Complementary use of laboratory and free-electron X-ray sources to study metal-based complexes.

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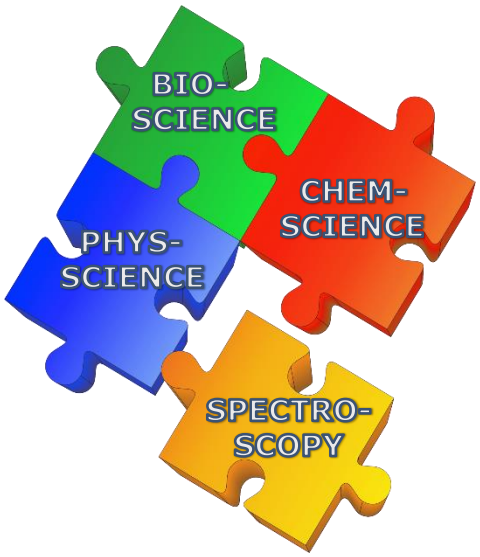
Jakub Szlachetko, Wojciech Błachucki, Anna Wach, Wiktoria Stańczyk, Rafał Fanselow, Wojciech Kwiatek

Department of Applied Spectroscopy

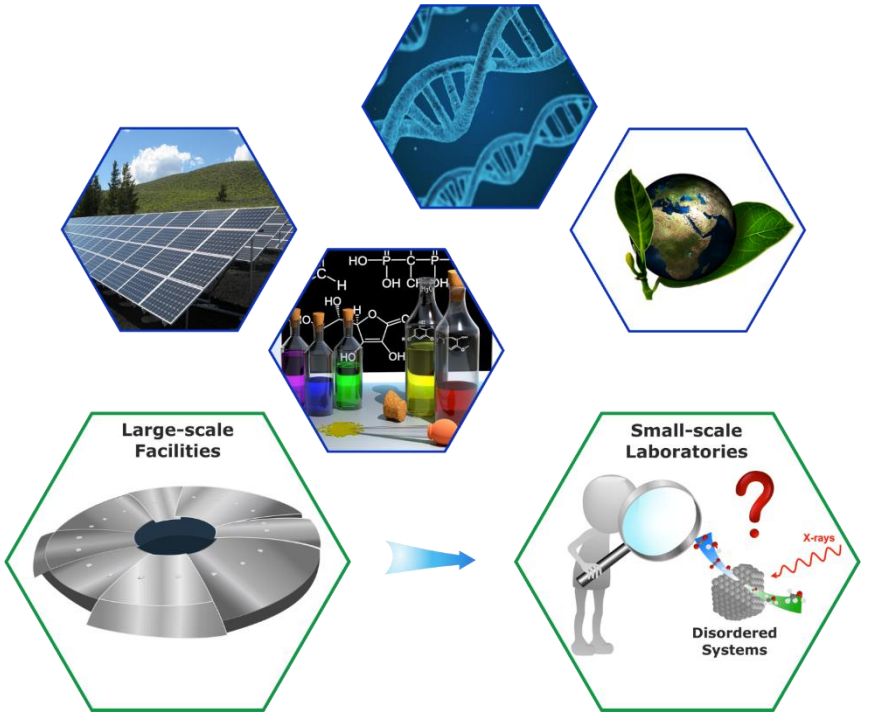
- X-ray spectroscopy applied to **bio**-science (DNA damage and repair mechanisms, interaction of metal-centred molecules with biological material)
- X-ray spectroscopy applied to **chemical** systems (charge transfer processes)
- X-ray spectroscopy applied to **nonlinear** interactions (core-core excitations, TPA)



Laboratory X-ray spectrometers/methods
(XAS/XES spectrometer setups, sample delivery systems, sample cells development)

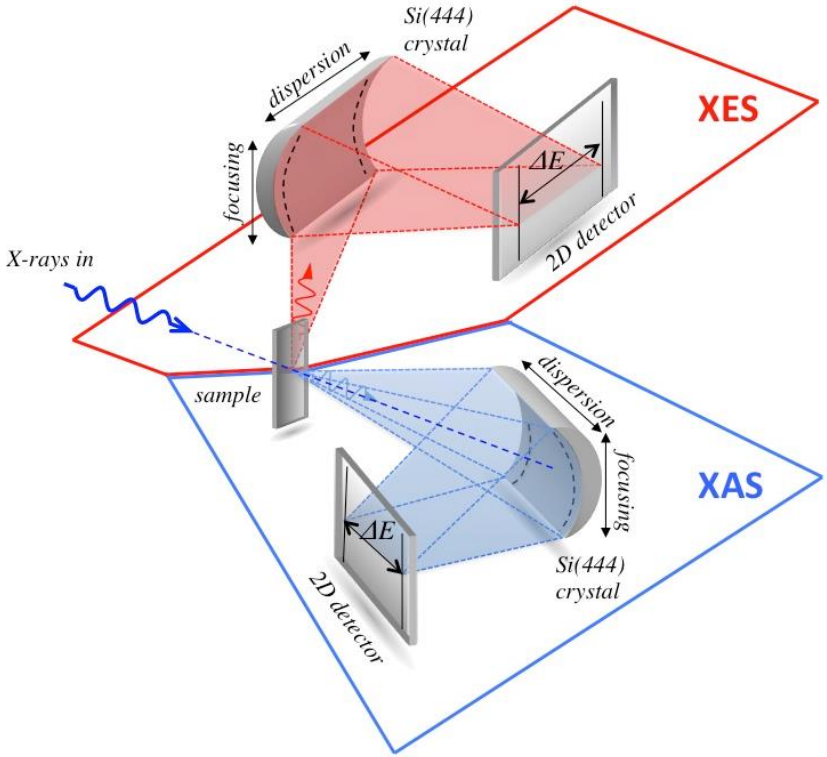
Synchrotron research
(spectroscopy on biological and chemical systems)

