Spectroscopy Program at NSLS-II

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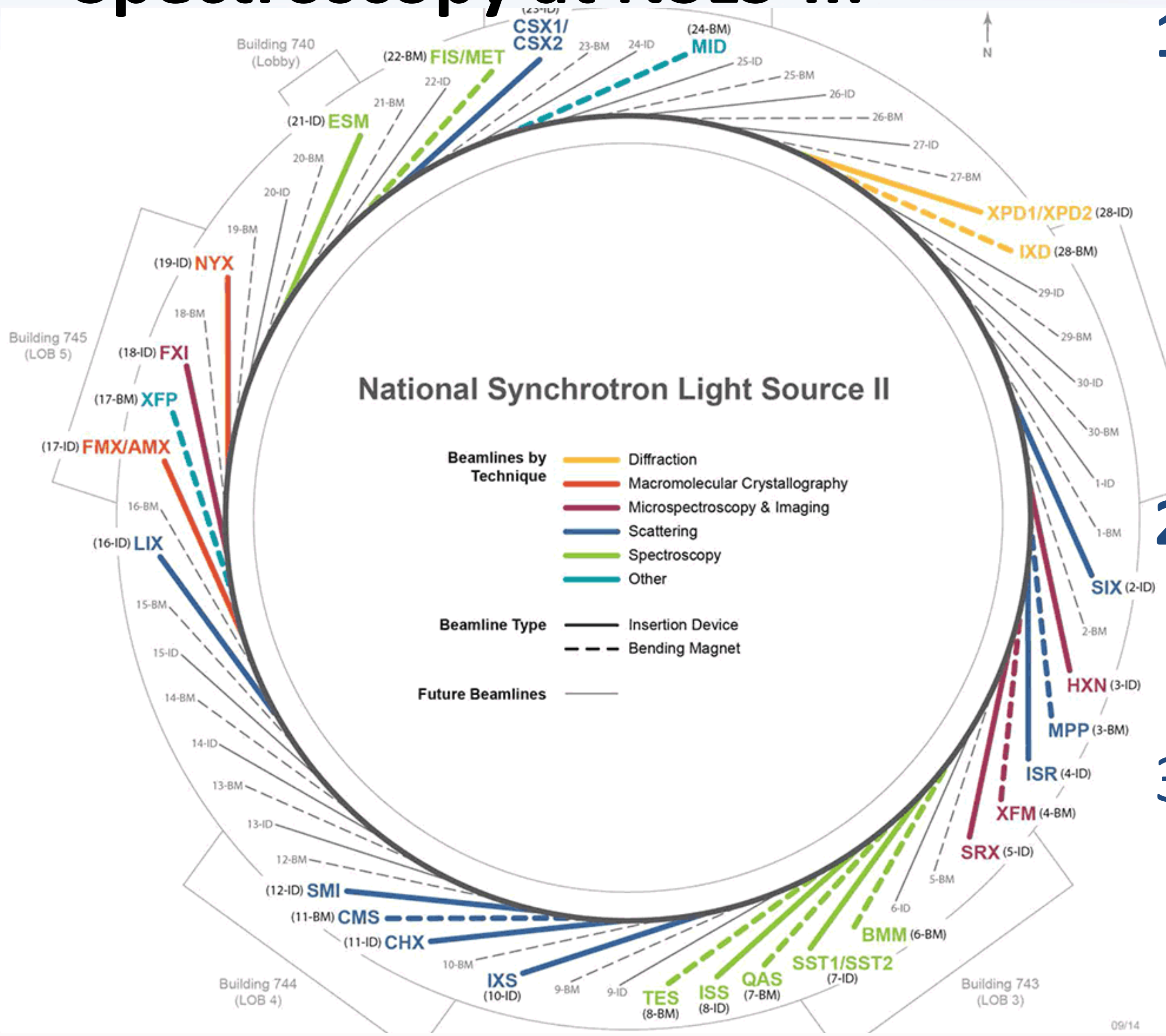
2 November 2016

Outline

- NSLS-II overview
- The Hard X-ray Program
  - The concept
  - The tools
  - The Method
- Conclusion

OVERVIEW: BEAMLINES/GROUPS

Spectroscopy at NSLS-II:



1. **Hard x-ray regime:**
   1. ISS
   2. QAS
   3. BMM (NIST)
   4. SRX (nano spectroscopy)
   5. HXN (nano spectroscopy)
   6. XFM
   7. SSRL: 2-2
2. **Tender**
   1. SST2 (NIST)
   2. TES
   3. SRX2
3. Soft X-ray
   1. CSX
   2. ESM
   3. SIX
   4. SST1 (NIST)

