Introduction to high-energy-resolution X-ray spectroscopies

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BME Physics

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1. Introduction

Literature:

- Vankó György: A szinkrotronsugárzás újszerű kémiai alkalmazásai: nagyfelbontású röntgenspektroszkópia - A kémia újabb eredményei 100. (Budapest, 2008)

By X-ray spectroscopies here I mean…

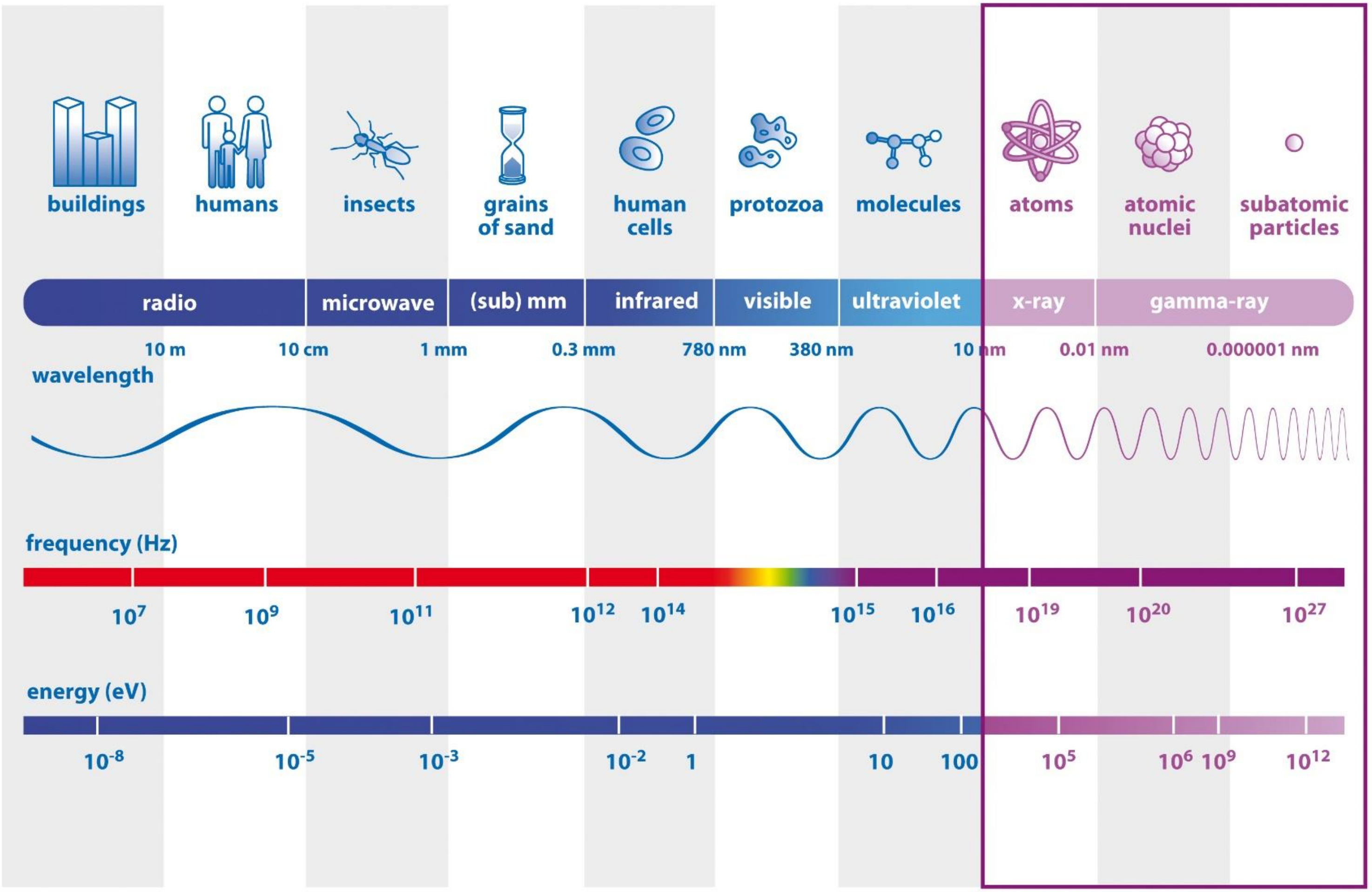
- Typically hard X-rays: 4-20 keV
  (but: soft X-rays below 1kV and tender regime between soft and hard)

- Absorption and emission of X-ray photons

- High energy resolution: better than the natural broadening of the signal

- Can be used with high spatial resolution
- Can be used with high time resolution
- Can be used to probe magnetic polarization

Spectroscopy with (hard) X-rays

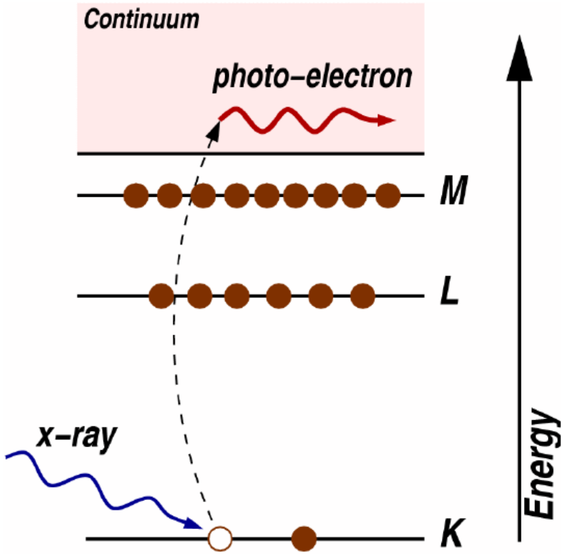


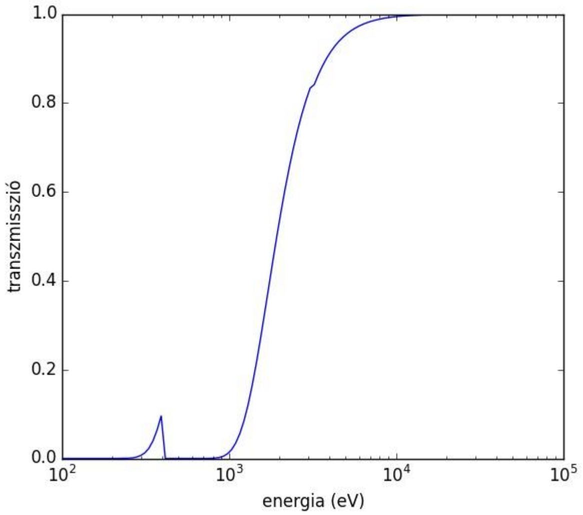
NMR (δ) FTIR (cm^{-1}) X-ray spectroscopies (eV)

FTMW (MHz) UV-Vis (nm) Mössbauer spectroscopy (mm/s)

Hard X-rays

- Typically: photoexcitation of core electrons of 3d/4d metals (e.g. 1s orbital of Fe is 7112 eV, http://xdb.lbl.gov/)
- Elemental selectivity: energy resolution is 2 orders of magnitude better that the distance between 2 absorption edges
- High penetration depth (bulk *vs.* surface)
- Gas phase, liquids, solids
- Not sensitive to air ↔ UPS, XPS, soft X-rays
- But similar methodology for soft or tender X-rays which work for low Z elements like C, N, O or S, Cl, P

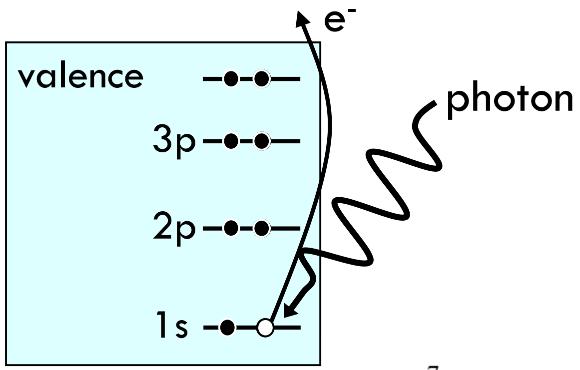


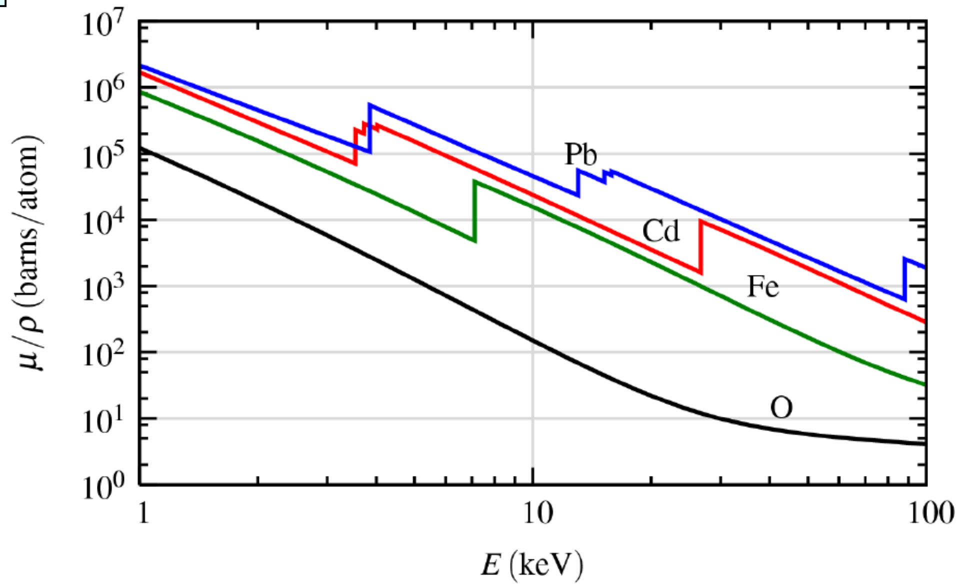


Element	K 1s
23 V	5465
24 Cr	5989
25 Mn	6539
26 Fe	7112
27 Co	7709
28 Ni	8333
29 Cu	8979
30 Zn	9659

Absorption and emission of X-ray photons

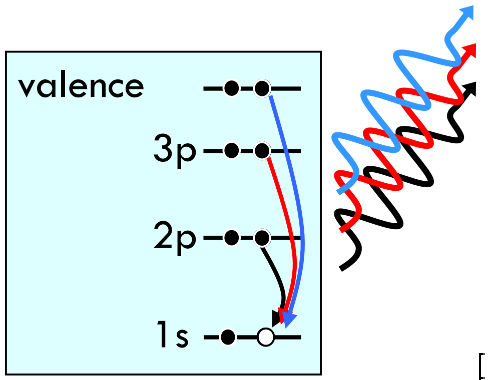
XAS: X-ray absorption spectroscopy



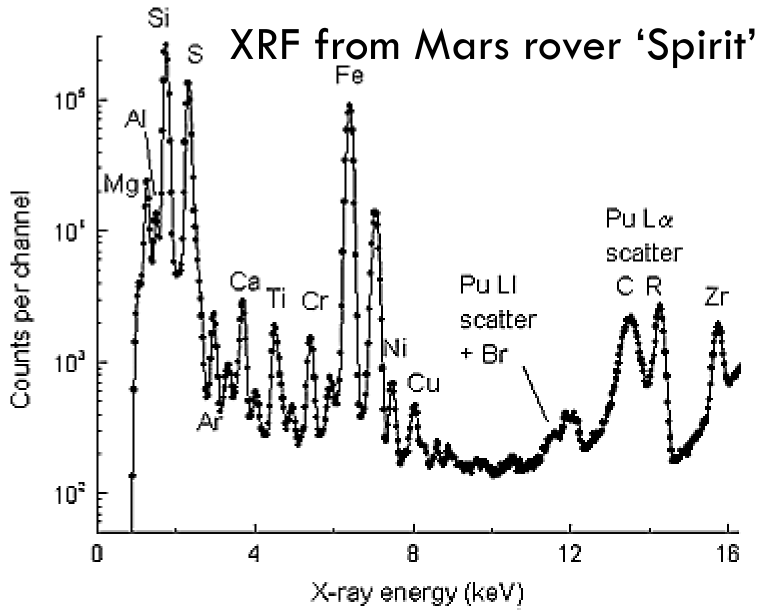


XES: X-ray emission spectroscopy

(XRF: X-ray fluorescence)

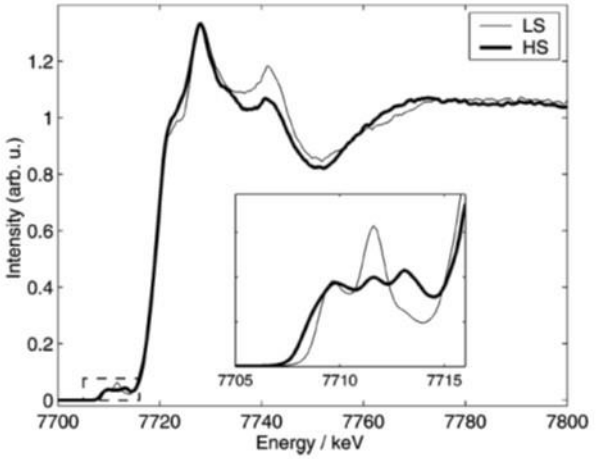


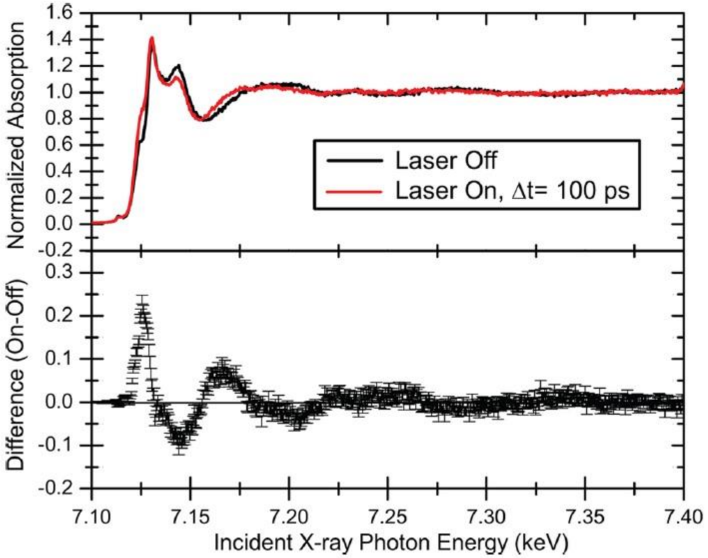
XRF from Mars rover 'Spirit'



High energy resolution: reveals the fine structure

- XANES: X-ray absorption near edge structure
- EXAFS: Extended X-ray absorption fine structure