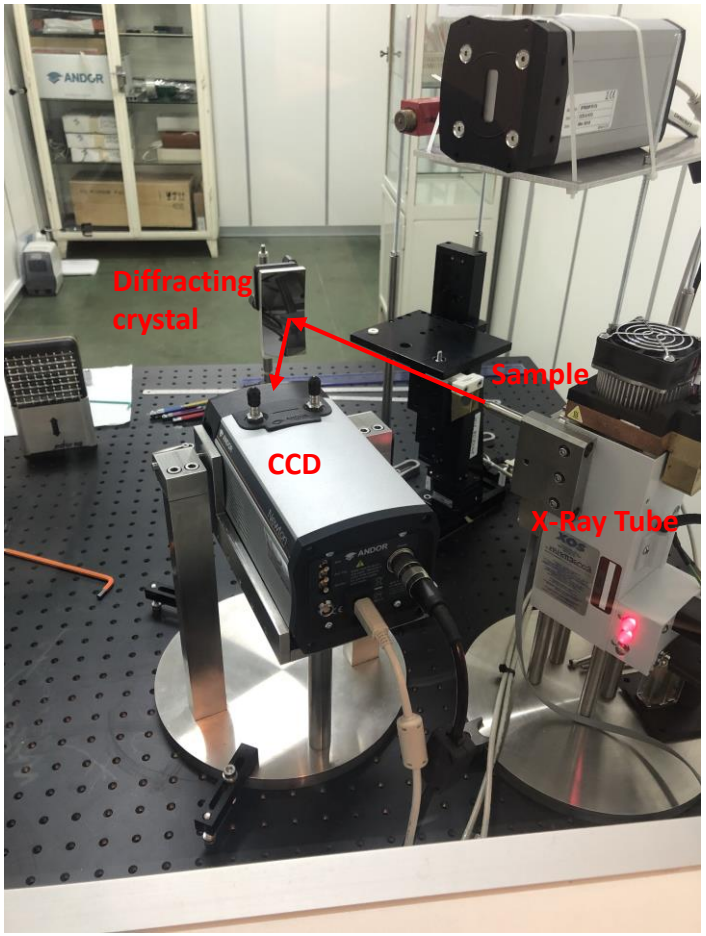
Science with **XFELs**
(dynamics, nonlinear interaction)



