# Review of QEXAFS and XRD capabilities

## Quick XAFS at X18A-X18B (NSLS) and its few applications.

Syed Khalid
Photon Sciences-Brookhaven National Laboratory

**WORKSHOP**
**In-situ Methods of X-ray Absorption Spectroscopy**

October 24, 2013

Brookhaven National Laboratory is operated by Brookhaven Science Associates for the US Department of Energy.

# ACKNOWLEDGEMENT


| | |
|---|---|
| Mechanical System: | Anthony Lenhard<br>Shu Cheung<br>Rick Greene |
| Detectors: | Tony Kuczewski<br>Dennis Poshka<br>Barrett Clay |
| Computer-stuff: | Zhijian Yin<br>Kate Feng Berman<br>Ivan So |
| Discussions: | Ned<br>Pete Siddons<br>Jon Hanson (BNL-Chemistry)<br>Simon Bare (UOP) |
| Contributions: | Ashtosh Ganjoo<br>Donald Sparks<br>Won-Sub Yoon<br>WOLOFGANG CALIEBE |

US Department of Energy Contract #DE-AC02-98CH10886

- Why we need Q-EXAFS?
- How the Hardware Works?
- How the Software Works?
- Applications: Example
    1. Catalysis
    2. Chalcogenites
    3. Batteries
    4. Environment
    5. ??

A Frenkel, S Khalid, J Hanson, M Nachtegaal, QEXAFS in catalysis research: Principles,Data Analysis and Applications, *In-Situ characterization of hetrogenious catalysis*, p. 23-48, John Wiley and Sons, Hoboken (2013).

# Time-scale

| | |
|---|---|
| months: | changes in nature, environmental sciences |
| days: | aging-processes of materials (extreme conditions) |
| hours: | radiation damage in organic systems, charging-discharging of batteries |
| minutes: | temperature-dependent chemical reactions (TPS, typical 5K/min) |
| seconds: | temperature-dependent chemical reactions, cooling-rates of -20K/s |
| ms: | chemical reactor-simulations, pulsed gas-supply, laser pump-probe |
| ps: | ligand-change |
| fs: | life-time of K core-holes |
| as: | electron-transfer |

month-minute scale feasible with conventional methods

ps, fs, as: FEL (and other, better sources or energy-domain)

s, ms: dispersive spectroscopy, QEXAFS

# Previous Experimental/Efforts

Scanning monochromators

1. Move monochromator as fast as possible, measure intensity as short a necessary
2. Mount monochromator directly on motor-axis
3. Piezo-QEXAFS (Ronald Frahm)
4. Cam (Ronald Frahm)

Problem: fast, reproducible rotation of monochromator
detectors: fast A/D-converter

Dispersive polychromator

cylindrically bent crystal, scattering plane in the (horizontal) ring-plane, polychromator disperses spectrum on linear detector

Problem: No $I_o$-measurement, no dilute samples
measure complete spectrum at the *same* time

Source: usually bending magnet (APS)
wiggler (Daresbury)
ESRF: tapered Undulator

Polychromator well understood
decent energy resolution, stable, glitches

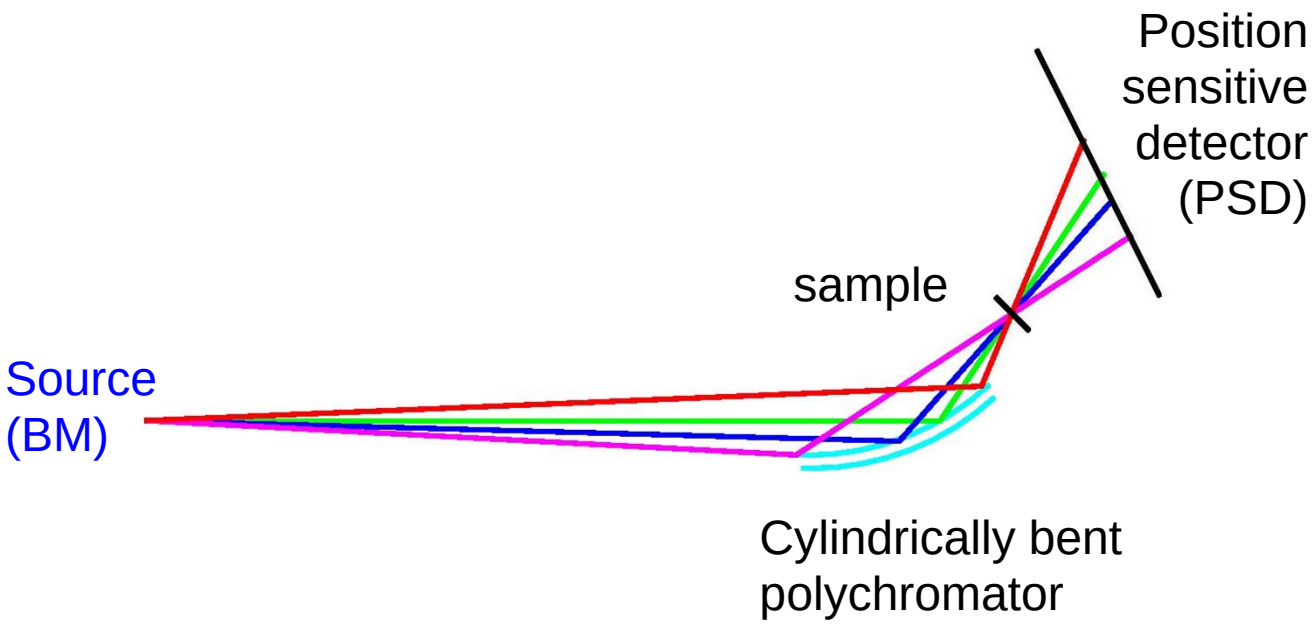
Group at ALS: Grating as real dispersive element

Detector: High counting rate, high spacial resolution, fast

Daresbury: Special detector: XStrip (Si-photo-diode array)[1]
ESRF: CCD in special operation mode

[1]Headspith et al., NIM A **512** 239-244 (2003)

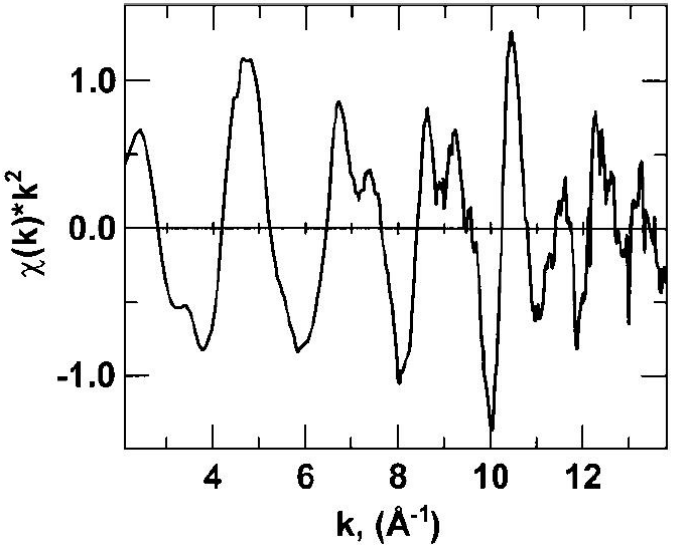
# Dispersive Polychromator



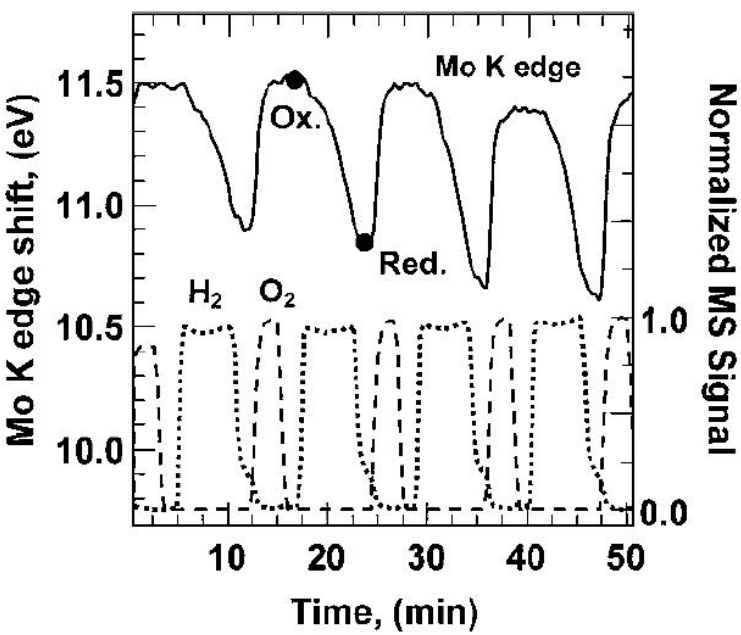

Sample not necessarily in focus
measure complete spectrum at the same time
only concentrated samples
time-resolution depends on detector and flux

# Experimental Results by Thorsten Ressler

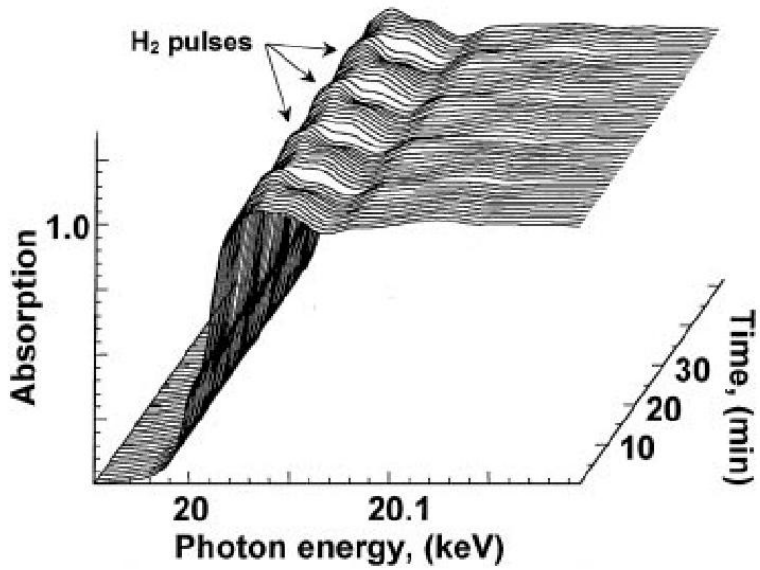
## Reduction/Oxidation of $MoO_{3-x}$ (ESRF)




Experimental $\chi(k)$ of $MoO_2$ measured in the energy dispersive mode in 30s, too many glitches at higher k

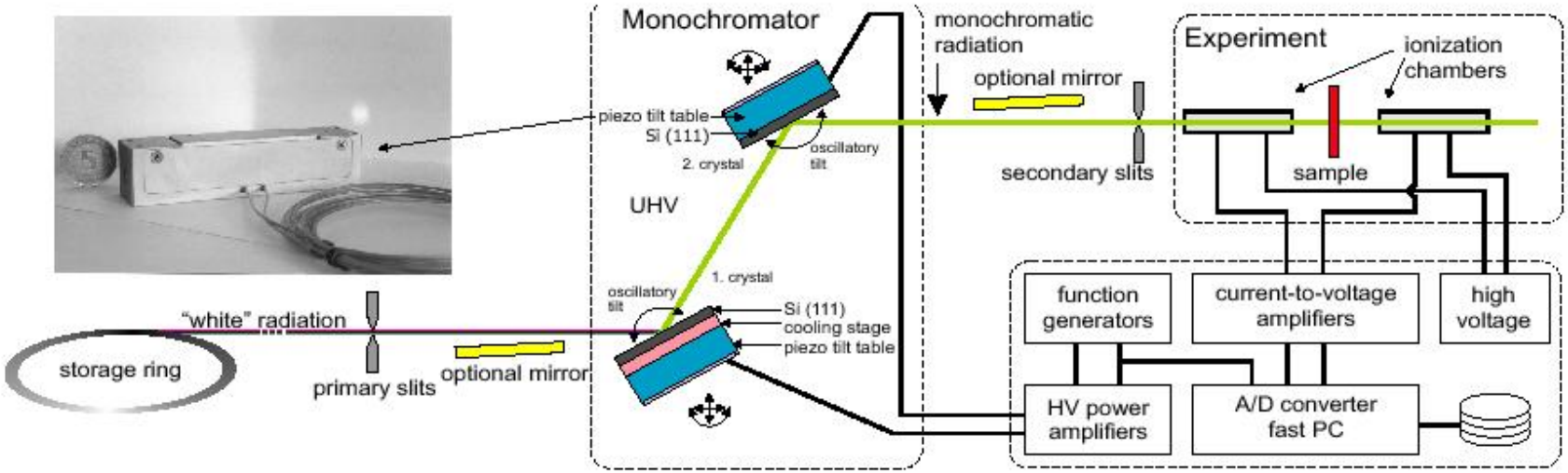



Flow $H_2$ and $O_2$ through sample, measure XANES and gas-composition




T. Ressler et al., J. Catal. **191** 75-85 (2001)

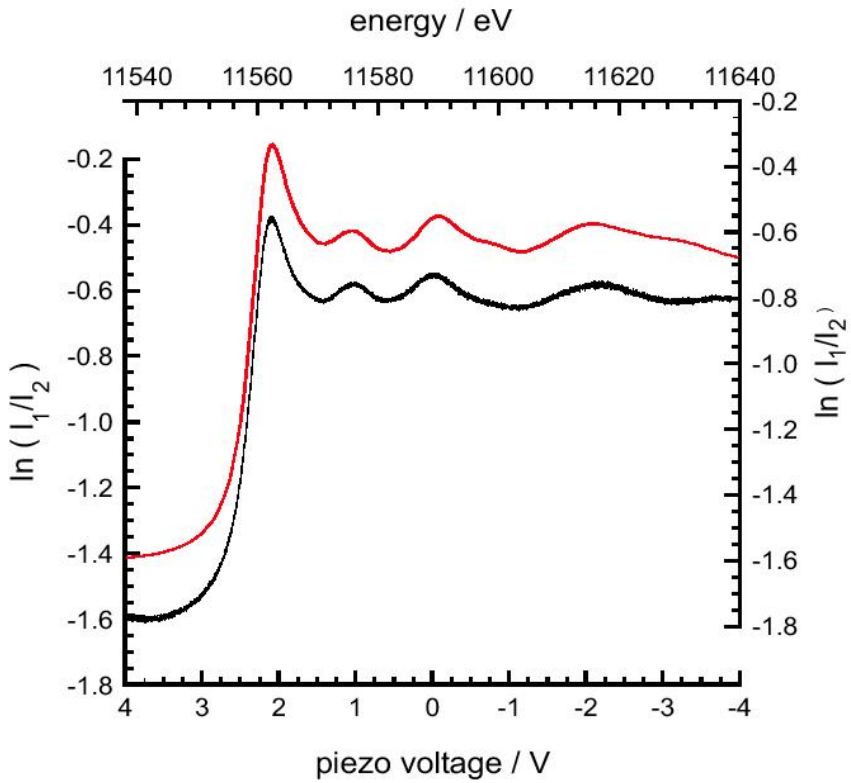
# Fast-scanning Monochromator – Piezo-QEXAFS
# Ronald Frahm's Group (Hasylab, DELTA)