BEAMLINES OVERVIEW

Beamline	Techniques	Available/phase	Energy range [KeV]	Group
ISS	EXAFS, RIXS, X-ELS….	available	4.5-36	ISS/PS
QAS	EXAFS/XRD	January 18	4.7-31	ISS/PS
BMM	EXAFS/XRD	July 17	4.5-25	NIST
SRX	Nano XAFS	available	4.6-25	SRX/PS
HXN	Nano XAFS	available	6-25	HXN/PS
SSRL 2-2	XAFS	available	5-25	ISS/PS
SST2	NEXAFS/XPS	July 17	1-7.5	NIST
TES	XAFS/micro-XAFS	available	1-8	PS
SRX2	XAFS/micro-XAFS	?	?	SRX/PS
CSX-2	XAFS/XMCD/ambient pressure XPS	available	0.27-2	CSX/PS
ESM	ARPES/XMCD/XAFS/PEEM	available	0.015-2	ESM/PS
SIX	RIXS	July 17	0.165-2.3	SIX/PS
SST1	NEXAFS/XPS/nano probe	January 18	0.1-2.2	NIST

Contacts and Main Players:

- NSLS2 beamlines:
  - Hard X-ray Spectroscopy (Program Manager): Klaus Attenkofer
    - ISS: Eli Stavitski / Klaus Attenkofer
    - TES: Paul Northrup
    - QAS: Steve Ehrlich
    - Lab Space: Khalid Syed
  - Soft X-ray Spectroscopy (Program Manager): Stuart Wilkins
    - ESM: Elio Vescovo
    - CSX2: Stuart Wilkins
    - SIX: Ignace Jarrige
  - Spectro-Microscopy (Program Manager): Lisa Miller
    - HXN: Young Chu
    - SRX: Juergen Thieme
- NIST beamlines (Program Manager): Dan Fischer
    - SST: Dan Fischer
    - BMM: Bruce Ravel
- Support Consortia:
    - SCC: Jingguang Chen (catalysis)
    - Case Western: Mark Chance (Bio)
    - Battery: currently under discussion
    - COMPRESS: ? (high pressure)

How to get beamtime:

- All important information can be found on: https://www.bnl.gov/ps/proposal-cycles.php
- Run cycle:

Cycle	Run Dates	General User Proposal Deadline
Spring 2017	Jan—April 2017	September 30, 2016
Summer 2017	May—Aug 2017	January 31, 2017
Fall 2017	Sept—Dec 2017	May 31, 2017

- User office: Gretchen Cisco (631-344-4703)
- Beam current:
  - typically 250mA (max 500mA)
  - schedule: https://www.bnl.gov/ps/nsls2/opschedule.php
- Proposal system
  - GUP are valid for 1 year (3 cycles); SC are valid for 1 cycle
  - Beamtime requests can be submitted against active proposals
  - Safety Approval Forms are valid for 1 cycle (needed submitted at least 14 days before experiment.

HARD X-RAY PROGRAM

Scientific Target Area:

The scientific program is focused on **battery-, electro catalysis-, catalysis-, bio-, and materials growth** communities.

Techniques Offered:

1. Conventional XAFS/EXAFS in transmission and fluorescence
2. Inelastic techniques allowing higher sensitivity to chemical bonding
3. Powder diffraction in combination with XAFS measurements

Beamlines:

1. ISS: high flux wiggler beamline
2. TES: Bending magnet beamline
3. QAS: Bending magnet (3-pole) beamline
4. Partner beamlines

Sample preparation and pre-characterization area

Specialized support by collaboration with partners:

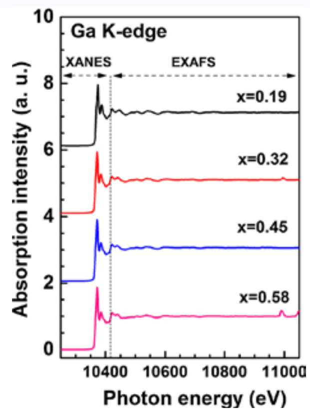
1. Case Western X-ray Consortium
2. Synchrotron Catalysis Consortium
3. Battery Consortium
4. In-house science program

Hard X-ray Spectroscopy: A Perfect Tool to Study Structure and Chemistry

Near Edge Spectroscopy

- Valence state
- Symmetry of absorber
- Electron density

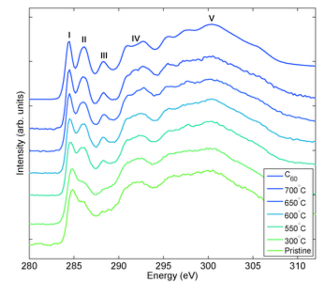
EXAFS



- Distance between neighbors
- Coordination number
- Somewhat kind of neighbor
- Somewhat particle size

J Mater Sci: Mater Electron (2014) 25:4800–4805

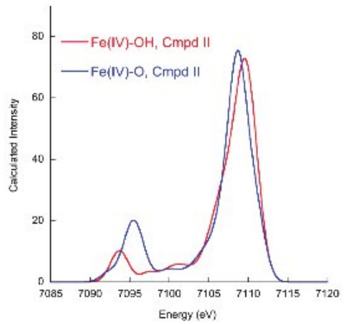
Energy Loss Spectroscopy



- Low Z-material at high energies
- High concentration
- Very similar to NEXAFS/EXAFS

