MAX PLANCK INSTITUTE
FOR CHEMICAL ENERGY CONVERSION

IN-HOUSE X-RAY SPECTROSCOPY AT THE MPI CEC UPDATE AND APPLICATIONS

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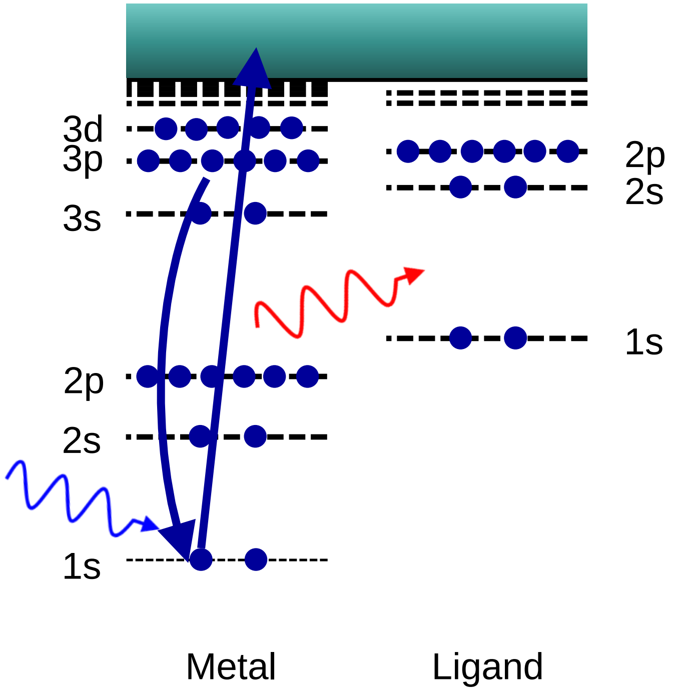
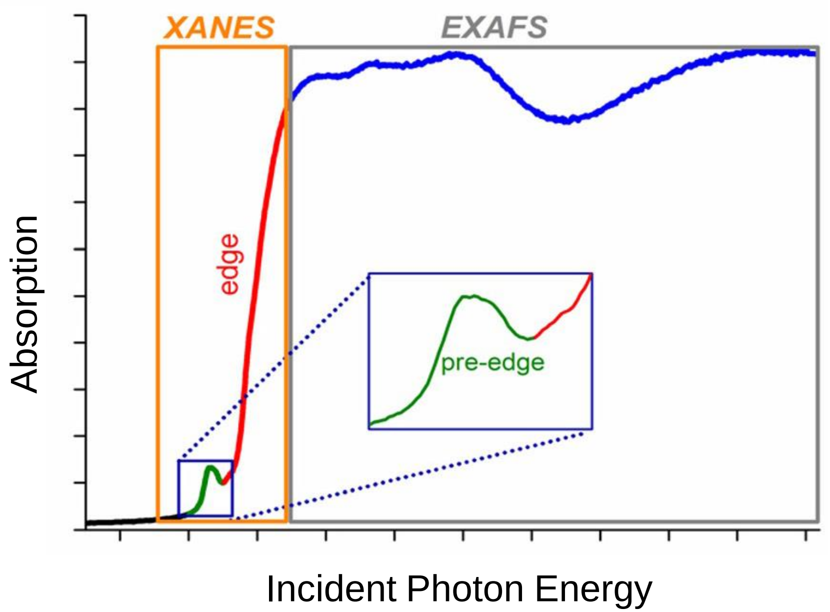
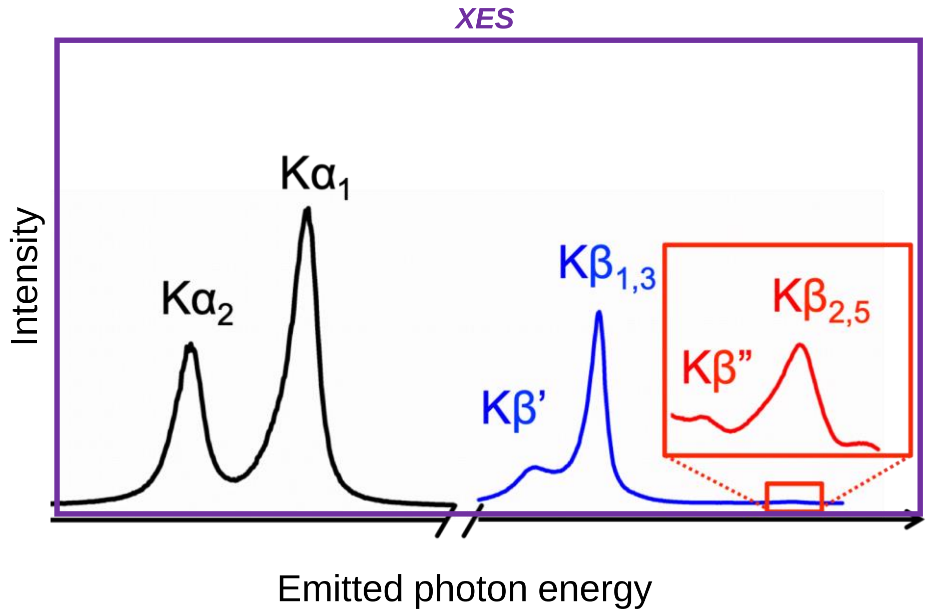
X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY







XANES
- pre-edge → local ligand field
- → oxidation state
- edge region → site symmetry

EXAFS
- → distance nearest neighbors
- → type of nearest neighbor
- → coordination number

XES
- Kβ main line → spin state, oxidation state
- → metal-ligand covalency
- VtC → ligand identity, bond length

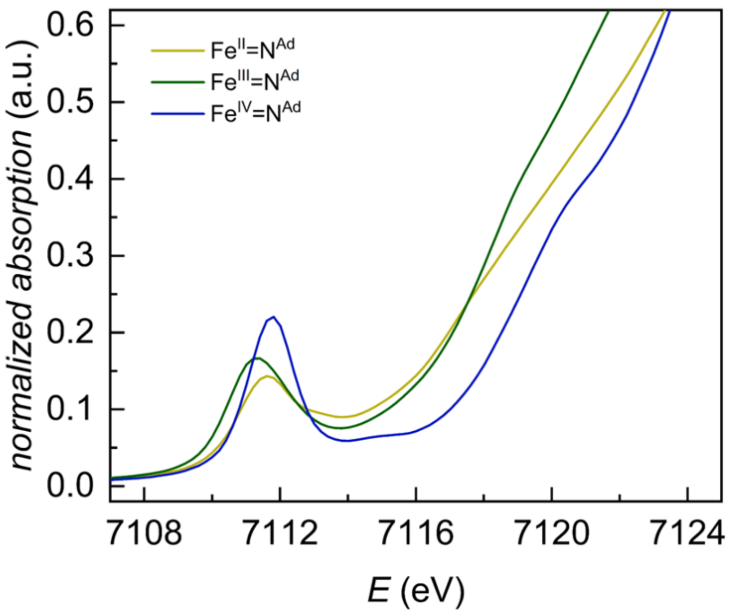
METAL-LIGAND BOND AND PRE-EDGE INTENSITY

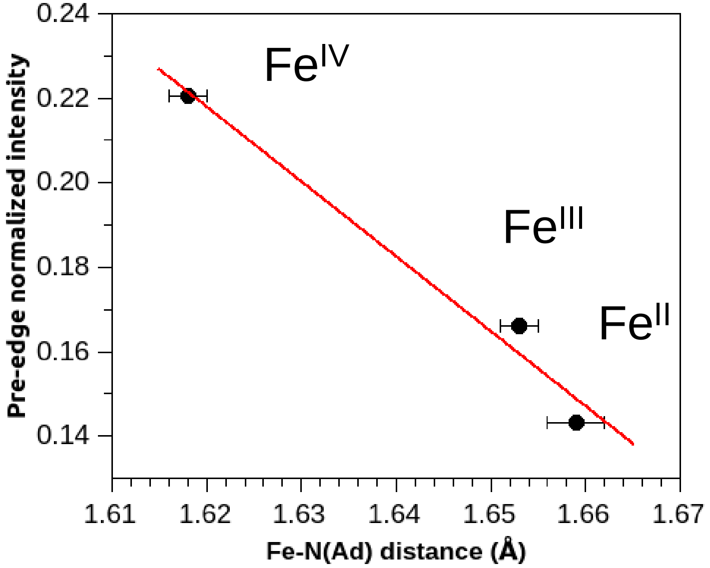
	$Fe–N^{Ad}$ (Å)	Calc. main pre-edge intensity*
Fe^{II}	1.659(3)	1.08
Fe^{III}	1.653(2)	2.64
Fe^{IV}	1.618(2)	4.06

* most intense calculated transition in the pre-edge region

Short, strong covalent bonds in non-centrosymmetric systems tend to increase pre-edge intensity

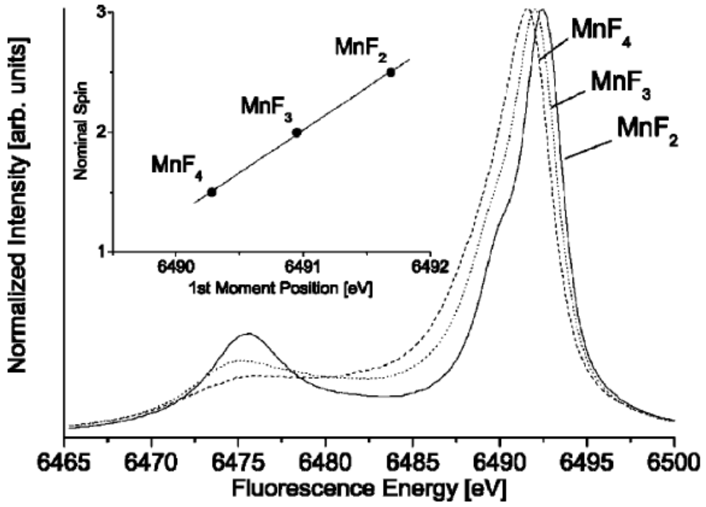
Experiment

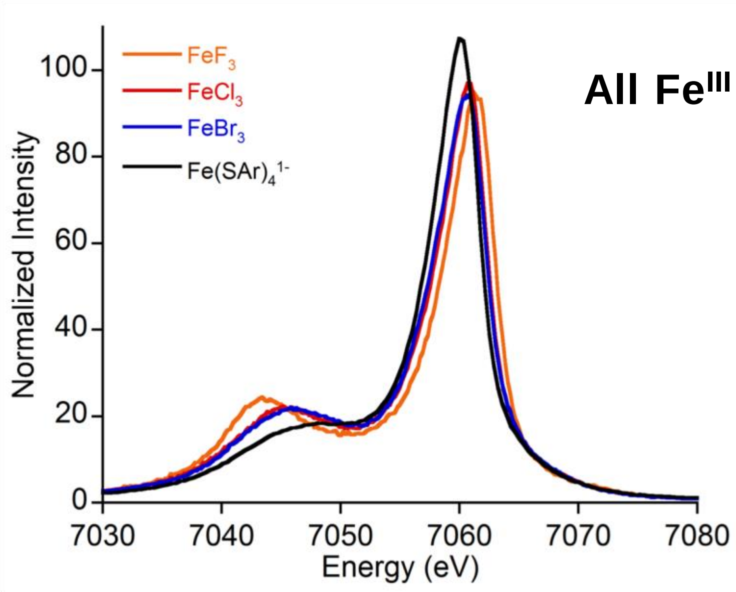




J. Am. Chem. Soc. 145, 2, 873-887 (2023).

XES: SPIN STATE AND COVALENCY





All Fe^{III} (d^5) HS

- $K\beta_{1,3}$ and Kβ' move closer together with decreasing spin state (i.e as 3p-3d exchange interaction decreases)
- Kβ lines reflect number of unpaired d electrons
- Require very little time to measure (minute(s) using SR) or minutes to hours with a stand-alone source.

Coord. Chem. Rev. 249, 65 (2005).

- Even for a series of high spin ferric compounds, large variations in the Kβ mainlines are observed
- Change in ΔE > of over 4.5 eV
- If nominal spin is known (by other methods) covalency can be extracted.
- Emphasizes importance of combined methods.

