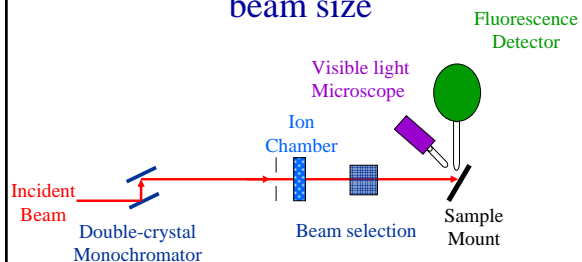


## Lecture 5.

### Spatially and temporally resolved XAS

X-ray microprobe provides spatial resolution – defined by beam size

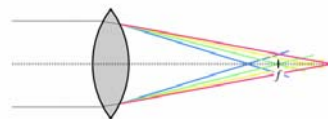


## Focusing x-rays

- Total external reflection: **Bent mirrors**, capillaries
- Bragg reflection from bent single crystals.
- Diffractive focusing elements: **Fresnel zone plates**
- Refractive focusing elements: Compound refractive lenses

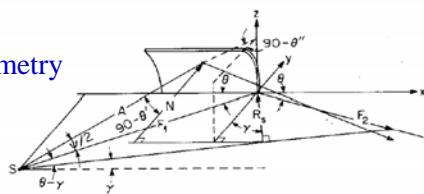
## Chromatic aberration

Important for zone plates and compound refractive lenses – make XANES, and especially EXAFS hard

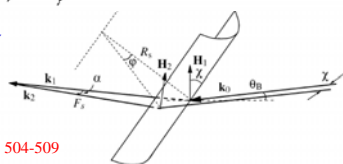


## Sagittal focusing

Bragg geometry

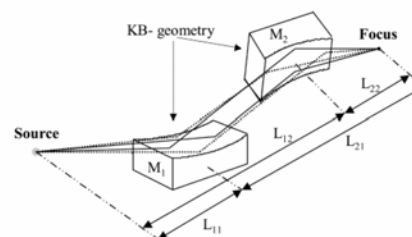


Laue geometry

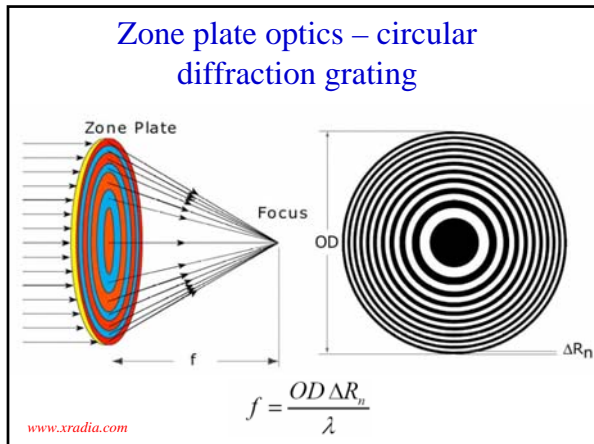


*J. Appl. Cryst.* (2001), **34**, 504-509

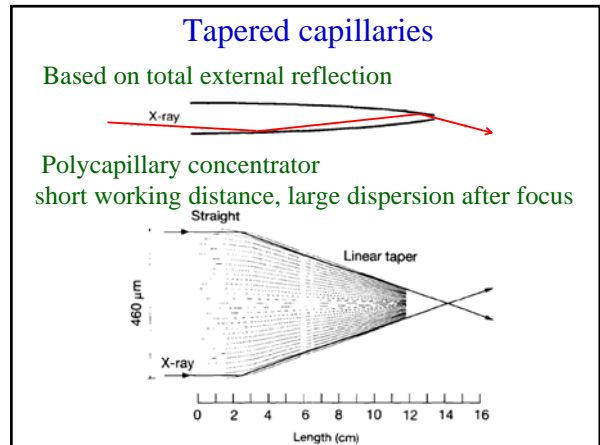
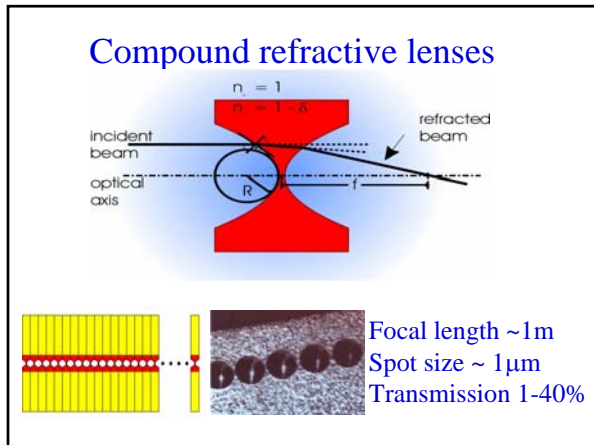
## Kirkpatrick-Baez mirrors