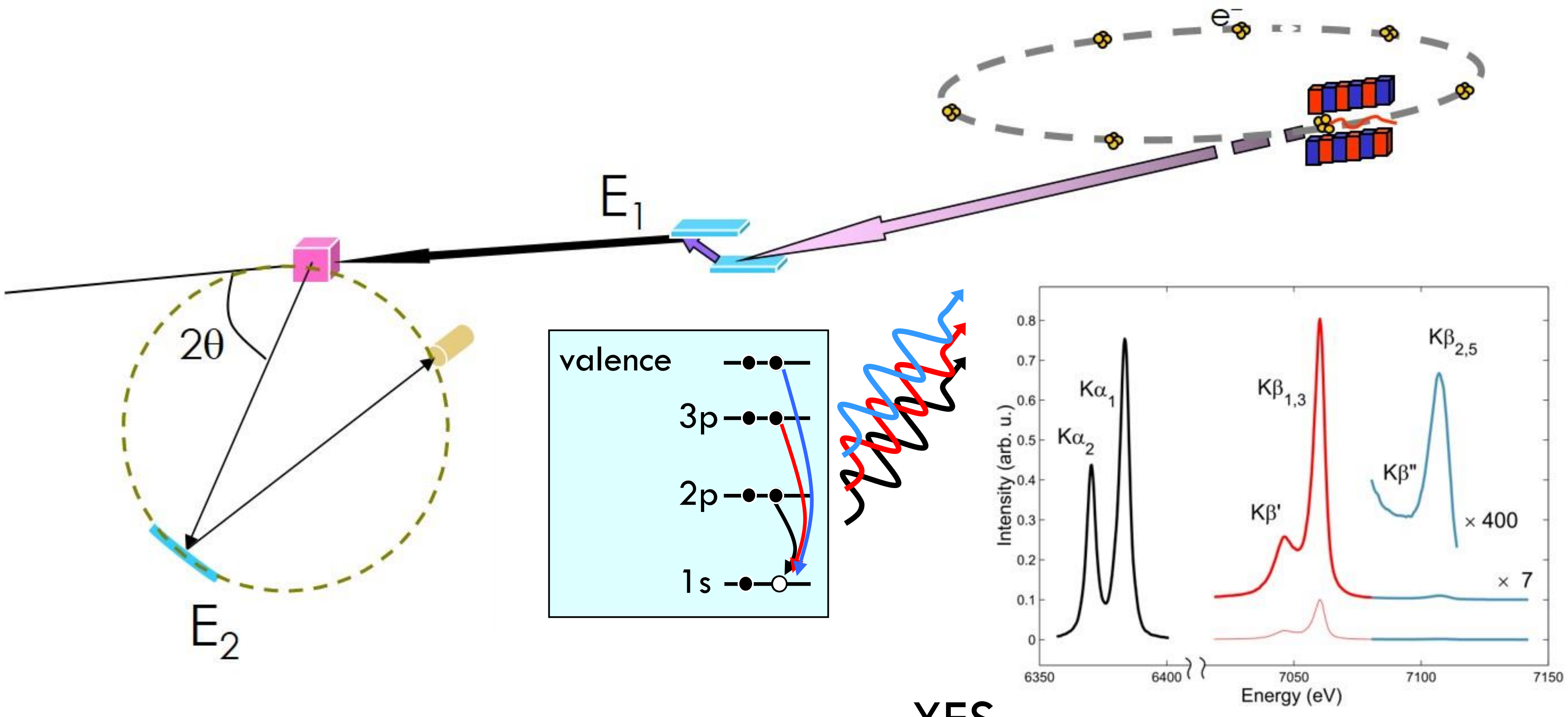


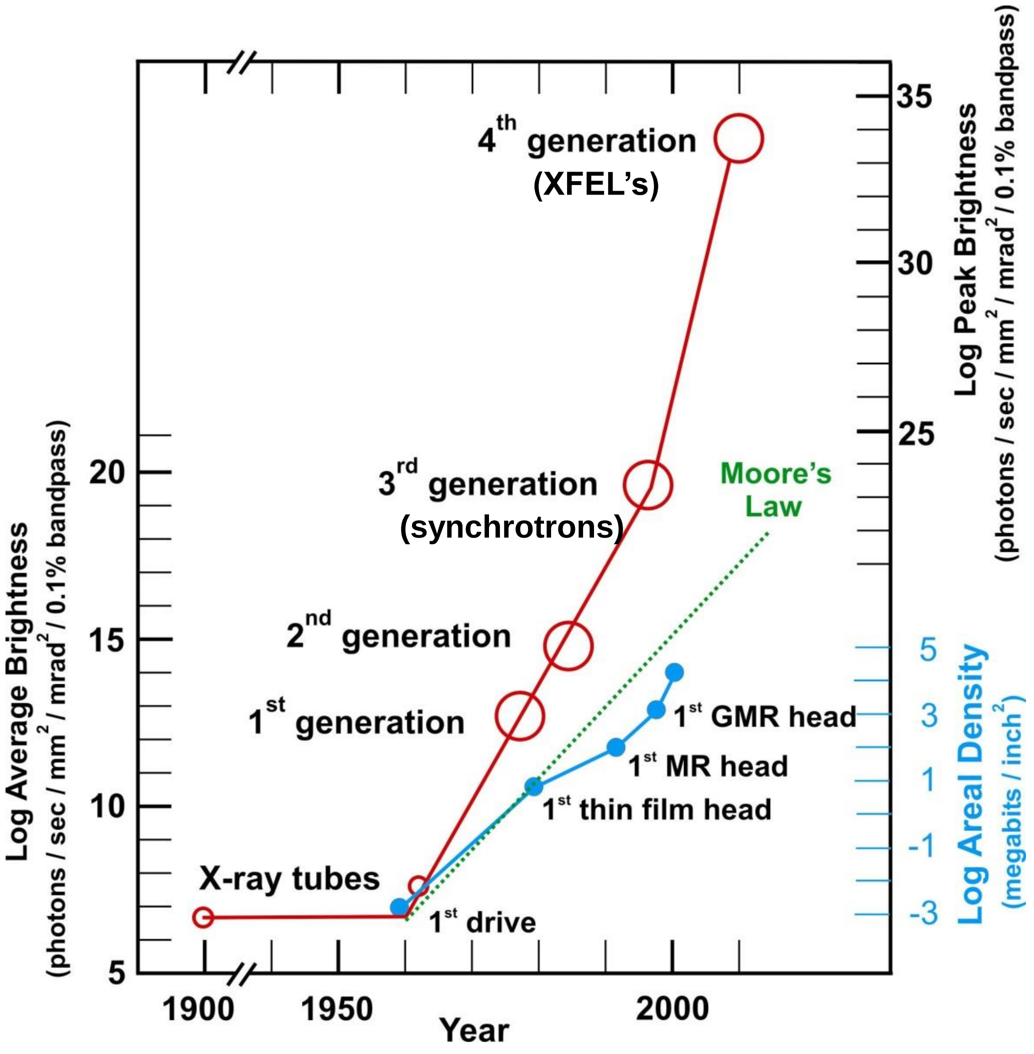
Figure from G. Vankó

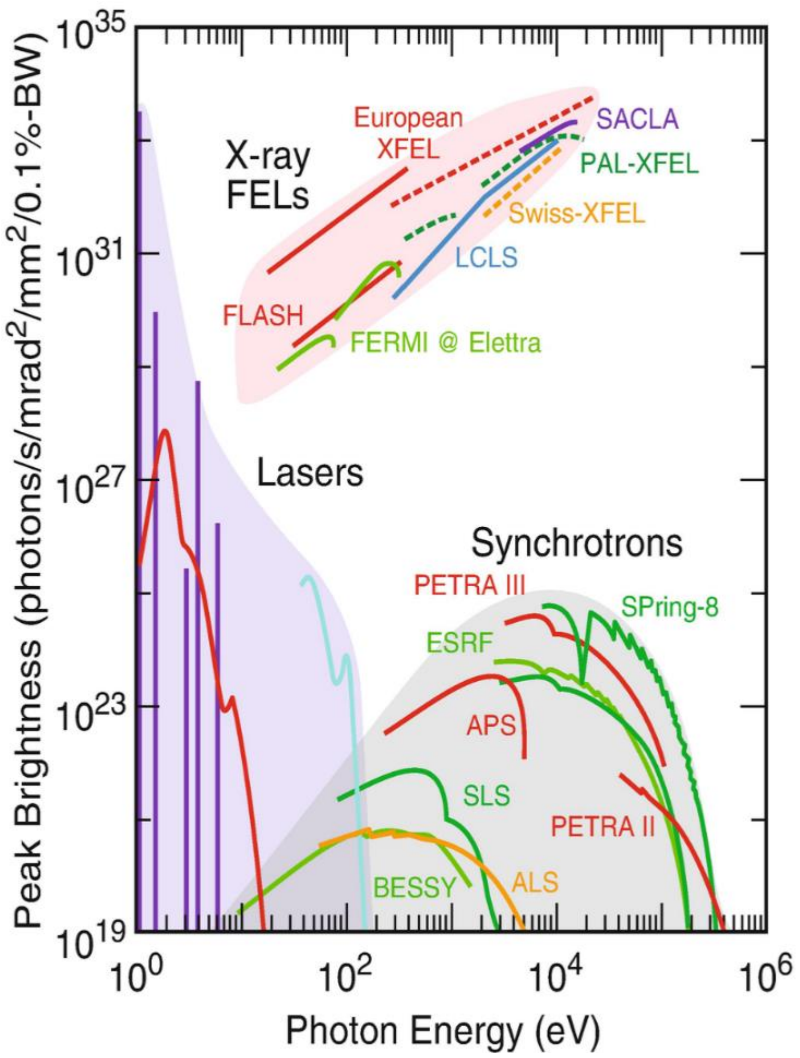
XES

How to get these spectra?

- X-ray sources
  - Synchrotrons
  - XFEL's
  - Laboratory sources
  - Laser based sources
- Detectors
  - Ionization chambers
  - Scintillators
  - Semiconductors
- Resolving by energy (or better wavelength)
  - Internal energy resolution of the detectors
  - Bragg diffraction on single crystals
  - Laue diffraction

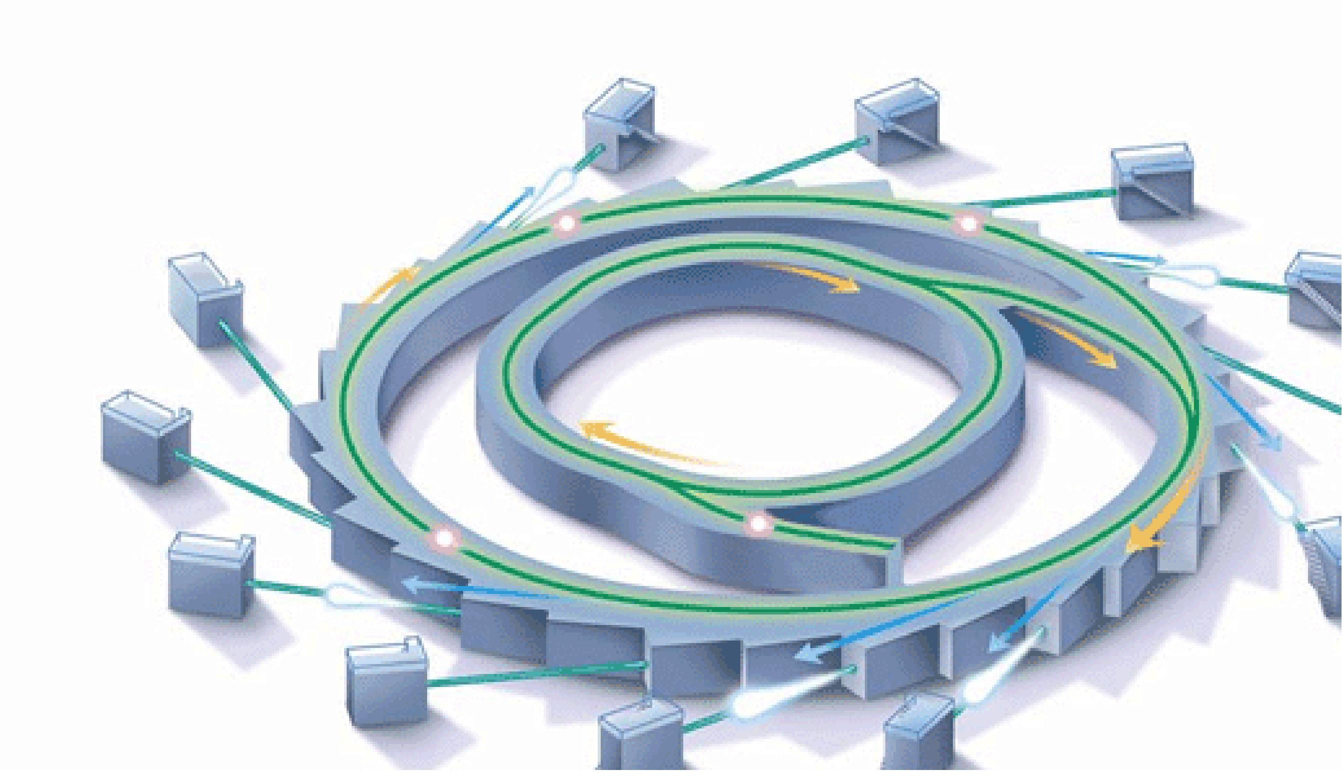
Evolution of X-ray sources





3^{rd} gen synchrotrons (90's -)

- high brilliance: 10^6–10^{12} times more than conventional laboratory X-ray tubes
- wide energy range (from infrared to hard X-rays)
- usually linearly polarized in the ring plane
- collimated (vertical divergence:
  20 μrad)
- pulsed radiation
  (pulse length: 10^{-11}–10^{-10} s,
  period time: 10^{-6}–10^{-8} s (tunable))
- **high demand and**
  high operational cost ca. €100M/a
  → €10k/day/experiment

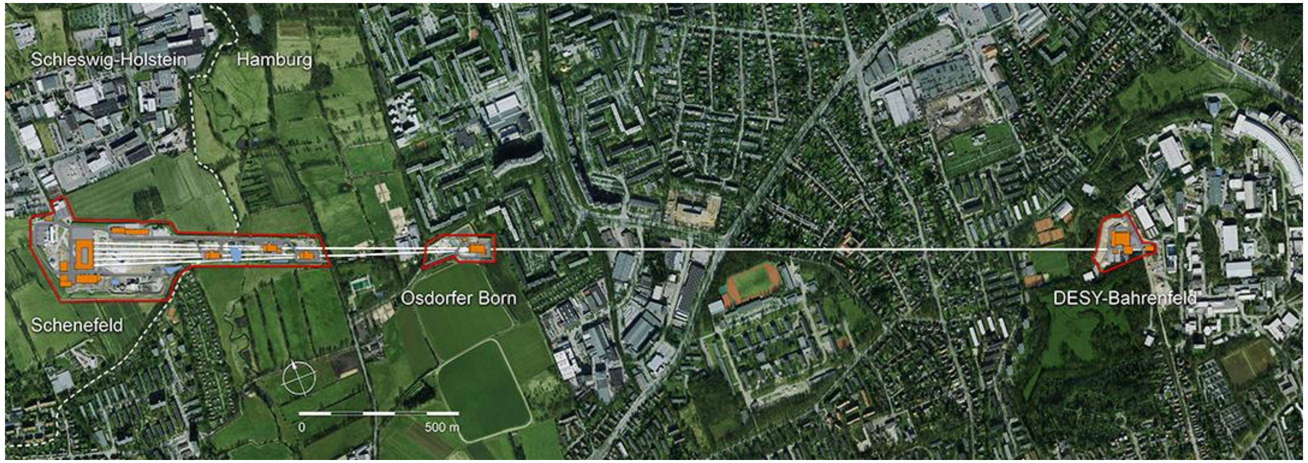


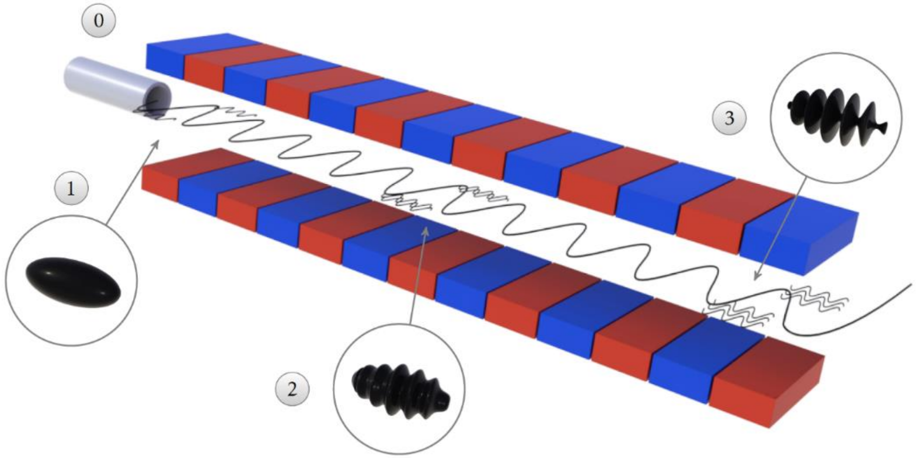
3rd gen synchrotrons (90's -)

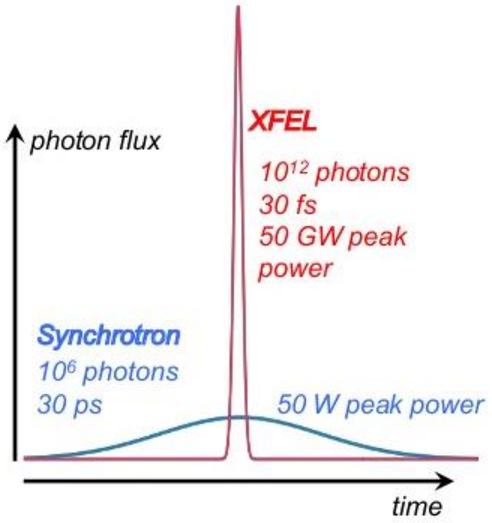
- 4 major synchrotrons (ESRF/EU, PETRA IV/DE, Spring8/Japan, APS/USA) and many smaller ones
- Beamtimes via accepted proposals (2/3 rounds per year, evaluated by international committees)
- Short, condensed beamtimes (few days)
- Local scientific and technical support
- Financial support through EU agencies for EU beamlines
- https://lightsources.org/

X-ray free electron lasers (10’s -)

- Long linear accelerators (few km), sometimes made of superconductors
- Nearly the speed of light electrons are driven through special magnets (undulators) to emit photons
- SASE (self-amplified spontaneous emission): the coherent electron and photon bunches align each other to form ultrashort pulses
- Result: ~10 fs long extreme intense (10^8 more peak brightness than synchrotrons) hard X-ray bunches

