Using Quick XAFS for Imaging Catalysts in Two and Three Dimensions

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Joint NSLS and CFN Users' Meeting
May 24, 2010

QEXAFS = Quick scanning EXAFS

QEXAFS using a conventional X-ray monochromator

QEXAFS–scan: Monochromator is moving continuously
EXAFS ≈ 5 s, XANES ≤ 1 s
0.002 – 0.05 s / data point

***Standard* EXAFS experiment with special software used**

⇒ **Fluorescence**, e-yield detection, **reflectivity** possible, wide energy range in one experiment (≈ 15 keV)

⇒ Easy combination with VU-Vis, Raman,… possible

⇒ **High intensity up to 10^{14} monochromatic photons/s with insertion devices**

BUT: ***Extremely* stable monochromator necessary**
⇒ crystals have to remain parallel within < 0.5" !

QEXAFS = Quick scanning EXAFS

578 Nuclear Instruments and Methods in Physics Research A270 (1988) 578–581
North-Holland, Amsterdam

QUICK SCANNING EXAFS: FIRST EXPERIMENTS

R. FRAHM
Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 2000 Hamburg 52, FRG

Received 18 December 1987 ⇒ **First measurements in July 1987!**

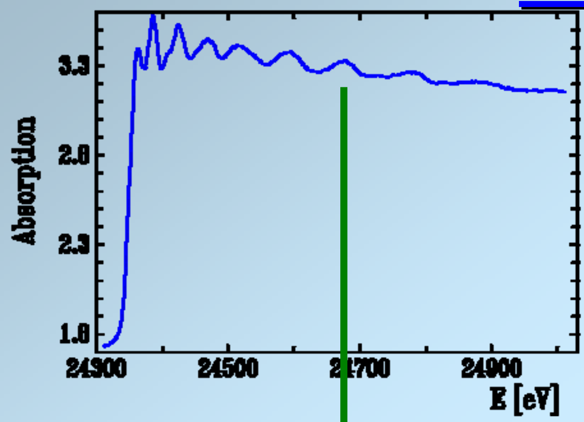
By speeding up a conventional X-ray monochromator by a factor of 100 using the quick scanning EXAFS (QEXAFS) mode the data collection time required for a typical EXAFS scan was reduced to a couple of seconds, making XANES scans in a split second possible. Typical absorption spectra of Fe and Cu foils taken in 3.5–10 s covering an energy region of up to 800 ev are shown. It is demonstrated that the normalized Cu-EXAFS and its Fourier transform agree very well with the results of a conventional step by step measurement. The new approach allows the use of fluorescence detection and hereby makes possible the time dependent investigation of the changes in structure or valence state of a wide variety of samples which are inaccessible for transmission spectroscopy.

First references:

R. Frahm: Quick scanning EXAFS: First experiments. Nucl. Instrum. Methods Phys. Res. A 270, 578 (1988)

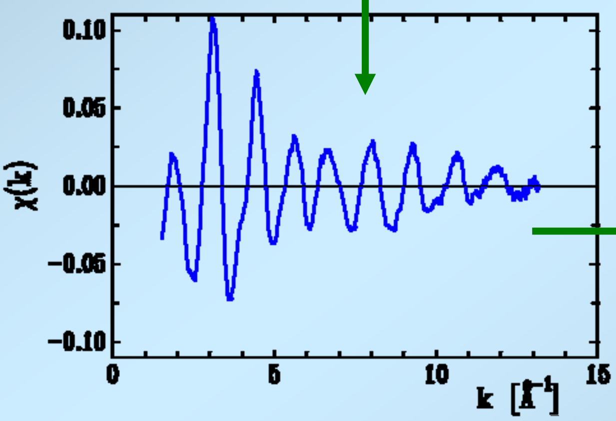
R. Frahm: New method for time dependent X-ray absorption studies. Rev. Sci. Instrum. 60, 2515 (1989)

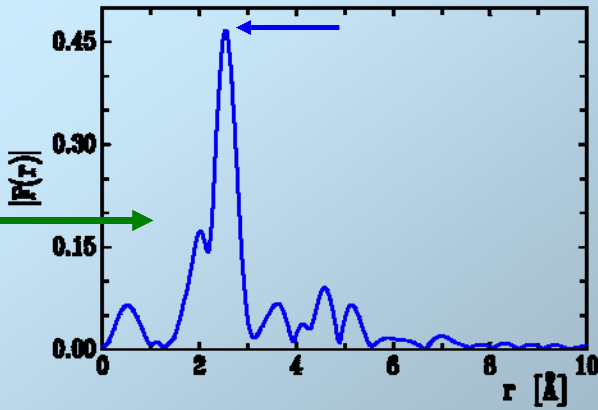
Very fast scan using standard monochromator: Pd foil (300 K)



QEXAFS in 0.81 s
0.002 s / data point

E_K = 24.348 keV,
Si(311) monochromator.



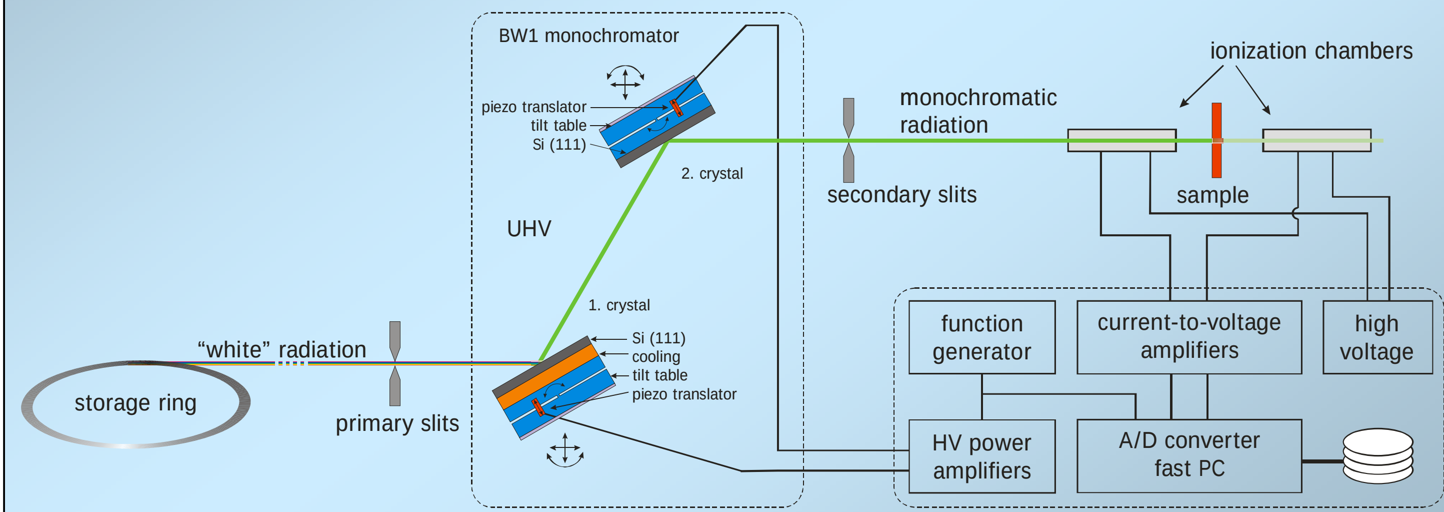


Getting faster:

Special monochromator systems

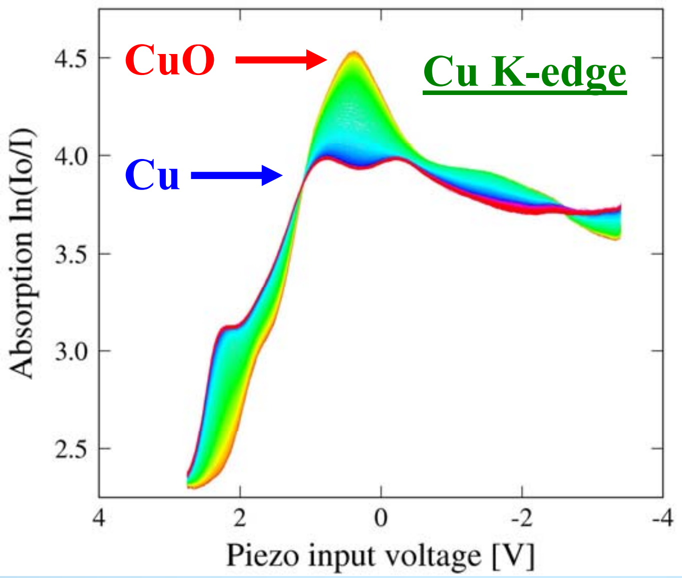
Piezo QEXAFS

- Oscillation of monochromator crystals by piezo tilt tables
- Operating frequency 10-300 Hz ⇒ ms range accessible



Setup for transmission measurement

Activation of a $CuO/ZnO/Al_2O_3$ catalyst



In situ reduction in H_2 atmosphere

Time resolution: **50 ms**

Simultaneous measurement of catalytic activity

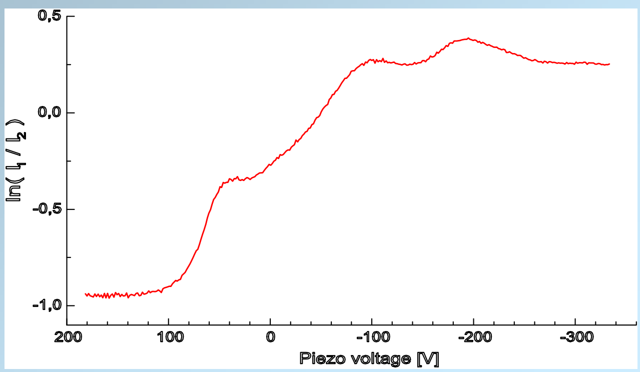
⇒ Cu particle size can be determined directly!

