Brookhaven National Laboratory

U.S. DEPARTMENT OF ENERGY

High-Energy-Resolution Spectroscopy

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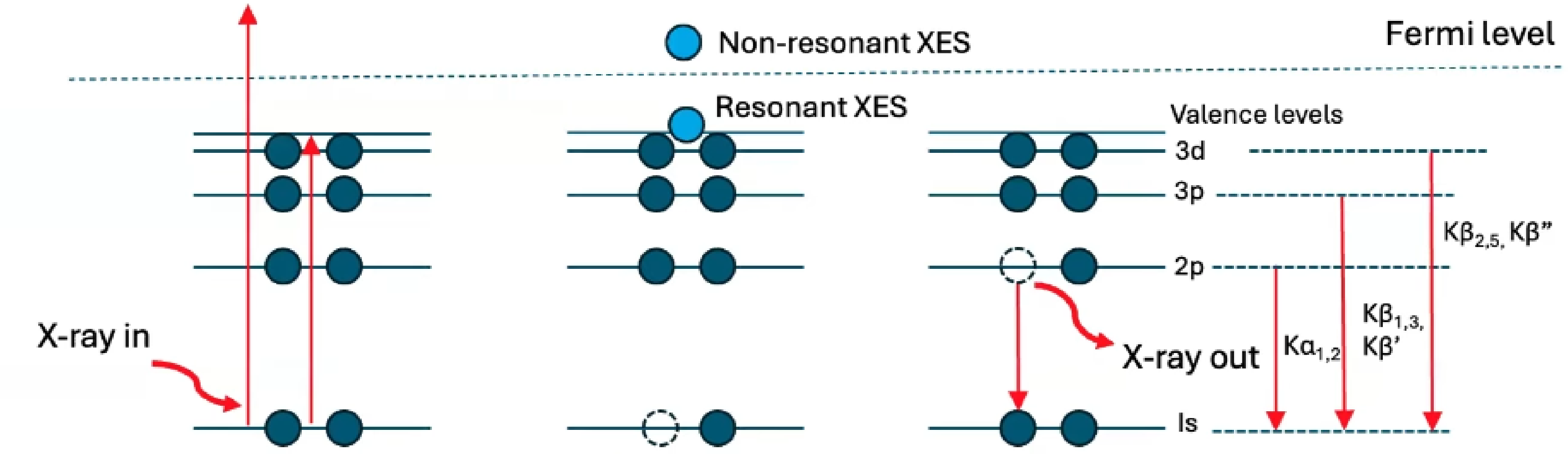
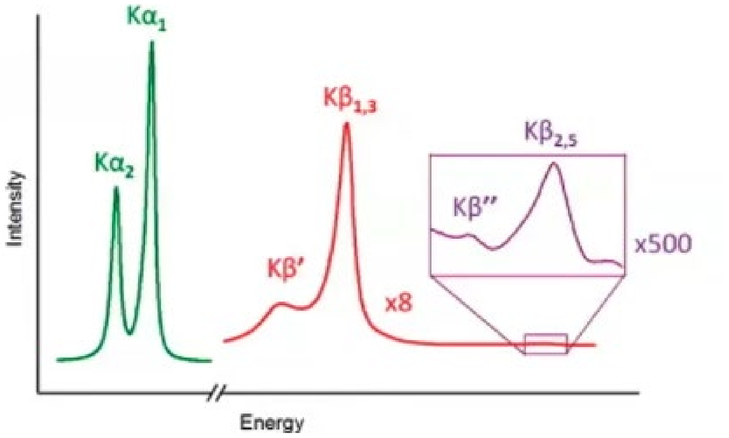
03.11.2026

@BrookhavenLab

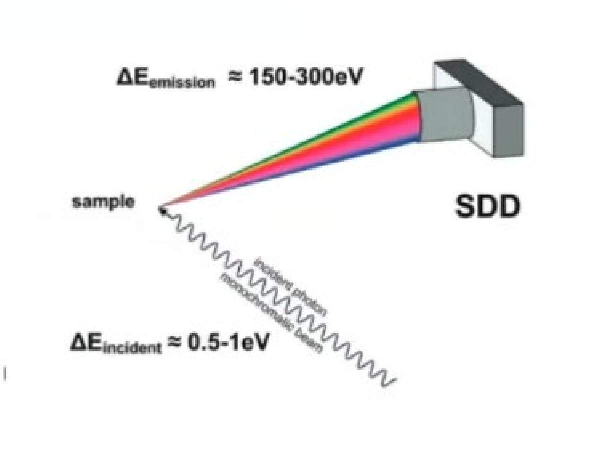
Emission lines

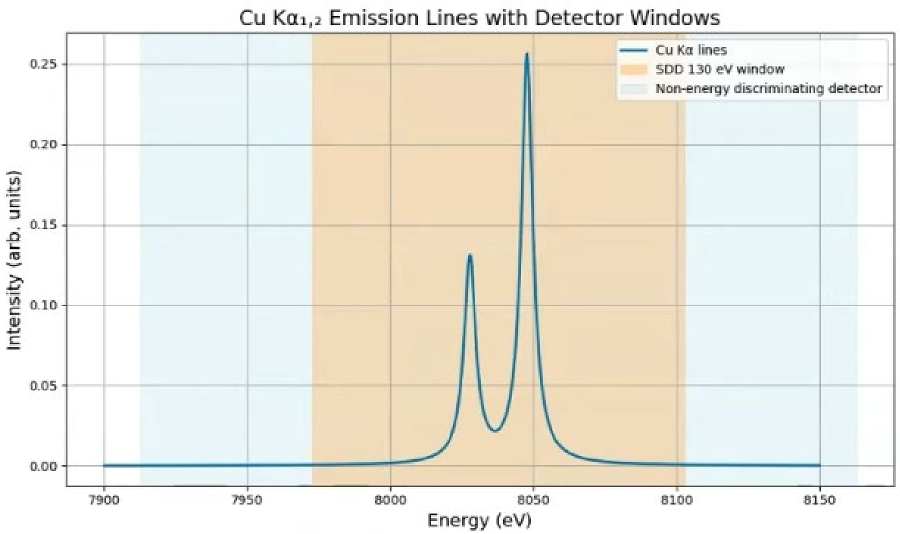




How to detect fluorescence

Modern synchrotron beamlines commonly use semiconductor detectors, typically based on Silicon or Germanium diodes, to detect X-ray fluorescence emitted from a sample.



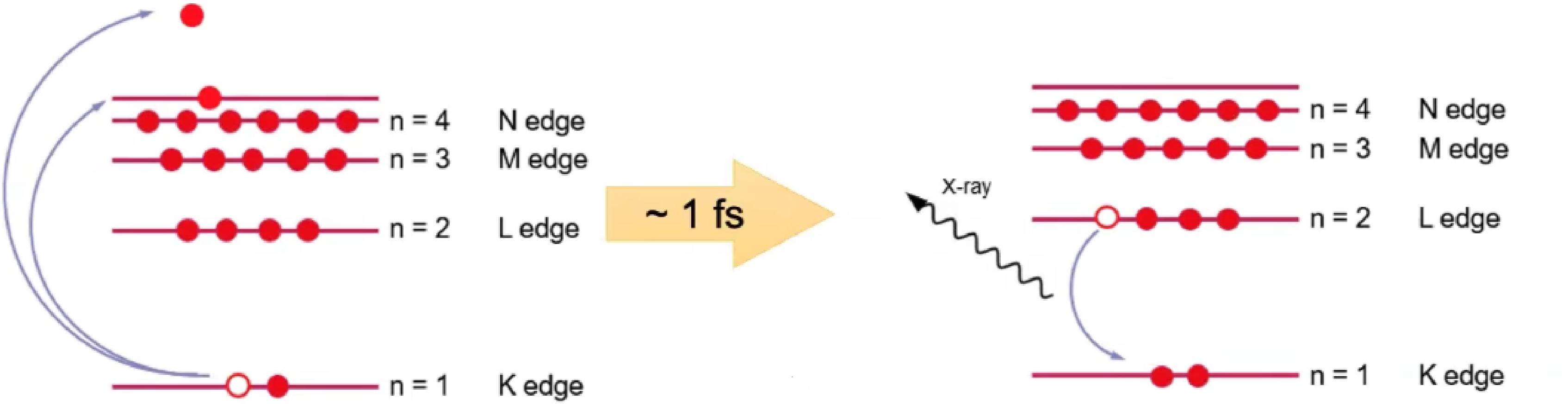


They provide:

- High quantum efficiency
- Ability to separate fluorescence lines from background
- “Good” energy resolution,

Core-hole lifetime broadening

Core-hole lifetime broadening refers to the **natural linewidth (energy uncertainty)** of an X-ray emission or absorption spectral line that arises because a **core-excited state (core hole) has a finite lifetime**.

