State of the art Quick-EXAFS: Applications in Catalysis

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QEXAFS = Quick scanning EXAFS

(“Stepper motor QEXAFS”)

Conventional EXAFS scan: Step by step mode
measuring time ≈ 15 min

QEXAFS–scan: Monochromator is moving (quasi)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} photons/s available**

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

QEXAFS = Quick scanning EXAFS

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)

Additional reading (more references in the text):

J.-D. Grunwaldt, D. Lützenkirchen-Hecht, M. Richwin, S. Grundmann, Bjerne S. Clausen, and R. Frahm. Piezo X-ray absorption spectroscopy for the investigation of solid-state transformations in the millisecond range. J. Phys. Chem. B 105, 5161 (2001)

M. Richwin, R. Zaeper, D. Lützenkirchen-Hecht, and R. Frahm. Piezo-XAFS - Time-resolved X-ray absorption spectroscopy. Rev. Sci. Instrum. 73, 1668 (2002)

C.G. Schroer, M. Kuhlmann, T.F. Günzler, B. Lengeler, M. Richwin, B. Griesebock, D. Lützenkirchen-Hecht, R. Frahm, E. Ziegler, A. Mashayekhi, D.R. Haeffner, J. D. Grunwaldt, and A. Baiker. Mapping the chemical states of an element inside a sample using tomographic X-ray absorption spectroscopy. Appl. Phys. Lett. 82, 3360 (2003)

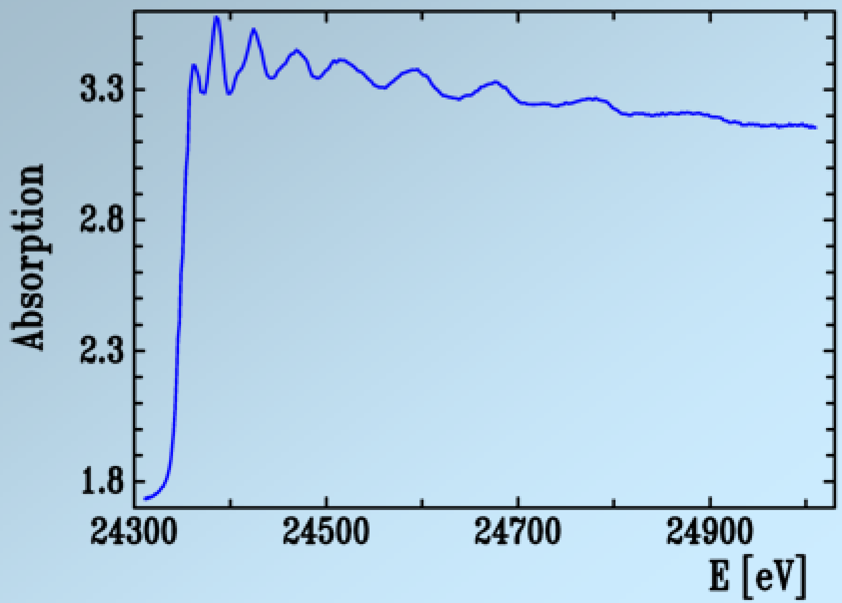
R. Frahm, M. Richwin, B. Griesebock, and D. Lützenkirchen-Hecht. Status and new applications of time-resolved X-ray absorption spectroscopy, Proc. 8th Int. Conf. Synchrotron Radiation Instrumentation, American Institute of Physics Proceedings 705, 1411 (2004)

R. Frahm, M. Richwin, and D. Lützenkirchen-Hecht. Recent advances and new applications of time-resolved X-ray absorption spectroscopy, Physica Scripta T115, 974 (2005)

D. Lützenkirchen-Hecht, J.-D. Grunwaldt, M. Richwin, B. Griesebock, A. Baiker, and R. Frahm. Monitoring of fast transformations in solid state chemistry and heterogeneous catalysis by QEXAFS in the second scale, Physica Scripta T115, 831 (2005)

J. Stötzel, D. Lützenkirchen-Hecht, E. Fonda, N. De Oliveira, V. Briois, and R. Frahm. Novel angular encoder for a quick-extended x-ray absorption fine structure monochromator, Rev. Sci. Instrum. 79, 083107 (2008)

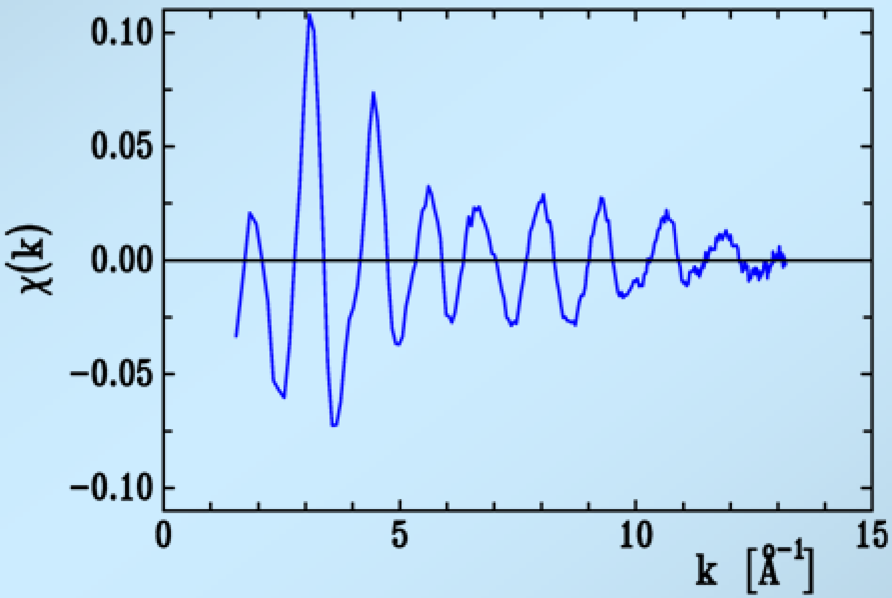
Very fast scans using stepper motors: Pd foil (300 K)

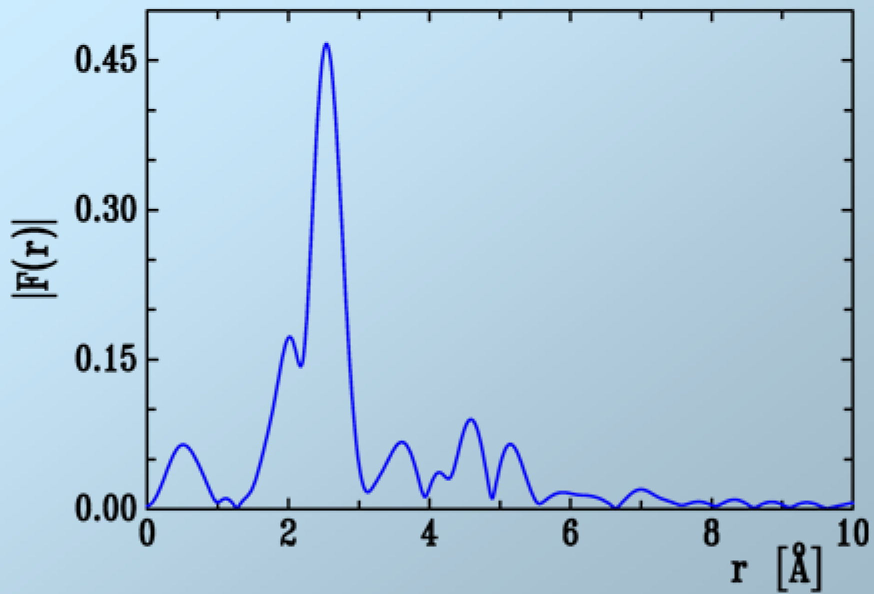


QEXAFS in 0.81 s
0.002 s / data point

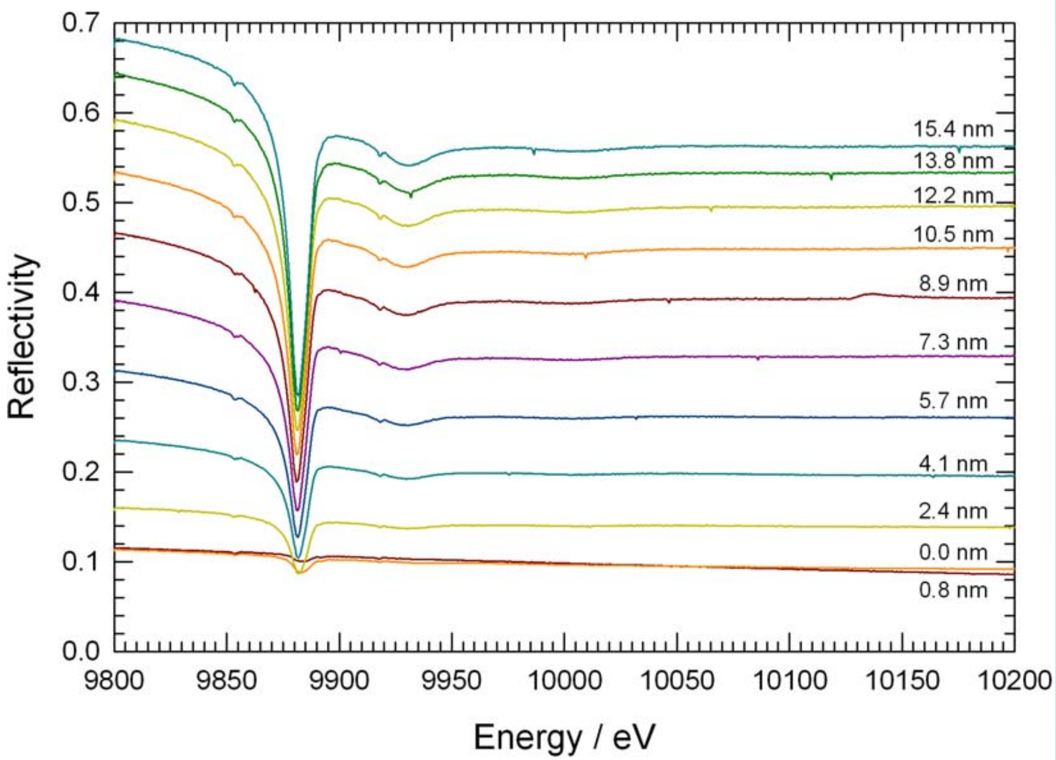
Energy range 700 eV
Si(311), channel cut,
E_K = 24.348 keV

Transmission measurement

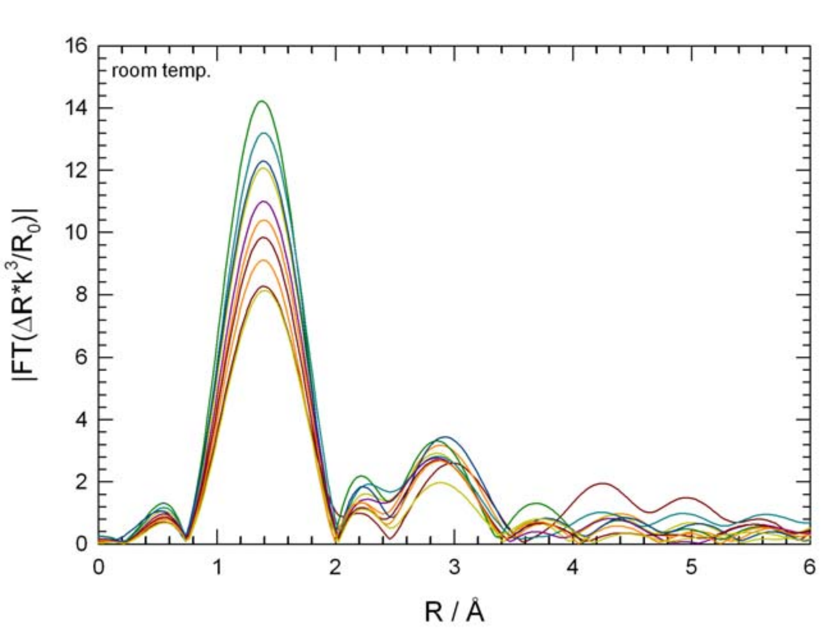




Time-resolved GIXAFS of sputtered Ta_2O_5-films



- glancing angle Θ = 0.22°.
  Θ_c(glass)=0.18°.
- ca. 22 s / spectrum
- growth rate 1.23 nm/min

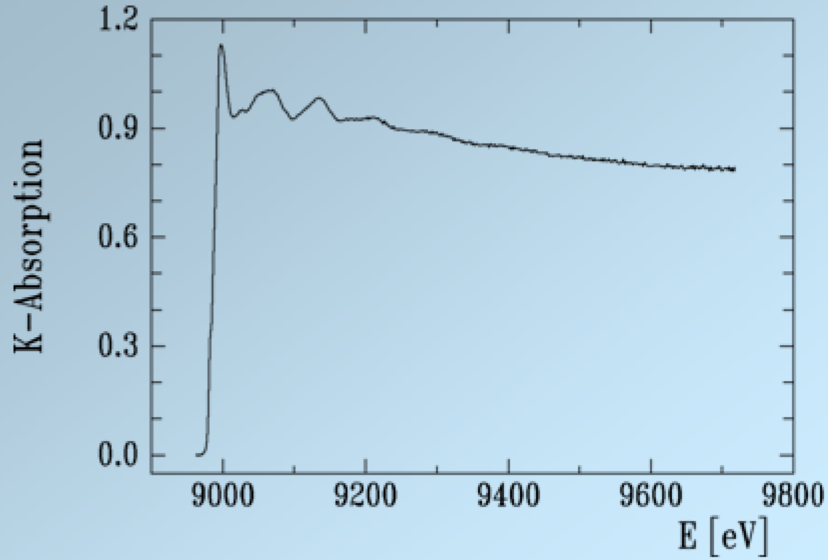


⇒ **data show growth of amorphous Ta_2O_5-films**

⇒ **detailed information about *in situ* thin film growth processes**

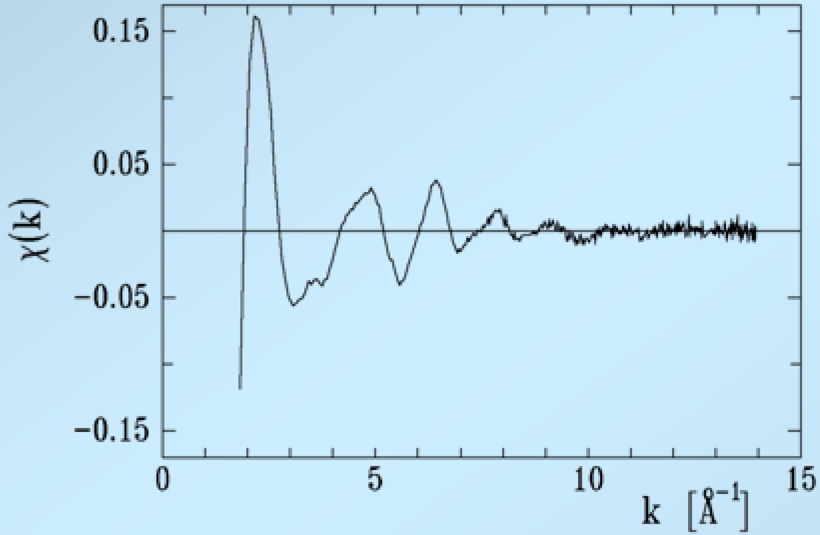
K. Bruder et al., Physica Scripta T115, 963 (2005)

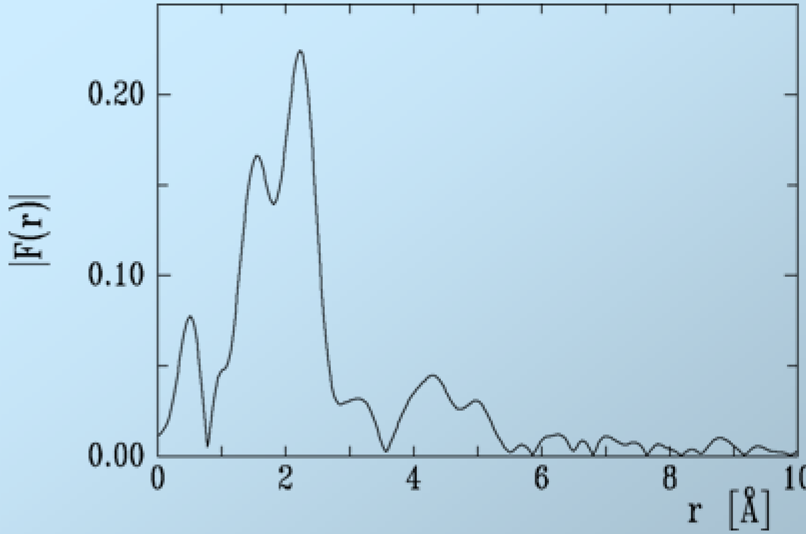
5 ML Cu on 500 Å W + 10 Å C, ex situ



Range 755 eV,
QEXAFS in 4.8 s,
0.01 s / point.