(Piezo-QEXAFS, collaboration with Haldor-Topsøe A/S)

Review:

B.S. Clausen, H. Topsøe and R. Frahm, Advances in Catalysis 42, 315 (1998)

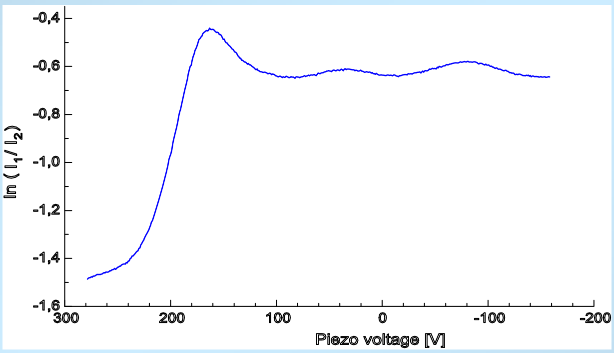
Very fast piezo scans using high speed ADCs



Cu K-edge, 111 Hz

4.5 ms/scan,

200 kHz sampling rate



Pt L_3-edge, 66 Hz

7.6 ms/scan,

200 kHz sampling rate

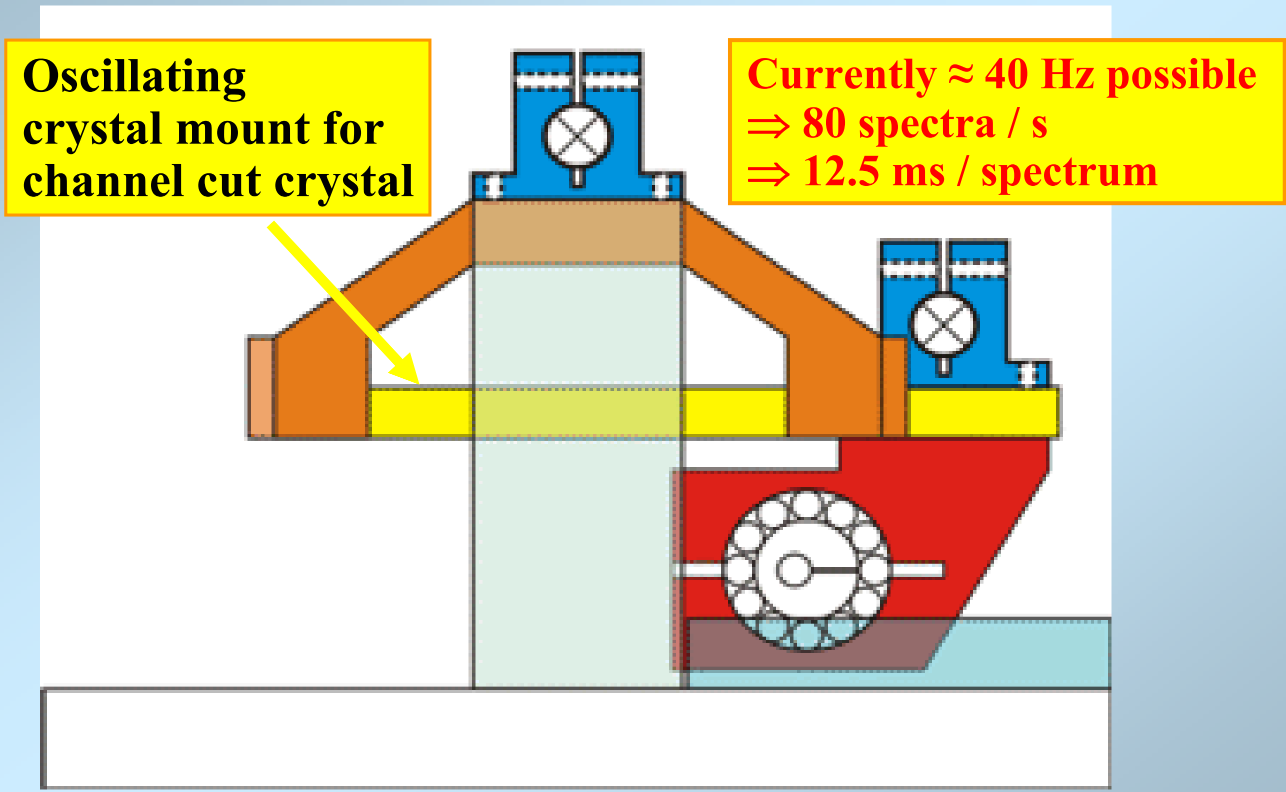
H. Bornebusch et al., J. Synchrotron Rad. 6, 209 (1999)

Piezo-QEXAFS with fluorescence detection:

D. Lützenkirchen-Hecht et al., J. Synchrotron Rad. 8, 6 (2001)

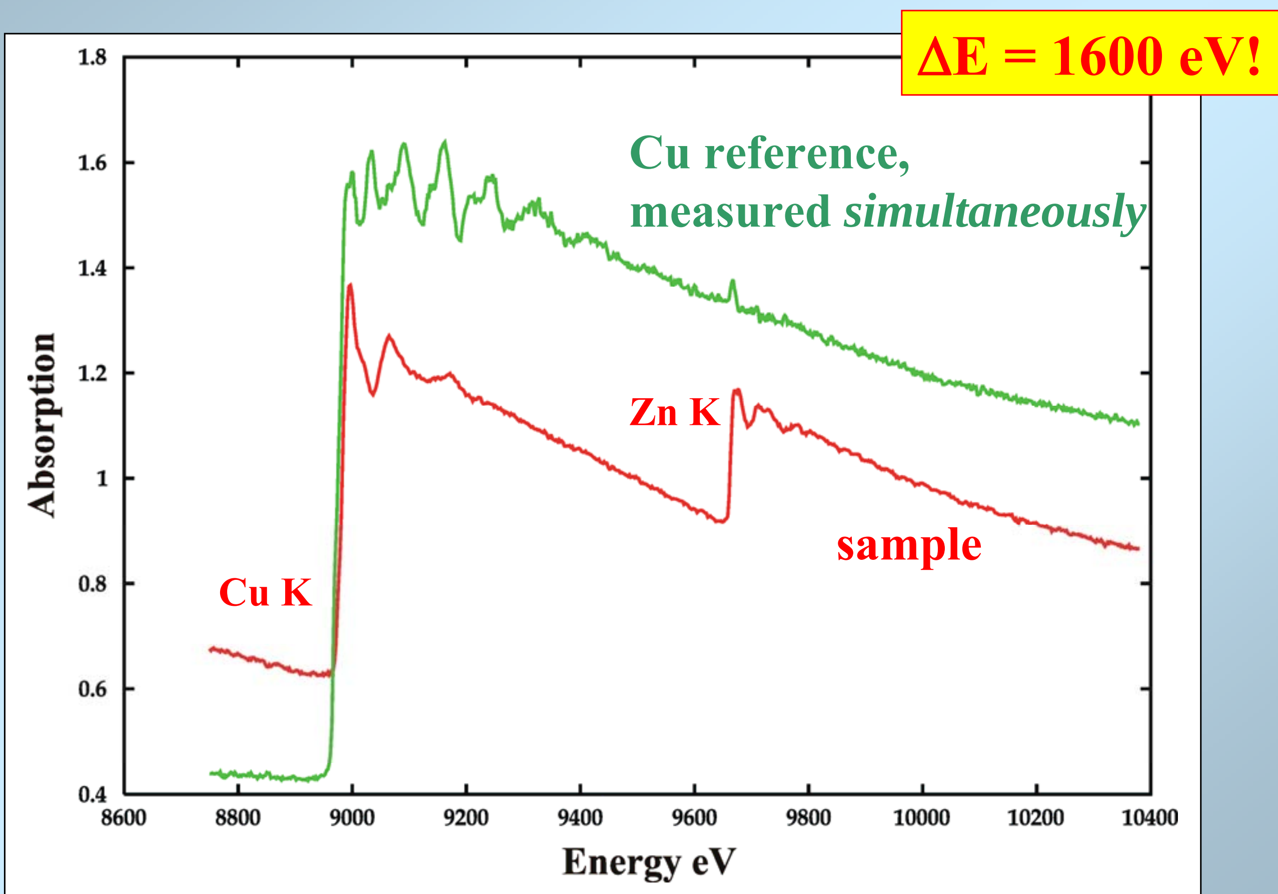
A novel fast monochromator: Drive system

Goal: Fast (ms), wide spectral range, continuous movement



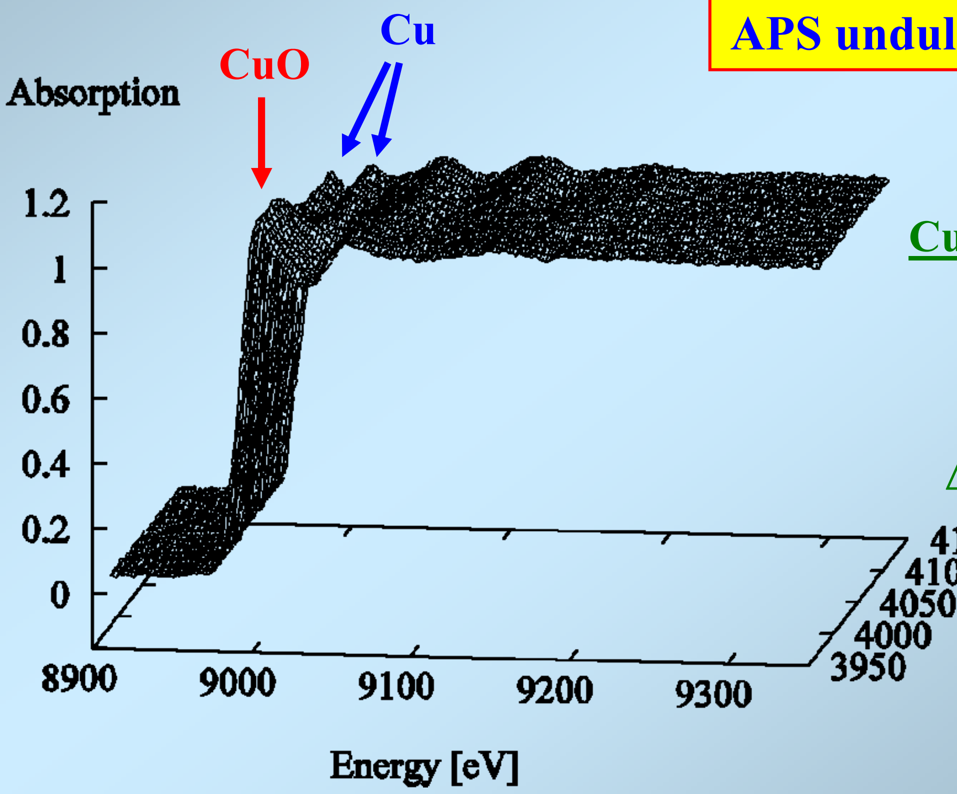
R. Frahm et al., AIP Proc. 705, 1411 (2004) and Physica Scripta T115, 974 (2005)