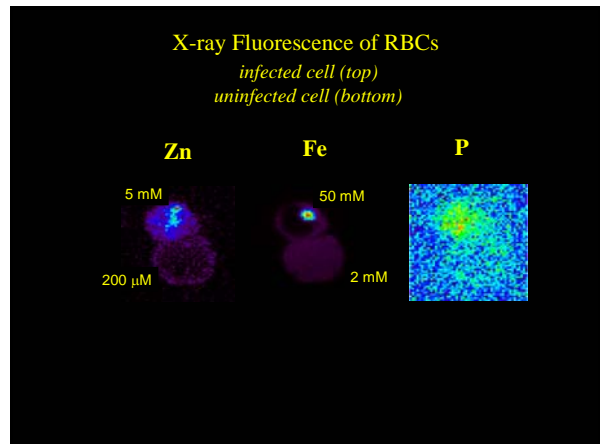
~1  $\mu\text{m}$  focus but no chromatic aberration

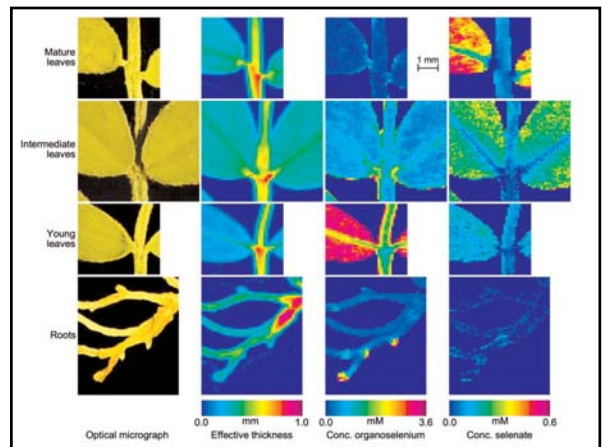
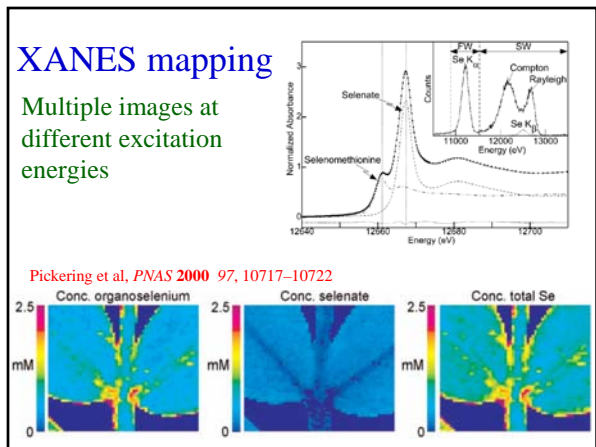
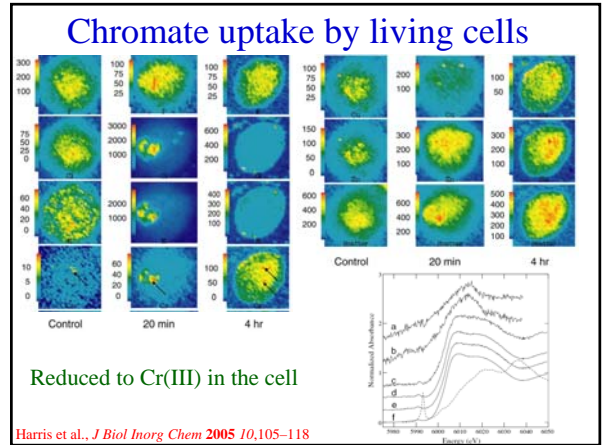
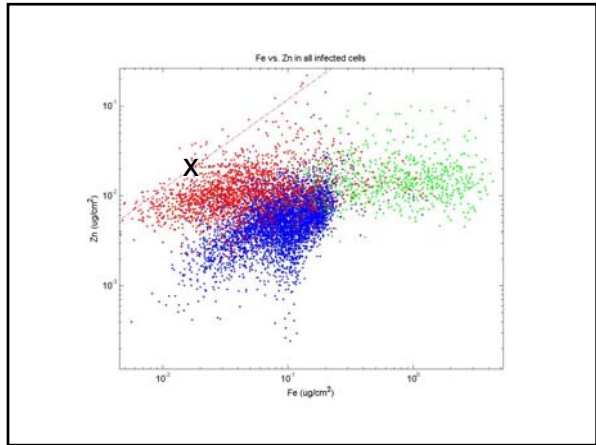
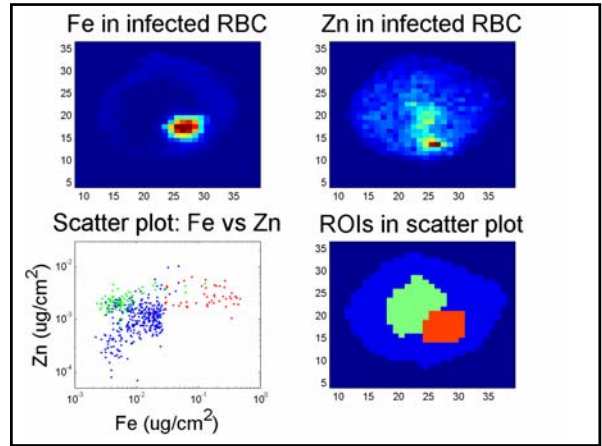
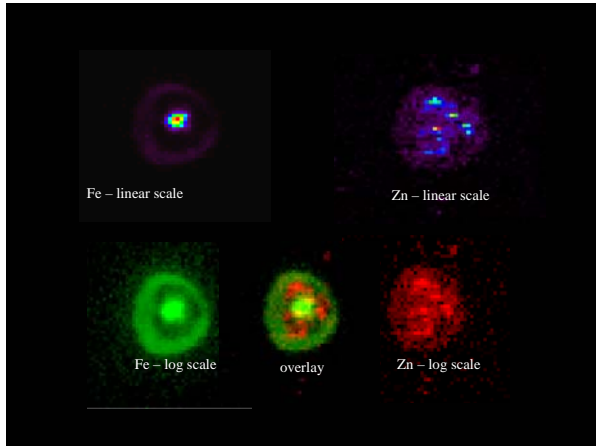