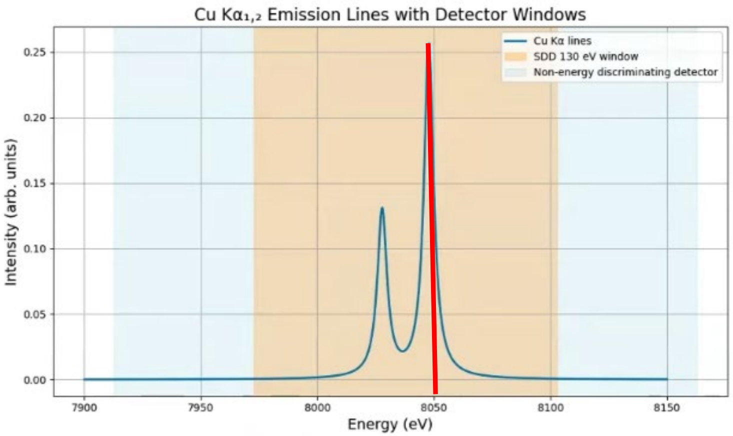


$$\Delta E \Delta t > \frac{\hbar}{2}$$

Because the core hole exists only for a very short time, its energy cannot be defined with perfect precision. This effect follows the **Heisenberg uncertainty principle**, specifically the energy-time relation

How do we overcome these limitations ?

Instead of measuring total fluorescence or a wide window of it we should only collect photons emitted in a very narrow window using crystal analyzers.
We use diffraction.



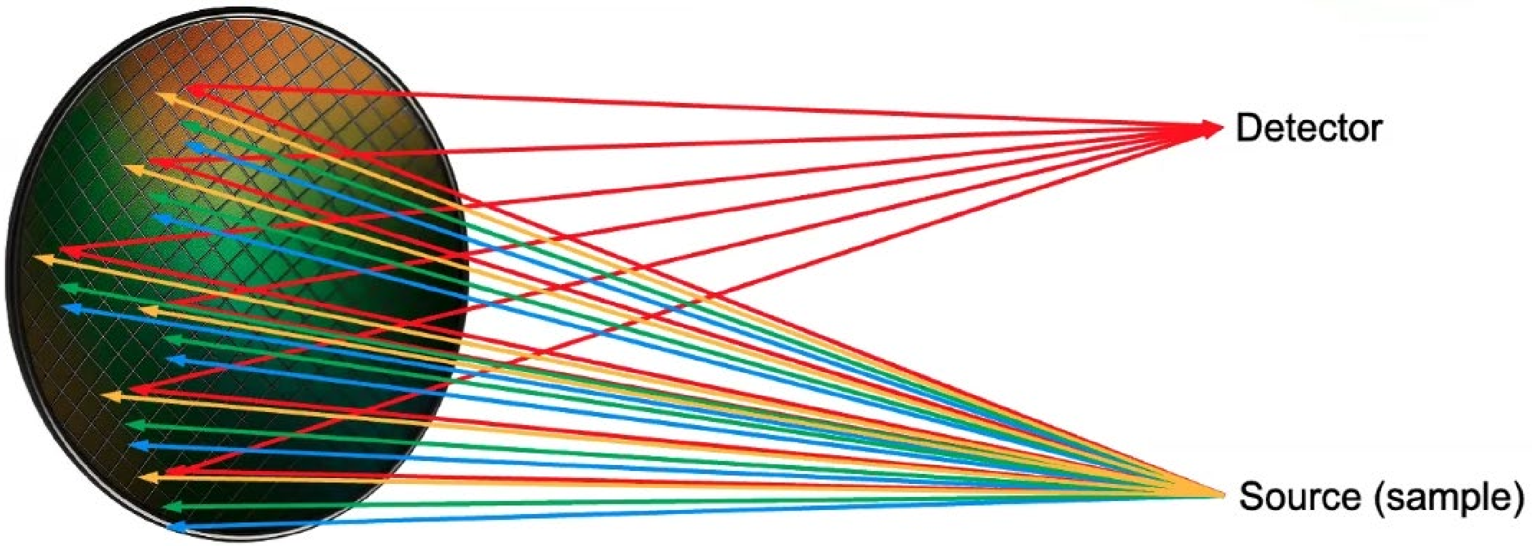
Bragg's law:

$$n\lambda = 2d \sin\theta$$

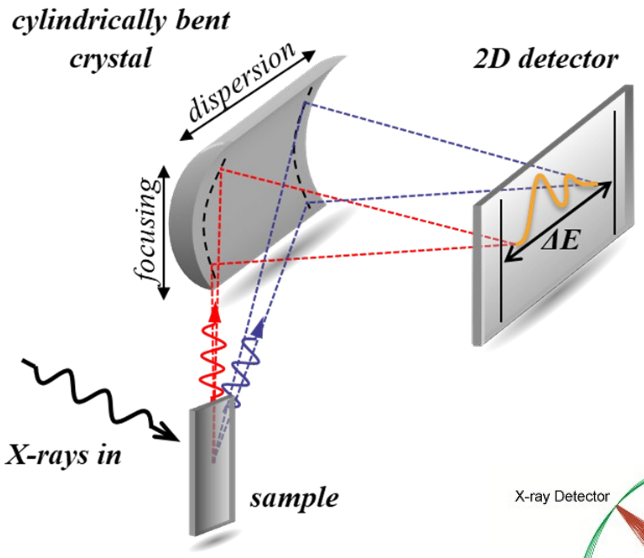
How do crystal analyzers work

X-ray monochromators expect collimated beam – crystals are flat

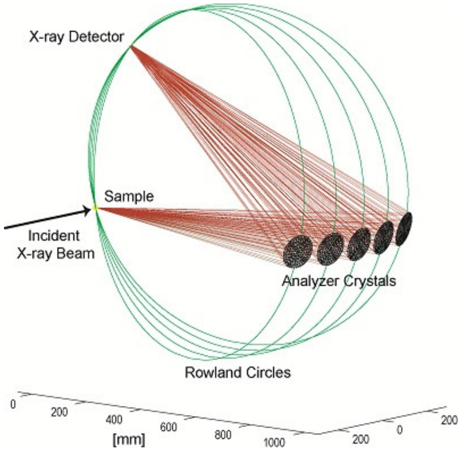
Photons coming from the sample to the crystal as divergent "beam" – we need to curve the crystals



Spectrometers for XAS and XES



- **<u>von Hamos geometry</u>**
- cylindrically bent crystal, which disperses the photon energy along one axis and focuses photons on the other axis
- No motorized crystals required

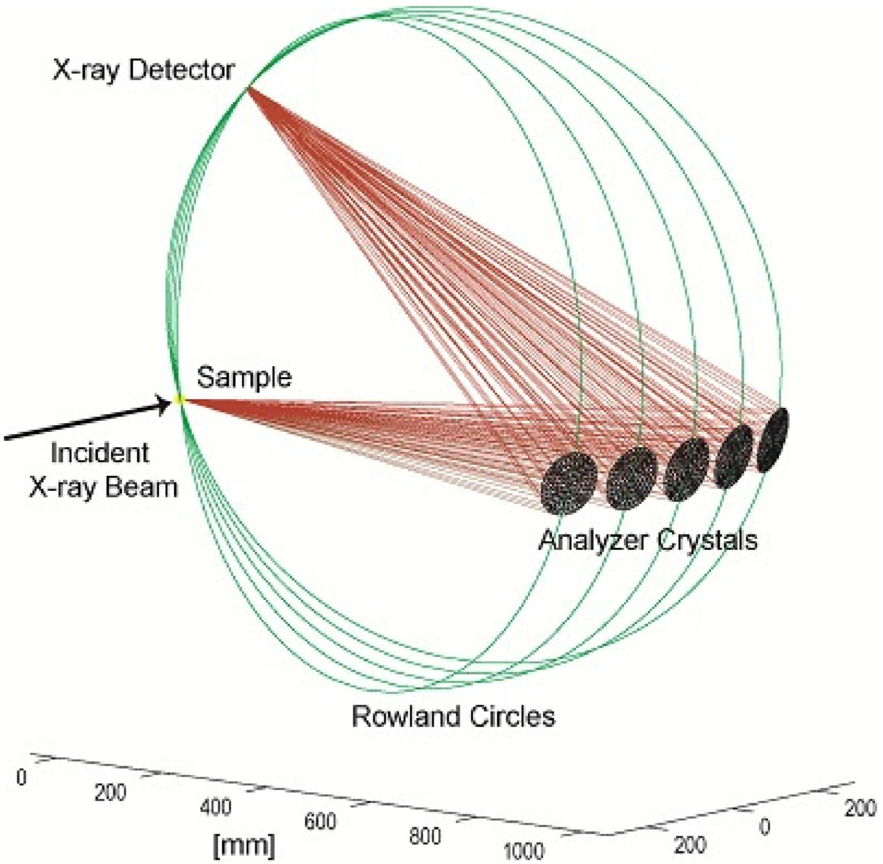


- **<u>Johann geometry</u>**
- More complex setup - motorized crystals that need to scan + moving detector
- Higher signal intensity