CuO/ZnO-catalyst: Single scan, 50 ms



CuO/ZnO-catalyst: Reduction

APS undulator 1-ID

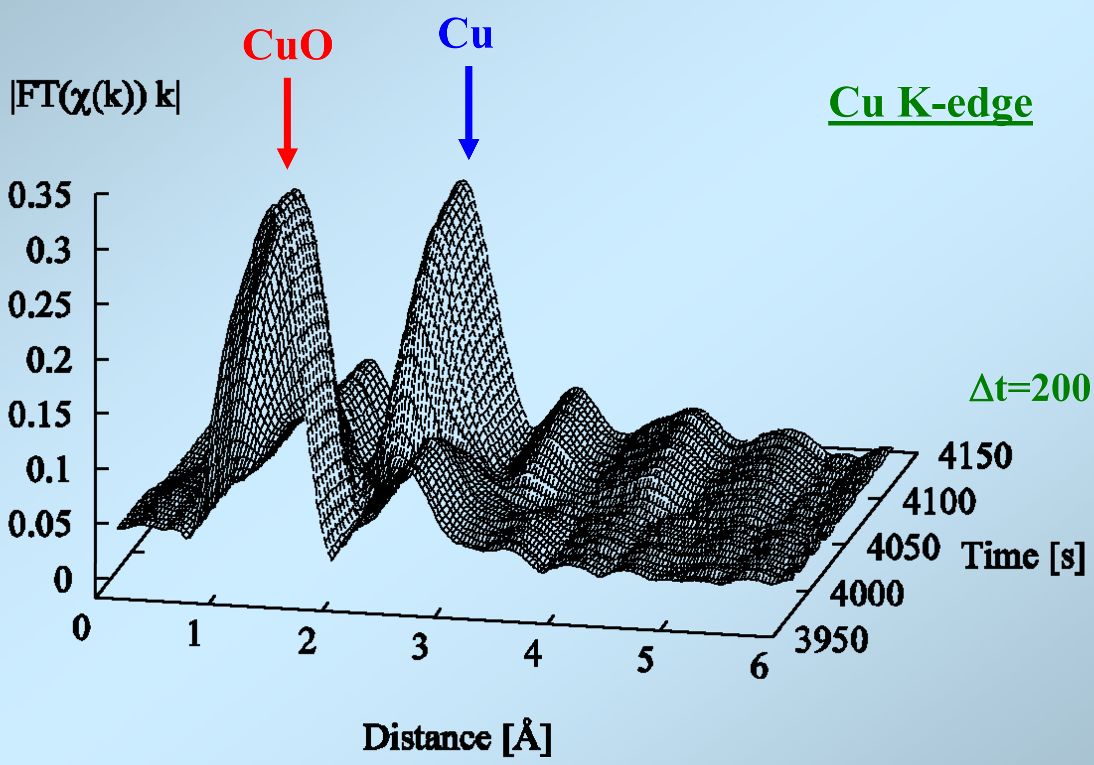


Cu K-edge

Δt=200 s

Collaboration with J.-D. Grunwaldt and A. Baiker, ETH Zürich

CuO/ZnO-catalyst: Reduction



Cu K-edge

Δt=200 s

Collaboration with J.-D. Grunwaldt and A. Baiker, ETH Zürich

Very important: Angular encoder

Renishaw encoder ⇒ Bragg angle ⇒ Photon energy

Properties:

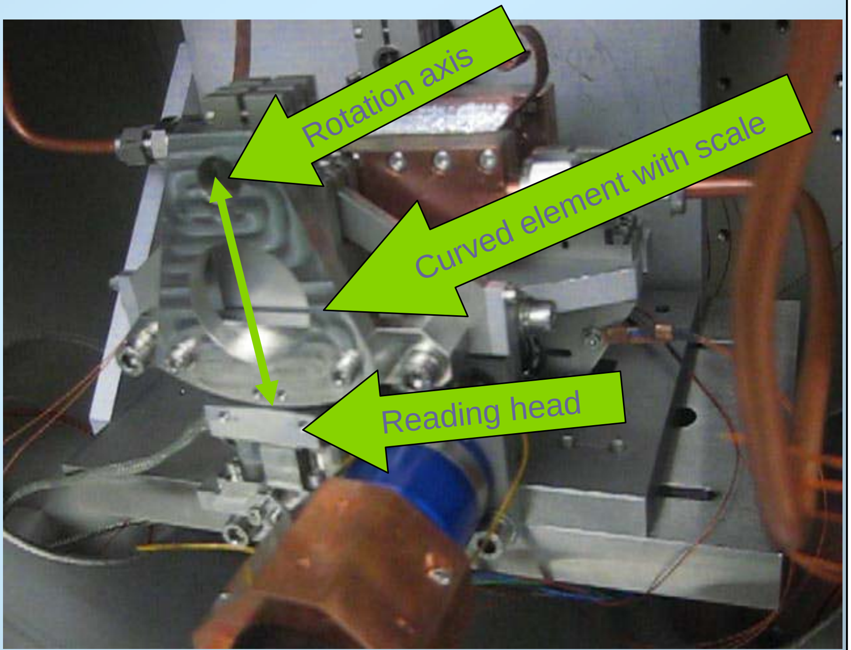
No mechanical connection

Vacuum compatible

Fast (~10 m/s)

High resolution (10 nm)

Collaboration with SOLEIL



Encoder signal:

Angular resolution:

ca. 0,03''

J. Stötzel et al., Rev. Sci. Instrum. 79, 083107 (2008)

First dedicated QEXAFS setup at the Swiss Light Source (SLS)

SLS:
2.4 GeV, 400 mA, top-up mode.

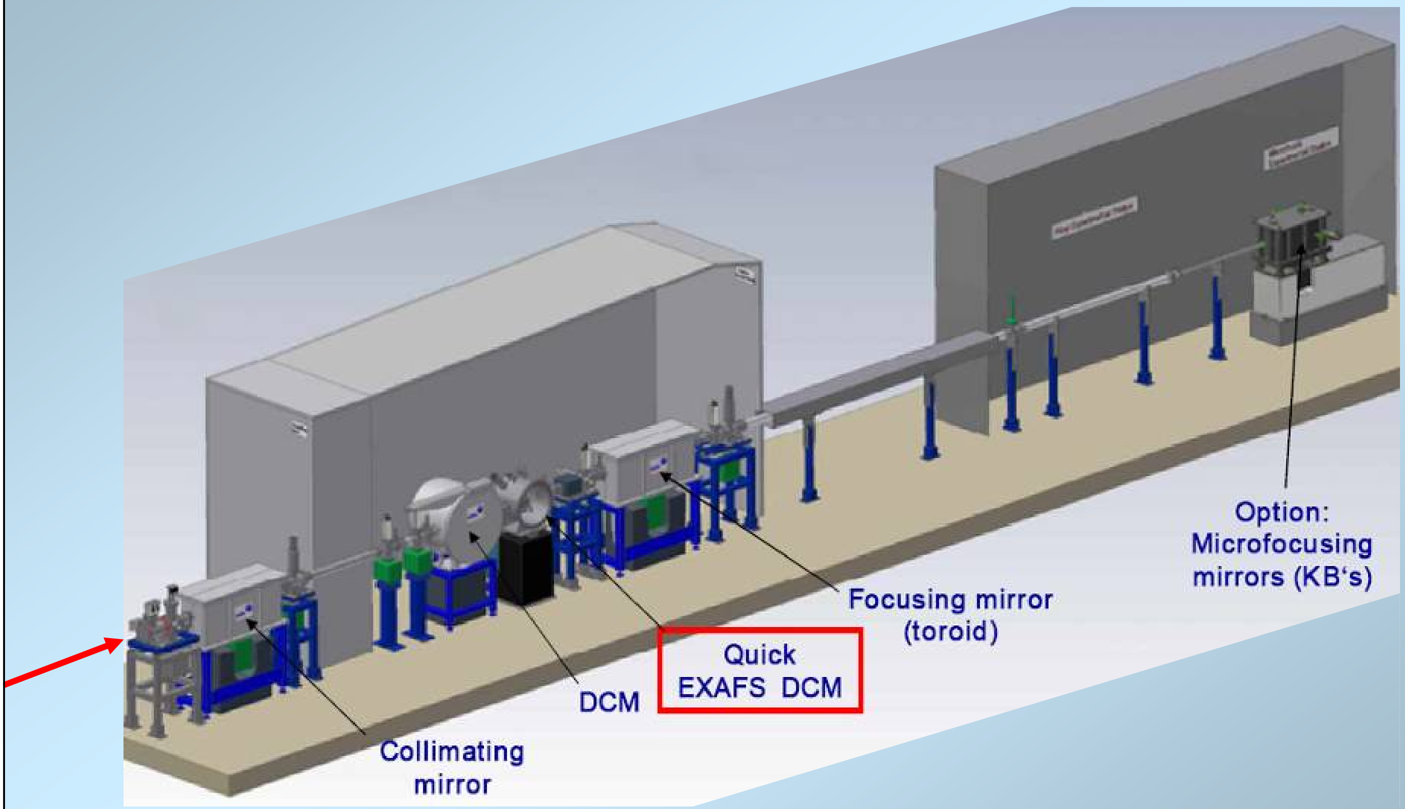
SuperXAS: Superconducting bending magnet (2.9 T) beamline, conventional DCM and QEXAFS monochromator in a row.

Crystal and monochromator change in < 5 min possible!

Large user demand: 30-50% of beamtime for QEXAFS.