Phys. Chem. Chem. Phys., 2016, 18, 5366-5371

Valence Band Emission Spectroscopy

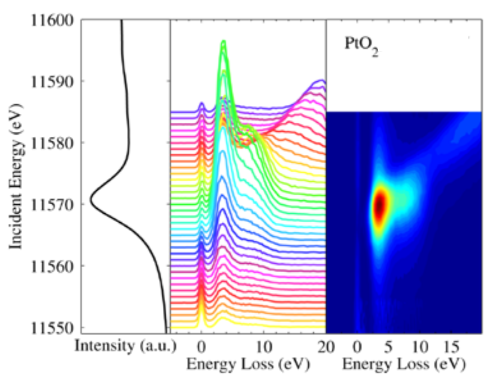


- Chemical compound
- Needs high concentration

Similar to XPS

J. AM. CHEM. SOC. 2010, *132*, 9715–9727

Resonant Inelastic X-ray Scattering

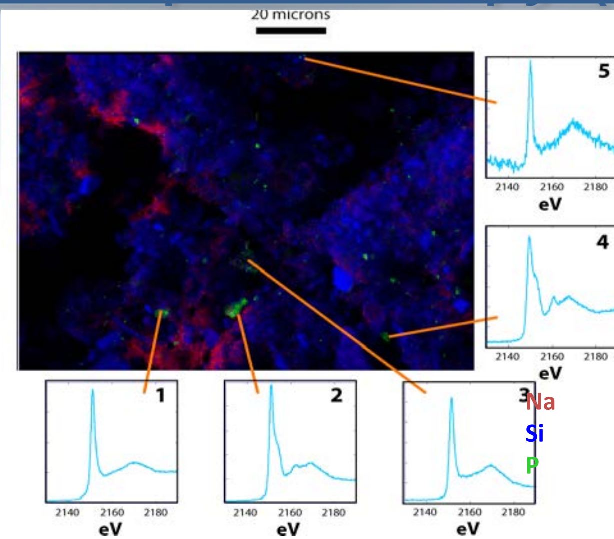


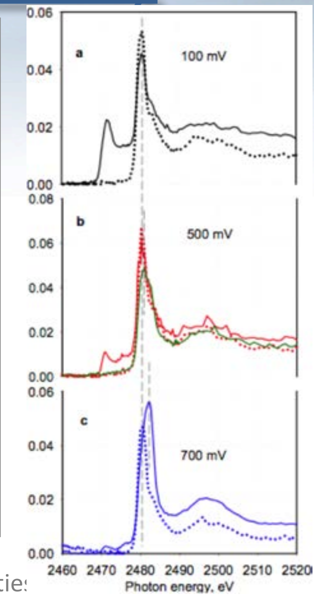
- Valence State
- Quantitative description of oxidation/reduction
- High sensitivity to small changes (capability to detect minority of atoms)

Tender-Energy X-ray Absorption Spectroscopy (TES)

TES at NSLS-II

- Will enable **spatially-resolved** and ***in-situ*** studies of speciation and local structure by x-ray absorption spectroscopy in a *non-vacuum environment*
- Chemical sensitivity to **key lighter elements** Mg through Ti, and advantageous heavier-element L and M edges
- Optimized for the **NSLS-II dipole bend** source -- high brightness over a tunable spatial resolution and energy scanning across 1.2-8 keV will be world-class





Example applications: Above: natural systems, e.g. P in sediments, exhibit species and distribution heterogeneities the submicron to mm scale. Diaz et al., *Science*, 320, (2008). At right, combined *in-situ* XAS and electrochemistry examines S speciation during poisoning of fuel-cell catalyst (Baturina et al., unpublished). TES will enable fast-scanning high-quality EXAFS and XANES at tunable spatial resolution to better address these and other real systems.

Examples of Science Areas & Impact

- **Catalysis**: Materials (zeolites, thin films, nanomaterials), reaction mechanisms and intermediate species, poisoning
- **Energy Materials**: Photovoltaic, fuel cell, battery and superconducting (nano)materials
- **Environmental/Earth Science**: Biogeochemical and redox processes, contaminant behavior and remediation
- **Climate**: Terrestrial and marine C cycling, carbonate (bio)mineralization, geologic record of climate change
- **Sustainability**: Nutrient (P, S, K, Ca, Mg, Fe) cycling, transport and bioavailability, biofuel/biomass productivity

Beamline Capabilities

Techniques: x-ray fluorescence and spectroscopic imaging, high-performance and *in-situ* EXAFS

Source: dipole bend magnet

Energy Range: 1.2 to 8 keV (optimized for 1.2-5 keV)

