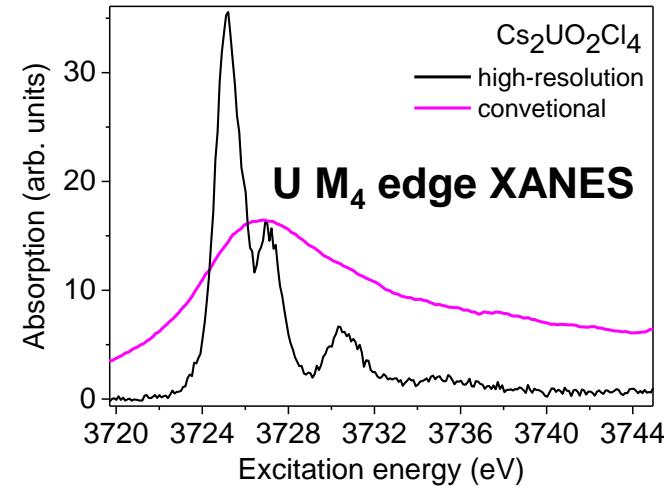
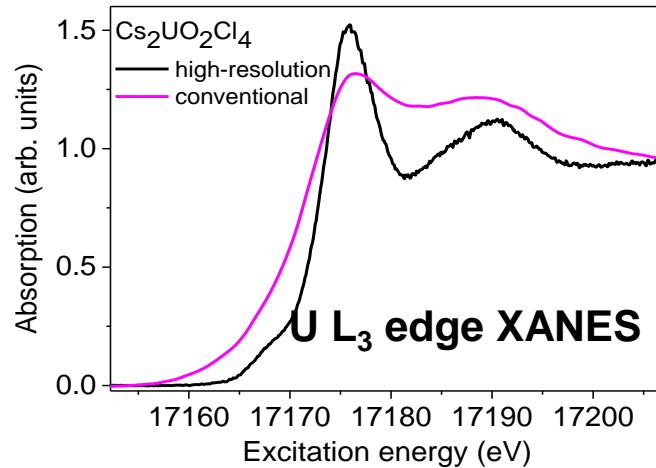


# X-ray absorption spectroscopy

Tonya Vitova

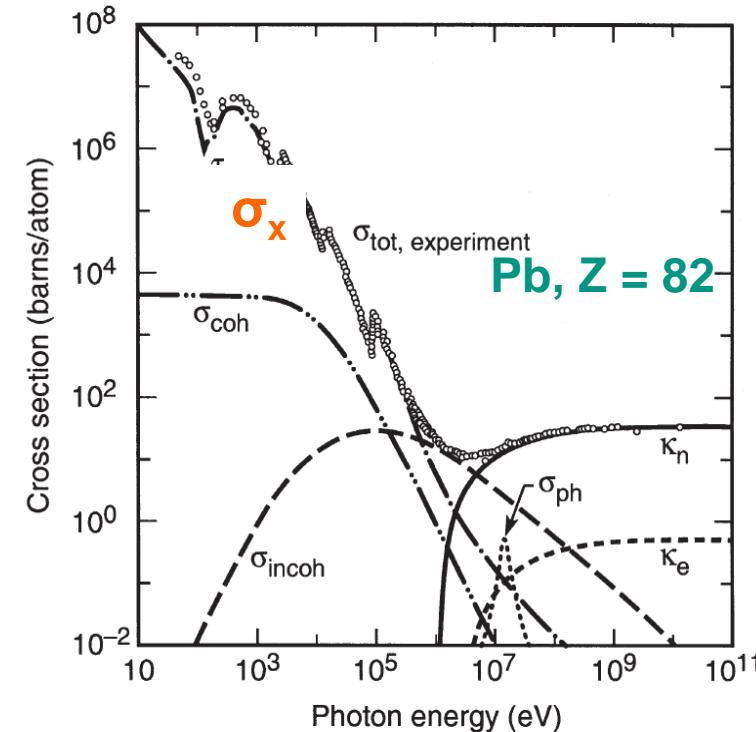
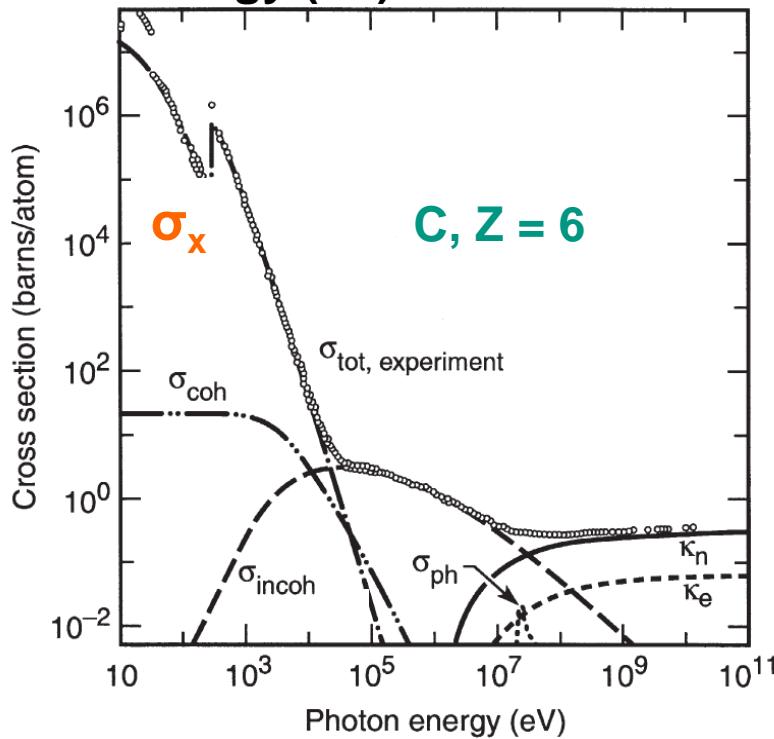
**European Summer School  
Radiochemistry and nuclear instrumentation  
(low level radioactivity) 21-25.08 2017**



- Basics of X-ray absorption spectroscopy**
- X-ray absorption near edge structure (XANES)**
- Extended X-ray absorption fine structure (EXAFS)**
- Experiment**

# Interaction of X-rays with matter

Cross section (barns/atom,  $1 \text{ cm}^2 = 10^{24} \text{ barn}$ ) as a function of photon energy (eV)



$\sigma_x$  – atomic photo-effect (electron ejection, photon absorption)

$\sigma_{coh}$  – coherent scatterings (Rayleigh scat.; atom neither ionized nor excited)

$\sigma_{incoh}$  – incoherent scattering (Compton scattering off an electron)

$\sigma_{ph}$  - photo nuclear absorption (e.g., followed by emission of a neutron)

$\kappa_n$  – pair production, nuclear field

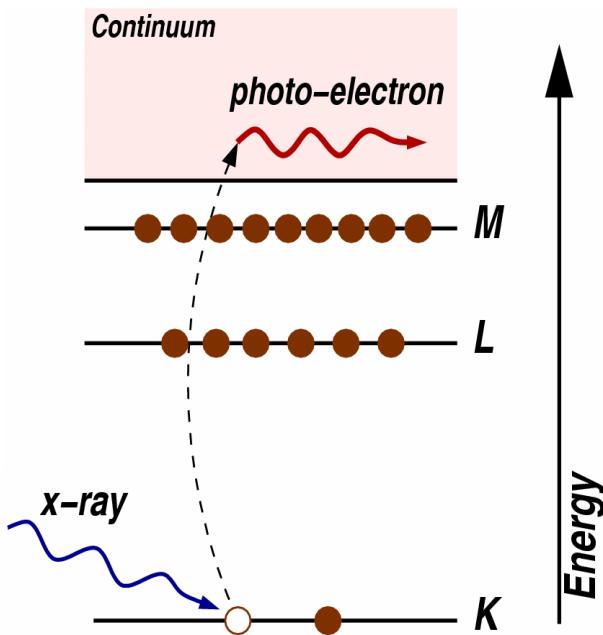
$\kappa_e$  – pair production, electron field

$\sigma_{tot}$  – total photon cross section

<http://xdb.lbl.gov/>

# Basics of X-ray absorption spectroscopy (XAS)

## Photo electric effect (Nobel Prize Einstein; 1921)



Atom absorbs a photon with energy  $E$  close to the binding energy of an electron in an atom

$$E = v h = hc/\lambda$$

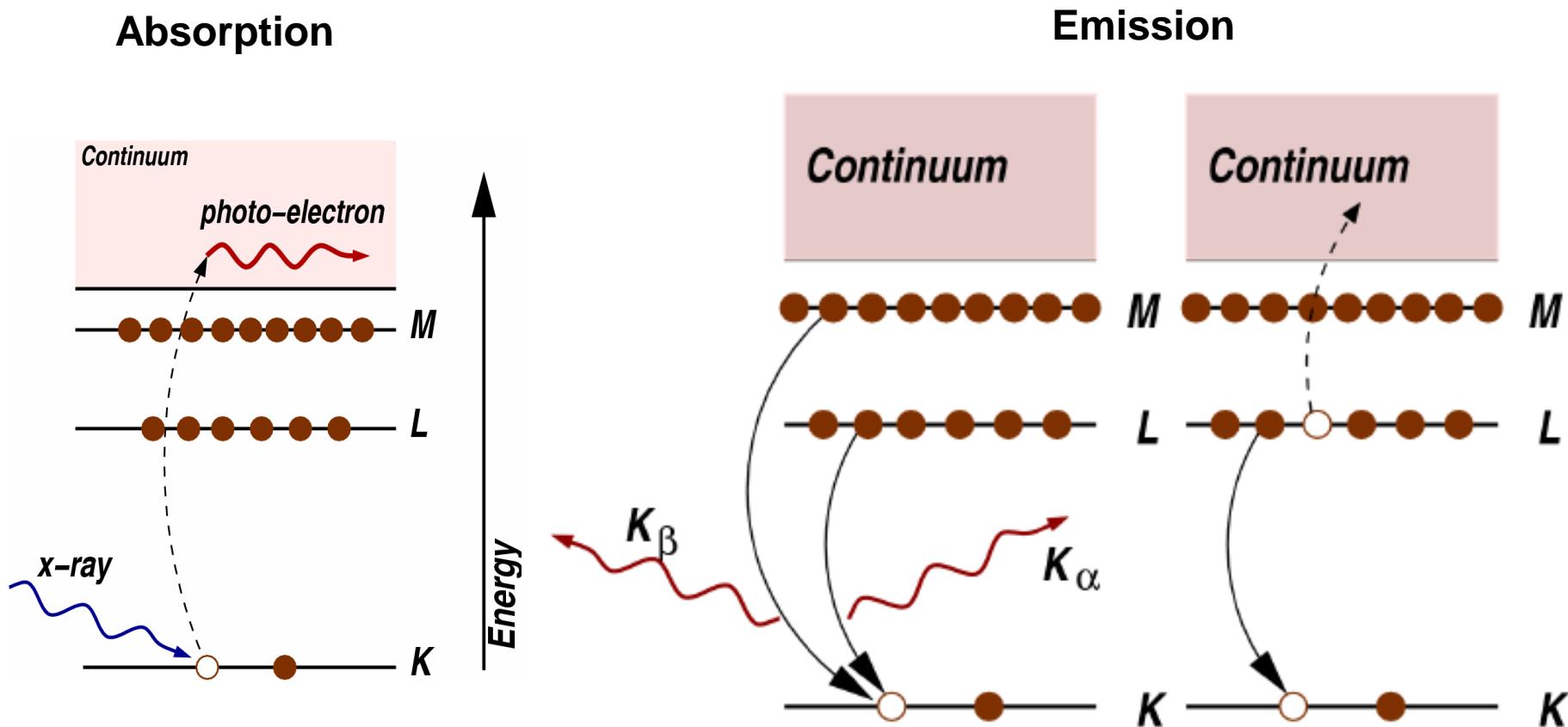
An electron in a tightly bound quantum core level is excited

*Matt Newville „The fundamentals of XAFS“, <http://xafs.org/Tutorials>*

# Basics of XAS

## Relaxation mechanisms of the atom

The excited atom relaxes by filling the core-hole with an electron from higher state (L/M..) and a photon ( $K_{\alpha}/K_{\beta} \dots$ ) /Auger electron is emitted.