J. Am. Chem. Soc. 136, 9453 (2014).

IN-HOUSE X-RAY SPECTROSCOPY FACILITIES AT THE CEC

XES
XAS
EXAFS

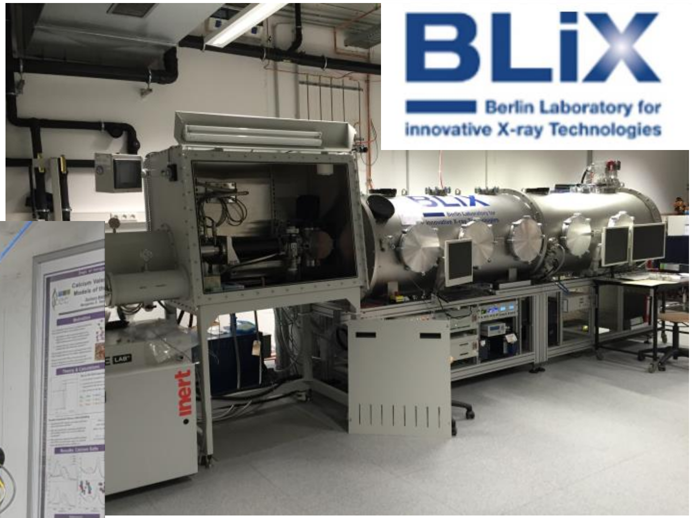
Hard X-ray radiation

EXAFS

Hard X-ray radiation

Talk from Carl

XANES
Hard X-ray radiation



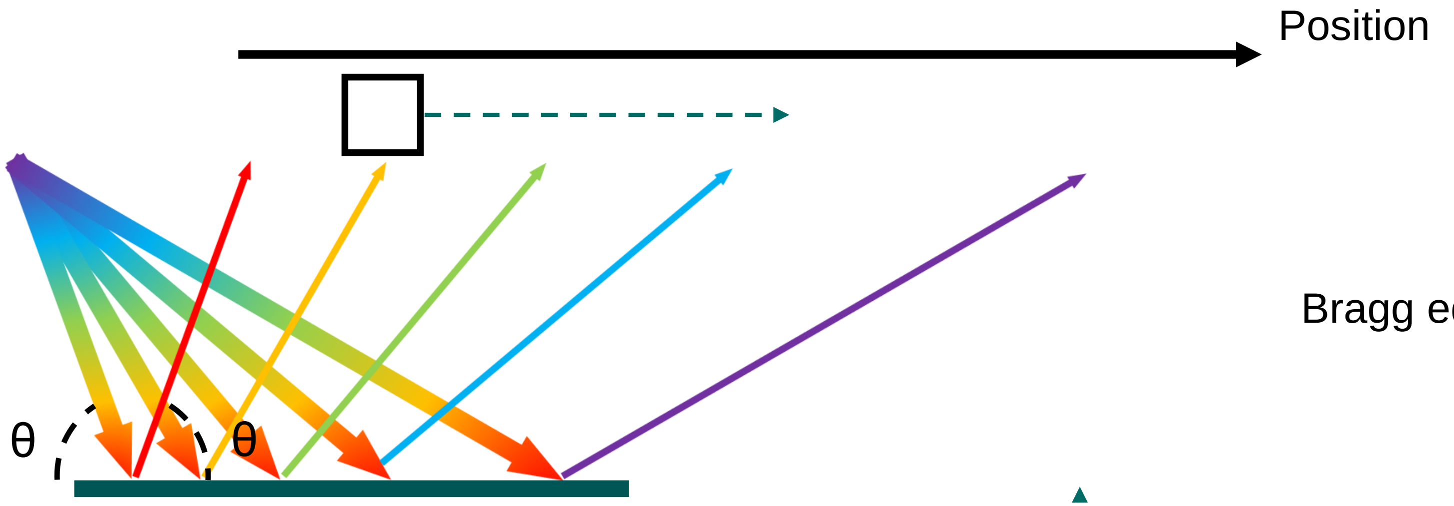
XES

Tender to hard X-ray radiation

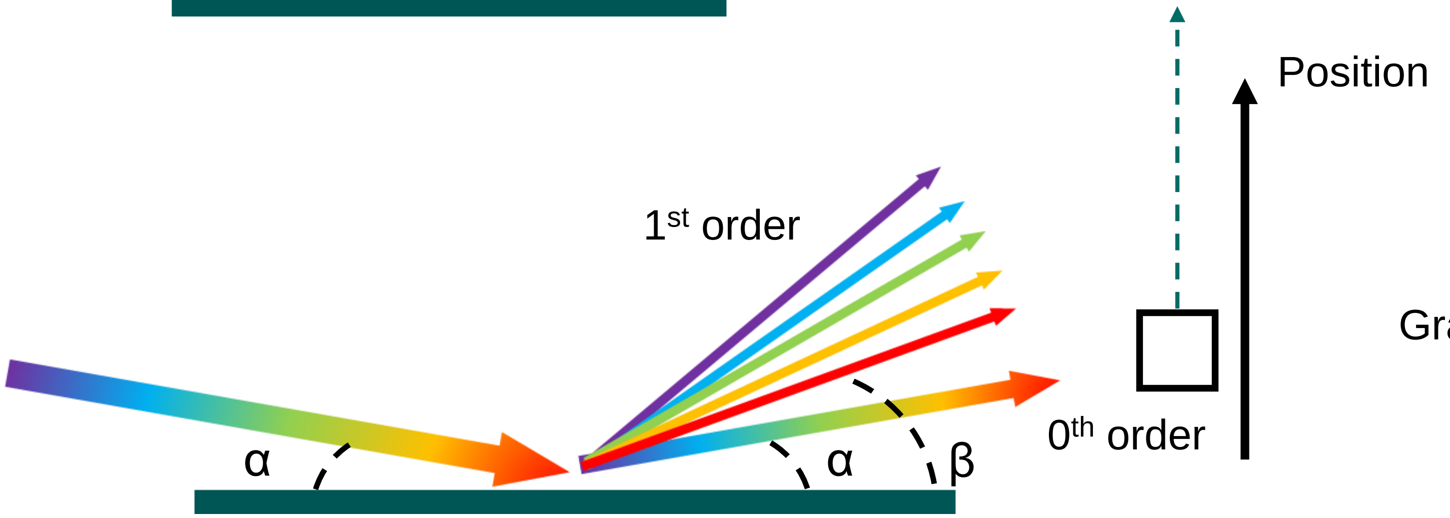
XAS

Soft X-ray radiation

SCANNING-TYPE SPECTROMETERS

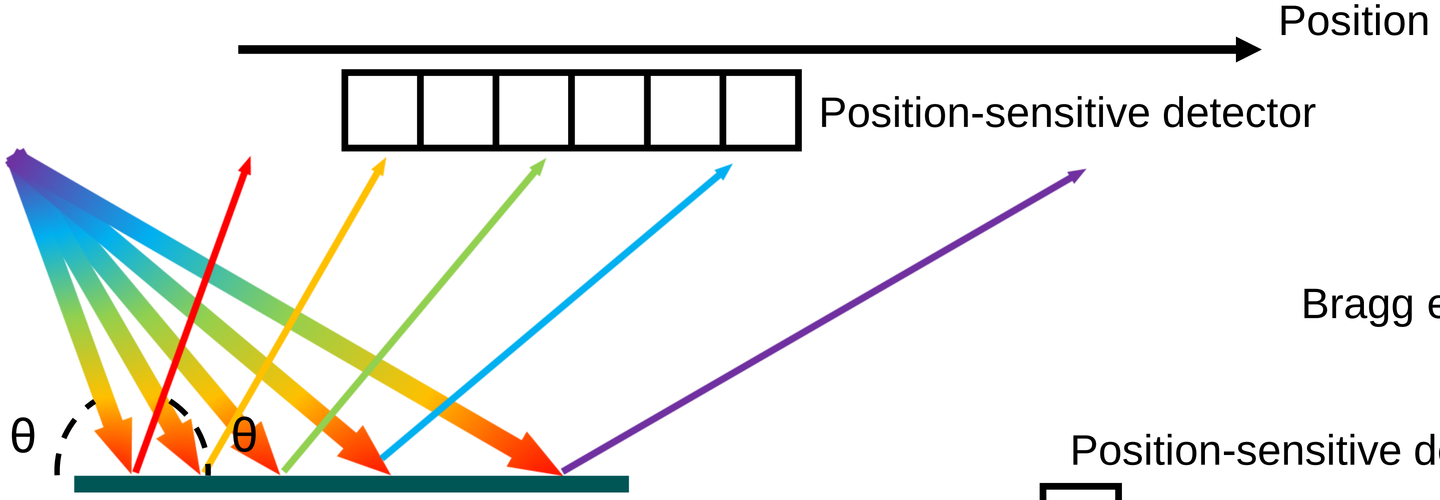


Bragg equation: $n\ \lambda = 2d \sin\theta$

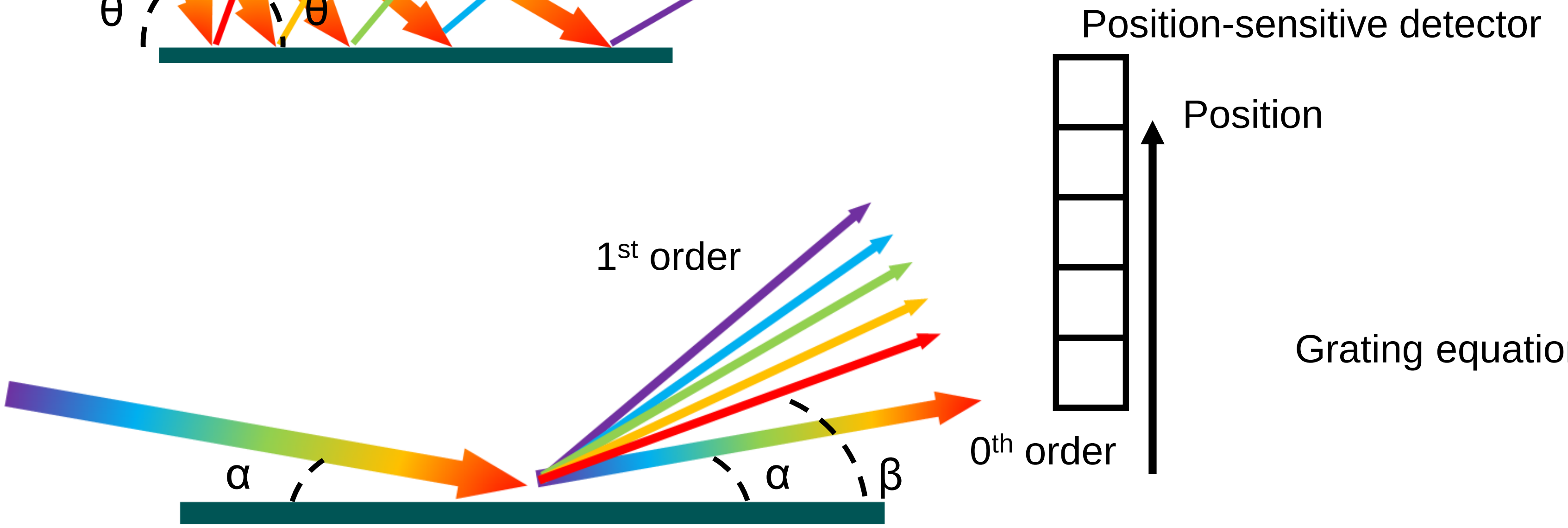


Grating equation: $n\ \lambda = d_0 \cos\alpha + \cos\beta$

DISPERSIVE-TYPE SPECTROMETER

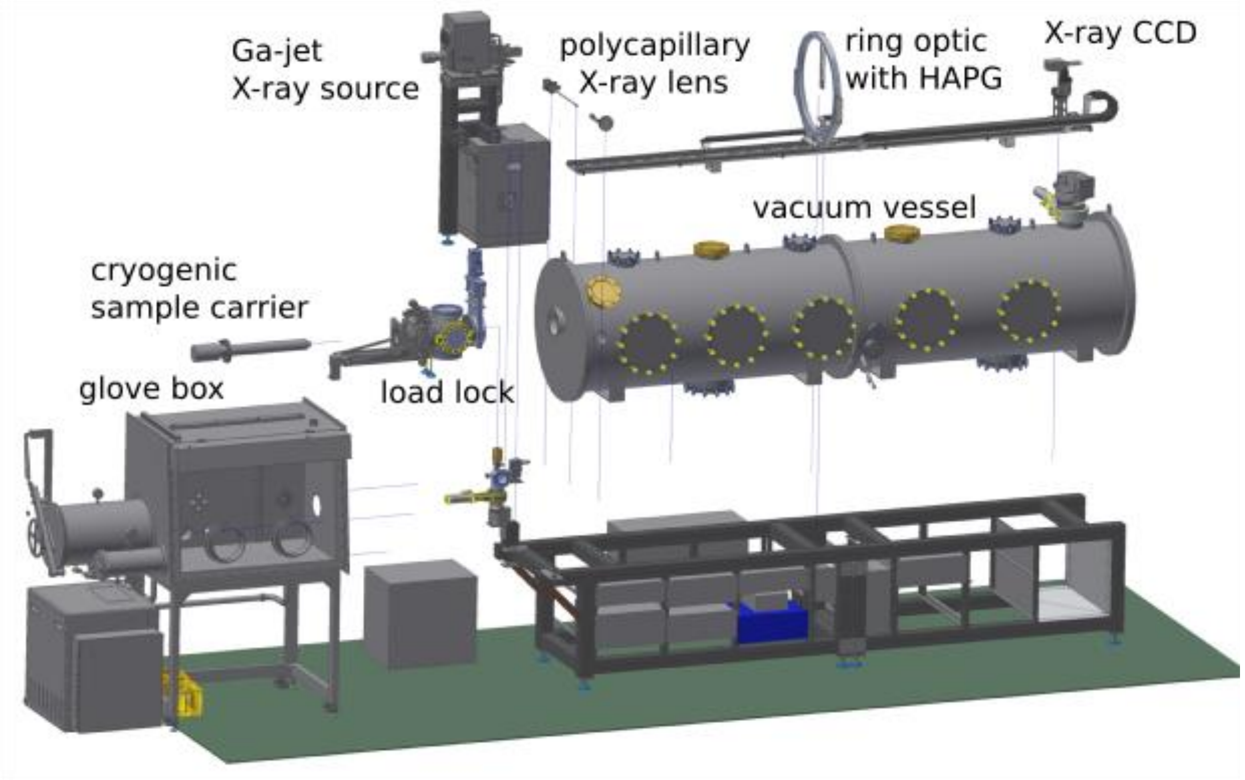


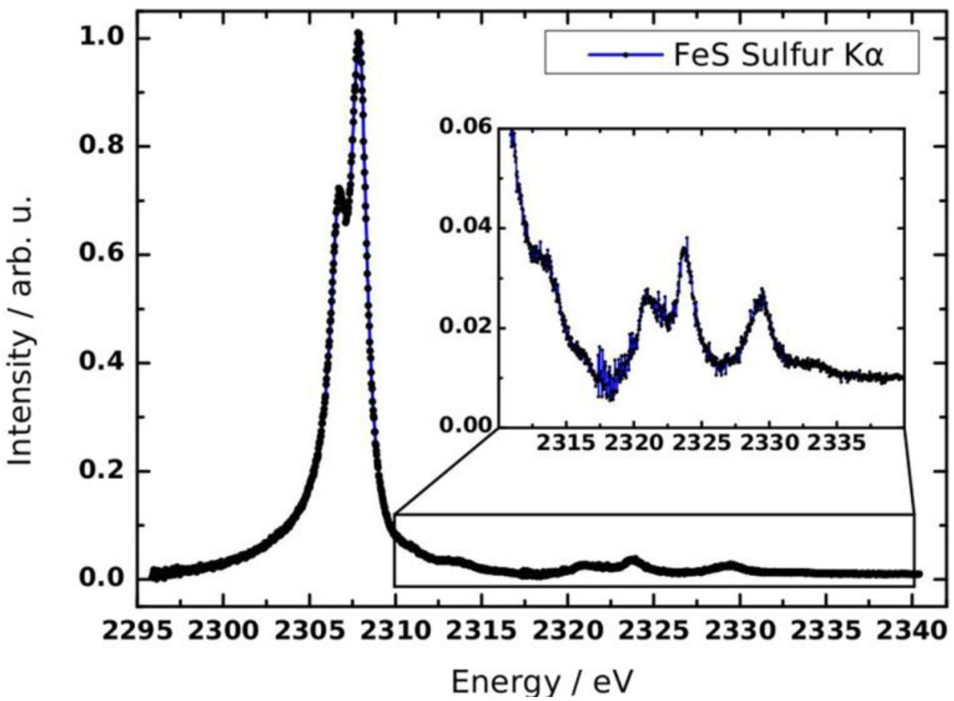
Bragg equation: $n\ \lambda = 2d \sin\theta$



Grating equation: $n\ \lambda = d_0 \cos\alpha + \cos\beta$

FULL CYLINDER VON HAMOS X-RAY EMISSION SPECTROMETER





Rev Sci. Instrum. 89, 113111 (2018).

DETECTION SENSITIVITY CONSIDERATIONS

- Photon flux

  Exp. determined photon flux for Ga Kα: $6.0(5) \times 10^{12}$ s^{-1} sr^{-1} at 200 W for 68% Ga, 22% In and 10% Sn

  J. Anal. At. Spectrom. 34, 1497 (2019).

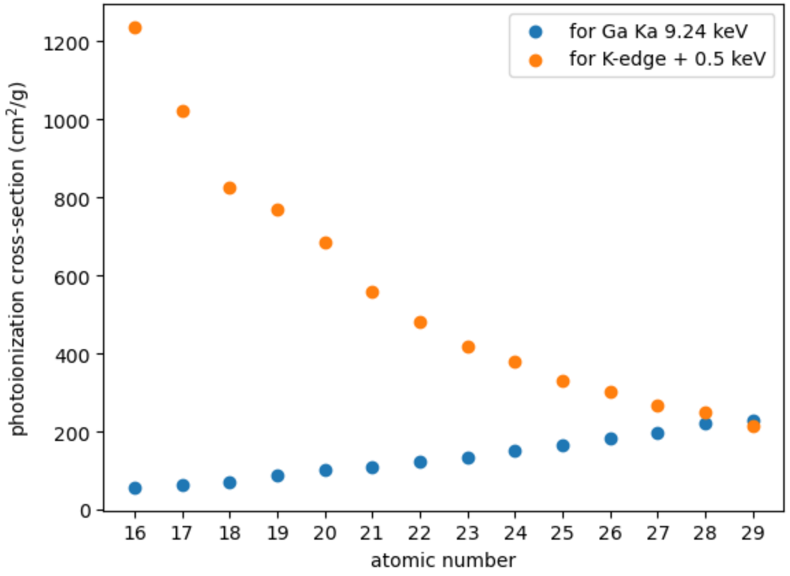
- Impact of focusing optics

  Modelled transmission and solid angle of acceptance reduce photoon flux by a factor 10^{-3}

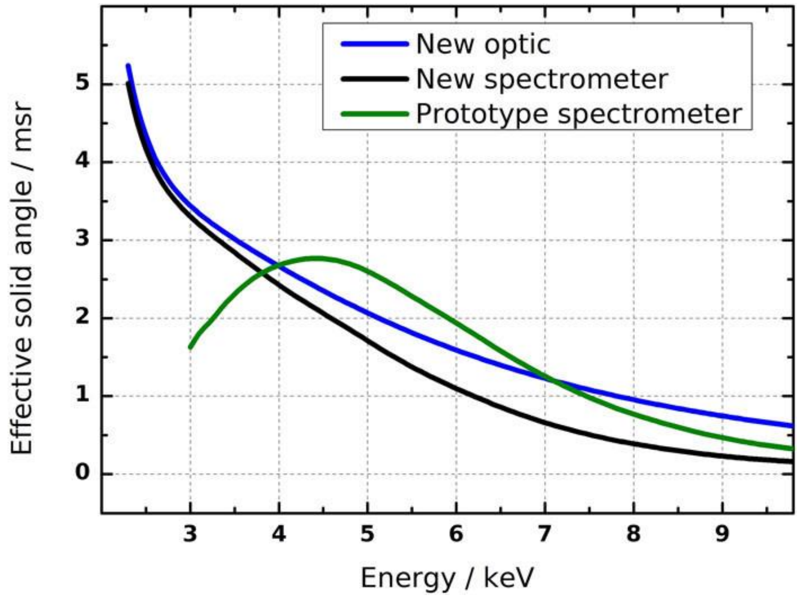
  J. Anal. At. Spectrom., 36, 2519 (2021).