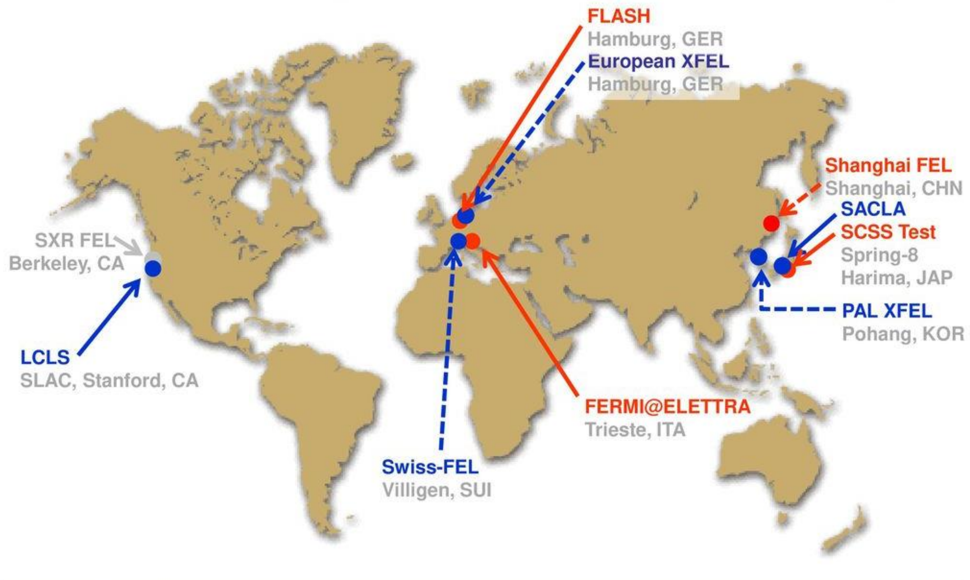






X-ray free electron lasers (10’s -)

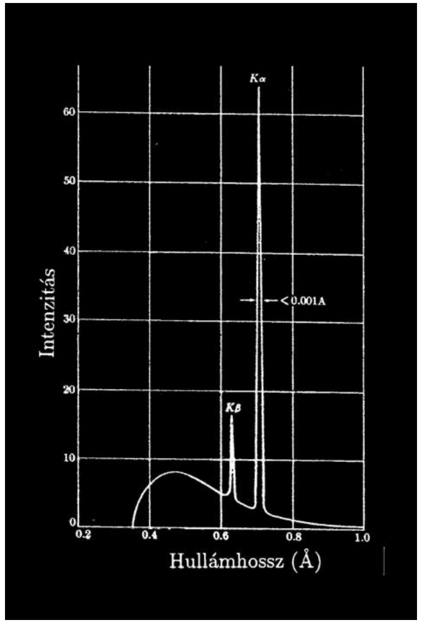
- 5 hard X-ray free electron lasers in operation (EuXFEL/EU, SwissFEL/CH, SACLA/Japan, PAL-XFEL/Korea, LCLS/USA)
- Extreme high load on the beamlines
- **€1B construction cost**
- **€1M/day/experiment**

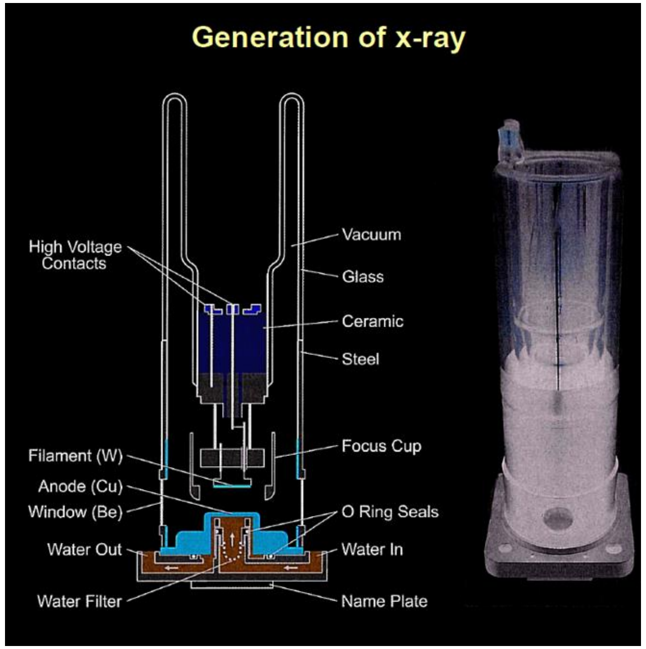


Thomas Tschentscher, European XFEL,
ESI 2013, CERN, 27/05/2013

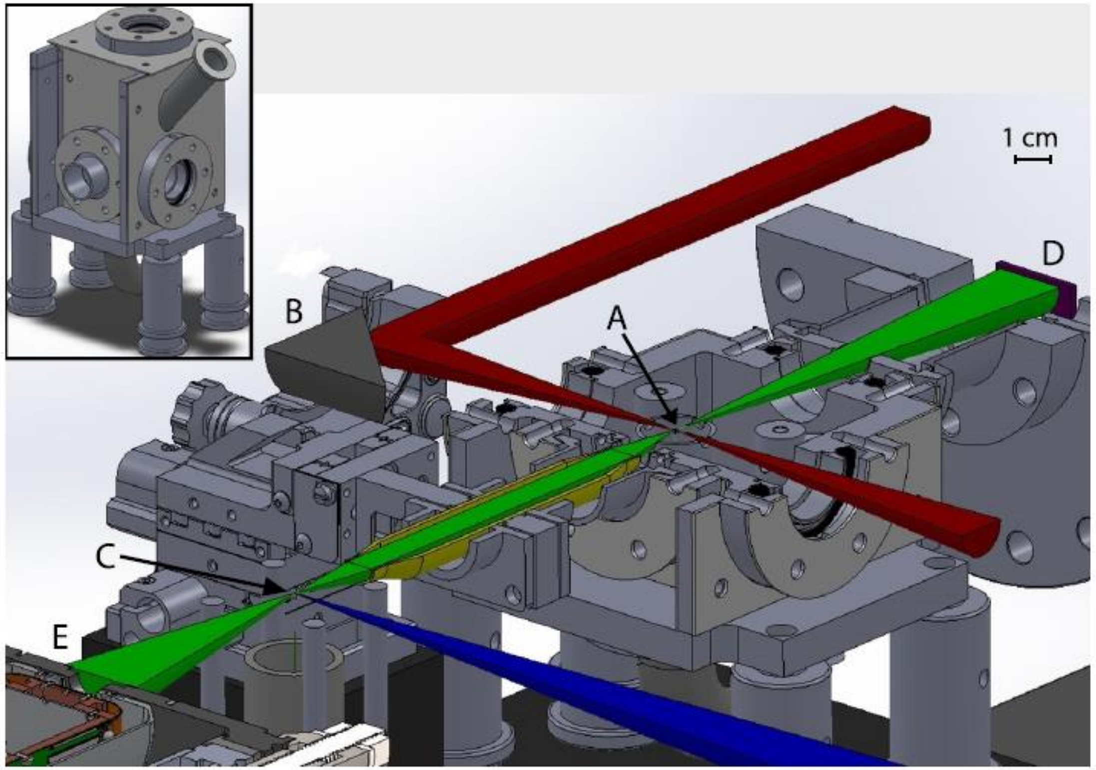
Laboratory X-ray sources

- **€0.01M investment, negligible running costs**
- Stable, well controlled intensity for long runs
- Can be focused to <100μm
- Not polarized, no time structure (CW)
- Broad bremsstrahlung + characteristic peaks of the anode
- Intended use: diffraction, imaging, XRF

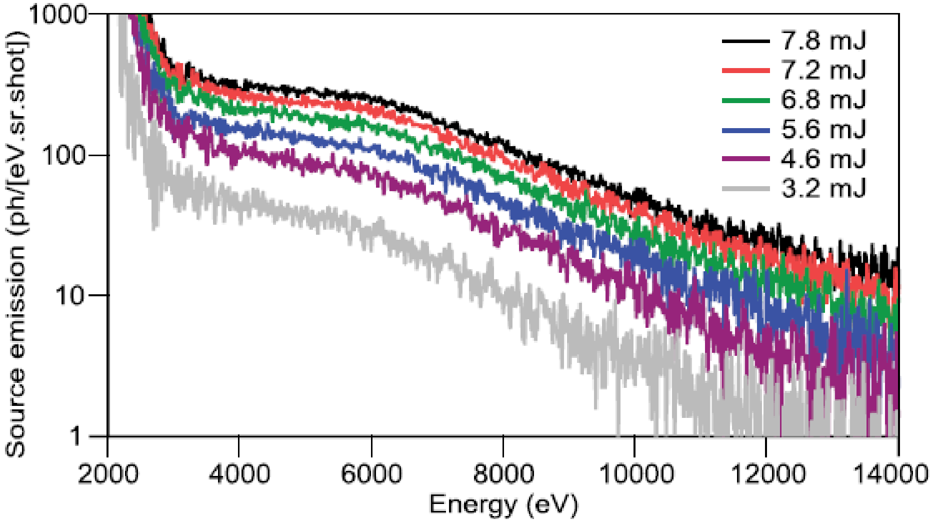


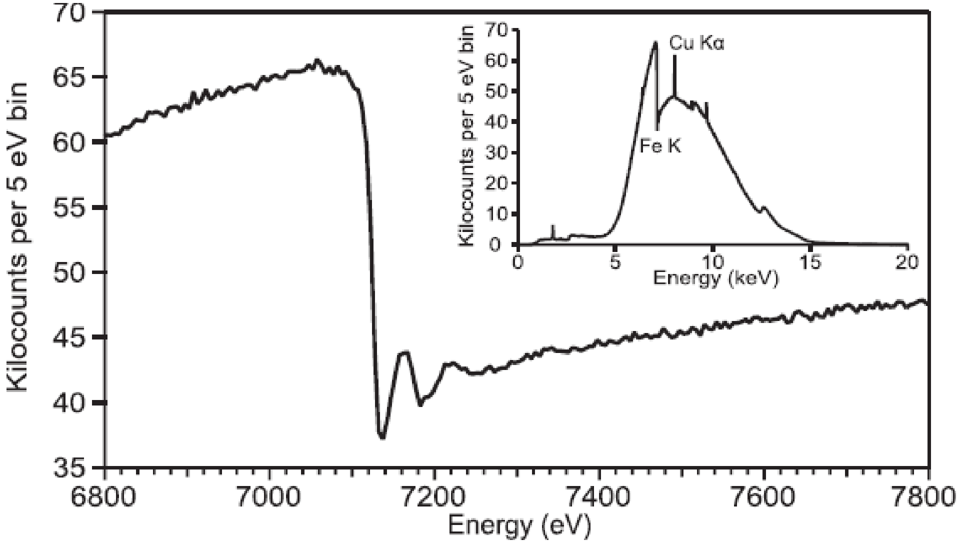


Laser plasma sources



A: water jet
B: mirror focusing the incident laser beam
C: sample
D: beam monitor
E: detector

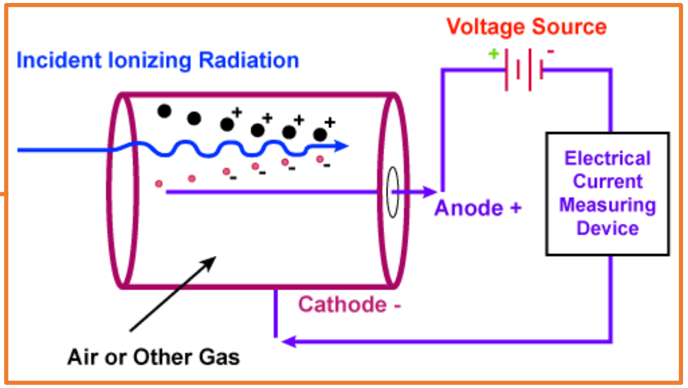


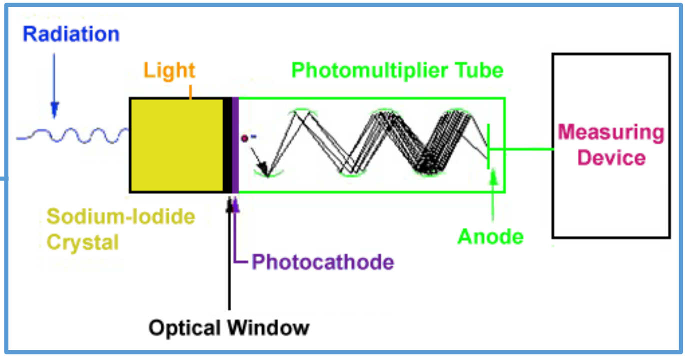


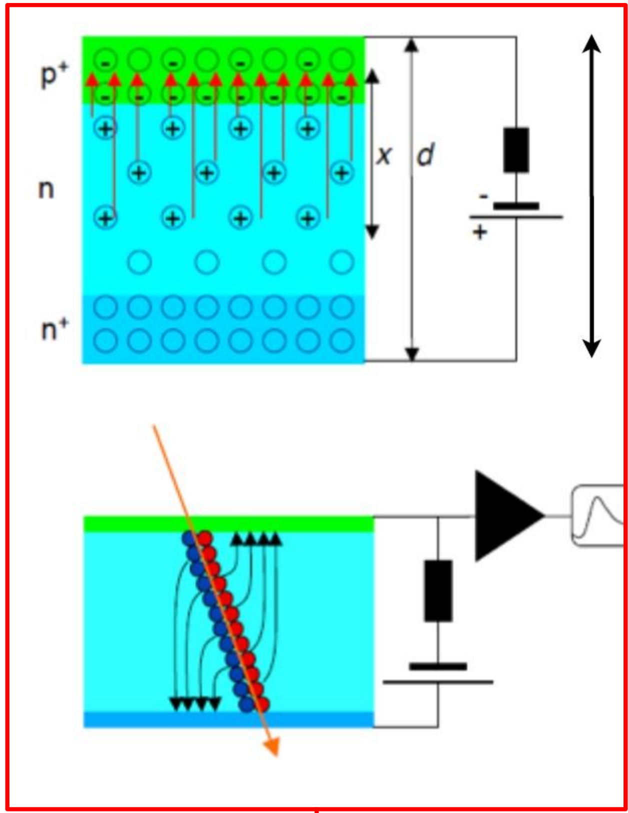
W. Fullagar, et al, Rev. Sci. Instrum. 78, 115105 (2007), Lund, Sweden
L. Miaja-Avila, et al., Struct. Dyn. 2, 024301 (2015), Boulder, Colorado, USA

Detection

- Ionization chambers:
  - Handle high photon fluxes
  - Good proportionality
- Scintillation detectors
  - Moderate energy resolution
  - Good efficiency
  - Slow
- Semiconductors
  - High energy resolution
  - Good efficiency
  - Fast (low deadtime)
  - Low background
  - Scalable – can easily be used for building 2D arrays