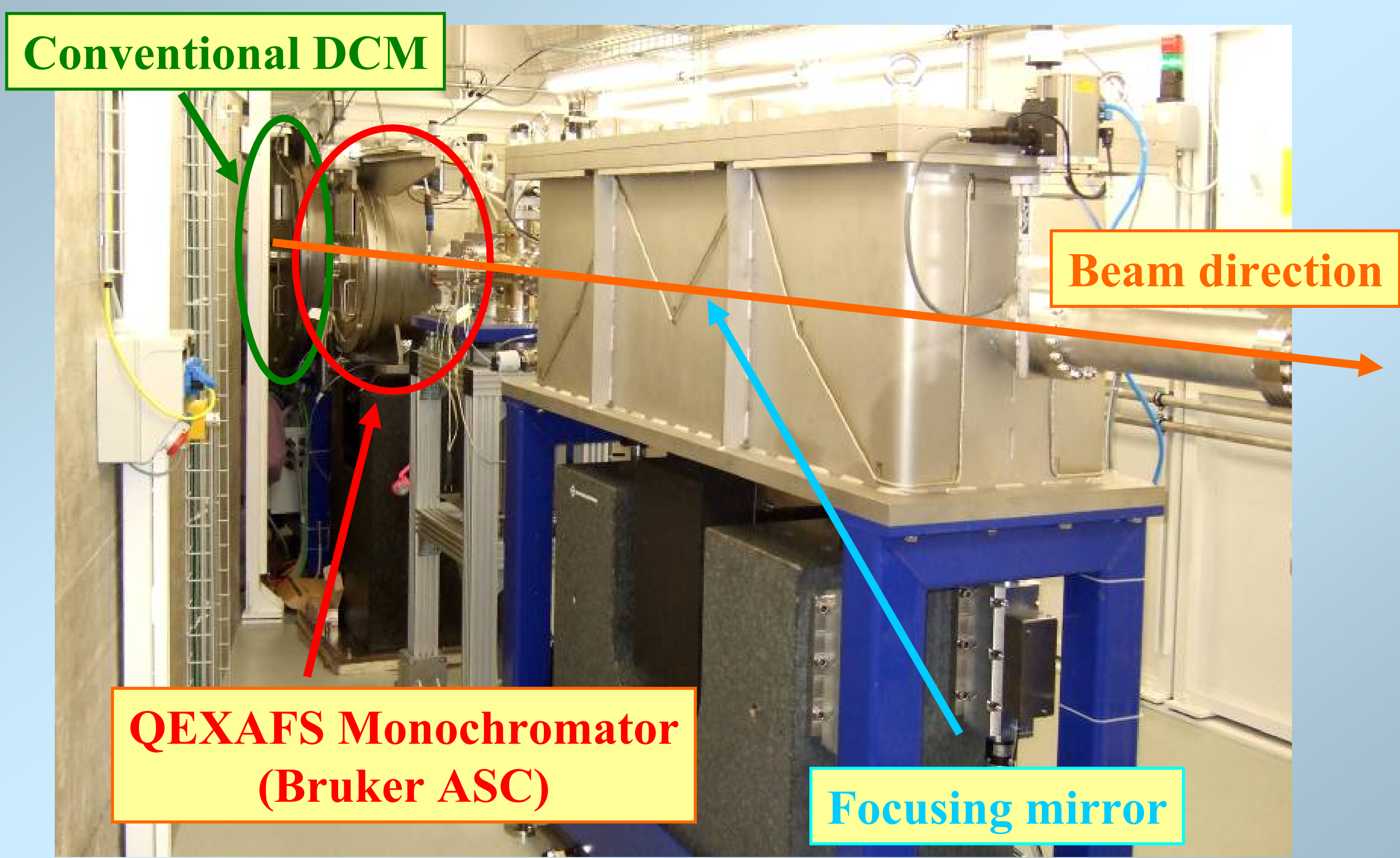
R. Frahm et al., AIP Conf. Proc. 1234, 247 (2010)

SuperXAS Beamline (X10DA) at the SLS

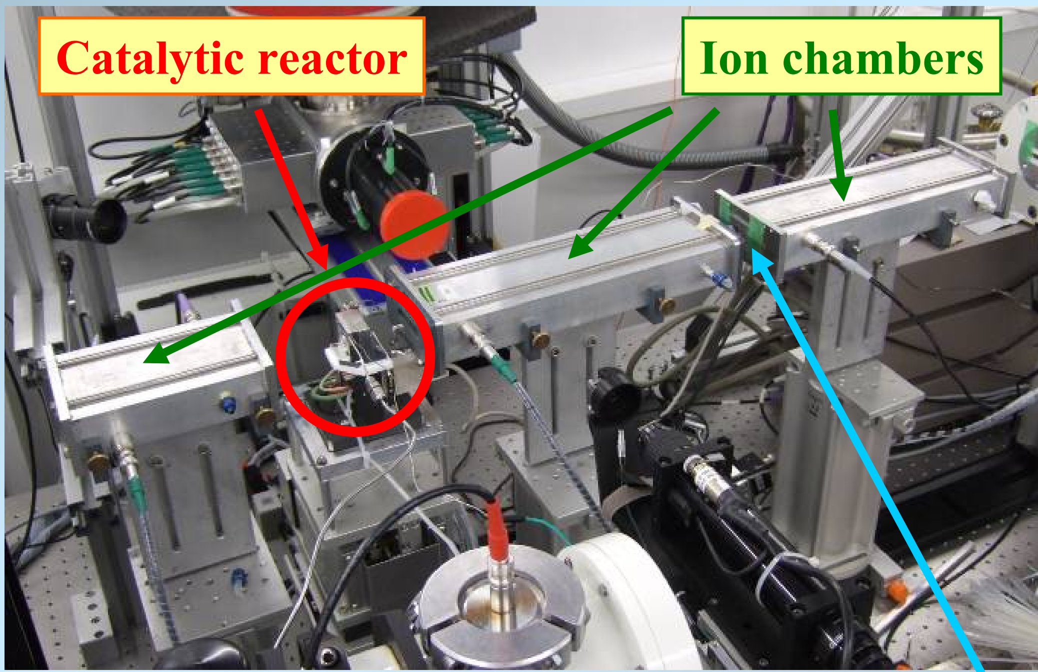


(Entire beamline delivered and installed by ACCEL, now Bruker ASC)

SLS XAFS beamline: Main hutch



QEXAFS at the SLS: Experiment



Reference sample

Data collection:
Up to 500 kHz, 16 bit ADCs

QEXAFS setup at the SLS

First permanently installed dedicated QEXAFS monochromator, in user operation since March 2008.

Commissioning time after first beam on monochromator: 24 h.
R. Abela and H. J. Weyer, Synchrotron Radiation News 21, No. 3, p. 32 (2008)

Catalysis research within first 7 days of operation by the groups of

Jeroen A. van Bokhoven (ETH Zurich)
J. Singh, E.M.C. Alayon, M. Tromp, O.V. Safonova, P. Glatzel, M. Nachtegaal, R. Frahm, J.A. van Bokhoven, Angewandte Chemie International Edition 47, 9260 (2008)

Jan-Dierk Grunwaldt (TU Denmark, now Univ. Karlsruhe)
J.-D. Grunwaldt, M. Beier, B. Kimmerle, A. Baiker, M. Nachtegaal, B. Griesebock, D. Lützenkirchen-Hecht, J. Stötzel, R. Frahm, Phys. Chem. Chem. Phys. 11, 8779 (2009)

Why does QEXAFS require high intensities?

The obvious fact: Better signal to noise ratio

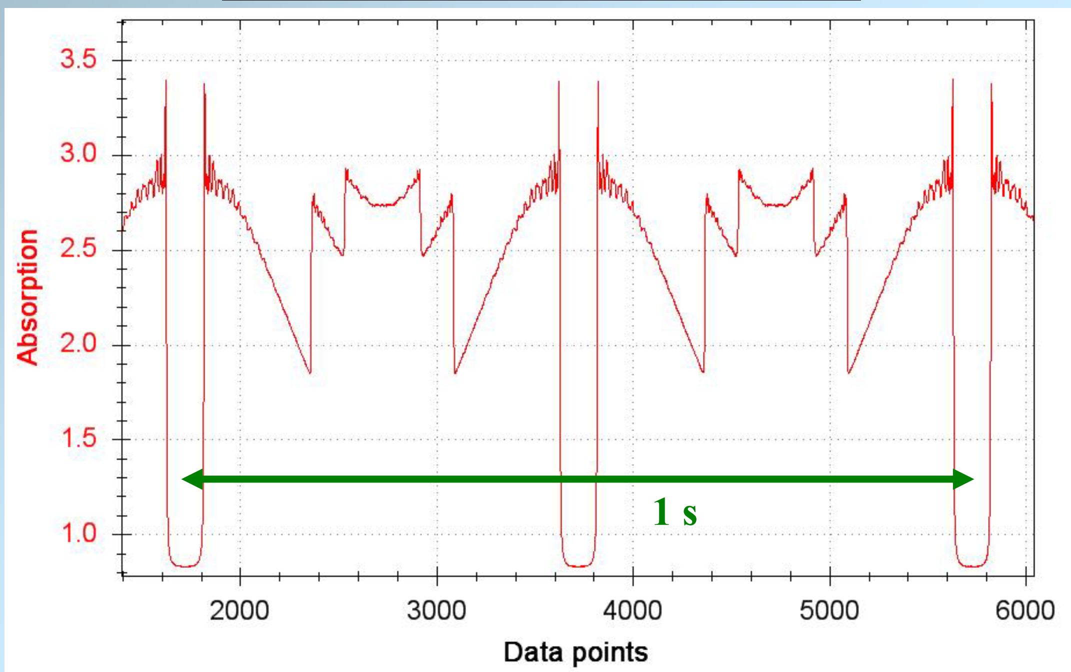
Now some experimental considerations:

Very important: Speed of current amplifiers

QEXAFS needs identical detector response times for fast measurements, otherwise I_0/I_1 becomes noisy!

QEXAFS needs fast detection systems, especially fast ion chambers and current amplifiers!