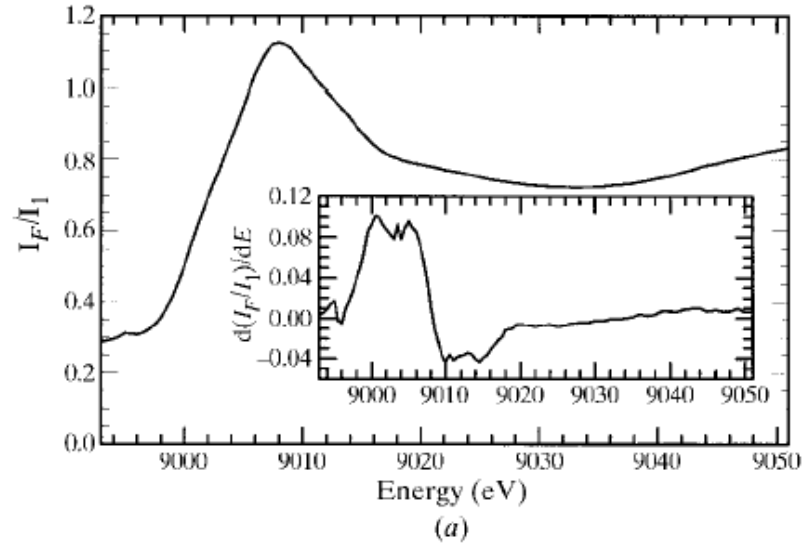

Piezo-driven tilt-tables for two separate crystals
tilt-tables with low hysteresis, no separate measurement of energy
HUGE beam-offset (150mm) really bad

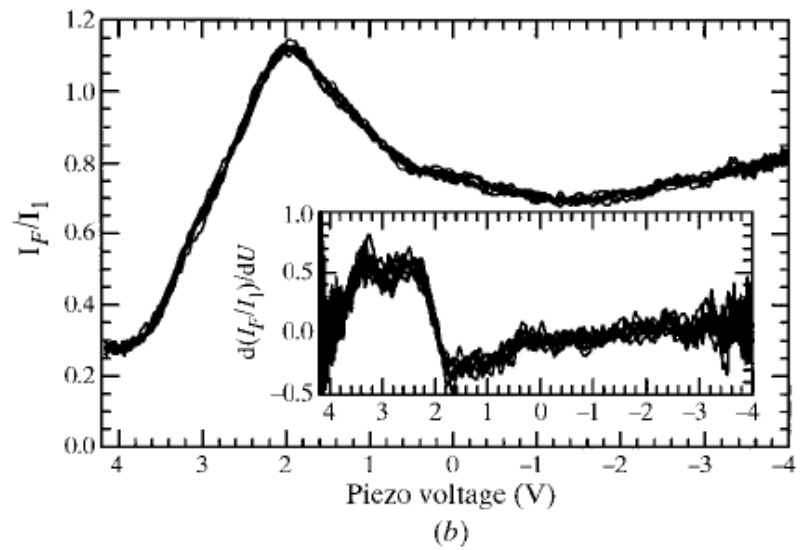
Lützenkirchen-Hecht, Grundmann, Frahm, J. Synchr. Rad. **8** 6-9 (2001)
Richwin, Zepper, Lützenkirchen-Hecht, Frahm, J. Synchr. Rad. **8** 254-256 (2001)

# Experimental Results




Pt $L_{III}$-edge: black 20 scans measured in one direction, 20Hz frequency on piezo (40scans/s)
red: conventional step-scan measurement

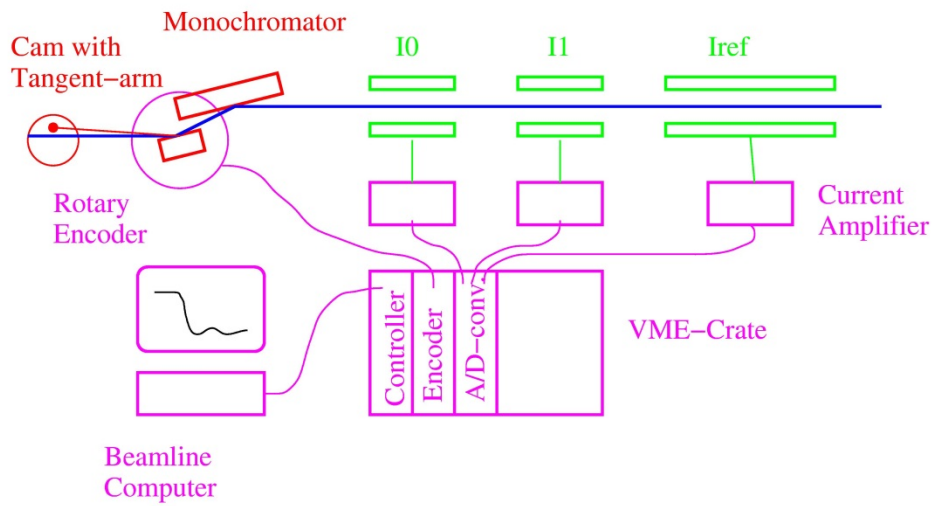


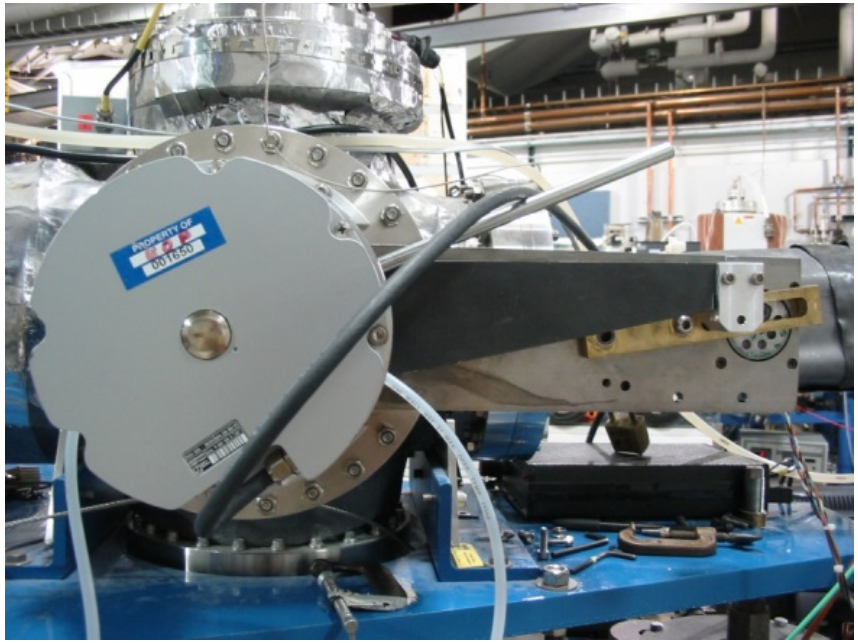




XANES of 10mmol/l $CuSO_4$-solution, top conventional step-scan measurement, bottom 10 'up' spectra in QEXAFS-mode (9.1Hz)
(inset: first derivative)

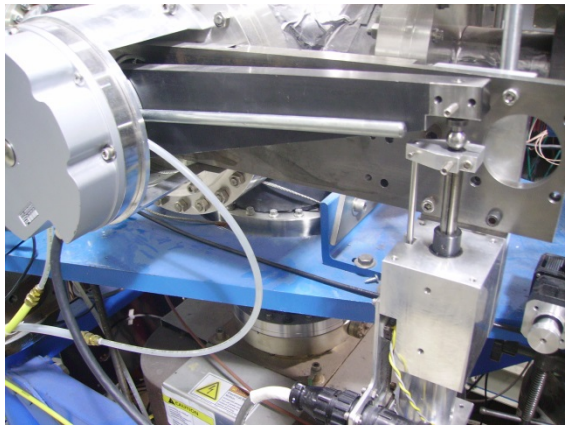
# How is it done?

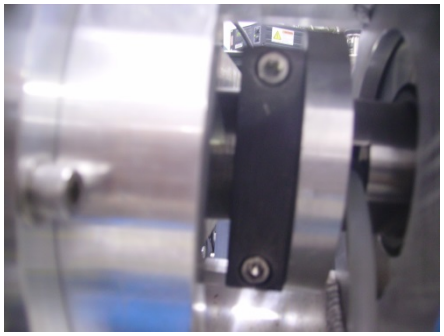
- Hardware at X18B
- Bragg angle changed continuously
  - Micro-stepping motor coupled to the monochromator
- Fast data acquisition
  - Data collected on the fly at 60K points per minute.
  - Achieved via VME technology
    - Heidenhain encoder
    - VME 32-Channel 12 bit Analogue to Digital converter (ADC)

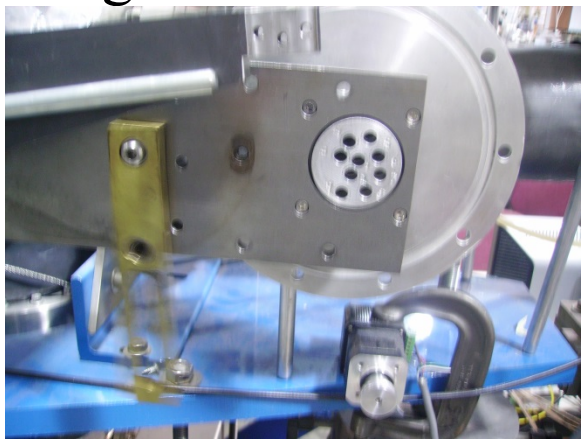


# Modification to the old X18B-QEXAFS design:







## Changes from the old version:

1. 60,000 data points / 15 seconds
2. Independent of VME crate
3. IK220 is the Linux computer readout for Heidenhein encoder
4. ADC is now 16 bit, also part of Linux computer.

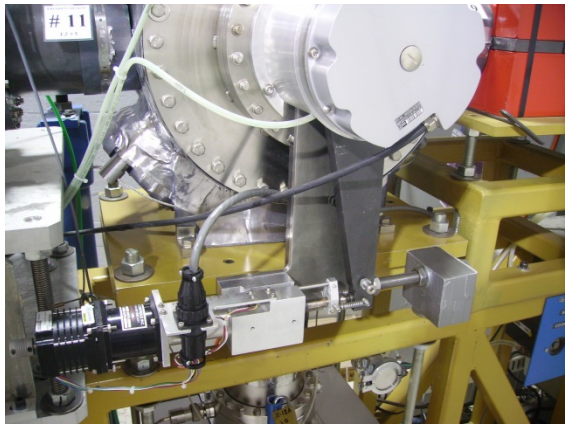
Reference:

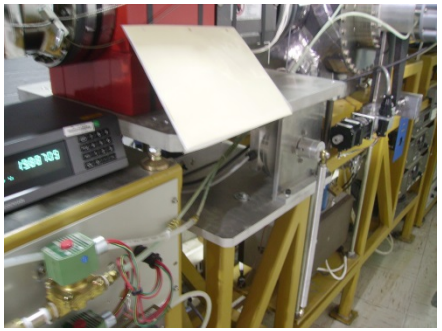

W Caliebe, I So, A Lenhard, D Siddons, Cam-Driven Monochromator for QEXAFS, *Radiat. Phys. Chem.*, Vol 75, p. 1962-1965, sponsored by University of Melbourne (2006). [77676]

S Khalid, W Caliebe, P Siddons, I So, T Lenhard, J Hanson, Q Wang, N Hould, M Ginder-Vogel, A Ganjoo, QEXAFS Instrument with Milli-Second Time Scale, Optimized for in situ Applications, *Rev. Sci. Instrum.*, **81**(1), 015105 (2010). [91089]

I So, D Siddons, W Caliebe, S Khalid, Hard Real-time Quick EXAFS Data Acquisition with All Open Source Software on a Commodity Personal Computer, *Nucl. Instrum. Meth. A*, **582**, 190-192 (2007). [79366]

# Q-EXAFS at focused beamline X18A





All the computer software and hardware is just a duplicate of modified X18B design.

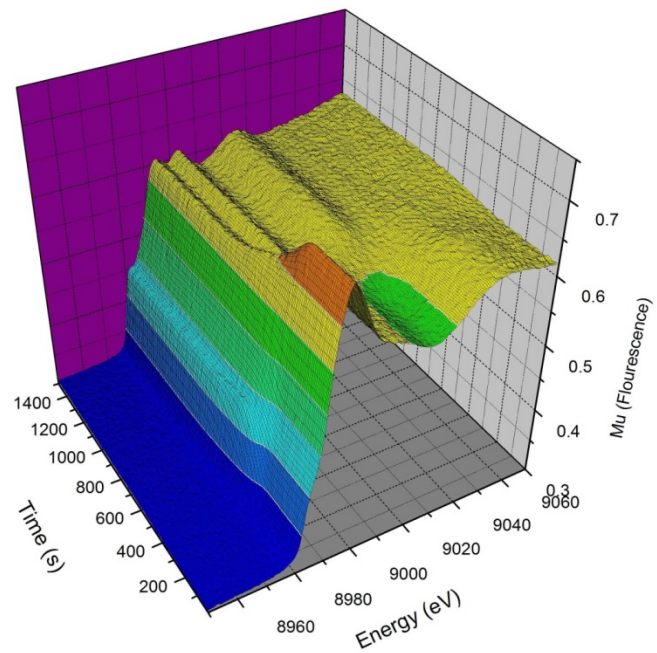
## Reference:


S Khalid, S Ehrlich, A Lenhard, B Clay, Hard X-rays QEXAFS Instrumentation with Scan Range 20 to 4000 eV, *Nucl. Instrum. Meth. A*, **649**, 64-66 (2011). [94598]

S Khalid, W Caliebe, P Siddons, I So, A Lenhard, J Hanson, Q Wang, A Frenkel, N Marinkovic, Q-EXAFS Instrumentation at beamline X18B, NSLS, BNL., Publicolor SNC prepared for 14th International Conference (2009).