Spatial Resolution, Flux: 1x1 mm to 1x1 μm; up to 3×10^{12} ph/sec flux

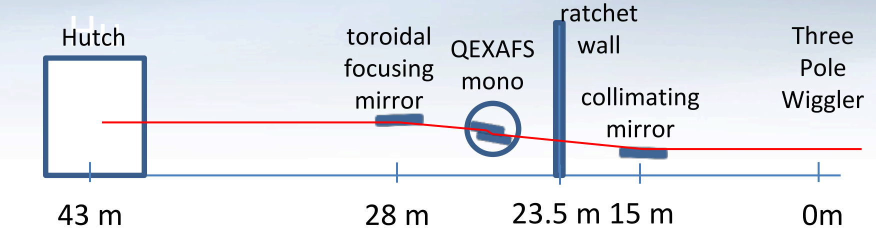
Quick X-ray Absorption and Scattering (QAS)

QAS at NSLS-II

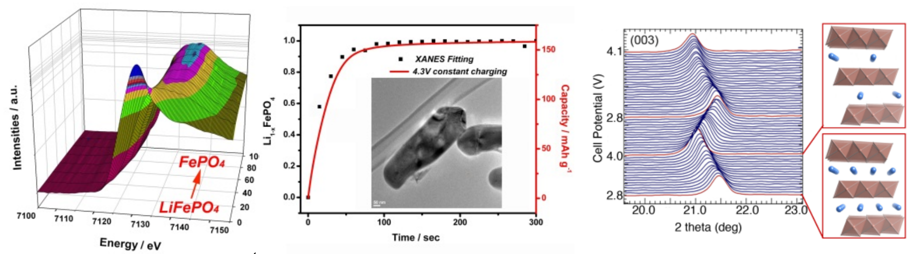
- Will enable in-situ and operando studies of complex nanoscale systems undergoing real-time transformations
- Will enable synchronous measurements of nanocatalysts by complementary techniques including IR, XAS, XRD, DAFS and mass spectrometry
- Will probe complex interactions in nanoscale systems at the time scale from tens of ms to hours and length scale from Å to µm

The Battery-Hub and QAS

- Will provide optimized in-operando sample environments and infrastructure for battery research community
- Will provide dedicated support effort for battery community
- Will allow to optimize detection and optics components to reduce detection limit, increase time resolution and to increase throughput
- Will provide hub-function for the access of the battery community



Beamline layout of QAS; the collimation mirror close to the source in combination with the fast scanning monochromator provides high flux and fast scanning capabilities



$LiFePO_4 \leftrightarrows Li^+ + e^- + FePO_4$

In situ monitoring of fast Li extraction kinetics of Li-ion battery material ($LiFePO_4$); the combination of in-operando quick EXAFS and X-ray diffraction provides reveals chemical and structural changes on all important length scales.

Beamline Capabilities

TECHNIQUES: XAFS and XRD

SOURCE: three-pole wiggler

ENERGY RANGE: 4.5 – 27 keV

TIME RESOLUTION: up to 10ms

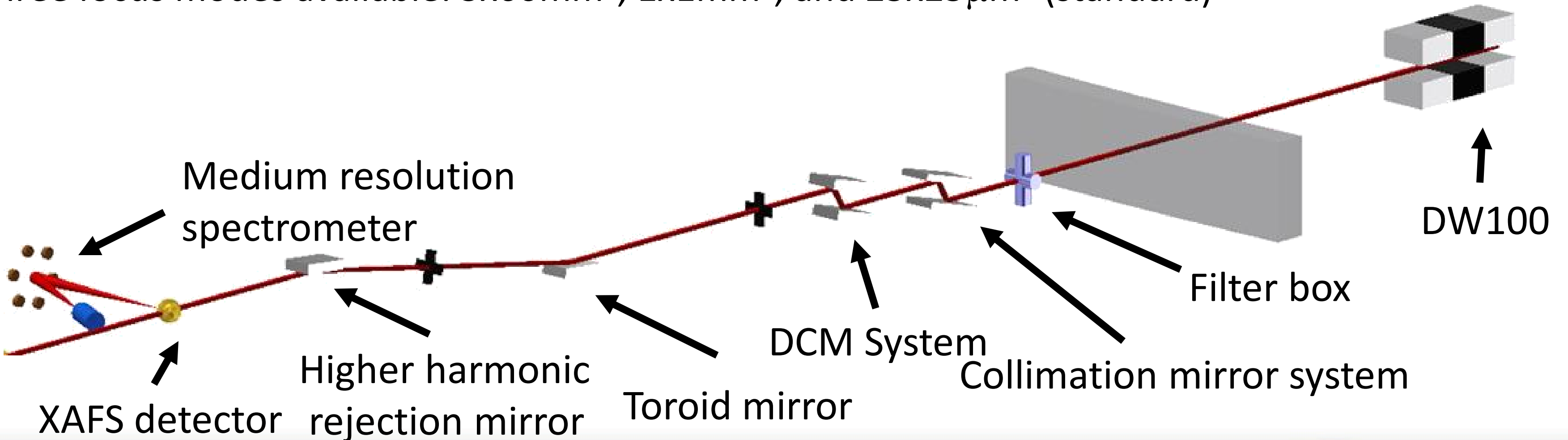
SAMPLE ENVIRONMENT: defined gas environment; 10K-1300K