QEXAFS at the SLS



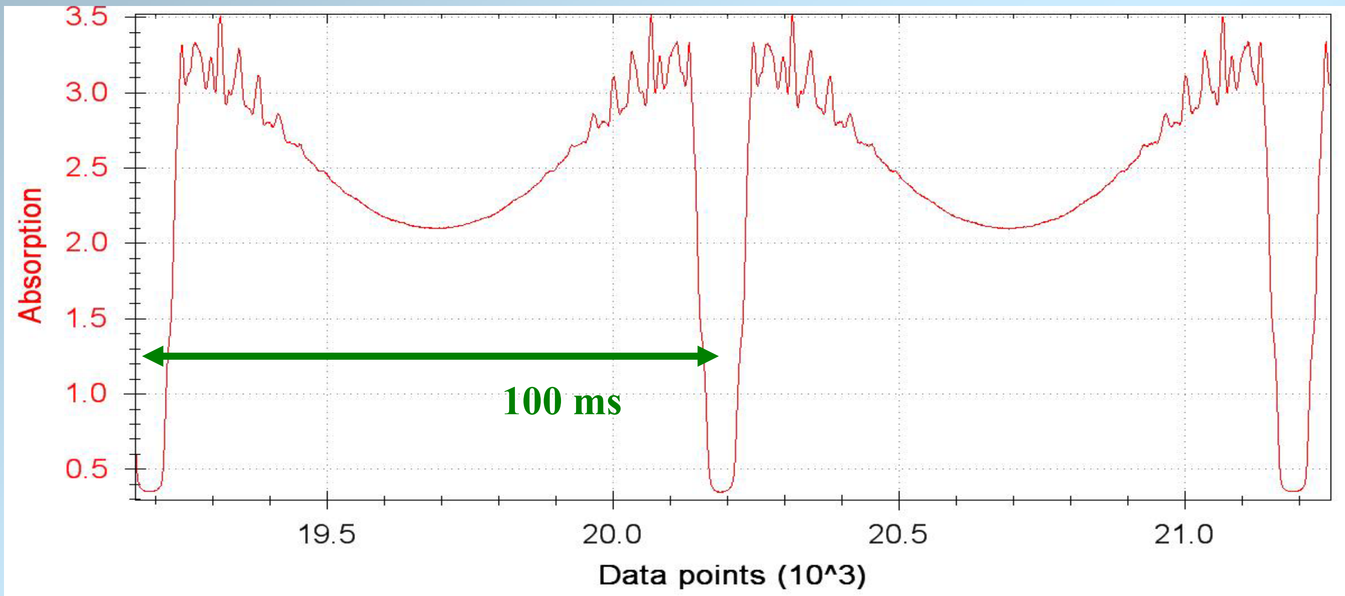
Pt L-edges, 2 Hz, 4 kHz sampling rate

E_{L3} = 11564 eV, E_{L2} = 13273 eV, E_{L1} = 13880 eV

Excentric used covers ±0.91° around a center Bragg angle of 8.98°
$\Rightarrow \Delta E$ = 2573 eV for Si(111)

QEXAFS at the SLS

ΔE ≈ 870 eV

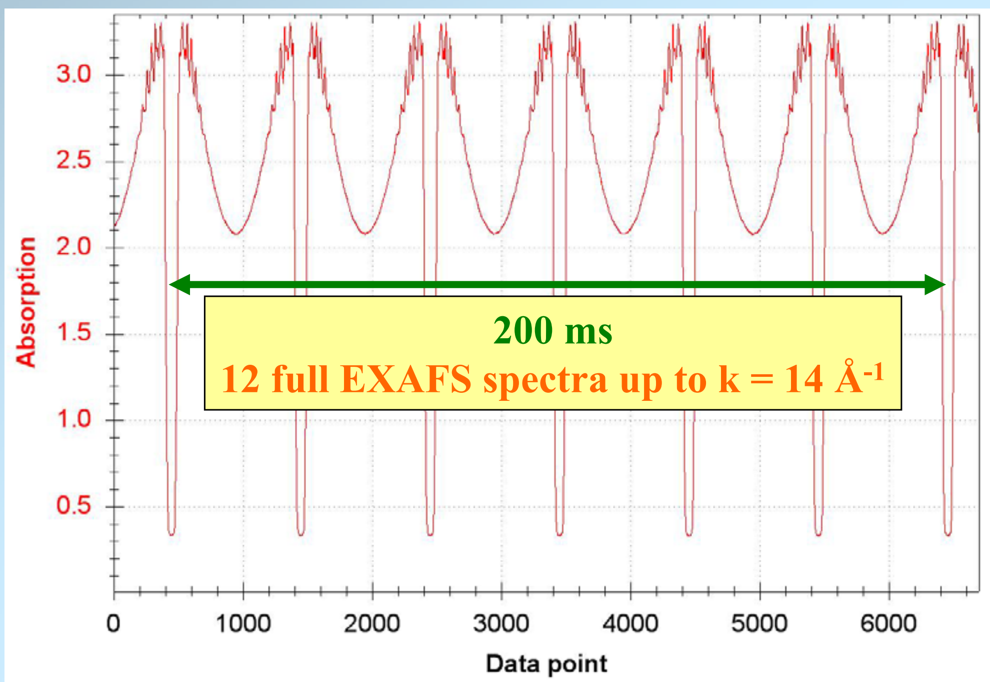


Fe K-edge in 50 ms

10 Hz, 10 kHz sampling rate , E_K = 7112 eV

Speeding up: 30 Hz ⇒ 60 spectra/s!

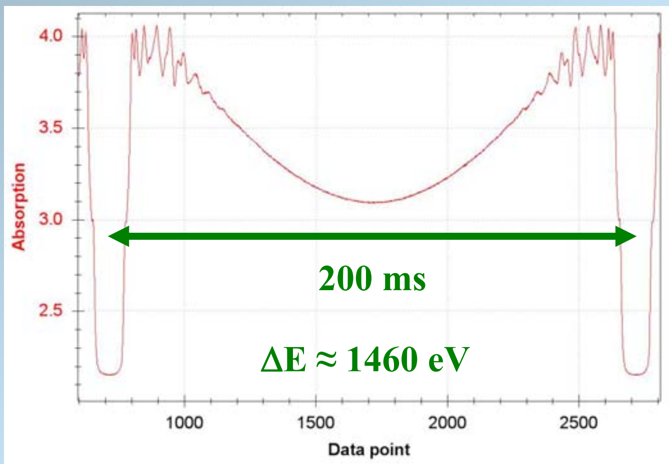
ΔE ≈ 870 eV

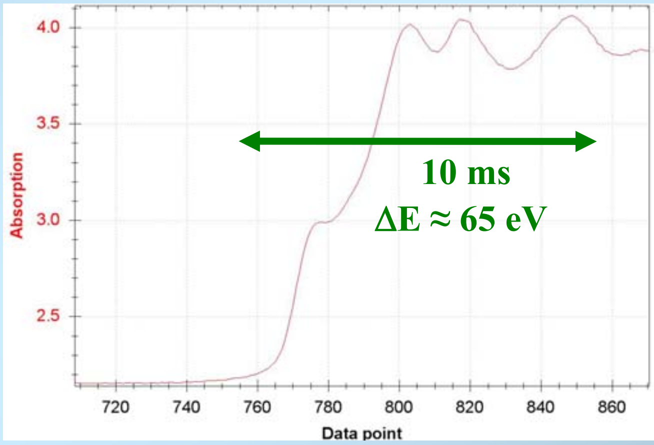


Fe K-edge in 16.6 ms

30 Hz, 30 kHz sampling rate , E_K = 7112 eV

QEXAFS at the SLS

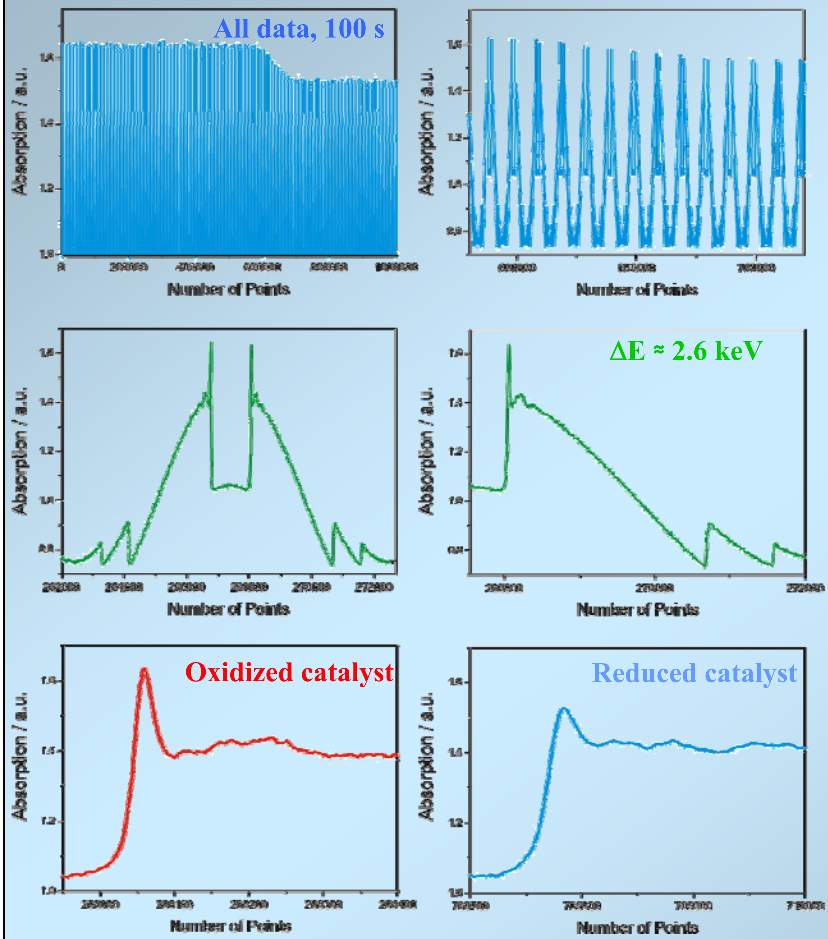




Cu K-edge in 100 ms

5 Hz, 10 kHz sampling rate, E_K = 8980 eV

Reduction of a Pt-Rh/Al_2O_3 catalyst



Pt L-edges

1 Hz oscillation frequency

⇒ 2 spectra/s

5% Pt -5% Rh / Al_2O_3 catalyst in 6% CH_4 / 3% O_2 / He atmosphere between 321 and 331° C sample temperature.