# Results from in situ Cu studies

- XANES Spectra of Copper oxide phase transformation
  - Resolved at 15s
  - Flourescence
- Reduction under 5% H2
  - CuO + H2 ↔ Cu + H2O
- Oxidation under 40% O2
  - Cu + 1/2O2 ↔ CuO
- Data collected at different temperatures for kinetics study

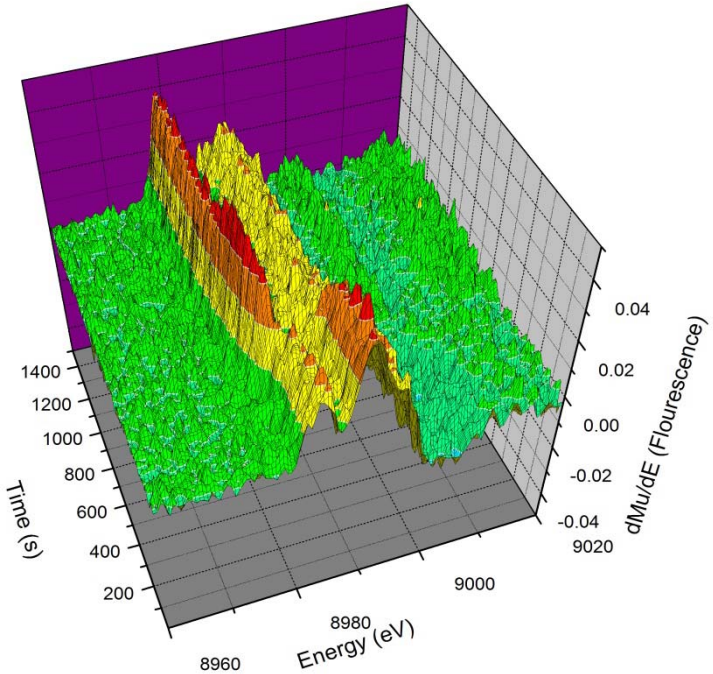



Data collected from CuO catalyst under flow of 5% H2 at 275K

# Kinetic Data Extraction

$$\left(\frac{\partial Mu(t,E)}{\partial E}\right)_t$$

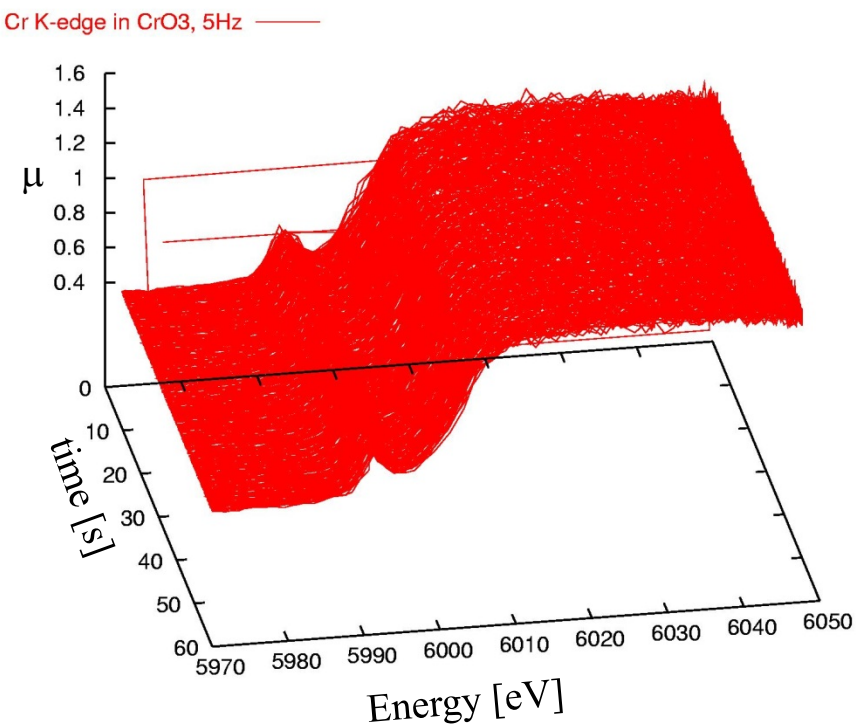
- First derivatives of absorption coefficient
  - Function of time and E
    - Assume time is constant over the course of one XANES spectra
  - Crop N' Chop uses numerical methods to determine derivatives
    - Smoothing Routine
  - Edge energy ($E_o$) often defined as max of derivative
- Crop N' Chop has functions that determine $E_o$

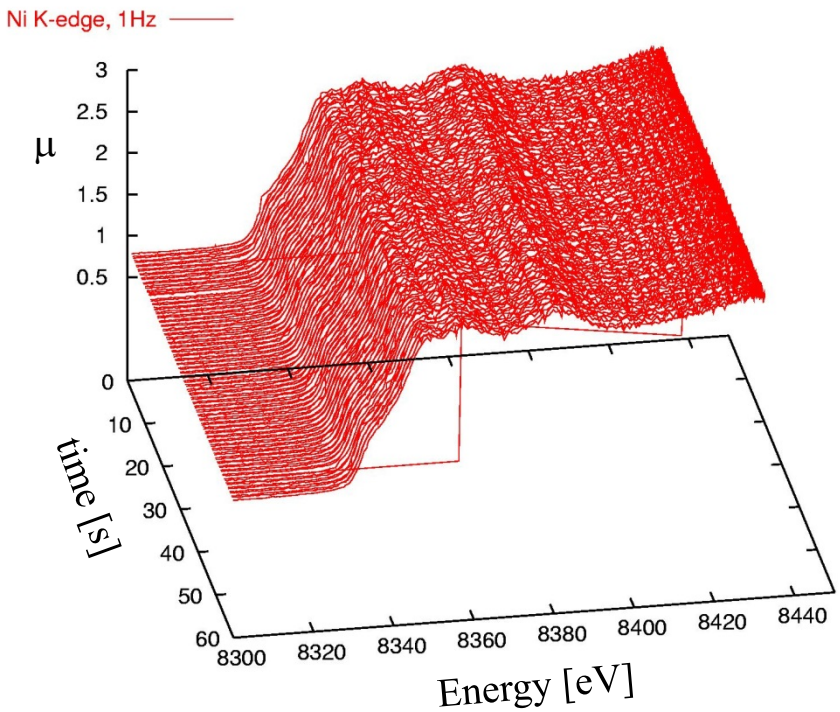



First derivative of Mu plotted over the course of a QXANES run. Cu(II) to Cu(O) transformation.

# Preliminary Results

Different speed and angle-range for standard reference samples (Ni, NiS, Cr, $Cr_2O_3$, $CrO_3$)

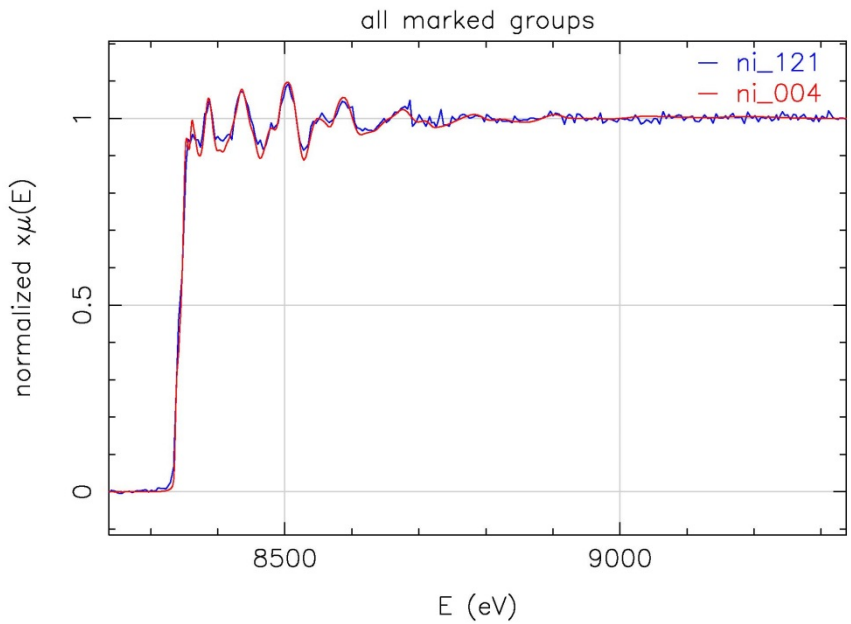


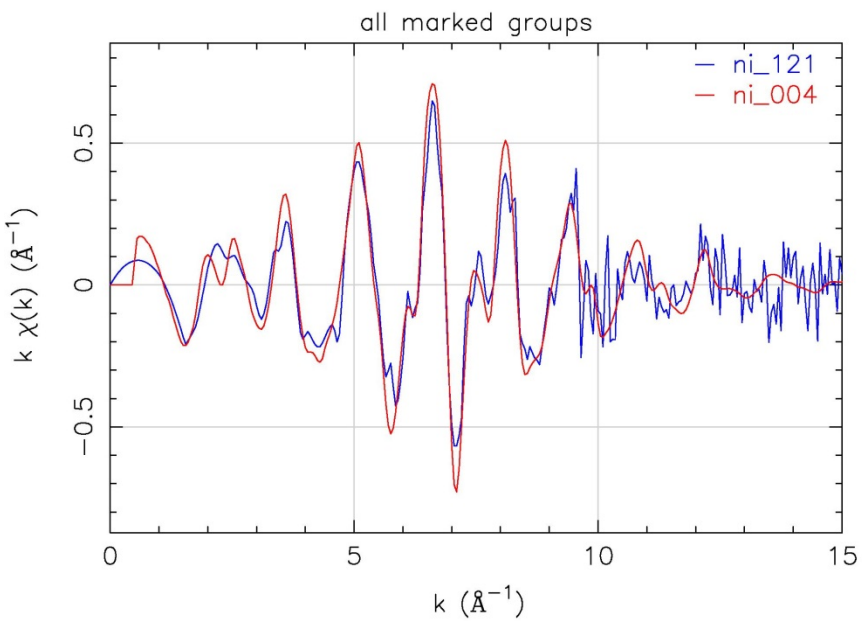

Relatively simple change of the angle-range for different edges

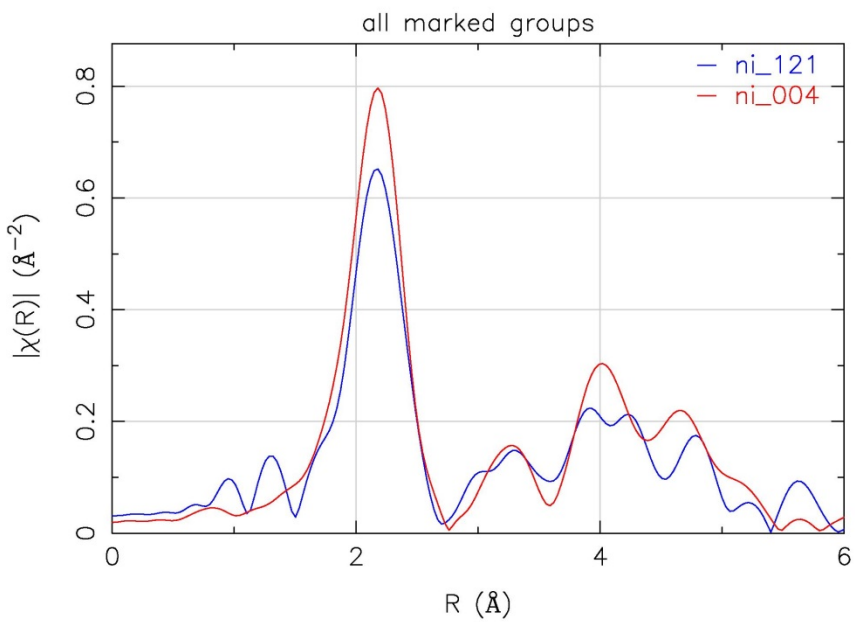
time to change between Ni and Cr: about 2 minutes

# Comparison to “conventional” Data



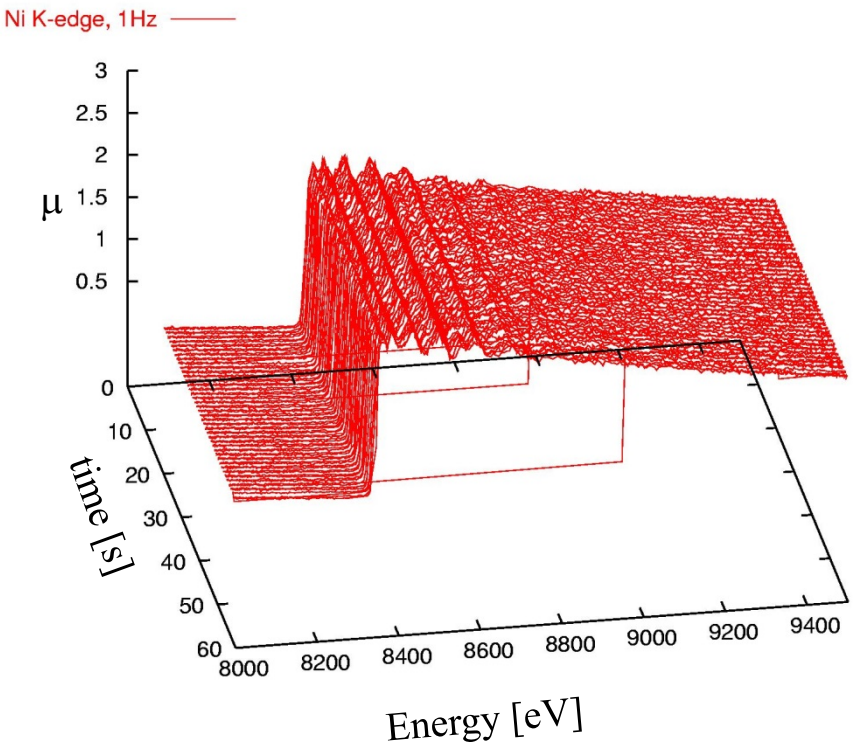

1 Scan collected in QEXAFS-mode
conventional scan collected at X19A

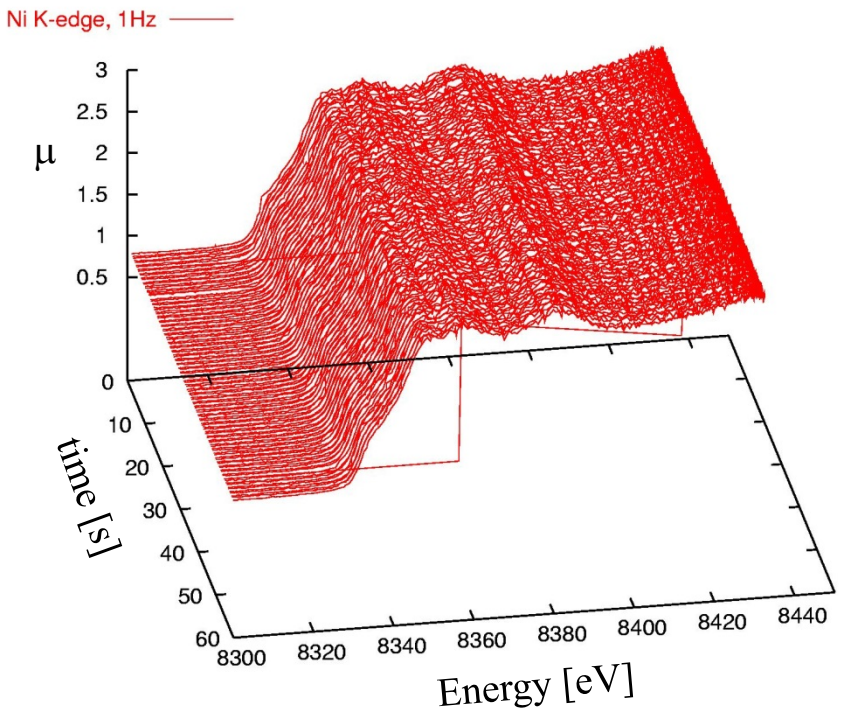


# Preliminary Results

Different speeds and different angular ranges for reference samples (Ni, NiS, Cr, $Cr_2O_3$, $CrO_3$)




Larger angle-range for EXAFS, smaller one for XANES, time to change between the two: about 2 minutes

# Intensity in Fluorescence Mode??

| | |
|---|---|
| Incident intensity: | $10^{10}$Hz |
| Absorption: | 50% |
| diluted sample: | 0.5% |
| Fluorescence yield: | 60% |
| Area of PIPS-detector: | $\pi*5^2/4$ |
| distance detector-sample: | $4*5^2*\pi$ |
| Al-foil in front of detector: | 2 |
| $\Pi$ | $10^6$Hz |
| measuring interval: | <1ms |

detector sees just 1000 photons

noise: 3%

# Copper Doped Ceria

## QEXAFS on $Cu_{0.2}Ce_{0.8}O_2$

Water Gas Shift reaction: Mix $H_2O$ and CO, and create $CO_2$ and $H_2$
Only method to produce large volumes of $H_2$!
Use catalysts to reduce temperature and increase yield.
Ce-based catalysts very popular since Ce can change between $Ce^{3+}$ and $Ce^{4+}$, can be used for oxygen-storage.
Add some other metals to improve catalysts.