*Matt Newville „The fundamentals of XAFS“, <http://xafs.org/Tutorials>*

### Nomenclature for Core Level Spectra

Orbital*	Label <sup>†</sup>	E <sup>‡</sup> (Ni)	E <sup>‡</sup> (O)
1s	K	8333	543
2s	L <sub>1</sub>	1008	42
2p <sub>1/2</sub>	L <sub>2</sub>	870	V <sup>§</sup>
2p <sub>3/2</sub>	L <sub>3</sub>	853	V <sup>§</sup>
3s	M <sub>1</sub>	111	
3p <sub>1/2</sub>	M <sub>2</sub>	68	
3p <sub>3/2</sub>	M <sub>3</sub>	66	
3d <sub>3/2</sub>	M <sub>4</sub>	V	
3d <sub>5/2</sub>	M <sub>5</sub>	V	

The absorption edges are named according to the principle quantum number of the excited electron

\* Orbital notation.

† Spectroscopic names (Barkla notation).

‡ Binding energies.

§ Valence state with a binding energy of a few eV.

Source: X-ray Data Booklet (2001) (LBNL, Berkeley).

K-edge: 1s initial state ( $n=1, l=0$ )  
L<sub>1</sub>-edge: 2s initial state ( $n=2, l=0$ )  
L<sub>2</sub>-edge: 2p ( $j=1/2$ ) initial state ( $n=2, l=1$ )  
L<sub>3</sub>-edge: 2p ( $j=3/2$ ) initial state ( $n=2, l=1$ )

# Basics of XAS

The absorption near edge structure is angular momentum selective

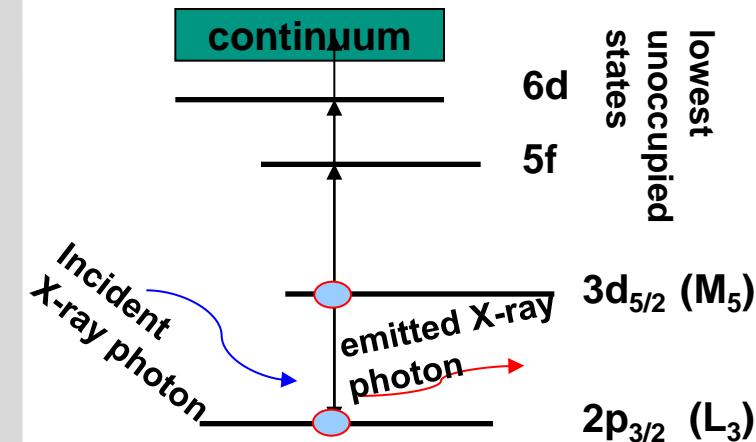
Dipole selection rule:

change in angular momentum quantum number

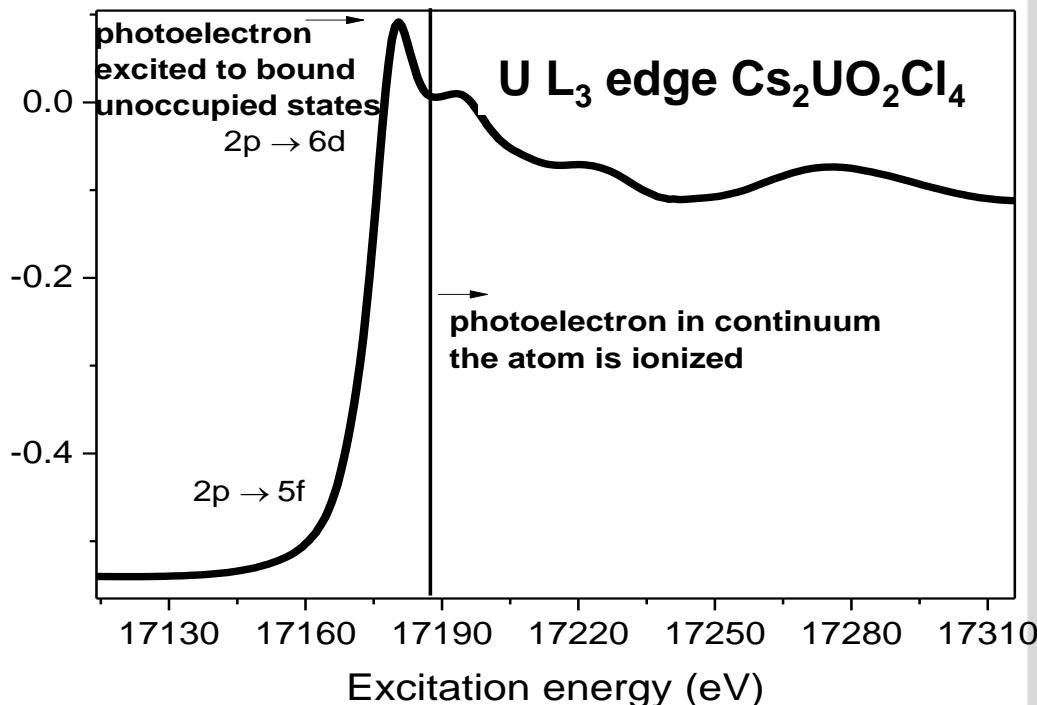
$\Delta l = \pm 1, \Delta j = 0, \pm 1$ : high-transition probability

$\Delta l = \pm 0, 2$ : quadrupole transition: low transition probability

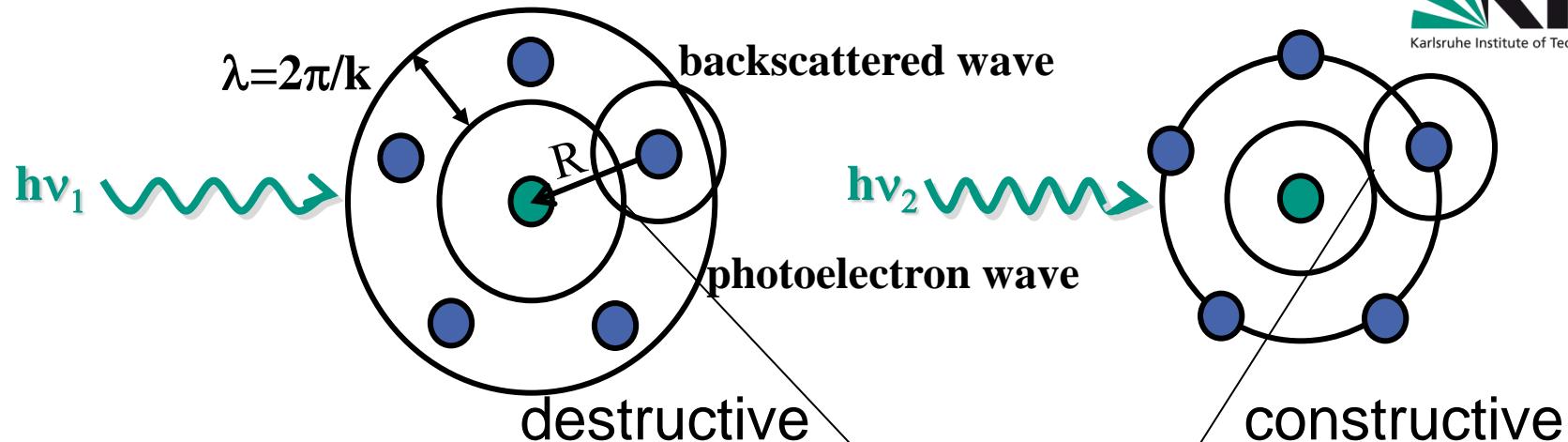
U(VI): valence configuration  $5f^0$



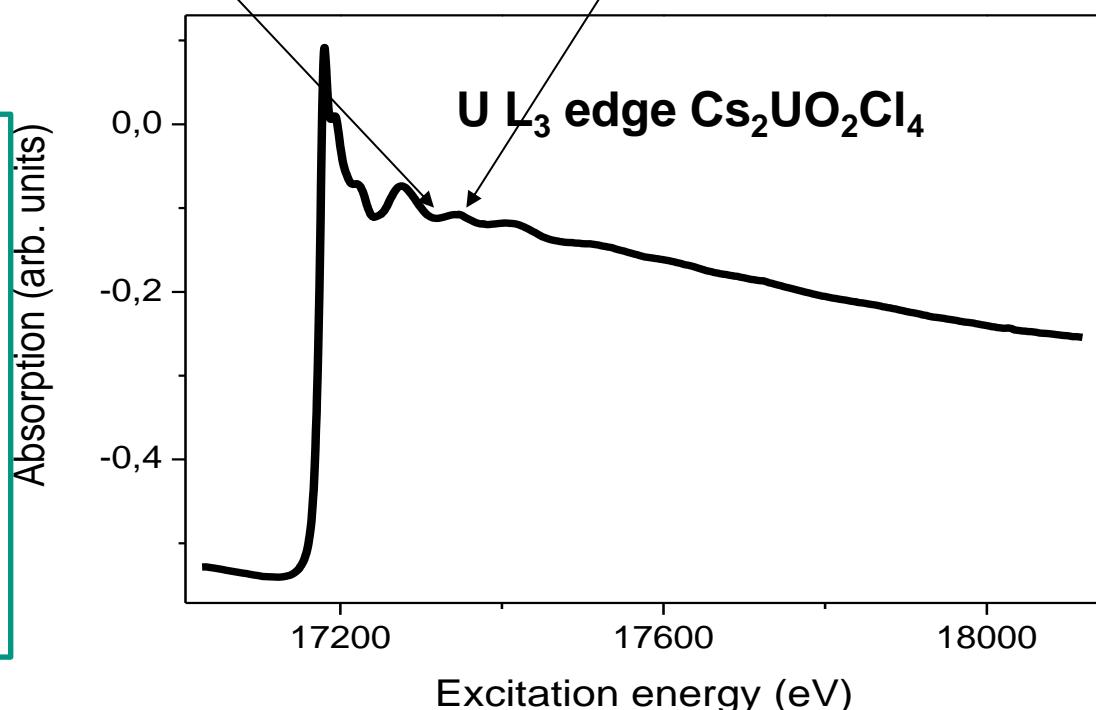
Absorption (arb. units)



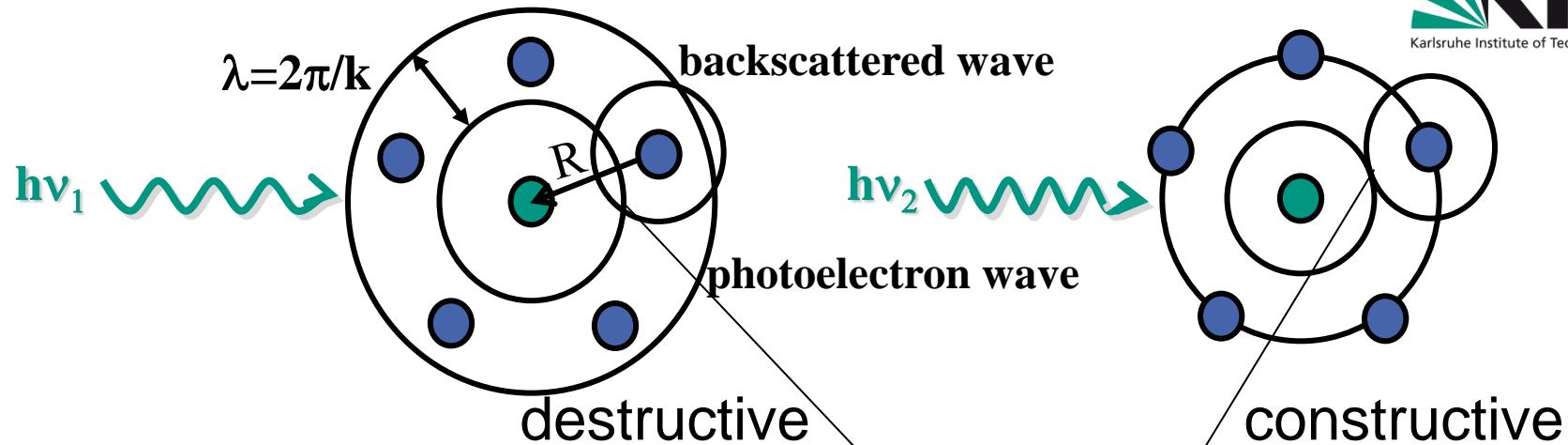
XAFS = X-ray absorption fine structure



The emitted photoelectron can be described as a spherical wave, which scatters from the surrounding atoms; the incoming and outgoing waves interfere constructively or destructively and as a result the absorption intensity is modulated