Fluorescence measurement, wiggler beam





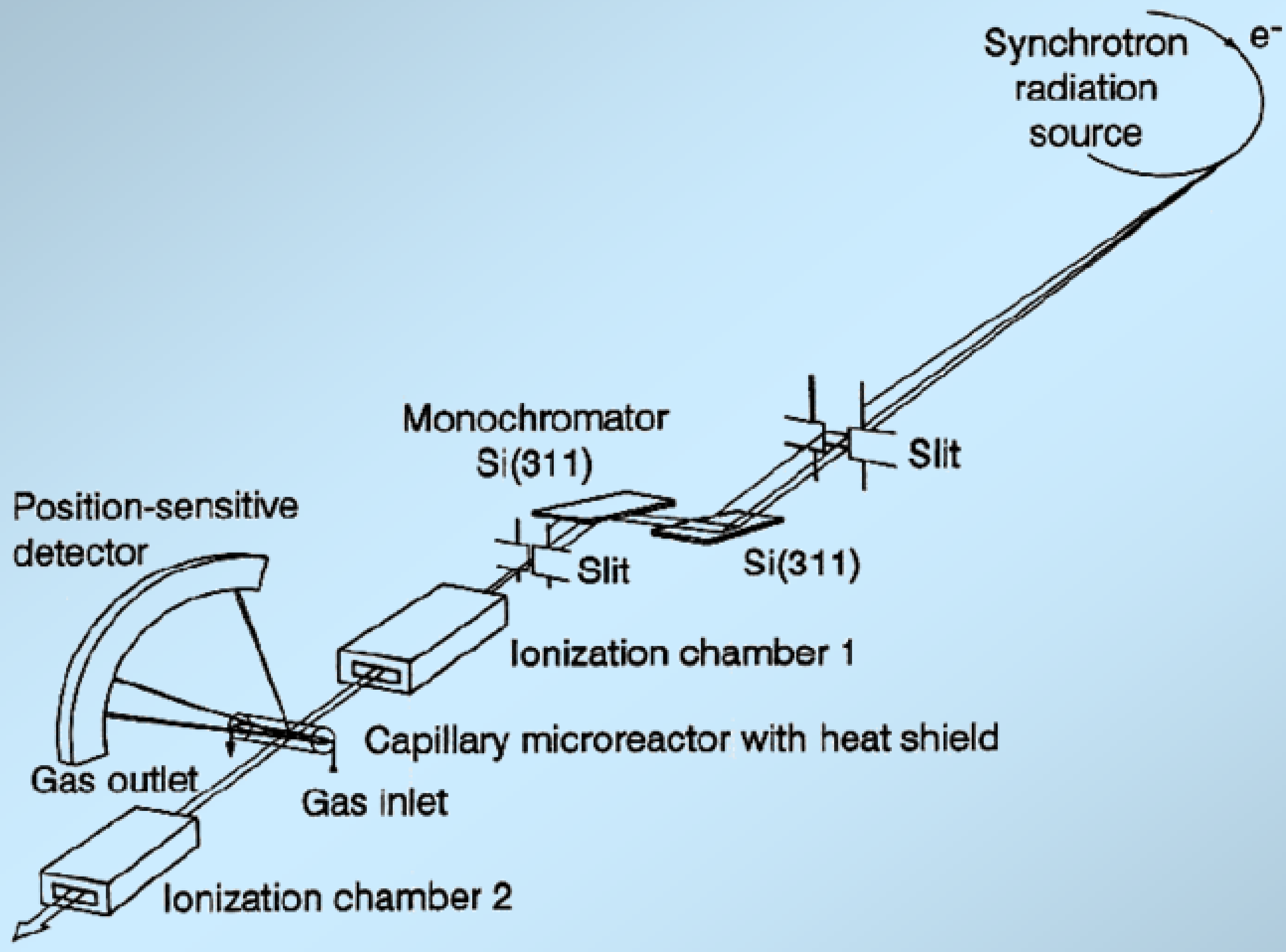
R. Frahm. Quick XAFS: Potentials and practical applications in materials science. In S.S. Hasnain, editor, X Ray Absorption Fine Structure, p. 731. Ellis Horwood Ltd., Chichester (1991)

Catalysts:

Small particles, big business

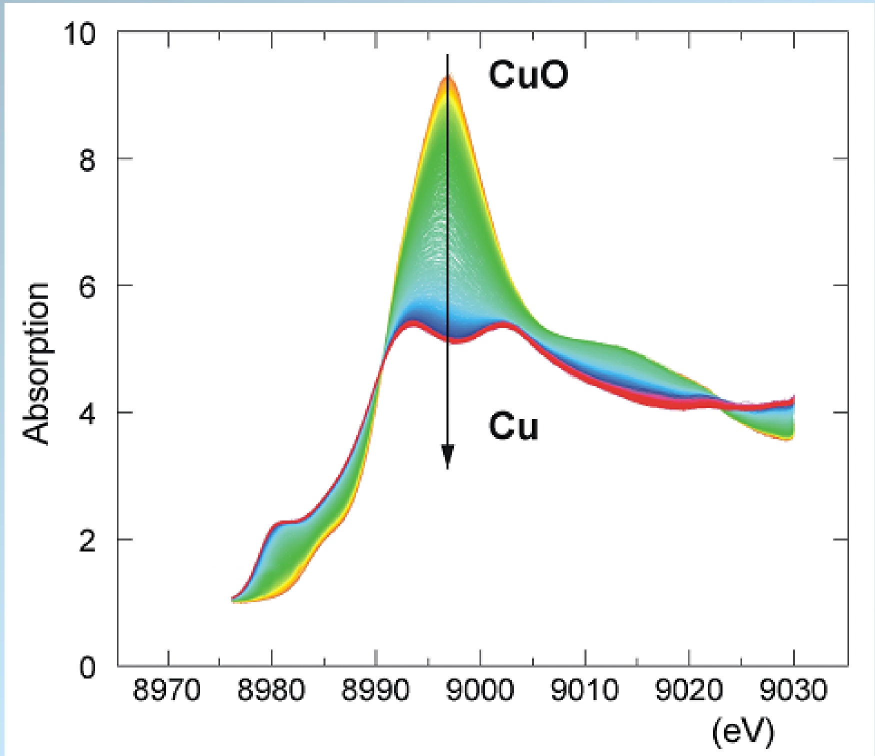
B.S. Clausen, H. Topsøe and R. Frahm: Application of combined X-ray diffraction and absorption techniques for in situ catalyst characterization. Advances in Catalysis 42, 315 (1998)

Combined setup: QEXAFS + XRD



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

Activation of a $CuO/ZnO/Al_2O_3$ catalyst



Cu K-edge

In situ reduction in H_2 atmosphere

Time resolution: **50 ms**

Simultaneous measurement of catalytic activity

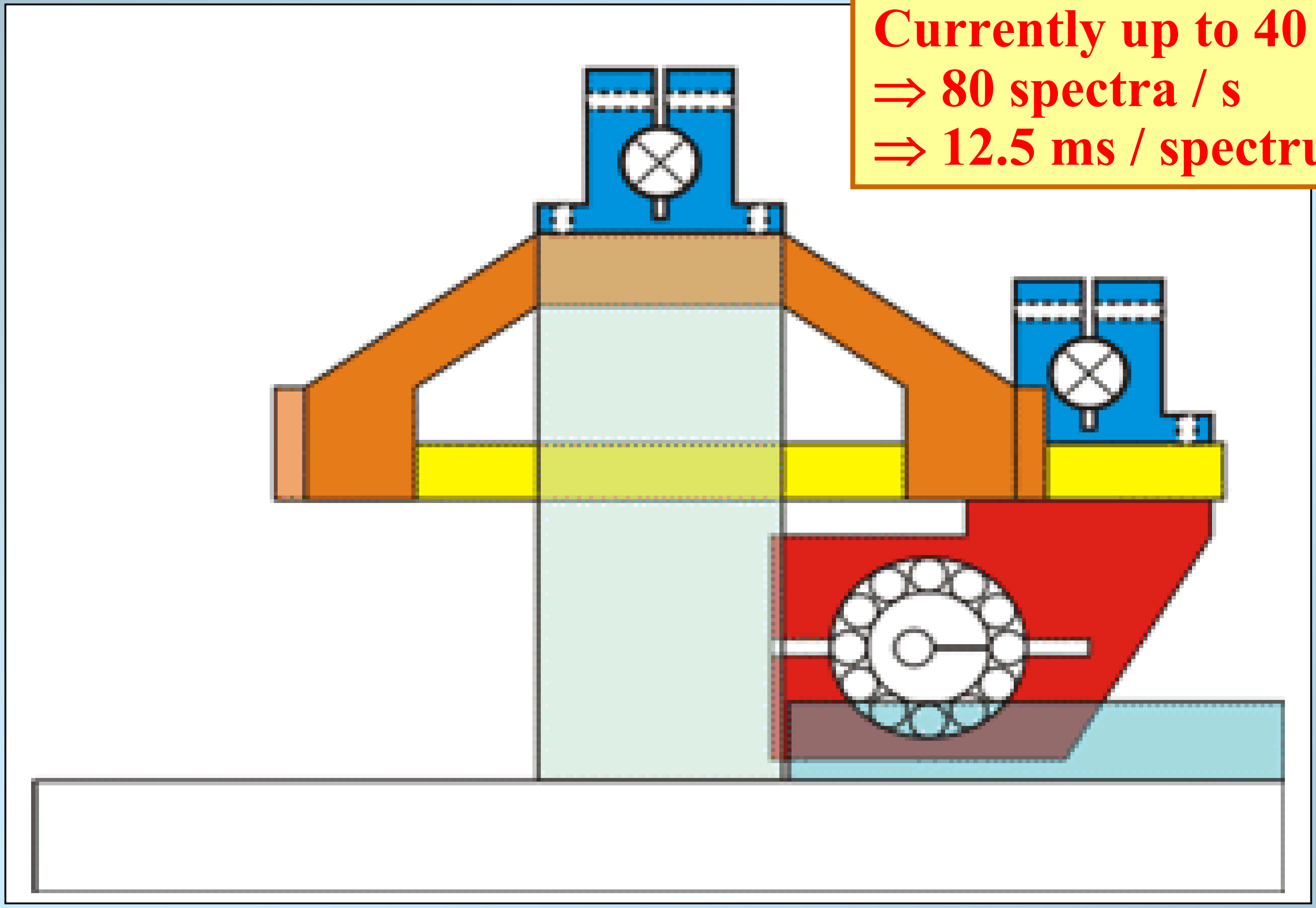
⇒ Cu particle size can be determined directly!

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

A novel fast monochromator: Drive system

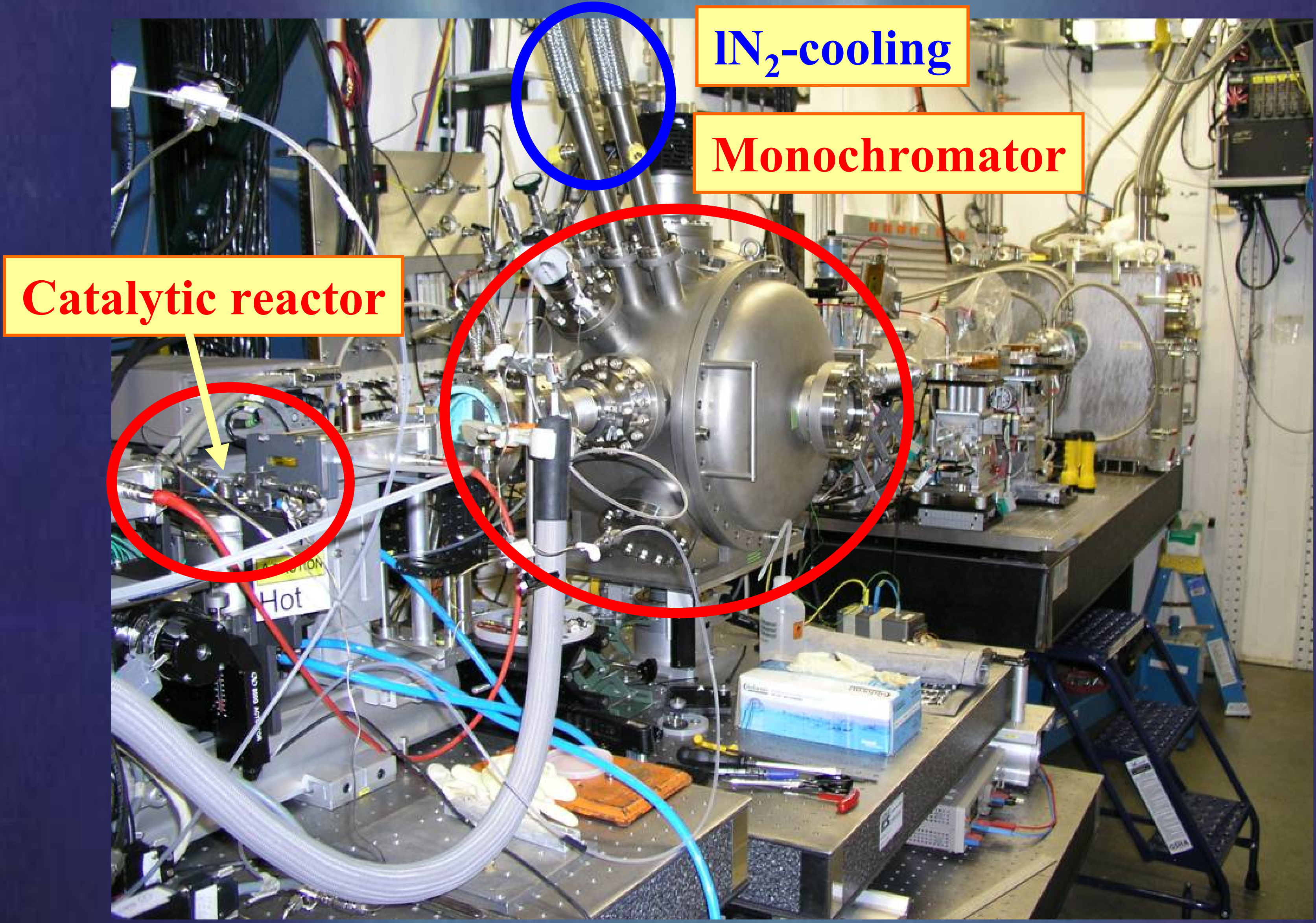
Goal: Faster (ms), wide spectral range, continuous movement

Currently up to 40 Hz possible
⇒ 80 spectra / s
⇒ 12.5 ms / spectrum

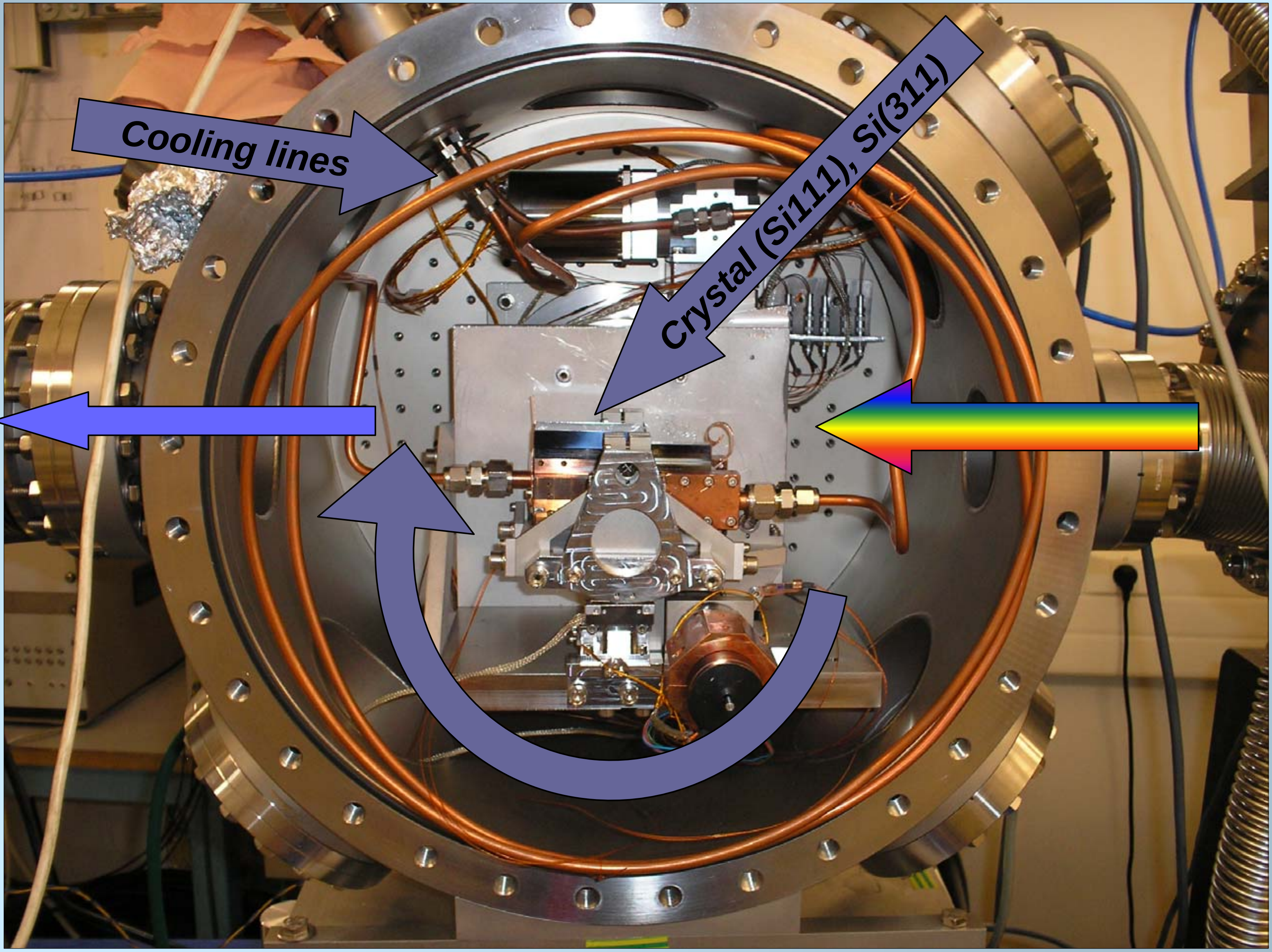


R. Frahm, M. Richwin, B. Griesebock, D. Lützenkirchen-Hecht, AIP Proc. 705, 1411 (2004)
R. Frahm, M. Richwin, D. Lützenkirchen-Hecht, Physica Scripta T115, 974 (2005)