EXPECTED START OF OPERATIONS: 2017

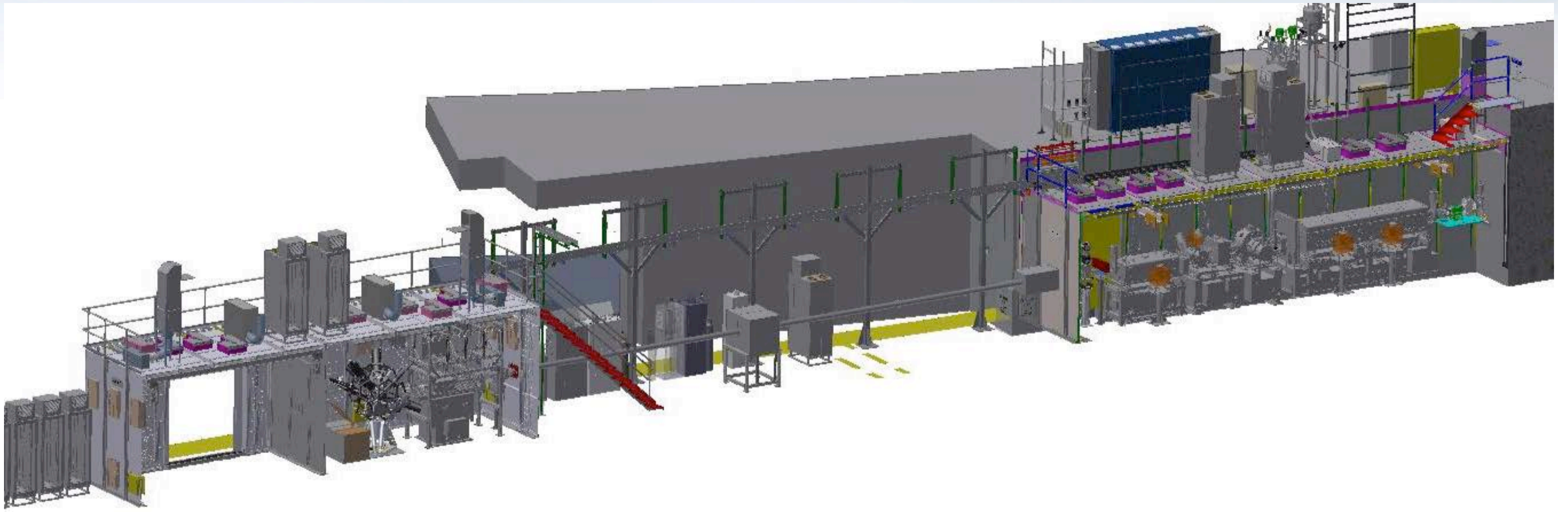
ISS Beamline Scope

- Hard X-ray Spectroscopy for chemical and structural analysis of functional materials
  - High flux fast scanning spectroscopy: *high throughput for operando experiments*
  - X-ray Absorption Spectroscopy on highly diluted systems: *complex multiphase materials*
  - Medium resolution emission spectroscopy: *increased chemical sensitivity*
  - Operando and in-situ conditions: *frontier chemical specificity under working conditions*

- Damping wiggler beamline designed for high flux, fast scanning capability, and large energy range:
  - Flux of up to 10^{14} Photons/s in a wide energy range
  - Energy range: 4.5KeV-36KeV
  - Scanning rate up to 20Hz with low and medium energy resolution
  - Three focus modes available: 3x60mm^2, 1x1mm^2, and 25x25μm^2 (standard)



ISS: A WORLD CLASS BEAMLINE



The ISS-Key Features: Photon delivery system

1. High flux beamline (~10^{14} photon/s) with wide energy range (4.5KeV-36KeV)
2. Variable energy resolution: $1.6x10^{-4}$, $5.6x10^{-5}$, $8x10^{-6}$ (limited energy range) Si(111), Si(111)/Si(220) (four bounce), Si(333)/Si(220) (four bounce)
3. Excellent high harmonic rejection (better than 10^{-4})
4. Capability to switch energy ranges quickly (3 overlapping energy configurations)
5. Fast scanning capabilities up to 20Hz (using bi-directional data collection)
6. Continuous scanning capability with arbitrary speed profile (constant in k-scans)
7. Variable focus size: $3x60mm^2$, $1x1mm^2$, and $25x25\mu m^2$ (standard)
8. Widow-less or window mode allows simplified and safe user operation