How are the measurements performed

HERFD-XANES

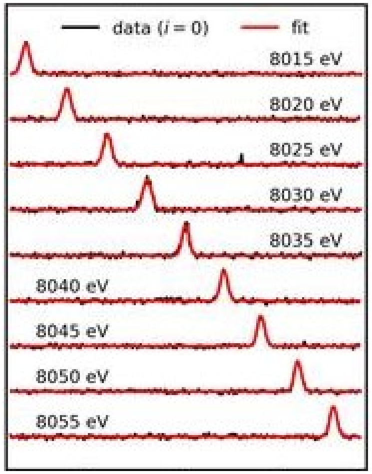
- Fix emission energy (spectrometer Bragg)
- Scan energy (monochromator)



XES

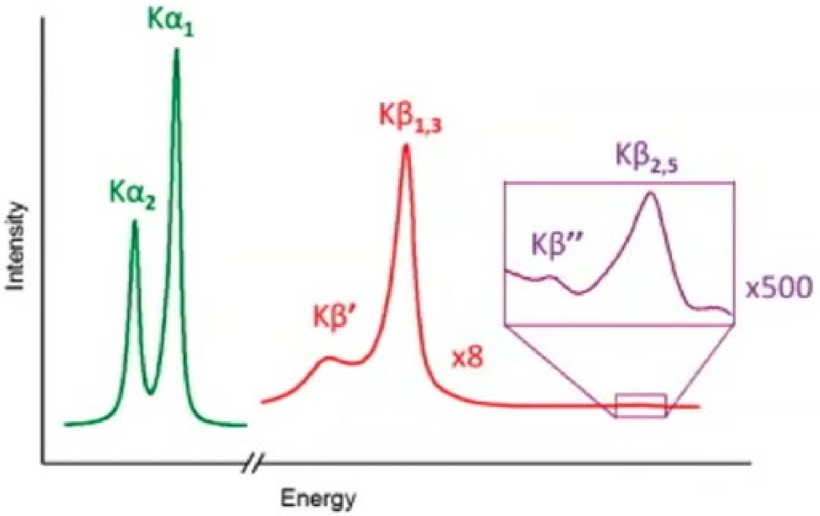
- Fix energy (monochromator)
- Scan emission energy (Johann)
  Or just collect (von Hamos)

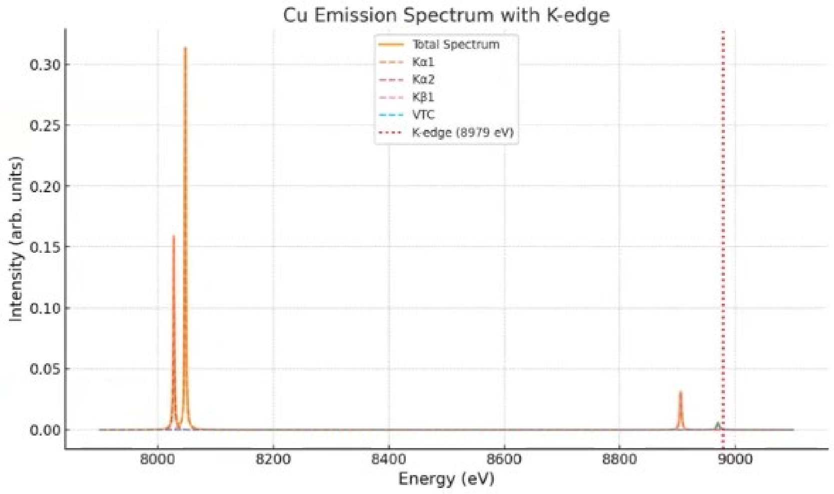
How do we know the energy ?
We can record elastic peaks

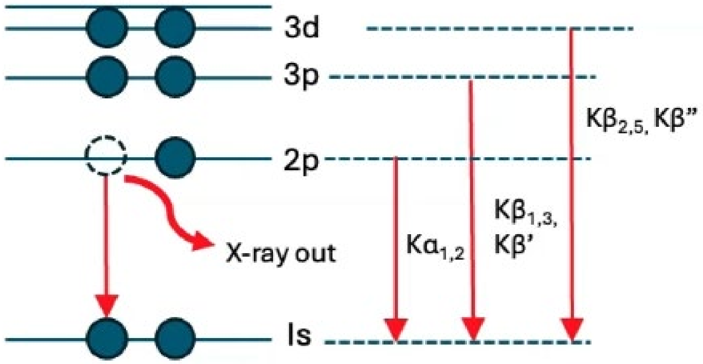


HERFD-XANES

High Energy Resolution Fluorescence Detected X-ray Absorption Near Edge Structure (HERFD-XANES)







- Kα lines are lowest in energy and are separated from the absorption edge energy by several hundred to several thousand eV
- Kβ lines lie closer to the edge
- K$\beta_{2,5}$/Kβ'', valence-to-core (VtC, v2c) transitions, lie only few eV away from the absorption edge

HERFD-XANES Examples: Copper

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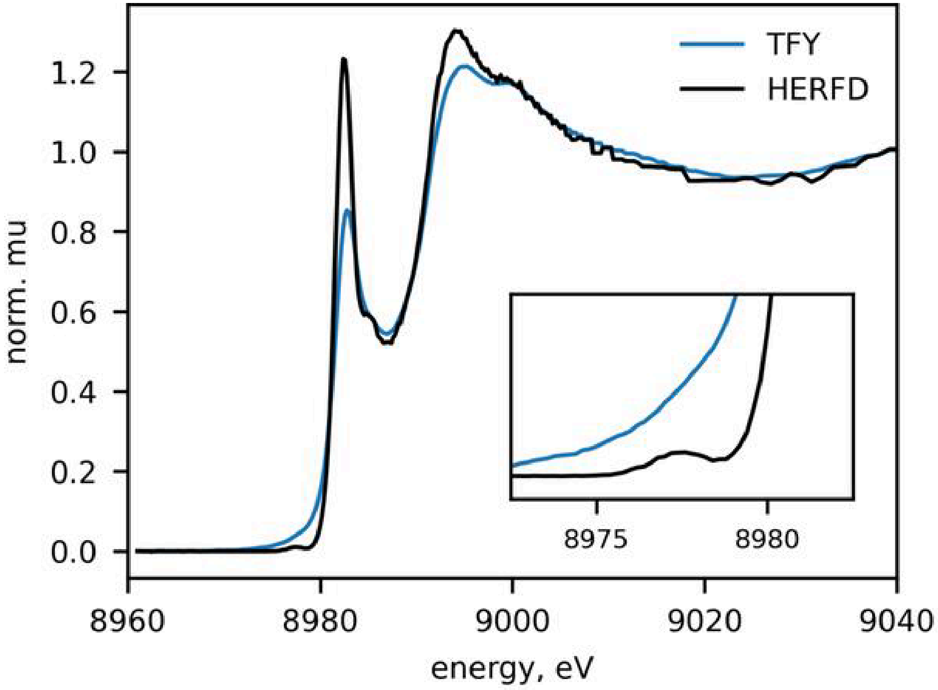

Problem from catalysis: what is the oxidation state of copper in selective catalytic reduction reaction:

- XANES shows evidence of Cu^{1+}
- HERFD-XANES allows to observe the pre-edge peak which is characteristic for Cu^{2+}

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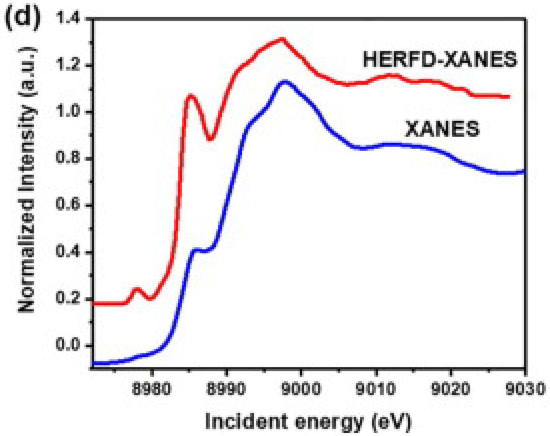
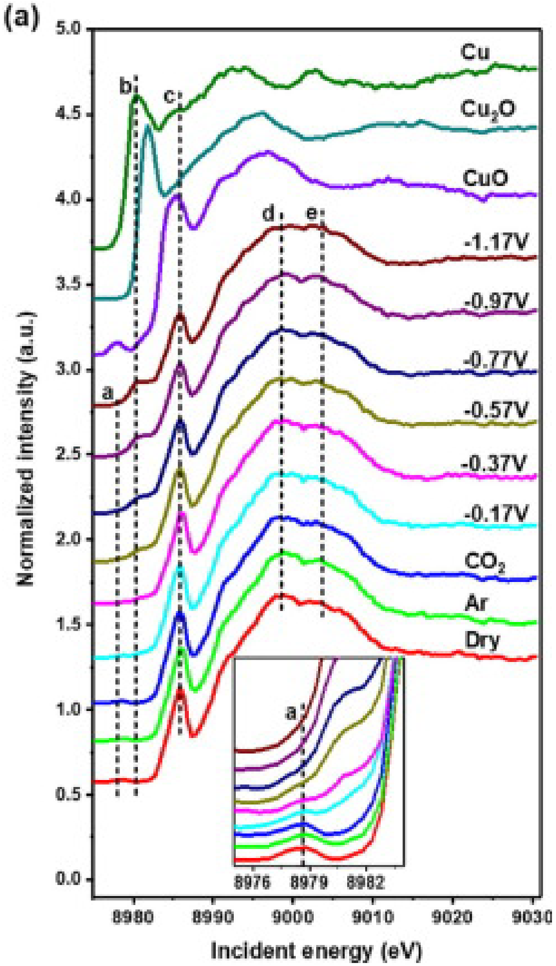
HERFD-XANES Examples: Copper