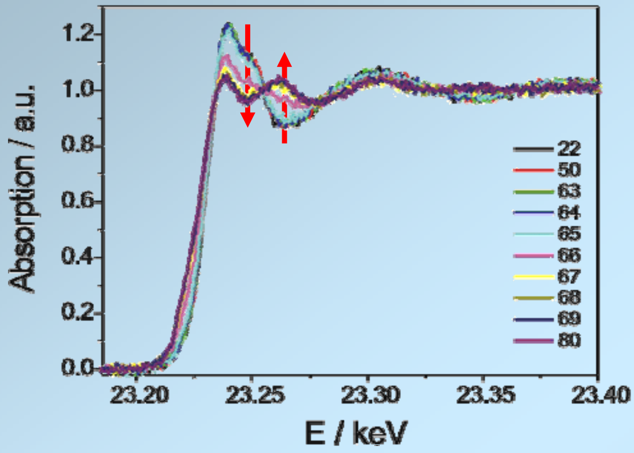
Data collected at the SLS.

Collaboration with J.-D. Grunwaldt.

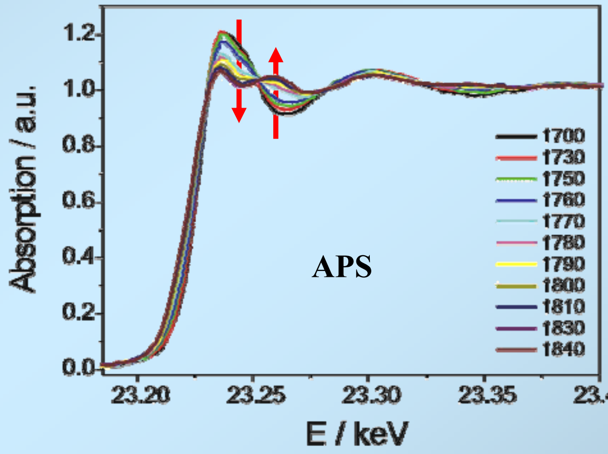
R. Frahm et al., Synchrotron Rad. News 22, No. 2, p. 6 (2009)

Ignition of a 2.5%Pt-2.5%Rh/Al_2O_3 catalyst

Heating over the ignition point in 6% CH_4 / 3% O_2 / He



HASYLAB, Si(311), 45 s/scan



APS, Si(311), 2 Hz, averaged for 10 s

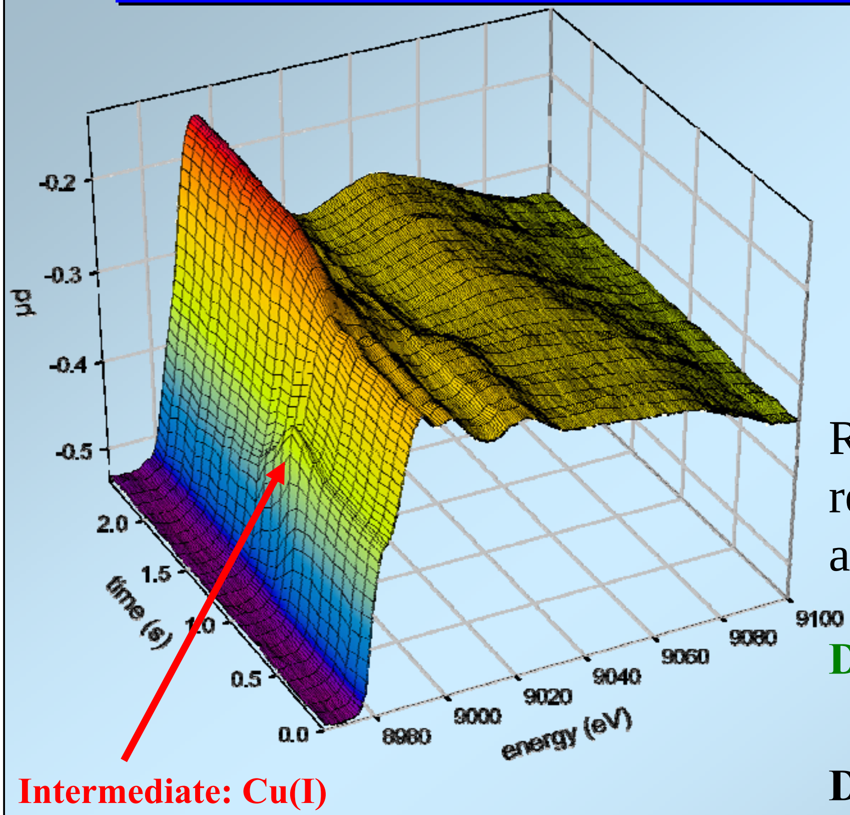
Rh K-edge

Catalytic partial oxidation (CPO) of hydrocarbons is a promising technology for the manufacture of synthesis gas (CO and H_2).

For methane: $CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2\ H_2$

J.-D. Grunwaldt et al., Phys. Chem. Chem. Phys. 11, 8779 (2009)

Fast re-oxidation of a Cu/Al_2O_3 catalyst



Cu catalyst on alumina

10 Hz oscillation frequency

⇒ 20 spectra/s, ΔE = 425 eV

Reduced in 5% H_2 / He, re-oxidized in 21% O_2 / He atmosphere.

Displayed region:

≈ 15 ms/spectrum

Data collected at the SLS.

Collaboration with J.-D. Grunwaldt (Univ. Karlsruhe)

Tomographic absorption spectroscopy:

Entering the 3rd dimension

µ-XAFS in 2D and 3D

Characterization of multi component samples on µm-scale

⇒ **Valence distribution of elements**

2D-mapping:

0.25 mm^2 with 5 µm resolution: 10.000 spectra

⇒ not feasible with conventional methods, 30 s/scan **⇒ 3.5 days**

⇒ oscillating QEXAFS at moderate 10 Hz **⇒ 8 min**

3D-Tomography:

Even more time consuming…

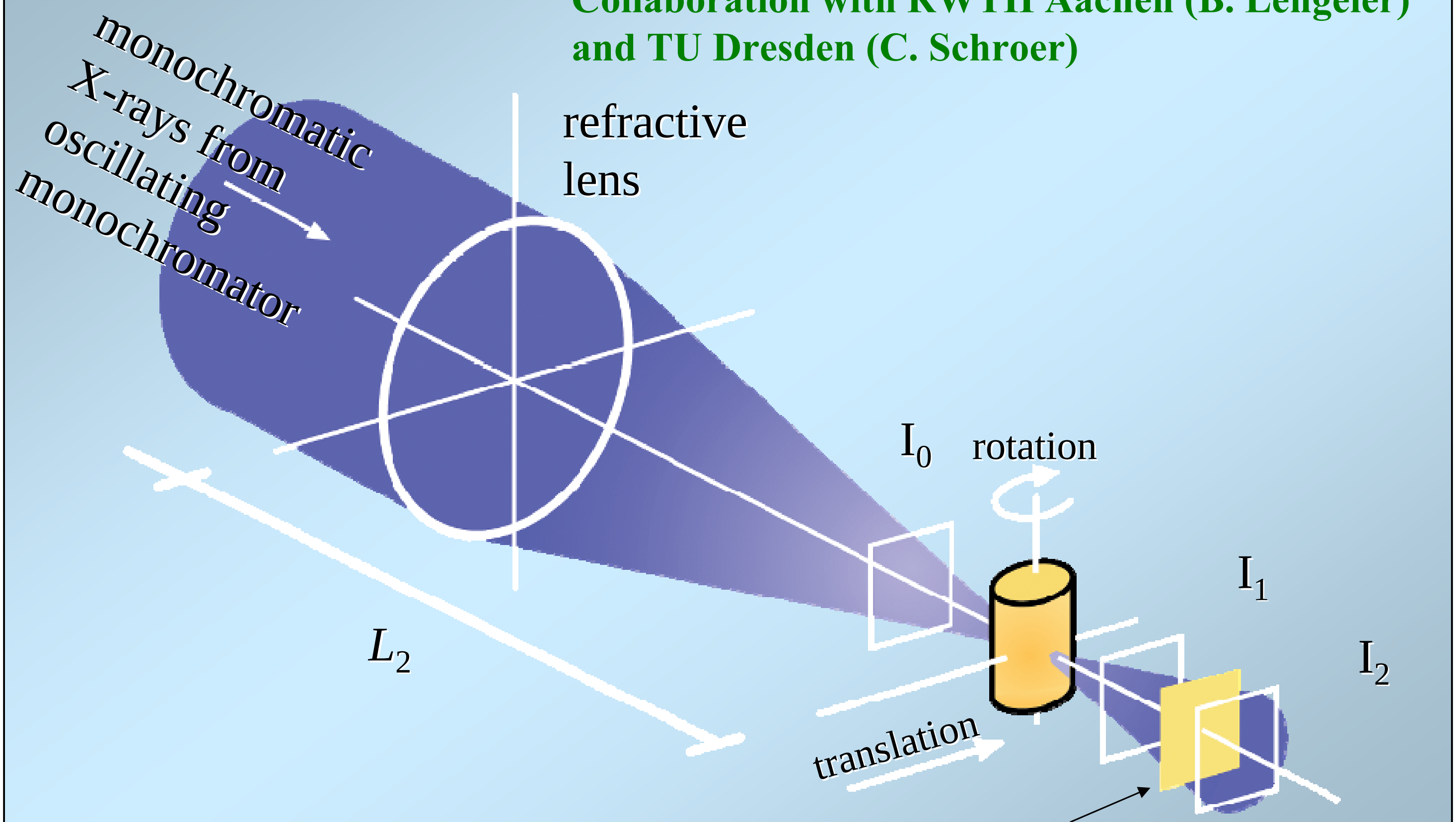
Experiments at ESRF (BM) and APS (tapered undulator)

Focusing with **X-ray lenses** ⇒ Focal size 6 µm x 2 µm.

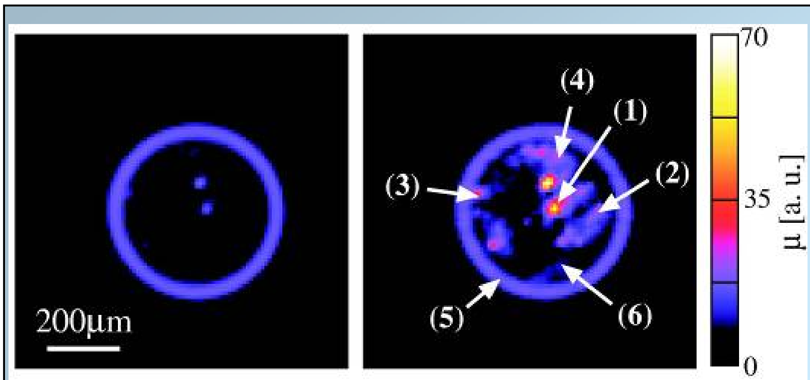
⇒ Even **dilute biological samples in fluorescence** mode possible!