- ### Zone plate trade-offs
- Thicker zones – higher energy, but harder to construct (high aspect ratio)
  - Smaller outer zone – better focus, but smaller working distance (Rayleigh limit=1.22 ΔR<sub>n</sub>)
  - Larger OD – longer working distance but harder to fabricate
- Typical values (hard x-ray):  
 ΔR<sub>n</sub>=100 nm; OD=300 μm; T=1.6 μm  
**\$45K**

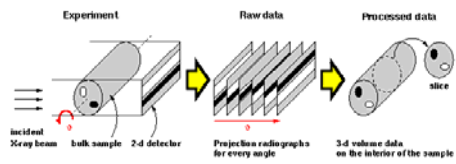


- ### Information from imaging
- Distribution
  - Concentration → Species mapping
  - Speciation

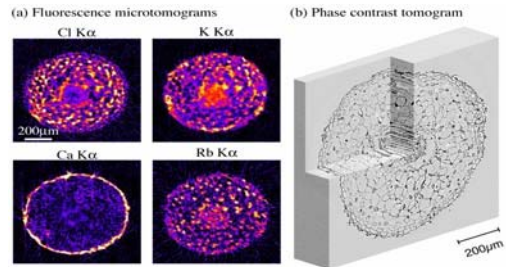




## Computer tomography – 3D images



## X-ray fluorescence microtomography

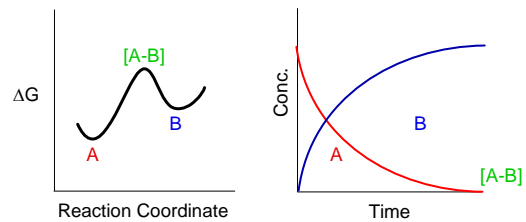


<http://www.institut2b.physik.rwth-aachen.de/>

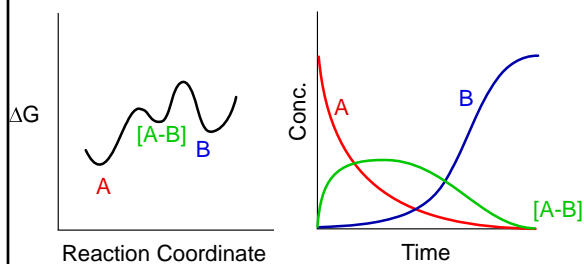
## Time-resolved XAS

- Rapid scanning monochromator (“QEXAFS”)
- Dispersive XAS
- Continuous flow
- Rapid freeze quench