HERFD (red) and traditional (blue) XANES of CuO

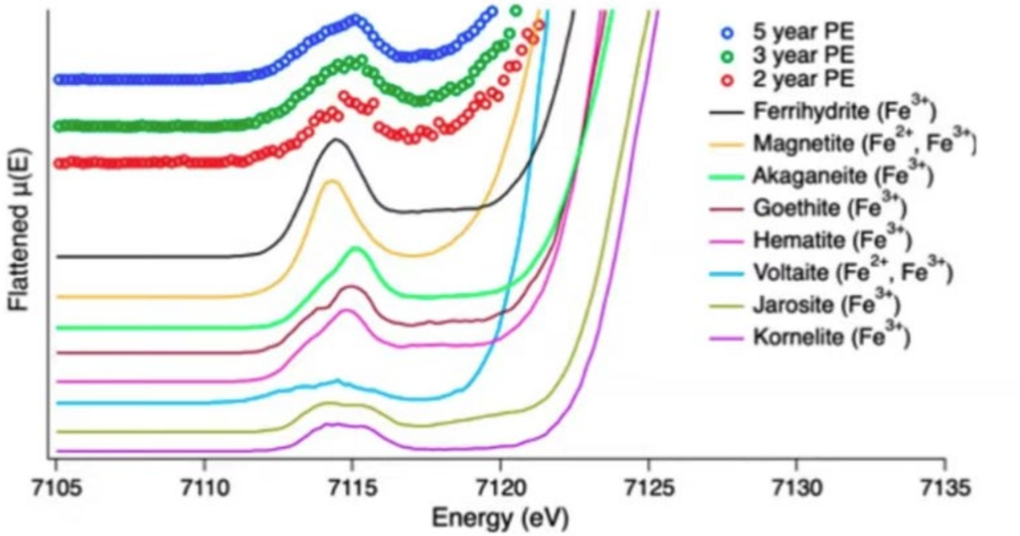


HERFD-XANES at various applied potentials vs RHE during ECO_2RR

HERFD XANES allowed to identify the state of copper during cycling that goes from Cu^{2+} to Cu^0

Journal of Energy Chemistry, 2022, 64, 1-7

HERFD-XANES more examples: Iron

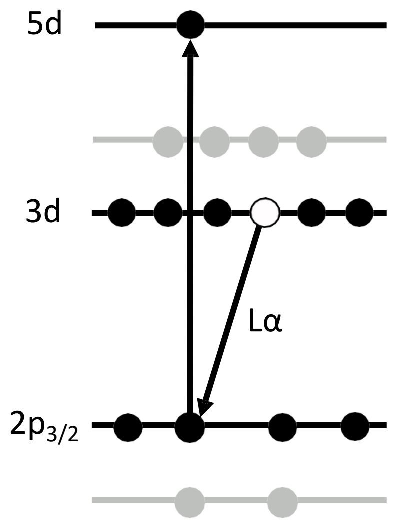


Environ. Sci. Technol. Lett. 2023, 10, 6, 538-542

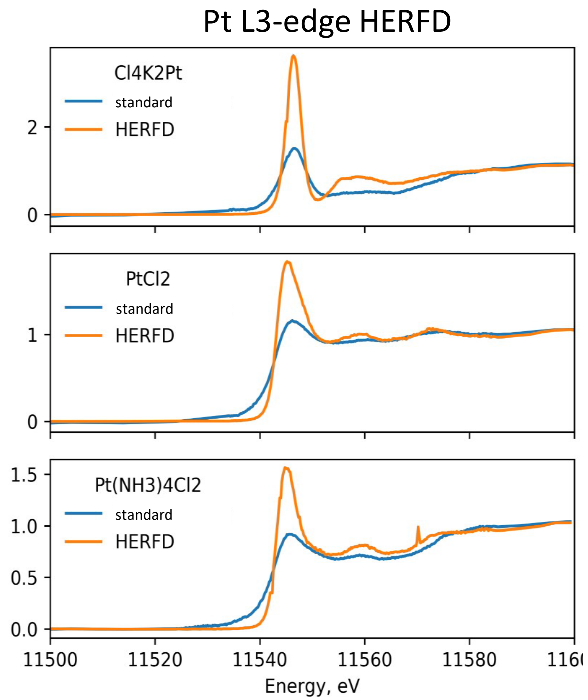
What are the iron species in aged microplastics

- As plastics age they accumulate contaminants (including ppm’s of heavy metals)
- Predominantly ferric species found in microplastics exposed to the environment for 2-5 years