XANES µ-tomography

Collaboration with RWTH Aachen (B. Lengeler) and TU Dresden (C. Schroer)

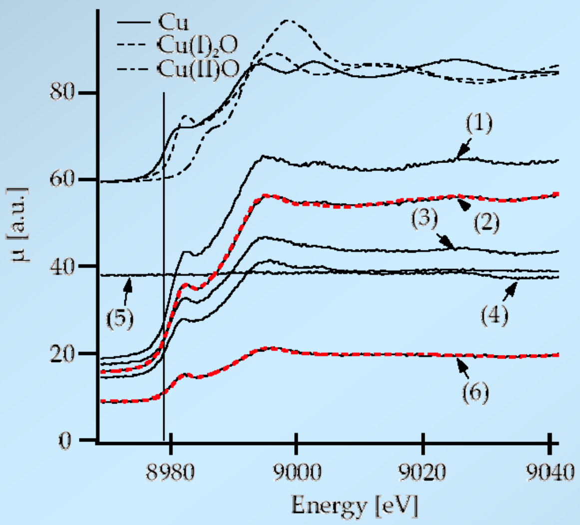


horizontal focus size: 6-10 µm



Cu/ZnO catalyst

Sample below / above Cu K-edge



Reconstructed spectra with references

Sample in glass capillary, outer diameter 500 µm, inner diameter 400 µm.

Beam size: 10 µm x 10 µm

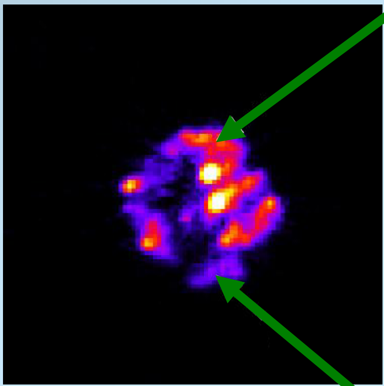
Reconstruction at different positions after several oxidation/reduction cycles:
What happens to the catalyst during catalysis?

All spectra can be decomposed into content of the Cu-oxides and Cu to answer this question!

C.G. Schroer et al., Appl. Phys. Lett. 82, 3360 (2003)

Cu/ZnO catalyst: Cu distribution

Cu > Cu(I) , 1.26 : 1



Average over whole cross section:

Cu : Cu(I) = 51 : 49

Cu < Cu(I) , 1 : 1.8

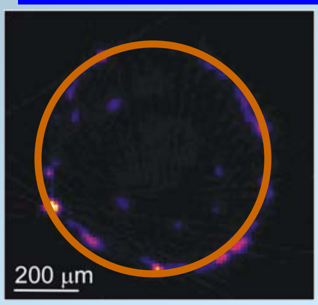
⇒ Very detailed in situ observation of behaviour of real catalysts!

Tomato root grown on a polluted (Zn, Pb) soil

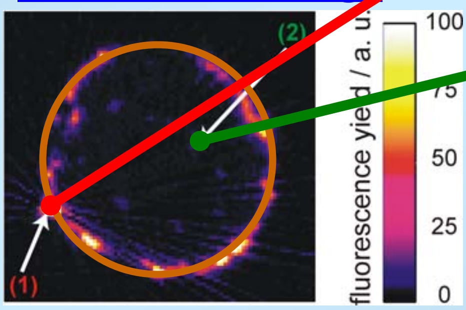
- Tomato root (diameter ~ 700µm)
- Low metal-ion concentration (<100 ppm):

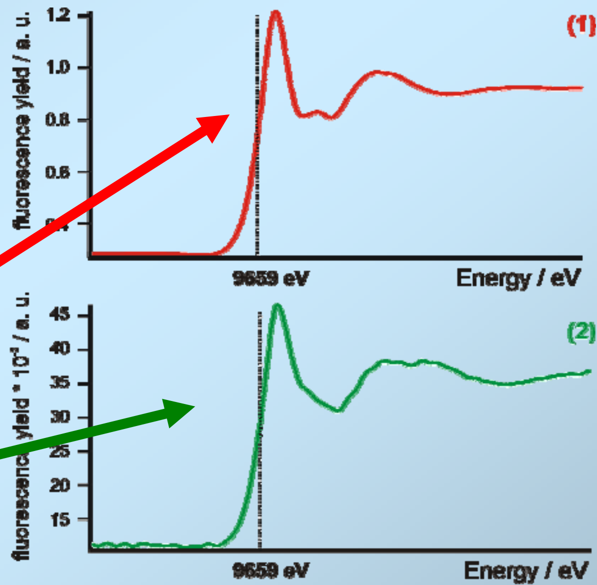
⇒ **Fluorescence tomography**, here: **Zn K-edge**

Below Zn K-edge



Above Zn K-edge





- Significant differences
- Zn concentrated in root bark

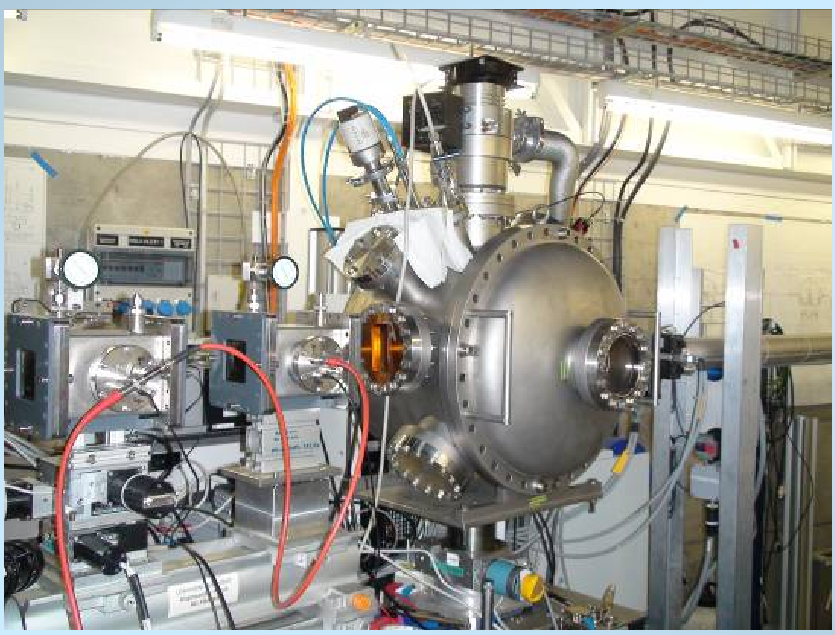
C. Schroer et al., Acta Phys. Polonica A 117, 357 (2010)

QEXAFS: Latest results (May 2010)

Remote controlled change of energy range

J. Stötzel, D.Lützenkirchen-Hecht, and R. Frahm:
A new flexible QEXAFS monochromator setup for time resolved X-ray absorption spectroscopy, Rev. Sci. Instrum., accepted (June 2010)

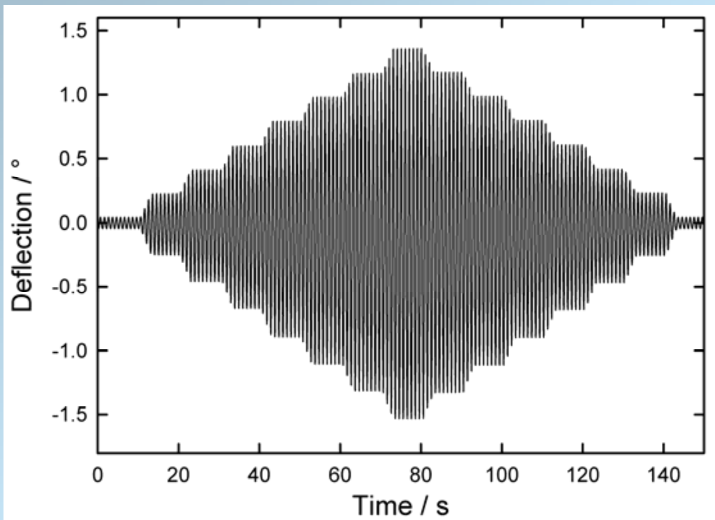
QEXAFS monochromator with improved drive system

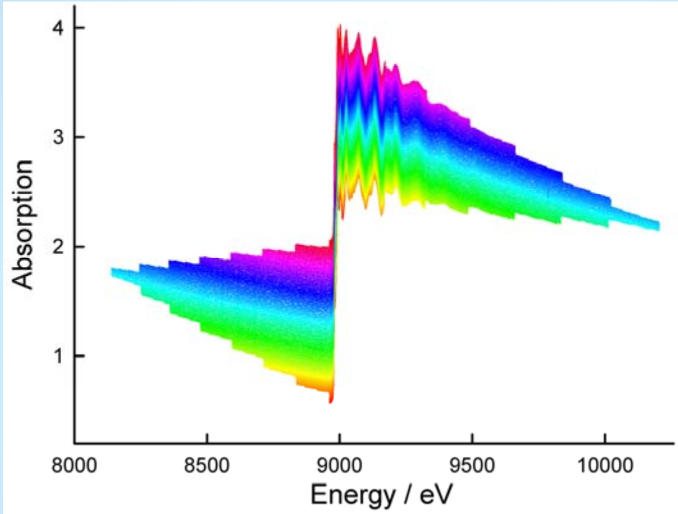


Setup at the Optics Beamline X05DA at the SLS (BM)

Optics beamline: U. Flechsig et al., Nucl. Instrum. Methods in Phys. Res. A 609, 281 (2009)