How does it work???

# Model

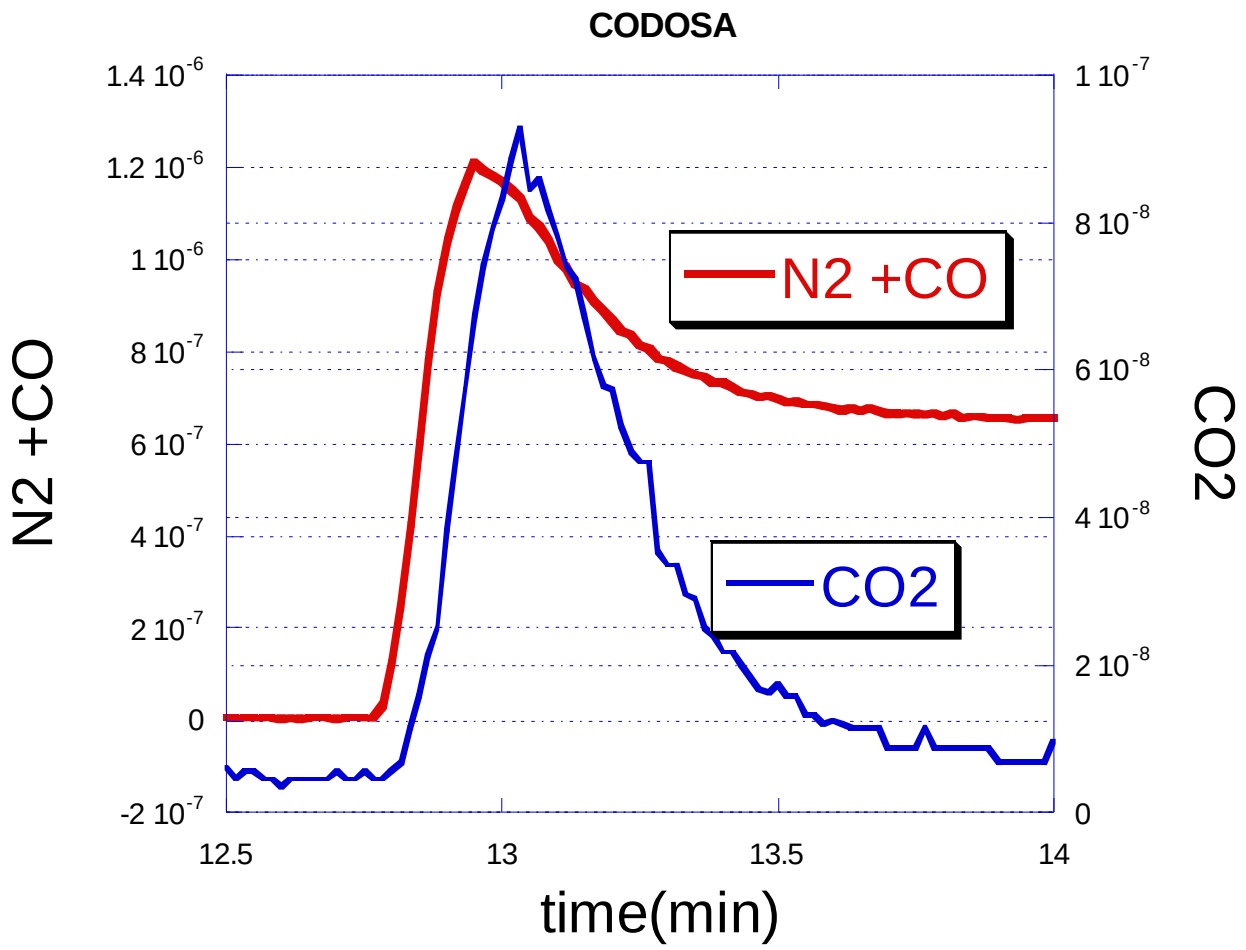
CO reacts with CuO and creates $CO_2$ and Cu

$\rightarrow$ Energy shift

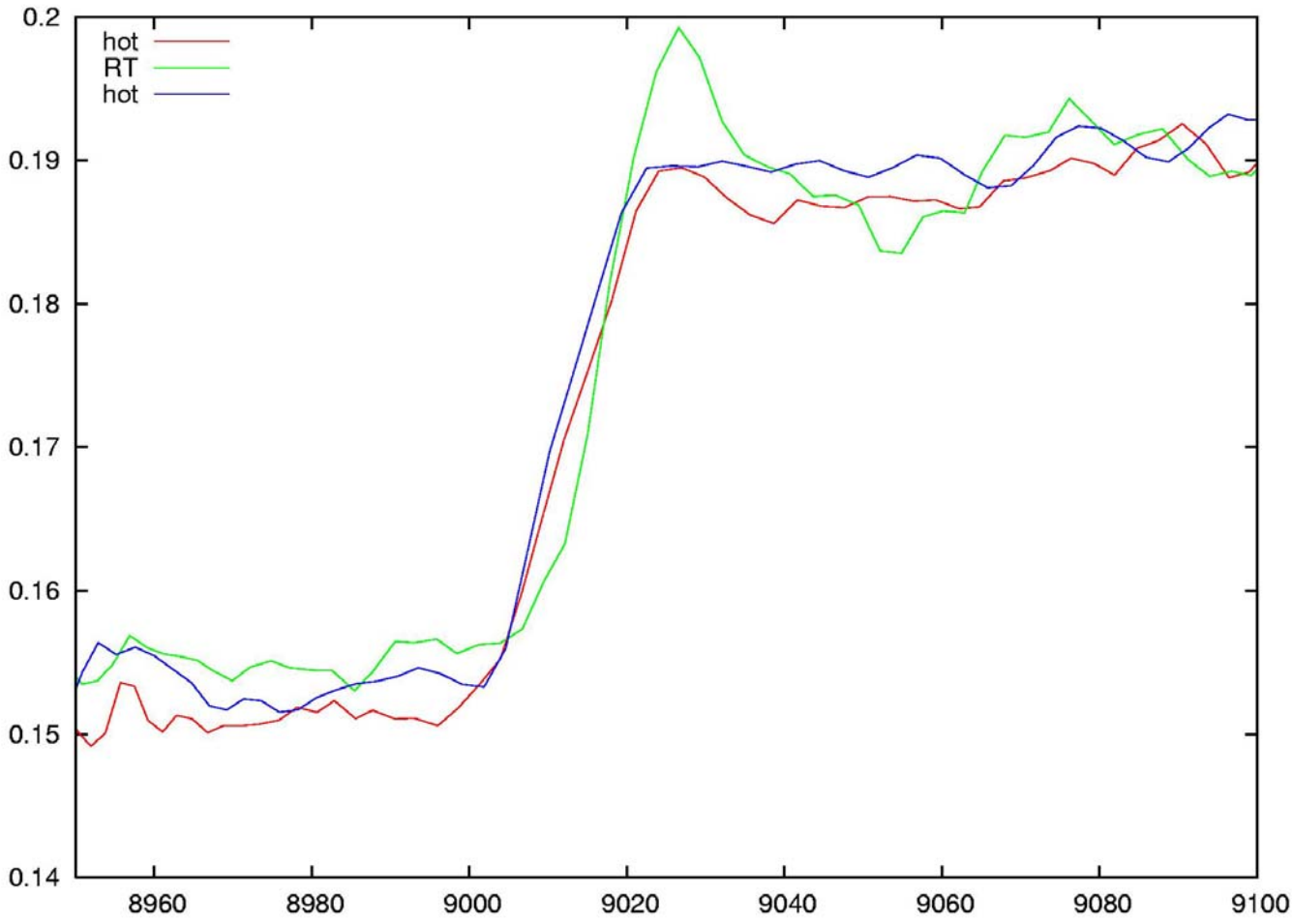
Cu moves from the core of the nano-particles to the outside

$\rightarrow$ Intensity increase

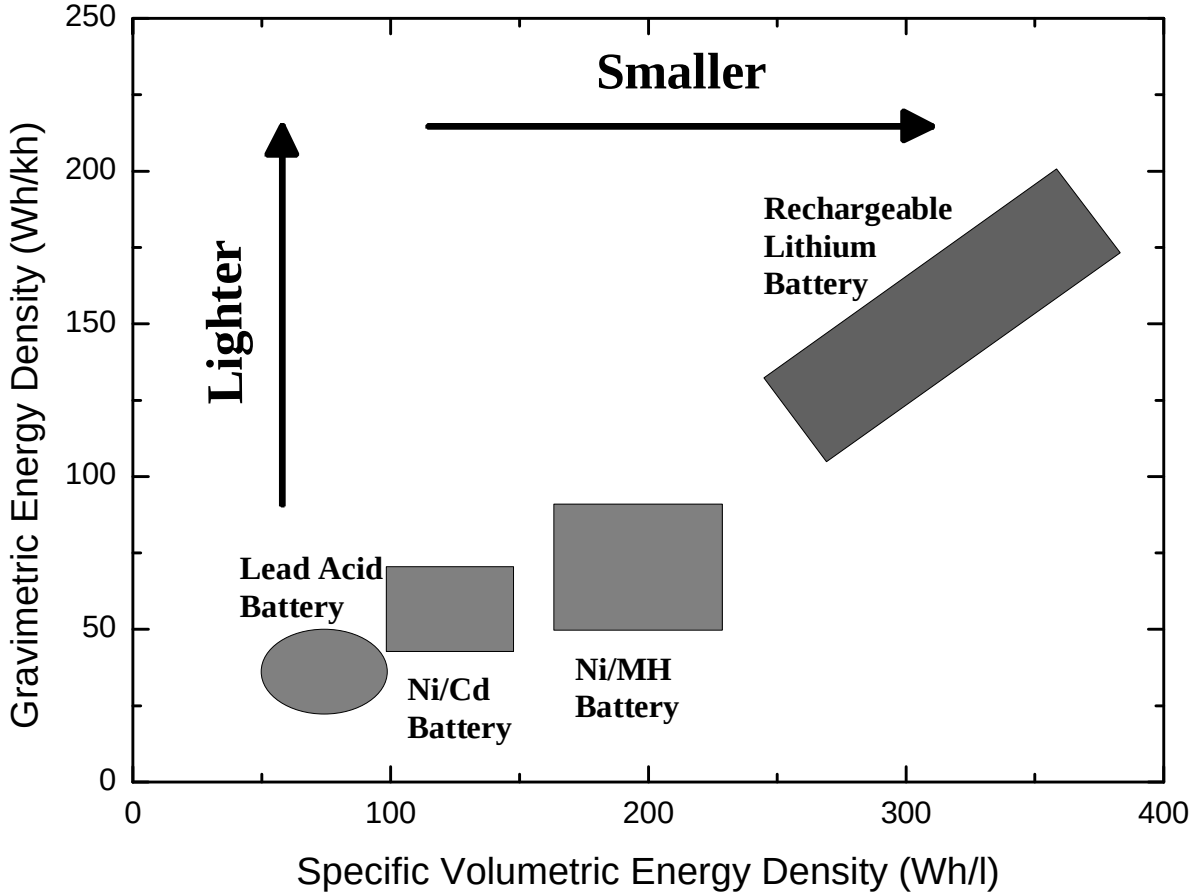
# Products and Reactants



# Comparison RT and hot sample *before* CO-exposure



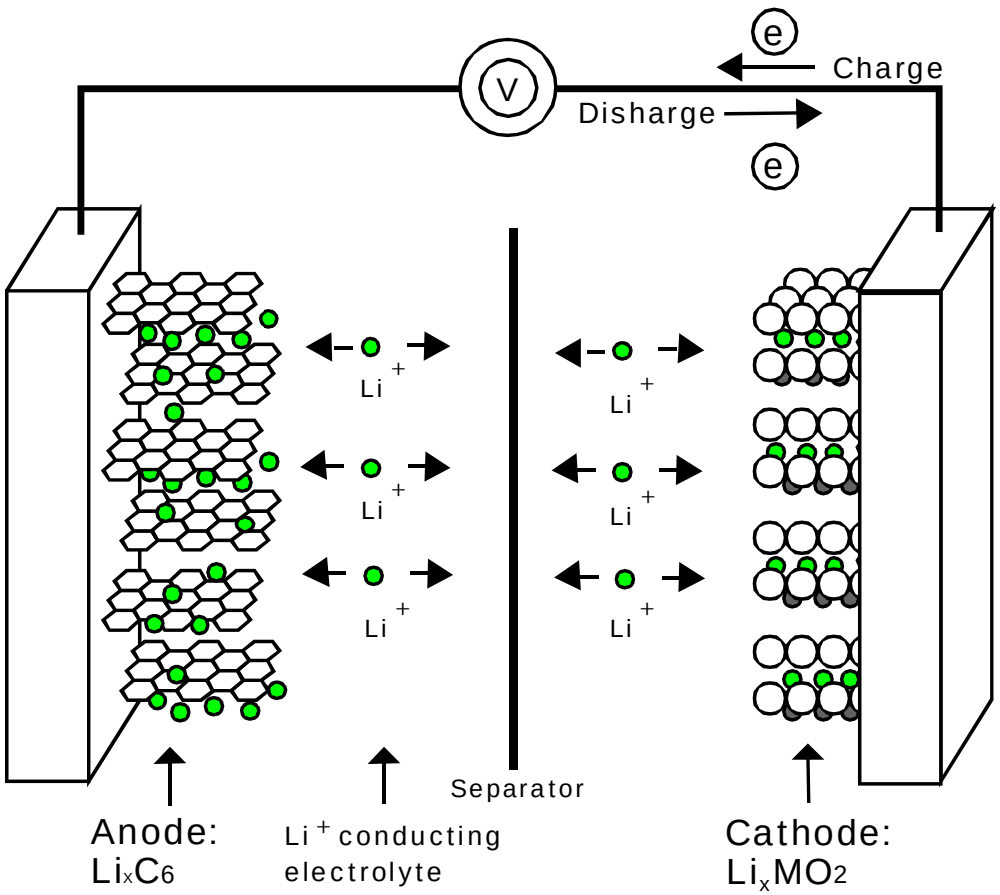
# Comparison of rechargeable batteries




**Comparison of the gravimetric and volumetric energy densities of rechargeable lithium batteries with those of other systems.**

BROOKHAVEN NATIONAL LABORATORY

# Li ion Rechargeable Batteries




- Cathode material
  : Li transition metal oxides
- Anode material
  : Soft and hard carbon
- Cathode reaction
  $LiMO_2 \rightarrow Li_{1-x}MO_2 + xLi + e^-$
- Anode reaction
  $Li_{1-x}C_6 + xLi + e^- \rightarrow LiC_6$

# Li ion Rechargeable Batteries

Lithium-ion batteries currently power millions of portable electronic devices all over the world. These cells have high energy densities, excellent cycle life, wide operating temperature ranges and long shelf lives.