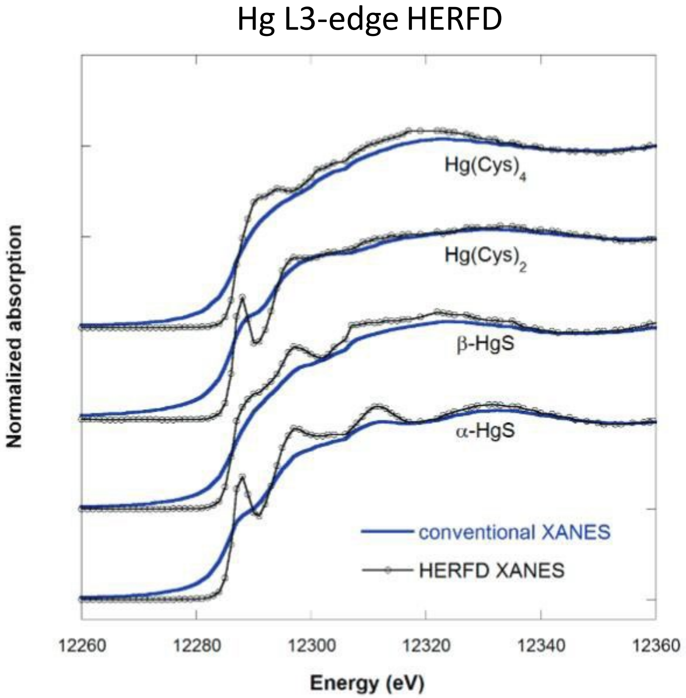
HERFD-XANES Examples: 5d metals



5d metals core-hole broadening can reach 6-8 eV

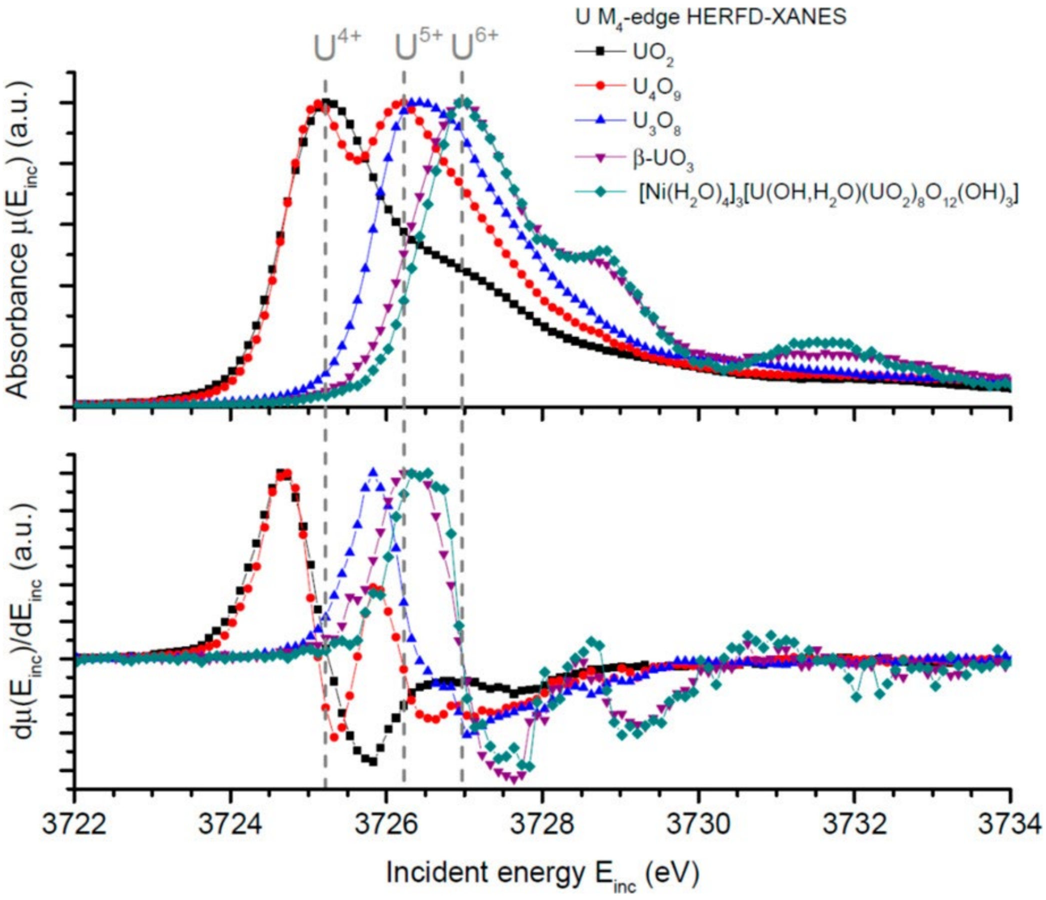


ISS data - samples from Bruce



J. Environ. Qual. 46:1146–1157 (2017).

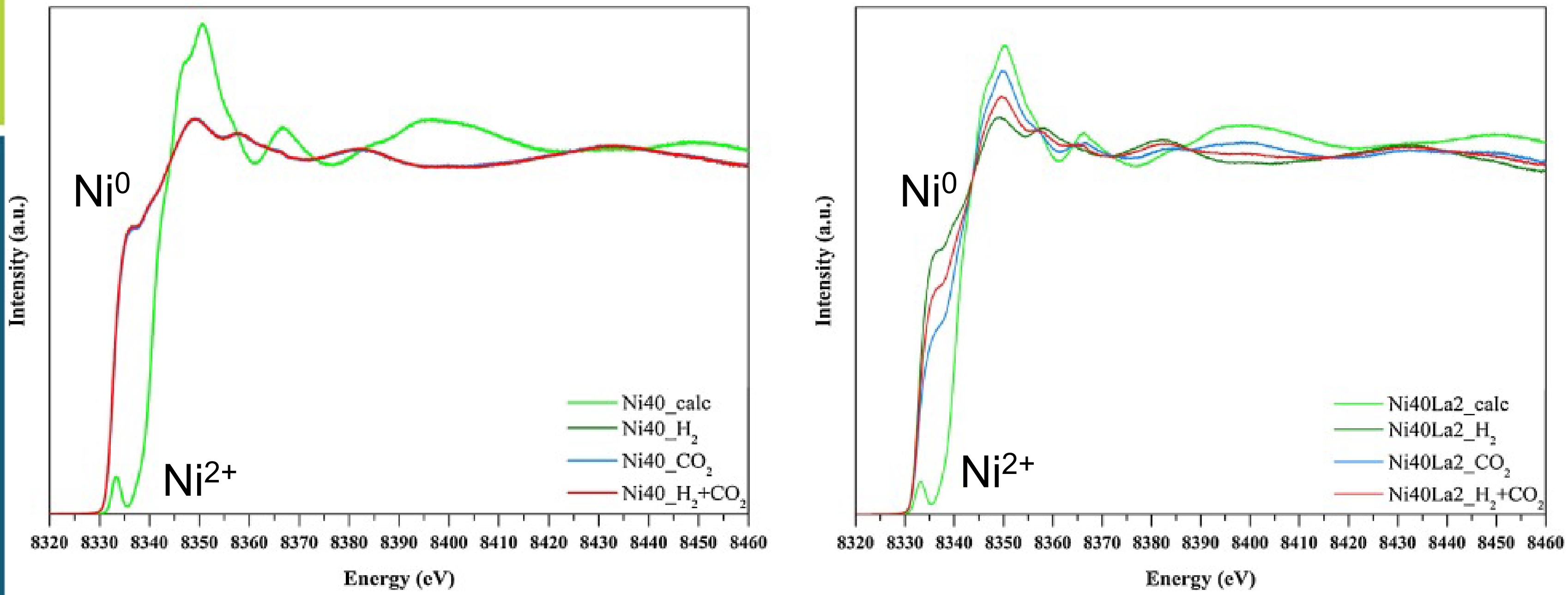
HERFD-XANES – Uranium M4 edge



U M4-edge HERFD−XANES spectra

- The U M_4-edge is more sensitive to uranium valence states than the U L_3-edge, making it better suited for identifying oxidation states in mixed-valence compounds.

HERFD-XANES – Ni catalyst for CO_2 methanation



Evolution of the Ni K edge HERFD-XANES spectra

- No redox changes for Ni40
- Oxidation of Ni under CO_2 atmosphere for La promoted sample
- Nice – but there is a problem -> self-absorption

X-ray emission spectroscopy

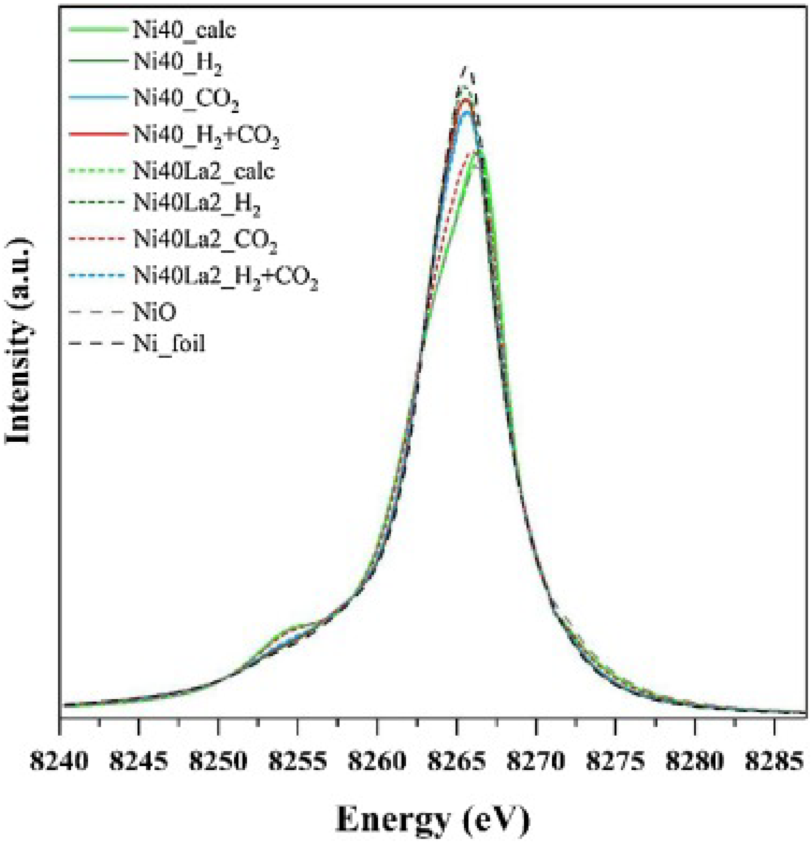


Fig. 1 Evolution of the Ni core-to-core Kβ XES

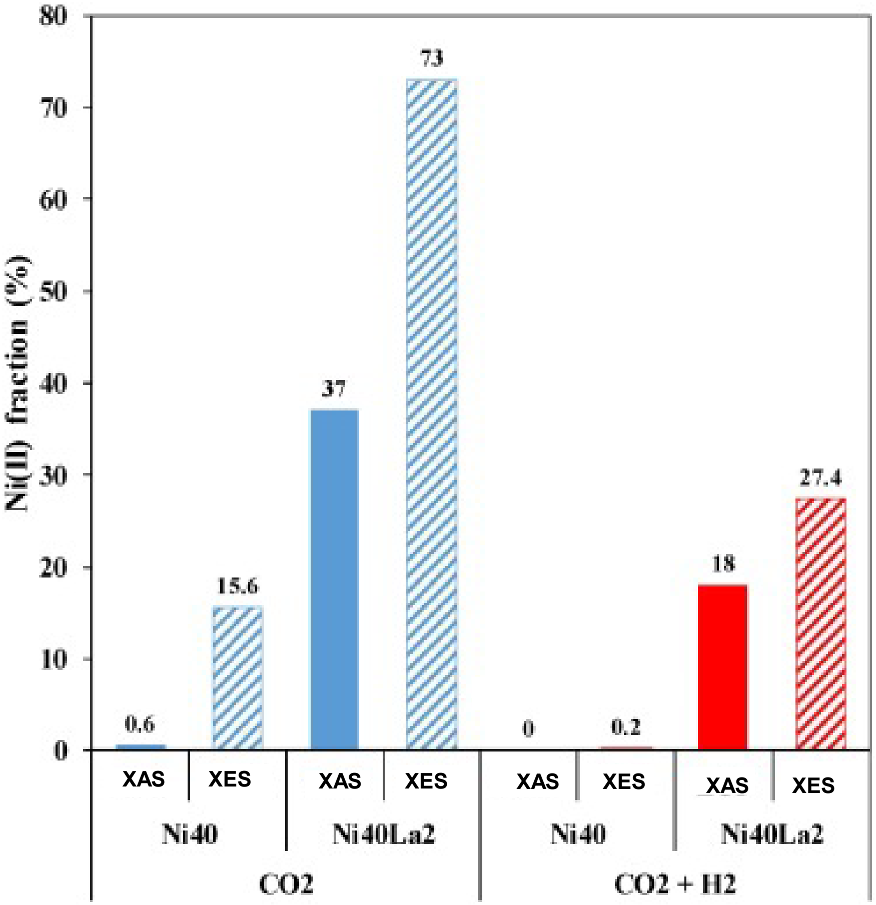


Fig. 2 Fraction of Ni^{2+} species (%)