→ 1×10^{10} s^{-1} Ga Kα photons (9.65 keV) at 250 W

- Atomic fundamental parameters: photoionization cross-section, fluorescence yield, trans. prob.



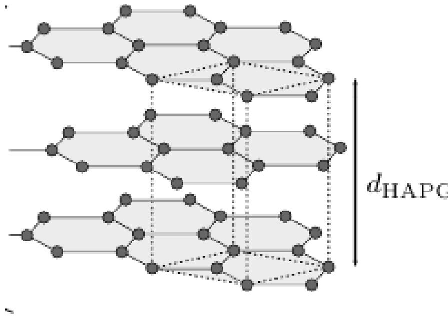
- Detection efficiency: solid angle of diffraction crystal, reflectivity, CCD efficiency



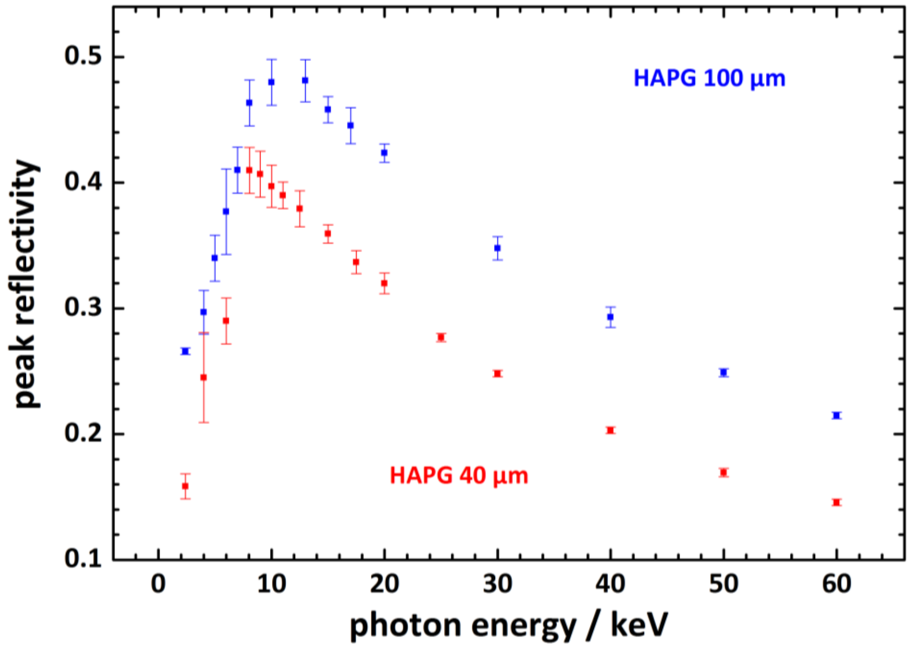
Rev Sci. Instrum. 89, 113111 (2018).

HIGHLY ANNEALED PYROLITHIC GRAPHITE

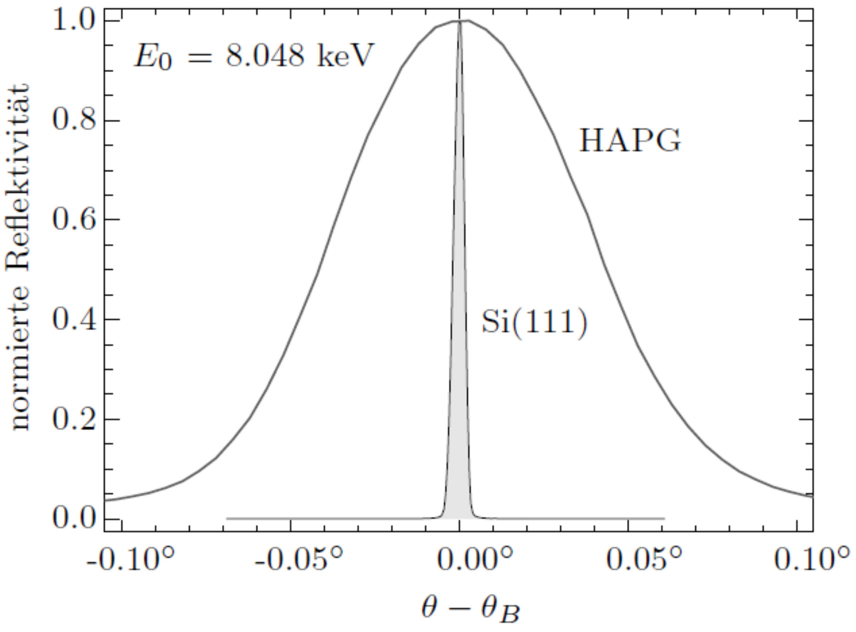
- mosaic crystal that has intrinsically a high integral reflectivity due to mosaic focusing
  → 5x times larger than that of pure crystals
- can be applied to optics with a small radius of curvature without lattice distortions
  → increased solid angle of detection can be realized



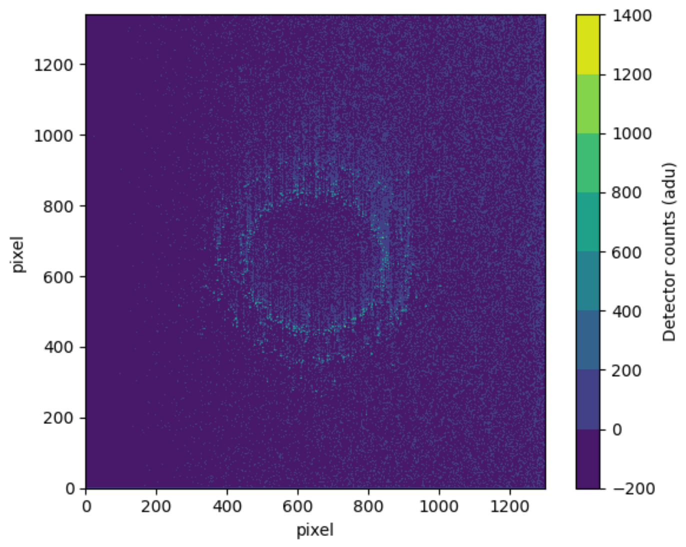
→ spectrometers with an increased detection efficiency can be realized