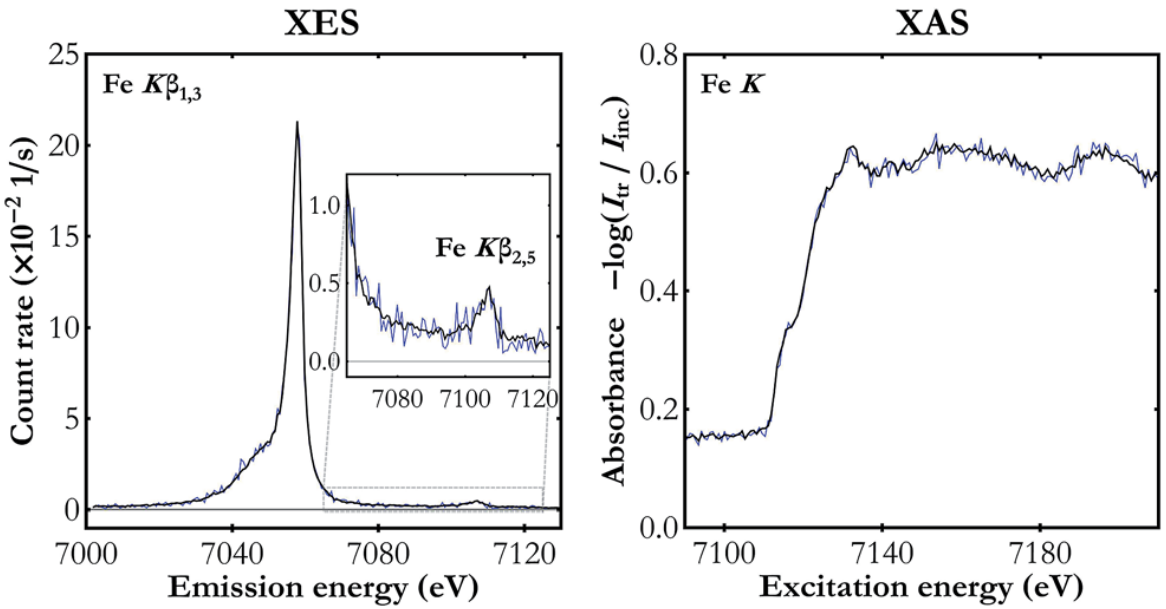
Laboratory setup

XAS/XES laboratory setup at IFJ PAN, Kraków





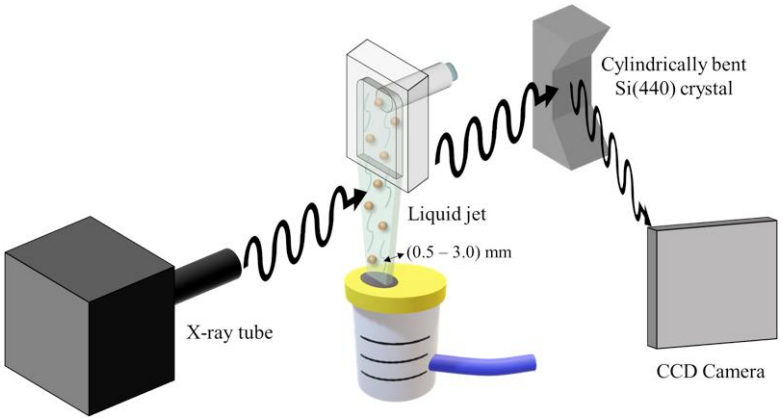
System performances (solids):



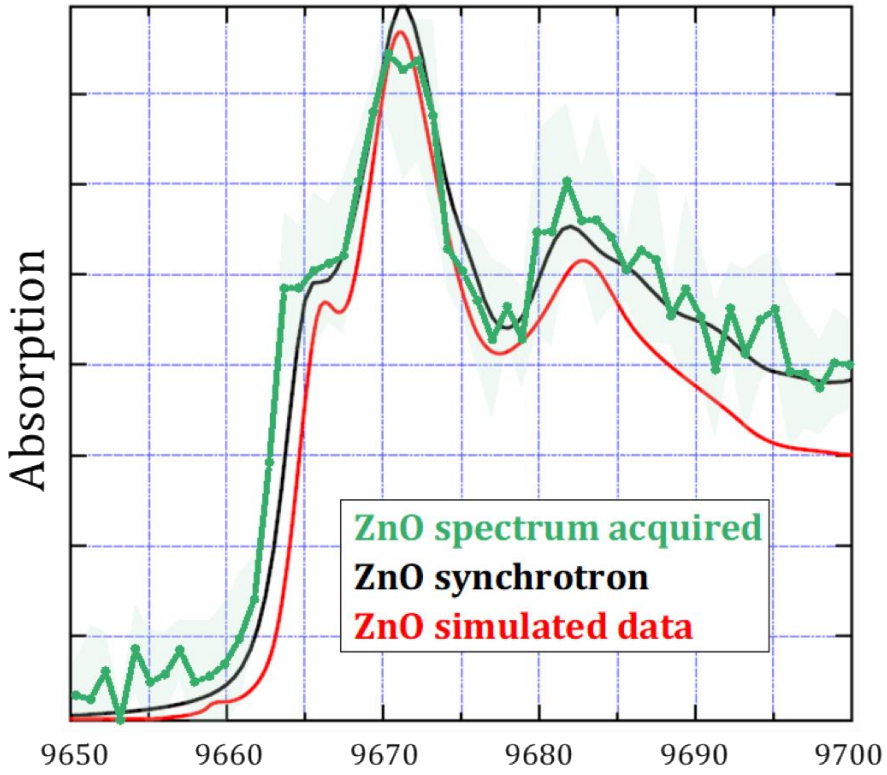
The simultaneous Fe Kb XES and Fe K-edge XAS measurement for two acquisition times: 2 hours (blue line) and 20 hours (black line)

W. Błachucki et al., *Journal of Analytical Atomic Spectrometry* **34**, 1409 (2019).

System performances (liquids):



ZnO in H2O



W. R. Faselow, *Synthesis of copper nanopraticles and characterization by means X-ray spectroscopy techniques*, master thesis (2020).

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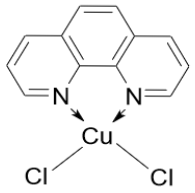
"Studies of the interaction of copper-based complexes with DNA by means of X-ray spectroscopy techniques"

Metal complexes in cancer therapy

Limitations of popular chemotherapeutics (i.e. cisplatin):

- high toxicity (side effects)
- primary or acquired resistance

- the development of new compounds (containing platinum or other metals) with modes of action different from that of cisplatin became an urgent task



