ADVANCED SPECTROSCOPIES: XAS AND XES



² Shelly Kelly and SPC team

EXAFS-50 Symposium Oct 30-31, 2023





OUTLINE

- Introduce Spectroscopy group and beamlines
- New S-25 due to APS-U
- Layout and technical specifications
- Commissioning data collected before shutdown
- Capabilities in development





SPECTROSCOPY GROUP



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SPECTROSCOPY MEASUREMENTS X-ray Absorption and Relaxation Processes

- Scan x-ray energy through absorption edge
 - record the total absorption of the sample (XAS)
 - record the total fluorescence of the sample
 - record partial fluorescence from the sample (HERFD)
- Set the x-ray energy above the absorption edge and record the energy of the fluorescent x-rays (X-ray Emission Spectroscopy: XES)
- Scan the x-ray energy far above the absorption edge and record the energy loss from interaction of core electrons with x-rays (X-ray Raman Scattering: XRS)

Combined with microprobe resolution and XRF mapping

The future will bring more image processing







SPECTROSCOPY GROUP Operates three beamlines at the APS

- 20-BM-B beamline is primarily dedicated to XAS.
- 9-BM-B,C beamline is a quick-scanning XAS capable of extended XAFS measurements in a few seconds.
 - optimized for low-energy measurements including P and S
 - full in-situ and operando catalyst studies with simultaneous infrared spectroscopy measurements.
- 25-ID-C/D has dedicated facilities for micro-XAFS, and an x-ray Raman spectrometer (LERIX) and provides multiple options for high-resolution fluorescence spectroscopy and x-ray emission spectroscopy.

20-ID program moved to 25-ID as part of APS-U







BASIC OPTICAL LAYOUT

Horizontal deflecting mirrors to separate two beamlines



28-MM UNDULATOR FOR BOTH BRANCH LINES

- Provides full coverage of our energy ranges
- Initial operation with Undulator A (dashed lines)







SECTOR 25 NEW BEAMLINE

Canted front end, both branches run independently





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S-25 COMMISSIONING

- Implement EPICS and Bluesky/Orphyd control system
- Test monos' motor temperature for consecutive scans
- Alignment of beams: front-end slits, mirror, masks, monos to end-station
 - Get central cone of ID: 'Crazy Steering Saves the Day'
- Align WB slits to mirrors, installation of encoders
- Implemented and initial testing of XAS-type energy scan
- Calibrate mono gaps for Si(111) and MTLs; establish motions for switching
- Verify energy range of MTLs; gap and height
- Verify energy resolution of Si(111) and MTLs and secondary Si(220)
- Verify energy calibration of monos over full range and repeated scans
- Improve mirror vacuum: bake and high power
- Activate and test mono internal feedback
- Establish protocol for mirror vertical translations for Pt, Si, and Rh and focusing





NEW CONTROLS FOR AGILE EXPERIMENTS

11

Python package based on Bluesky and Ophyd

- Common interface to devices with/without EPICS support (e.g. XMAP vs Xspress3).
- Scan data goes into a database with rich meta-data
- Work in progress: Adaptive scans can make decisions about acquisition in realtime







Research at BMM : Synchronous, Multimodal, Machine-Driven Experiments

Nearly identical Pt/Zr binary alloys co-deposited on silica were placed at BMM and at PDF, a total scattering beamline at NSLS-II. The measurement at PDF is much faster than at BMM, so PDF can quickly map out the phase space of the sample. Machine agents consume the PDF data, find regions of scientific value, and direct BMM to measure XAS on the Pt L_3 and Zr K edges in those regions.

Zr-rich



Bruce Ravel with Dan Olds and Phil Maffettone (NSLS-II) at BMM watching machines run our beamlines.



|X(R)| (A⁻³)

Machine agents direct BMM to move to relevant positions on a common coordinate system and begin XAS measurement.



PDF

GUI FOR ROUTINE OPERATIONS User interface uses Ophyd devices

- Creates and launches Bluesky plans for experiments.
- Bluesky Queueserver executes a queue of scans on a separate computer, so GUI cannot interrupt acquisition.
- Data browser allows searching the database for past scans.





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DISPERSIVE XANES MAPPING

Spatial maps of absorption and edge-shift derived from spatially resolved Dispersive XAS on Mn-oxide









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- Range of Si crystals available: Si(111), (100), (110), (211), (311), (773), (911)
- Common edges: Cr, Mn, Fe, Co, Ni, Cu, Zn, As, W, Au, Hg, Pb, U, Ce





HERFD EXAMPLES AT S-25

From thin films to bulk foils





- Absorption edge features become more pronounced
- Sample differences are more apparent

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LOW ENERGY RESOLUTION INELASTIC X-RAY SCATTERING (LERIX)

LERIX-II : Probing soft x-ray transitions with hard x-rays.