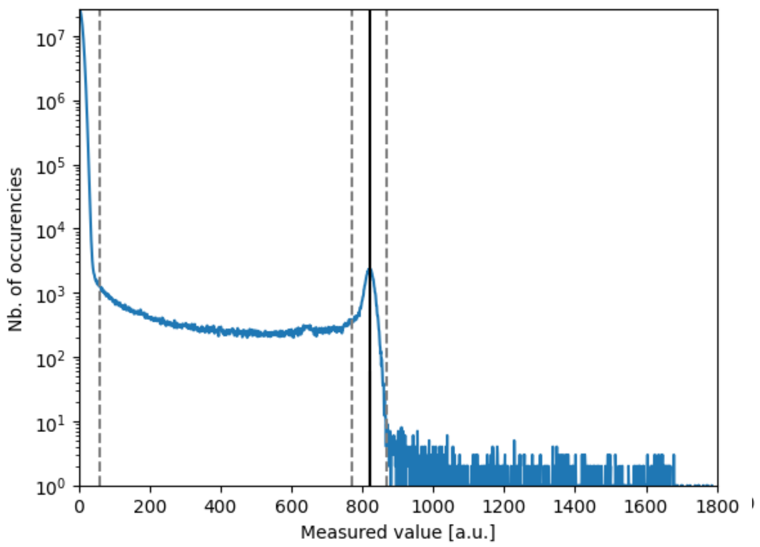


J. Appl. Cryst. 48, 1381-1390 (2015)

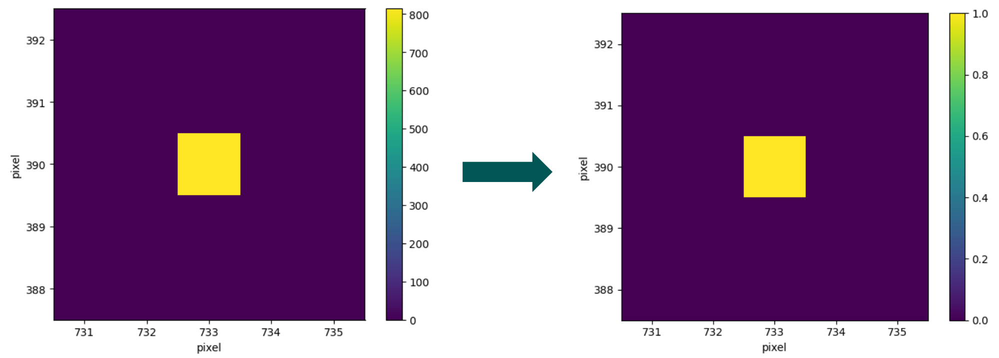


SINGLE PHOTON IMAGE EVALUATION

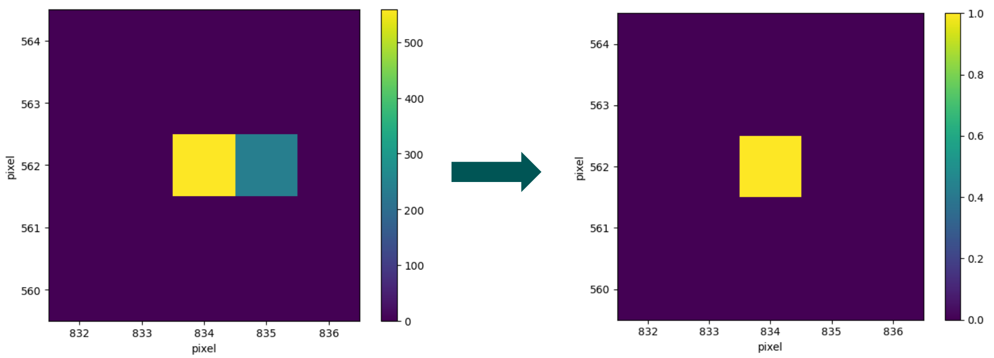




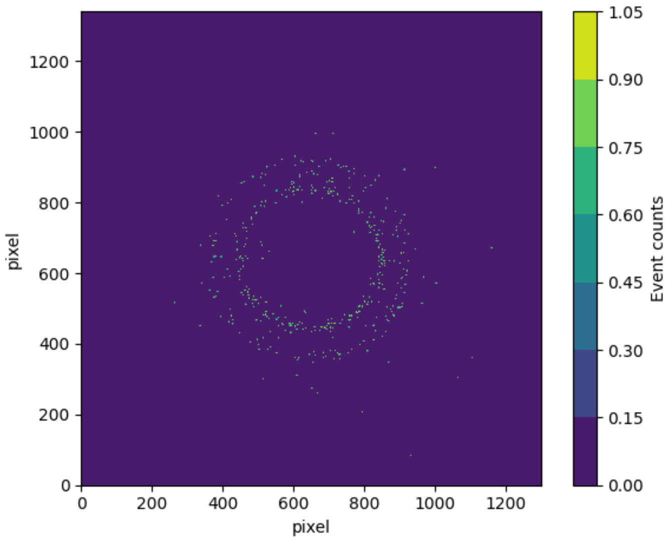
1 pixel event

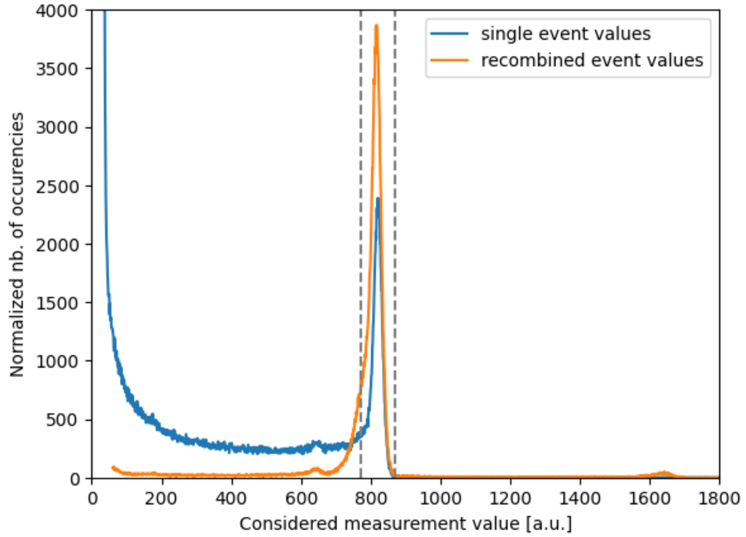


2 pixel event

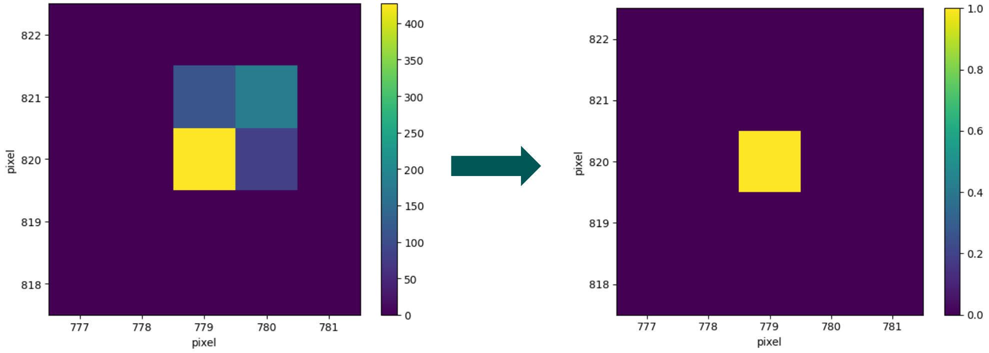


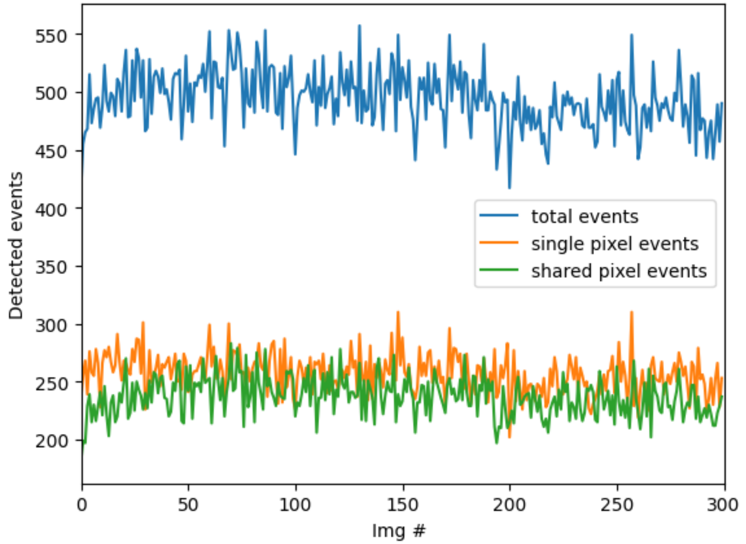
SINGLE PHOTON IMAGE EVALUATION



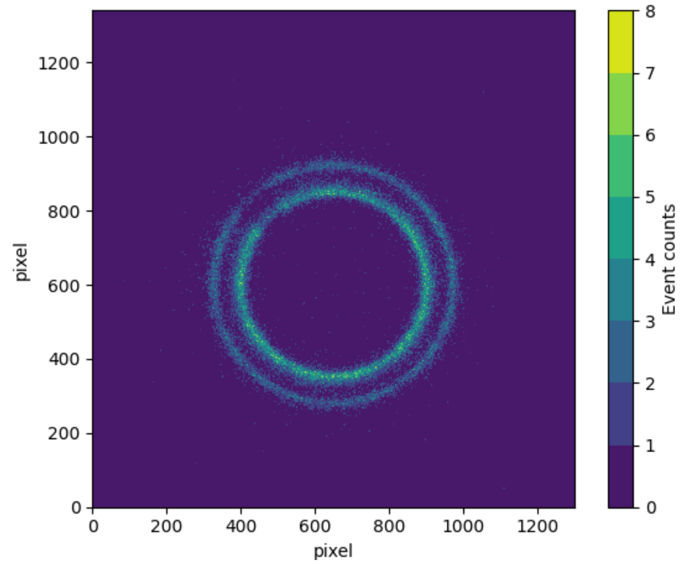


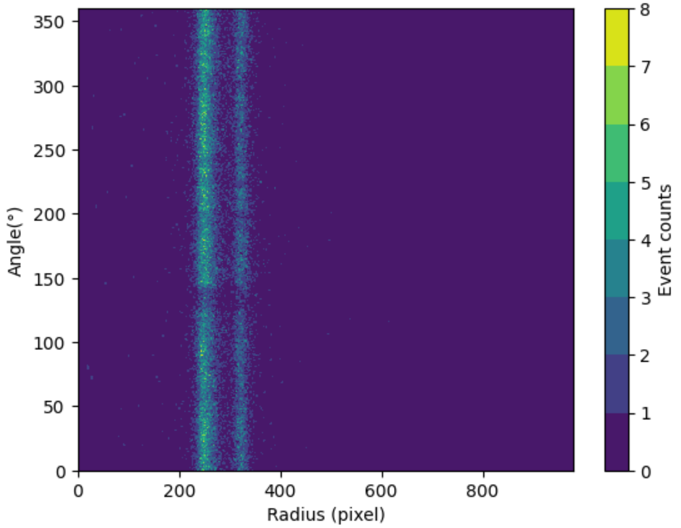
4 pixel event

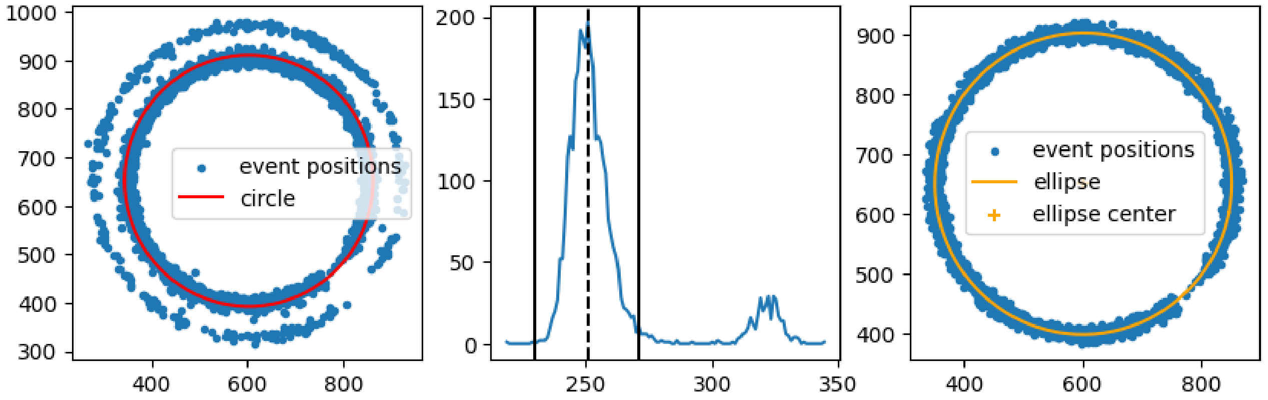


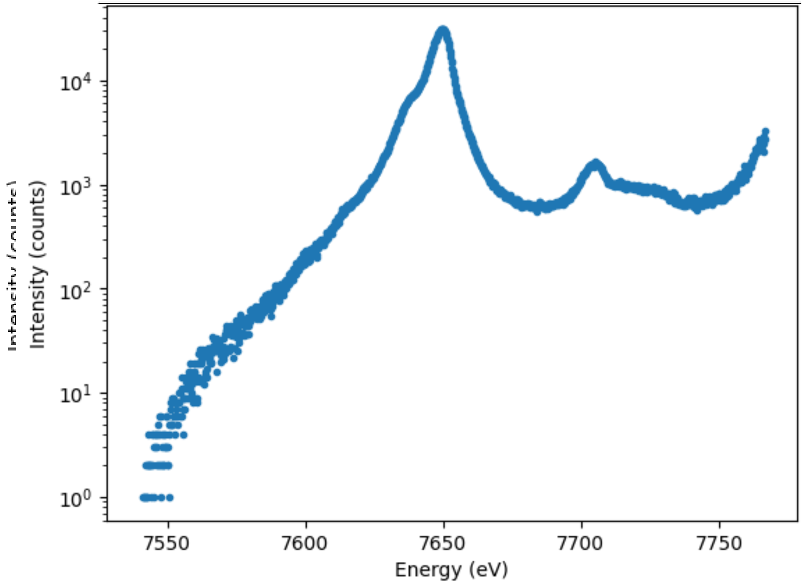


FROM IMAGE TO SPECTRUM







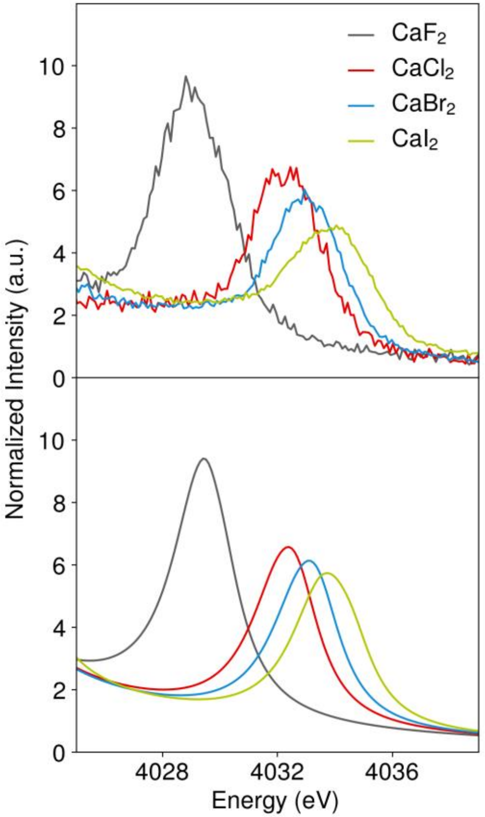


- Using a reference line, assign energy to radius
- change in measurement position, will result in change in radius
- at new position, assign radius to energy

CALCIUM VALENCE-TO-CORE XES

LabXES Spectrometer

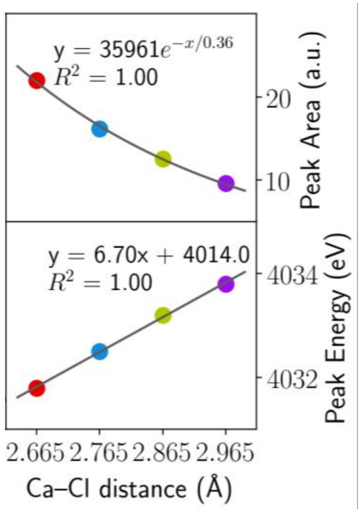
Density Functional Theory



Calculations with artificial Ca–Cl distances help understand structure–spectrum relationships

- Energy depends on the electronegativity / intrinsic ionisation energy of the ligand
- Peak areas increase exponentially as distance becomes shorter
- Peak energies decrease linearly as distance shortens

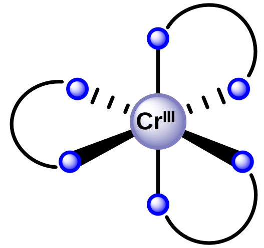
Compound	Coordination	Halogen Pauling Electronegativity	Average Ca–X Distance (Å)
CaF_2	8 (O_h)	3.98	2.366
$CaCl_2$	6 (O_h/D_{4h})	3.16	2.745
$CaBr_2$	6 (O_h/D_{4h})	2.96	2.885
CaI_2	6 (O_h)	2.66	3.117

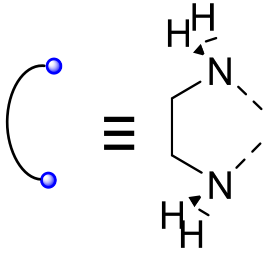


Inorg. Chem. 58, 16292 (2019).