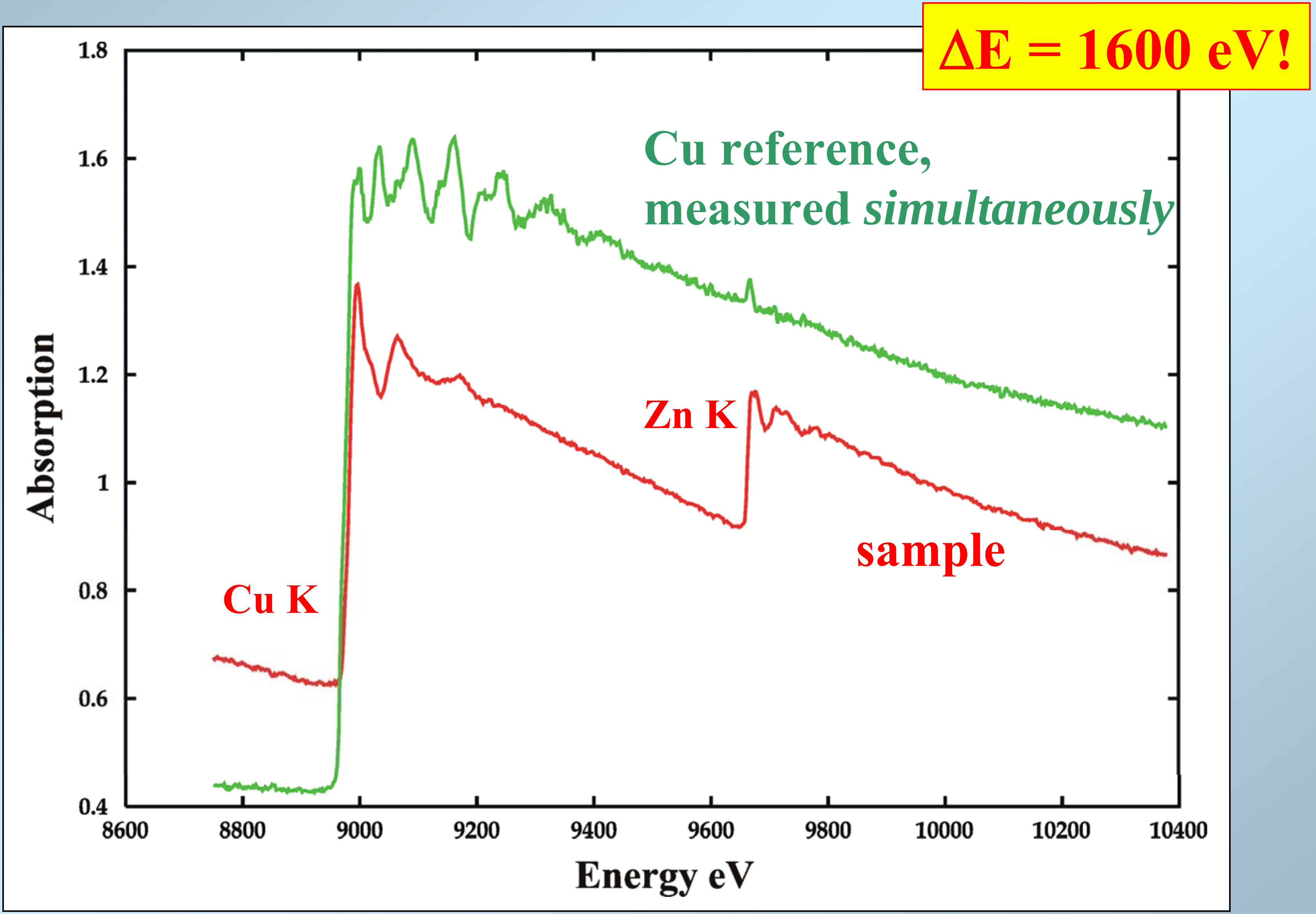
Experiments at APS undulator 1-ID



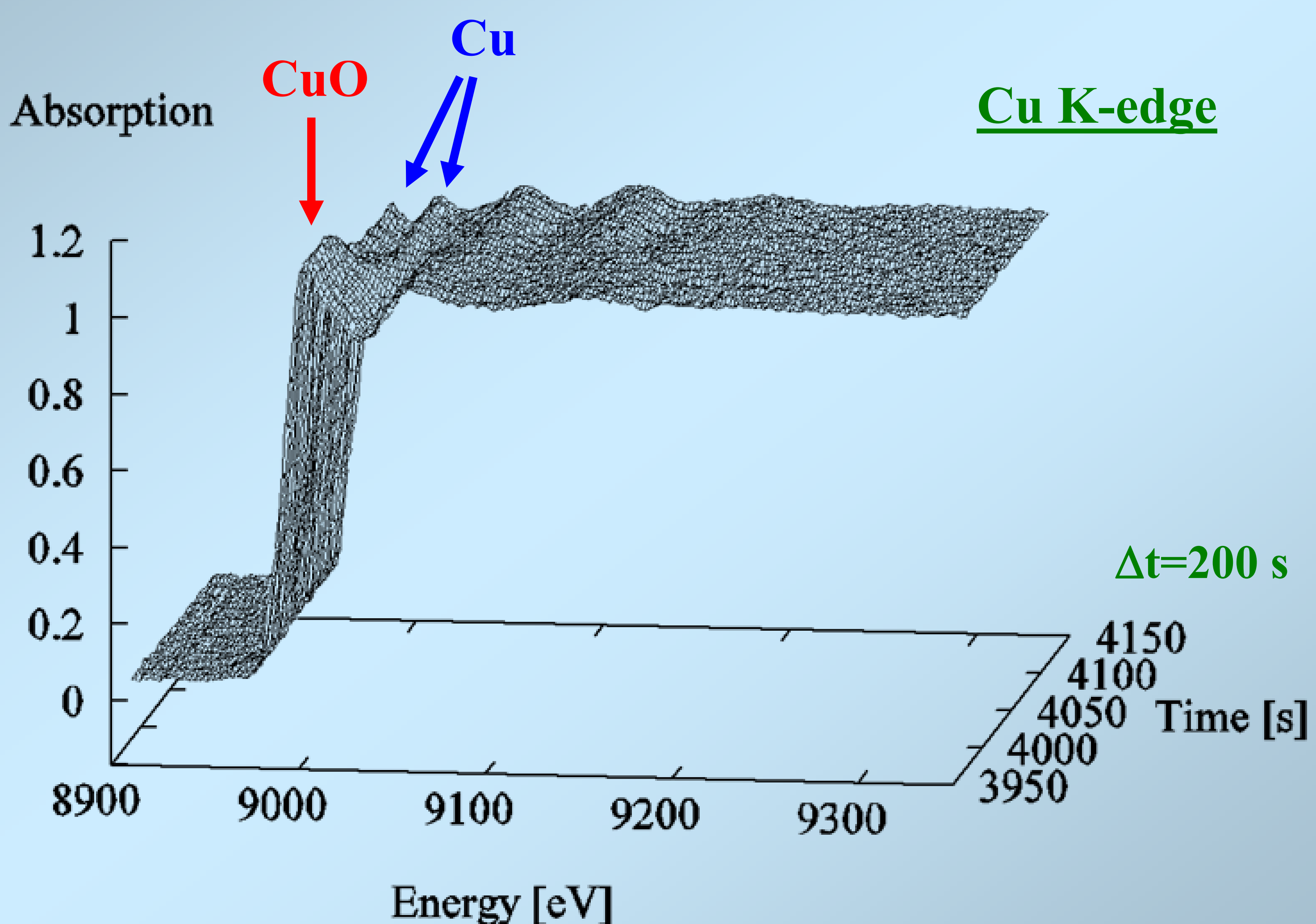
Monochromator



CuO/ZnO-catalyst: Single scan, 50 ms

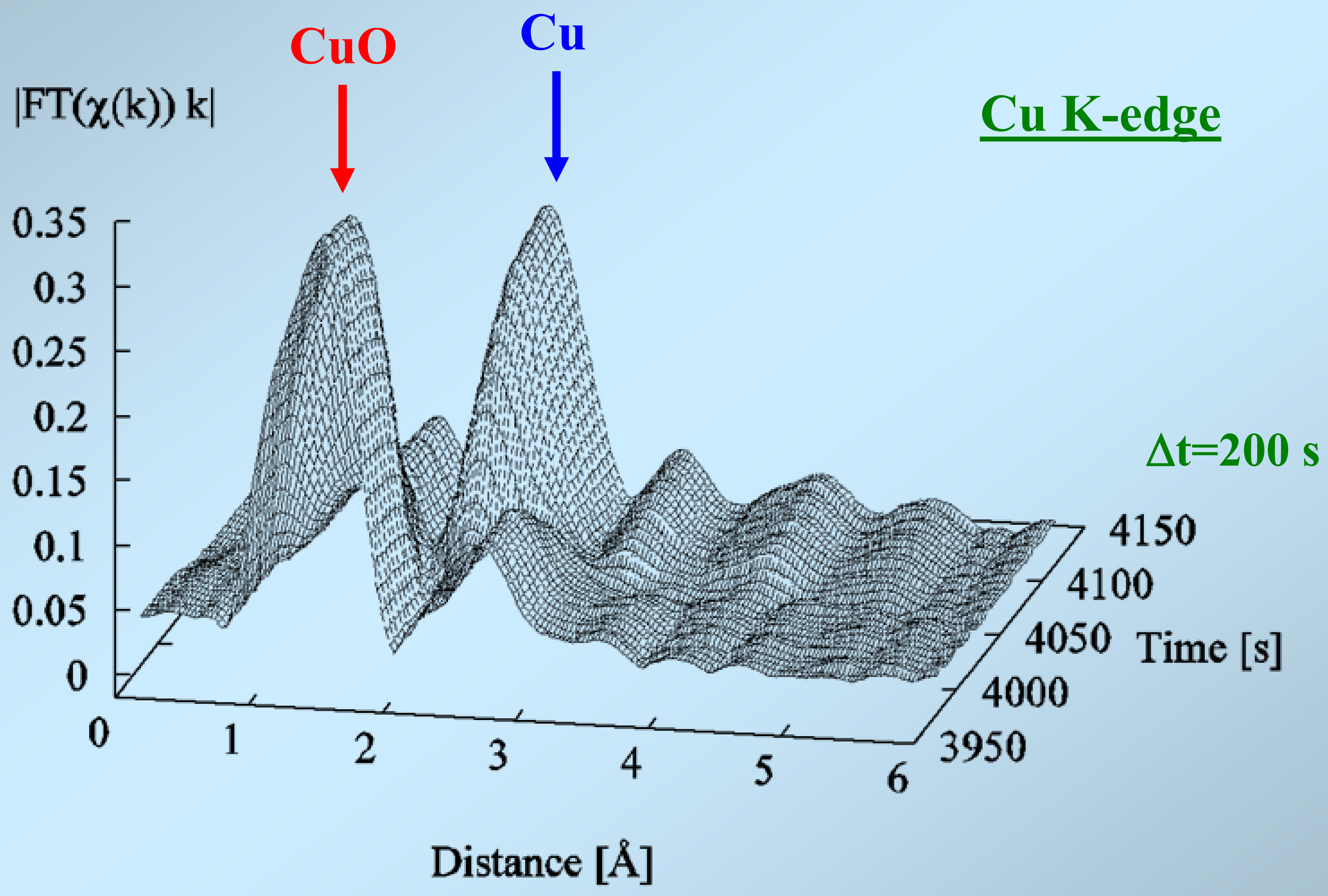


CuO/ZnO-catalyst: Reduction



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

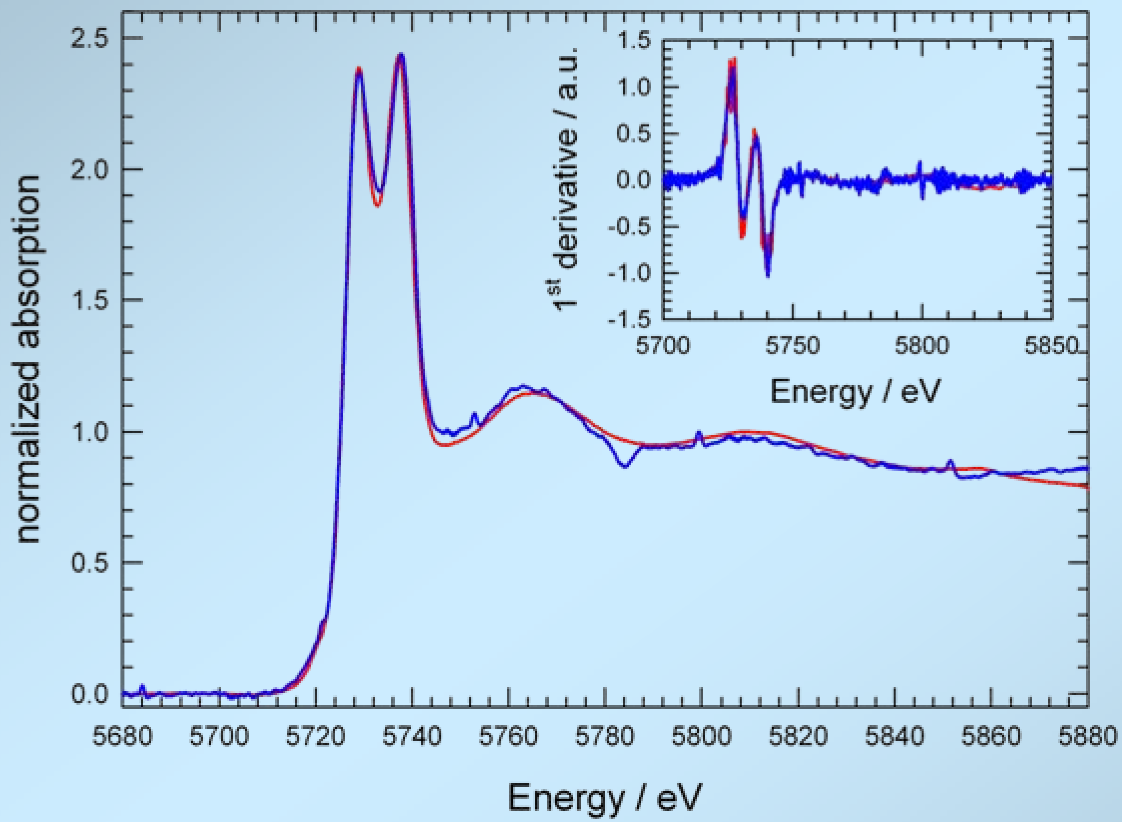
CuO/ZnO-catalyst: Reduction



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

DCI-Lure, beamline D44

"Time-resolved study of the oxidation of ethanol by cerium(IV) using combined quick-XANES, UV-Vis, and Raman spectroscopies",
B. Briois et al., J. Phys. Chem. A, 109, 320 (2005)

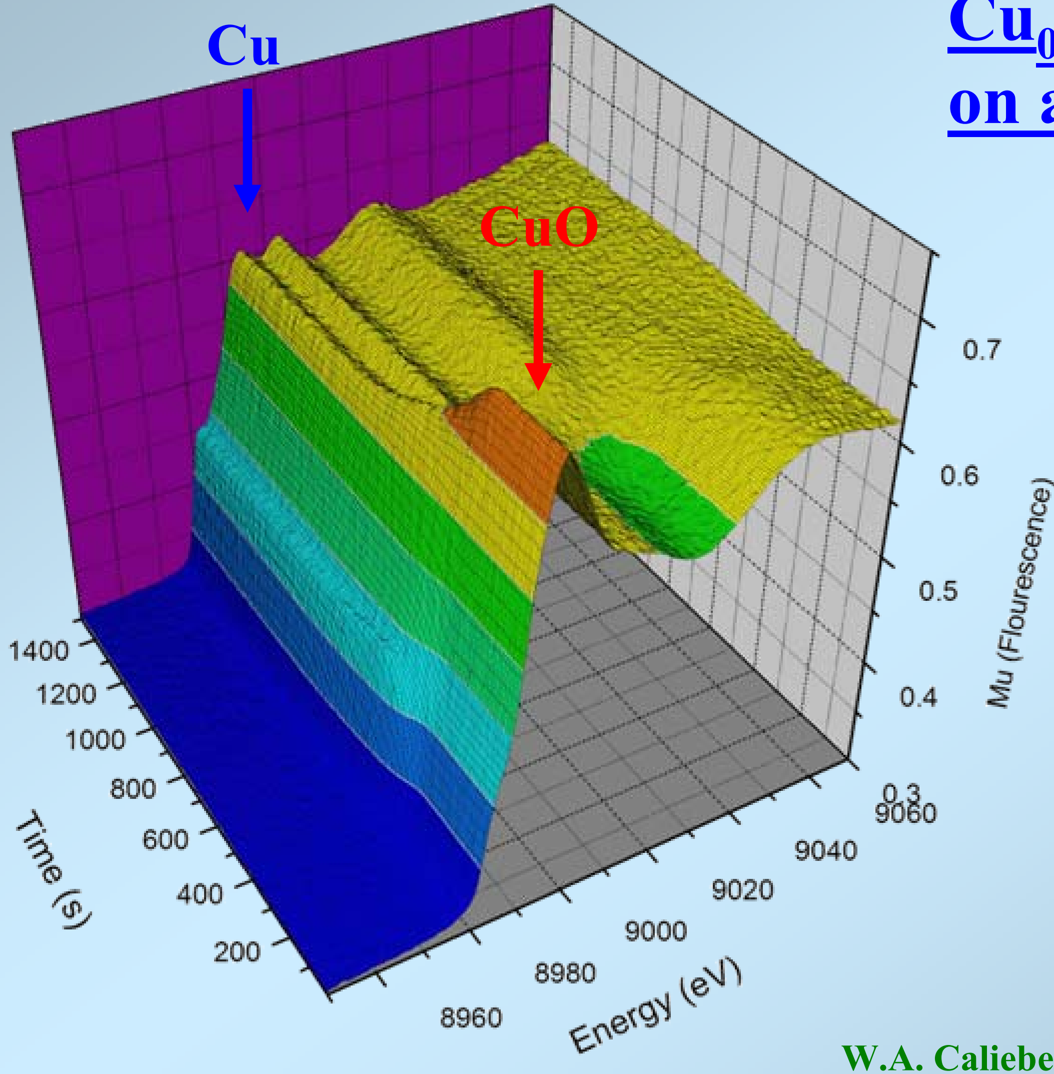


Ce L_3-edge

Q-XANES, 5 s
Stepscan, 20 min

Q-XANES, ΔE=200 eV, usable speed limited by intensity to 1-2 Hz

QEXAFS monochromator at the NSLS



$Cu_{0.2}Ce_{0.8}O_2$ catalyst on alumina, Cu K-edge

Time resolution: 15s / scan, Si(111), NSLS bending magnet beamline X18B

Reduction under flow of 5% H_2 at 275 K.

$$CuO + H_2 \Rightarrow Cu + H_2O$$

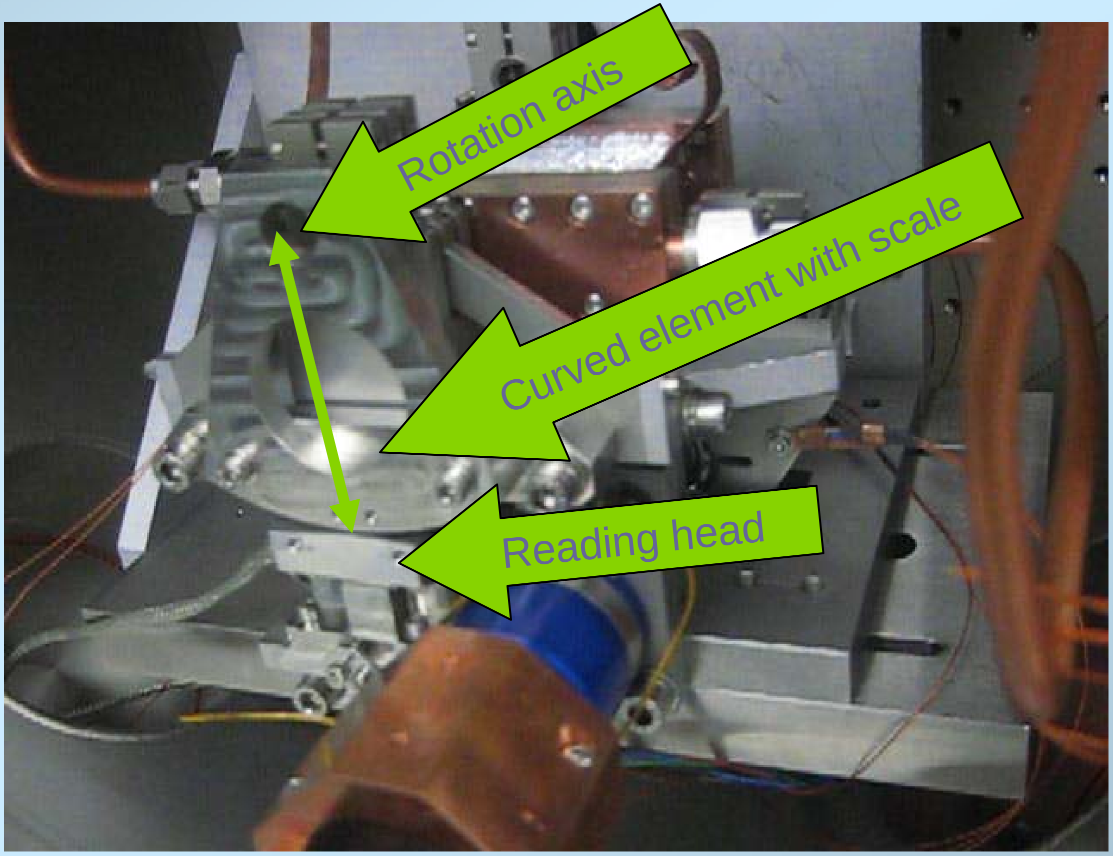
Data collected in *fluorescence*, Canberra PIPS detector, 1 channel.