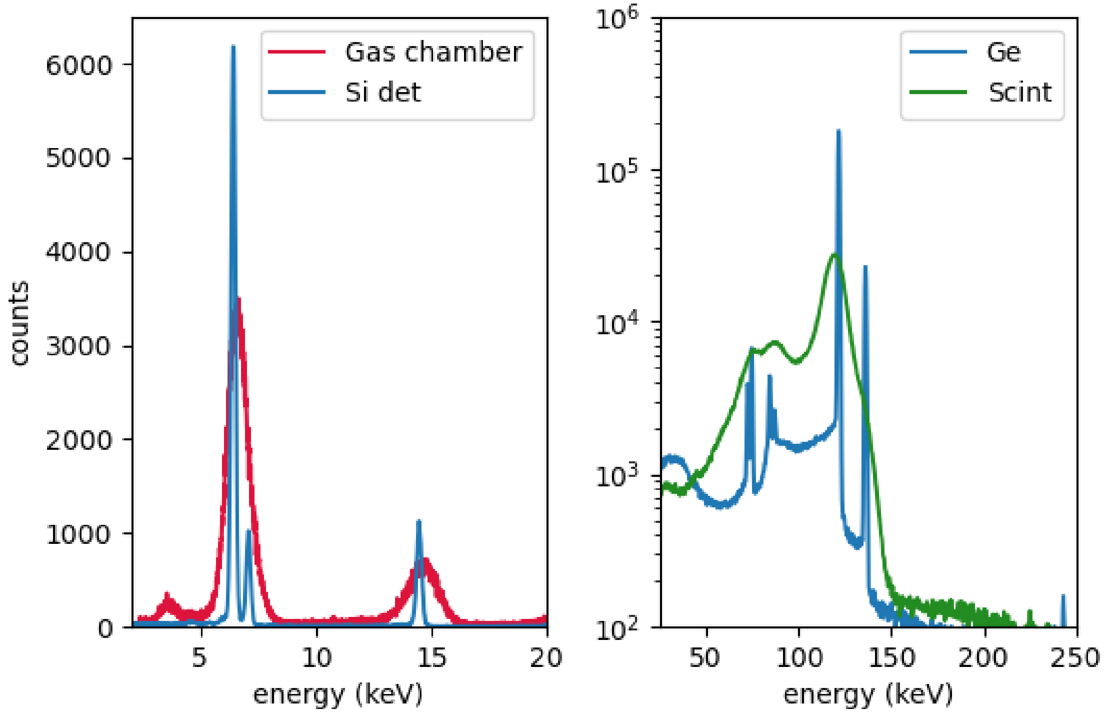


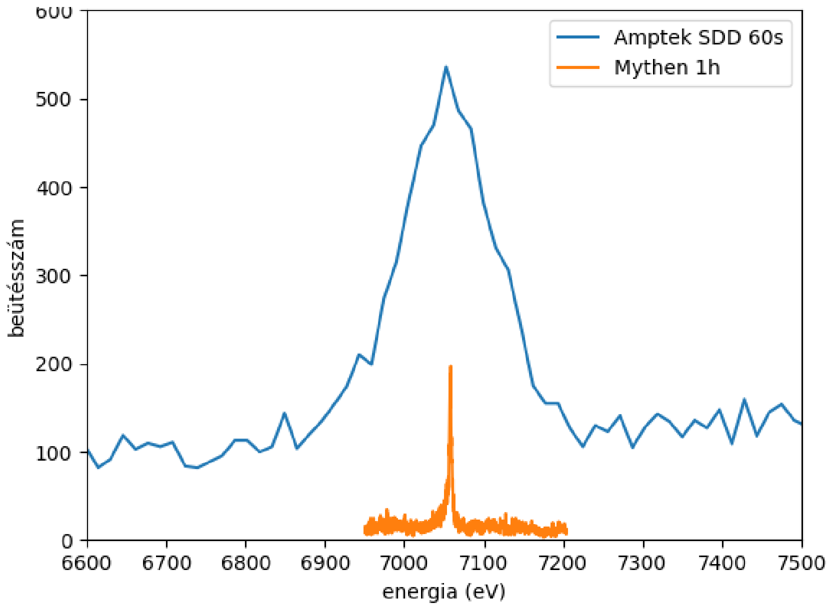




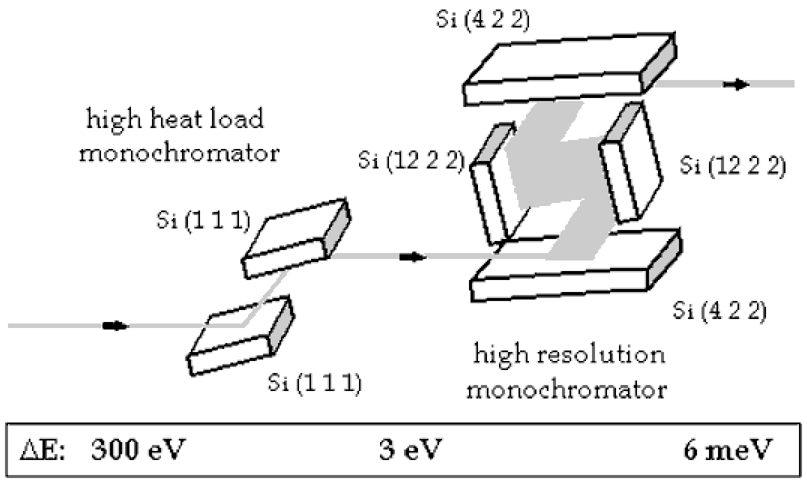
Resolving by energy

- Internal energy resolution of the detectors: discriminating by the signal height of the amplified electronic signal
- Depends strongly on the detector's working principle
- Typically: scintillators < ion chambers < semiconductors
- Best energy resolution: Silicon Drift Diodes (SDD),
  ca. 10^2 eV at several kV's
  ($= 10^{-1}\ E/E_0$)
- But! Fine structure needs at least $10^{-3}\ E/E_0$

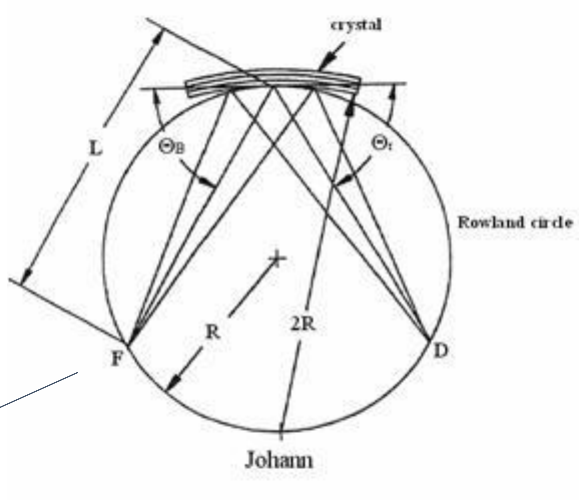


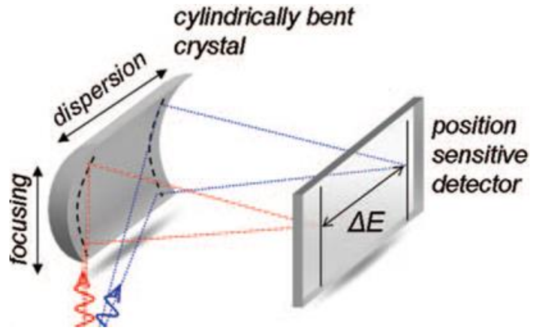


Resolving by wavelength



- Bragg diffraction or Laue diffraction
- Well know (*d*) diffracting single crystal analyzer
- Photons with different wavelengths will diffract at different Bragg angles
- Subsequent monochromators at high intensity synchrotron beamlines
- Smaller single crystals (Si,Ge, etc.) in spectrometers
    - Scanning mode (Rowland circle, Johann geometry with spherically bent crystal)
    - Static mode (von Hámos geometry with cylindrical crystal)





2. X-ray Absorption Spectroscopies

Literature:

- M. Newville: Fundamentals of XAFS ,Reviews in Mineralogy & Geochemistry Vol. 78 pp. 33-74, 2014
- http://gbxafs.iit.edu/training/xafsoverview.pdf
- *X-Ray Absorption – Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, ed. by D. C. Koningsberger and R. Prins, John Willey (1988)
- A. L. Ankudinov, B. Ravel, J. J. Rehr, S. D. Conradson, Phys. Rev. B 58, 7565 (1998)
- F. de Groot: High-Resolution X-ray Emission and X-ray Absorption Spectroscopy, *Chem. Rev.* 2001, *101*, 1779-1808

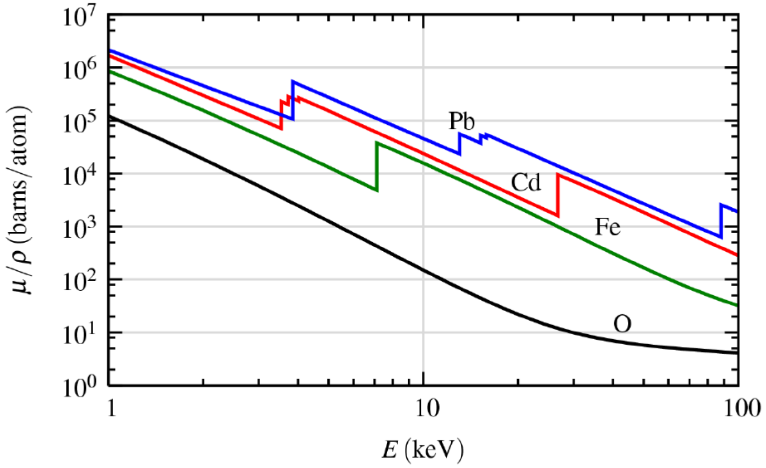
The X-ray absorption effect

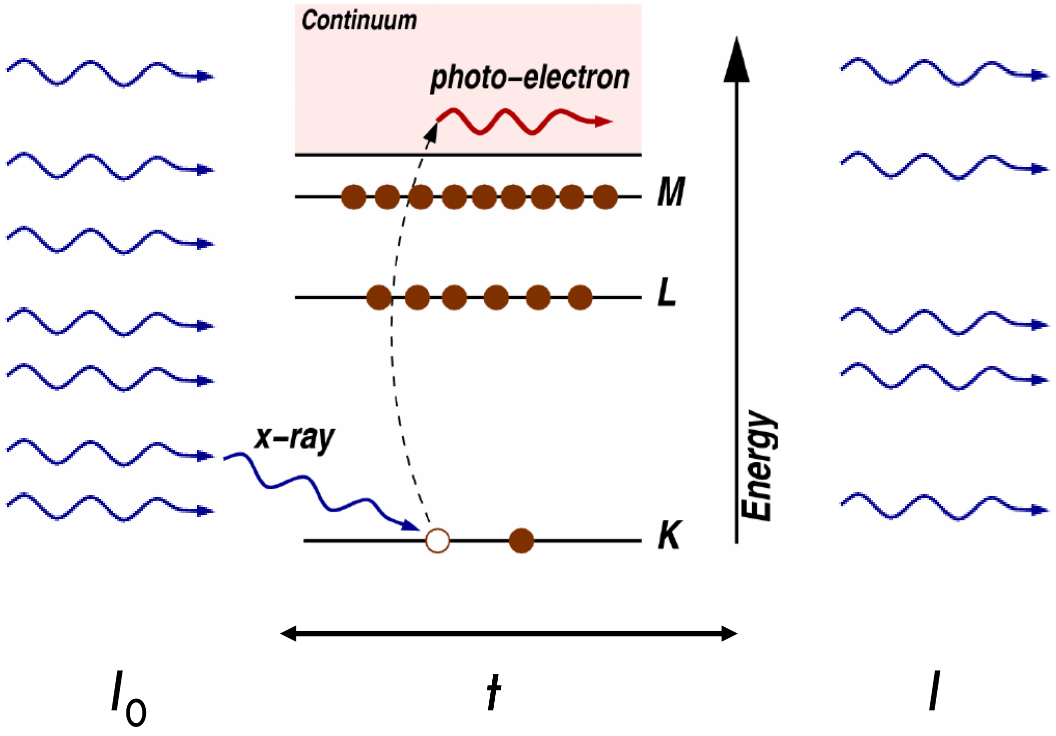
- Photo-electric effect (Albert Einstein, Nobel Prize in Physics, 1921)

- Beer–Lambert law: $I = I_0 e^{-\mu t}$,

- Quantity to measure: μ vs. E

- $\mu \approx \frac{\rho Z^4}{A E^3}$





The X-ray absorption coefficient

- Photoabsorption via Fermi's golden rule:

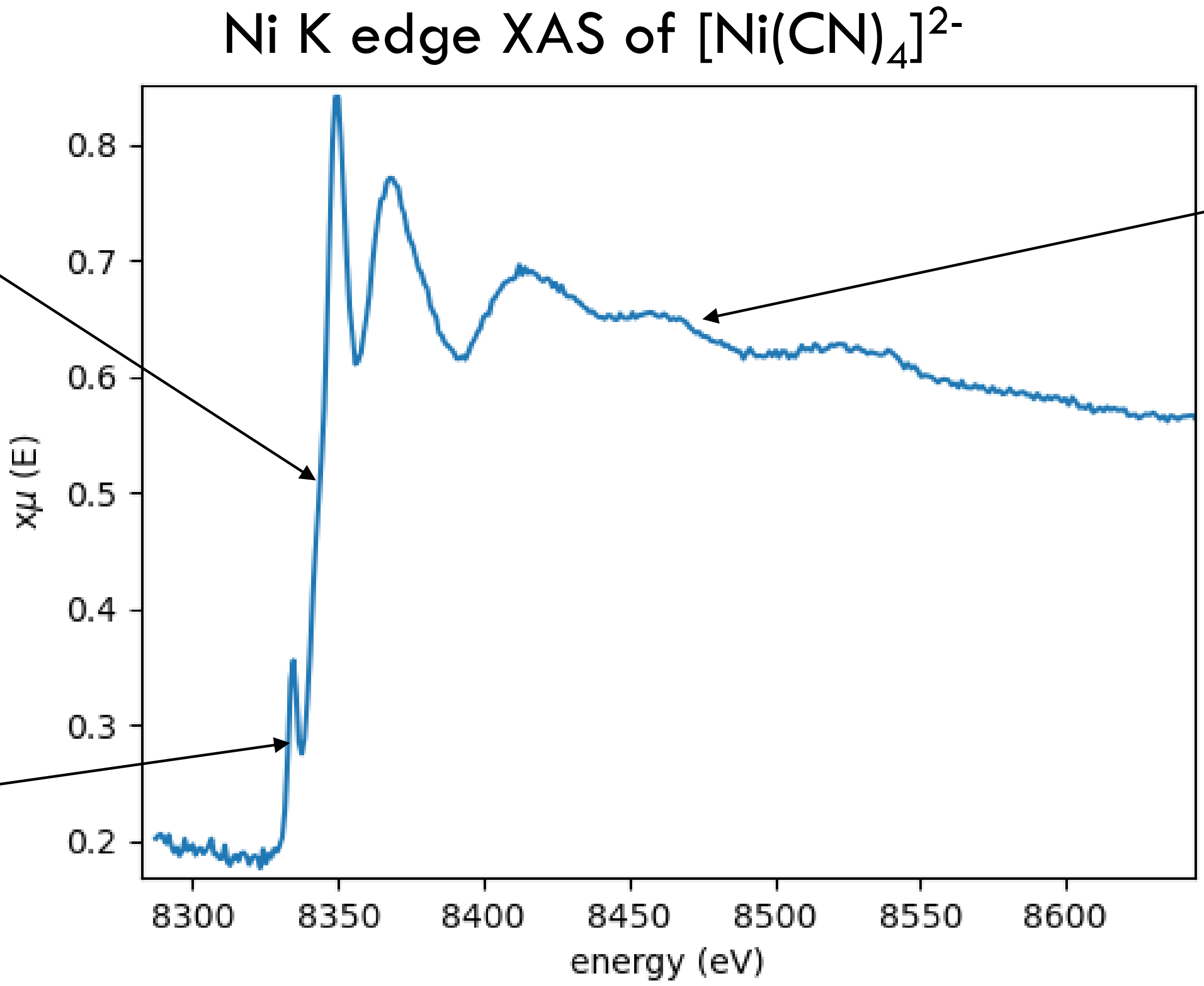
$$\mu \propto \left| \langle f \middle| \hat{e} \cdot r e^{ik \cdot r} \middle| i \rangle \right|^2 \delta_{E_f - E_i - \hbar\omega}$$

- Final state = initial state with a continuum electron (ϵ) added and a core electron removed (c)
- All inactive electrons neglected, thus the series of delta functions become the density of states (ρ):

$$\mu \propto |\epsilon|\hat{e} \cdot r|c\rangle|^2 \cdot \rho$$

- XAS intensity becomes a measure of the DOS

What can be seen with high energy resolution?