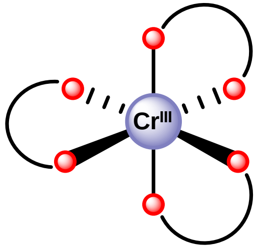
ELECTRON-/ENERGY-TRANSFER PHOTOCHEMISTRY

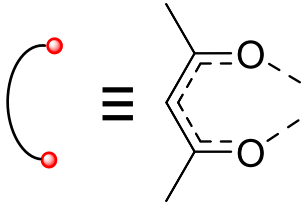
• A



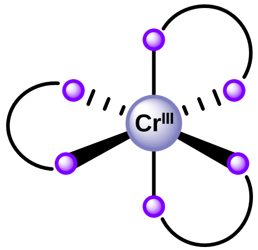


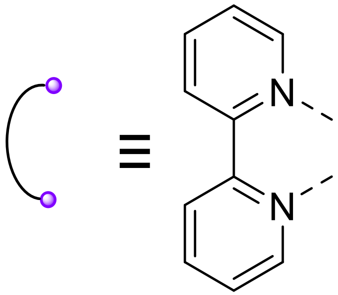
• C



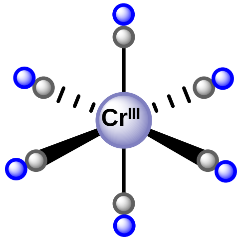


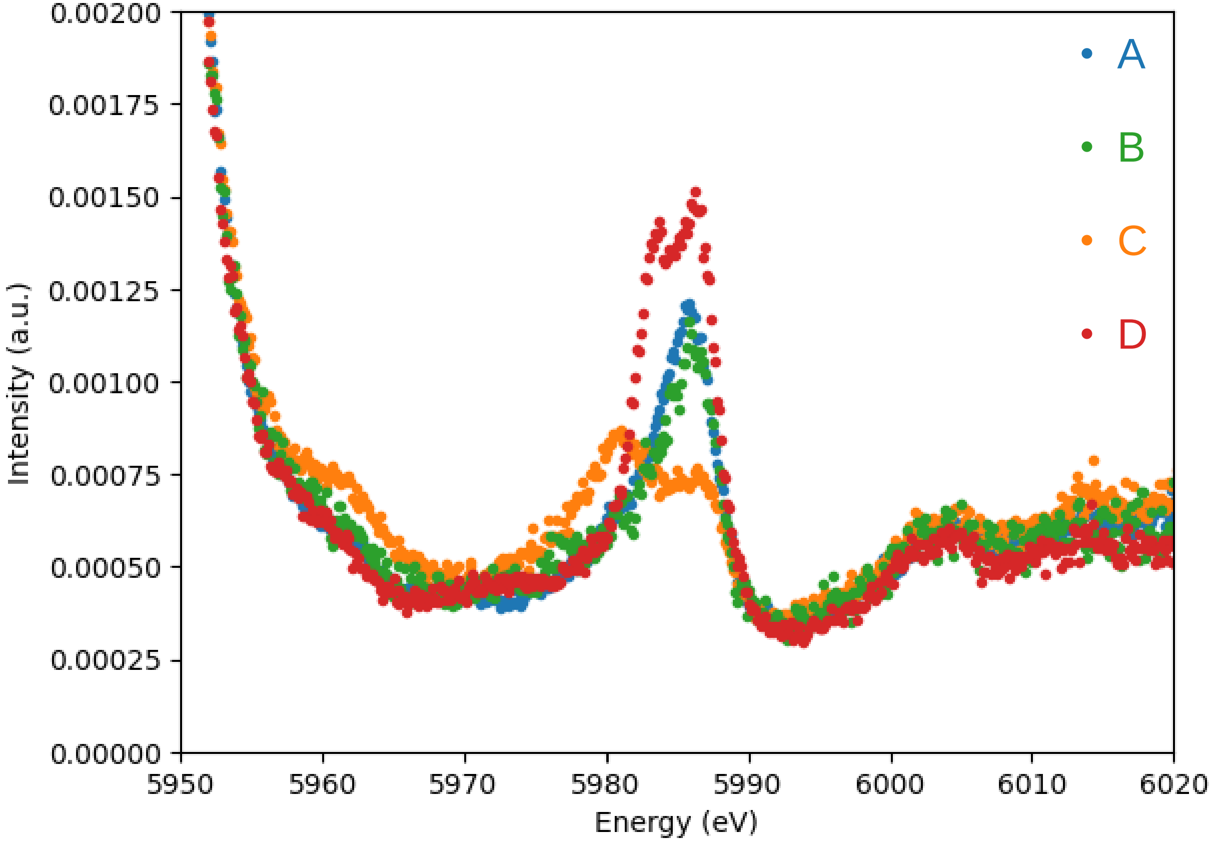
• B





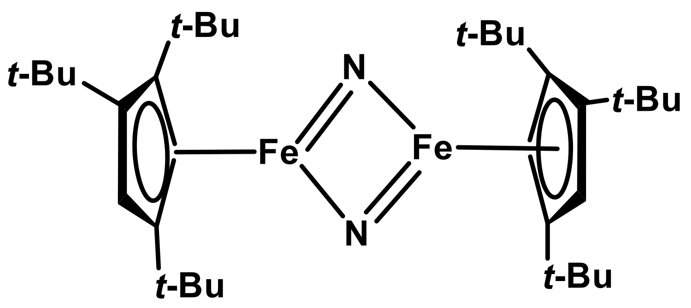
• D



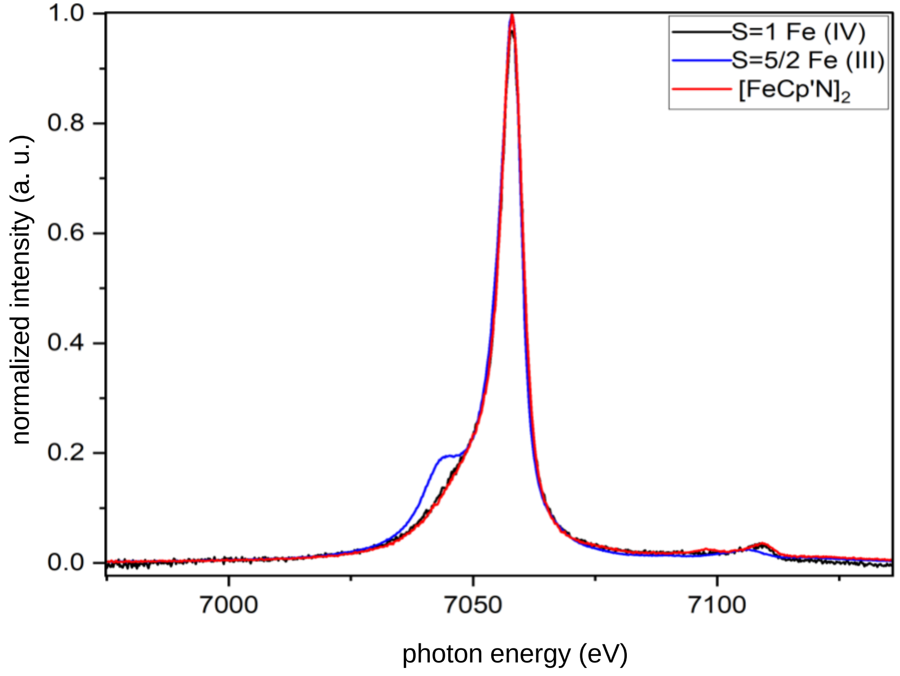


Courtesy of Issiah B. Lozada

INVESTIGATION OF IRON DIMERS

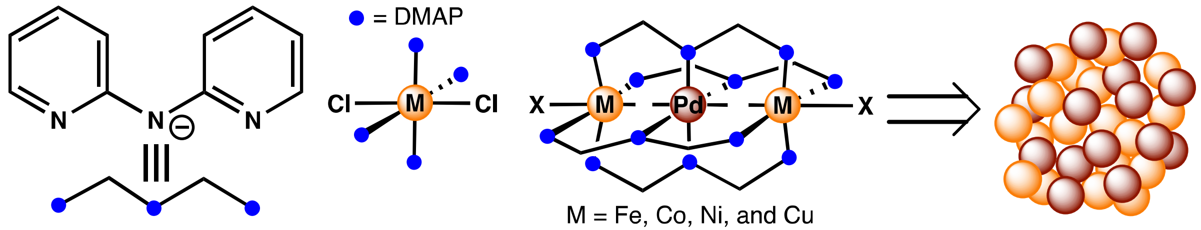


- Fe centers, supported by substituted cyclopentadiene bridging nitride groups.
- the Fe atoms are coupled with strong antiferromagnetic interactions
  → diamagnetic behavior by the system
- determination of oxidation states by widely employed magnetometric techniques like SQUID is complicated



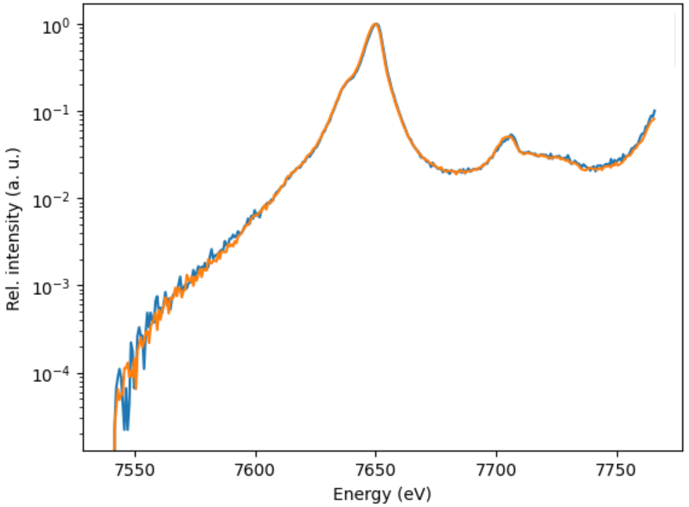
Courtesy of Vishwashri Srinivasan

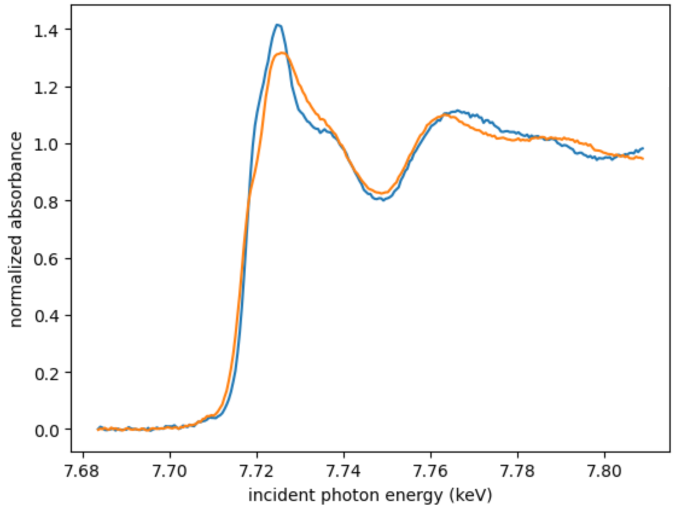
DIRECT H_2O_2 SYNTHESIS FROM H_2 AND O_2



- Concentration of H_2O_2 produced limited by concentration of H_2/O_2 in gas mixture (explosive risk)
- Interest in on-site production and consumption
- > 95% selectivity (Au-Pd, Sn-Pd)
  > 99% H_2 utilization (Au-Pd, Sn-Pd)
- H_2O_2 decomposition by catalyst must be minimized
- Productivity and H2O2 degradation rate modified via introduction of secondary metals and support material
- Goal: Understand effects of secondary metals on the electronic structure of Pd and which effects are beneficial towards catalysis.

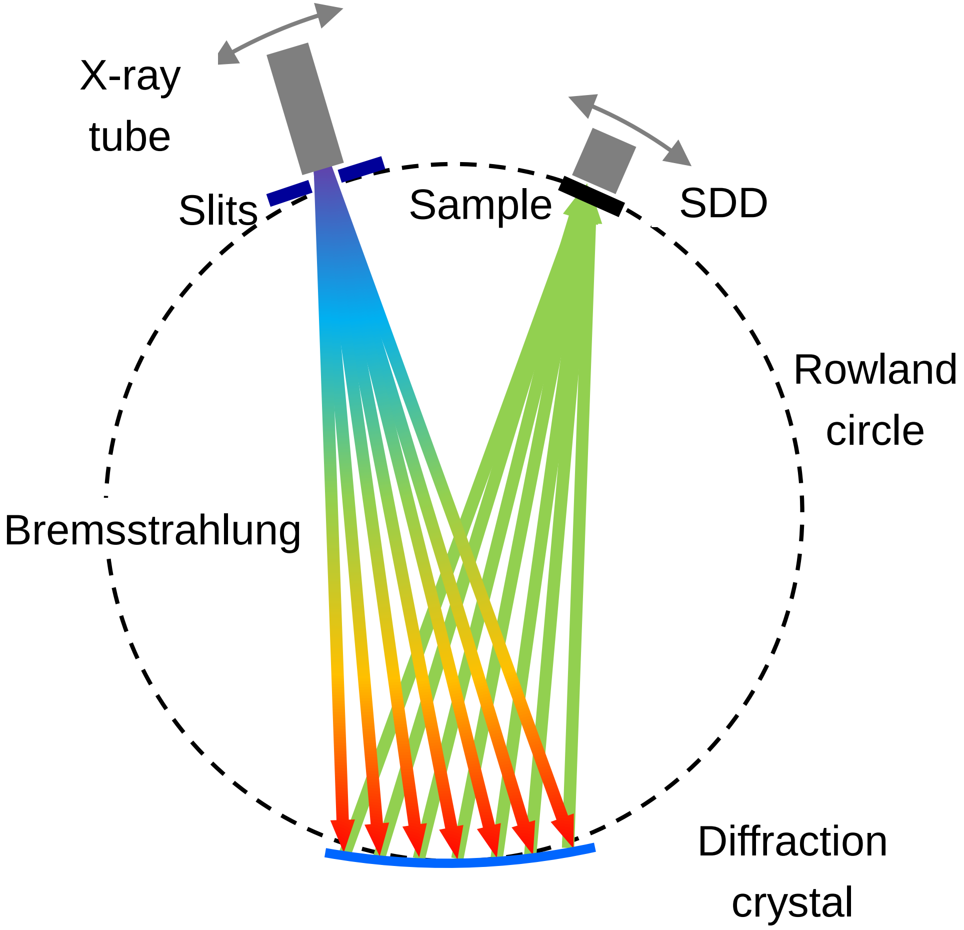
MCl2(pyridine)4 (M = Co)
MPdM complexes (M = Co)





Courtesy of Anna G. Scott

EASYXES-100 SETUP DEVELOPMENT



Configuration for
X-ray absorption spectroscopy

Rev. Sci. Instrum. 90, 024106 (2019).

EASYXES-100 SETUP DEVELOPMENT

Automatized overpressure regulation on the He flowbox

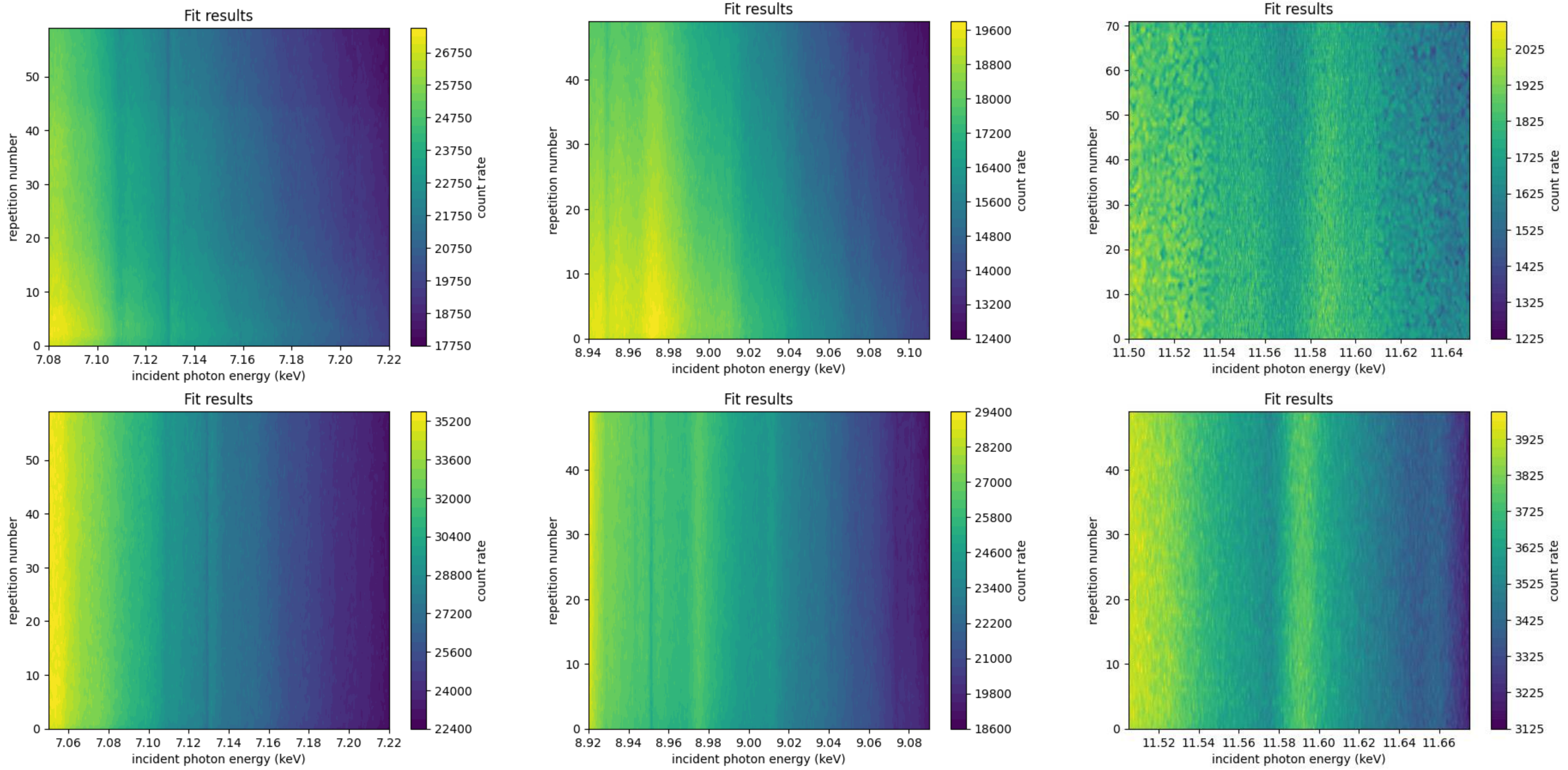
Rev. Sci. Instrum. 90, 024106 (2019).