W.A. Caliebe et al., Rad. Phys. Chem. 75, 1962 (2006)
W.A. Caliebe et al., HASYLAB Annual Report 2006, p. 283
S. Khalid et al., in preparation (2009)

Next improvement: Angular encoder

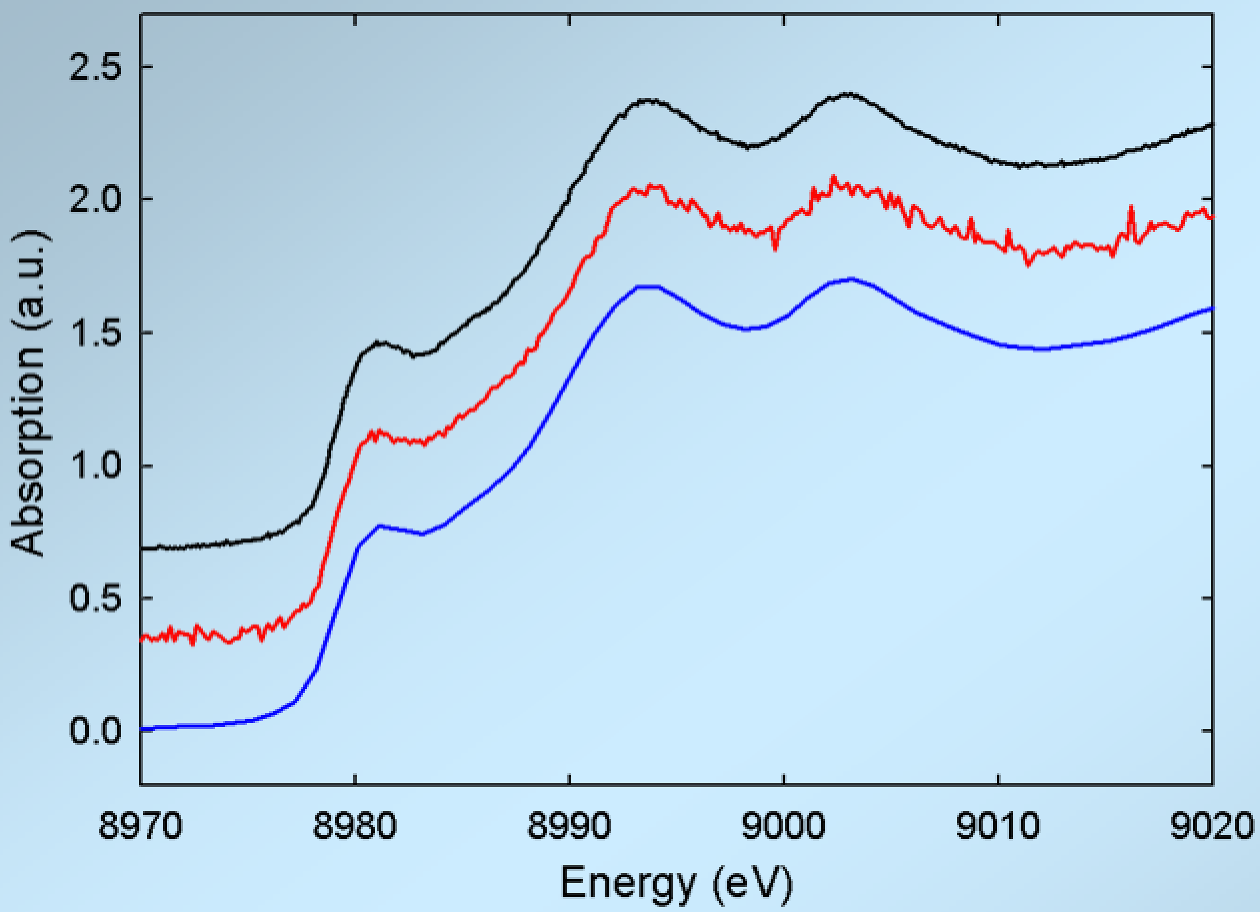
Renishaw encoder ⇒ absolute angular scale

Properties: No mechanical connection, vacuum compatible,
fast (~10 m/s), high resolution (10 nm) ⇒ 0.03“ in Bragg angle



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

First QEXAFS experiments at SOLEIL



≈ 600 ms / XANES (0.1 Hz)

≈ 5 ms / XANES (11 Hz)

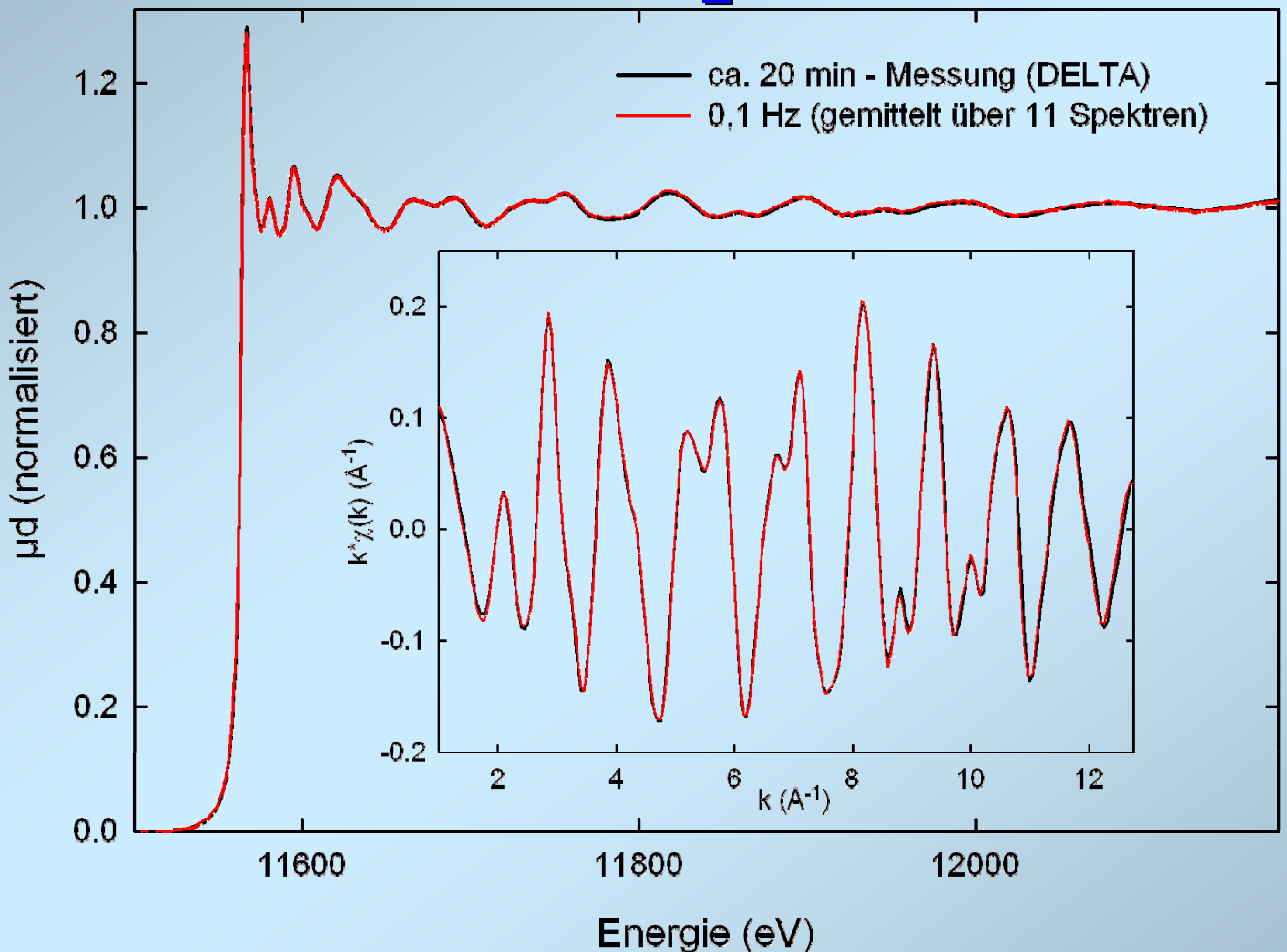
Step scan (HASYLAB)

Cu metal foil, XANES region

Noise of detector system is currently the limiting factor at SOLEIL

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

Pt L_3-edge



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

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, and J.A. van Bokhoven, Angewandte Chemie International Edition 47, 9260 (2008)

Jan-Dierk Grunwaldt (TU Denmark, Lyngby)

J.-D. Grunwaldt, M. Beier, B. Kimmerle, A. Baiker, M. Nachtegaal, B. Griesebock, D. Lützenkirchen-Hecht, R. Frahm, submitted for publication

QEXAFS setup at the SLS

Responsible beamline scientist:

Maarten Nachtegaal, maarten.nachtegaal@psi.ch

First description of QEXAFS setup:

M. Nachtegaal et al., Proc. MEDSI 2008 / Pan-American SRI 2008, June 10-13, Saskatoon, Canada, submitted for publication

Beamline homepage:

http://sls.web.psi.ch/view.php/beamlines/superxas/index.html

Dedicated QEXAFS setup at the SLS

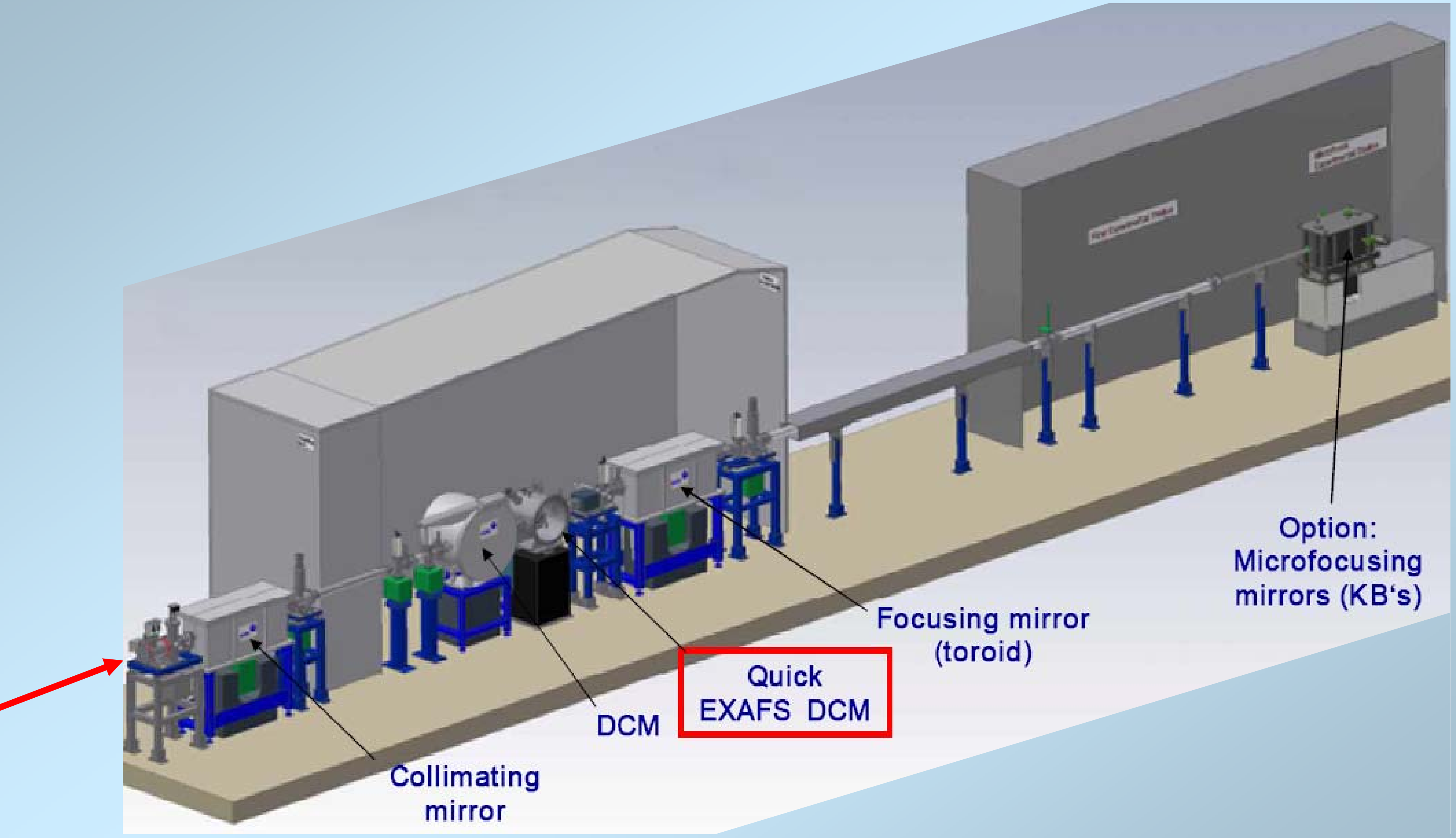
SuperXAS: **Superconducting bending magnet (2.9 T) beamline, conventional DCM and QEXAFS monochromator in a row.**

Crystal and monochromator change in < 5 min possible!

Typical intensity of monochromatized beam:

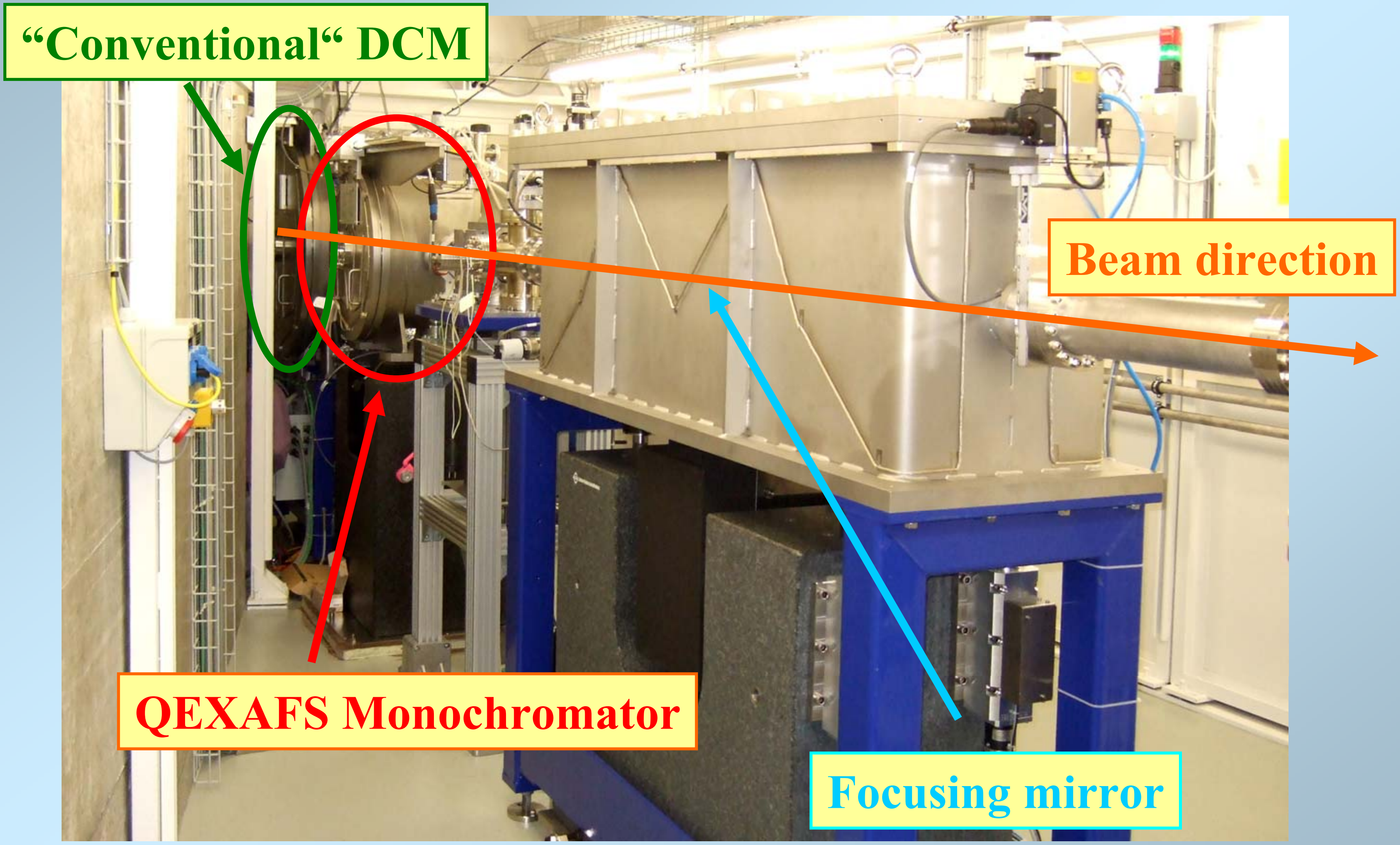
10^{12} photons/s at 400 mA ring current, top-up mode is used.