- In both cases (XAS and XES) the trend is the same, but…

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XES

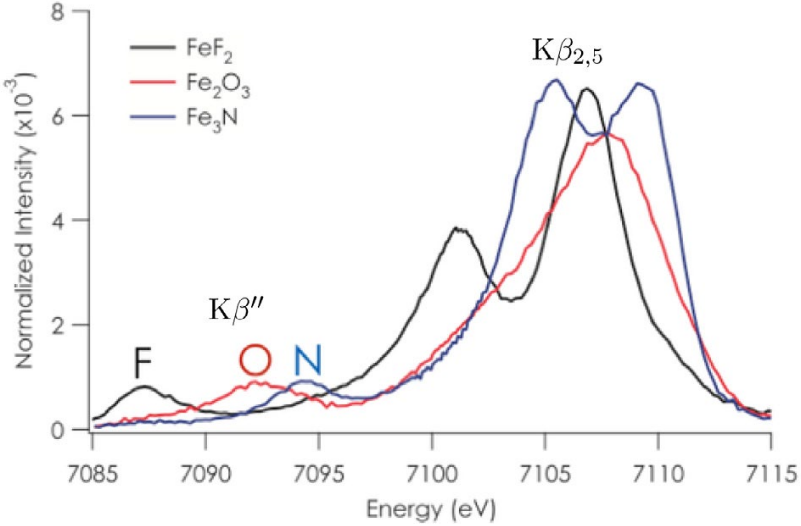
Chemical sensitivity of emission lines

The Kα and Kβ lines are split due to spin-orbit coupling

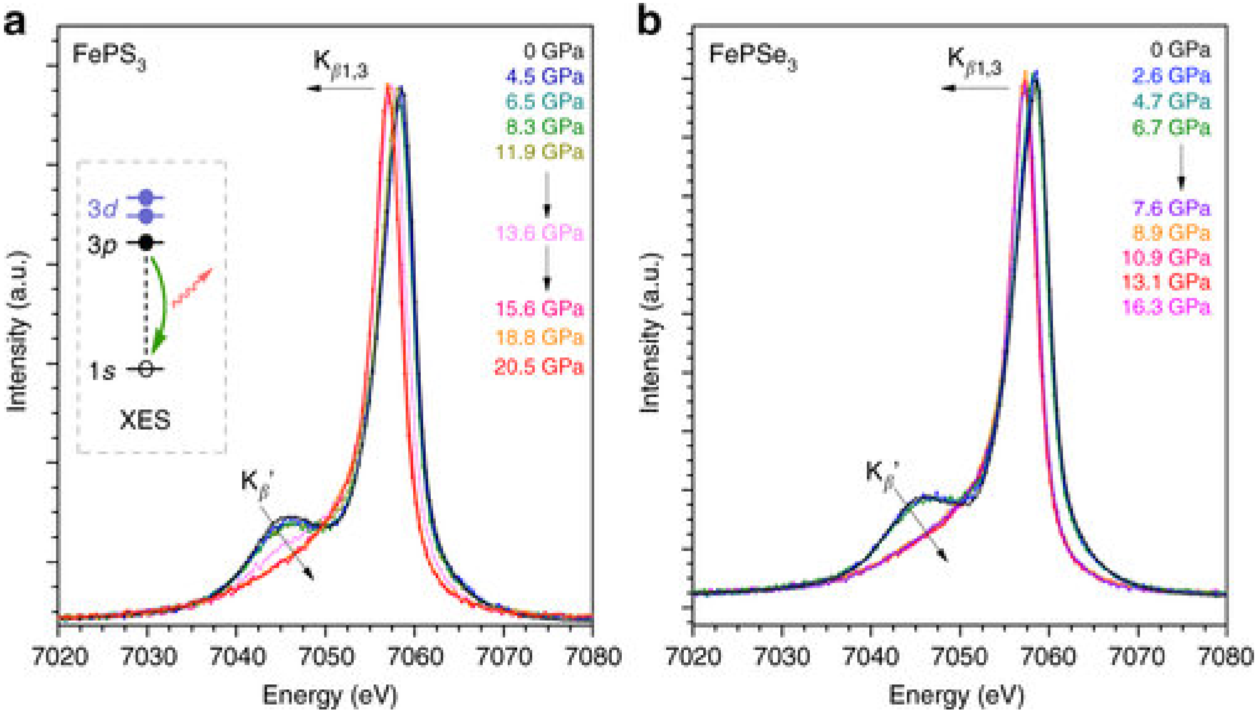
- $K\alpha_{1,2}$ splitting is due to 2p spin-orbit coupling,
- Kβ is split due to 3p-3d electron exchange interaction,

The valence-to-core transitions directly reflect the configuration of electron orbitals that participate in the chemical bond

- Light element ligands will strongly affect Kβ'' position and spectral shape allowing to discriminate between light elements bound to the emitter,



X-ray Emission Spectroscopy core-to-core (ctc)

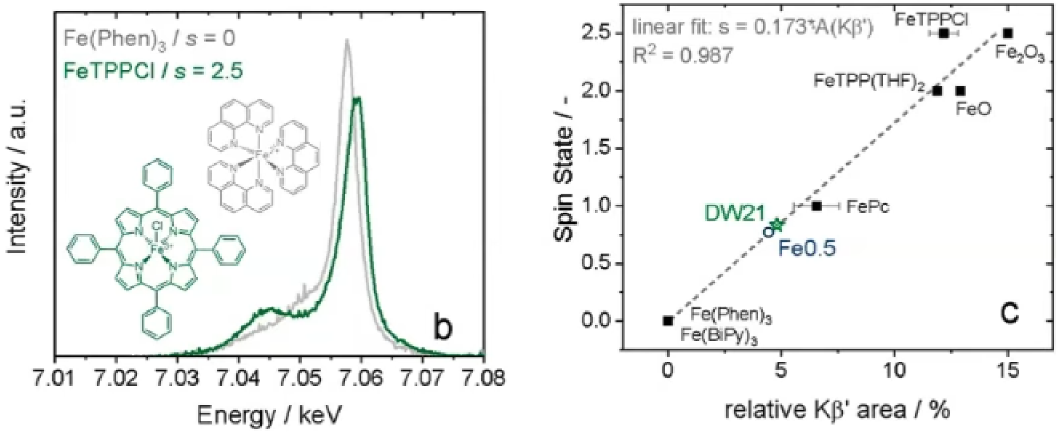


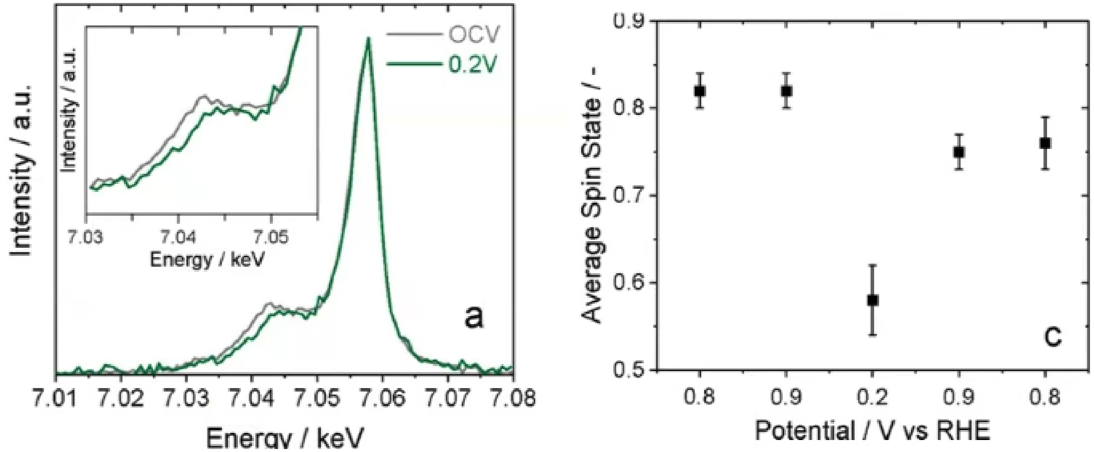
- Spin state transitions as well as oxidation state can be easily followed

More examples

- You can easily determine average spin state by analysis of XES spectra

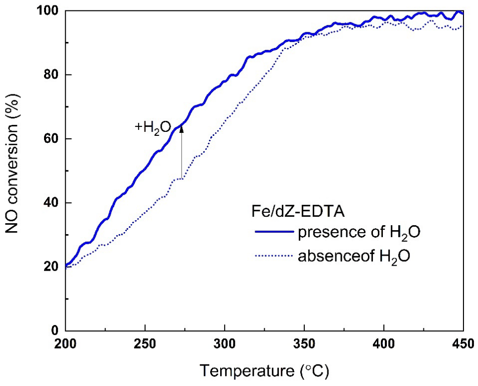
- This approach revealed a reversible spin state transition in the Fe/N/C