SETUP DEVELOPMENT ON EASYXES-100 INSTRUMENT

Fe K | Cu K | Pt L_3

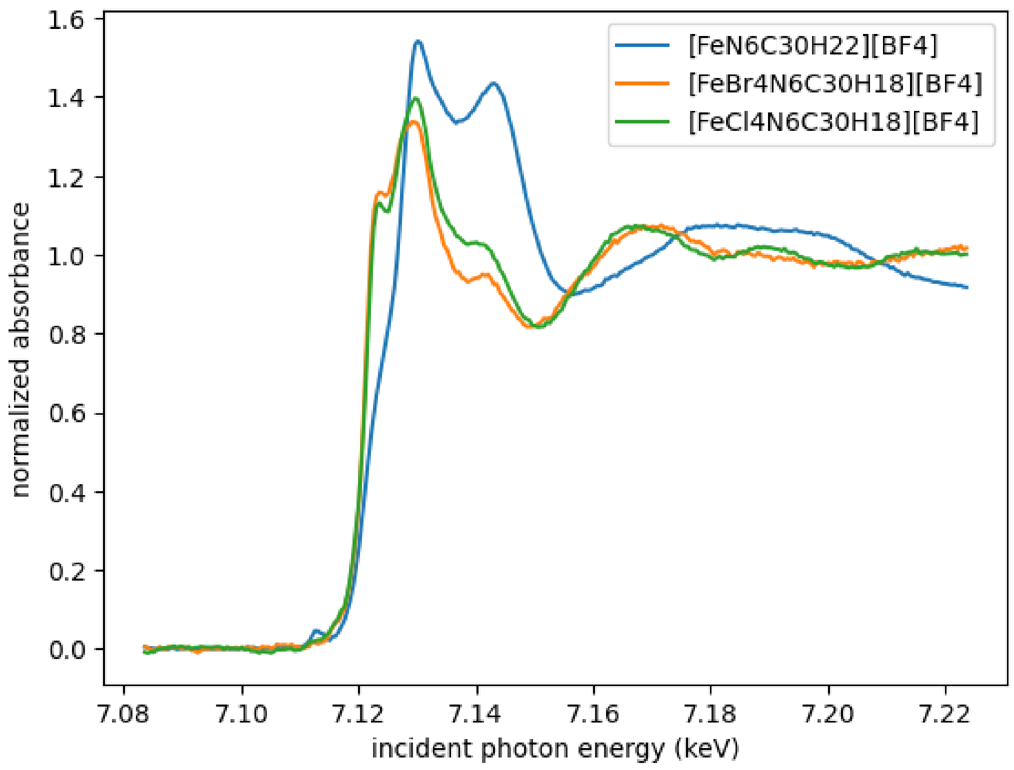
without automatized overpressure regulation

with automatized overpressure regulation



XANES MEASUREMENTS

Interlaboratory comparison



LABXANES INSTRUMENT

source

Liquid metal jet as a high-power micro-focused X-ray source

optic

Cylindrically curved Si or Ge crystals

Cuts with forbidden 2nd diffraction order

detector

Single-photon counting EIGER2R hybrid CMOS 2D pixelated detector

fast readout & position sensitive detection

setup

Slitless geometry

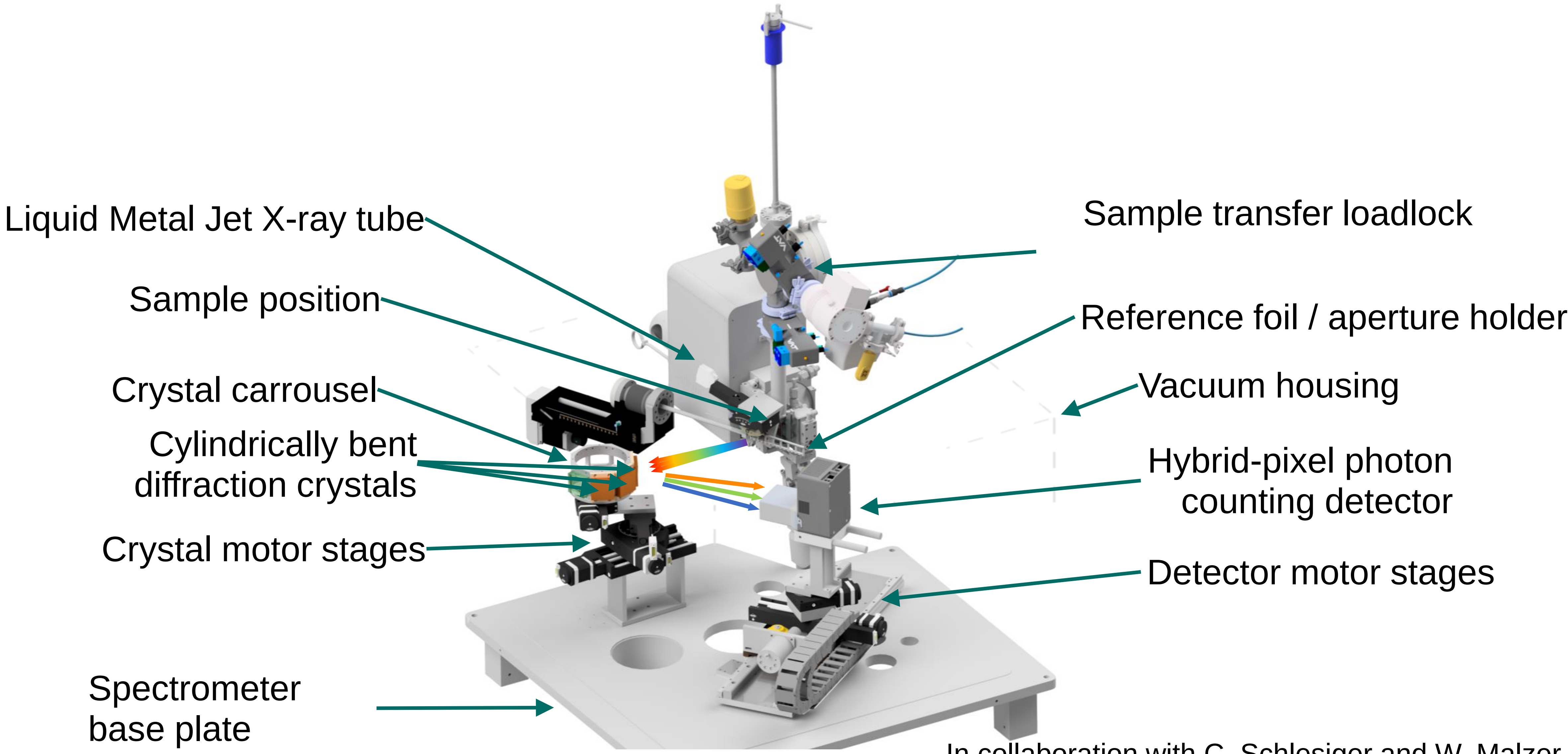
Peltier element for sample cooling or heating

characteristics

Technique(s)	XANES
Type	Dispersive
Geometry	von Hamos (R = 350 mm)
Source	Metal-Jet X-ray tube
Dispersive Element	cylidnricaly crved Si or Ge crystals
Detector	Eiger
Energy range	5 keV - >11 keV
K edges	Ti → Zn
L edges	Cs → Ir
Sample Cooling	Yes (Peltier)
Options	-
Energy window	> 0.2 keV
Resolving power E/ΔE	> 4000
Measurement time	to be commissioned

In collaboration with C. Schlesiger and W. Malzer

LABXANES SPECTROMETER

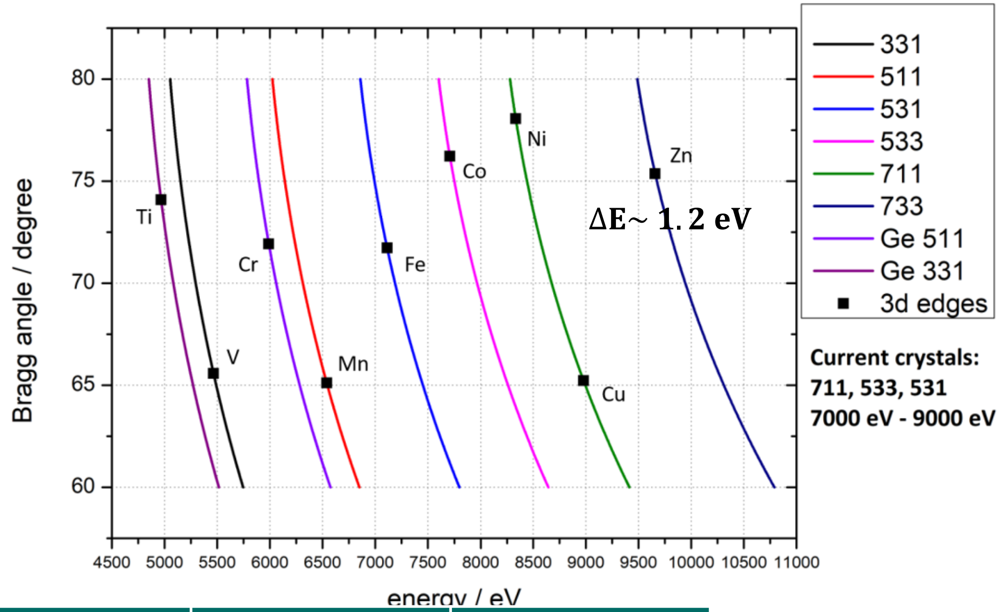


In collaboration with C. Schlesiger and W. Malzer

DESIGN PERFORMANCE

Considerations on crystal selection

- selection of crystal cuts: measurement at high Bragg angle ($n\ {}^{hc}/_{E} = 2d\ \sin\theta \rightarrow {}^{\Delta E}/_{E} = \cot\theta\ \Delta\theta$)
- pure Si or Ge crystals: better resolving power, but lower reflectivity compared to synthetic or mosaic diffraction crystals
- radius of curvature R: impacts solid angle of det-ection ($\Omega \sim {}^{1}/_{R^2}$) and resolving power (${}^{\Delta E}/_{E} \sim {}^{1}/_{R}$)
- crystal cuts with forbidden 2nd diffraction order:
  allows using fast read-out detectors without energy discrimination capabilities



Current crystals:
711, 533, 531
7000 eV - 9000 eV

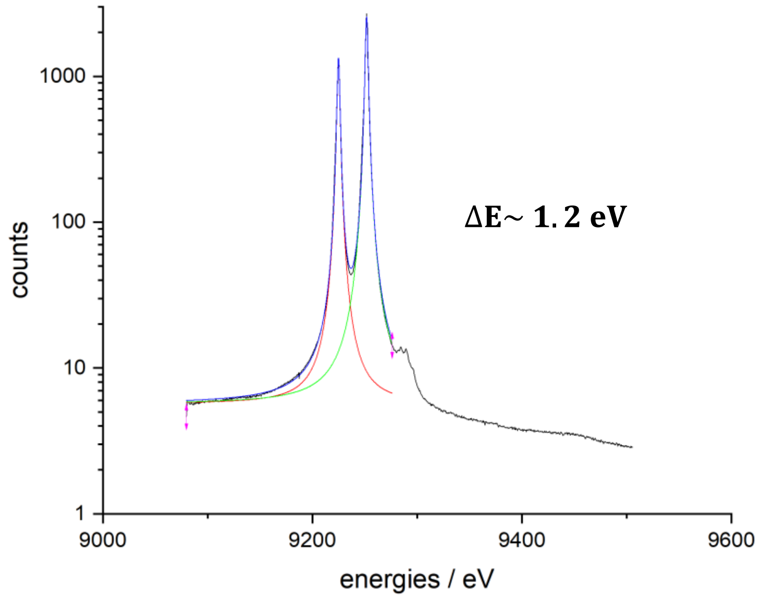
	Bragg angle	source contr.	crystal contr.	detector contr.	overall ΔE	energy range
Fe-K (7112 eV) @ Si 531	71.2°	0.13 eV	1.23 eV	0.24 eV	1.26 eV	278 eV
Ni-K (8333 eV) @ Si 533	63.9°	0.21 eV	1.73 eV	0.39 eV	1.79 eV	432 eV
Ni-K (8333 eV) @ Si 711	78.0°	0.10 eV	1.15 eV	0.18 eV	1.17 eV	222 eV
Cu-K (8979 eV) @ Si 711	65.2°	0.22 eV	2.20 eV	0.40 eV	2.26 eV	448 eV

In collaboration with C. Schlesiger and W. Malzer

DESIGN PERFORMANCE

Estimated resolving power and energy range covered

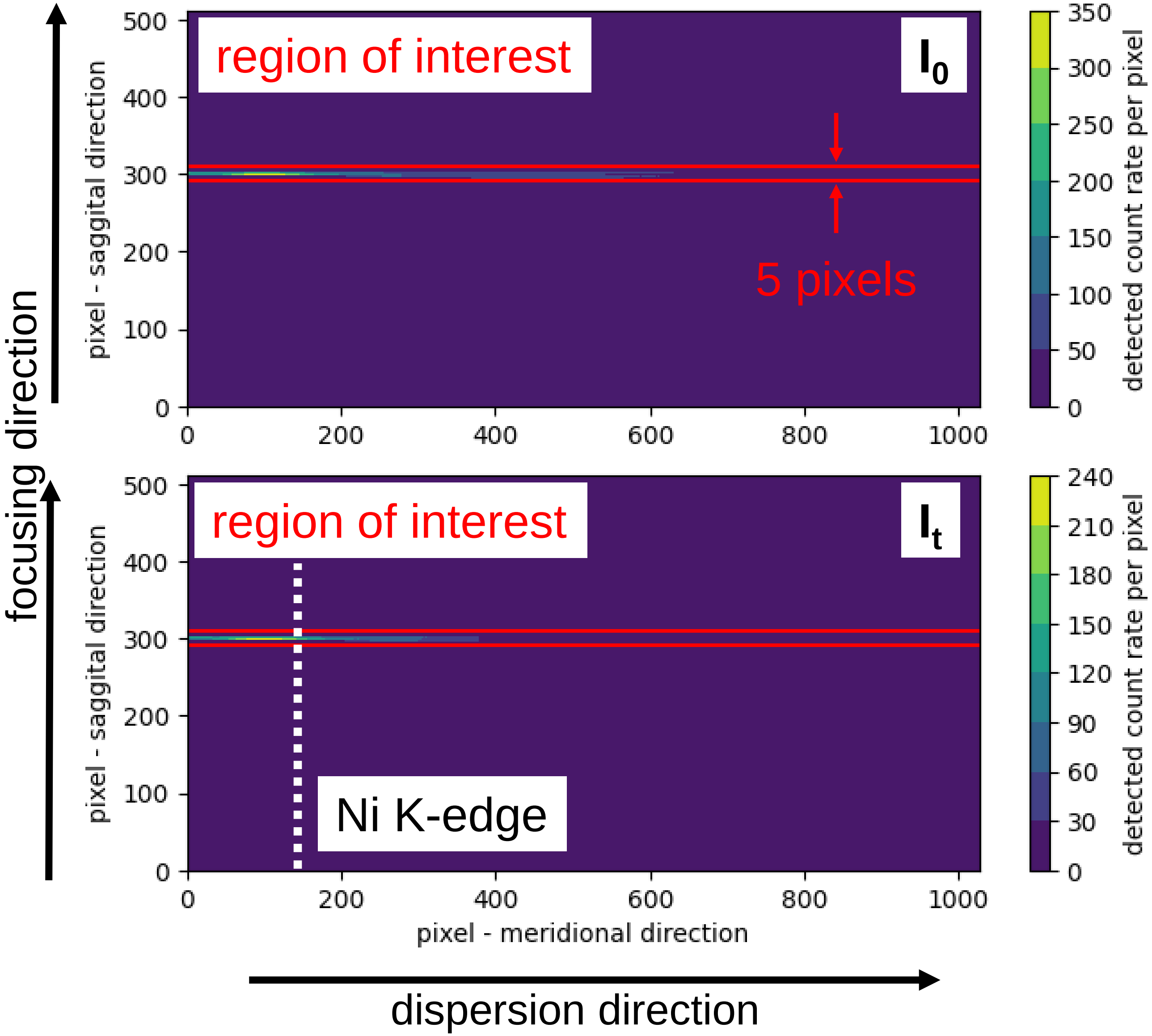
- source size ($s = 20$ µm) of the liquid metal jet: $\Delta E/E = s \cos\theta / R$
- crystal (R = 350 mm, d = 300 µm): stress-strain and penetration depth effects calculated using pyTTE [A.-P. Honkanen and S. Huotari, IUCrJ 8, 102 (2021)]
- detector pixel size (p = 75 µm) in dispersion direction: $\Delta E/E = p \cos\theta / 2R$
- energy range covered defined by crystal and detector dimensions in dispersion direction