SuperXAS Beamline (X10DA) at the SLS

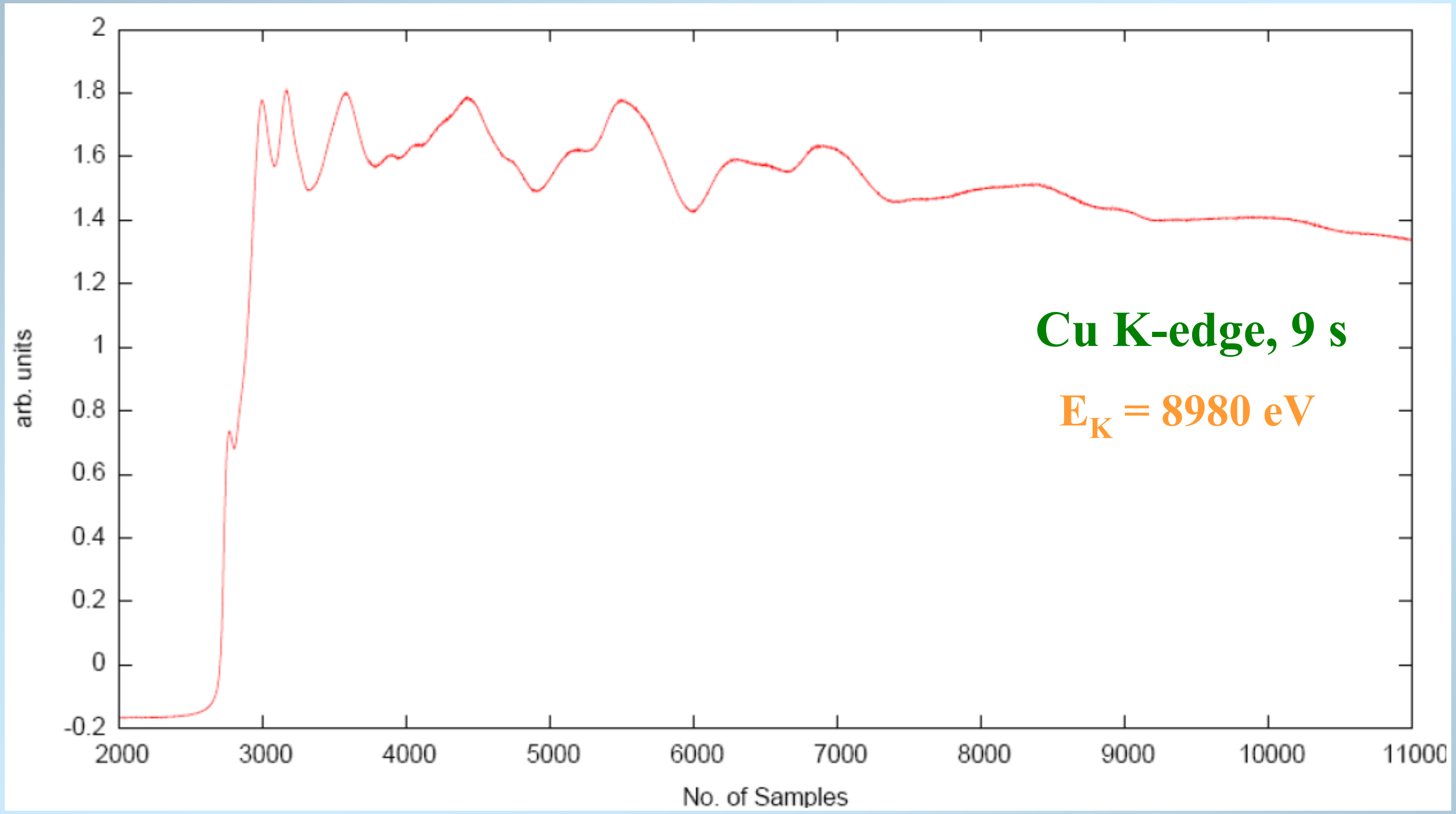


Entire beamline delivered and installed by ACCEL

SLS XAFS beamline: Main hutch

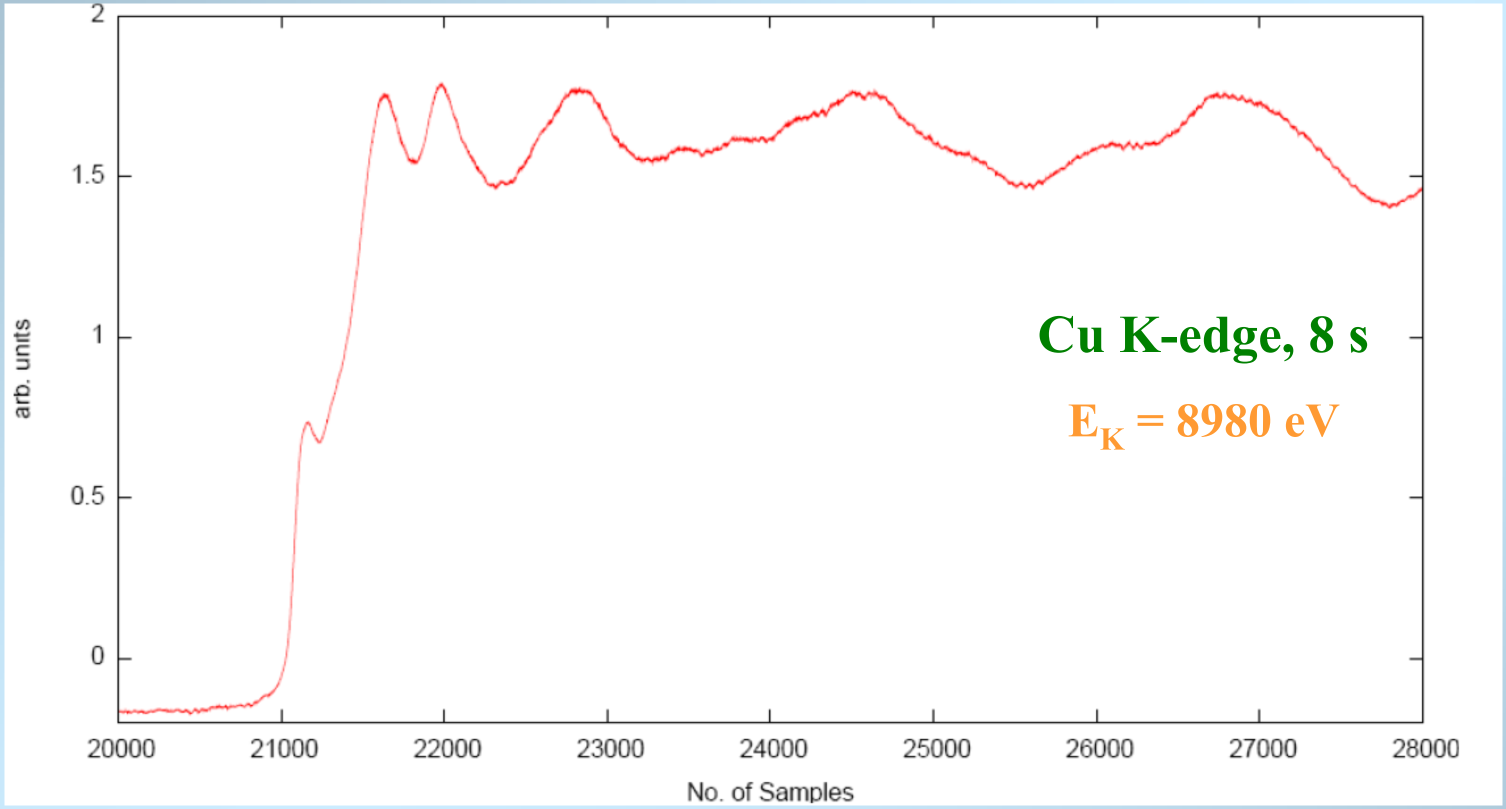


Conventional monochromator – SuperXAS at the SLS



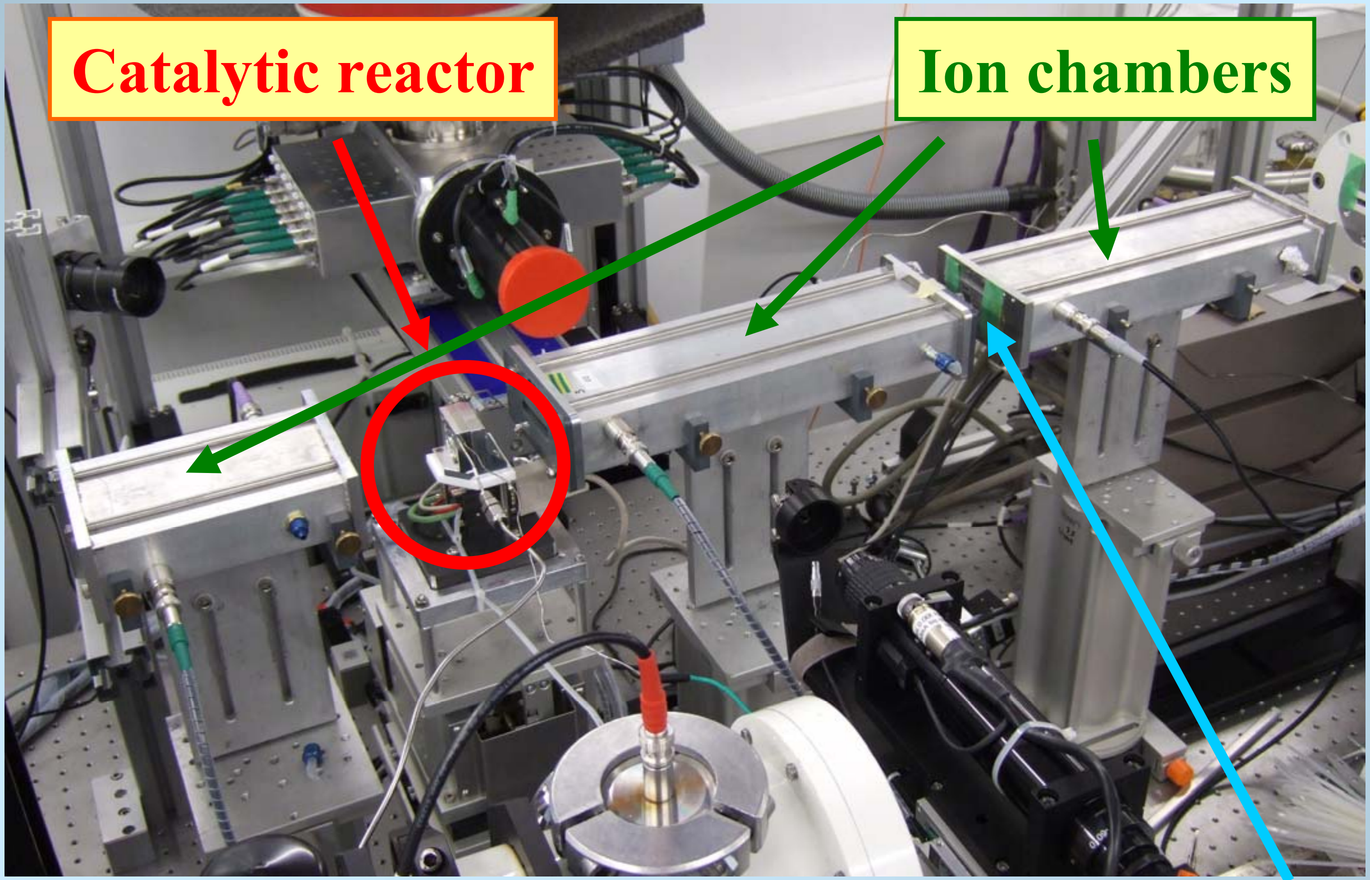
Si(111), 1 kHz sampling frequency

Conventional monochromator – SuperXAS at the SLS



Si(311), 1 kHz sampling frequency

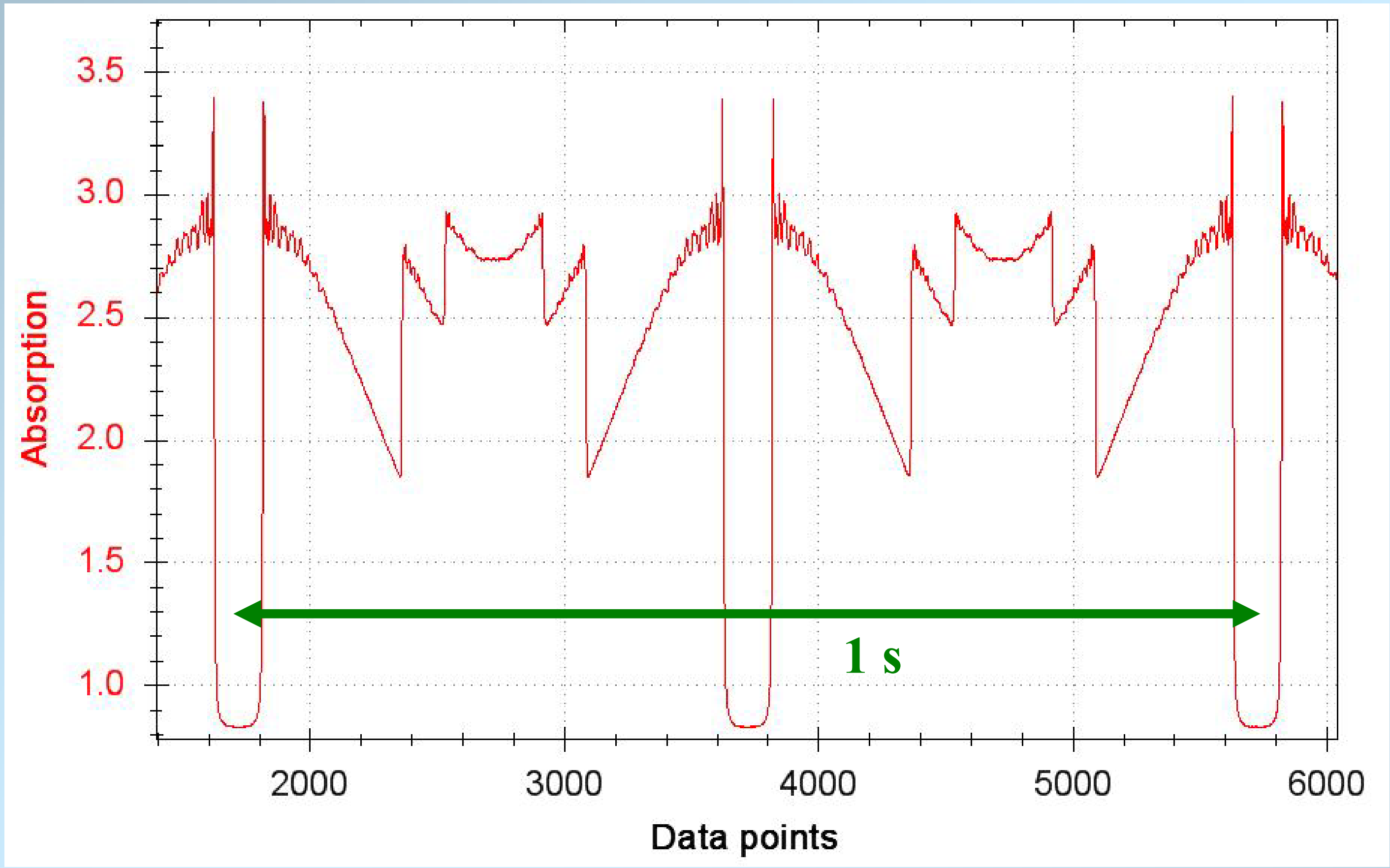
QEXAFS at the SLS: Experiment



Data collection:

Up to 500 kHz, 16 bit ADCs

QEXAFS at the SLS



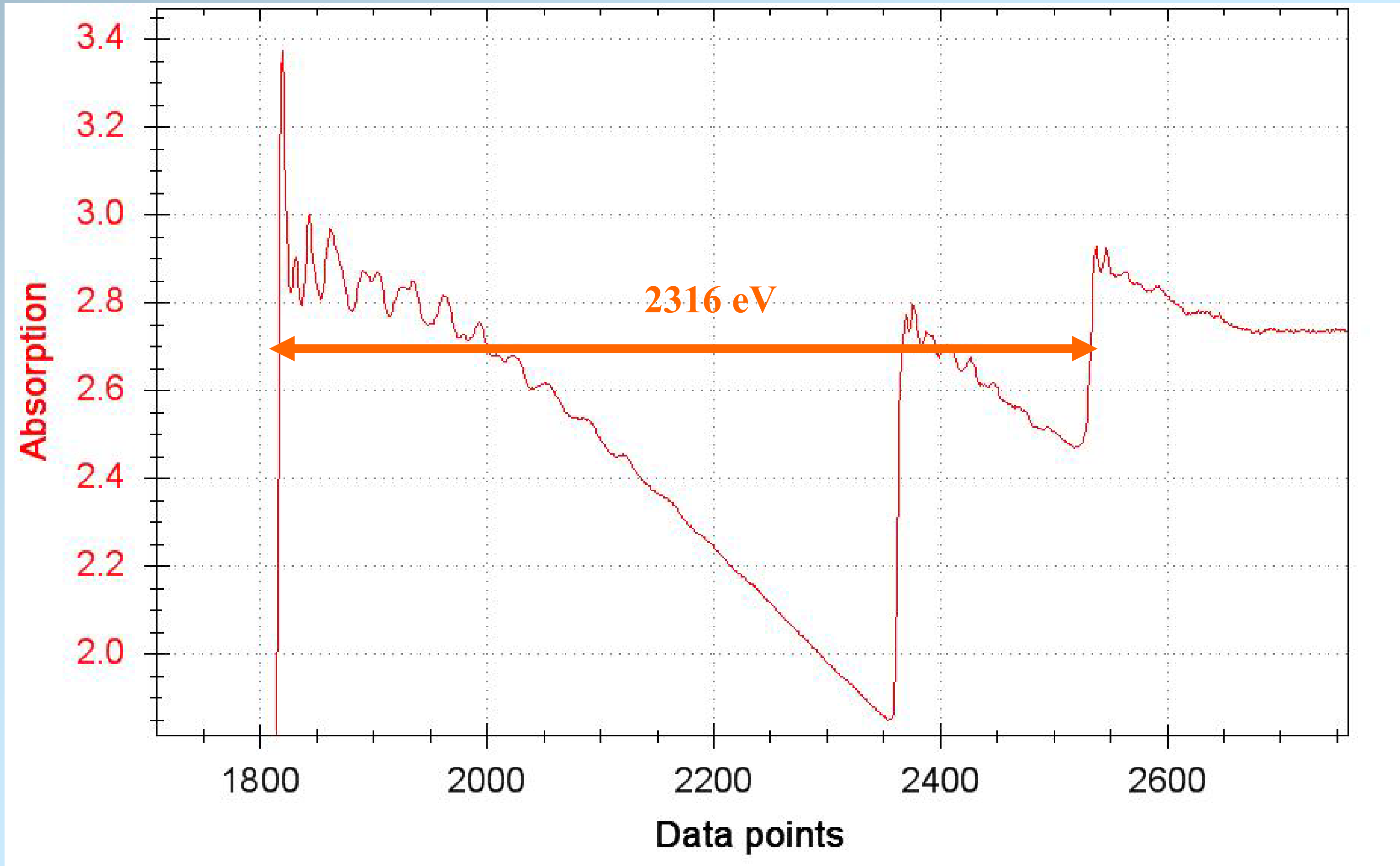
Pt L-edges, 2 Hz, 4 kHz sampling rate

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°
⇒ ΔE = 2573 eV for Si(111)