- Low energy electron transitions with hard x-rays
 - Transitions from core shells of light elements
 - Transitions from higher shells of heavier elements
- Eliminates several complications of soft x-ray absorption
 - Hard x-rays are more easily combined with complex sample environments such as in-situ, in-operando, high pressure (diamond anvil), and liquid cells
 - Bulk sensitive (hard x-rays)
 - Free of self absorption (non-resonant)
- Sensitive to non-dipolar transitions
 - Momentum transfer dependent, can be minimized or enhanced
 - Access aspects of electronic structure unavailable in XAS







PROOF OF PRINCIPLE LERIX-II DESIGN

S-25 testing LERIX-II design using half-meter analyzers



XRS with Sample imaging

Background and sample scattering can be spatially separated on the area detector to improve signal to noise levels



X-RAY EMISSION SPECTROSCOPY

Sensitive to spin state, valence, ligands

- Collection time from 30 sec to a few minutes
- Multilayer Monochromator after APS-U will allow sub-second integration time: mapping

Area detector

Sample

KB mirrors





RESEARCH ARTICLE | FEBRUARY 08 2012

Vertical energy gradient

A plastic miniature x-ray emission spectrometer based on the cylindrical von Hamos geometry \oslash

Incident X-ray



Von Hamos crystal analyzers

B. A. Mattern; G. T. Seidler; M. Haave; J. I. Pacold; R. A. Gordon; J. Planillo; J. Quintana; B. Rusthoven



X-RAY EMISSION SPECTROSCOPY

Sensitive to spin state, valence, ligands

- Collection time from 30 sec to a few minutes
- Multilayer Monochromator after APS-U will allow sub-second integration time: mapping

Example: distinguishing Ni and NiCl₂ in a battery electrode

Bowden et al, J. Power Sources 247, 517-526 (2014)



LI-ION BATTERY: COBALT XES Kbeta peak position varies with battery potential



- Change in spin/oxidation state is the important information.
- Single shot measurements on sub-second integration time after APS-U





SPECTROMETER FOR MULTI-ELEMENT XES

Large area detectors enable multiple element non-resonant XES

- Simultaneous XES spectra from nickel/manganese/cobalt on alumina cathode
- Simultaneous measurement
- Incident x-ray energy 8400 eV



Sun, C.-J.; Solovyev, M. A.; Heald, S. et.al. Advanced X-Ray Emission Spectrometers. US Patent 2023/0288352 A1, 2023.







NEXT GENERATION SPECTROMETER

Different crystals used for each element to satisfy Braggs Law to reflect required fluorescent x-ray energy







Sun, C.-J.; Solovyev, M. A.; Heald, S. et.al. Advanced X-Ray Emission Spectrometers. US Patent 2023/0288352 A1, 2023.

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ML GENERATED ROI FOR QUICK IMAGE TO SPECTRA CONVERSION

Image processing made easy









https://doi.org/10.1107/S1600577522006786



BONANZA GOLD MECHANISM Microprobe XRF and Spectroscopy

Extremely high-resolution SR-µXRF mapping of arsenian pyrite reveals that bonanza-style gold mineralization was caused by gold flocculation from electron transfer near arsenic-rich bands.



500 µm x 500 µm (50,451 pixels) ▲ ASK ▲ FeK ▲ AuL ▲ AgK Colour - Colours scaled independently

The distribution of electrum (Au, ■ + Ag, ■) on the edges of corroded pyrite grains (Fe, ■) with As banding (As, ■) as fine as <2 µm (single pixel thickness!)



400 µm x 400 µm (40,401 pixels) Microscopic metallic gold grain (2 pixels wide, ■) within the As band (As, ■) on the edge of a pyrite grain (Fe, ■).



Microscopic gold within arsenian pyrite growth zone is metallic Au⁰ and not lattice bound Au⁺¹



Dr. Neil R. Banerjee, P.Geo. Dr. Lisa L. Van Loon, C.Chem. XRF data analysis in Peakaboo (https://peakaboo.org) Beam spot size: <2 µm x <2 µm Energy: 26 keV

DEVELOPMENTS TOWARD LARGE MAPPING

Fly scanning sample positioner and variable focus

- Fly scanning sample positioner
 - 4 hour measurement using weak Fe-57 source with 18 minutes (7.5%) overhead
- Easy/rapid and reliable beam size adjustment using Be lenses
 - Initial measurements made at 20-ID







30mm x 30mm 21x21 points 30sec/point









GRAZING INCIDENCE PT EXAFS Pt monolayer on SrTiO₃ (001) substrate

- Oxide supported noble metal nanoparticles are widely used as heterogeneous catalysts; playing an important role for the societal shift from a fossil-fuel to renewable energy sources.
- Studies of highly diluted monolayer and single atom catalyst are difficult, but necessary with catalyst development at the atomic-scale.
- Initial measurements show full EXAFS scans can be used to determine interfacial Pt-O bond







https://doi.org/10.1103/PhysRevLett.128.206801

CHALLENGES WITH RESOLVING LN-LIGAND **COMPLEX STRUCTURES IN SOLUTION**

Ab initio molecular dynamics (AIMD)

- Ln³⁺ ions are reactive
 - Hydrolysis reactions, ligand degradation
- What molecules coordinate the Ln³⁺ ion in solution?
 - Highly dynamic first coordination sphere
 - Ligands are flexible and can rearrange their conformation when binding
 - Ligand/anion/solvent molecules compete for binding
- Unlike crystals or solids, structures in solution are not restricted in space
 - Harder to resolve experimentally or computationally

To resolve structure computationally, approach needs sampling due to dynamic nature of solutions, and consider chemical US. DEPARTMENT OF VIS. DEPARTMENT VIS. DEPARTMENT VIS. DEPARTMENT VIS. DEPARTMENT VIS. DEPARTMENT VIS. DEPART VIS. DEPARTMENT VIS. DEPARTM







VERIFYING COMPUTATIONAL STRUCTURES WITH EXAFS



ANION CHANGES THE LN COORDINATION ENVIRONMENT

- Eu-terpyNO₂ complex with nitrates, in acetonitrile, does not have solvent molecules in the first coordination sphere.
- Solution structure is similar to crystal, same species in complex, different conformation.
- When the anion is changed to triflate, solvent (acetonitrile) molecules will coordinate the Eu3+ ion



Summers et al., 2023, Inorg. Chem., 62, 5207 - 5218



QUESTIONS? AND FEEDBACK