$Cu(1,10\text{-phen})Cl_2$

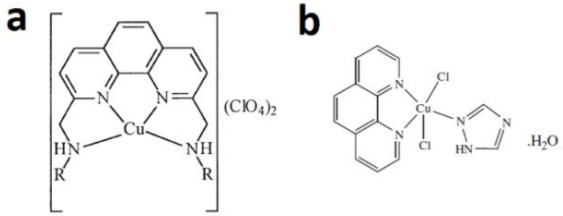
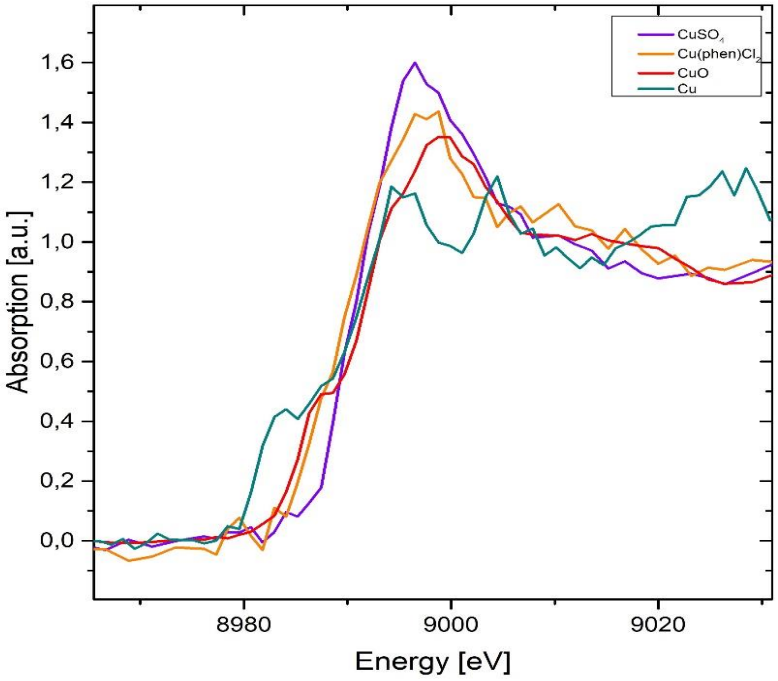


Fig. 2. Structural formula of a.) complex $(CuL)(ClO_4)_2$[17] and b.) complex $[Cu(phen)TzCl_2]H_2O$ [18].

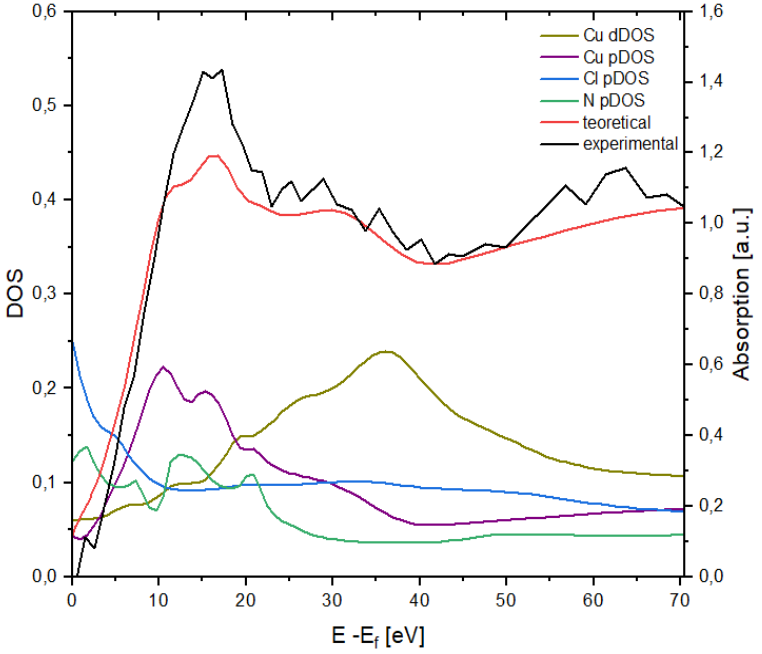
- Cytotoxicity
- Mechanism of action
- Mechanism of action, activity vs structure

Chemical information

Preliminary results (XAS)



XAS spectra of different copper samples, obtained in laboratory conditions.



Results of theoretical calculations of XAS spectrum and density of states (DOS)

Future perspectives:

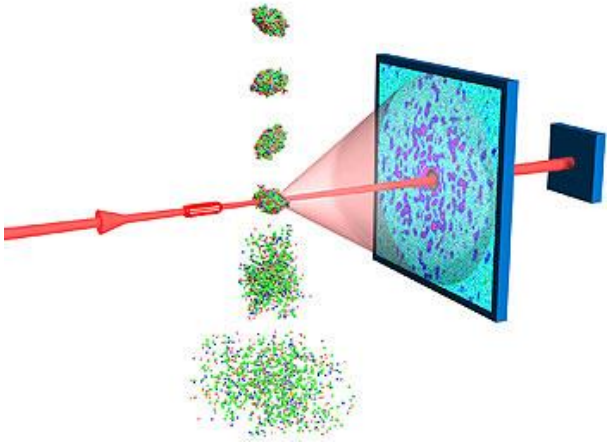
- Simultanous XAS/XES experiments of bio-samples
- Liquid biological samples (low concetration)
- BioLab on site (living cells experiments)

