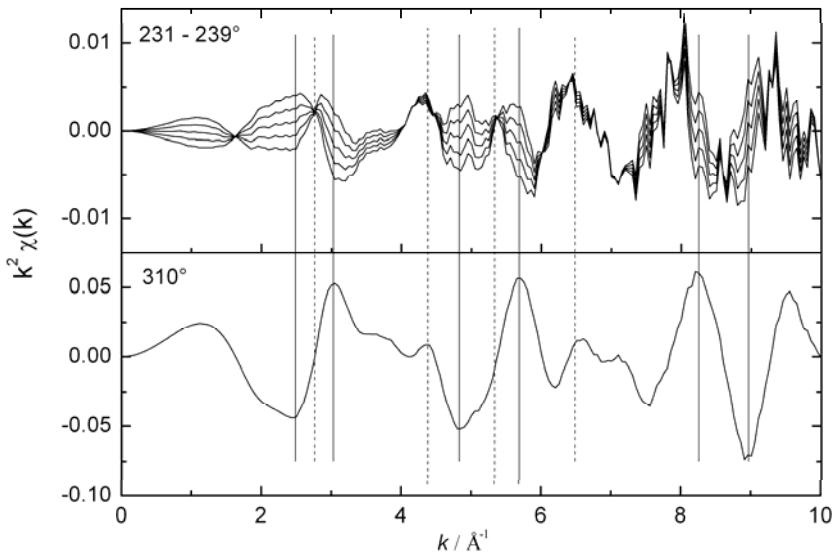


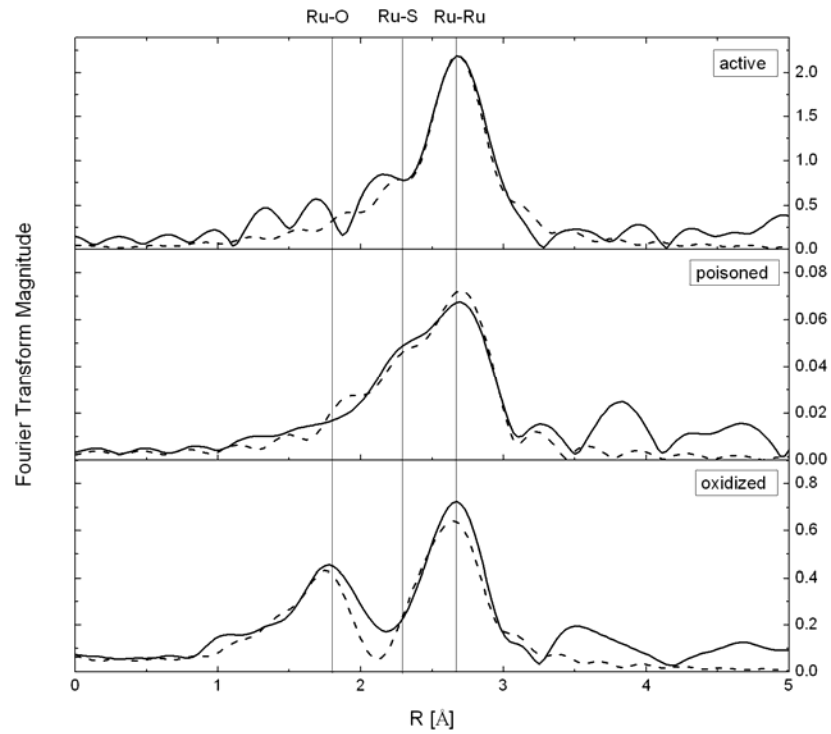
König, Schildhauer, Nachtegaal *J. Catal.* (2013) doi: 10.1016/j.jcat.2013.05.002

- We can select Φ such that the demod. spectrum contains only one phase
- For every Φ, we can analytically derive the correct scaling factor

More complex excitation

Comparison of two phase angles





Demodulated spectra

- Minor species (Ru-S) can be differentiated from major species (Ru-O)
- Detection and quantification of Ru-S
- Ru-S is formed and removed
- Coordination number 0.07 ± 0.02

König, Schildhauer, Nachtegaal *J. Catal.* (2013) doi: 10.1016/j.jcat.2013.05.002

Experimental considerations

How should an experiment be designed to be suitable for modulated excitation spectroscopy?

- Highly automated setup → periodic switching, automated data logging
- $f_{measurement} >> f_{excitation}$ → Quick XAS
- Reproducible processes → steady state(s) should be reached
- (Stable beamline, continuous data collection)

What kinds of experiments can be imagined?

Batteries, fuel cells, (photo)catalysis, functional materials, magnetism...

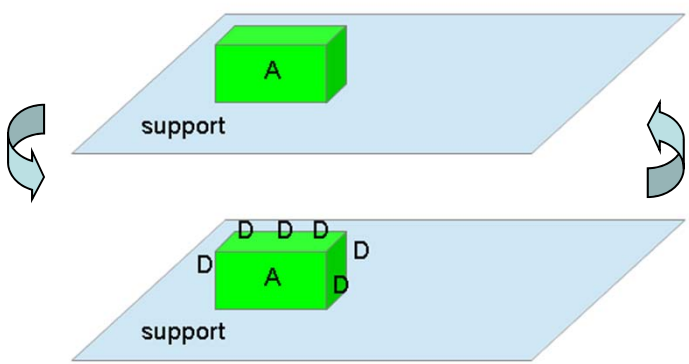
Outlook

What the future might bring:

- Integration with other techniques (XRD, Raman, Infrared...)
- More complex reactions (e.g. Multi-step reactions)
- Analysis of kinetics (higher orders of k)
- More experimental applications

Summary

Pros	Cons
Improved precision	Much effort required
More details than standard XAS	Careful analysis needed
Comes for free, no extra equipment	No standards defined (yet)
General concept, can be applied to many methods and questions	Some information about reaction is required for quantification



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