QEXAFS at the SLS

ΔE ≈ 2570 eV

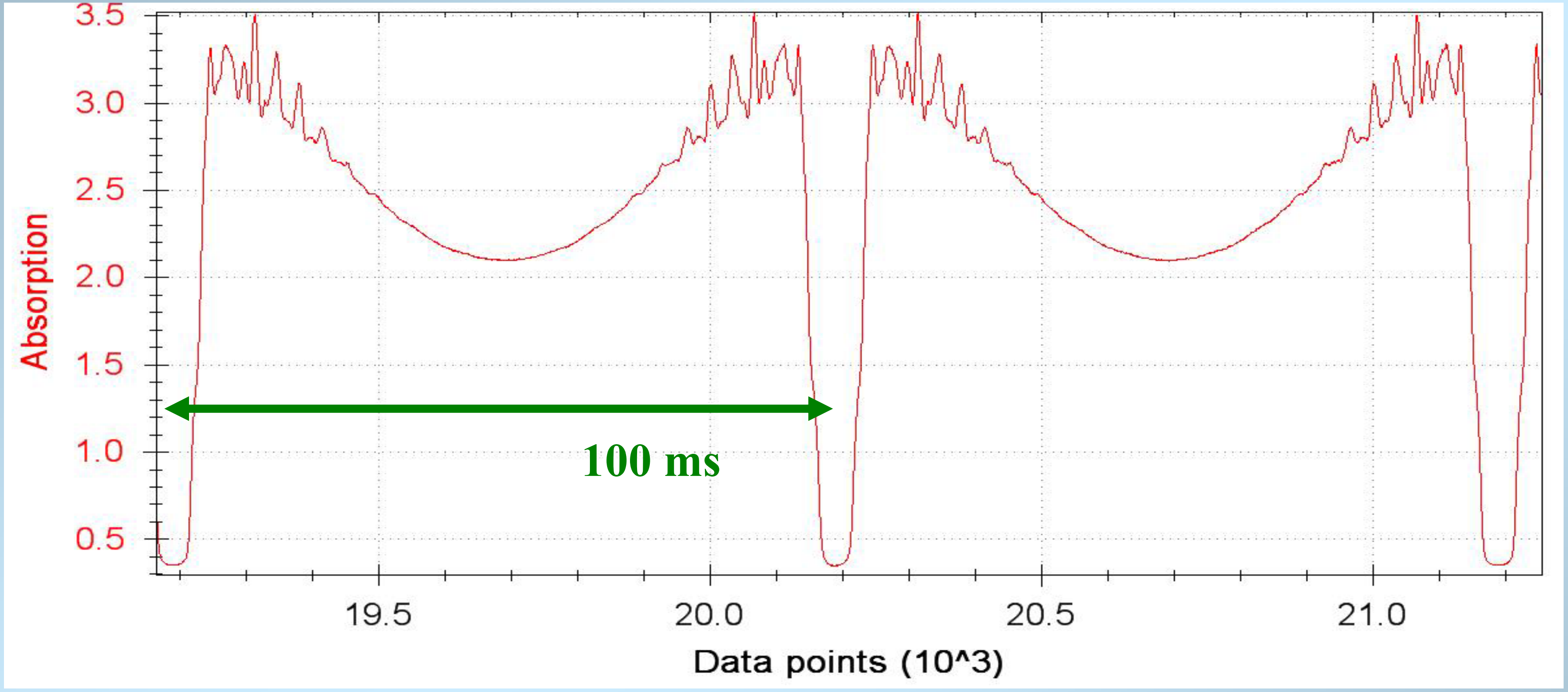


Pt L-edges, 2 Hz, 4 kHz sampling rate

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

QEXAFS at the SLS

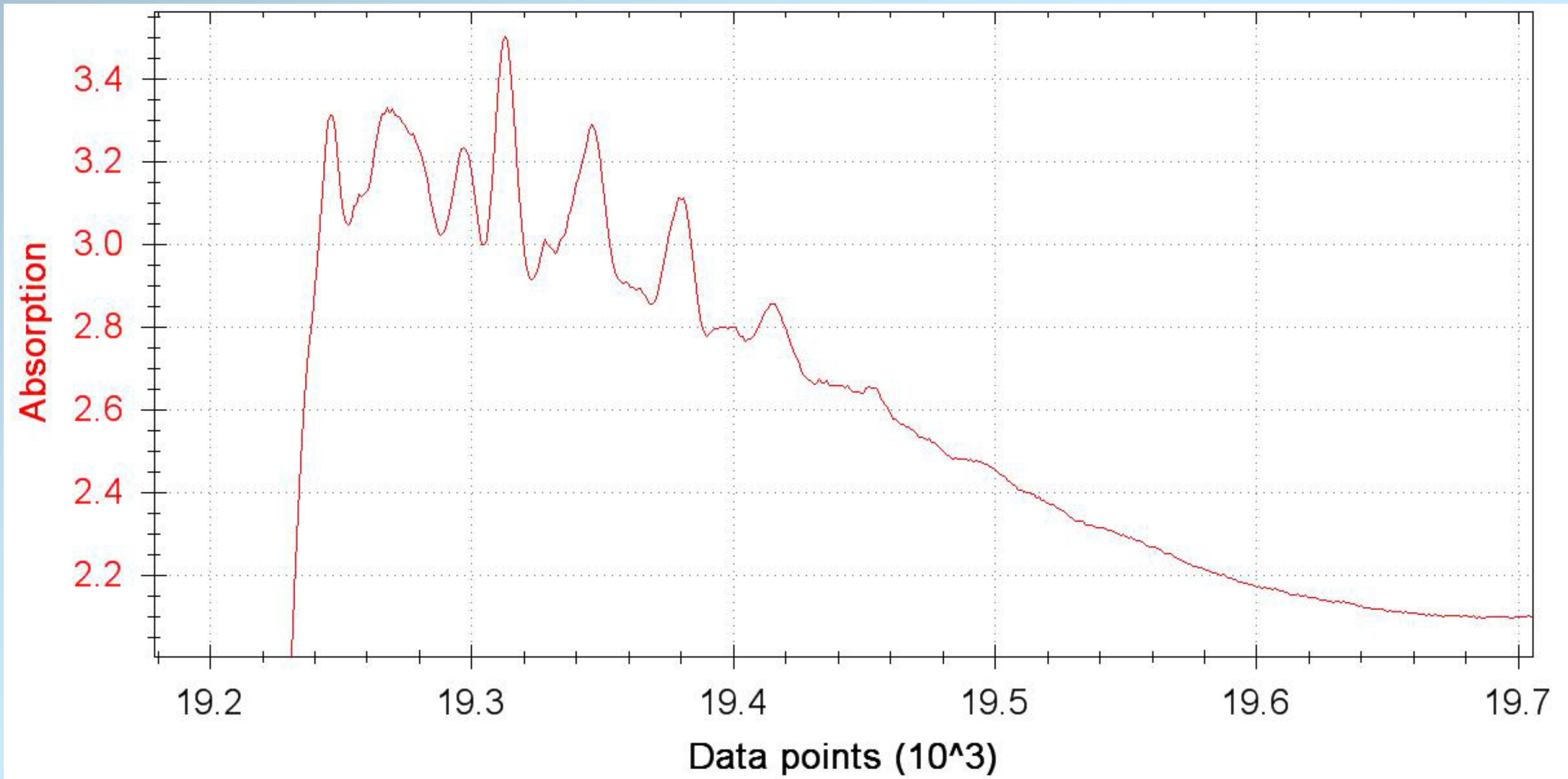
ΔE ≈ 870 eV



Fe K-edge in 50 ms

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

QEXAFS at the SLS

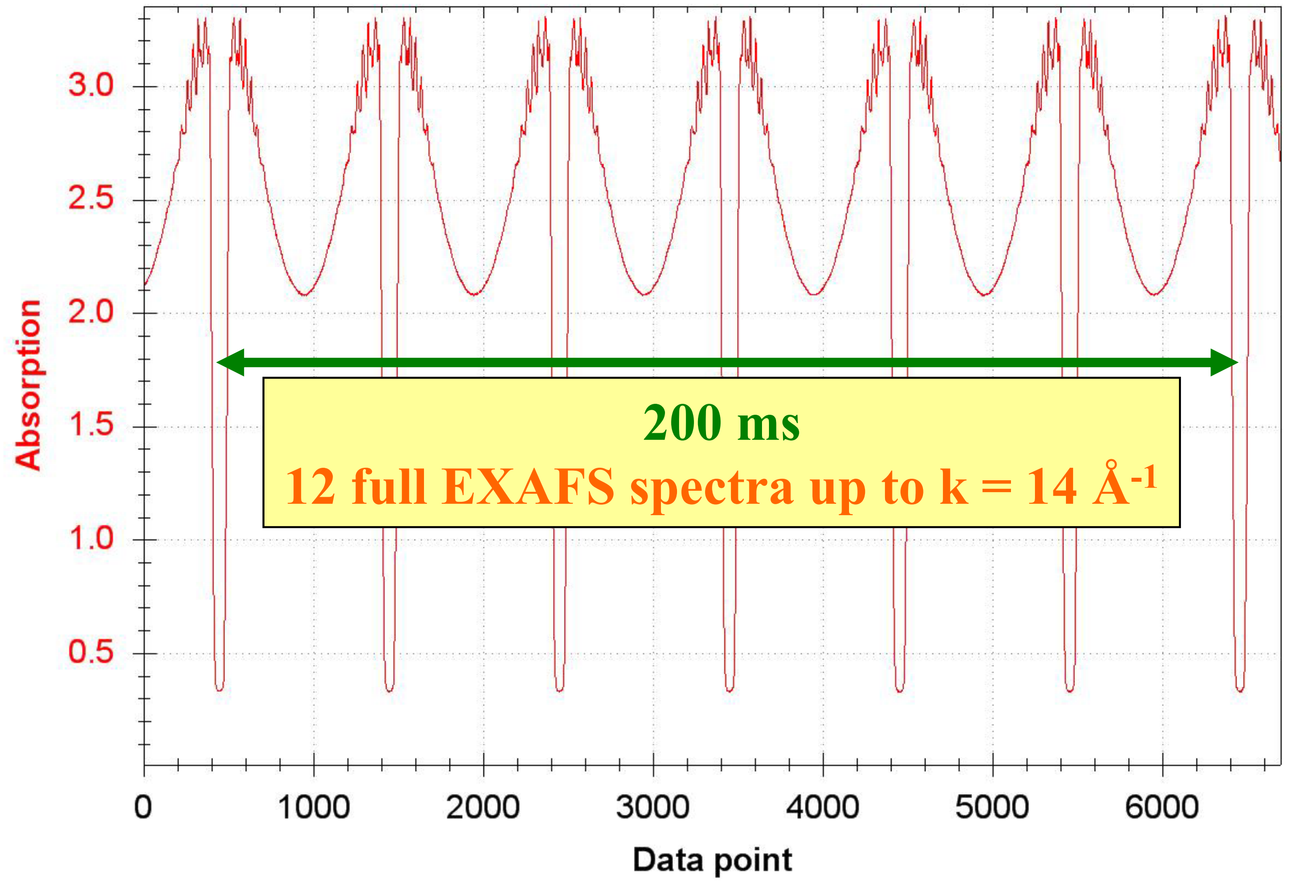


Fe K-edge in 50 ms

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

Speeding up: 30 Hz ⇒ 60 spectra/s!