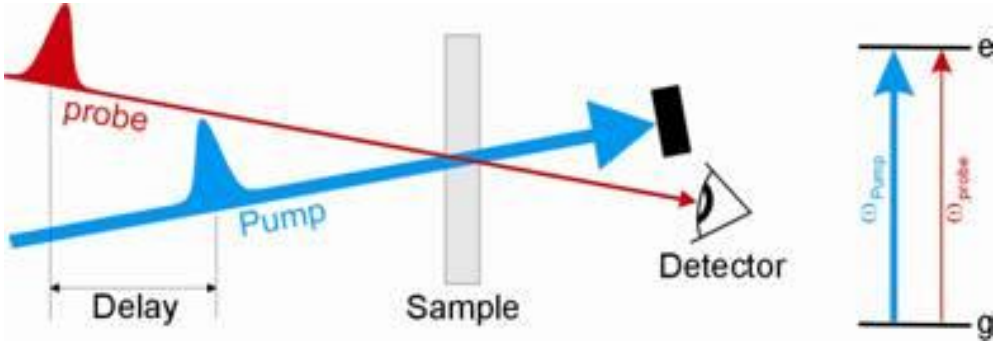
Free Electron Lasers

Free Electron Lasers

Three types of experiments benefit from the high peak flux from an XFEL:

1. **Single-shot experiments** that need lots of photons in a short pulse
2. **Pump-probe measurements** where the short pulse allows measurement of fast dynamics
3. **Nonlinear X-ray experiments** that depend nonlinearly on the number of incident X-ray photons





X-ray induced sample damage

X-ray induced damage to radiation-sensitive samples is a phenomenon well-known in X-ray community in the energy range of hard X-rays.

Sample exposition to X-rays:

Photo-reduction Photo-oxidation
(sample and matrix dependent)

Reducing effects of the X-ray sample damage:

- Liquid jet samples, samples circulations
- Cryo-cooling techniques
- Use of XFEL radiation: *Probe-before-destroy* methodology

Challenge of X-ray radiation damage is well recognized but rarely studied systematically.

X-ray damage with XFEL pulses: Experimental setup

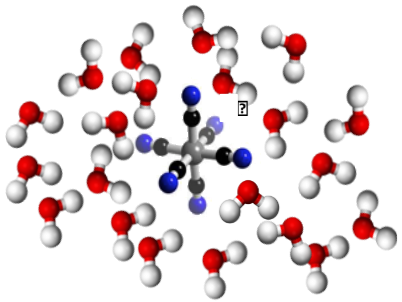
Linac Coherent Light Source

https://lcls.slac.stanford.edu/overview

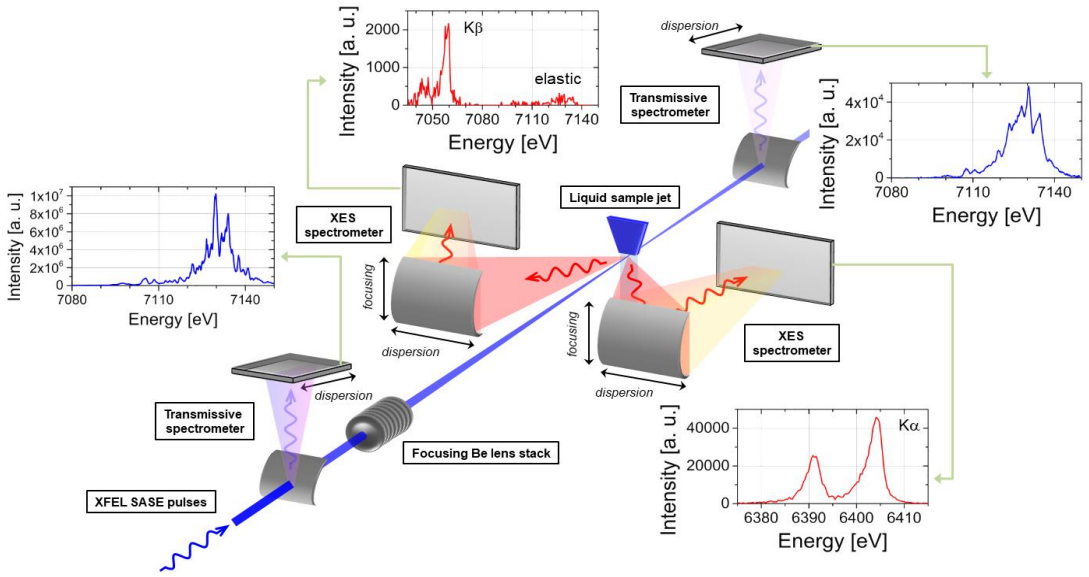
Beam parameters & sample:

XPP station of LCLS
7200eV (above Fe K-edge)
Pulse length = 30fs
3-6 x 10^{11} photons/pulse
Down to 3 x 3 um^2 beam size

Sample: 100 mMol hexacyanoferrate(II)
$(Fe(CN)_6/H_2O)$



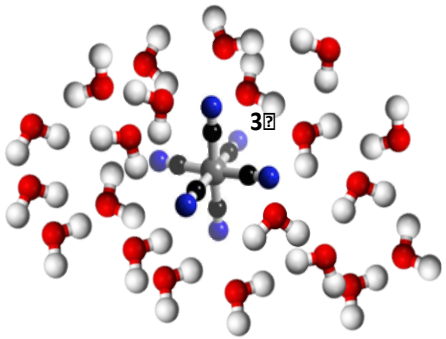
X-ray spectroscopy setup to track electronic structure changes:



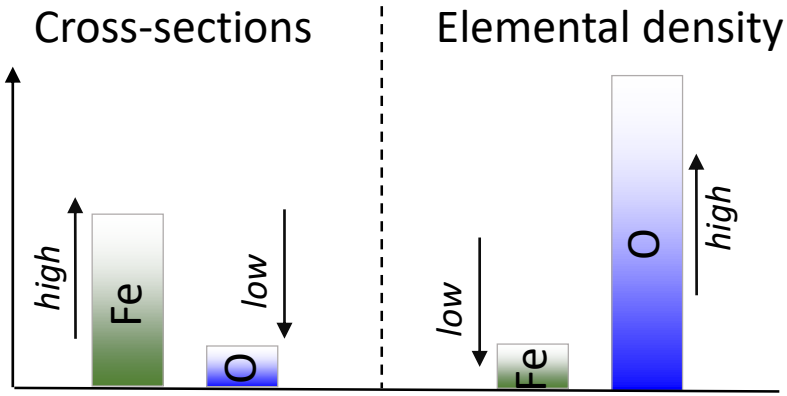
$K\beta_{1,3}$ X-ray emission signal as a probe of chemical and spin state of Fe metal center

Molecules electronic damage with XFEL pulses
X-ray interaction with matter

What are the physical processes leading to the Fe X-ray induced damage?



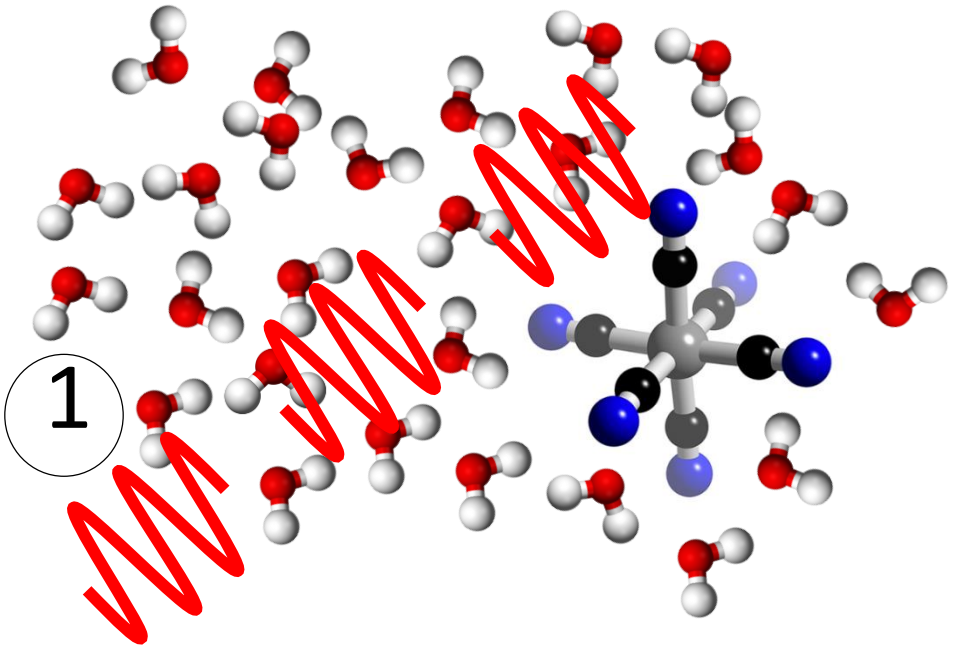
X-ray interaction with sample



95% of X-rays are absorbed by Oxygen

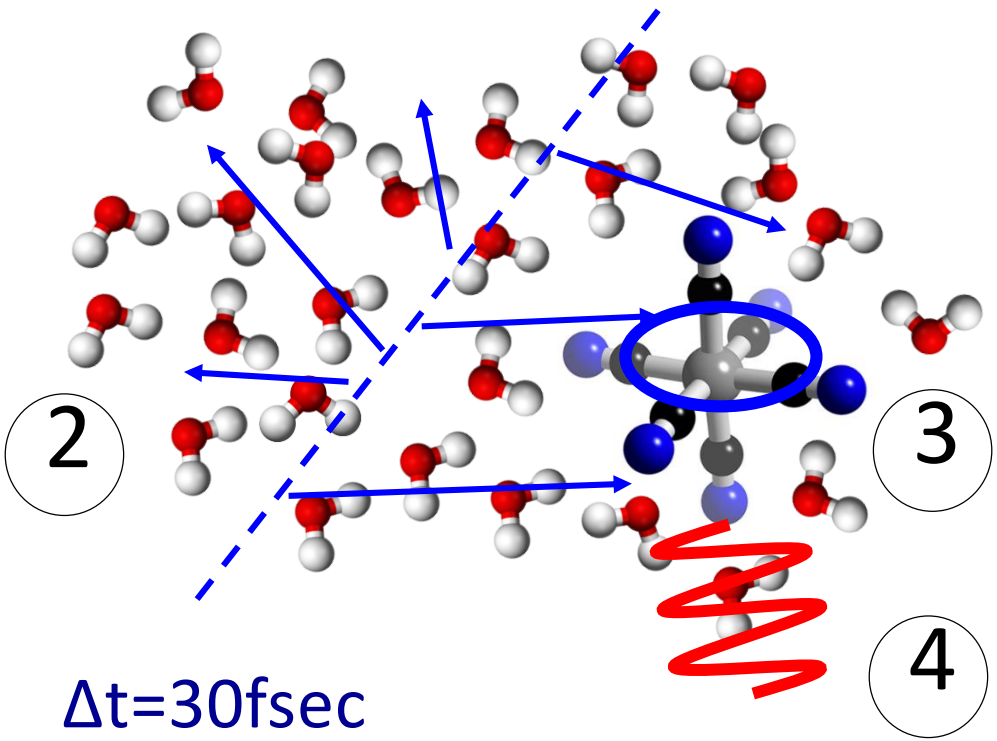
W. Blachucki et al., Structural Dynamics, 6, 024901 (2019).