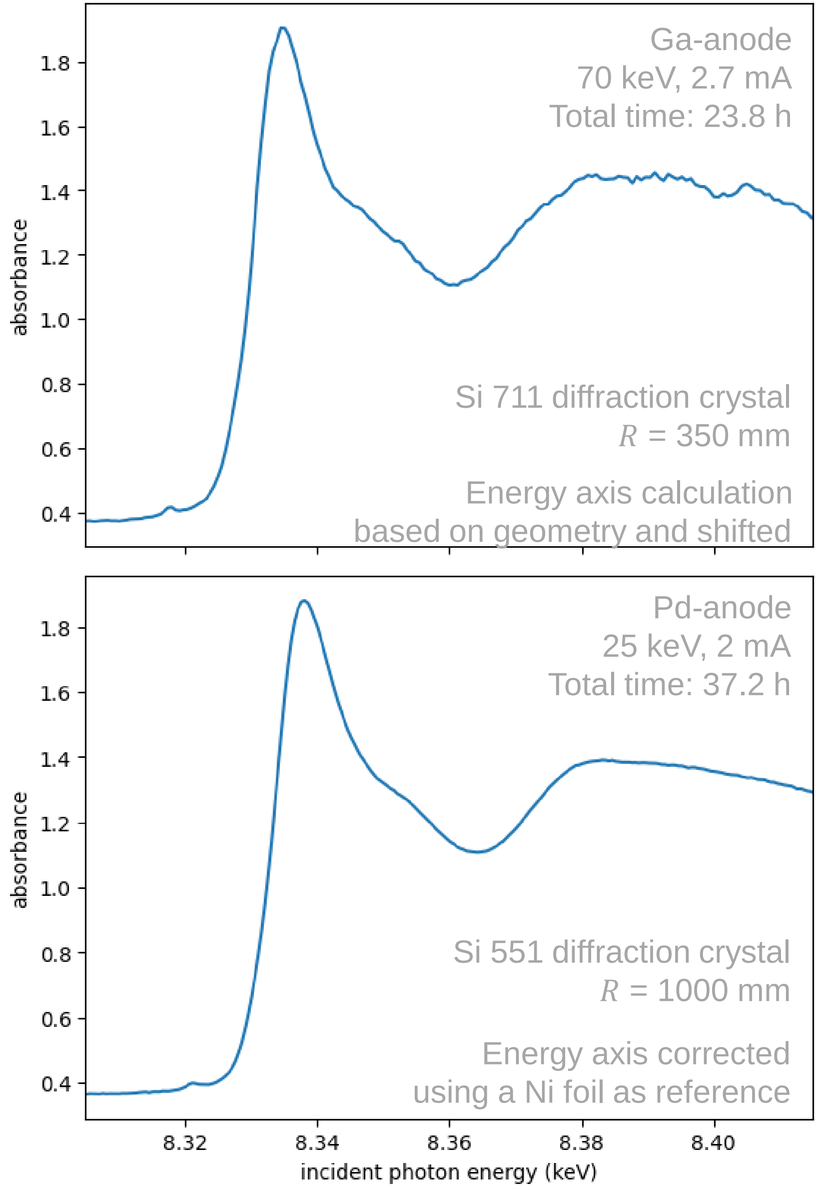


	Bragg angle	source contr.	crystal contr.	detector contr.	overall ΔE	energy range
Fe-K (7112 eV) @ Si 531	71.2°	0.13 eV	1.23 eV	0.24 eV	1.26 eV	278 eV
Ni-K (8333 eV) @ Si 533	63.9°	0.21 eV	1.73 eV	0.39 eV	1.79 eV	432 eV
Ni-K (8333 eV) @ Si 711	78.0°	0.10 eV	1.15 eV	0.18 eV	1.17 eV	222 eV
Cu-K (8979 eV) @ Si 711	65.2°	0.22 eV	2.20 eV	0.40 eV	2.26 eV	448 eV

In collaboration with C. Schlesiger and W. Malzer

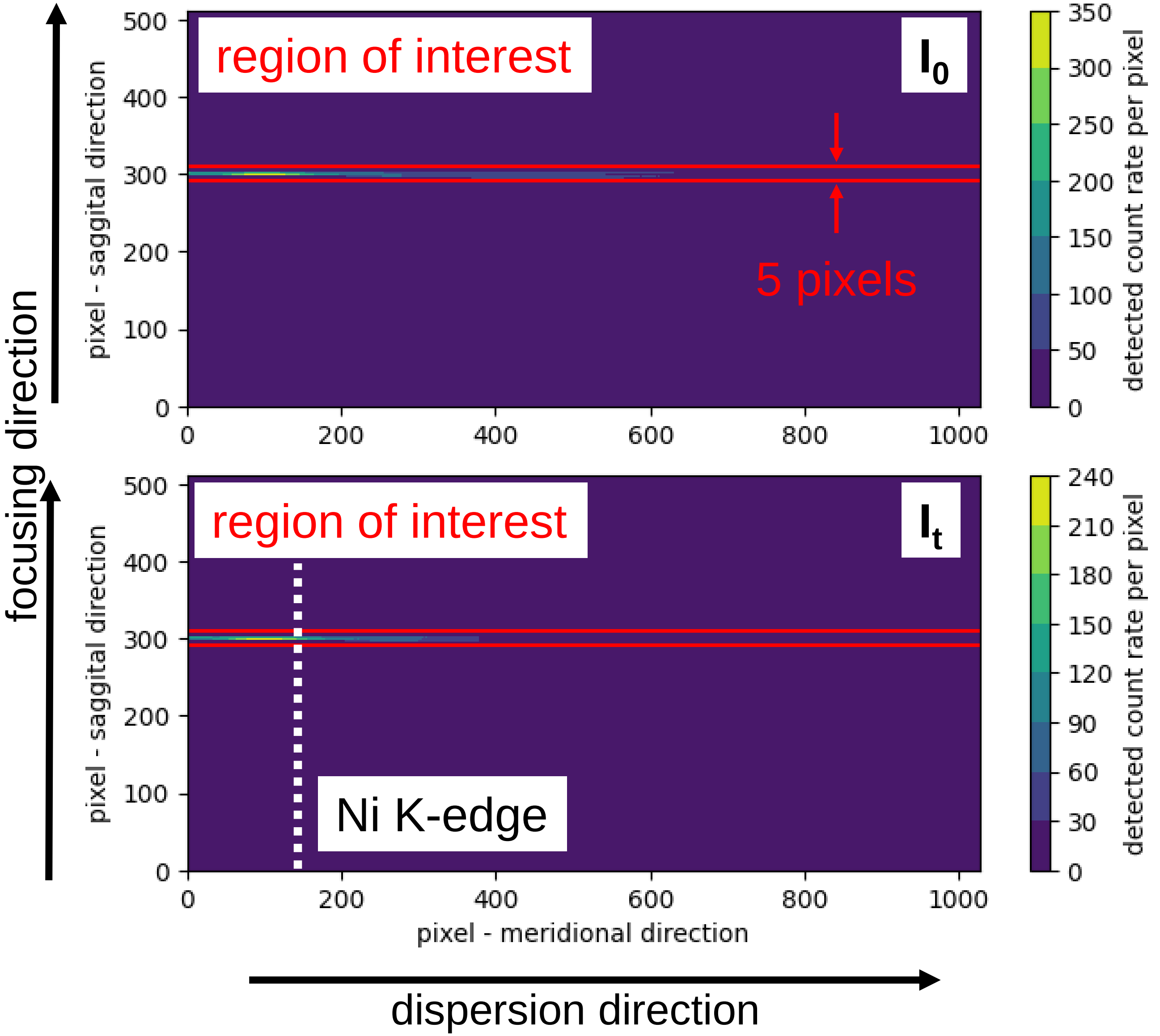
LABXANES OPERATION

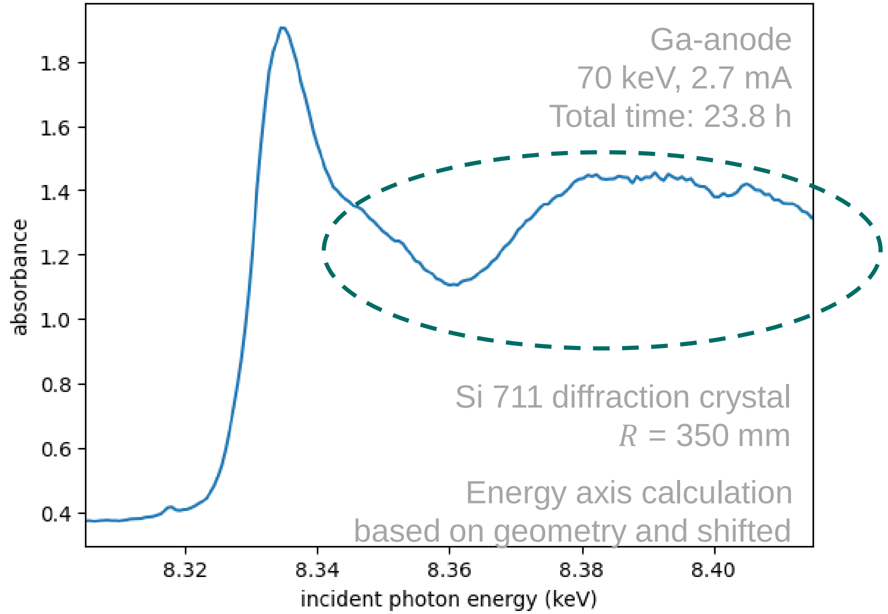


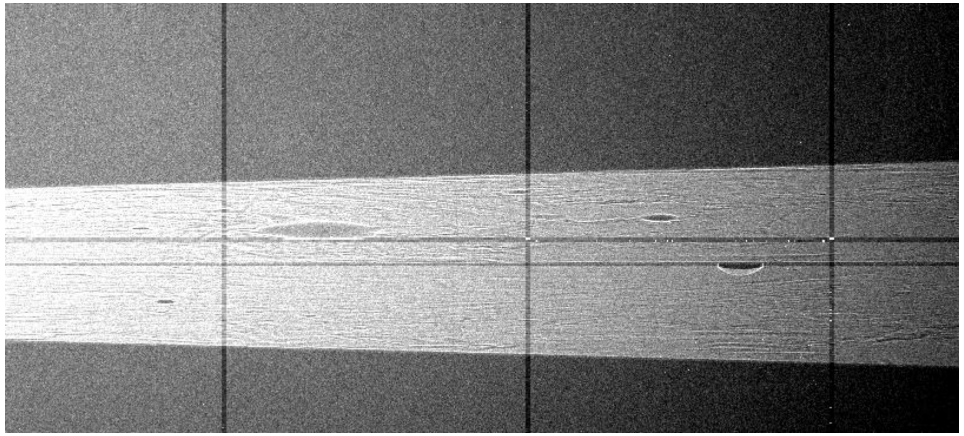


In collaboration with C. Schlesiger and W. Malzer

LABXANES OPERATION

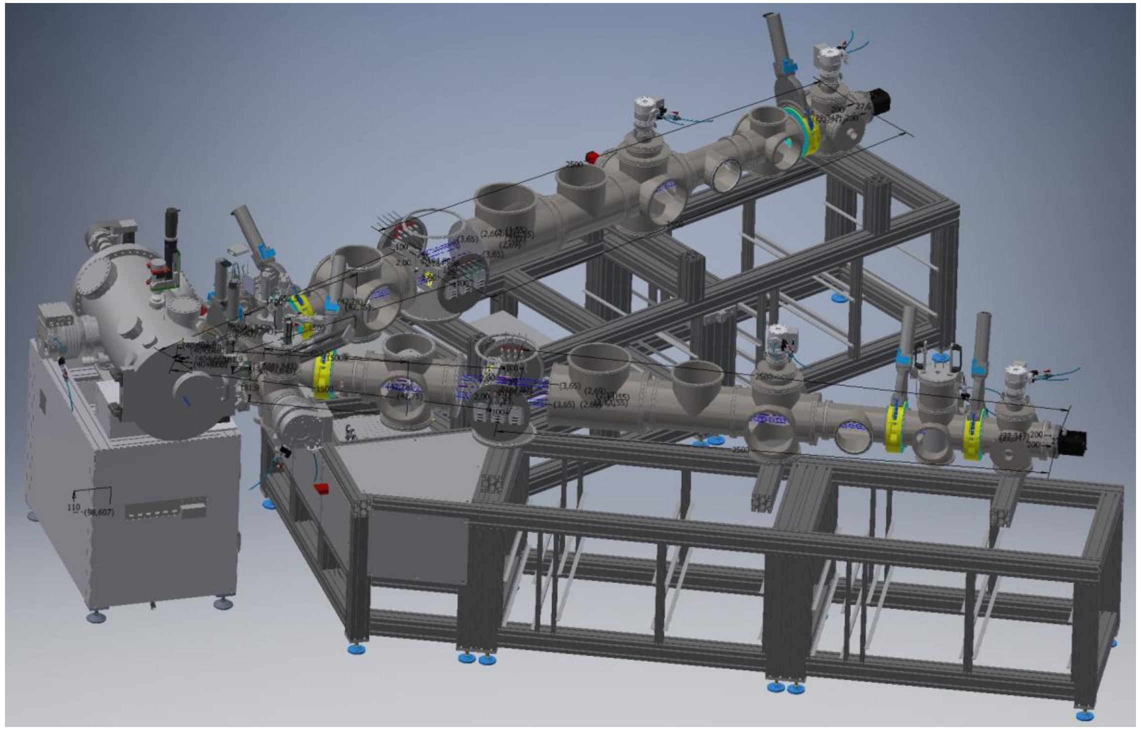






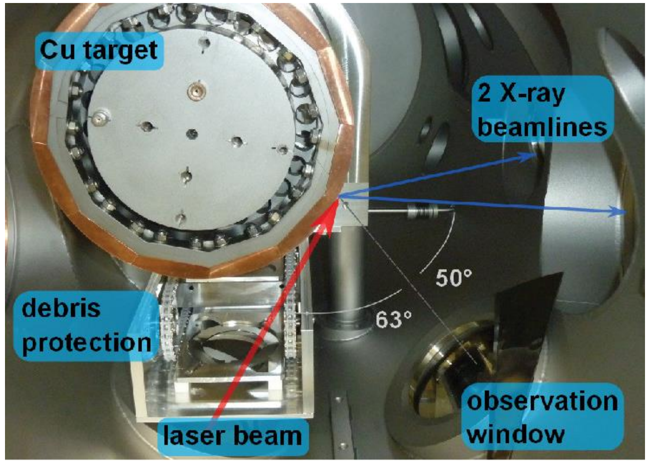
In collaboration with C. Schlesiger and W. Malzer

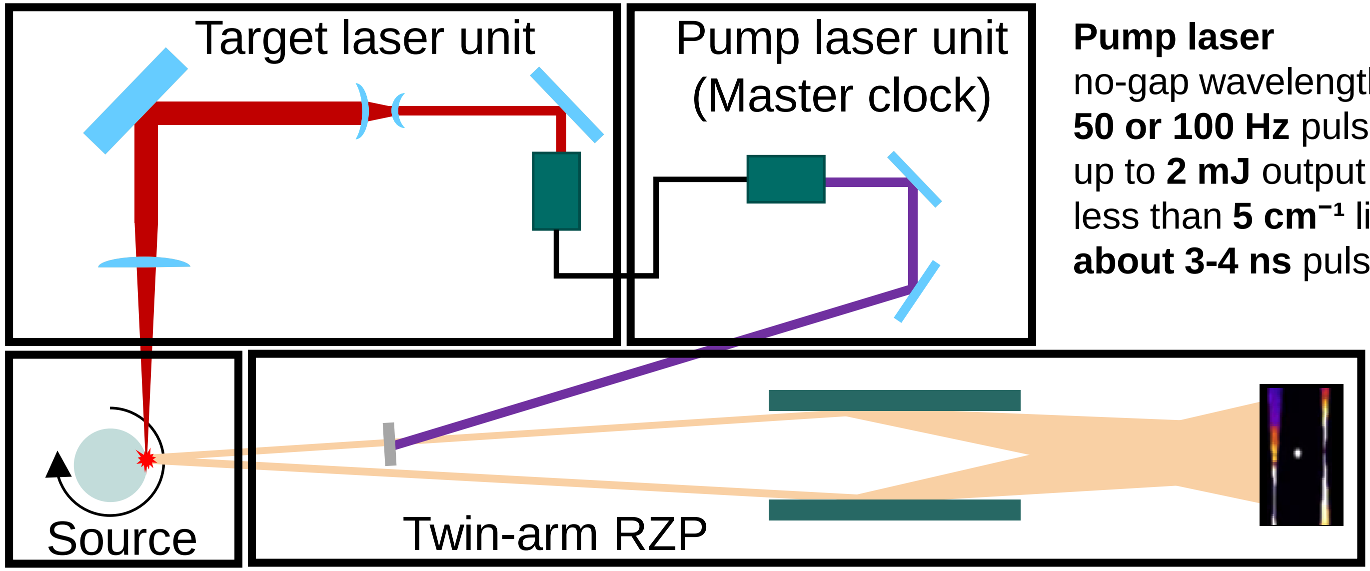
LPP SOURCE WITH 2 TWIN-ARM RZP SPECTROMETERS