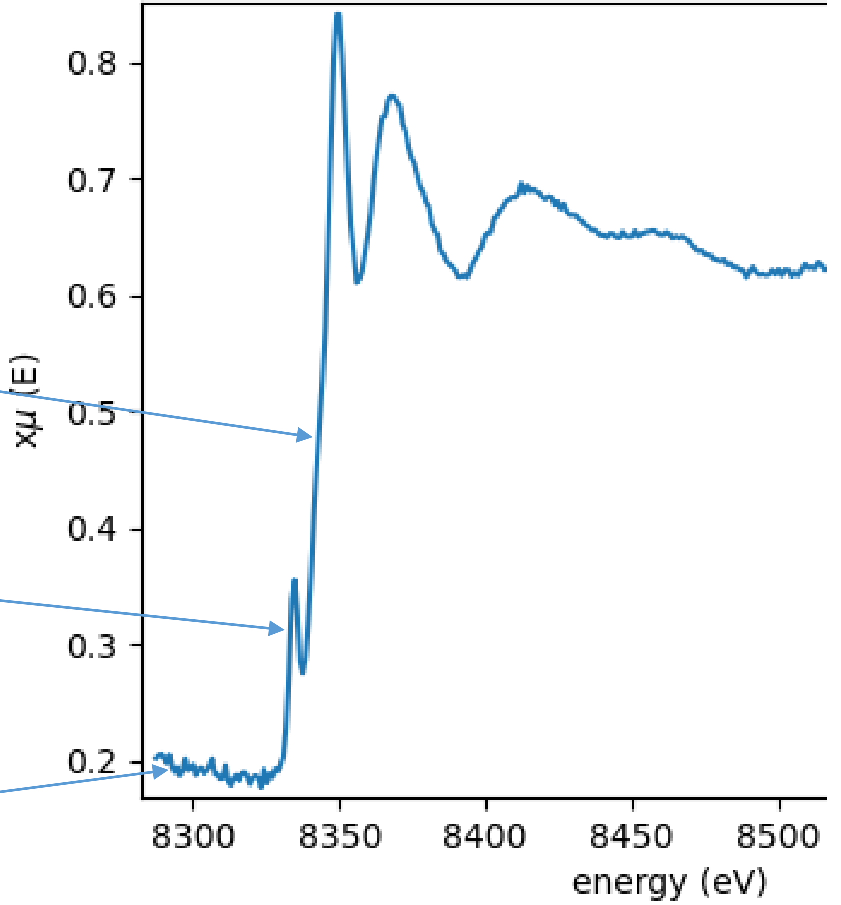
Precise position of the edge jump

Pre-edge features

Wiggles after the edge

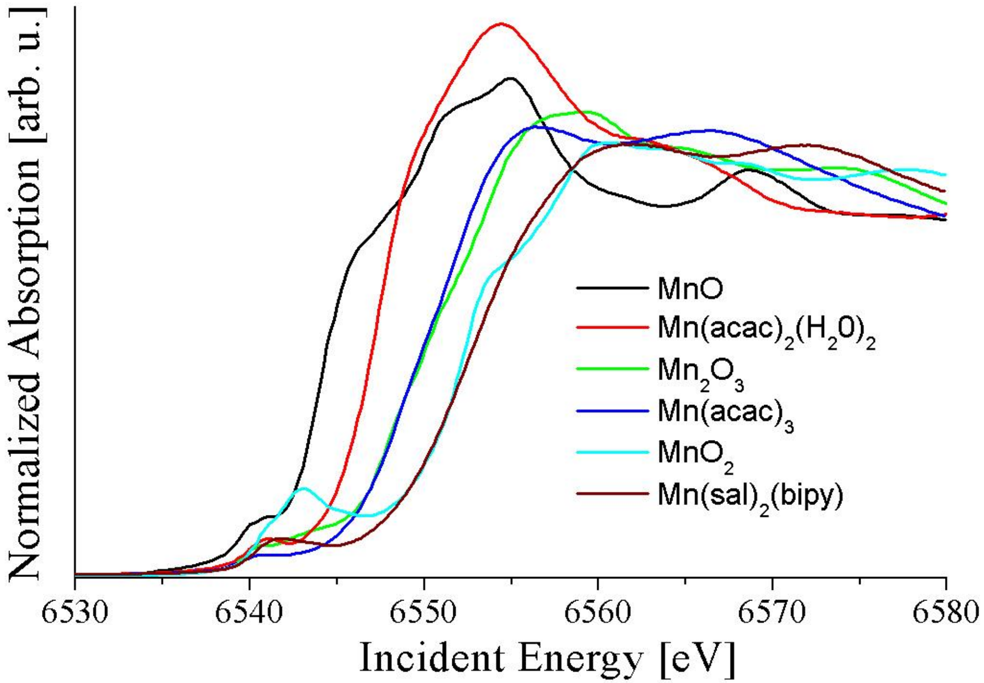
XANES – region near the absorption edge

- Dipole transition matrix is ca. 137 times stronger than quadrupole, typical case is to excite 1s electron to empty 4p orbital in 3d transition metals (or 2p → 5d)
    - ➢ Edge position reflects the lowest lying empty orbitals (LUMO or conduction band)
    - ➢ Pre-edge peaks appear due to mixing the quadrupole and dipole orbitals (1s → 3d'ish)
- Absorption is small if $\hbar\omega < (E_f - E_i)$
    - ➢ Baseline before the edge

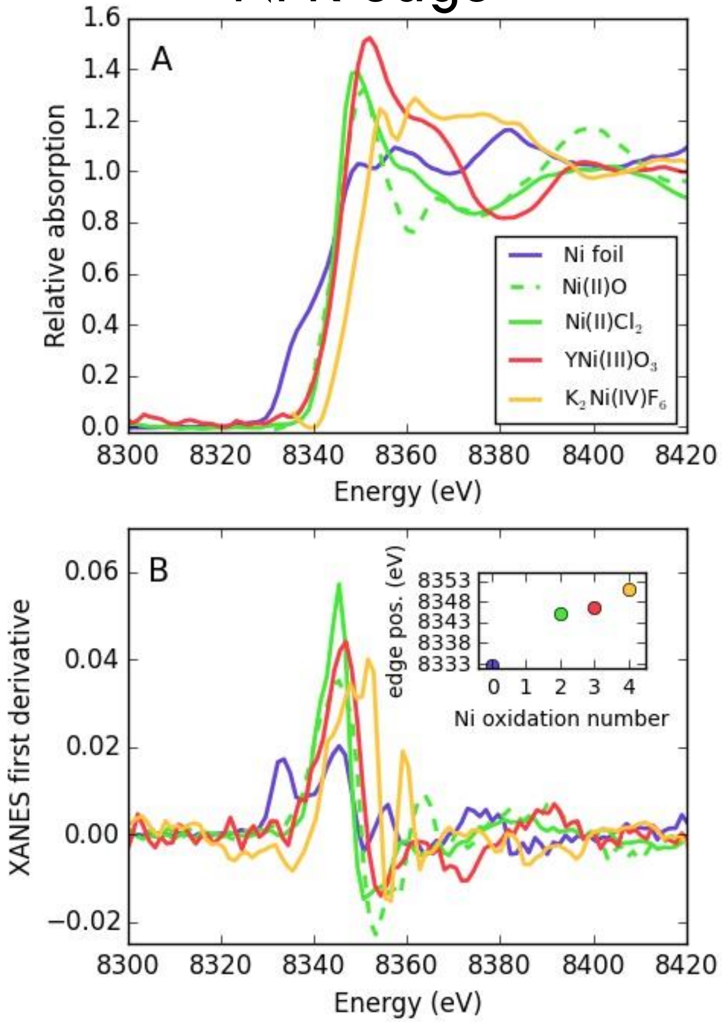


XANES – typical applications

Mn(II) $3d^5 \rightarrow$ Mn(IV) $3d^3$

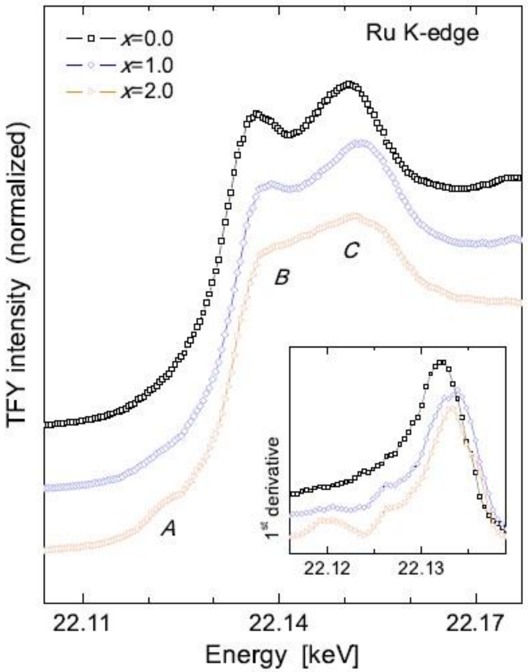


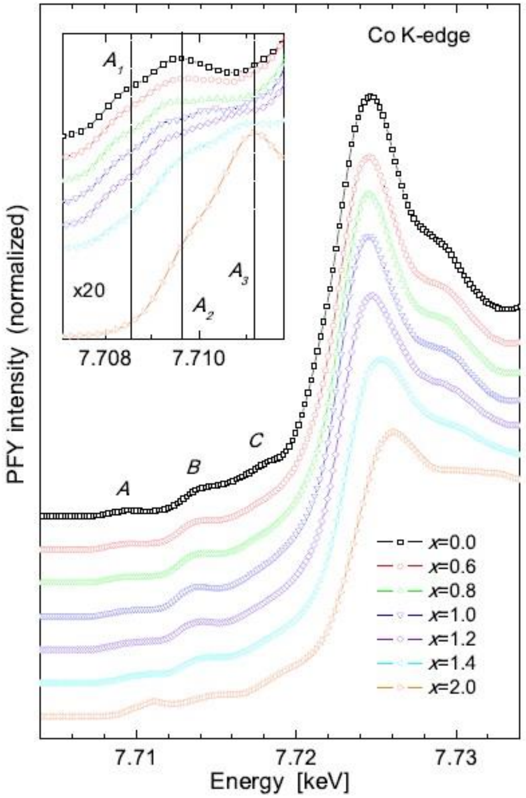
Ni K edge

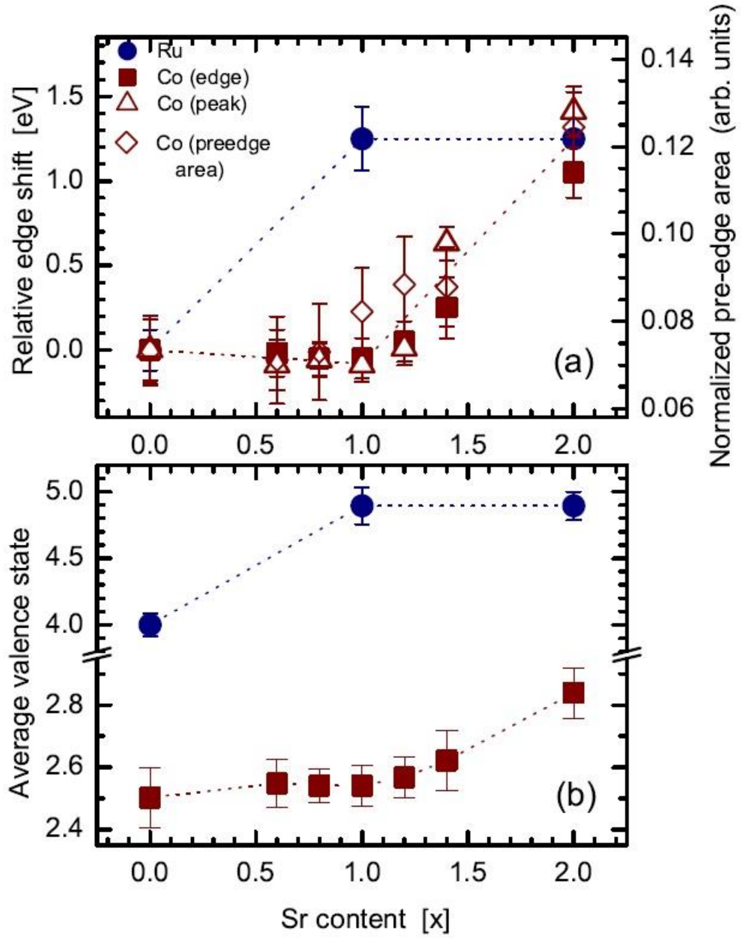


XANES – typical applications

$La^{3+}_{2-x}Sr^{2+}_{x}(CoRu)^{(6+x)+}O_6$ perovskite

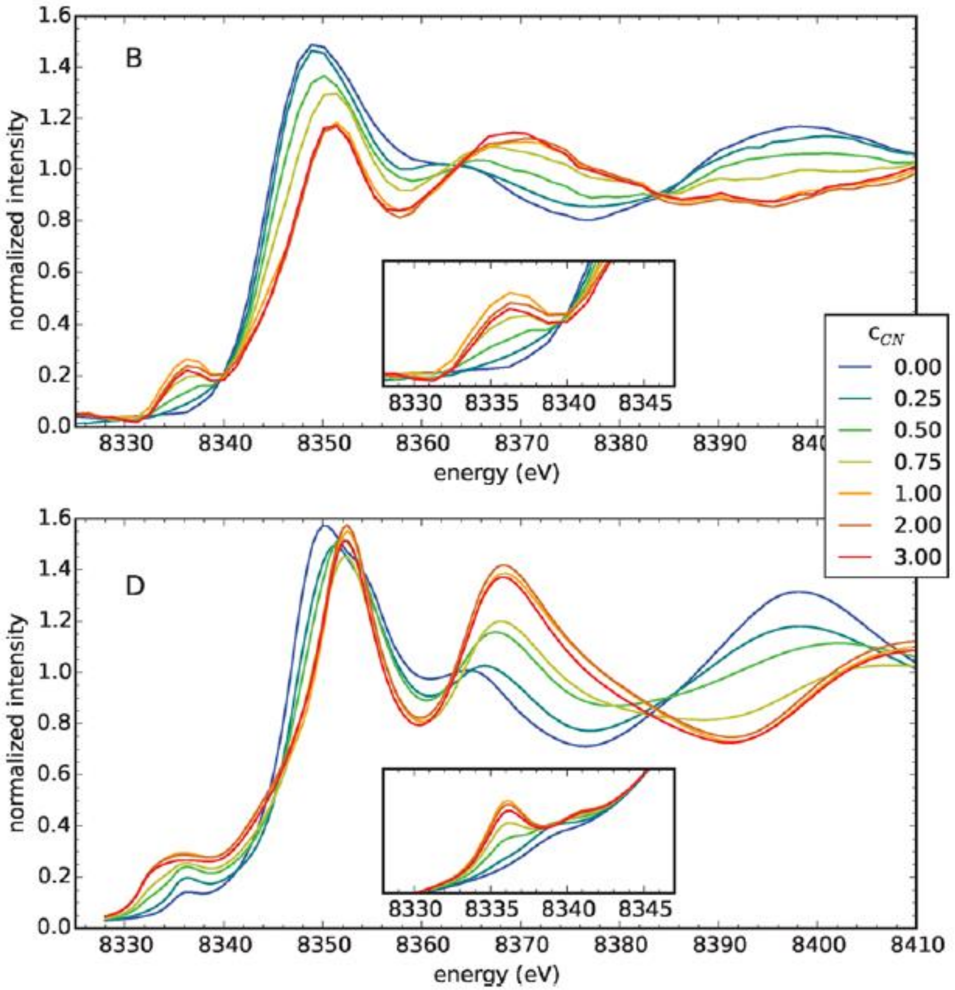


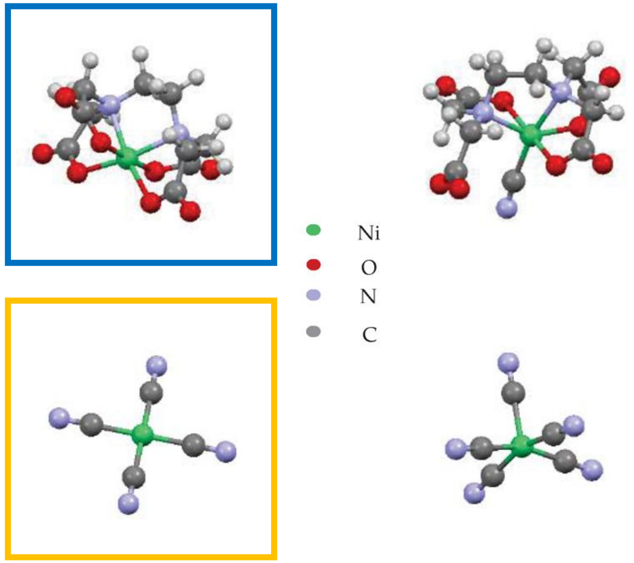




XANES – typical applications

- Pre-edge vanishing with increasing symmetry
- From square planar to octahedral Ni^{2+}

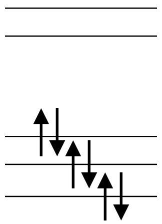




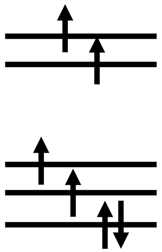
XANES – spin state dependence

- Not only the density of states, but also the spin density affects the fine structure of the XANES spectrum
- An example: Co^{3+} ion ($3d^6$) in