Cu K-edge, change of energy range



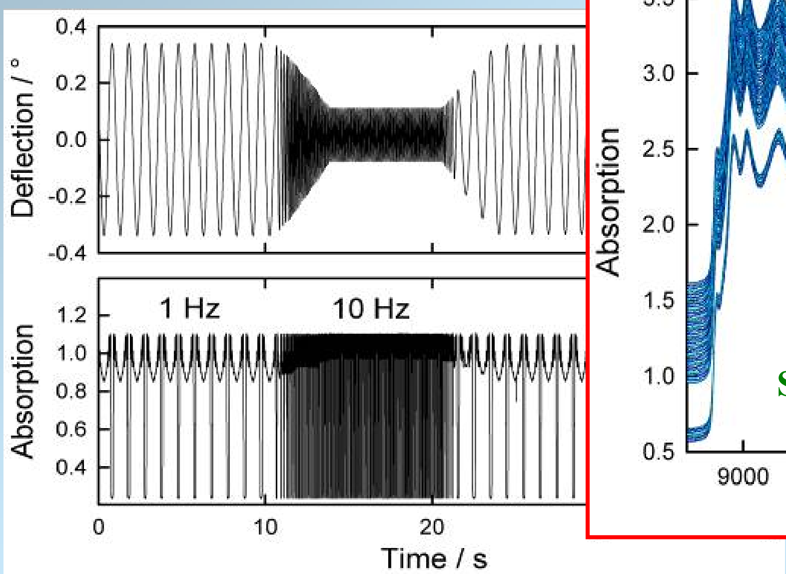


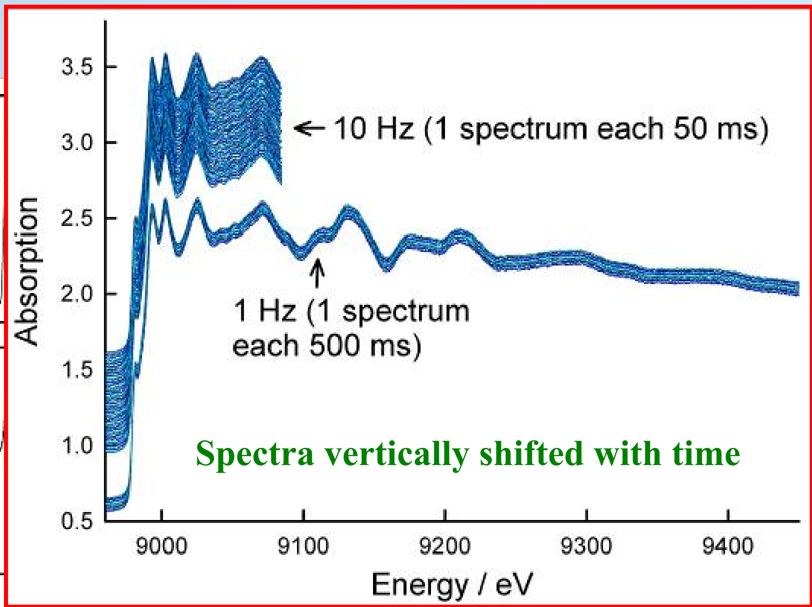
Spectra vertically shifted with time

Change from ΔE = 60 eV to 2070 eV and back,
central Bragg angle remains fixed

Cu K-edge, change of range and frequency

Δθ = 0.68°, ΔE = 460 eV   Δθ = 0.19°, ΔE = 125 eV





Repeated change of Δθ and *f* and start Bragg angle after 10 s

QEXAFS: Perspectives

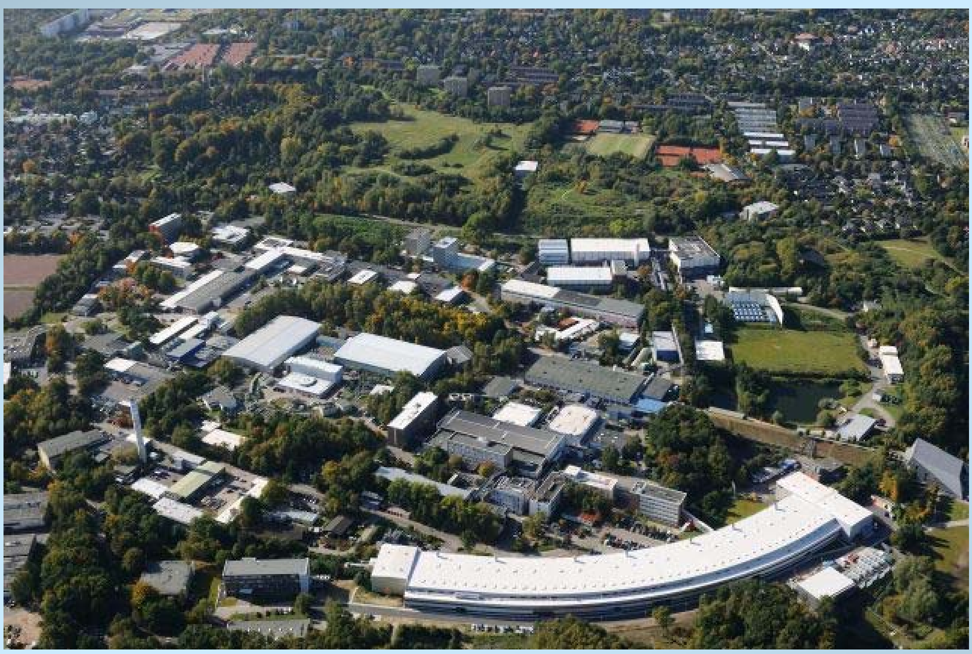
QEXAFS benefits from high intensity sources

High intensity sources allow

- better time resolution: **EXAFS scan in few ms**
- time resolved **fluorescence studies in the ms-range**

  ⇒ very dilute samples (especially also for **biology**)
- smaller focal size **< 20 nm** possible
- time resolved **nano imaging**, **nano tomography**, minute/seconds time scale

PETRA III at DESY, Hamburg



2304 m circumference, 6 GeV positrons, 100 mA (200 mA)

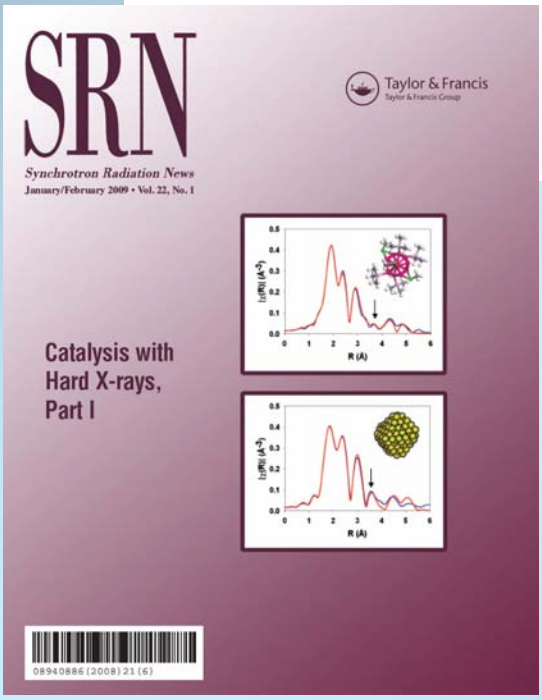
Funding granted for a QEXAFS monochromator at an insertion device beamline.

More about QEXAFS

GUEST EDITORIAL

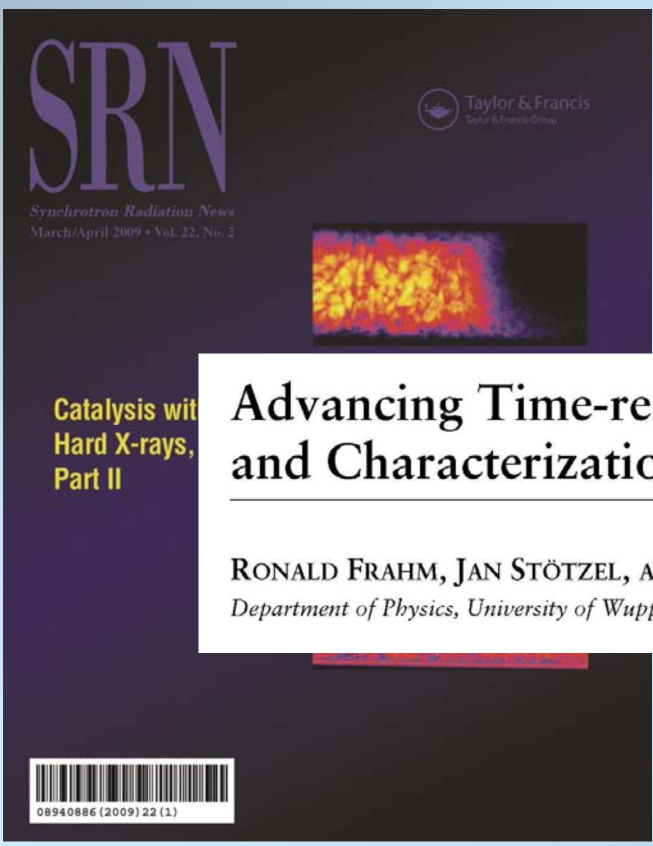
A.I. Frenkel and J.-D. Grunwaldt

Synchrotron Studies of Catalysts: From XAFS to QEXAFS and Beyond



SRN Vol. 22, No. 1
(January/February 2009)

More about QEXAFS



Part II contains a review about QEXAFS in the March /April issue.

Advancing Time-resolved Methods in Monitoring and Characterization of Catalysts

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SRN Vol. 22, No. 2
(March /April 2009)

Acknowledgements

Univ. Wuppertal: D. Lützenkirchen-Hecht, J. Stötzel, diploma and thesis students
ETH Zürich: J. Singh, J.A. van Bokhoven, A. Baiker
Univ. Karlsruhe: J.-D. Grunwaldt
RWTH Aachen: B. Lengeler
TU Dresden: C. Schroer
Univ. Dortmund: Departments of chemistry and physics
APS: A. Mashayekhi, D.R. Haeffner
SOLEIL: E. Fonda, V. Briois
SLS: M. Nachtegaal, U. Flechsig, M. Harfouche, M. Willimann, R. Abela
Bruker ASC: T. Waterstradt, M. Schwoerer-Böhning, W. Diete

Sources and collaborations:

APS, Chicago
LURE / SOLEIL Paris
Dortmund
Swiss Light Source Villigen

QEXAFS = Quick scanning EXAFS

Additional references:

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