ISS: A WORLD CLASS BEAMLINE

The ISS-Key Features: Endstation capabilities

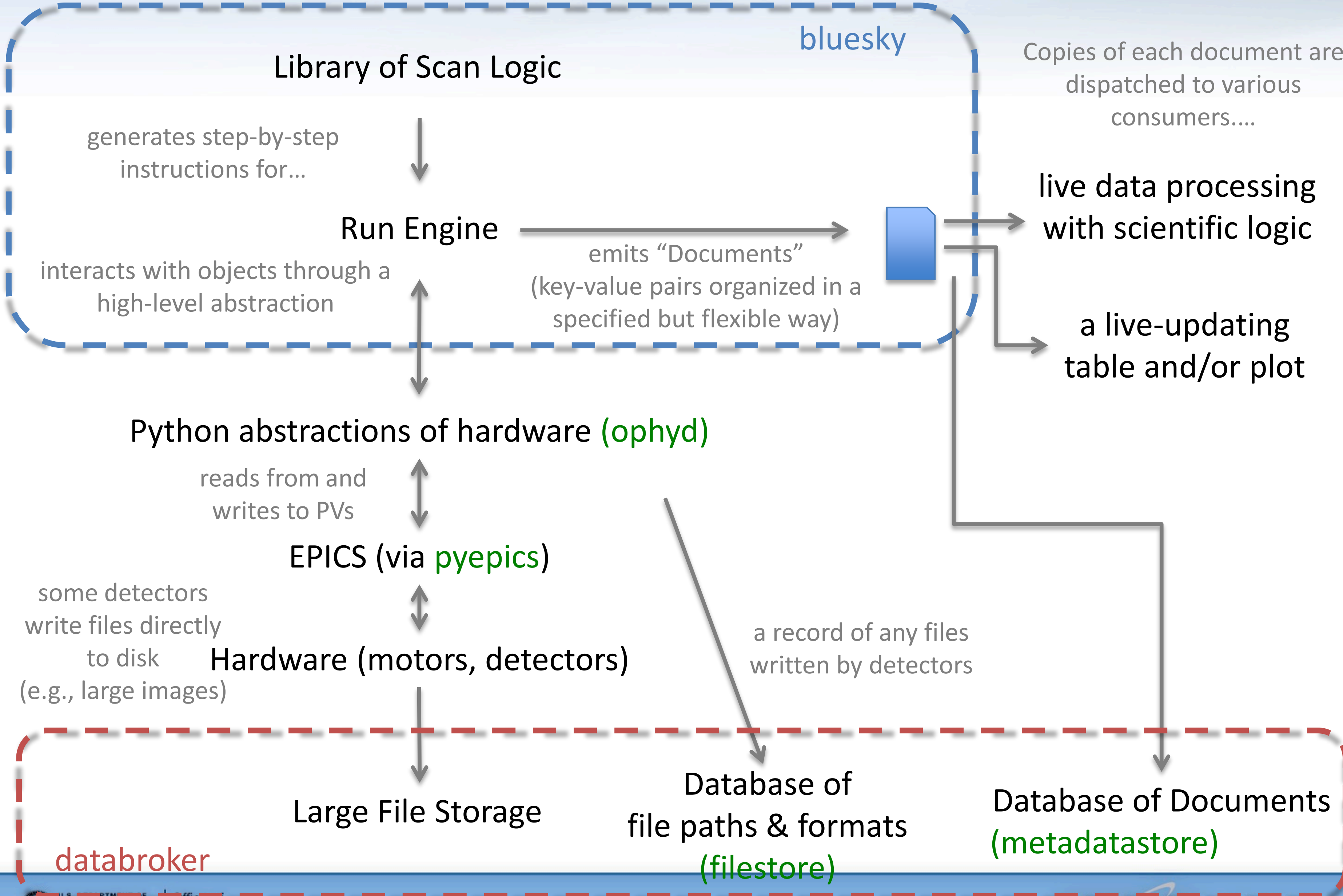
1. High flexibility for user: Optimized setup or “open field”
2. Large solid angle detection platform with integrated sample environment
3. Sample positioning system allows wide range of spectroscopic techniques (including grazing incidence techniques and “liquid scattering” geometry)
4. Fully integrated gas handling system with
   - Gas and liquid sources (up to four) available
   - Inert, flammable, and toxic gasses; highly toxic gasses can be included at any time
   - Fast gas switch capability (less than 1 sec)
   - System is fully PLC/computer controlled
   - Professional safety standards
5. Novel sample handling concept
   - Sample robot allows high throughput for operand and in-situ experiments (8 electrical 3 gas connections)
   - Sample handling is tuned for remote/mail-in access (barcode system)
   - Fully enclosed sample environment (inert gas or vacuum) from sample preparation to measurement
   - Double sample containment allows a wide range of samples
   - Individual sample unit is modular and allows a wide range of experiments (heterogeneous catalysis, liquid samples/stop-flow, batteries, fuel cells, growth reactors [ALD, MOVPE, CVD]…)
   - system allows “intelligent” samples (optional microprocessor)

Data acquisition scheme

- **Goal: distributed and flexible DAQ system**
  - –Reduce overhead New strategy is required to avoid frequent triggering to reduce overhead
  - –Match scanning speed / requirements for quick experiments (beam damage)
  - –Allow for addition of new devices/detectors

- **Approach:**
  - –Asynchronous data collection
  - –Encoder data stream is collected and time-stamped
  - –Detector signals are time-stamped and time correlated with the motor position to retrive a “conventional scan
  - –A time-stamped trigger is send to the detector controller to begin data collection