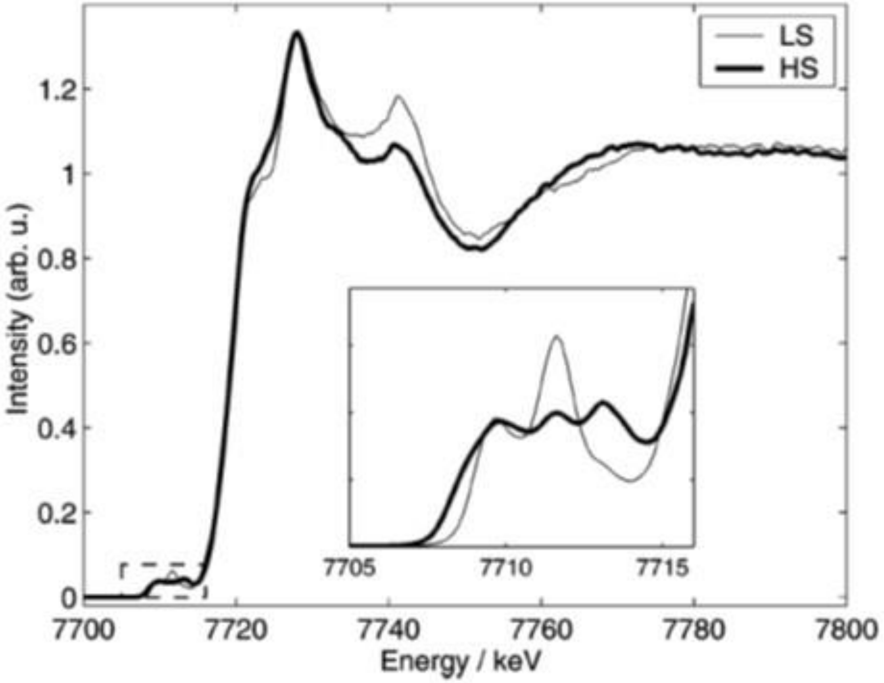
low spin state ($t_{2g}^6 e_g^0$)



and high spin state ($t_{2g}^4 e_g^2$)

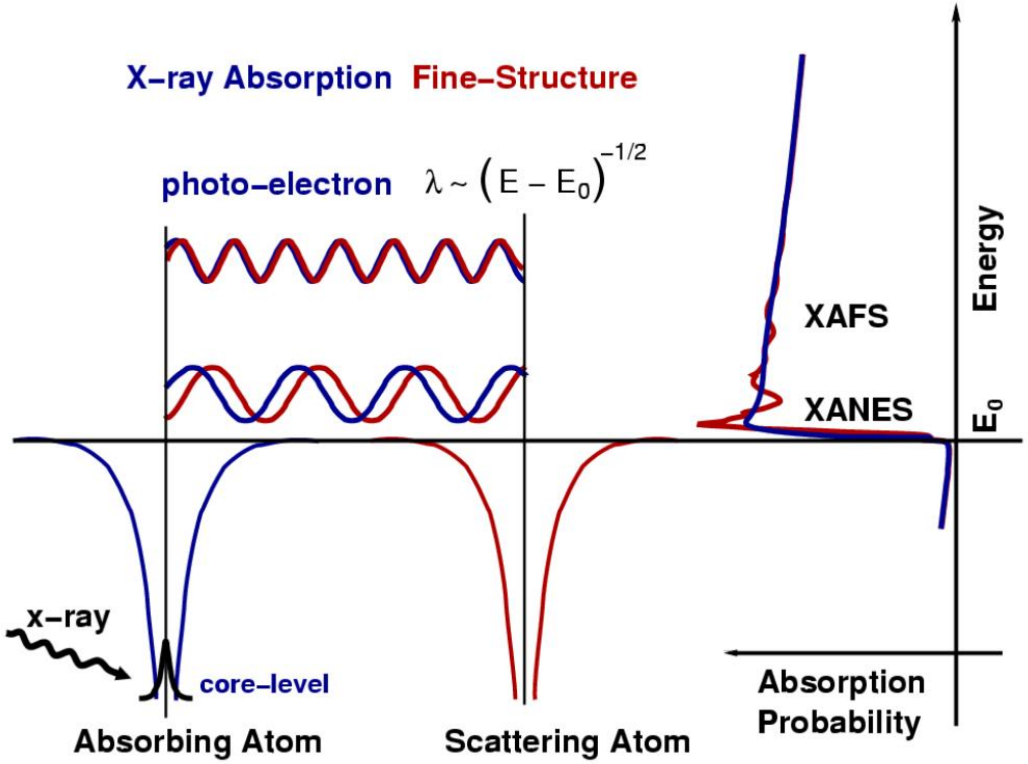


in $LaCoO_3$ perovskite



EXAFS – behind the absorption edge

- If the incident X-ray energy is high enough, the photoelectron will be excited to the continuum with λ
- If the excited atom has no neighbors, the absorption coefficient is not perturbed (blue line)
- The photoelectron wave can scatter back from the neighboring atoms and modify the absorption coefficient resulting in an interference pattern (red line)



The EXAFS equation

- Removing the isolated atom contribution (μ_0) and the edge jump gives the fine structure function:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E)}$$

- It is converted to wave number scale $\chi(k)$ and usually multiplies by k^2 or k^3 to account for the dumping nature of $\chi(k)$

- The final equation is:

$$\chi(k) = \sum_i N_i F_i(k) \frac{S_0^2}{kR_i^2} e^{\frac{-2R_i}{\lambda}} e^{-2\sigma_i^2 k^2} \sin(2kR_i + \varphi_i(k))$$

Scattering amplitude

Disorder

Damping

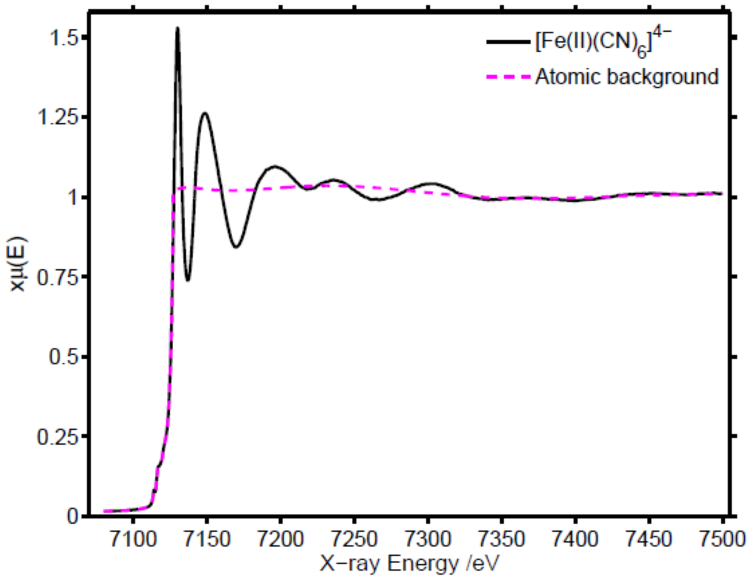
The EXAFS equation

$$\chi(k) = \sum_i N_i F_i(k) \frac{S_0^2}{kR_i^2} e^{\frac{-2R_i}{\lambda}} e^{-2\sigma_i^2 k^2} \sin(2kR_i + \varphi_i(k))$$

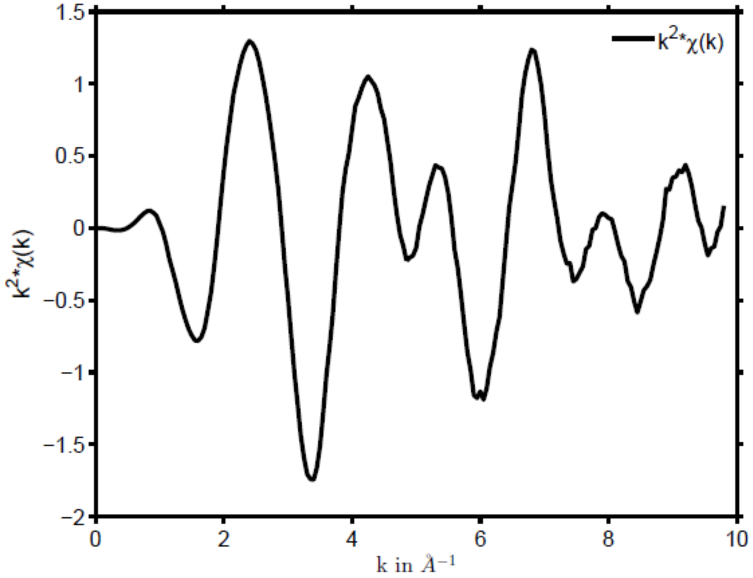
Parameters to handle:

- ***R_i*** distance between the absorber and scatterer (in case of multiple scattering, half of the total travelling path)
- ***N_i*** number of scattering atoms in the *i^{th}* shell (=coordinantion number)
- ***F_i*** effective backscattering amplitude
- ***S_0^2*** amplitude reduction factor
- ***λ*** mean free path of the photoelectron (the probability of returning before the core hole fills up or the photoelectron scatters inelastically)
- ***σ^2_i*** Debye-Waller factor
- ***φ_i*** effective scattering phase shift

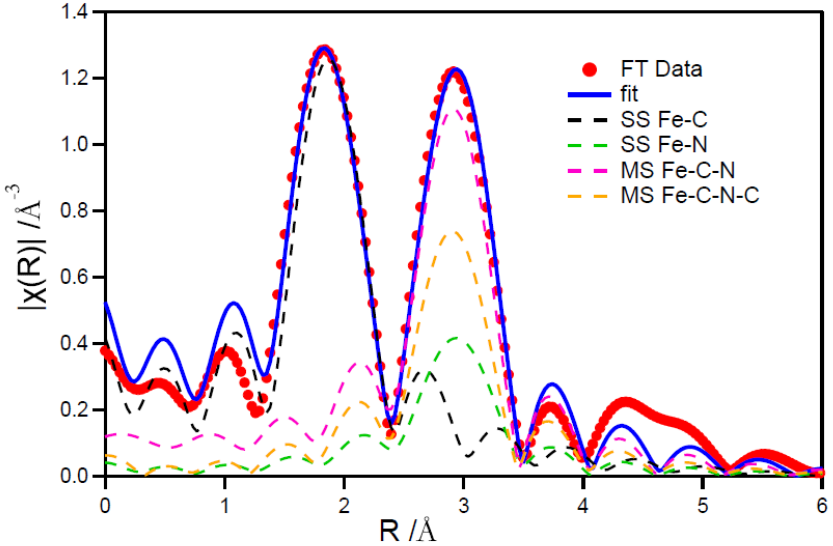
EXAFS example: $[Fe^{II}(CN)_6]^{4-}$



data reduction



Fourier transformation and fit



3. X-ray Emission Spectroscopies

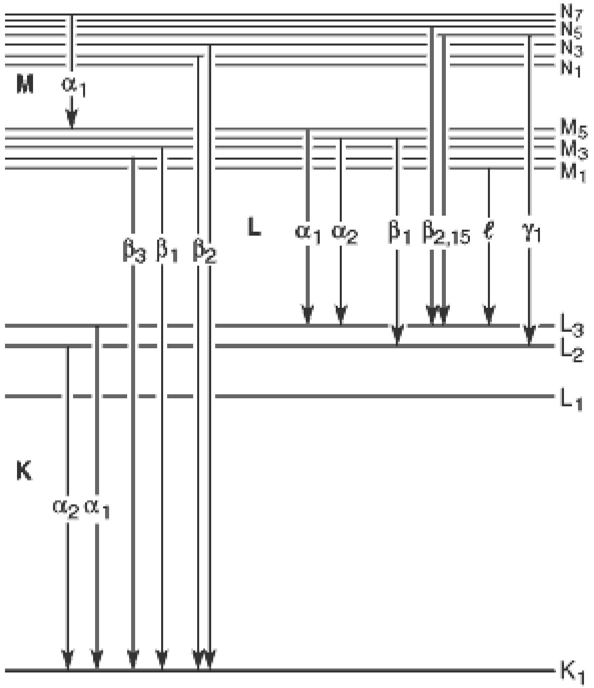
Literature:

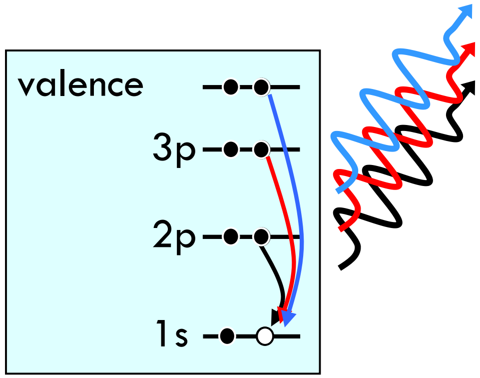
- F. de Groot: High-Resolution X-ray Emission and X-ray Absorption Spectroscopy, *Chem. Rev.* 2001, *101*, 1779-1808
- P. Glatzel, U. Bergmann: High resolution 1s core hole X-ray spectroscopy in 3d transition metal complexes-electronic and structural information, Coordination Chemistry Reviews 249 (2005) 65–95

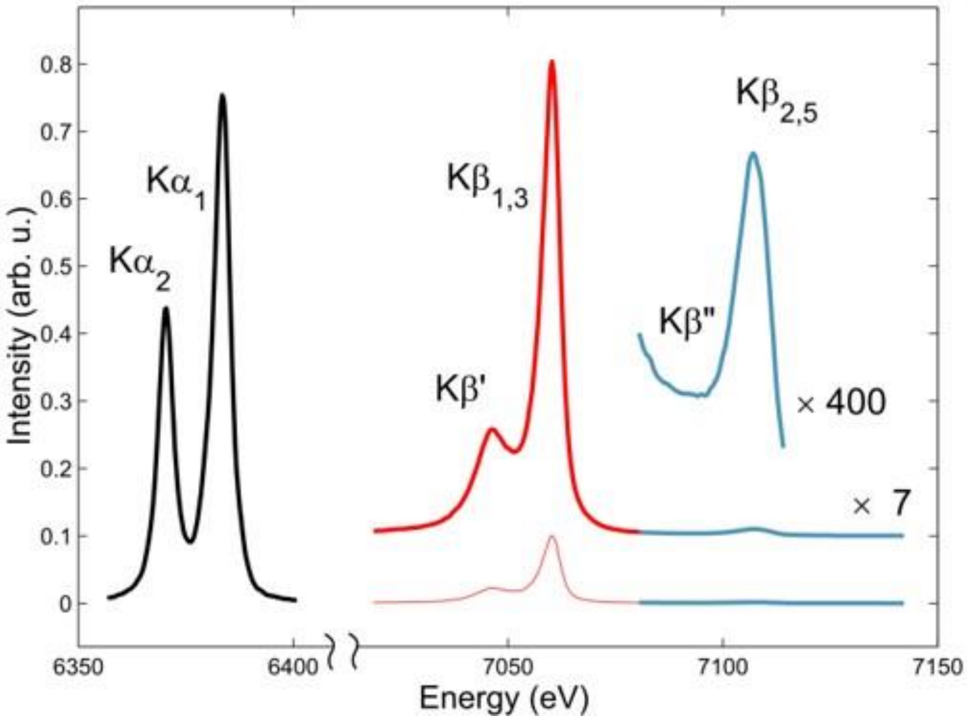
X-ray emission

- Photon-in photon-out process: after creating the core hole, an electron from outer orbitals will fill the hole, the energy difference will be (sometimes) emitted by an X-ray photon
- Core-to-core features (1s2p, 1s3p) sensitive mostly to the spin density via electron-electron exchange interaction, which is bigger on Kβ
- Spin-orbit coupling is stronger on Kα_1 and Kα_2 lines (associated with $2p_{3/2}$ and $2p_{1/2}$, respectively, typically 15-20 eV), but weaker on Kβ (ca. 1-2 eV)

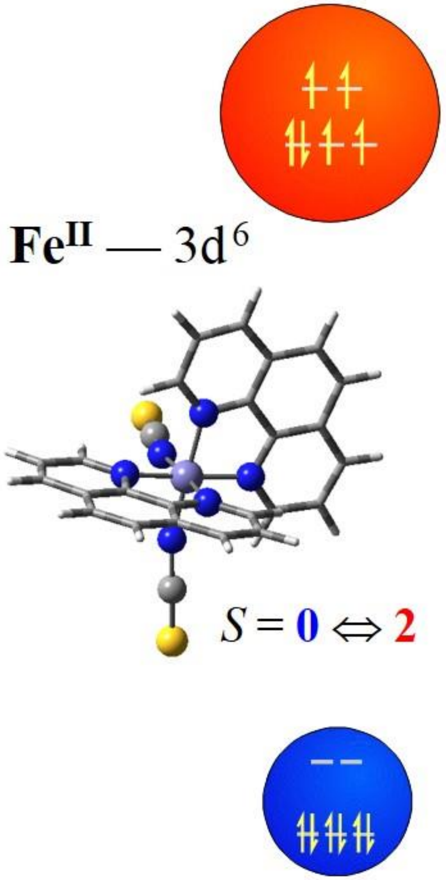
Nomenclature:

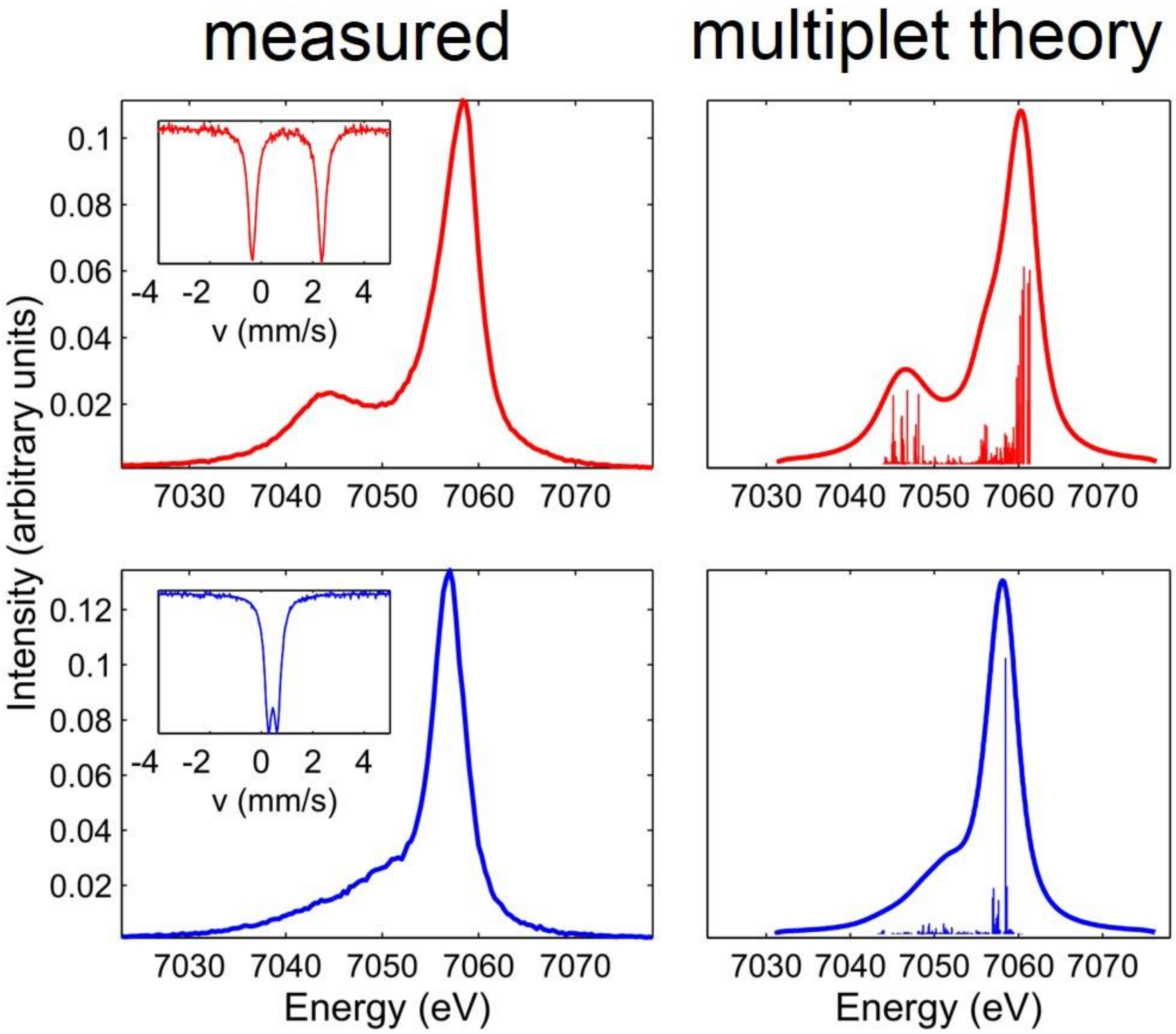






Sensitivity of ctc XES





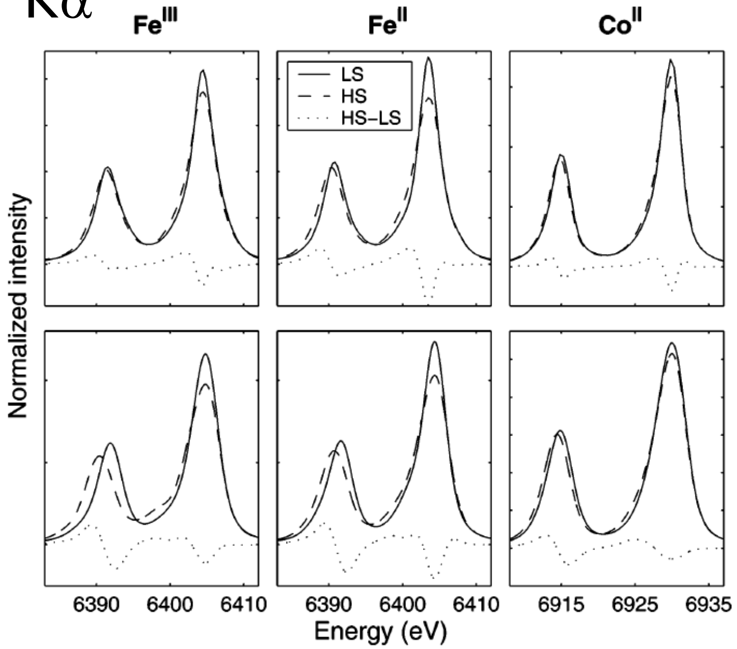
G. Vankó, F. de Groot, *Phys. Rev. B* **75** (2007) 177101.

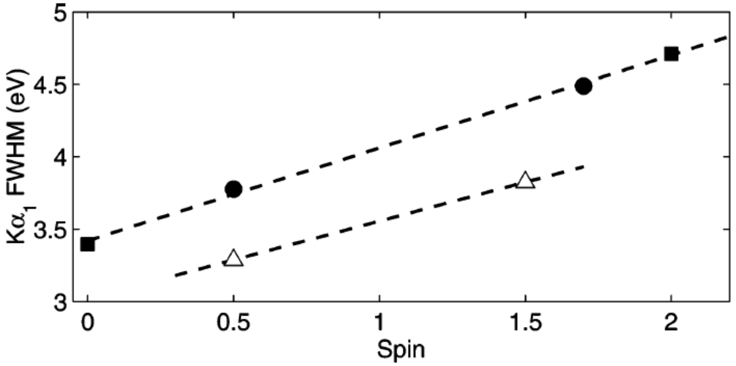
Evaluating XES spectra

- After rigorous normalization peak widths can be used to track spin state

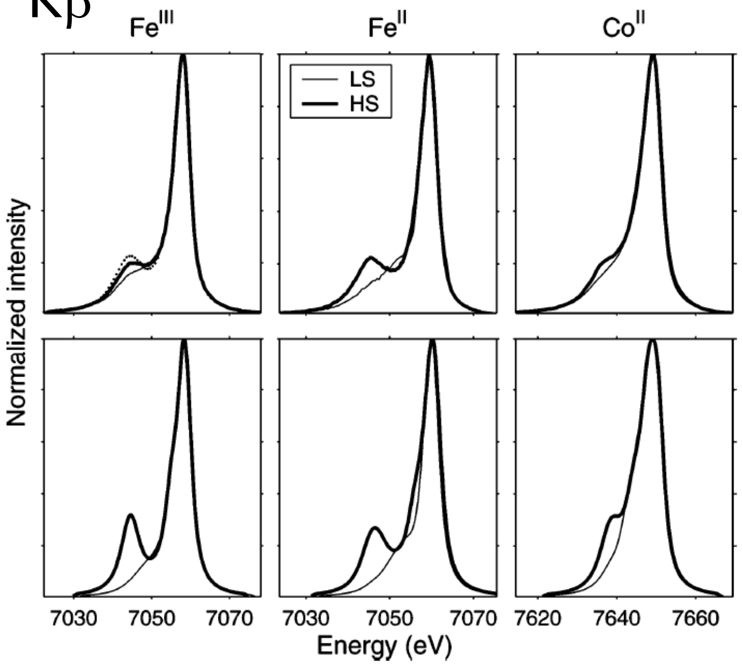
- IAD: integrated absolute difference, footprint compared to references