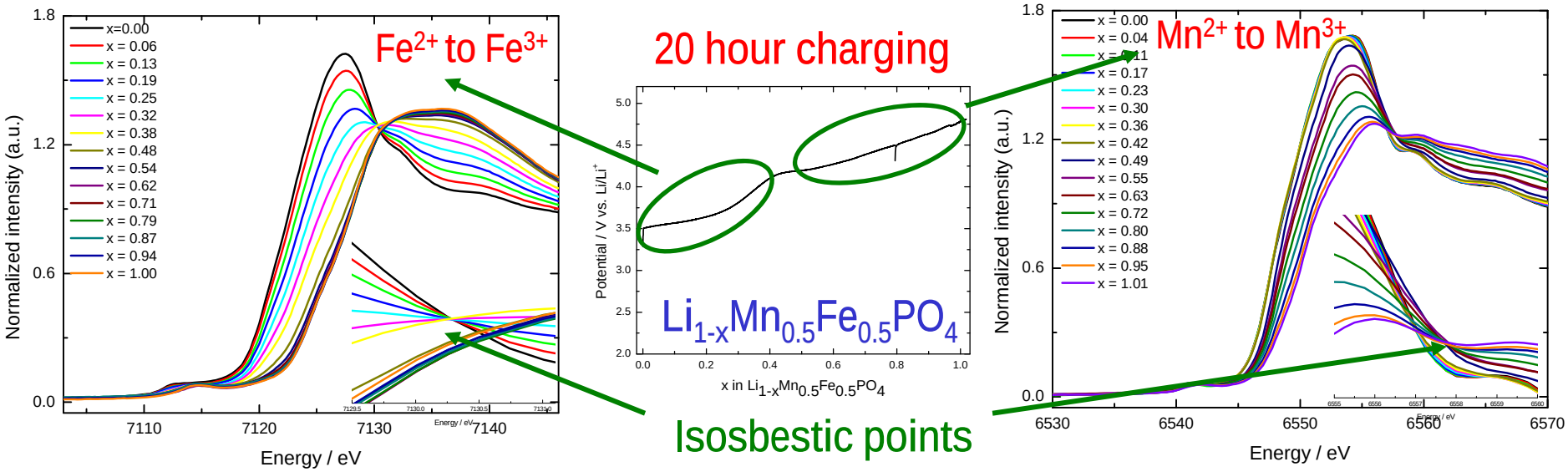
The success in commercial electronics make lithium-ion battery technology well positioned to move into electric vehicle applications. Problems of power-fade in lithium-ion cells are the major technical barriers that have to be overcome for these more demanding applications.

BROOKHAVEN NATIONAL LABORATORY

# In-situ XAS technique

## well suited for Li rechargeable battery systems

In-situ Mn and Fe K-edge XAS $Li_{1-x}Fe_{0.5}Mn_{0.5}PO_4$, electrodes during charge




However, most of high power battery systems cycle within an hour:

- XAS scan should be acquired within a minute to follow the changes in local structure and electronic property of electrode materials during charge/discharge

Fast XAS technique is needed for high power battery systems !!!

# NSLSII and beyond ....

- shorter pulses (11ps)
- higher brightness
- measure time-resolved bunches
- need for better detectors
    - more intensity
    - better time-resolution

## QAS: Quick Absorption Spectroscopy:

This is one of the Next-Gen beamlines at NSLS-II with high priority.
It will be at a three-pole-wiggler, using X18A monochromator and moving mechanism. Hutch, mirror and end station equipment from NSLS beamlines.

Hopefully operational in 2015.

# Kinetics of Chromium Oxidation by Manganese Oxides in Real Time using Quick-Scanning XAFS Spectroscopy

**G. Landrot, R.V. Tappero, J. Fitts, D.L. Sparks**

# Introduction

- The kinetics of important chemical processes (e.g., redox and adsorption) in natural systems such as soils are often rapid.

- A large portion of the reaction process is complete before the first data points can be collected using traditional batch and flow techniques.

# Introduction (suite)

- By measuring the initial reaction rates (system far from equilibrium) one can determine chemical kinetics parameters that are devoid of mass transfer phenomena.

➡ ***These parameters are needed to develop precise models for predicting the fate and transport of contaminants in soil and water environments.***

- So far, few studies on real-time kinetics of environmentally important reaction mechanisms at the molecular scale have been carried out.

# Kinetics of Chromium Oxidation by Manganese Oxides in Real Time using

# Quick-Scanning XAFS Spectroscopy

• Chromium considered as potentially toxic in the environment.

- **Cr(III)** rather immobile due to its limited solubility

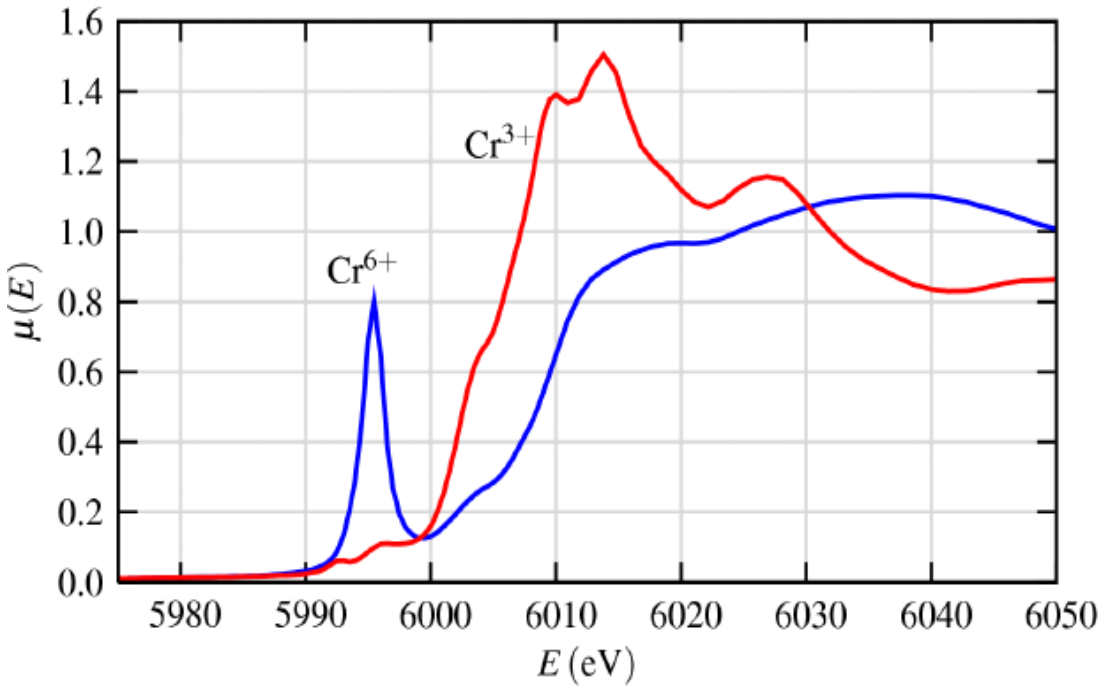
- **Cr(VI)** soluble. It is a carcinogen, an irritant, and a corrosive.

➡ **Cr (VI) toxic , Cr(III) less toxic**

• Manganese Oxides are the principle oxidizing agents for Cr(III) in soil systems

# An ideal System (1)

- Cr(III) and Cr(VI) easily recognizable and can be differentiated in the XANES regic

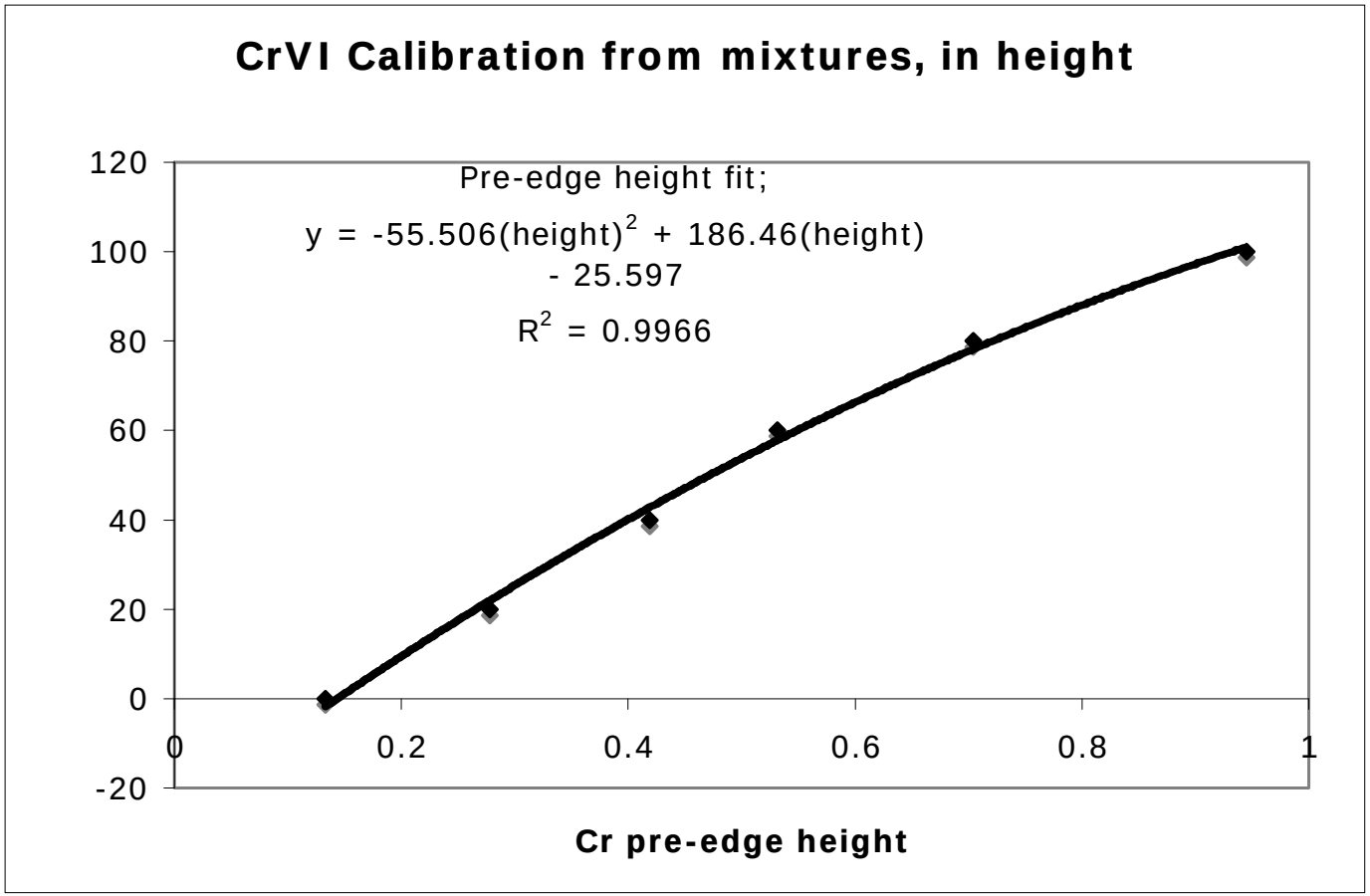



***From M. Newville, "fondamental of XAFS", 2004***

***Thus, one can easily follow the oxidation reaction from Cr(III) to Cr(VI) as time goes by.***

# An ideal System (1)

- Cr(III) and Cr(VI) Standard mixtures* ran at NSLS, X11A. Calibration done from Cr(VI) pre-edge height

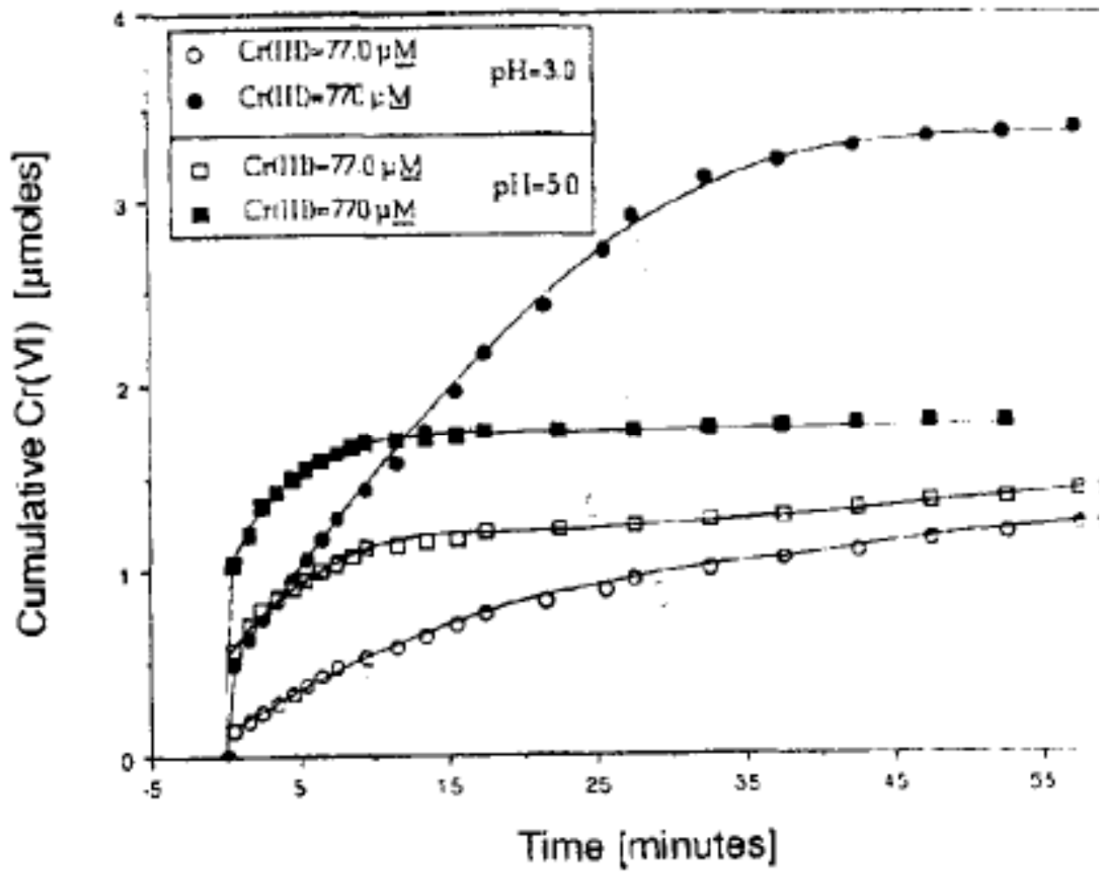



*Mixtures: 0% CrIII 100% CrVI -- 20% CrIII 80% CrVI -- 40% CrIII 60% CrVI -- 60% CrIII 40% CrVI --