# Basics of XAS

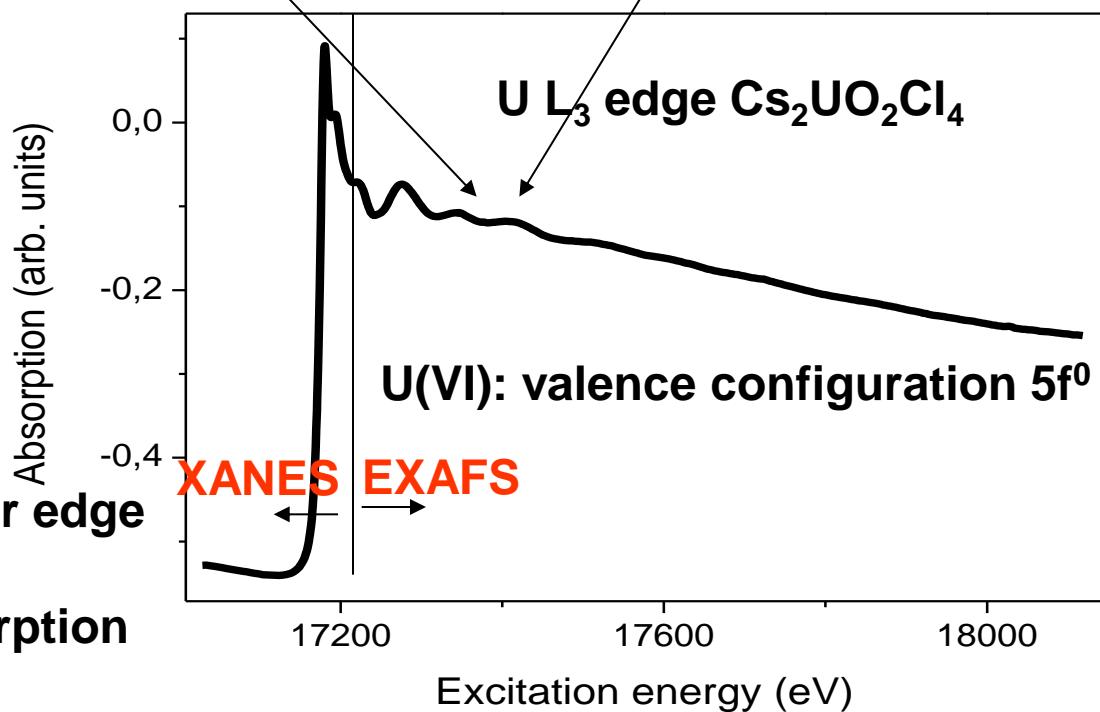


**XAFS:** X-ray absorption fine structure

**XAFS = XANES + EXAFS**

**XANES:** X-ray absorption near edge structure

**EXAFS:** Extended X-ray absorption fine structure





## Absorption in transmission mode:

**Beer-Lambert Law**

$$I_t = I_o e^{-\rho \mu_m x}$$

$$\mu \equiv \rho \mu_m x = \ln\left(\frac{I_o}{I_t}\right)$$

## Absorption in fluorescence mode:

$$\mu \sim I_{\text{fluo}} / I_0$$

$\mu_m$ : mass absorption coefficient

$\rho$ : density

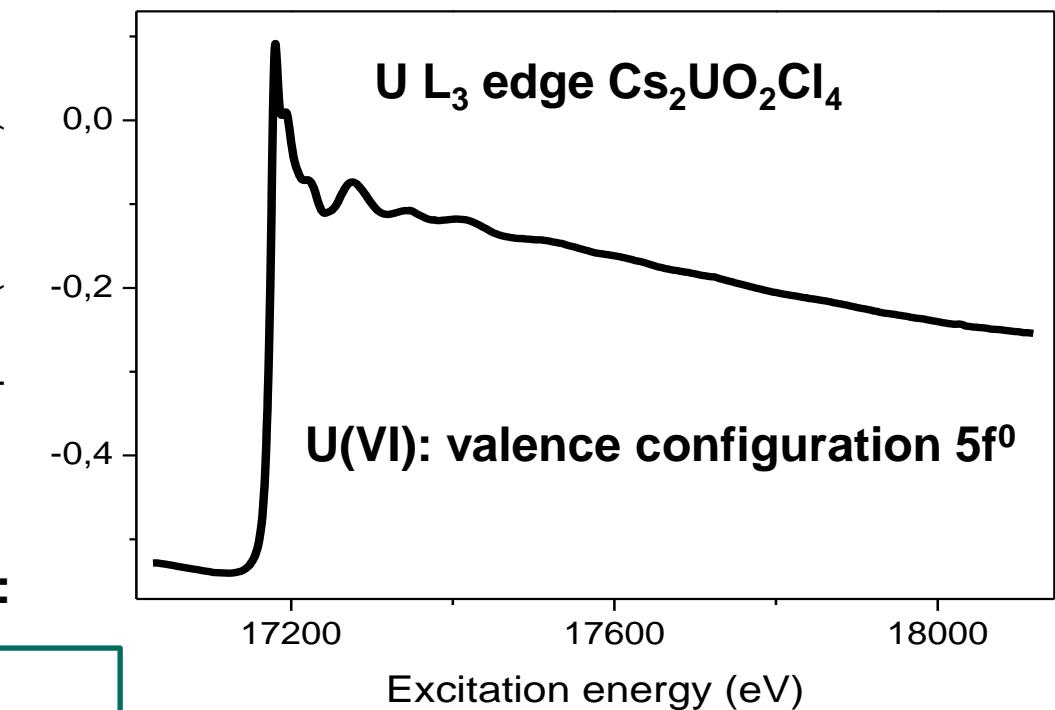
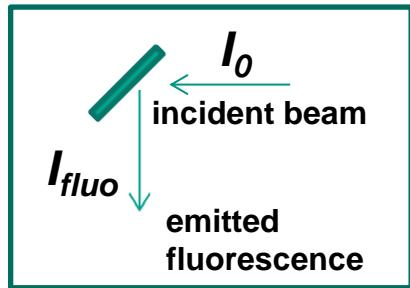
$\mu$ : absorption

$x$ : thickness of sample

$I_0$ : incident X-ray intensity

$I_t$ : transmitted X-ray intensity

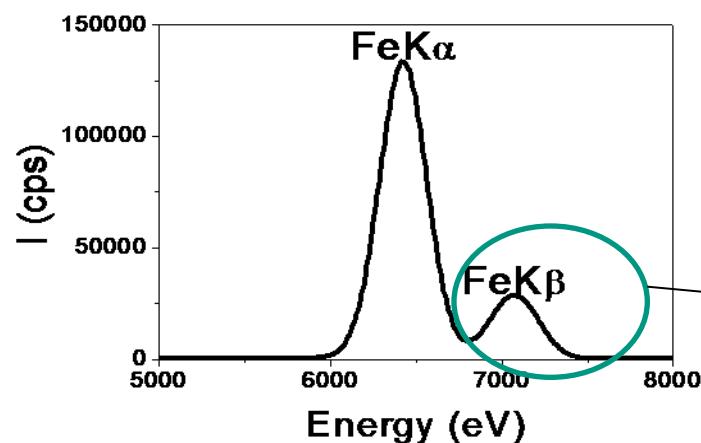
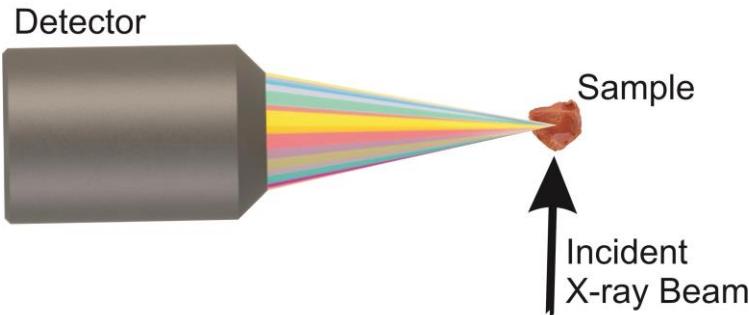
$I_{\text{fluo}}$ : intensity of emitted fluorescence



**The XAFS spectrum measures the absorption intensity ( $\mu$ ) as a function of the energy of the incident X-ray photon**

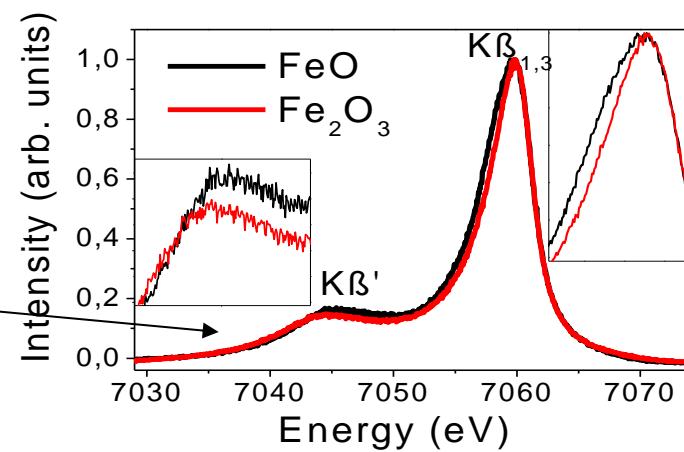
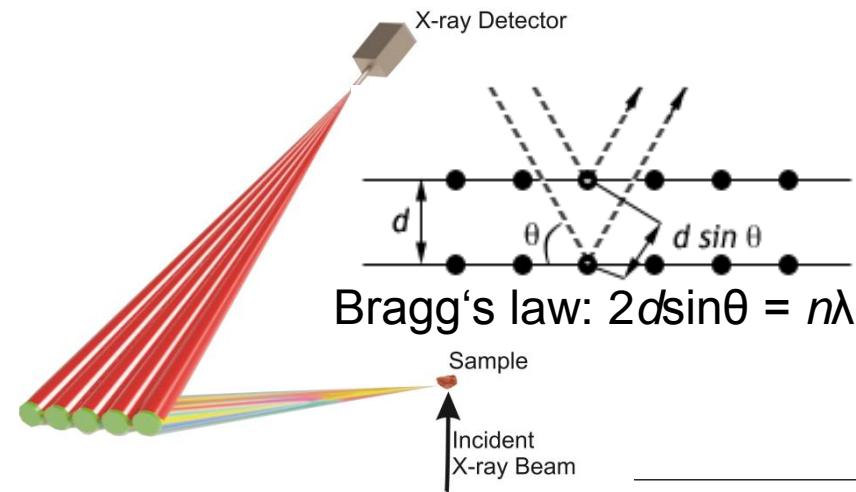
# **Basic principles of High energy resolution-X-ray emission spectroscopy (HR-XES)**