## Can TR EXAFS be used to determine structure of transition state?

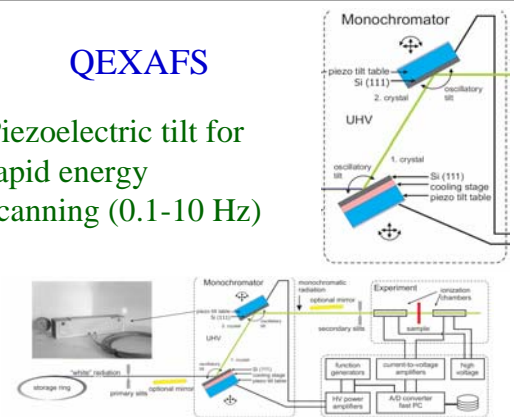


If intermediate builds up to significant concentration, can be studied by XAS



## QEXAFS

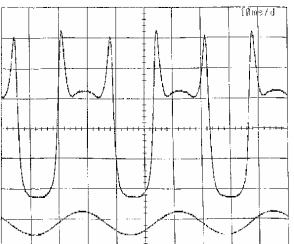
Piezoelectric tilt for rapid energy scanning (0.1-10 Hz)




*J. Synchrotron Rad.* (2001), 8, 354±356

### QEXAFS

Absorbance



Piezo voltage

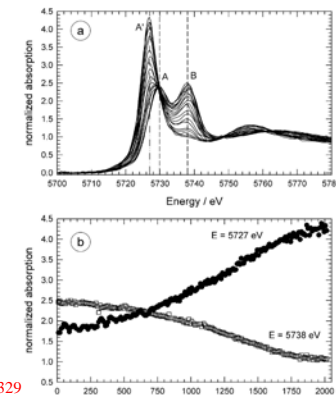


Good time resolution (if recyclable or concentrated)  
Compatible with any (fast) detection method

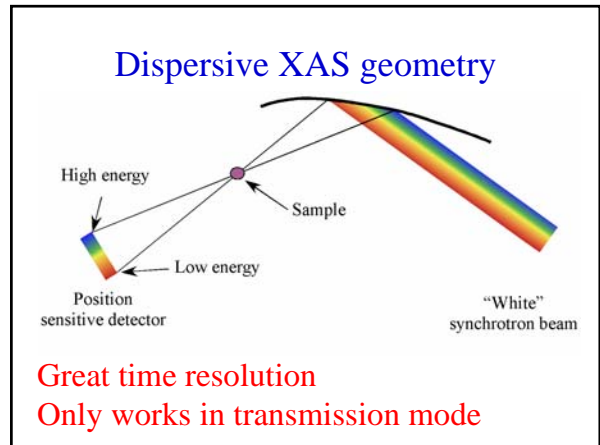
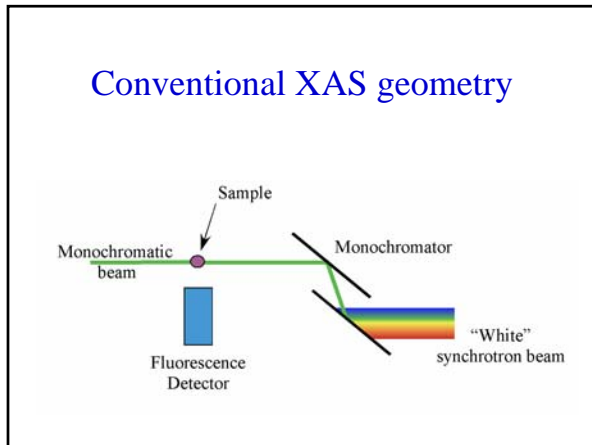
<http://schulzeundschultze.amphy.uni-duesseldorf.de/~frahn/QEXAFS/piezo.html>