80% CrIII 20% CrVI -- 100% CrIII 0% CrVI

# An ideal System (2)

- The Oxidation of Chromium from Cr(III) to Cr(VI) on MnO2 (0.1g/L) **is relatively fast**

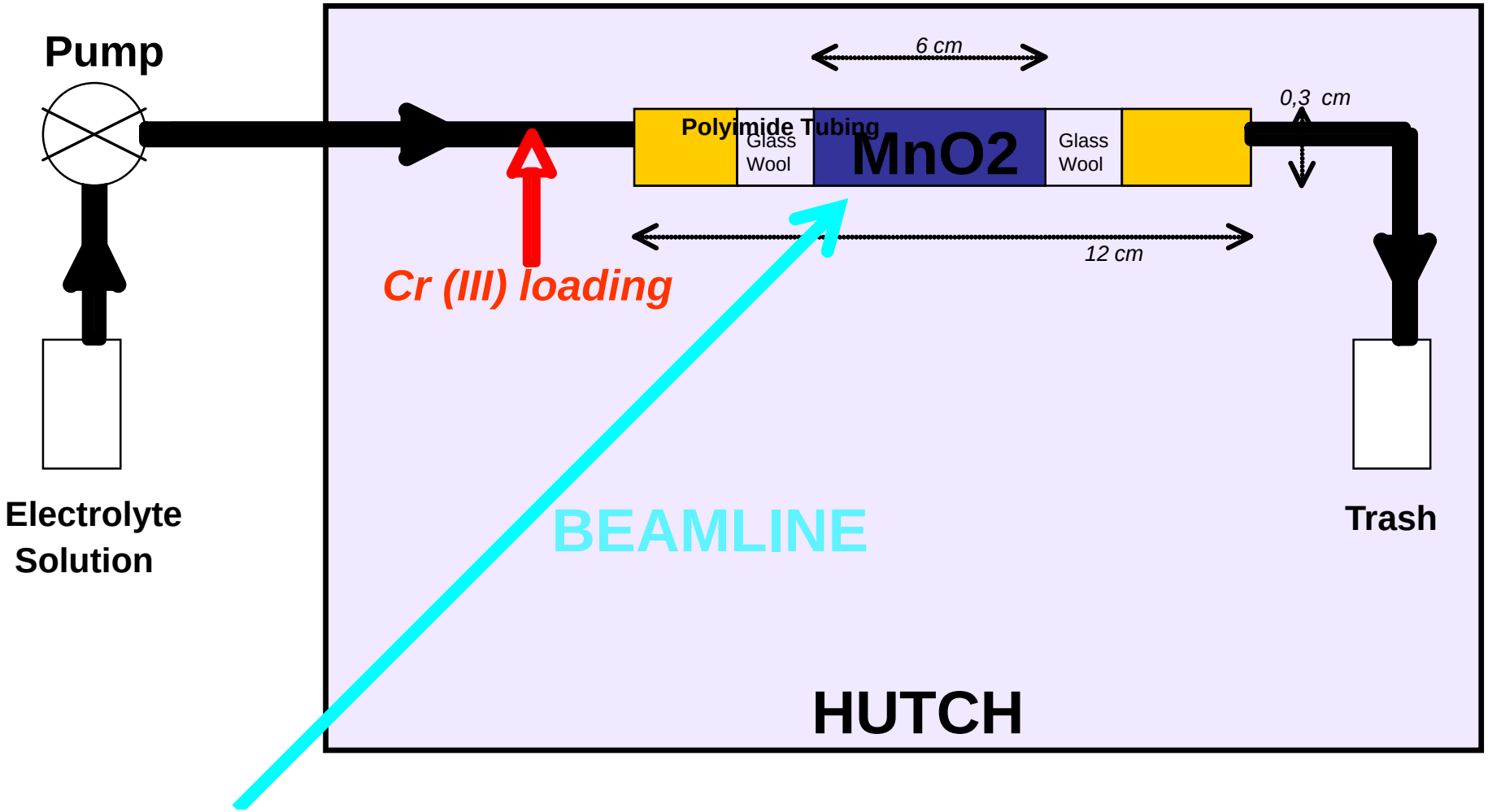



***From S. Fendorf and R. Zasoski, 1992***

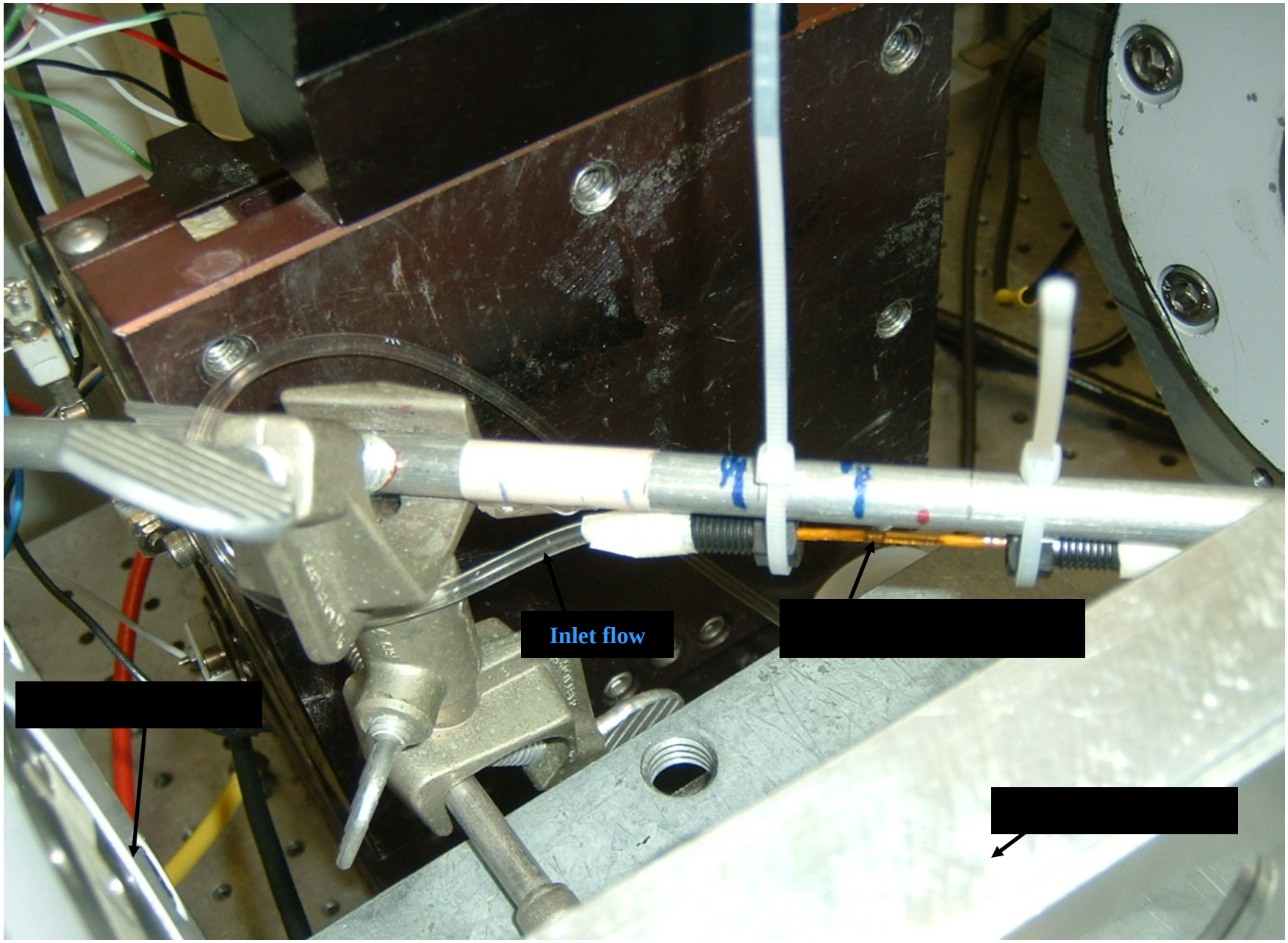
*Note: At pH greater than 3.5, a surface alteration induced by Cr(III) limits the extent of oxidation (Fendorf & Zasoski, 1992)*

# Flow through System

- Cell : Small Polyimide tubing filled with MnO2 and placed in the beamline's path



# Flow through System



# QEXAFS and chalcogenide glasses

- Why do we need QEXAFS for photoinduced structural changes in amorphous chalcogenides?

- What information can we get from QEXAFS?

- How can we correlate the changes obtained from QEXAFS to other photoinduced changes?

# a-chalcogenides

**Very sensitive to near bandgap light illumination**

*Photo-induced structural changes*

- Bandgap light affects volume, viscosity, optical properties, electrical properties, mechanical properties, (photo-induced structural changes)

**Applications of photoinduced changes in ChG's**

**Optical information storage (DVDs)**

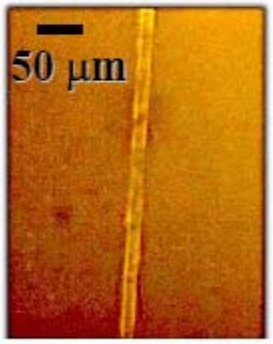
**Channel waveguide fabrication**

**Flexible optics**

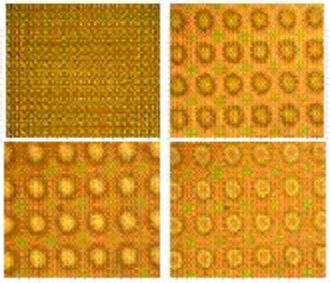
**Micro fabrication of IR optical components**

**Opto-mechanical nano-transducers**

**Photoresistors …**



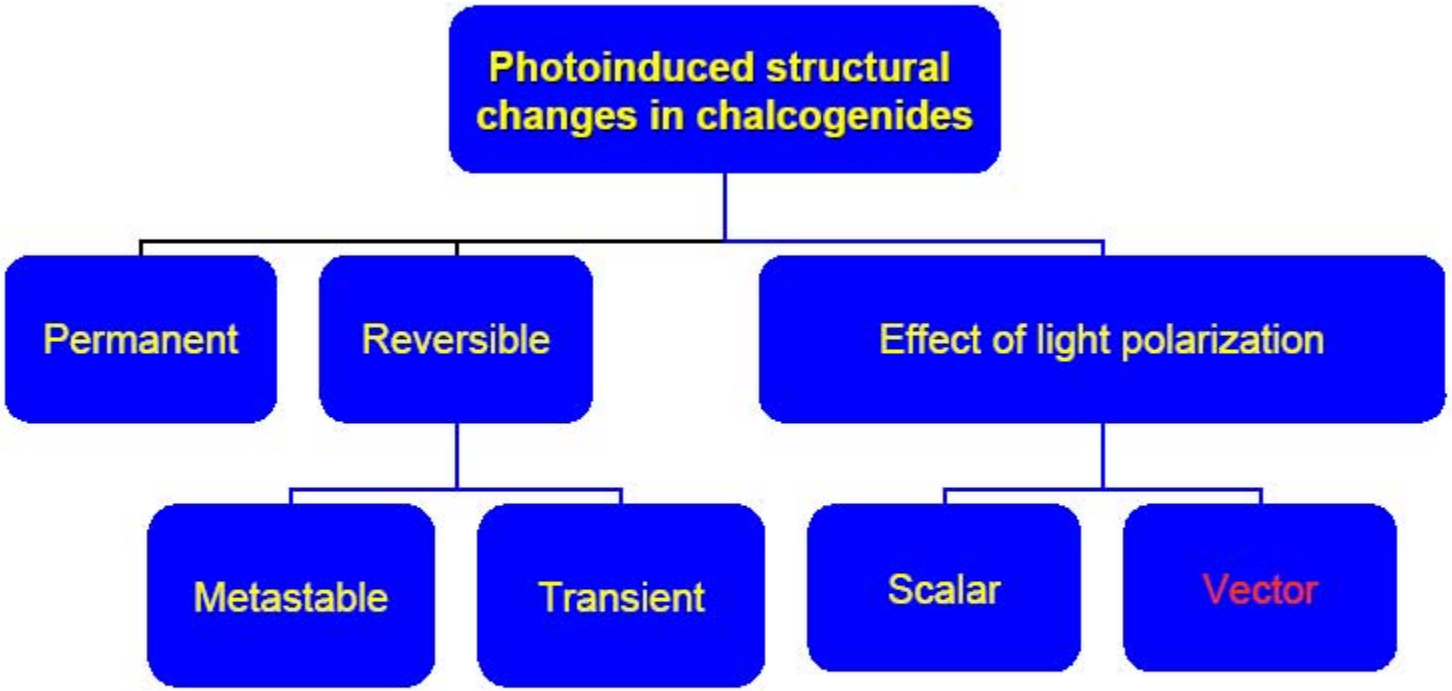

**Channel Waveguides (a-GeSbSe)**



**Micro lenses (a-$As_2S_3$) ($\phi$:14 μm)**

LEHIGH UNIVERSITY

Center for Optical Technologies

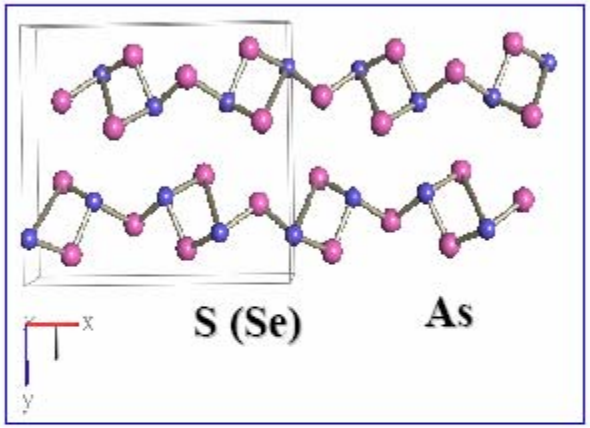



Permanent: cannot be recovered without remaking the glass
Metastable: recovered on heating to ~Tg
Transient: recovered on removing of the light
Scalar: do not depend on the polarization of the light
Vector: depend upon the polarization of the light