## Conventional fluorescence mode set-up

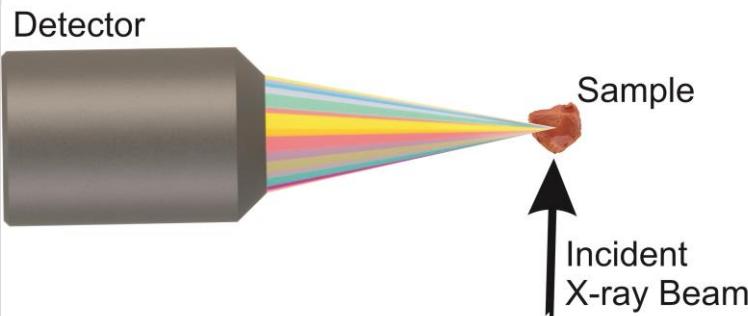


**FWHM >110 eV**

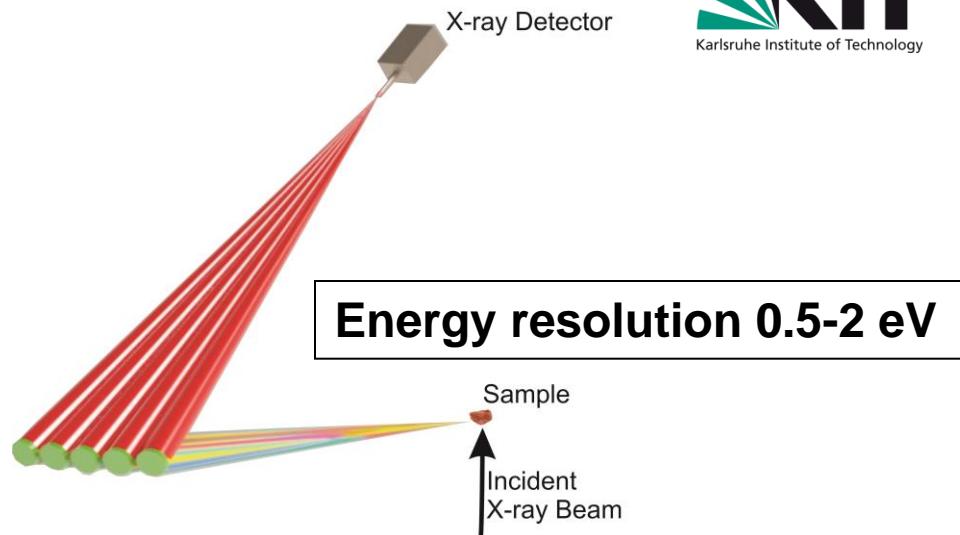
## High-resolution fluorescence mode set-up



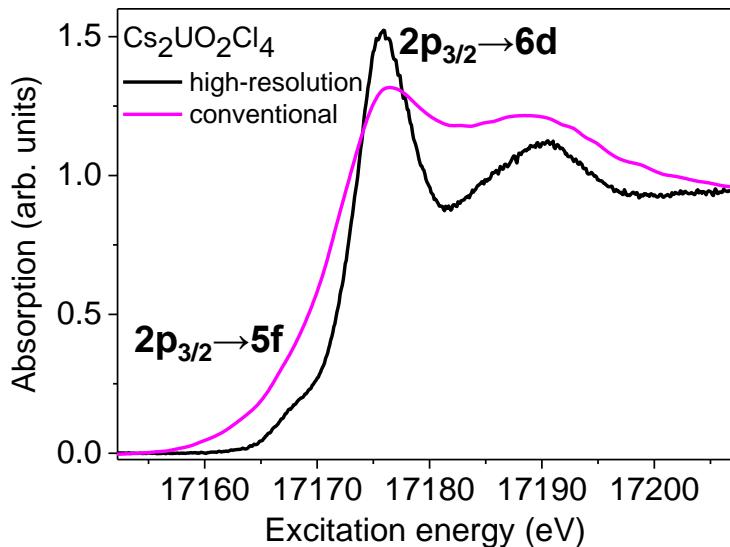
**FWHM <5 eV**



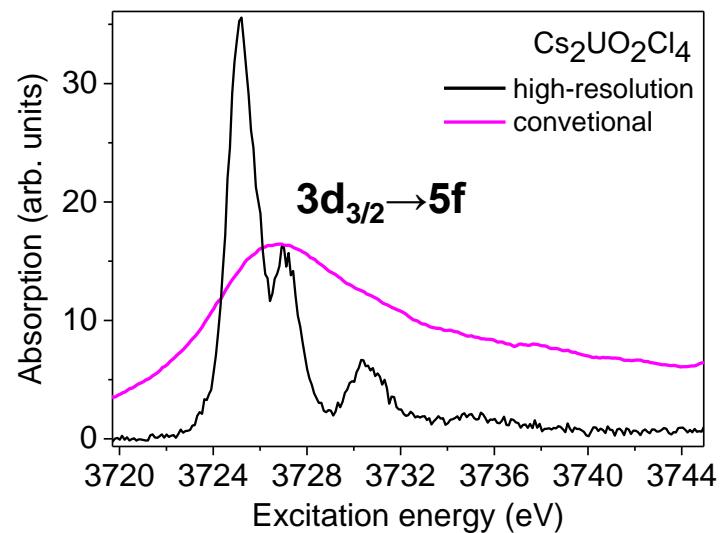
**Energy resolution > 100 eV**



## $\text{U}^{6+}: 5\text{f}^0 6\text{d}^0$ U L<sub>3</sub> edge XANES



## U M<sub>4</sub> edge XANES

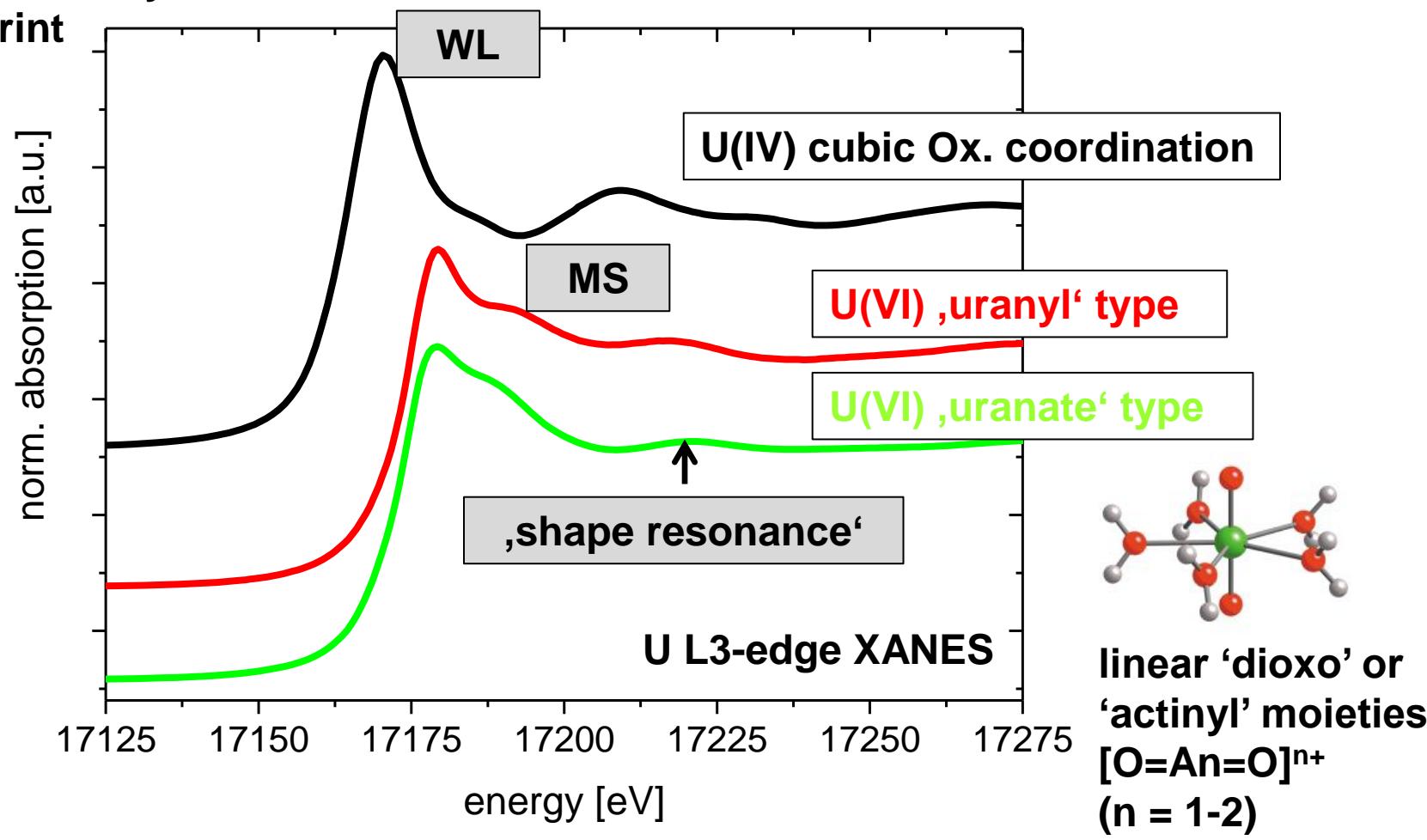


T. Vitova et al. PRB 82, (2010) 235118; Inorg. Chem. 2015, 54, 174; Nature Communication 8, (2017) 16053

# XANES

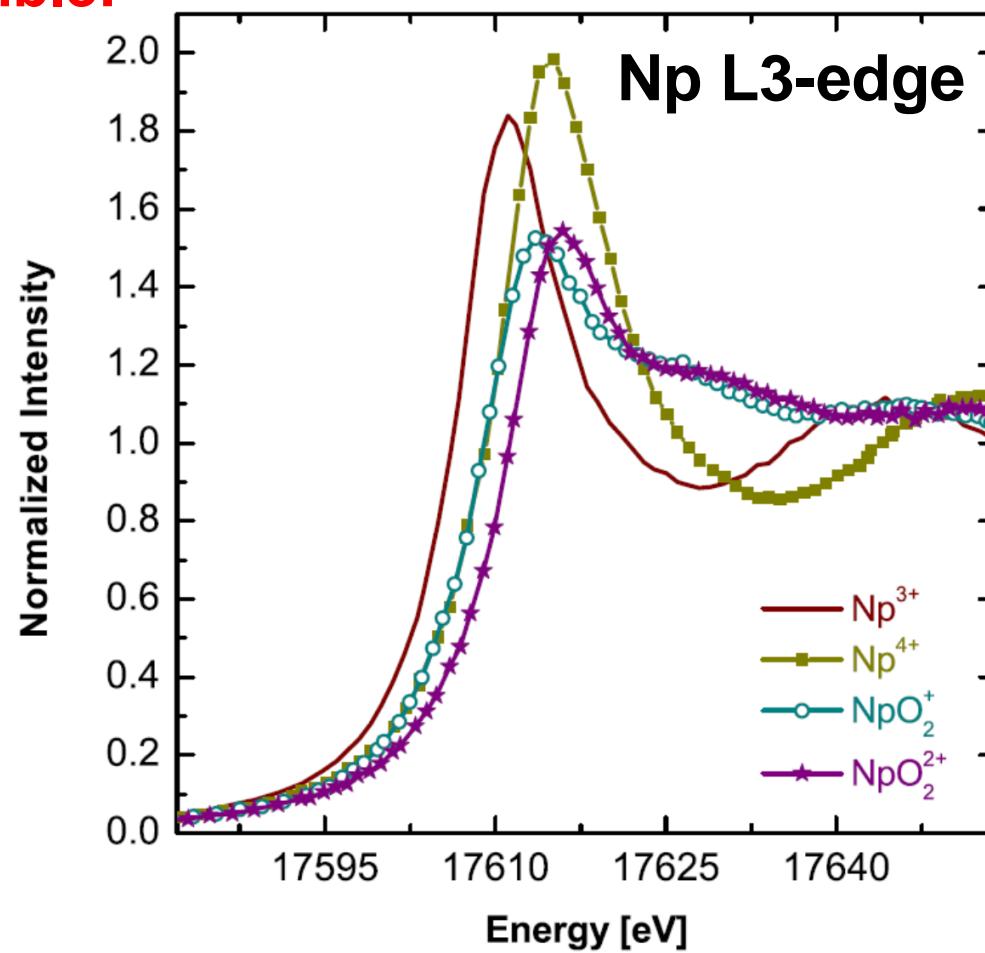
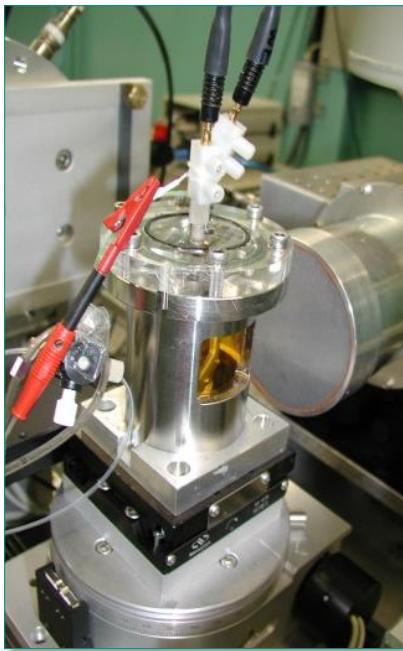
XANES is sensitivity to oxidation state and local structure of the absorbing atom

actinide / actinyl /actinate  
fingerprint



e.g.: S. Conradson, P. Allen, M. A. Denecke

In-situ speciation possible:

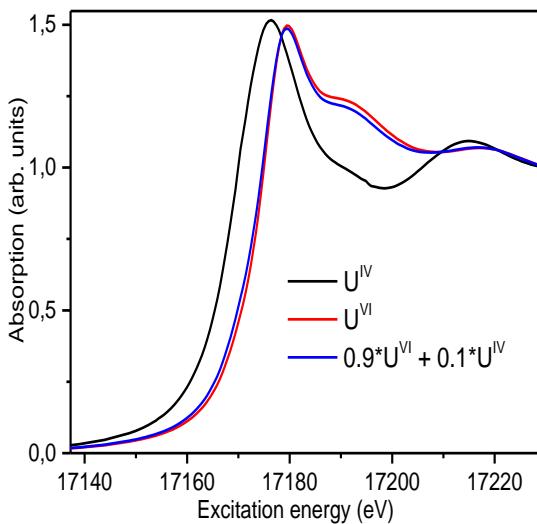


Np L<sub>3</sub>-XAFS /  
electrochemistry,  
ANKA INE-BL

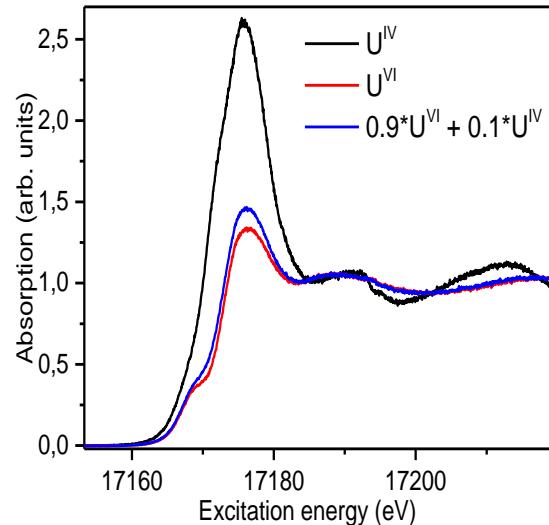
X. Gaona et al., Radiochimica Acta, 100 (2012)

759

## $U\text{ L}_3$ edge XANES

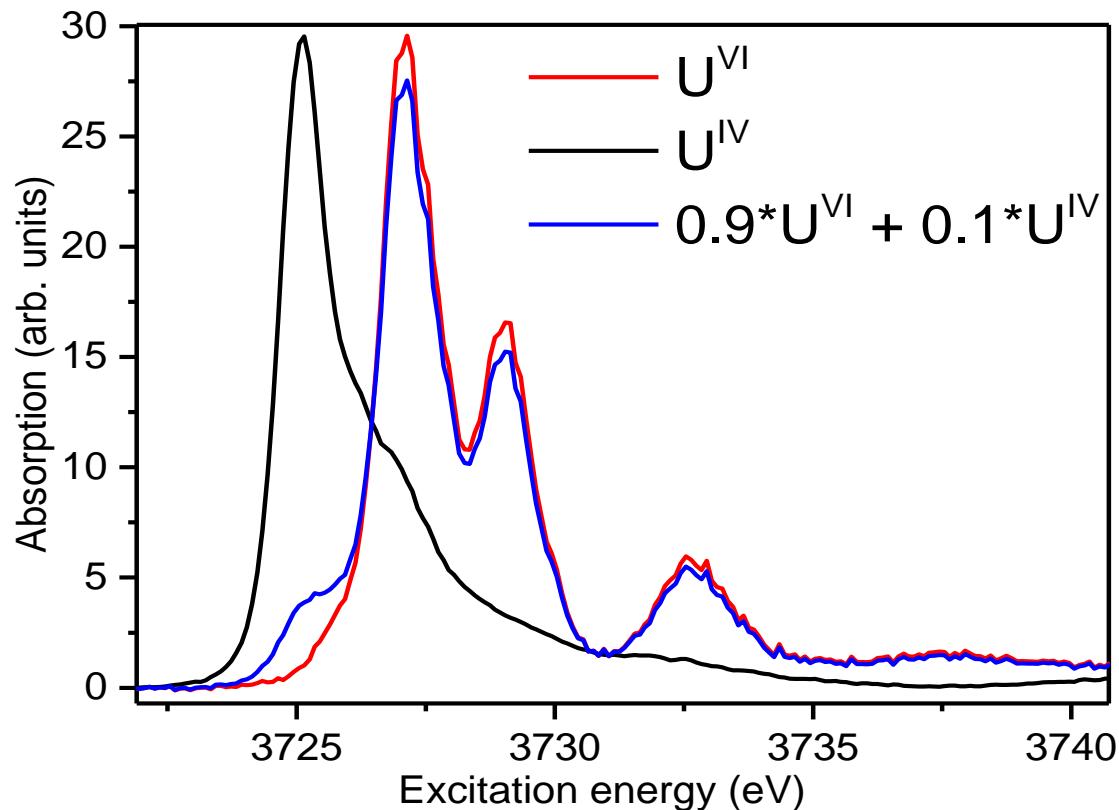


## $U\text{ L}_3$ edge HR-XANES

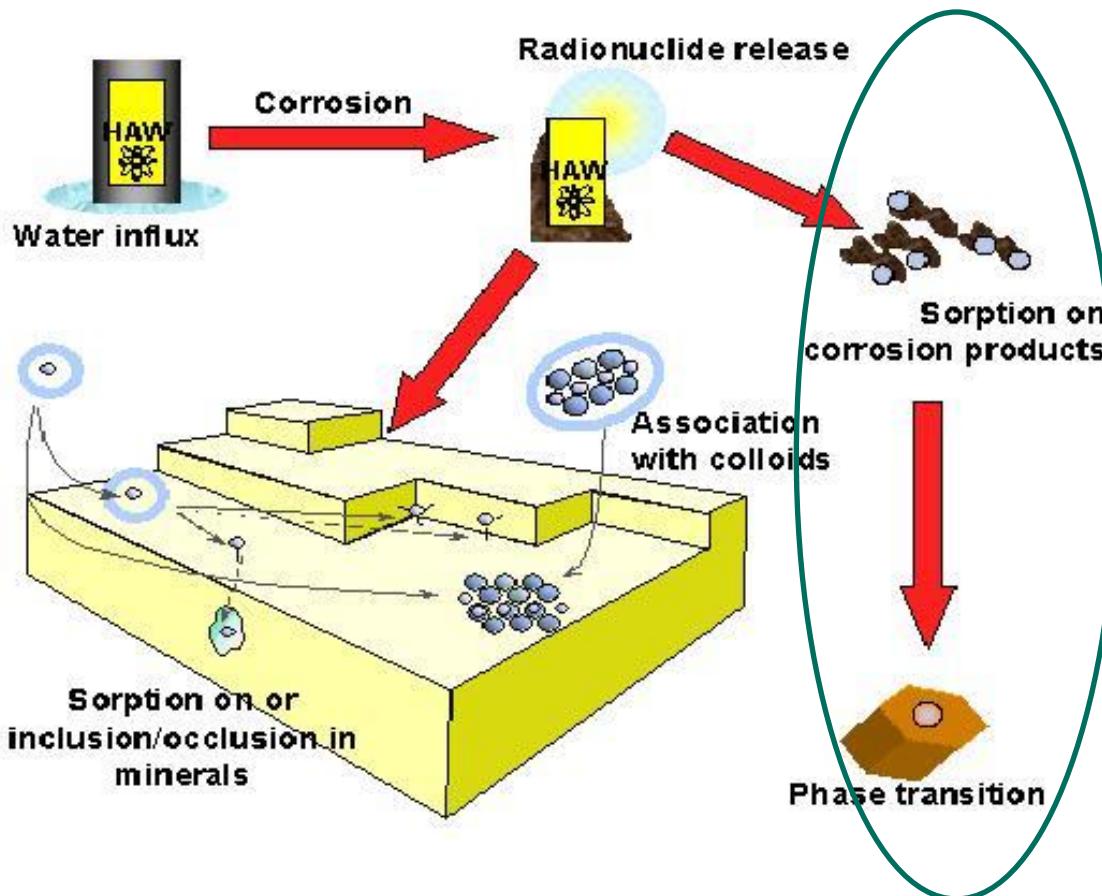


**U  $\text{L}_3$  or U  $\text{M}_4$  HR-XANES is more sensitive to U oxidation states?**

## U $\text{M}_4$ edge HR-XANES



# Mechanisms of U<sup>VI</sup> interaction with magnetite

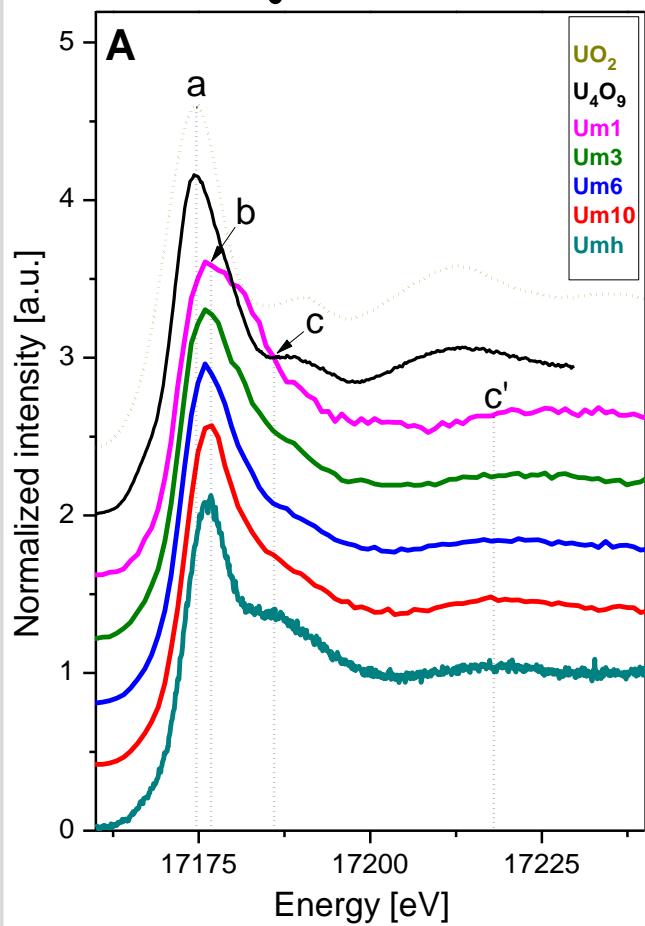


- Iron oxides can form on corroded canister walls and interact with radionuclides released from waste forms
- Reduction mechanisms of U by Fe<sup>II</sup> present in Fe<sub>3</sub>O<sub>4</sub> (magnetite)?