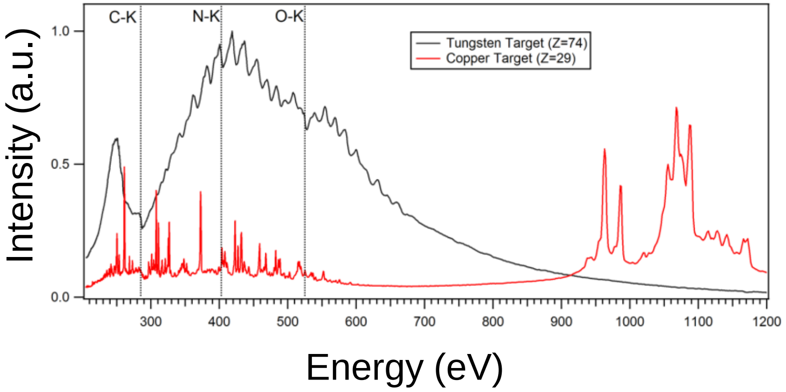
LPP SOURCE WITH 2 TWIN-ARM RZP SPECTROMETERS

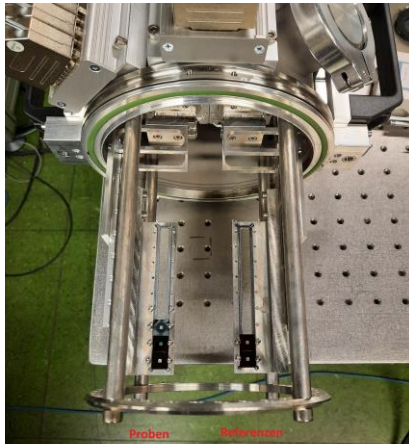
Probe laser
190 mJ at 1064 nm pulse energy
100 Hz pulse repetition rate
pulse duration of about **3 ns**

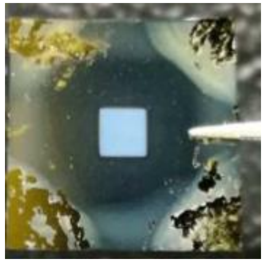


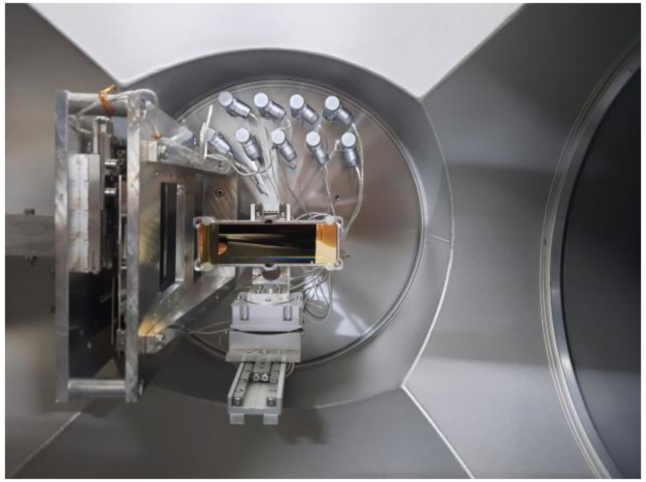


Pump laser
no-gap wavelength tuning **192 - 2600 nm**
50 or 100 Hz pulse repetition rate
up to **2 mJ** output pulse energy **in UV**
less than **5 cm⁻¹** linewidth
about 3-4 ns pulse duration

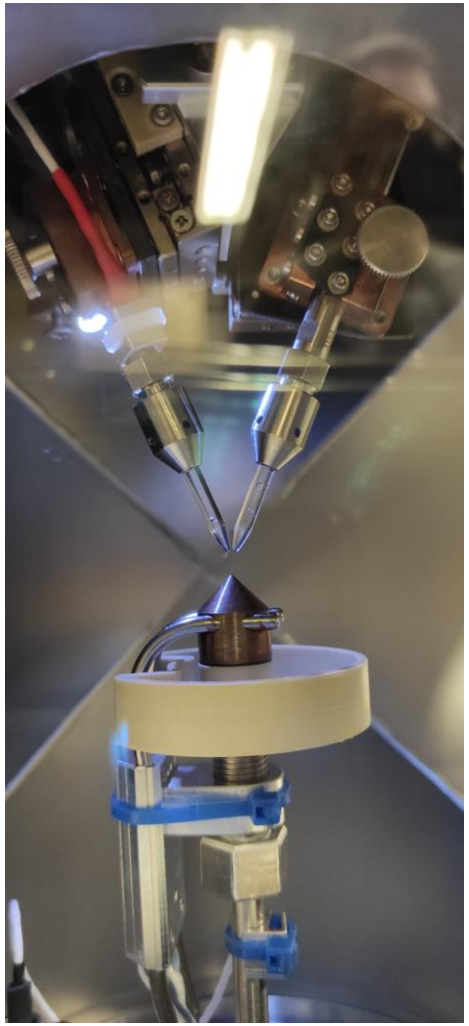






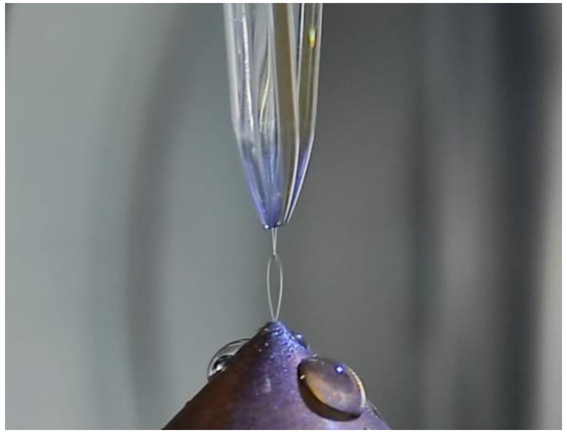


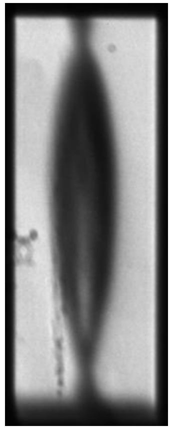
FLAT JET TO PROBE SAMPLES IN SOLUTION



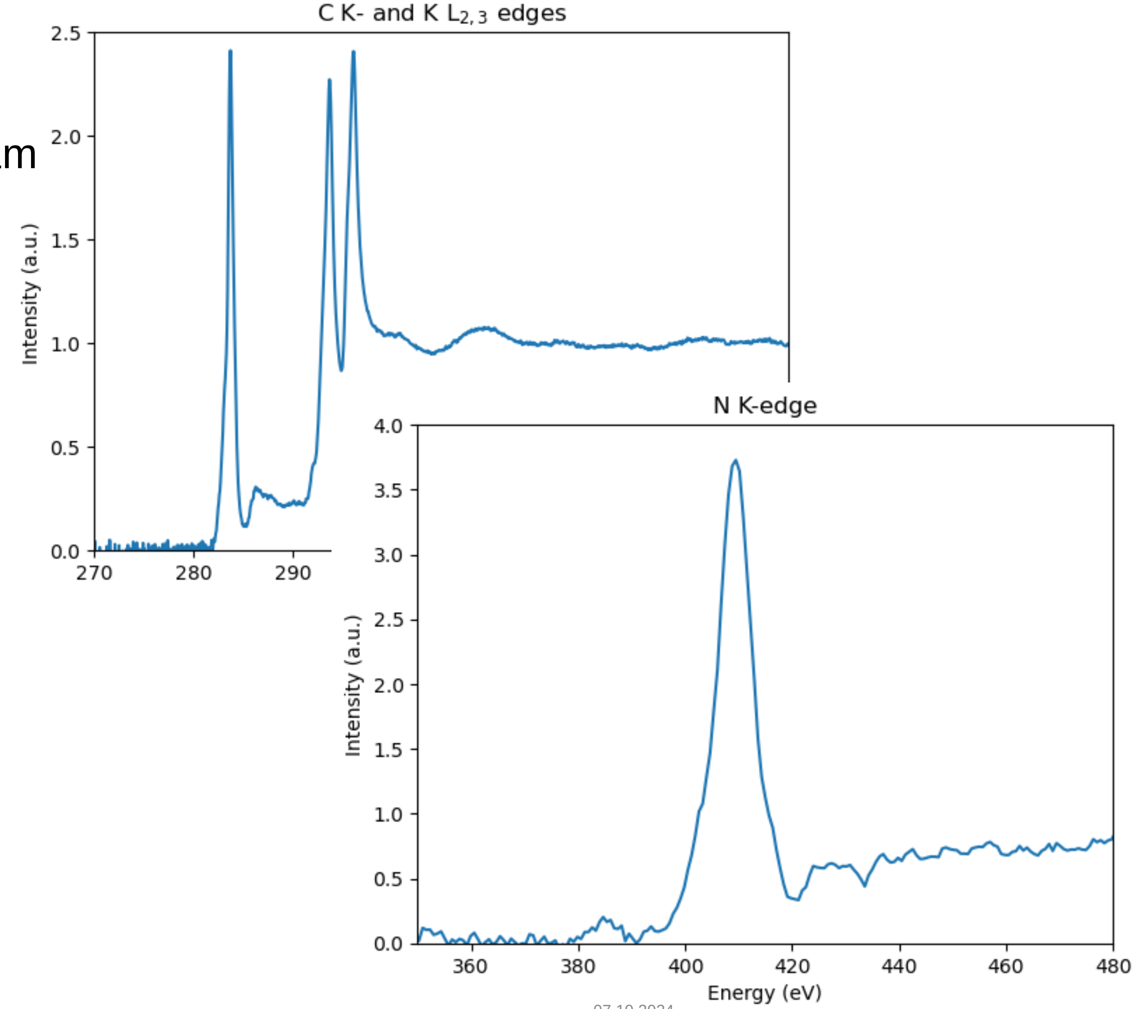
Leafshaped liquid sheet with thicker rims and diminishing thickness of the median cross section (from top to bottom)

- Sheet thickness: 0,5 µm – 3 µm
- Area of minimal curvature: 100 µm x 100 µm to 500 µm x 500 µm (depending on jet size)
- Thickness stability: <1%
- Spatial stability <1 µm
- Temperature from -20° to +100° C



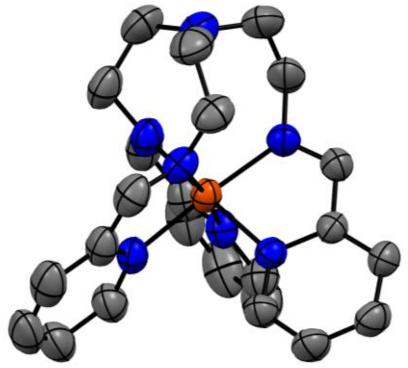


130 mMol K3[Fe(CN)6]
20000 pulses for sample and for reference

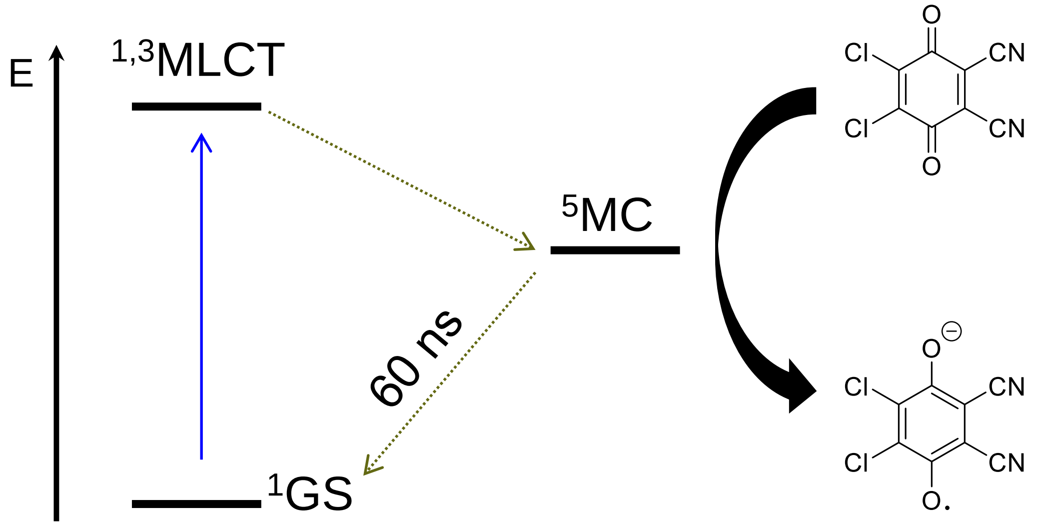


INVESTIGATION OF LONG-LIVED EXCITED STATES

Electron-Transfer Photochemistry of MC States



Inorganica Chim. Acta, **2004**, *357*, 2390.



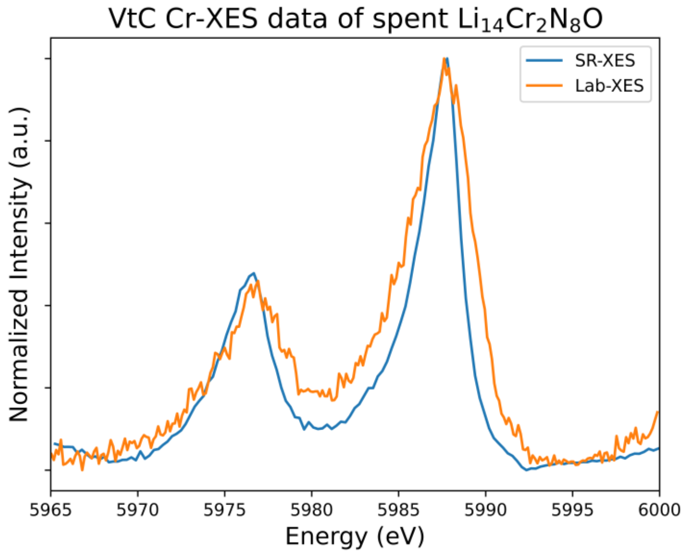
J. Am. Chem. Soc., **2000**, *122*, 4092.
J. Am. Chem. Soc., **2020**, *142*, 16229.

- Electron transfer from ^{5}MC state (localized in metal center)
- Investigation of transfer mechanism in a photoredox reaction

Courtesy of Issiah B. Lozada

OUTLOOK

- For XES: comparison of data collected across a range of elements between PINK beamline and in-house XES spectrometer
- Development of sample environments to accomodate different needs within the department on Inorganic Spectroscopy at the CEC
- Move towards time-resolved measurements in the soft X-ray energy range
- Commissioning of the new in-house XANES spectrometer with cross-comparison to the exisiting spectrometer



Thank you for your attention

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Technische Universität Berlin

BLiX Berlin Laboratory for innovative X-ray Technologies