ΔE ≈ 870 eV

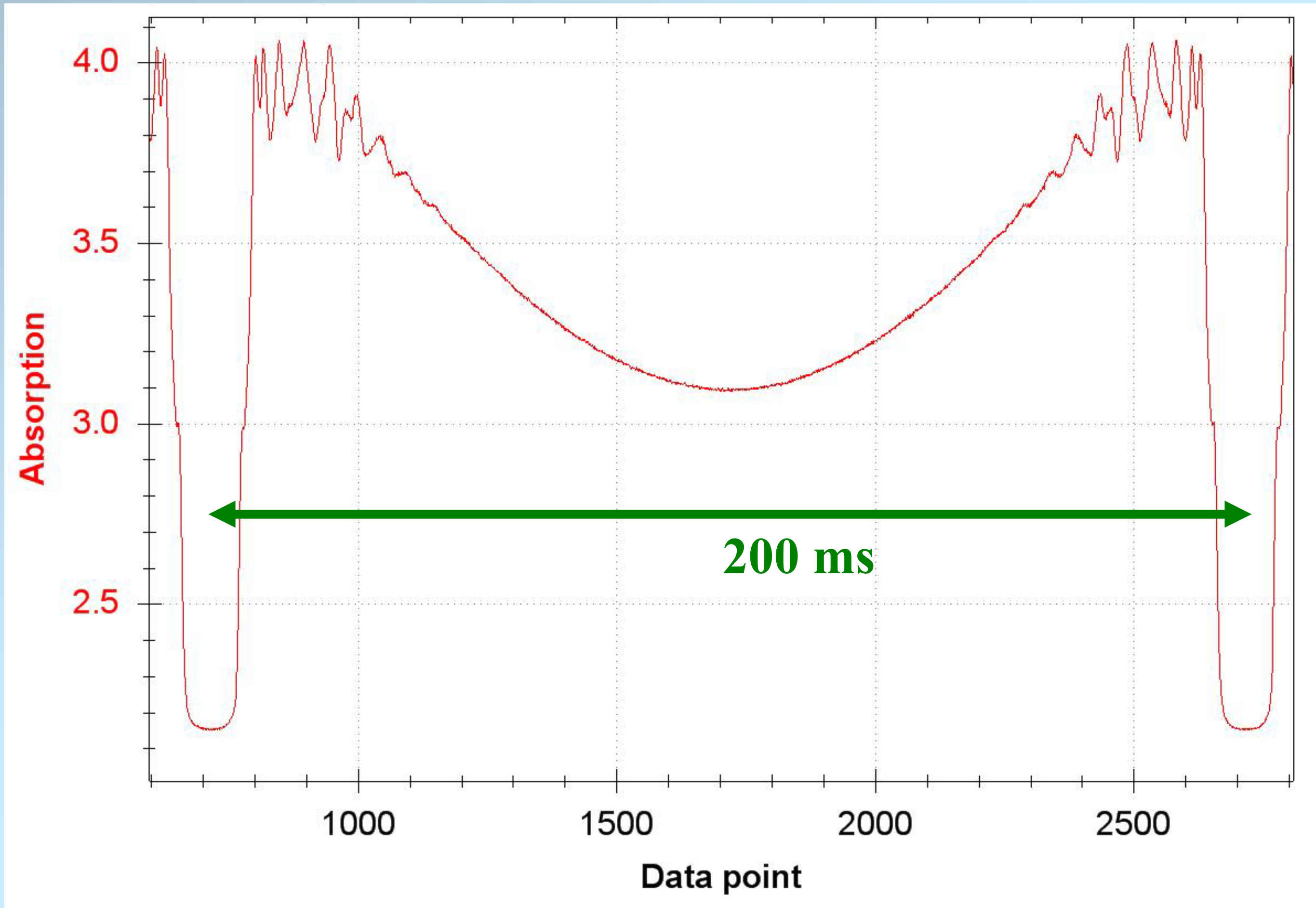


Fe K-edge in 16.6 ms

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

QEXAFS at the SLS

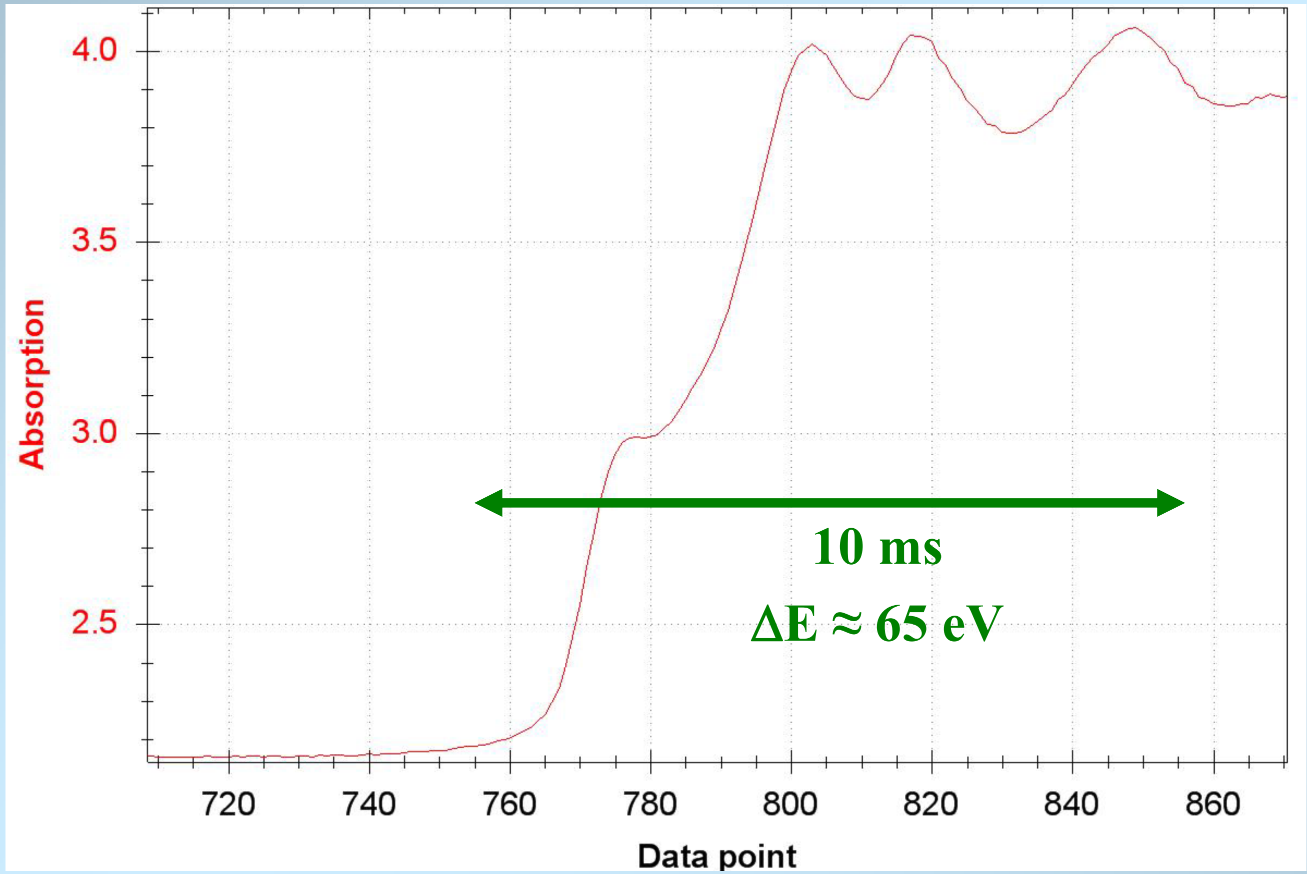
$\Delta E \approx 1460$ eV



Cu K-edge in 100 ms

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

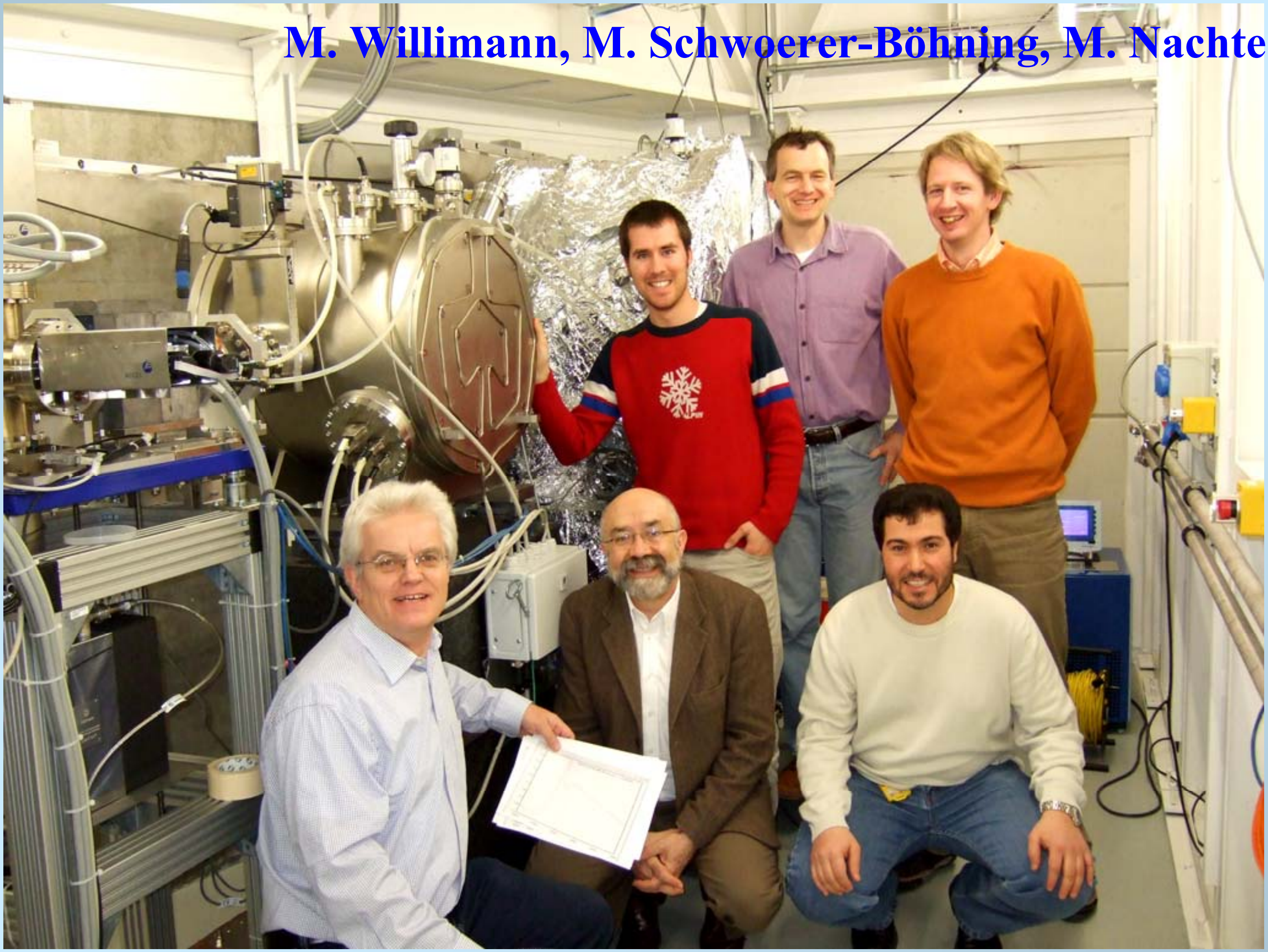
QEXAFS at the SLS



Part of Cu K-edge in 100 ms

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

QEXAFS at the SLS



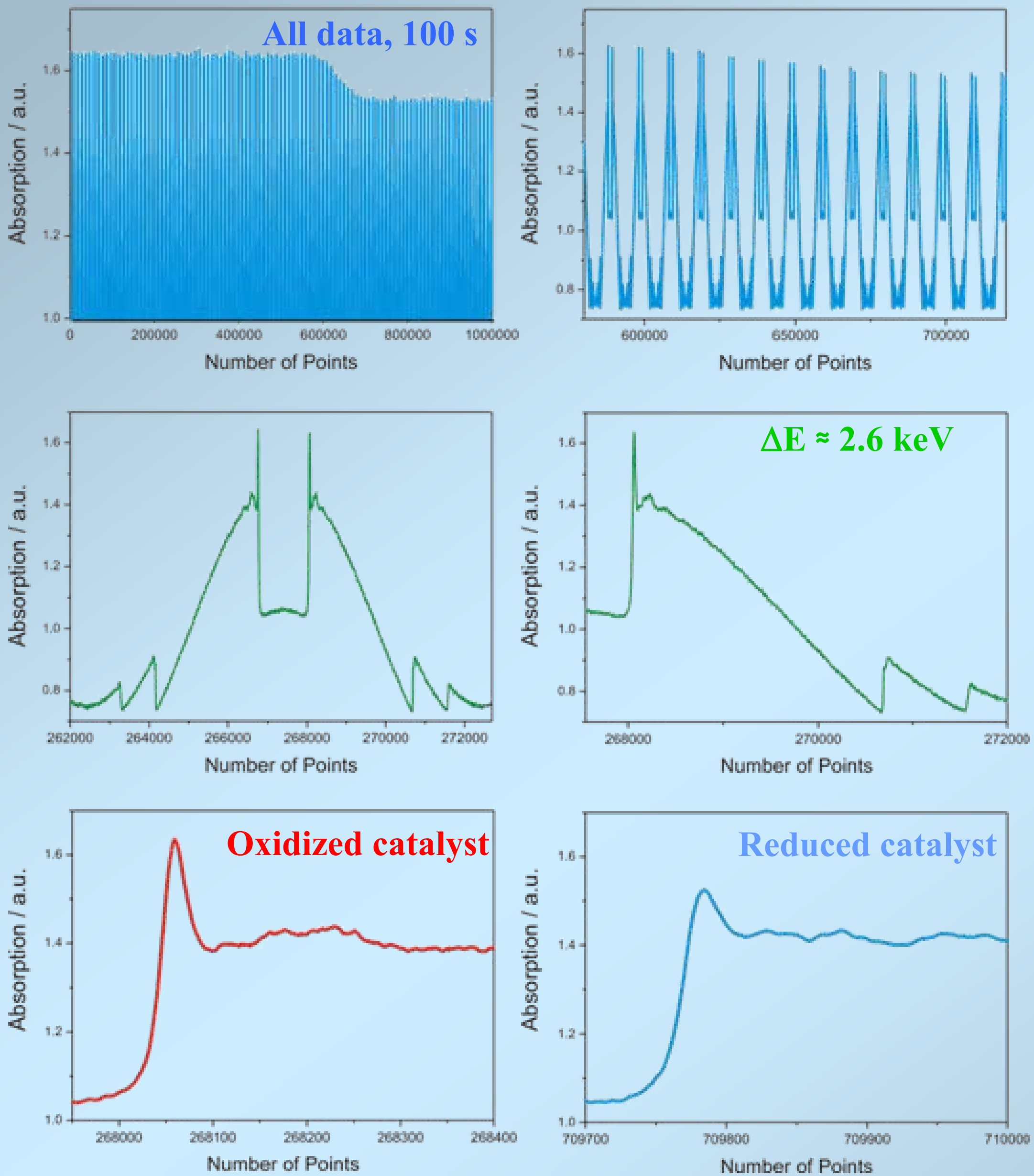
M. Willimann, M. Schwoerer-Böhning, M. Nachtegaal

R. Frahm, R. Abela, M. Harfouche,

At the QEXAFS monochromator in the Super-XAS beamline

(see Synchrotron Radiation News May/June 2008)

Reduction of a Pt-Rh/Al_2O_3 catalyst



Pt L-edges

1 Hz oscillation frequency

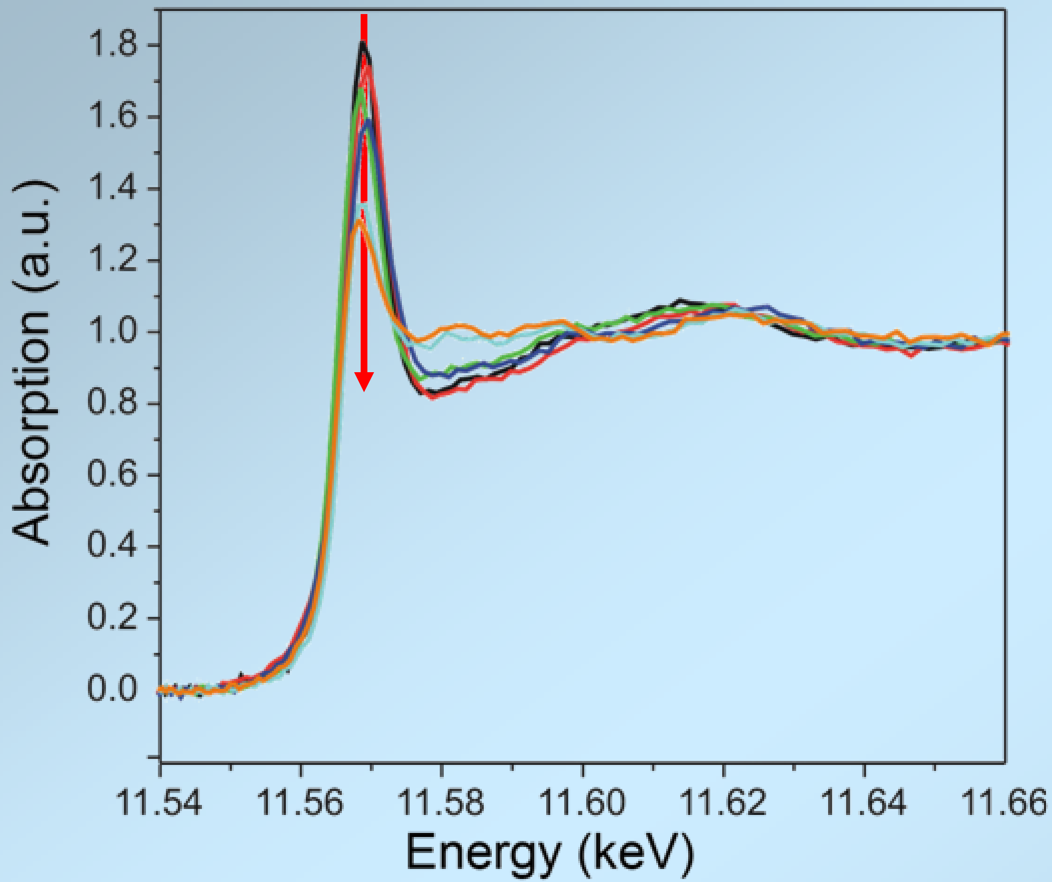
⇒ 2 spectra/s

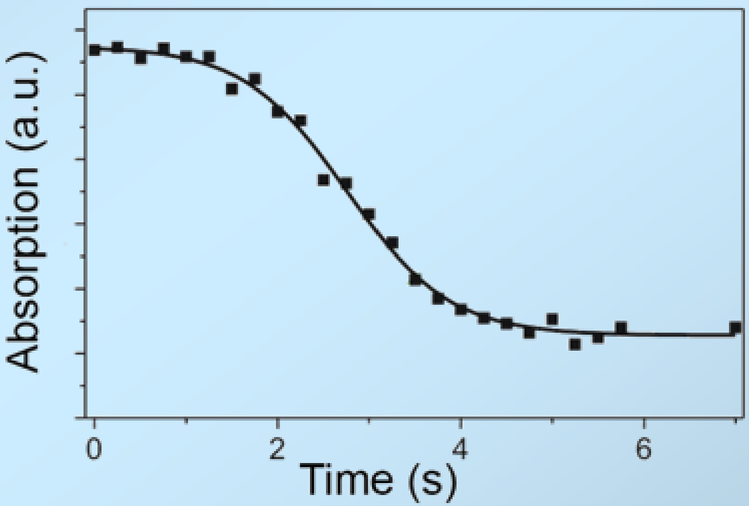
5% Pt -5% Rh / Al_2O_3 catalyst in 6% CH_4 / 3% O_2 / He atmosphere between 321 and 331° C sample temperature.

Data collected at the SLS.

Collaboration with J.-D. Grunwaldt (TU Denmark, Lyngby)

Reduction of a Pt-Rh/Al_2O_3 catalyst





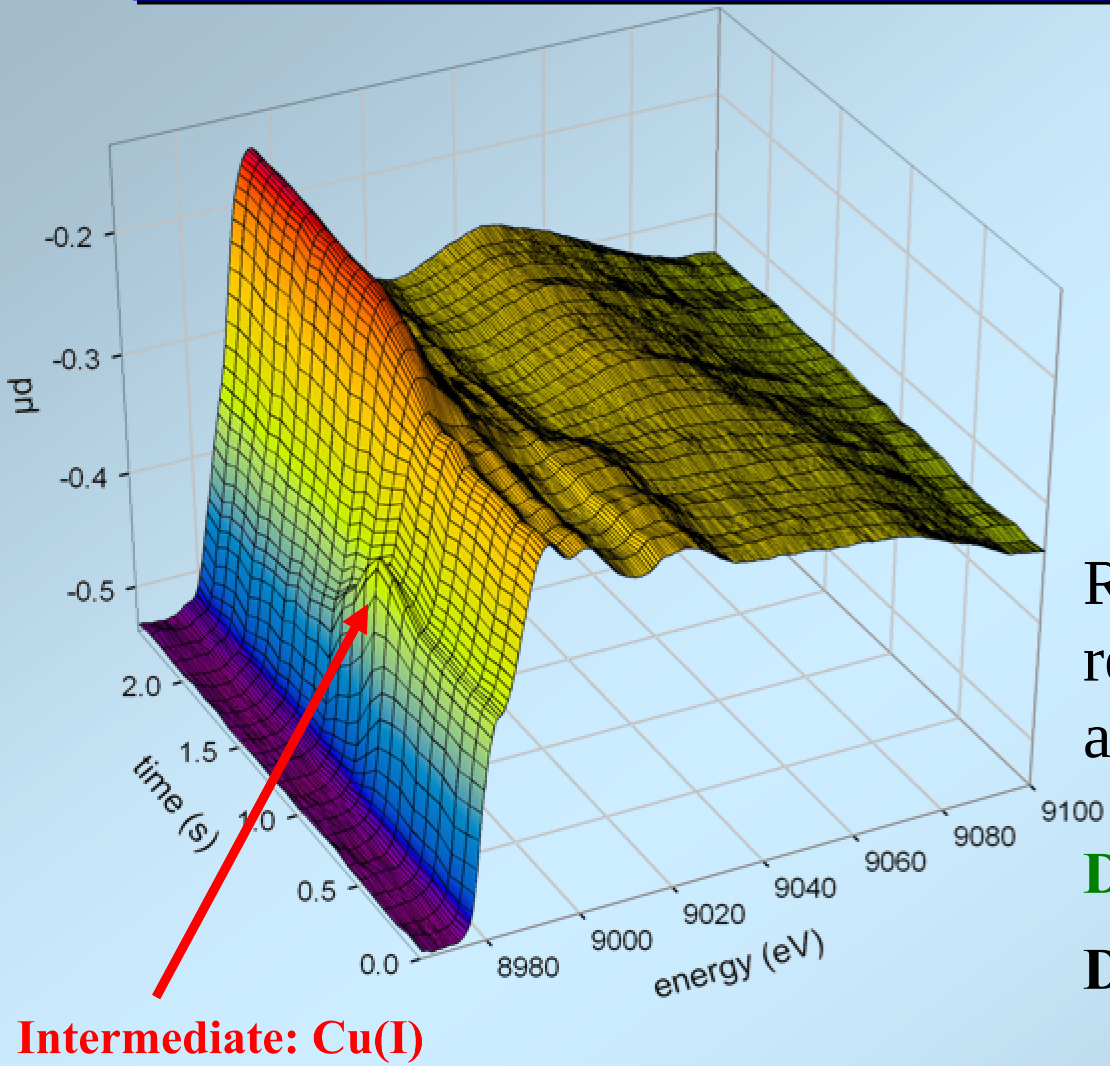
Pt L_3-edge

2 Hz oscillation frequency ⇒ 4 spectra/s

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

Collaboration with J.-D. Grunwaldt (TU Denmark, Lyngby)

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

Data collected at the SLS.