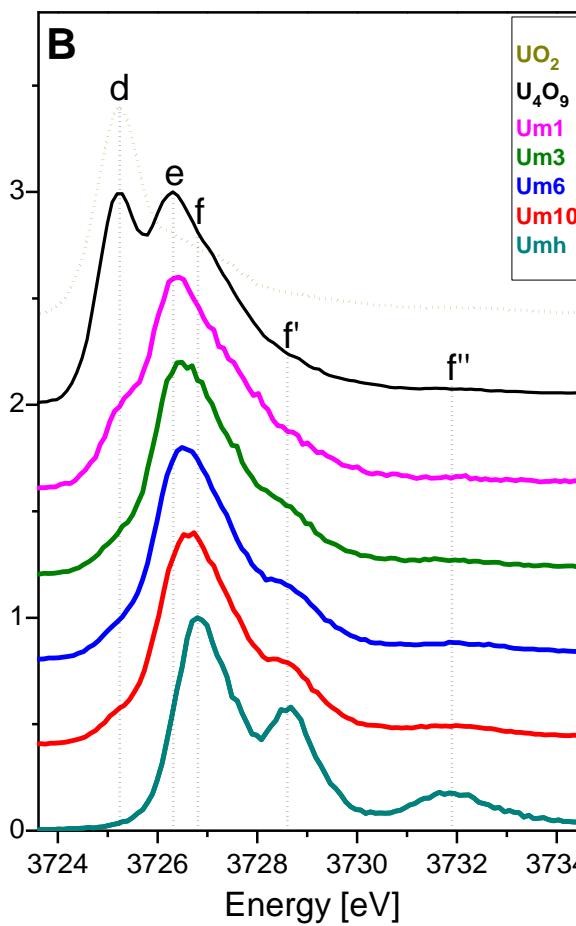
U<sup>V</sup> stabilized in presence of magnetite is assumed but unambiguous detection remains difficult:

Reliable redox form speciation methods needed

## U L<sub>3</sub> HR-XANES



## U M<sub>4</sub> HR-XANES



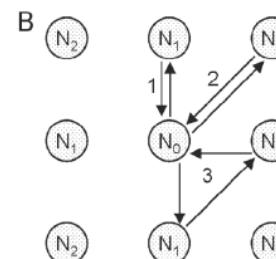
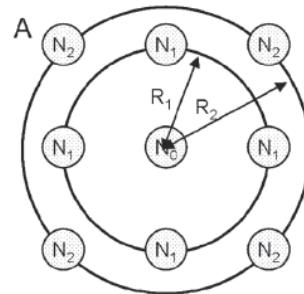
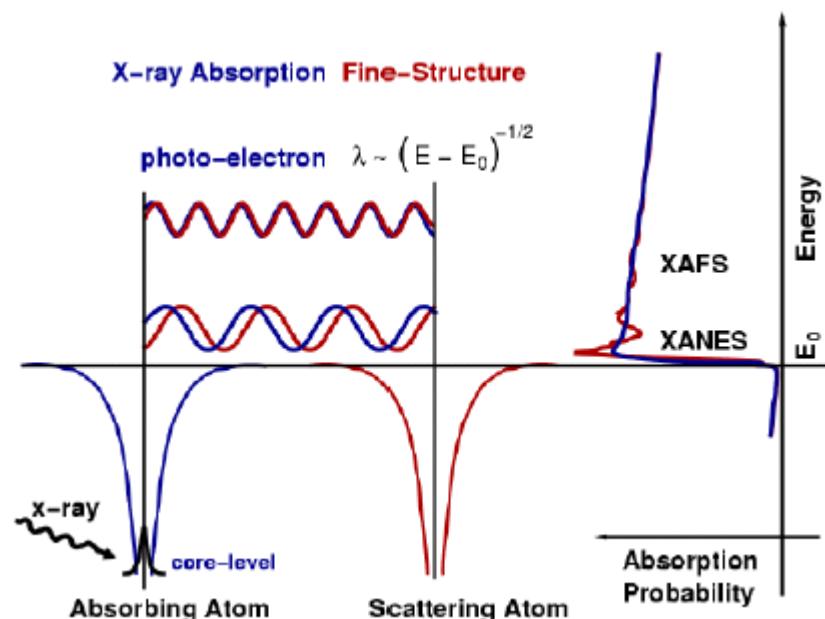
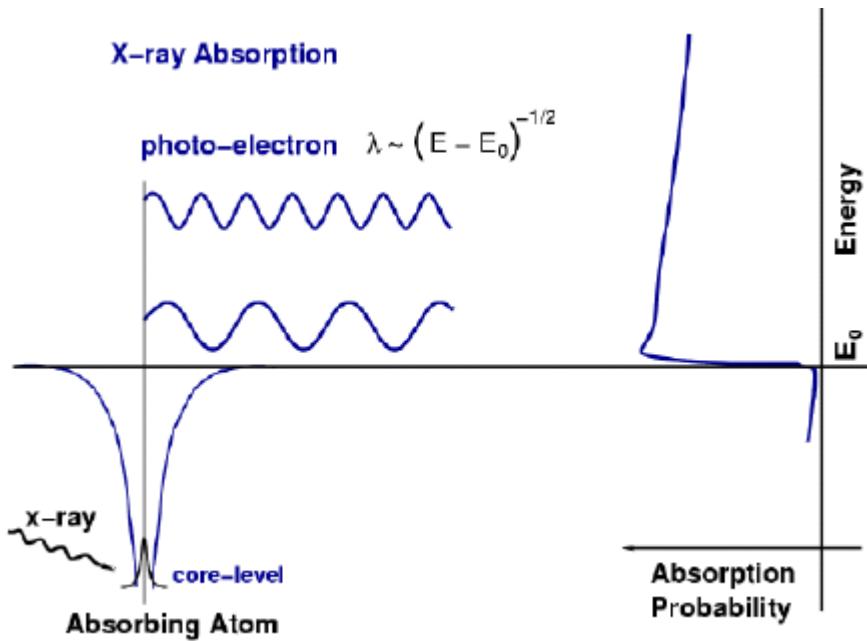
**Only U M<sub>4</sub> HR-XANES detects:**

- $U^{IV}$ ,  $U^V$  and  $U^{VI}$  in the same sample
- Increase of  $U^{VI}$  with total U concentration

# X-ray absorption fine structure (XAFS)

## X-ray absorption near edge structure (XANES)

## Extended X-ray absorption fine structure (EXAFS)

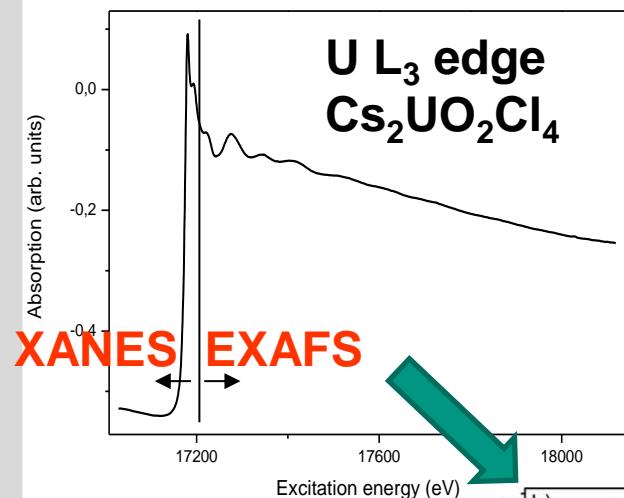


**A:** coordination spheres marked with circles and radius  $R1$  or  $R2$   
**B:** single (1, 2) and multiple scattering paths (3)

Tutorial of Bruce Ravel:

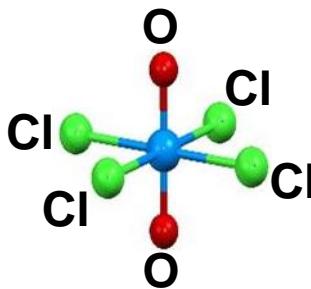
<https://github.com/bruceravel/XAS-Education/downloads>

# Extended X-ray absorption fine structure (EXAFS)



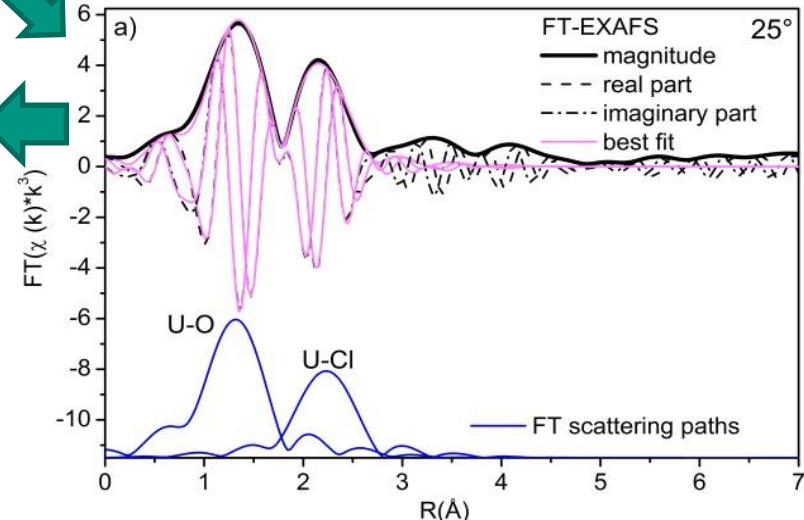
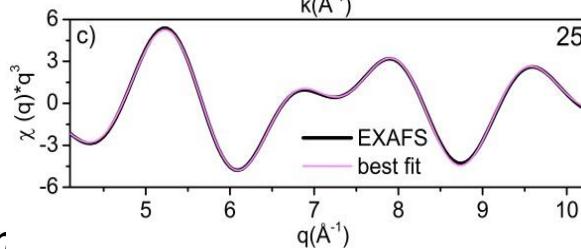
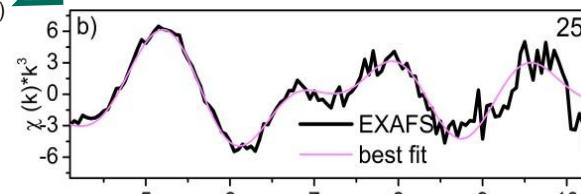
## What can we learn from EXAFS?

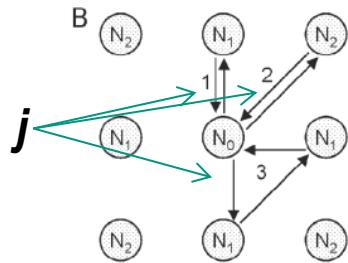
- ❖ Interatomic distances ( $\Delta R \pm 0.02 \text{ \AA}$ )
- ❖ Type ( $\Delta Z \pm 5$ ) and number of near neighboring atoms ( $\Delta N \pm 50\%$ )
- ❖ Structural disorder
- ❖ Short range atomic order (5-10  $\text{\AA}$ )



Circles: coordination.  
spheres with different  
radius

Arrows: single and  
multiple scattering paths





$$\chi(k) = \frac{S_0^2}{k} \ell^{-1} \sum_j N_j |f_j(k, \pi)| \frac{e^{-2Rj/\lambda(k)}}{R_j^2} e^{-2k^2\sigma^2} \sin \{2kR_j + 2\Phi_{ca}(k) + \Phi_j(k, R_j)\}$$