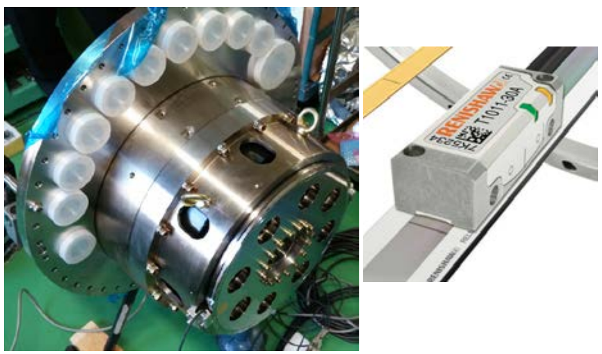
NSLS-II data collection scheme



DAQ scheme

- Fly scan
  - Motion trajectory is loaded into a motion controller (DeltaTau Power PMAC)
  - Acquisition starts (on EPICS time)
  - Controller is commanded to begin trajectory execution

GPS clock → DAQ box



DCM encoder → DAQ box → DAQ box

Ion chamber → DAQ box

Absolute time Motor position

```
2015-02-19 16:38:47.719599368 55684 402434
2015-02-19 16:38:47.719699312 55682 402435
2015-02-19 16:38:47.719799256 55680 402436
2015-02-19 16:38:47.719899200 55678 402437
2015-02-19 16:38:47.719999152 55676 402438
2015-02-19 16:38:47.720099096 55673 402439
2015-02-19 16:38:47.720298984 55670 402440
2015-02-19 16:38:47.720498872 55667 402441
2015-02-19 16:38:47.720598816 55665 402442
2015-02-19 16:38:47.720798704 55662 402443
2015-02-19 16:38:47.720998600 55659 402444
2015-02-19 16:38:47.721298432 55655 402445
2015-02-19 16:38:47.721698208 55650 402446
2015-02-19 16:38:47.721898096 55647 402447
2015-02-19 16:38:47.722197936 55643 402448
2015-02-19 16:38:47.722397824 55640 402449
2015-02-19 16:38:47.722597712 55637 402450
2015-02-19 16:38:47.722697656 55635 402451
2015-02-19 16:38:47.722797600 55633 402452
```

Absolute time IC current


```
2015-02-19 16:38:47.719599368 55684 402434
2015-02-19 16:38:47.719699312 55682 402435
2015-02-19 16:38:47.719799256 55680 402436
2015-02-19 16:38:47.719899200 55678 402437
2015-02-19 16:38:47.719999152 55676 402438
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2015-02-19 16:38:47.722597712 55637 402450
2015-02-19 16:38:47.722697656 55635 402451
2015-02-19 16:38:47.722797600 55633 402452
```
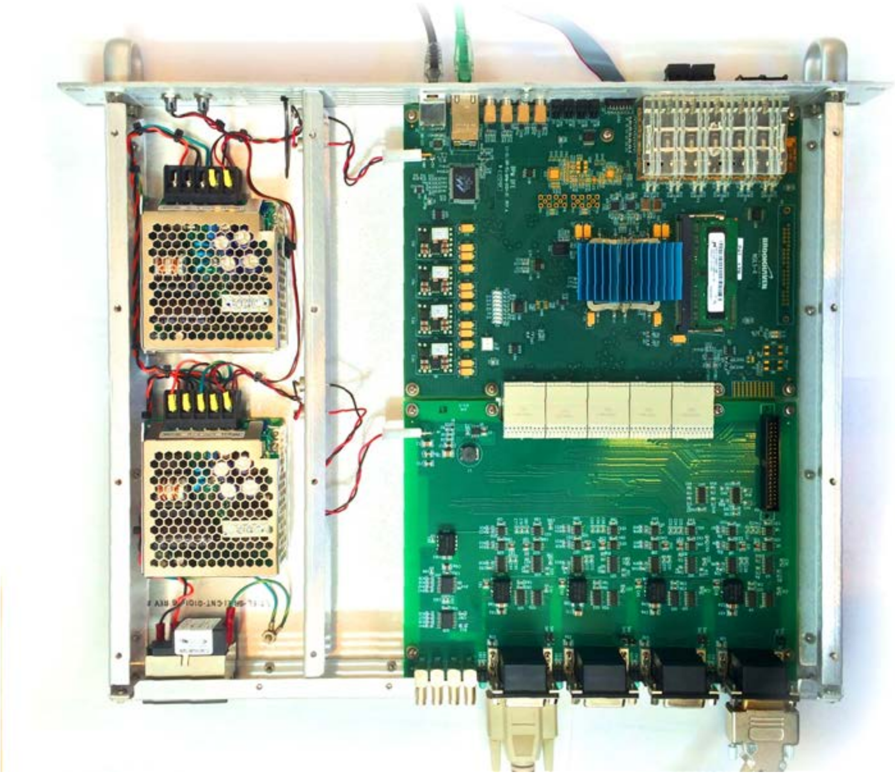

Beamline Encoder Interface Box

- Platform shared with accelerator BPMs and Cell Controllers;
- 2U chassis;
- Handles 4 incremental quadrature encoders with digital RS-422A interface and output frequency up to 10 MHz;
- XILINX Virtex-6 FPGA processes signals from an encoder, associates it with GPS timestamp latched through fiber connection;
- Data stream is buffered and sent to the server using TCP/IP stack, with server side running EPICS IOC;
- Filtering and compression techniques applied;
- Diagnostics for missing steps/packets;
- Additional GPIO for custom triggering.