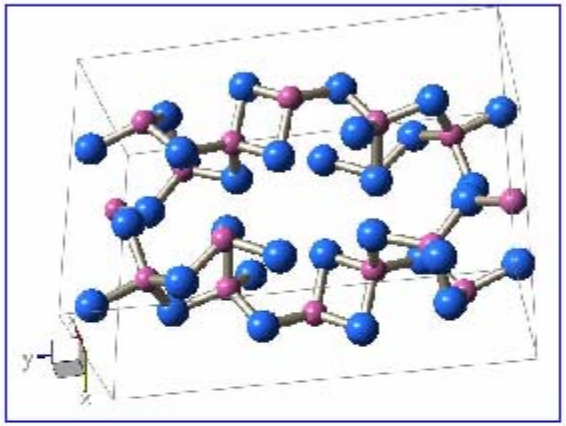
LEHIGH UNIVERSITY

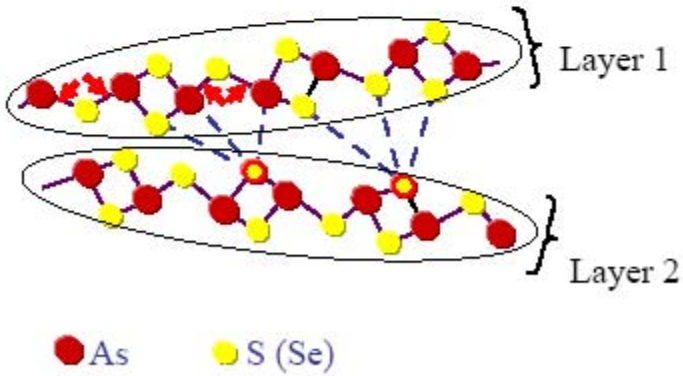
Center for Optical Technologies

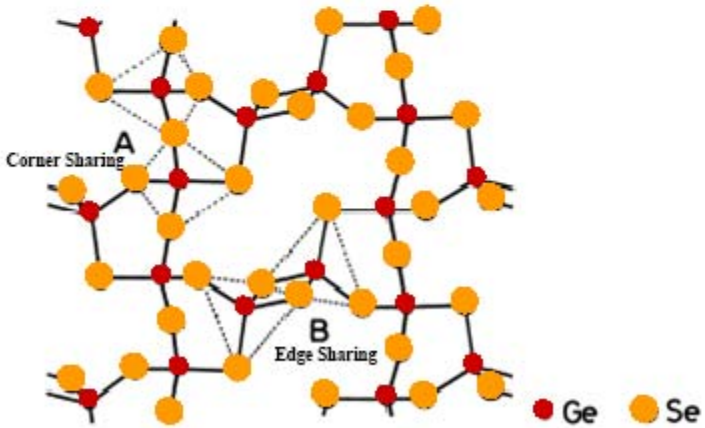
## Structure of $As_2S(Se)_3$



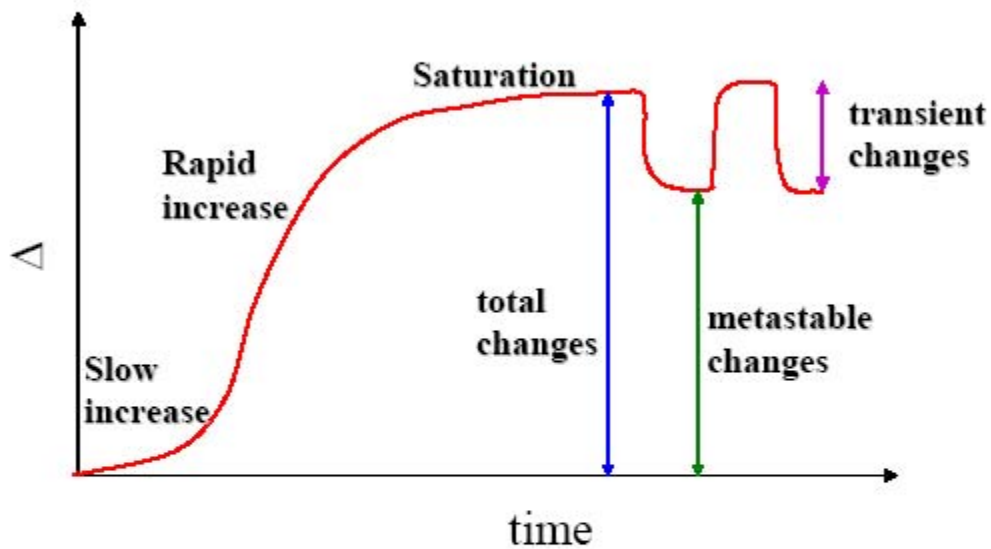

## Structure of $GeSe_2$





## Typical behavior of various photoinduced changes in amorphous chalcogenides



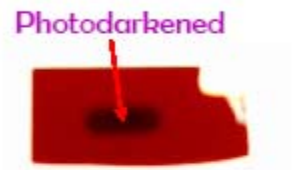
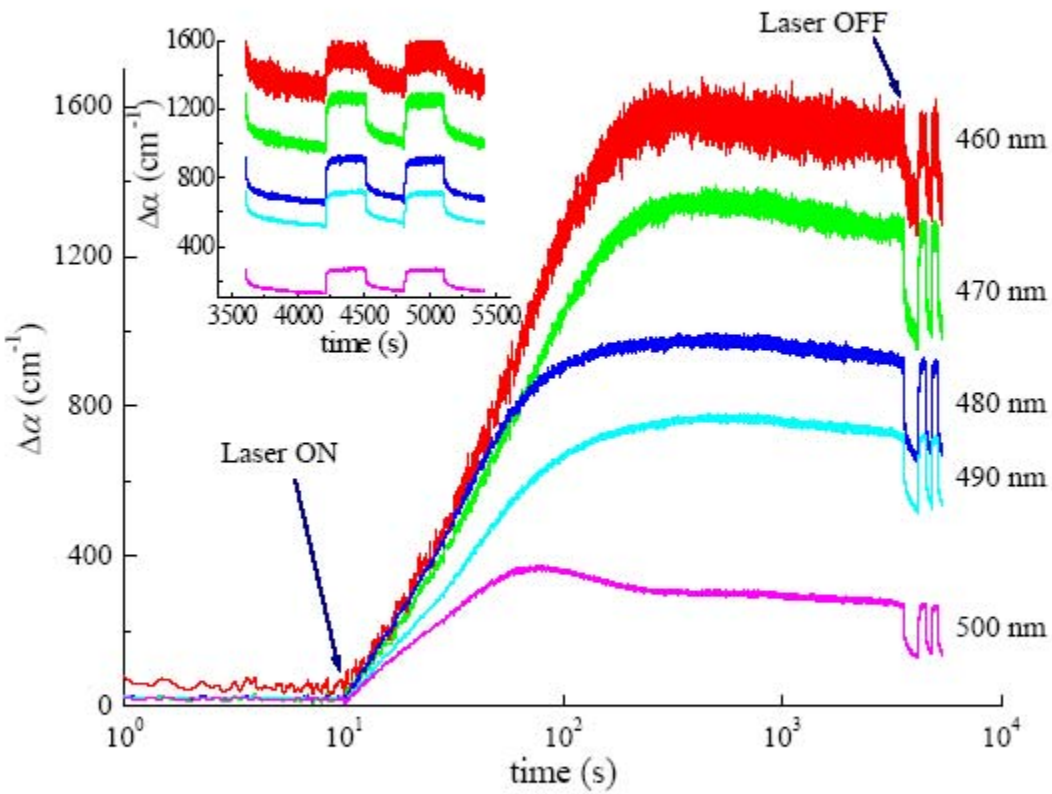




Photo darkened $As_2Se_3$ film

Total changes are a combination of transient and metastable changes
Transient changes decay once the illumination is switched off
The kinetics are generally explained by a stretched exponential behavior

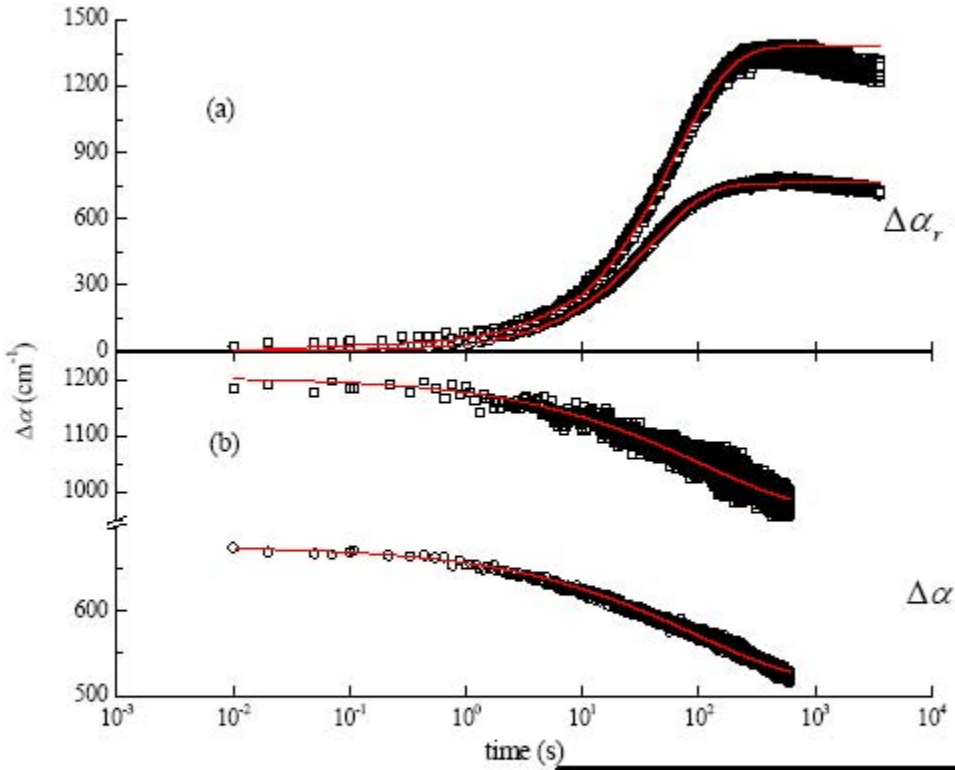
Kinetics of most of the changes in optical properties are known and time constants are estimated

## Time evolution of photoinduced changes in absorption coefficient




A. Ganjoo, H. Jain, Phys. Rev. B, 74, 024201 (2006)

## Kinetics of photoinduced changes (rise and decay) in absorption coefficient



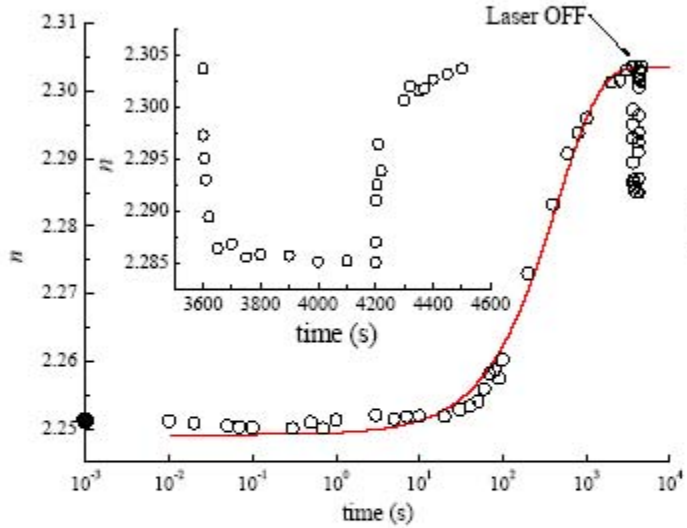

$$\Delta\alpha_r = \Delta\alpha_{Sr}\left[1-\exp\left\{-\left(\frac{t}{\tau_r}\right)^{\beta_r}\right\}\right]$$

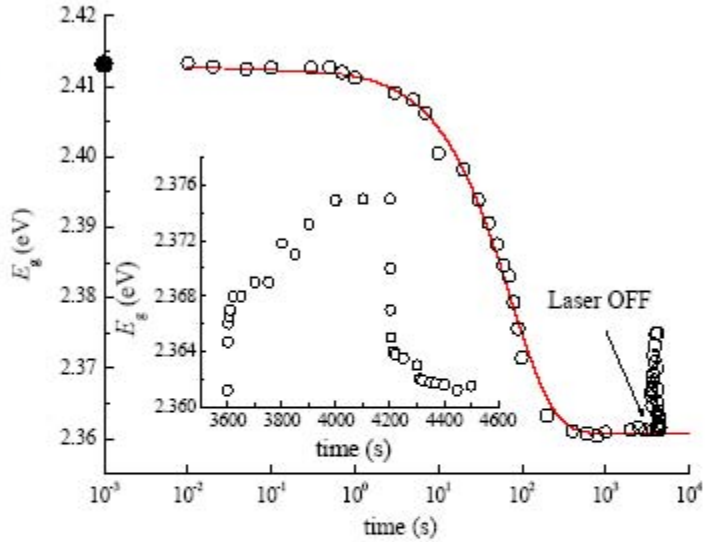
$$\Delta\alpha = C\left[\exp\left\{-\left(\frac{t}{\tau_d}\right)^{\beta_d}\right\}\right]+\Delta\alpha_{Sd}$$

**Time constants of photoinduced changes can be estimated**

| $\lambda$ (nm) | $\tau_r$ (sec) | $\beta_r$ | $\Delta\alpha_S$ ($cm^{-1}$) | $\tau_d$ (sec) | $\beta_d$ | $\Delta\alpha_S$ ($cm^{-1}$) | C |
|---|---|---|---|---|---|---|---|
| 470 | 61.50 | 0.87 | 1380 | 105.66 | 0.45 | 960 | 244.9 |
| 490 | 38.48 | 0.87 | 760 | 93.03 | 0.45 | 512 | 164.5 |