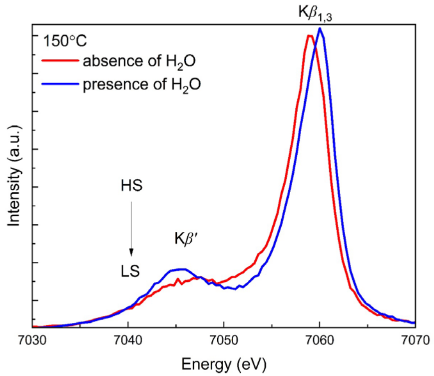


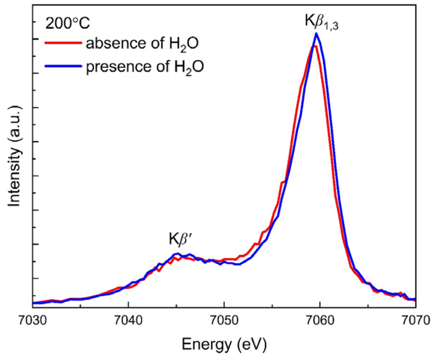


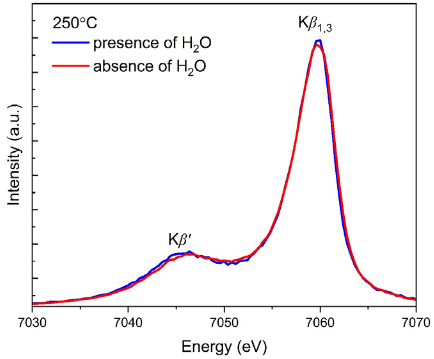
More examples

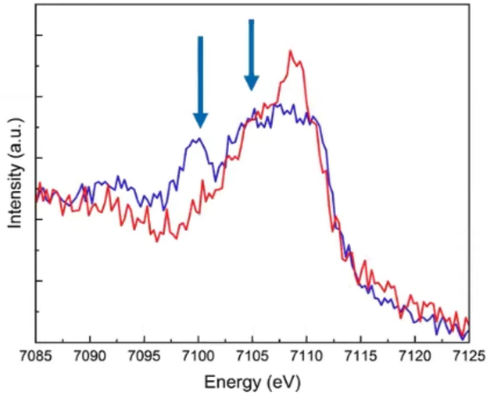
- *In situ* XES data (K*β* mainline) revealed that Fe gradually undergoes transition from high spin (HS) Fe^{2+} species to low spin (LS) Fe^{2+} under NO/NH_3 at lower temperatures.





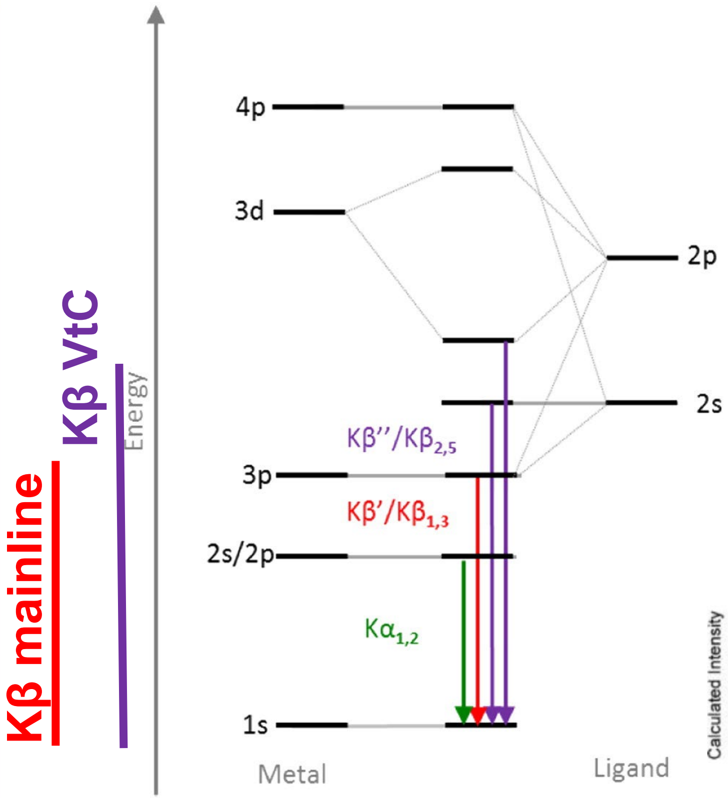




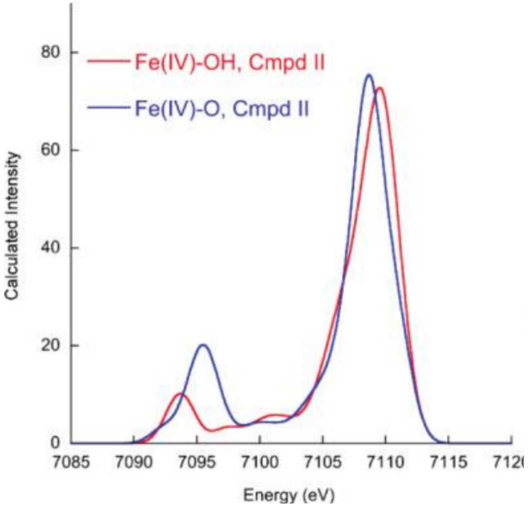


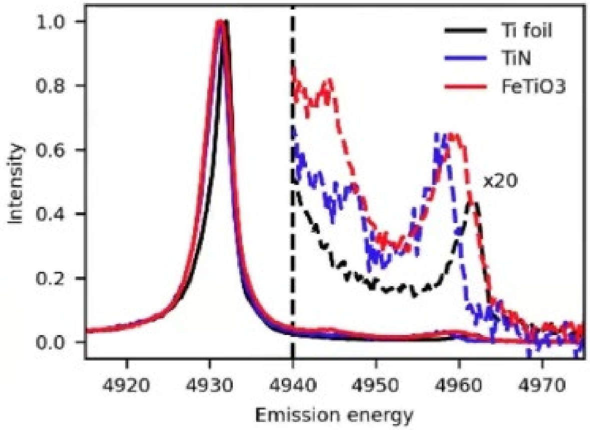
Direct evidence of adsorption on Fe – not visible with other spectroscopic tools (IR, UV-Vis)

More on valence-to-core XES



- Valence-to-core emission spectroscopy (vtc) probes the chemical environment around the element particularly its ligand and bonding.

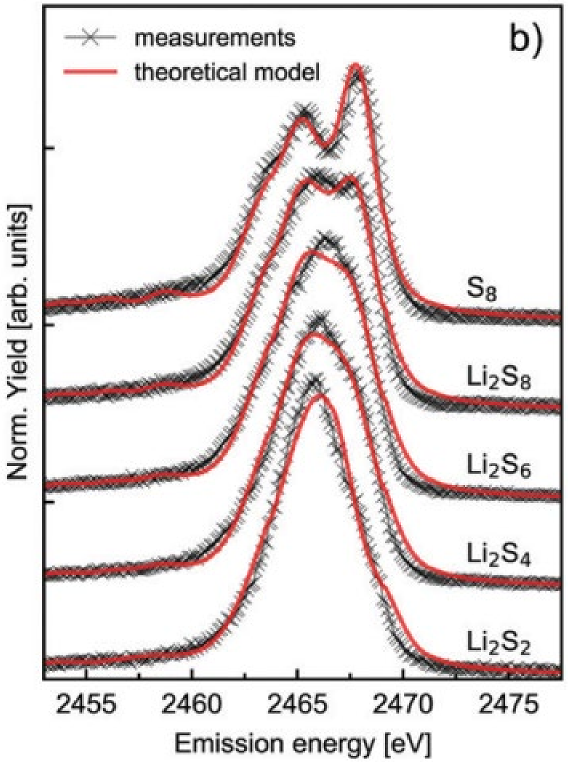




More examples – sulfur speciation

- Conventional XAS is generally not sensitive to the specific type of polysulfide species formed during battery cycling,

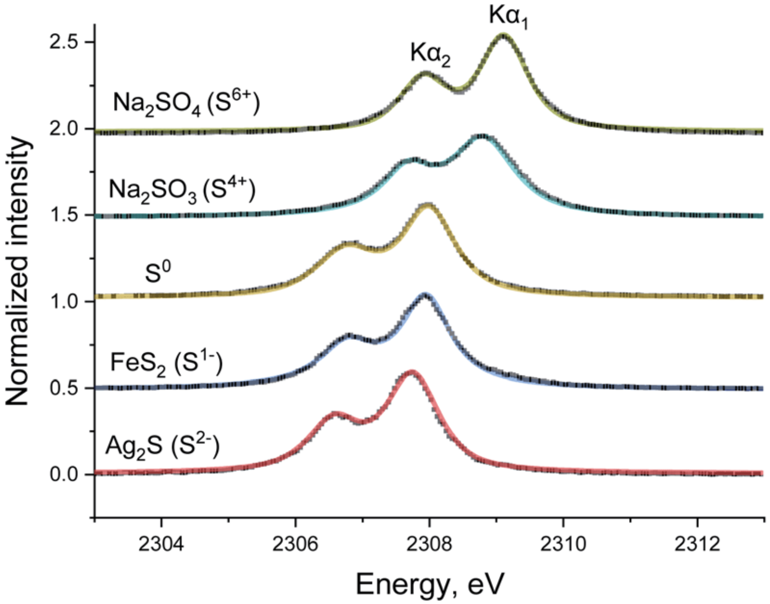
- valence-to-core XES can directly probe ligand electronic states and therefore distinguish different sulfur environments.