$|f_j(k, \pi)|$

**backscattering amplitude**

$2\Phi_{ca}(k) + \Phi_j(k, R_j)$

**total phase shift**

$S_0^2$

**amplitude reduction factor**

$\lambda(k)$

**mean free path length**

$\sigma^2$

**mean square displacement (Debye-Waller)**

$N$

**coordination number**

$R$

**path length**

**Calculated  
with the FEFF  
code**

**Determined  
by modeling the  
experimental  
spectrum**

Popular data analyses program package: <https://bruceravel.github.io/demeter/>

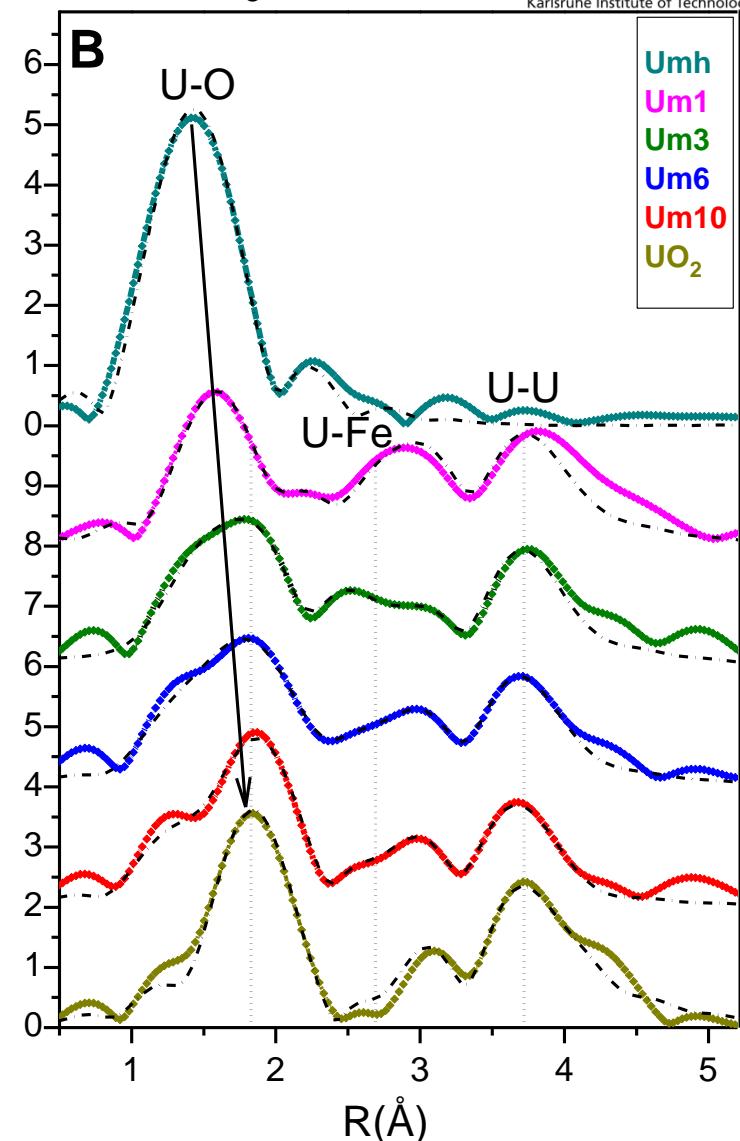
FEFF code: <http://monalisa.phys.washington.edu/feffproject-feff.html>

# $U^{VI}$ co-precipitated with magnetite: after 147 days

UL<sub>3</sub> EXAFS



- Non-stoichiometric  $UO_{2+x}$  nanoclusters
- $U^{VI}$  incorporates in octahedral Fe sites



I. Pidchenko et al., Environ. Sci. Technol. 51 (2017) 2217

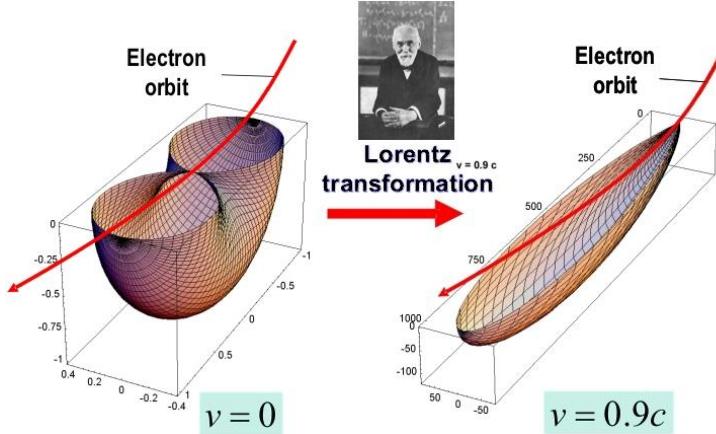
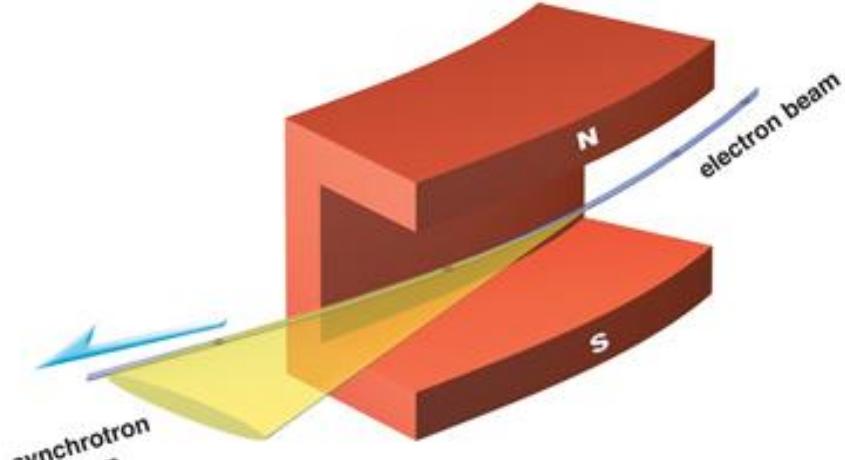
## Generation of “Synchrotron Radiation”



**electro- (bending) magnet**

■ Deflection of relativistic ( $v$  approx.  $c$  !) electrons by magnetic fields:

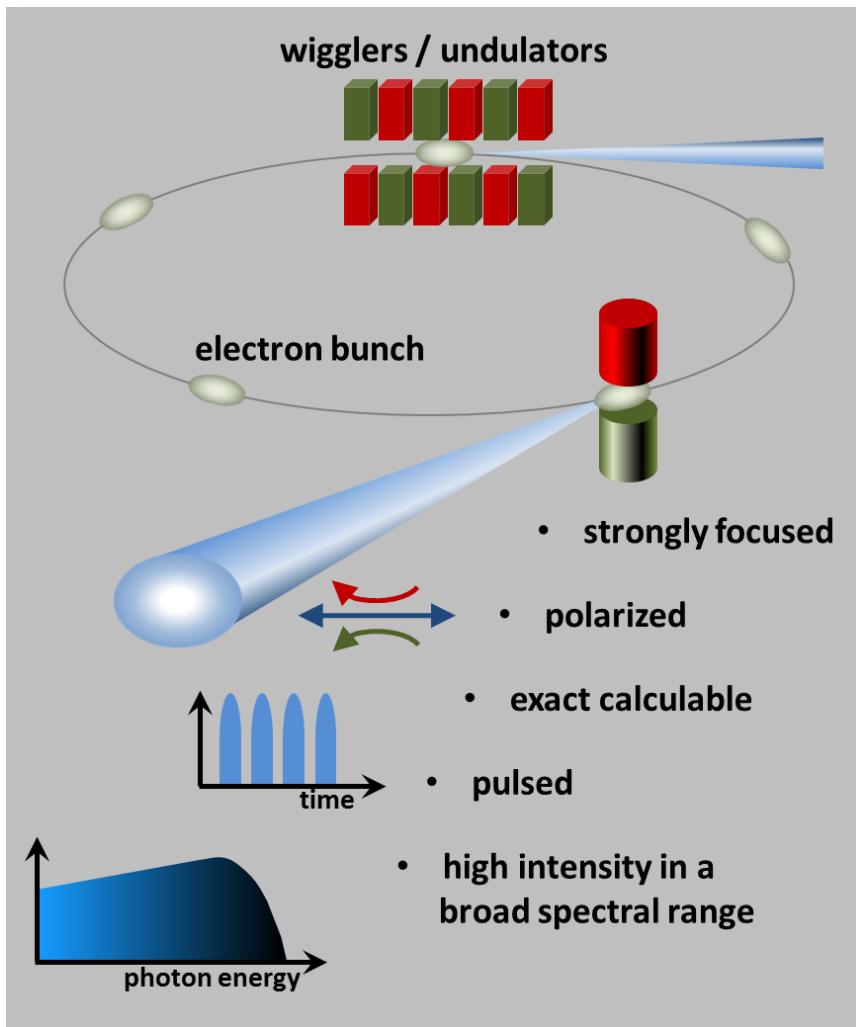
$$\text{Lorentz force } \vec{F} = q\vec{v} \times \vec{B}$$



Synchrotron light...

...has many colors!





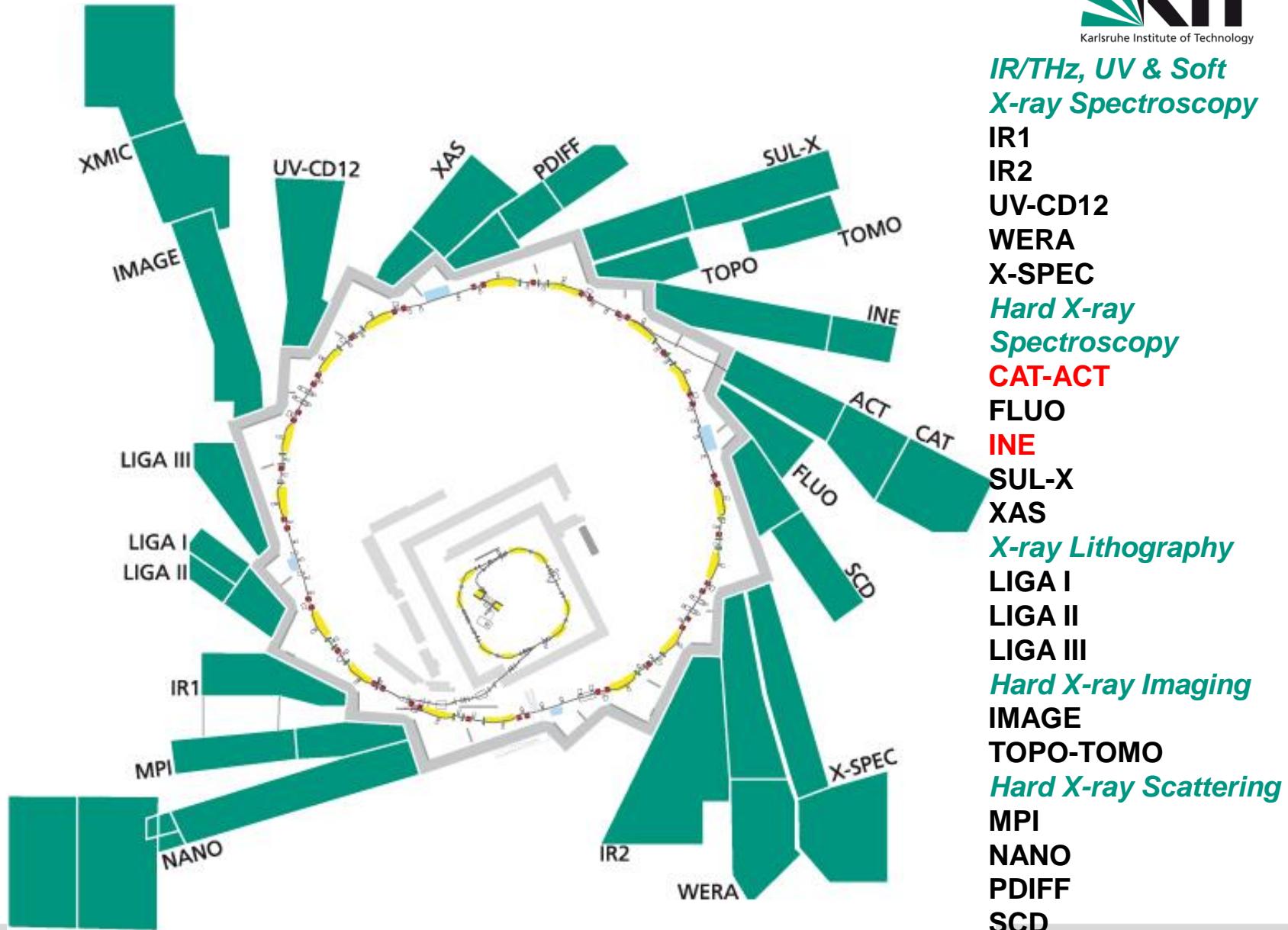
## Properties of Synchrotron Radiation:

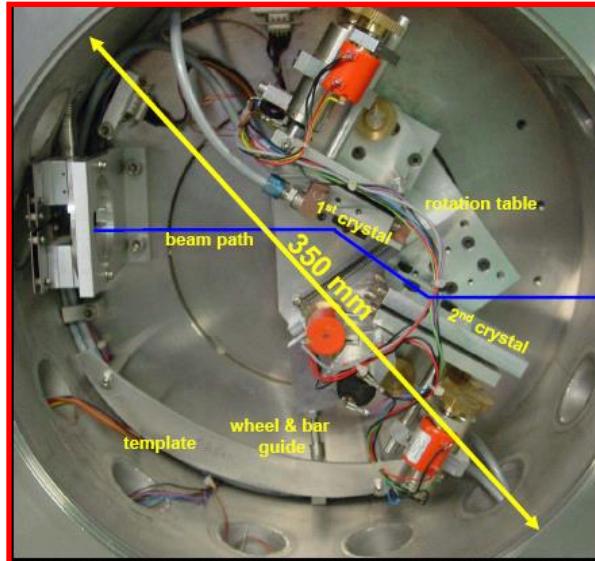
- Broad spectral range from infrared/THz to hard X-rays
- High intensity and brilliance
- Strongly focused in forward direction of electron path
- Polarized
- Partially coherent (correlated phase)



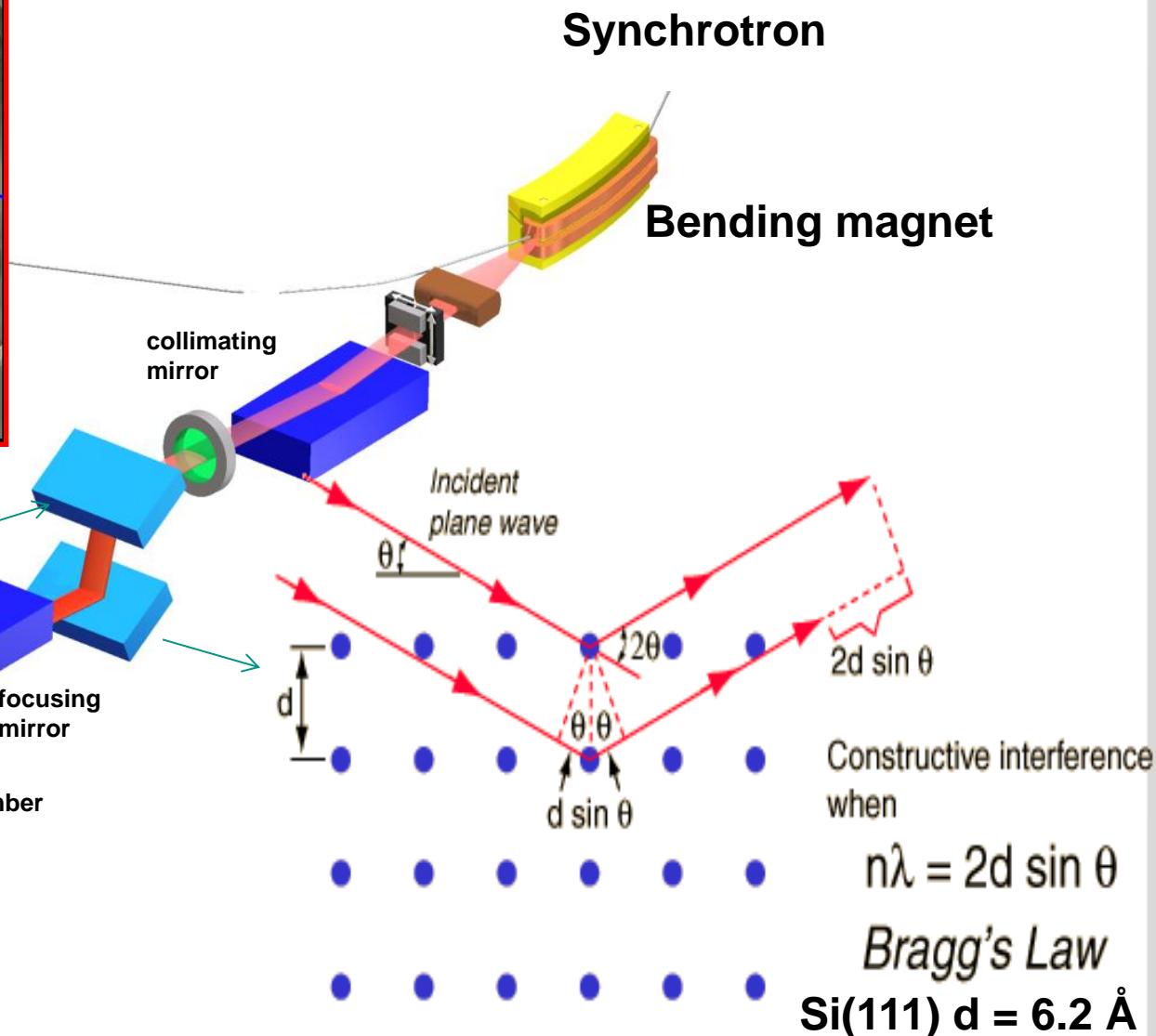
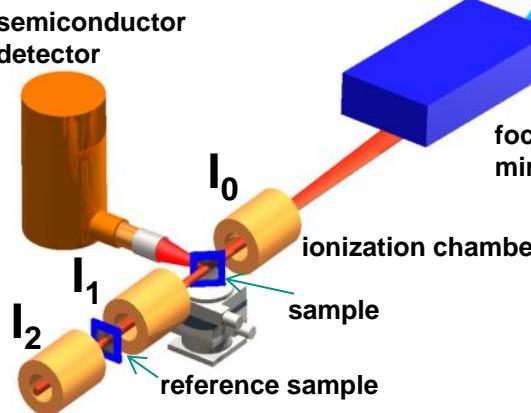
**Model of the Ångström-Source KArlsruhe  
ANKA ( $1\text{\AA} = 10^{-10}\text{ m}$ )**

# Synchrotron radiation: ANKA

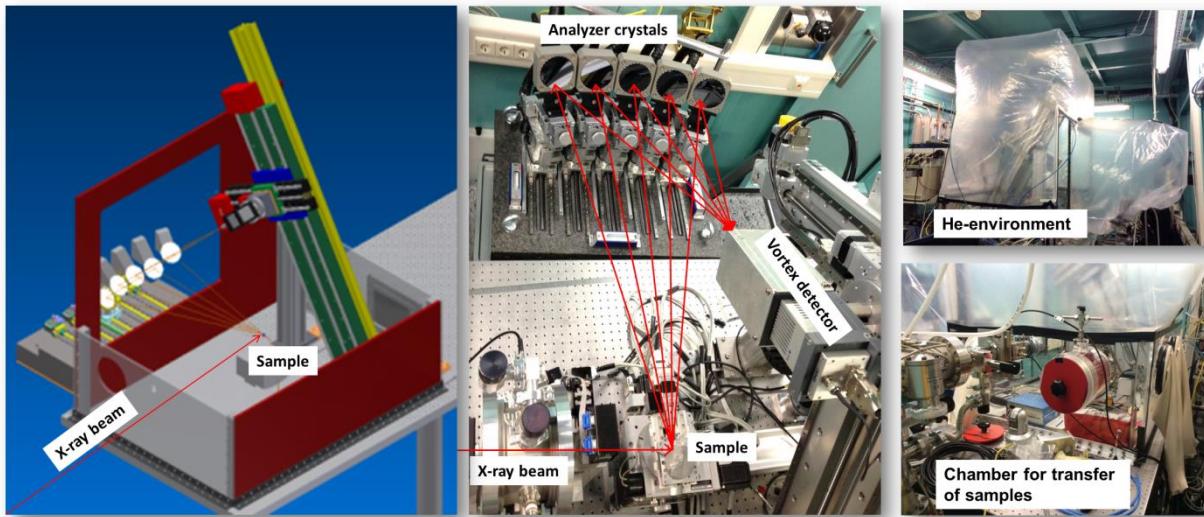




**Double crystal monochromator (DCM)**



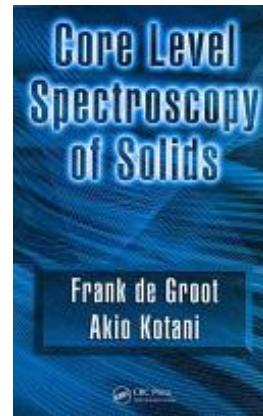
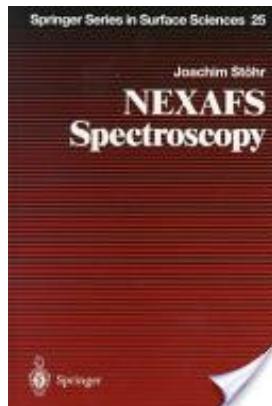
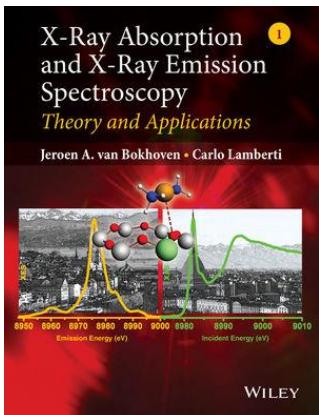
# High energy resolution X-ray emission spectrometer at the CAT-ACT Beamline, ANKA, KIT, Karlsruhe, Germany



J. Rothe et al, Rev. Sci. Instrum. 83 (4) (2012) 043105, A. Zimina et al., Rev Sci Instrum 2017, submitted

The X-ray absorption fine structure (XAFS) spectrum is

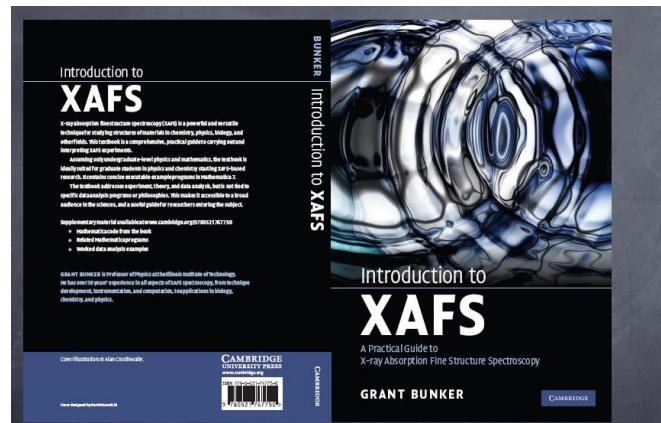
- 1) Element selective:** every atom of a selected element is probed
  - 2) (usually) Bulk sensitive and non-destructive**
  - 3) Sensitive to oxidation state and local symmetry of the probed atom**
  - 4) Sensitive to short range (5-10 Å) order around the probed atom (EXAFS)**
  - 5) Sensitive often and to long range order (XANES)**
  - 6) Allows qualitative and quantitative analyses**
  - 7) Allows *in-situ* investigations: following a chemical reaction, variations of temperature/pressure, time-resolved experiments etc.**
  - 8) INE-Beamline: 1000 ppm (EXAFS), 100 ppm (XANES)  
CAT-ACT Beamline: 100 ppm (EXAFS)**
- ...



See tutorials in:  
[www.xafs.org](http://www.xafs.org)

For example from:  
Bruce Ravel  
Matt Newville  
Shelly Kelly  
Grant Bunker...

<http://onlinelibrary.wiley.com/book/10.1002/9781118844243>



- Kelly, S D, Hesterberg, D and Ravel, B. Analysis of soils and minerals using X-ray absorption spectroscopy. In *Methods of soil analysis, Part 5 -Mineralogical methods*; Ulery, A. L., Drees, L. R., Eds.; Soil Science Society of America: Madison, WI, USA, 2008; pp 367.