## Kinetics of photoinduced changes (rise and decay) in refractive index and optical bandgap



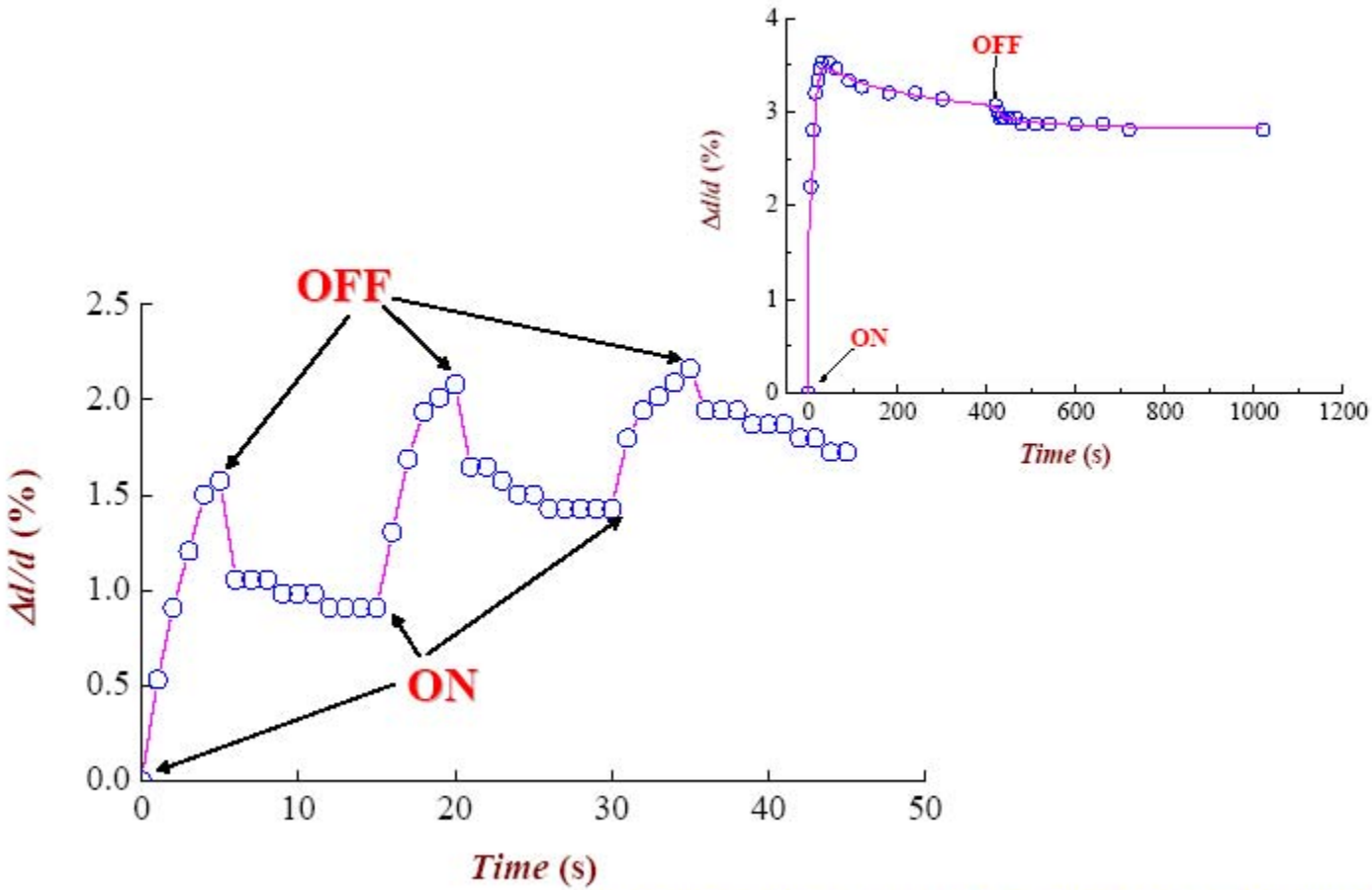




$\tau$ = 456.3 sec

$\tau$ = 73.5 sec

A. Ganjoo, H. Jain, Phys. Rev. B, 74, 024201 (2006)

## Time evolution of Transient and metastable photoinduced changes in volume




A. Ganjoo et al., Appl. Phys. Lett., 74, 2119 (1999)

Changes in optical properties are related to changes in structure of a material

Photoinduced changes in optical properties e.g., absorption coefficient, optical bandgap, refractive index all related to changes in structure

Kinetics of changes in optical absorption, refractive index, optical bandgap, volume known (time evolution of changes studied)

What are the kinetics and time constants for changes in structural parameters (nearest neighbor distances, Debye Waller factor, coordination number)

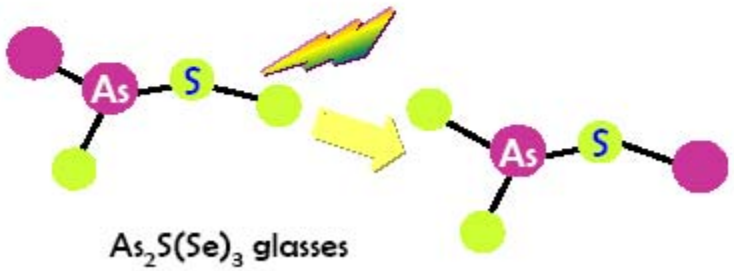
What are their kinetics (???)

Do photoinduced changes in structure and optical parameters have the same origin and kinetics

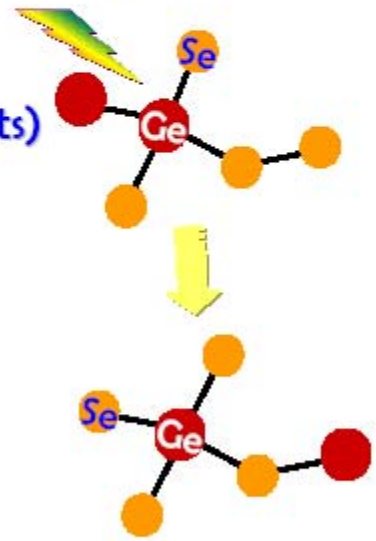
This information is very useful in switching, writing and related applications

## What causes photoinduced structural changes in amorphous chalcogenides

- Bond breaking (at the weaker homopolar bonds)
- Conversion of homopolar bonds into more stable heteropolar bonds
- Bond switching
- Reduction of defects (bonding, coordination defects)

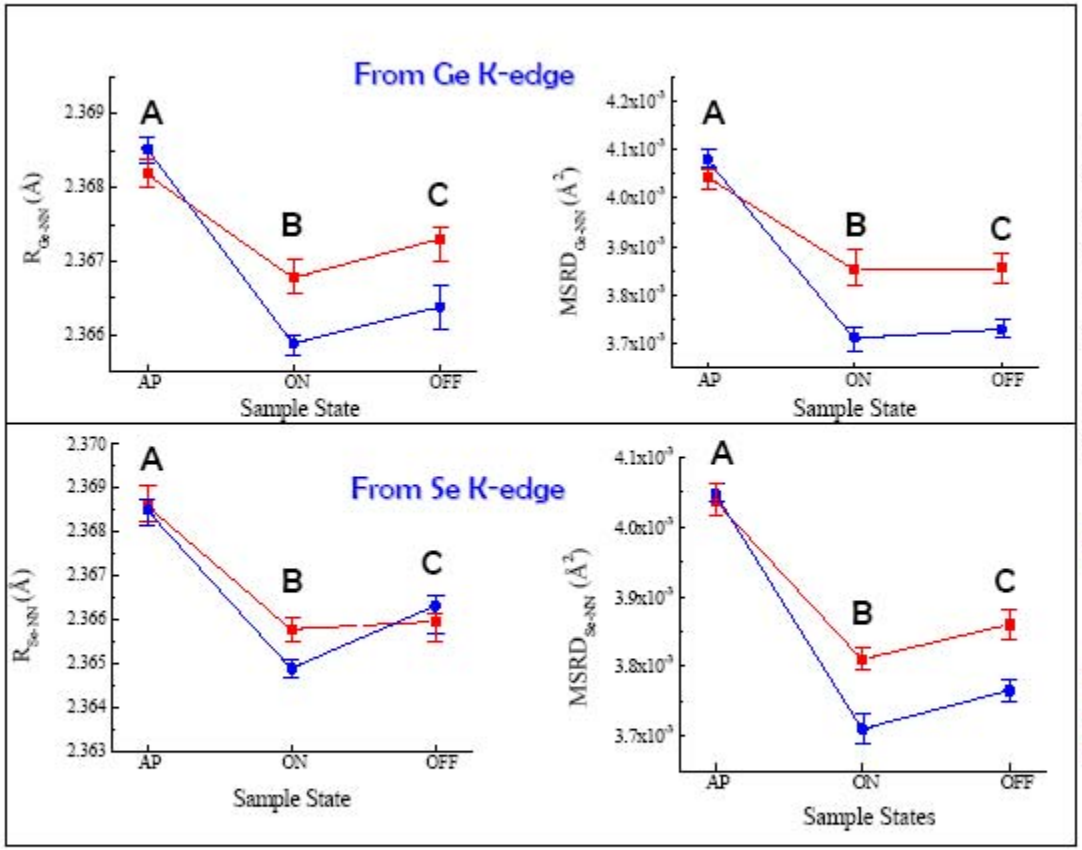



$As_2S(Se)_3$ glasses




$GeS(Se)_2$ glasses

## Photoinduced structural changes as studied by normal in-situ EXAFS (a-$GeSe_2$)




Normal EXAFS gives us the information about changes before any illumination, at the saturation stage and at the metastable state

(time required to collect each scan ~45 mins.)

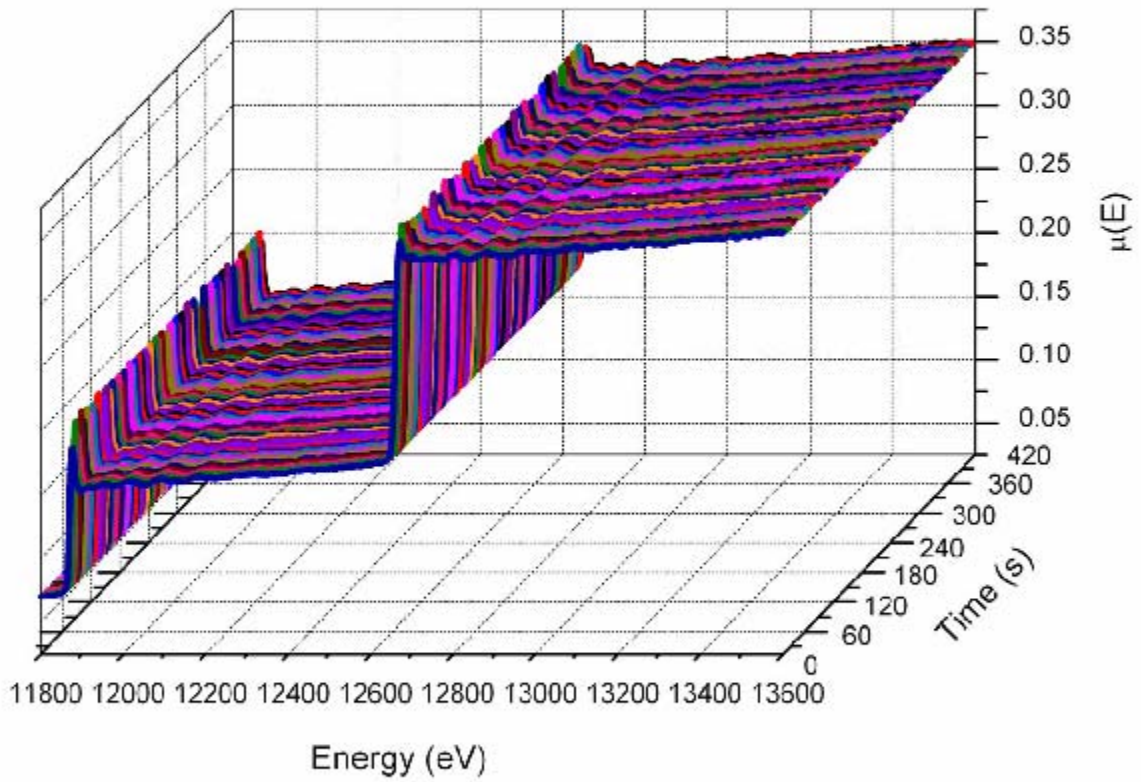
Kinetics of changes are not measured

How the changes go from A to B to C is not known

Nearest neighbor distances

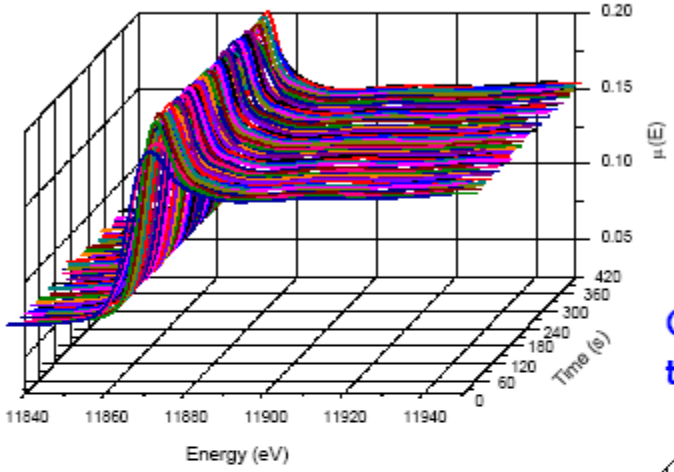
Debye-Waller factor

## In-situ QEXAFS in $\alpha$-$As_2Se_3$ films

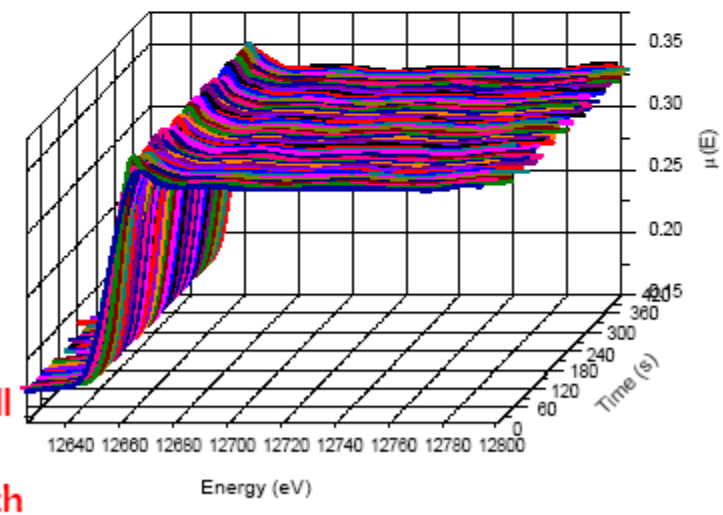



Data collected every 5 seconds

QEXAFS As K-edge with illumination time (measured every 5 sec)




QEXAFS Se K-edge with illumination time (measured every 5 sec)




Analysis of the in-situ QEXAFS data will give us the kinetics of the changes with illumination time, thus providing us with time constants and related parameters

## What do we expect from QEXAFS?

Measurements using QEXAFS can provide us with the time evolution of changes in structural parameters, which can give us the kinetics of the changes

From the kinetics, we can estimate the time constants and other useful parameters

We can then correlate the kinetics of changes in structural parameters with the kinetics of changes in optical properties

From the correlation, we can understand the photoinduced structural changes fully

The dynamics of bond breaking/switching can be known from the kinetics of structural changes

Proper information for improving the time constants and their uses in various applications

# ACKNOWLEDGEMENT


| | |
|---|---|
| Mechanical System: | Anthony Lenhard<br>Shu Cheung<br>Rick Greene |
| Detectors: | Tony Kuczewski<br>Dennis Poshka<br>Barrett Clay |
| Computer-stuff: | Zhijian Yin<br>Kate Feng Berman<br>Ivan So<br>Nathan Hould |
| Discussions: | Ned<br>Pete Siddons<br>Jon Hanson (BNL-Chemistry)<br>Simon Bare (UOP) |
| Contributions: | Ashtosh Ganjoo<br>Donald Sparks<br>Won-Sub Yoon<br>WOLOFGANG CALIEBE |

US Department of Energy Contract #DE-AC02-98CH10886