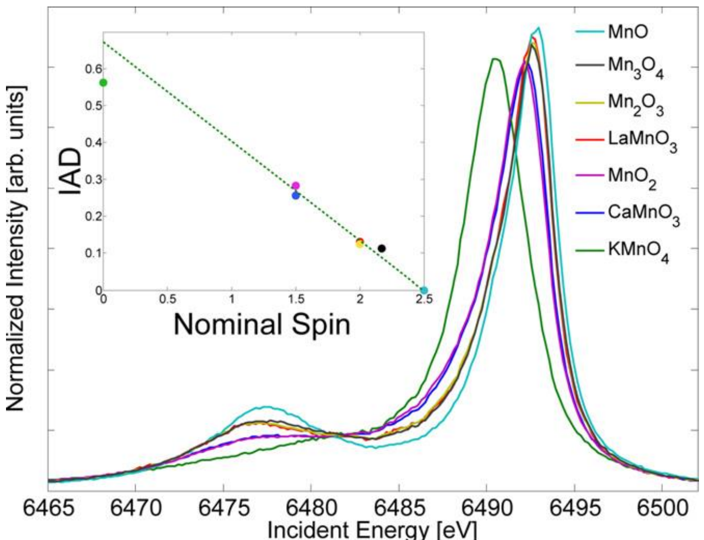
Kα



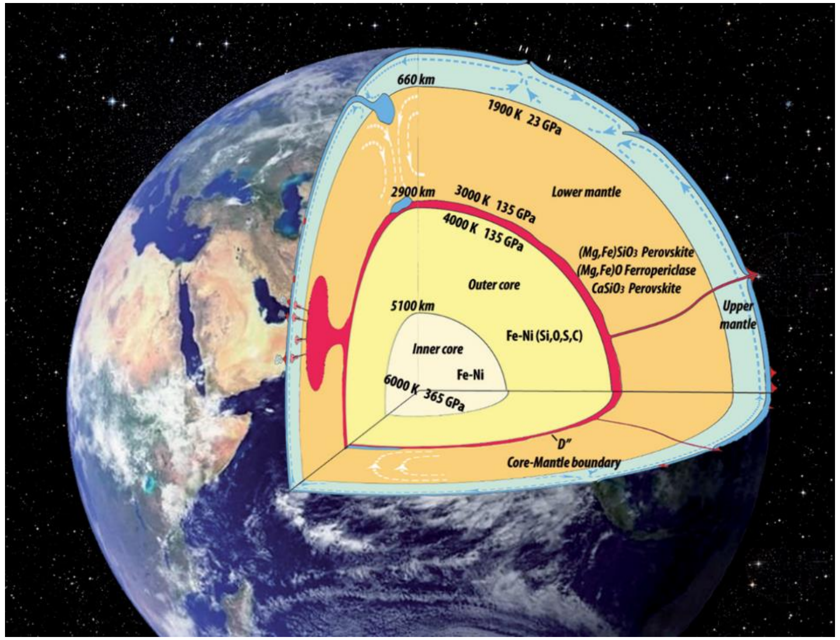


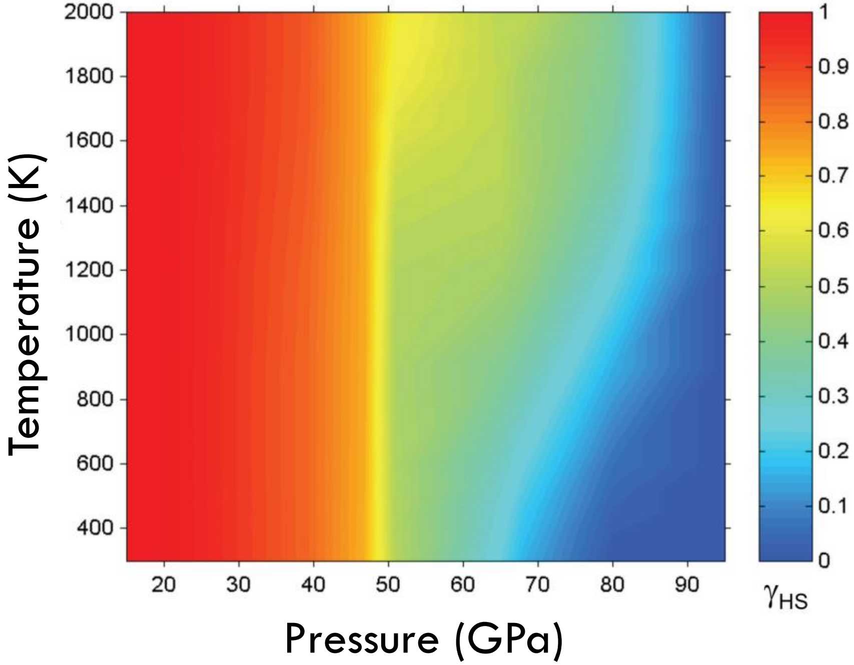
Kβ

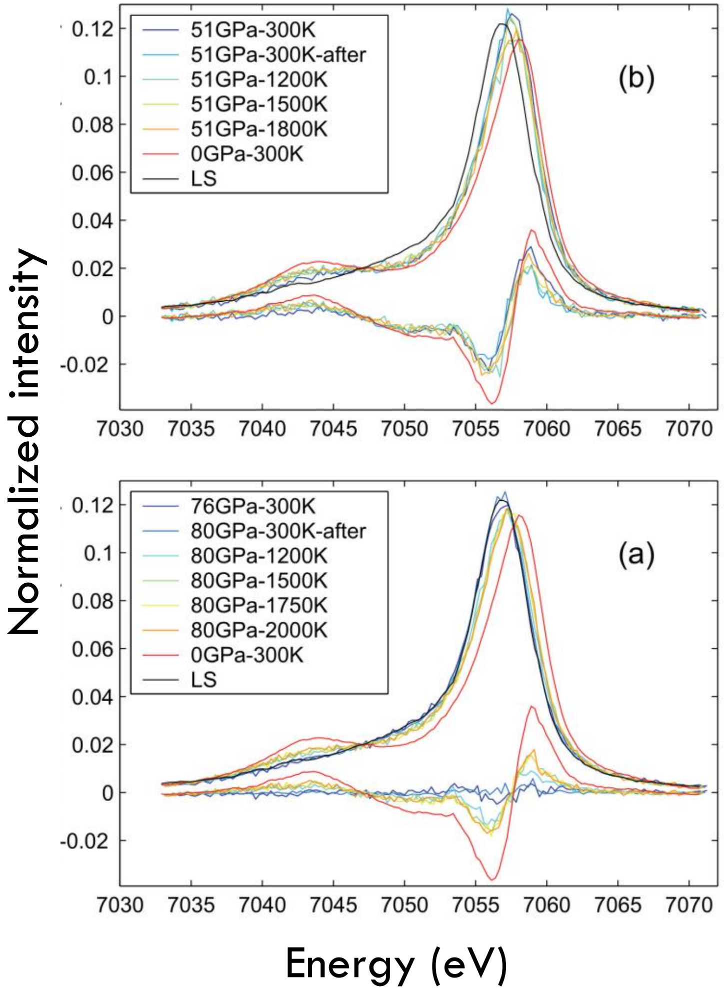


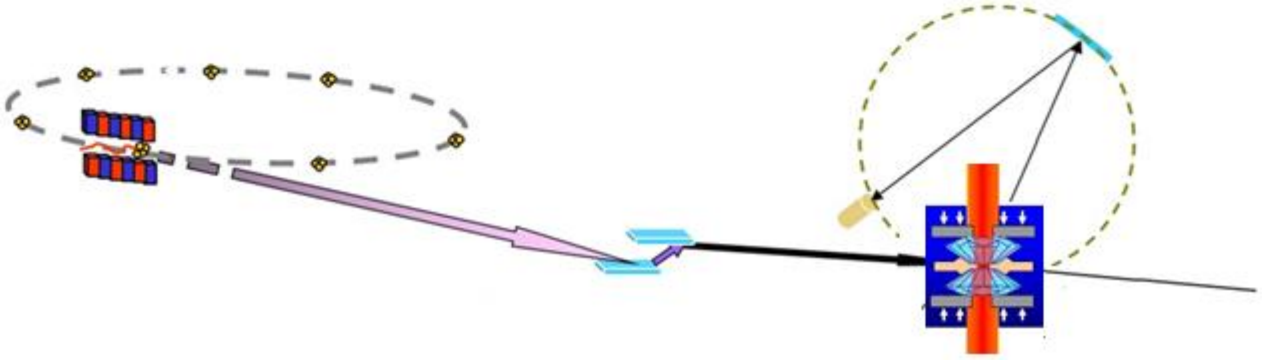


XES example: Earth’s mantle

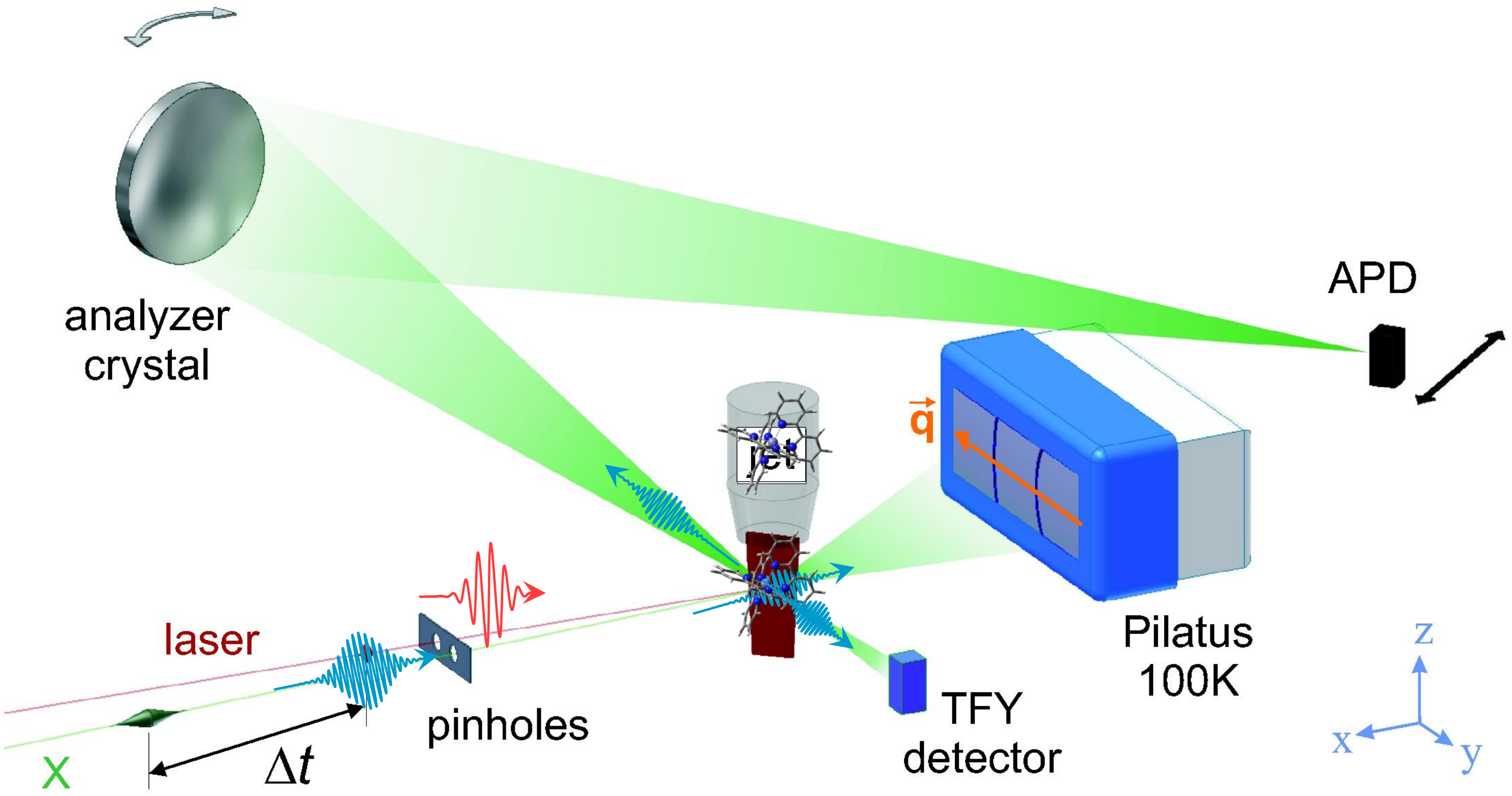








XES example: ultrafast processes

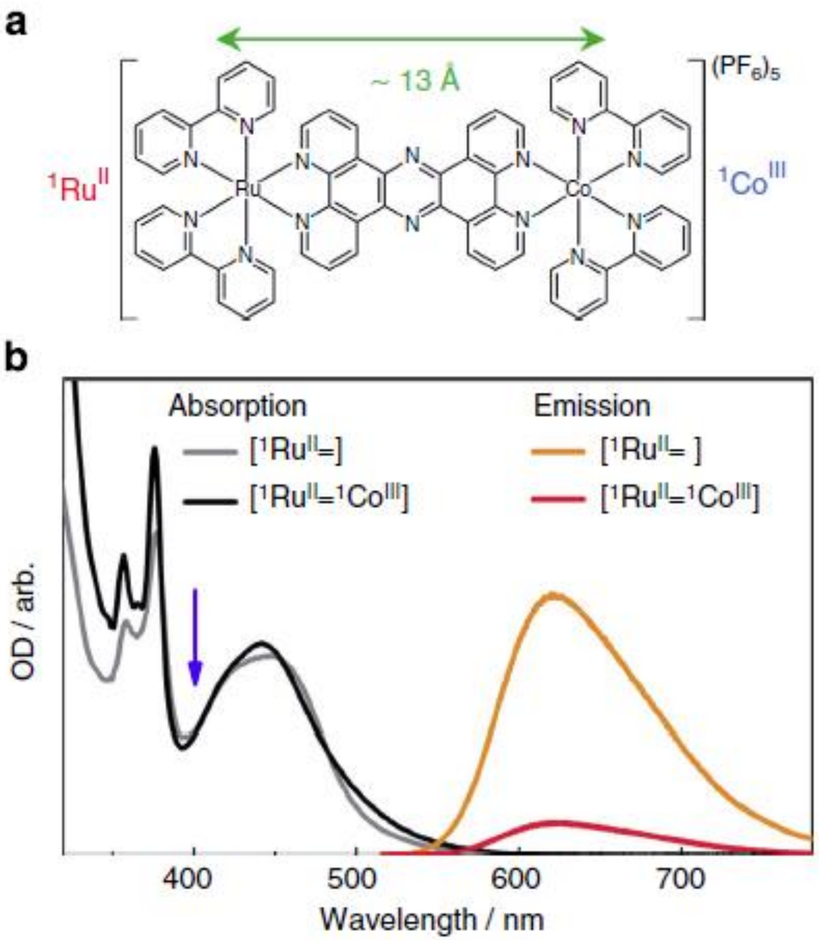


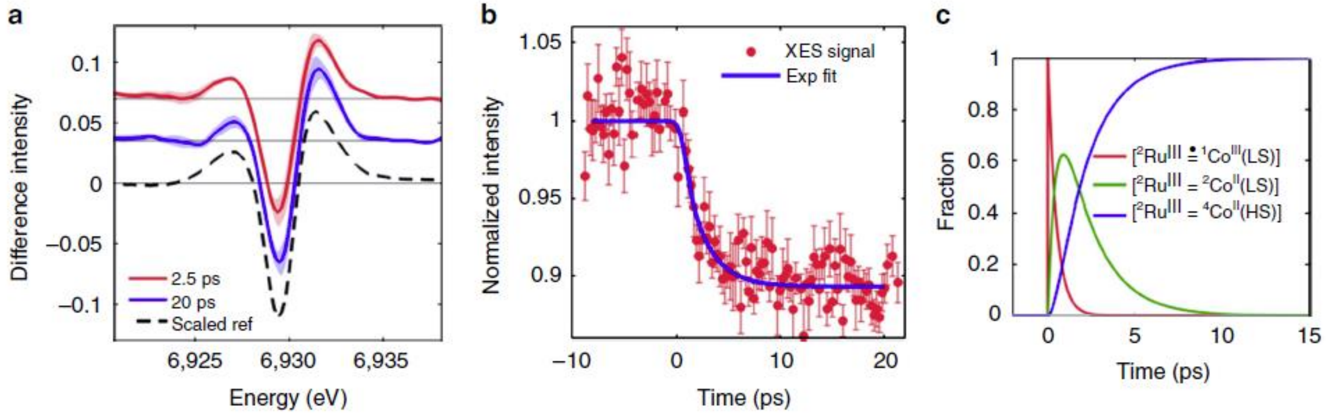
Courtesy of G. Vankó

XES example: ultrafast processes

$[(\mathrm{bpy})_2{}^1\mathrm{Ru}^{\mathrm{II}}(\mathrm{tpphz}){}^1\mathrm{Co}^{\mathrm{III}}(\mathrm{bpy})_2]^{5+}$

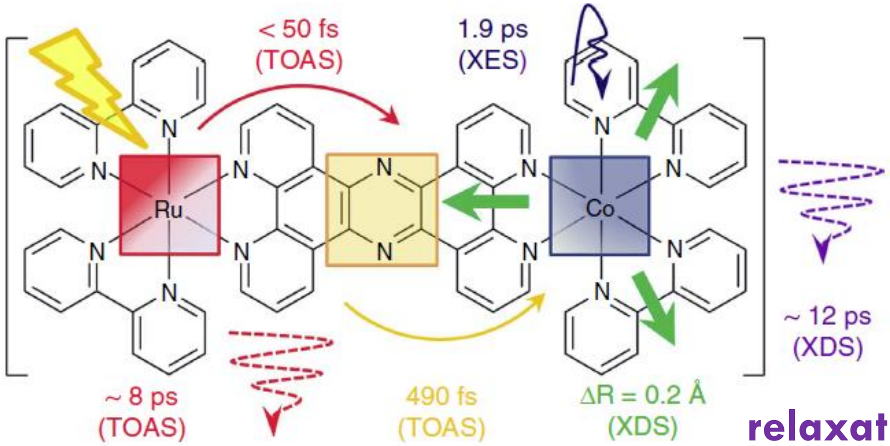
(bpy=bipyridine, tpphz=tetrapyrido phenazine)





electron leaves the Ru site, transfers through the bridge, leaves the bridge

electron transfer, spin-flip

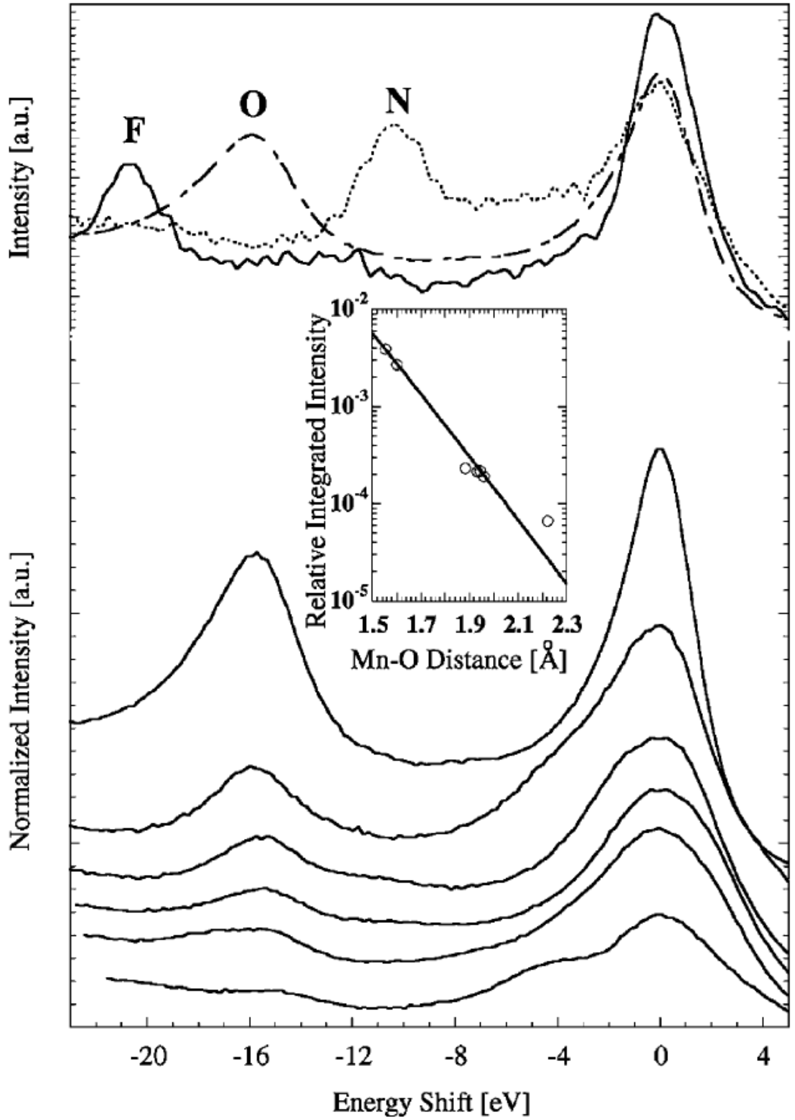


relaxation and energy release into the solvent

Valence-to-core XES

- valence orbitals: chemistry!
- vtc XES reflects ligand orbitals mixed with the core ion's orbitals
- XPS has the same final state but shows also the 3d orbitals of the core ion (different selection rules!)
- vtc XES is bulk sensitive

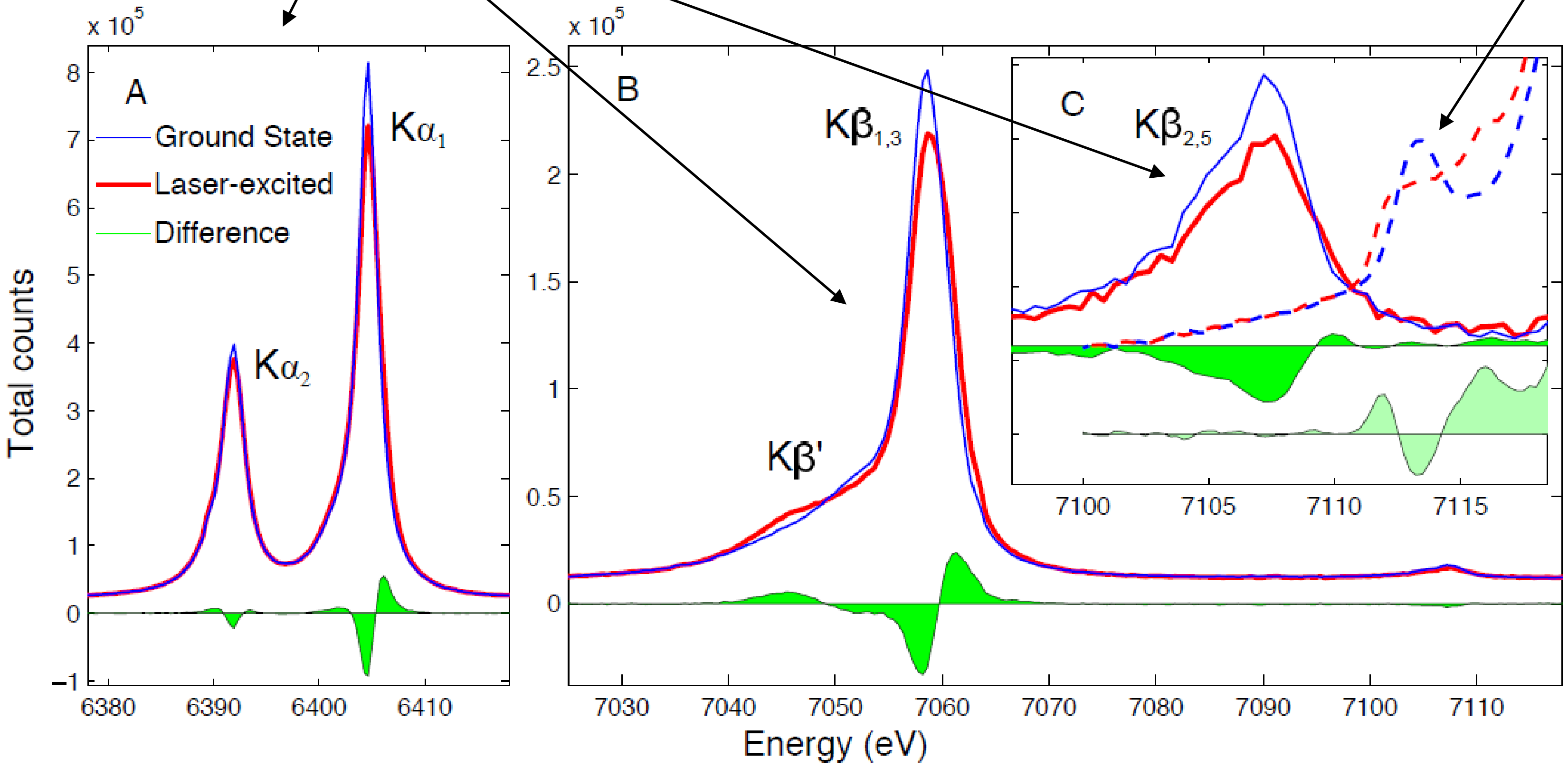
Mn vtc XES



From XES to XAS

XES peaks

XANES pre-edge



$[Fe(CN)_6]^{2-}$

- XES probes the highest occupied states
- XAS probes the lowest unoccupied states
- Difference would be the valence gap, but XES has a different electronic core structure (core hole!)

Combining XAS and XES

- $1s2p_{3/4}$ resonant XES spectra
- Scanning bot the incident and fluorescent X-ray energy
- Spectral features separate better

- High Energy Resolution Fluorescent detection XANES: scanning XAS via a specific fluorescent energy
- Overcoming the 1s core hole broadening