### QEXAFS investigation of oxidation of EtOH by Ce(IV)

t=5 sec  
[Ce]=0.1 M



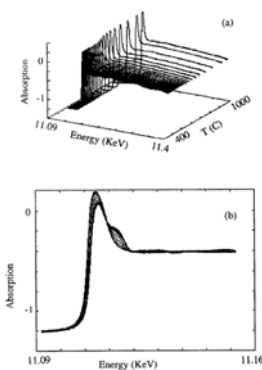
*J. Phys. Chem. A* **2005**, *109*, 320-329



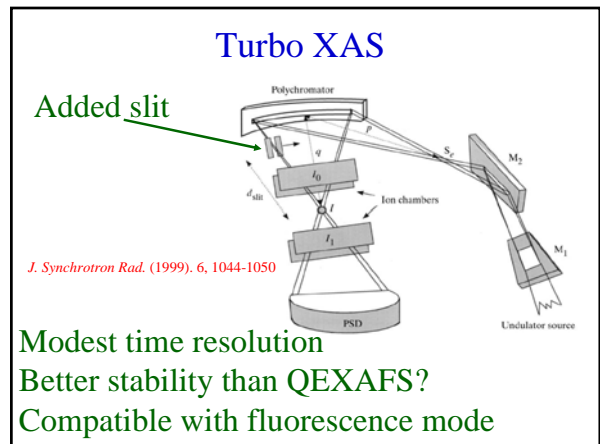
### Dispersive XAS of Ge solidification

EXAFS – 520 ms/spectrum

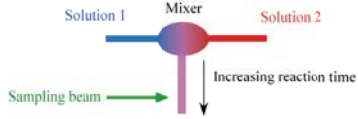
XANES – 120 ms/spectrum



*J. Synchr. Rad.*, **1999** *6* 146



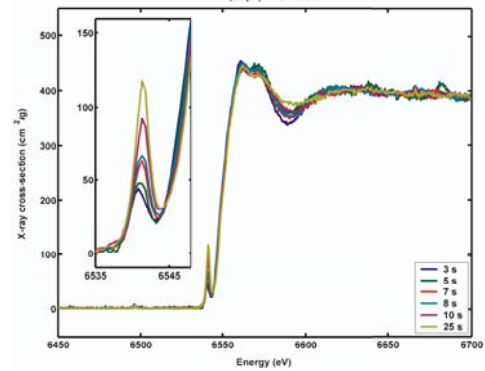
## Flow system can be used for time resolved measurements



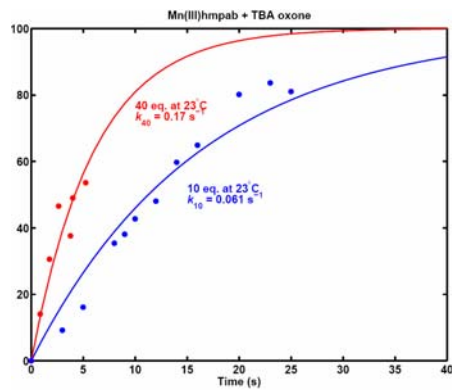
Requirements (for reasonable sample volumes):

- Rapid scanning
- Small sample (i.e., small beam)

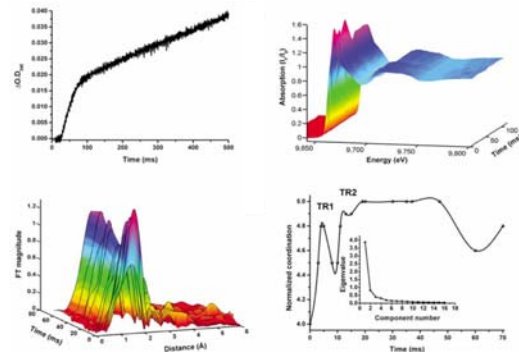
## Oxidation of Mn(III)hmpab by oxone



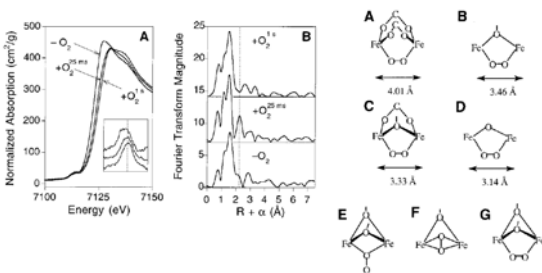
## Reaction appears to be first order in Mn and oxone



## Rapid freeze quench is (the best?) solution to time-resolved EXAFS



## Peroxo-diferic ferritin



Hwang et al, *Science*, 2000, 287, 122

## X-ray photoreduction of photosynthetic oxygen evolving complex