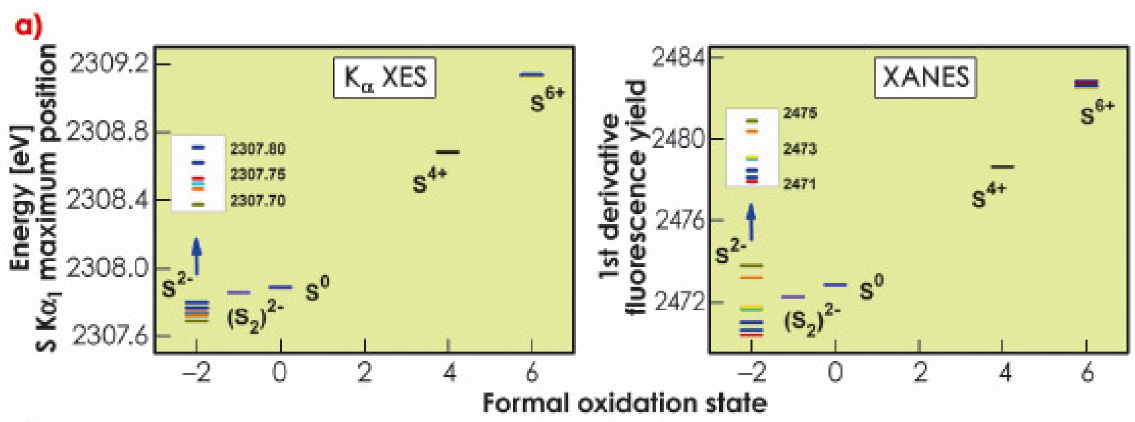
Chem. Commun., 2021, 57, 7573

Local charge density – XAS vs XES

- Quantitative sulfur speciation by simple linear fitting.



Considerably higher accuracy as probe of local charge compared to XANES



Anal. Chem. **81**, 6516 (2009).

Advantages of XES

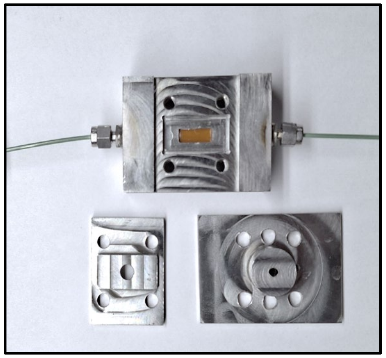
- Significantly less influence of self-absorption effect (compared to XANES),

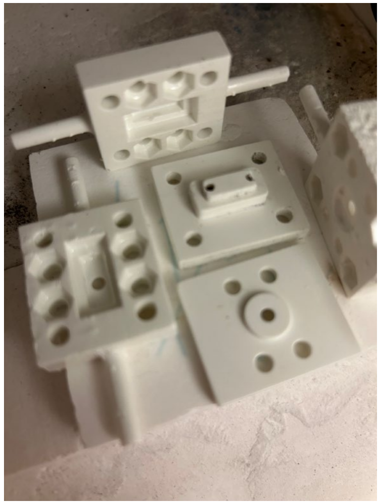
- You do not need to scan the energy (monochromator),

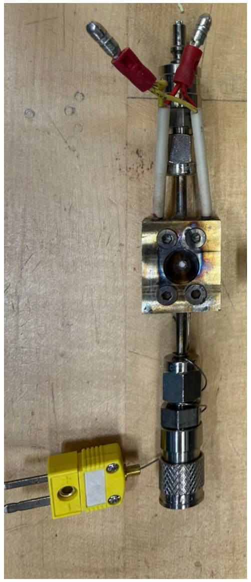
- If you use multiple cylindrically curved crystals and an area detector you can measure multiple elements simultaneously,

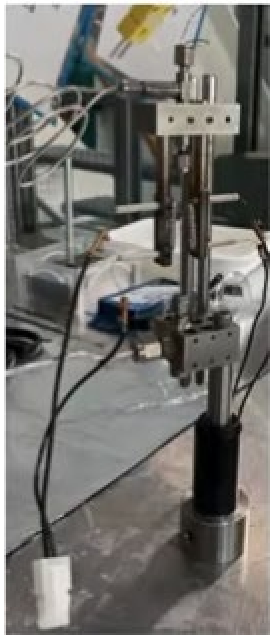
Practical considerations – sample environments

- Most sample environments that are compatible with conventional XAS (especially fluorescence) will work for high-energy-resolution experiments

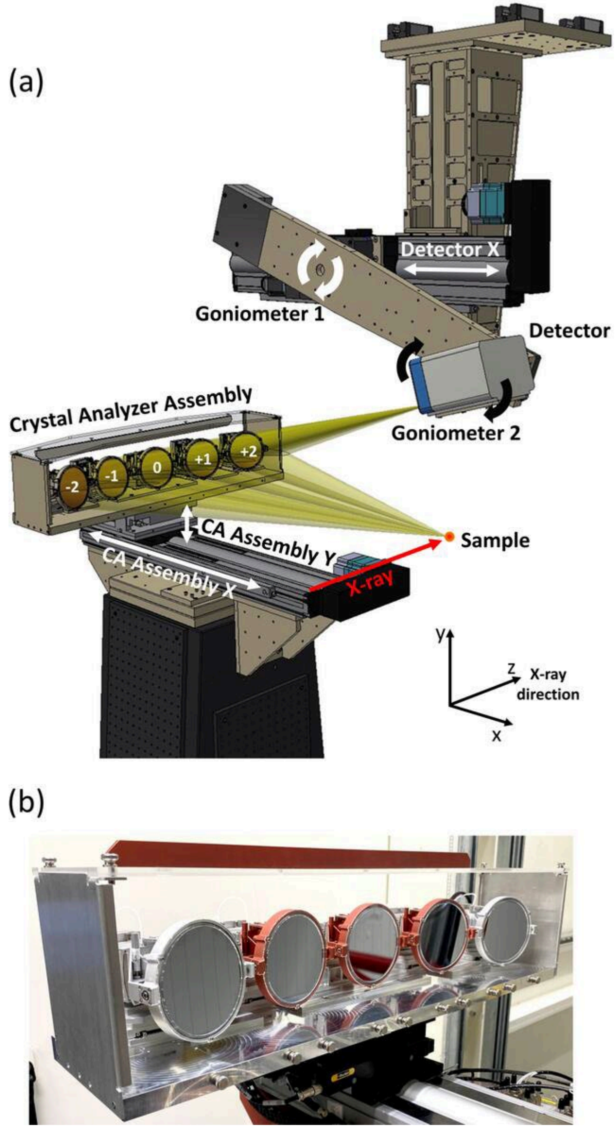








Where can you do it?



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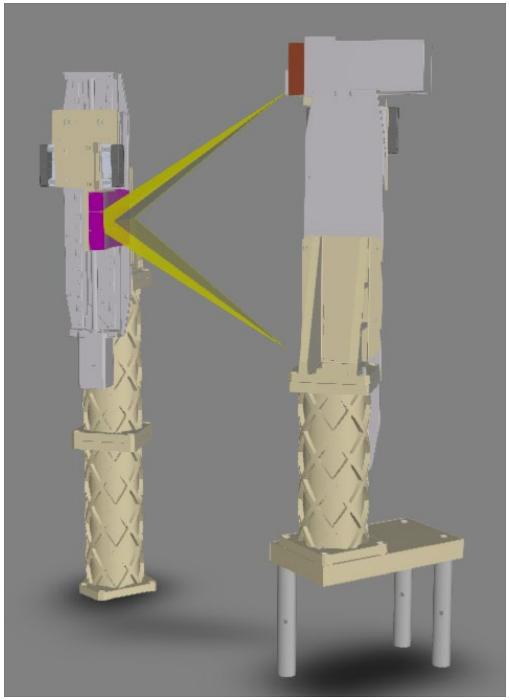
Akhil
Tayal

Jorge
Moncada



Soon also at TES (von Hamos geometry)

NSLS-II/CFN User Meeting - Workshop

NSLS-II & CFN Users' Meeting

We welcome all first-time, current, and future users

The Users' Meeting will be hosted by Brookhaven National Laboratory and will take place on April 21–23, 2026 with Extended Workshops scheduled for May 5-6, 2026.

Thursday, April 23	Workshop 7 - High Energy Resolution Spectroscopy for Operando Studies
	Workshop 8 - Building a U.S. EUV Research Ecosystem: Community Drivers for a Dedicated NSLS-II EUV Beamline Capabilities
	Workshop 9 - Characterizing Amorphous Materials: Seeing Order in Disorder
	Workshop 10 - AI Showcase