Collaboration with J.-D. Grunwaldt (TU Denmark, Lyngby)

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…

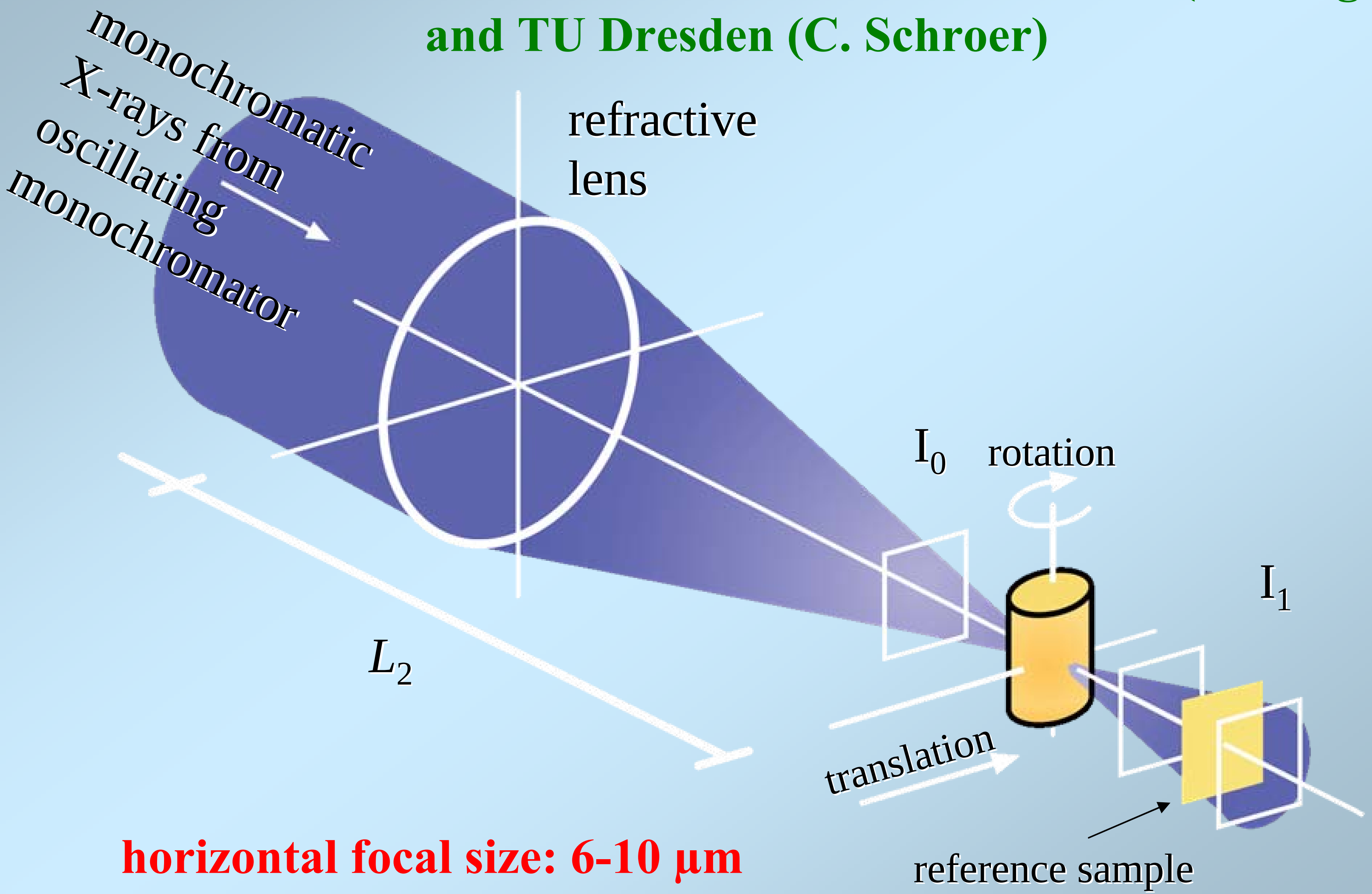
Experiments at the ESRF (BM) and the **APS (tapered undulator)**

Focussing 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 focal size: 6-10 µm

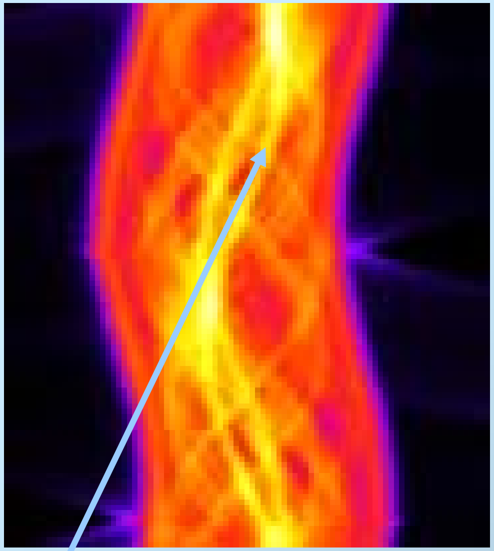
Data measured at the APS

Acquisition of tomographic data set:

- 102 projections
- 91 points per projection

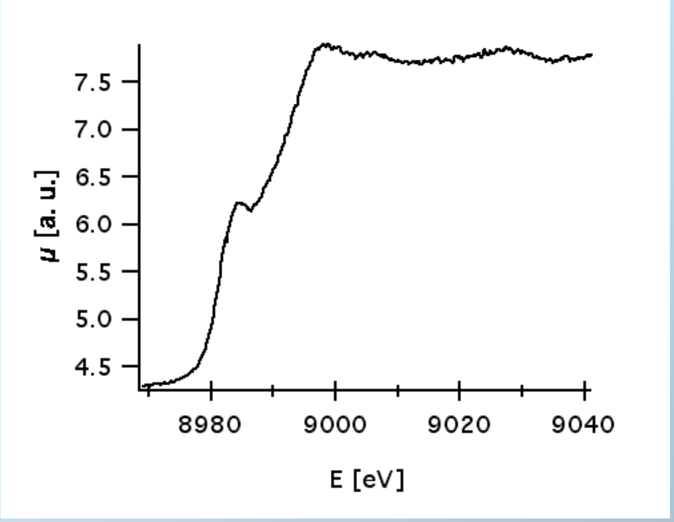
At each position in the scan:

- acquire 10 spectra in 1 second
- sampling rate: 100 kHz

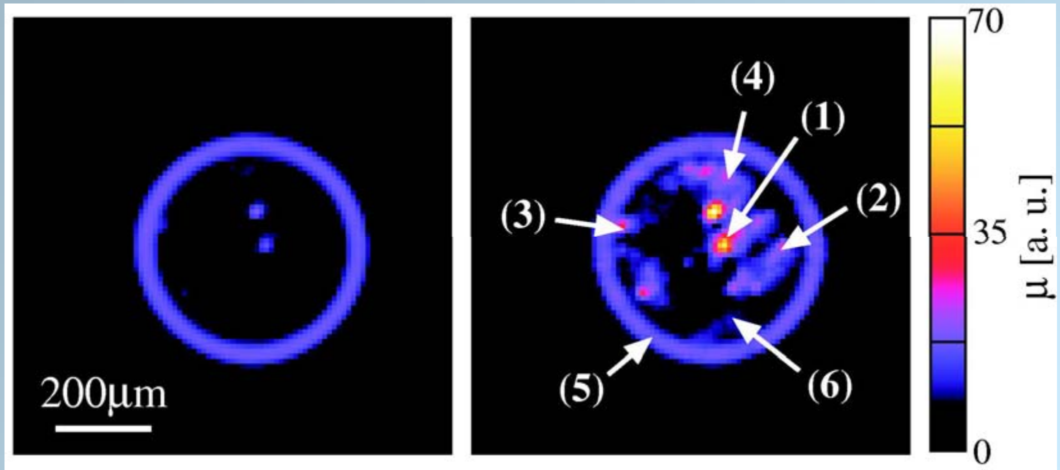


over 90.000 spectra
with 10^4 points each
> 7 GByte of raw data

Near edge spectrum:



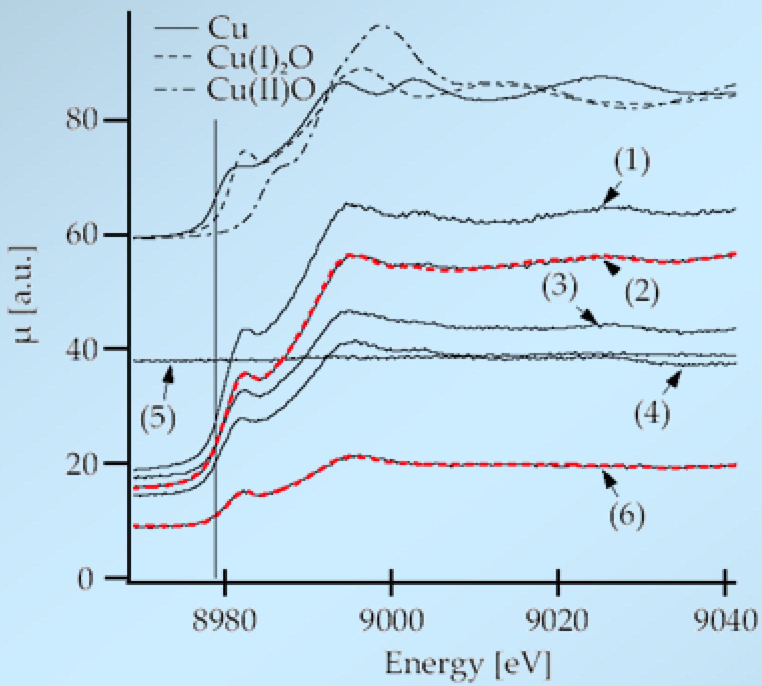
Sample:
CuO/ZnO catalyst in glass capillary



Cu/ZnO catalyst

Measurements at the APS

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

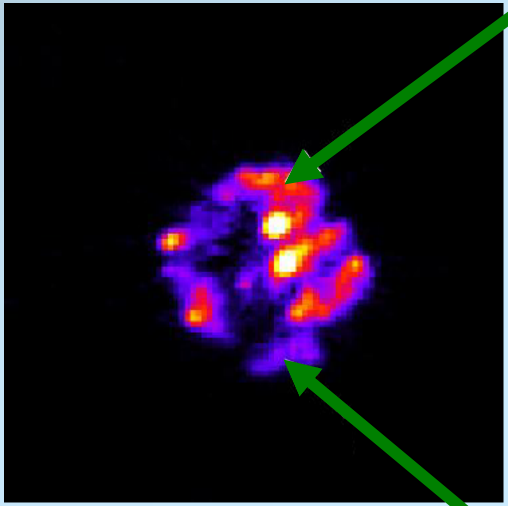
Reconstruction at different positions after several oxidation/reduction cycles:
What happens to the catalyst during catalysis?

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!**

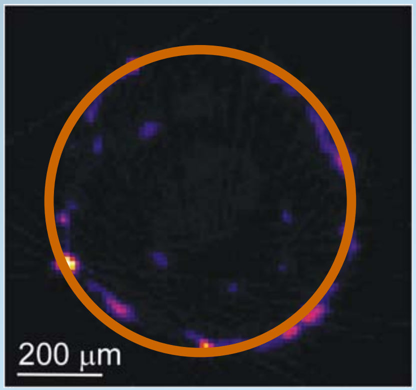
Tomato root grown on a polluted (Zn, Pb) soil

(Measurements at the APS)

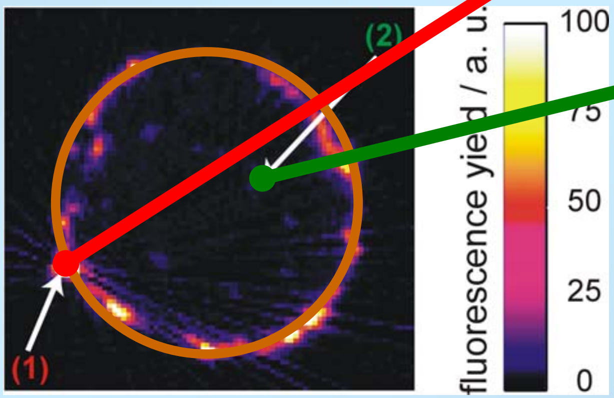
- Tomato root (diameter ~ 700µm)
- Low metal-ion concentration (<100 ppm):

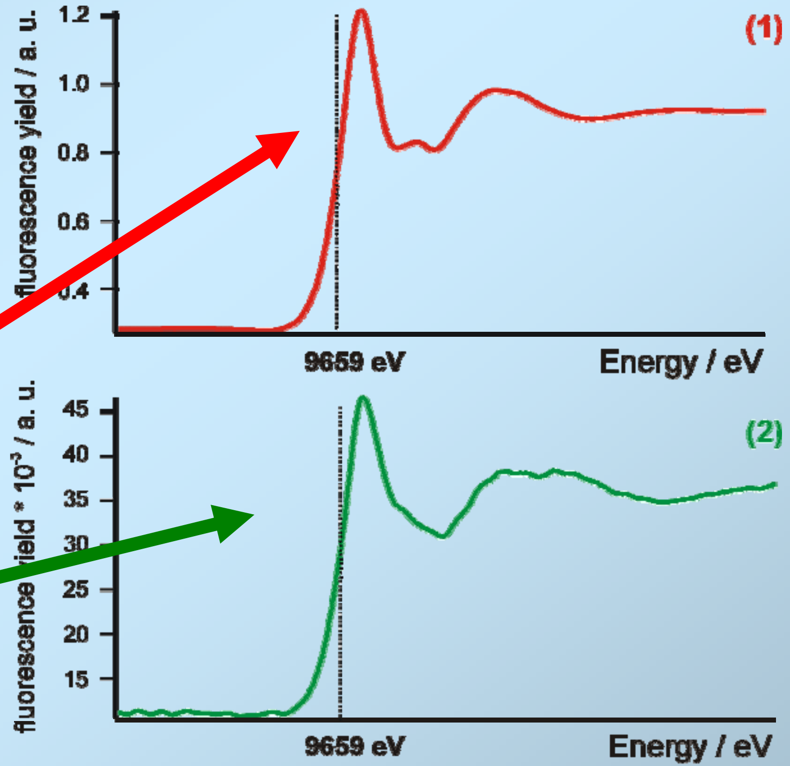
⇒ **Fluorescence tomography**, here: **Zn K-edge**

Below Zn K-edge



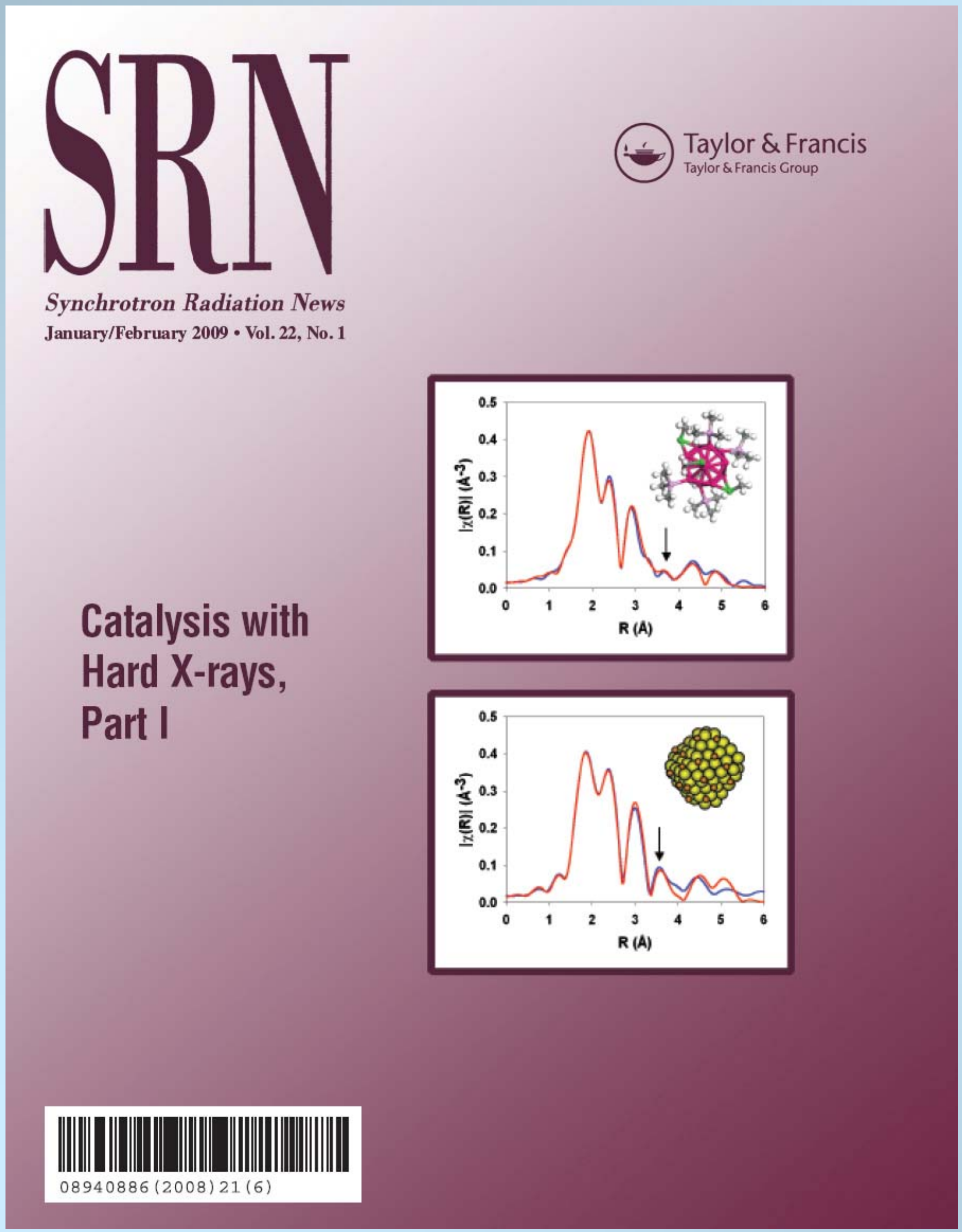
Above Zn K-edge





- **Significant differences**
- **Zn concentrated in root bark**

QEXAFS: Perspectives



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

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