Inception of X-ray damage of molecules in solution

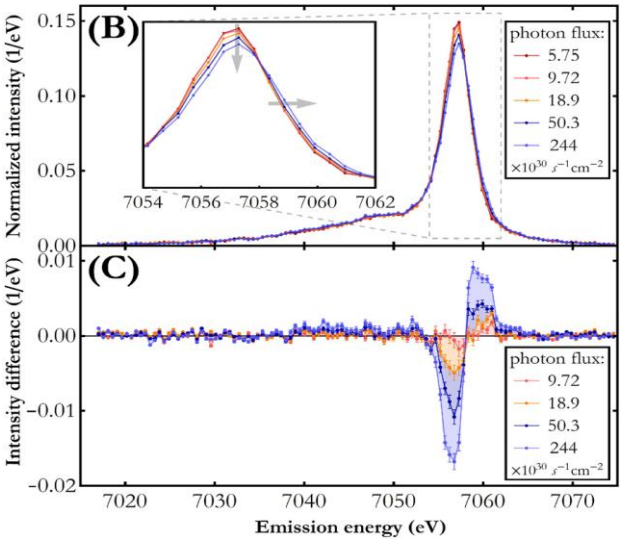


- X-ray interaction with solvent

Inception of X-ray damage of molecules in solution



- X-ray interaction with solvent
- Generation of energetic electrons
- Electron – impact Fe ionization
-



Highly charge state molecule with preserved atomic positions

Inception of X-ray damage of molecules in solution Quantitative and qualitative analysis

Monte-Carlo simulations* with fundamental atomic parameters:

Calculated distribution of Fe charge state:

1 electron hole-Fe3+ : **29**%

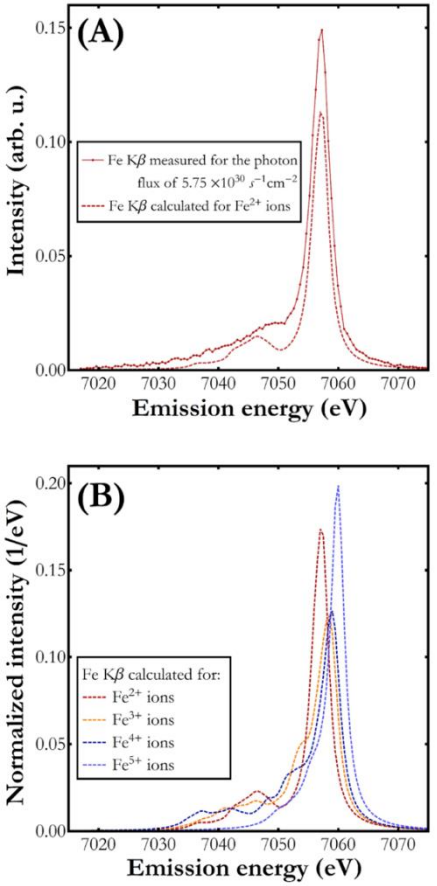
2 electron hole-Fe4+: **31**%

3 electron hole-Fe5+ : **12** %

4 electron hole-Fe6+: **4** %

*Fe- electron impact and the following Auger decays are considered

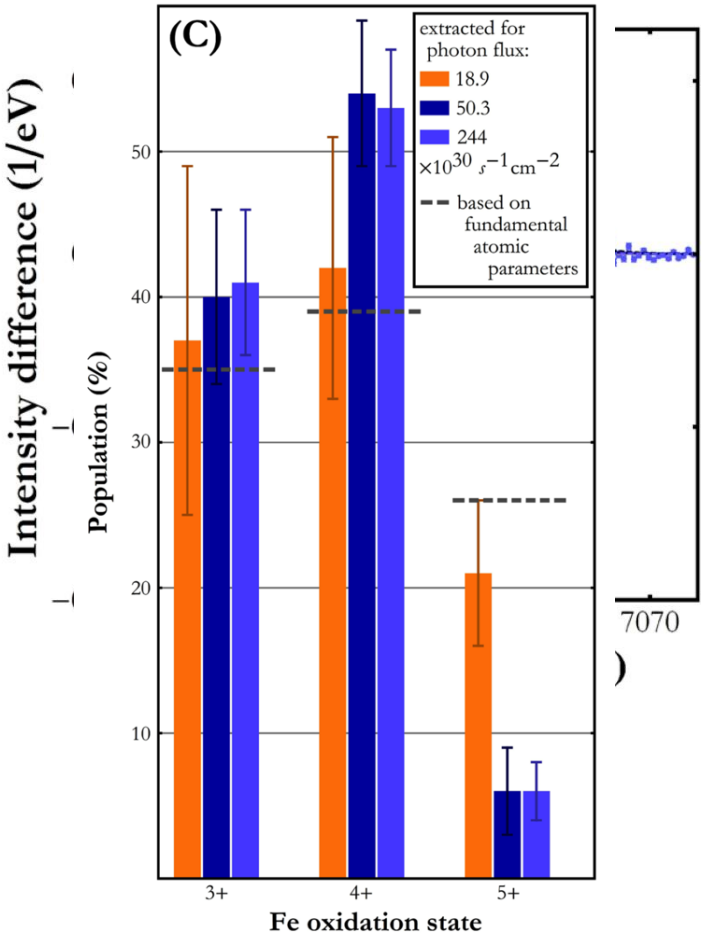
Spectral calculations using crystal-field multiplet (CFM) at different oxidation states. The electronic structure of the hexacyanide complexes were evaluated within the DFT.



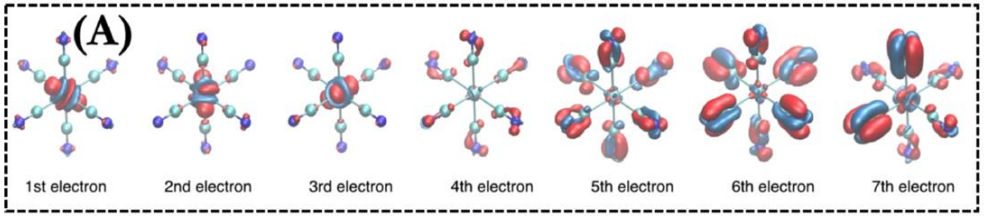
W. Blachucki et al., Structural Dynamics, 6, 024901 (2019).

Inception of X-ray damage of molecules in solution
Quantitative and qualitative analysis

Charge state distribution



Mechanism of the high Fe valence state creation



Charge density difference maps upon subsequent electron loss.

- First electron is removed from a metal-dominated t_{2g} orbital. At the same time electron density increases along Fe-C bond.
- The next two steps, metal t_{2g}-centered oxidations (FeV state).
- Further electrons removal leads to gradual loss of spin, accompanied with electron flow from the ligands to the metal.
- The system thus approaches Fe(IV) species rather than Fe(VI) when more electrons are lost (Fe(V) state is highest accessible)

E. Källman & M. Lunberg

UPPSALA UNIVERSITET

Inception of X-ray damage summary:

- X-ray photons induce solvent ionization within sub-fs leading to the formation of solvated electrons. The travel range of these electrons amounts in average to tens of nm and the electrons may reach the nearest Fe atoms in less than 1 fs. Fe electron-ionizations increase Fe oxidation state (without affecting molecule's atomic positions).

- Analysis showed creation of Fe species with distribution of higher oxidation states. DFT predicts Fe5+ state as highest accessible, lack of electrons is compensated with charge donation from ligands.

- Mechanism should be valid for on samples embedded in, e.g., solutions or in matrices

Complementarity

Lab setups:

- Constant access @ home institution
- Principal analysis (chemical structure, oxidation state)
- In case of processes – define the initial and final state

Free Electron Lasers:

- Unique X-ray properties
- Exceptional temporal resolution

Using both approaches gives opportunity of detailed sample analysis.

Acknowledgments

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Thank you for your attention!

Line	Part Number	Description
1	X-Beam	Superflux PF X-Beam with Mo anode

Superflux PF X-Beam with Mo-anode x-ray tube and a polycapillary focusing x-ray optic
- *Max voltage: 50KV; Max beam current: 1.0mA; Max power: 50W*
- *Output focal distance (OFD) of the polycapillary optic: 21.0mm*
- *Focal spot: <= 100 um, FWHM, at 10 keV*
- *Intensity gain at 17.4 keV (vs. a 50um pinhole 100mm from the source): >= 1000*
- *Output x-ray intensity (Mo K lines) at full power: >= 5.0E8 photons/sec*
- *Output beam divergent angle: > 3 degrees*
- *Stability: Better than +-1% for at least eight hours with x-ray tube temperature within +- 2 degrees Celsius*
- *Air Cooled, oil free packaging*
- *Built-in safety shutter and cooling fan*
- *8-position filter wheel (filter materials not included)*
- *Equipped with four mounting holes*
- *Dimensions: no greater than 40cm X 40cm X 40cm*
- *Net weight: ~7.0 kg*