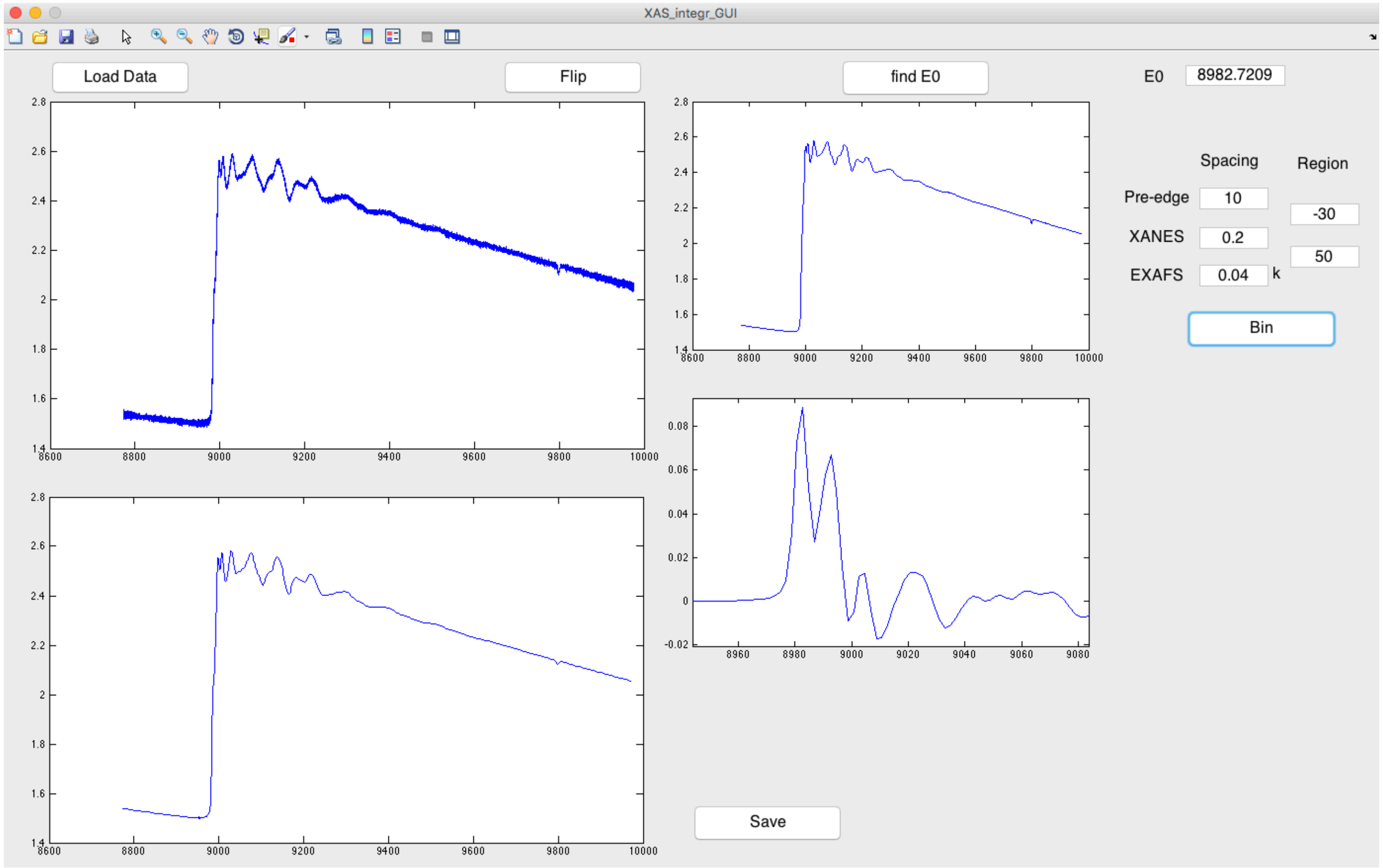


Beamline Data Acquisition Box

- Similar mechanical design, but 1U chassis;
- Up to 8 analog inputs can be populated:
  - 16-bit, 1MS/s, ±10V;
  - Buffered input;
  - Adjustable sample rate with optional averaging.
- Same logic patterns and EPICS driver;
- Detector signals timestamped and sent to the server for post-analysis;
- 8 analog outputs (16-bit, ±10V, 10kHz) 16 configurable DIO (LVTTL, up to 10MHz) for PWM, triggering, event counting.

EXAFS data folding and binning

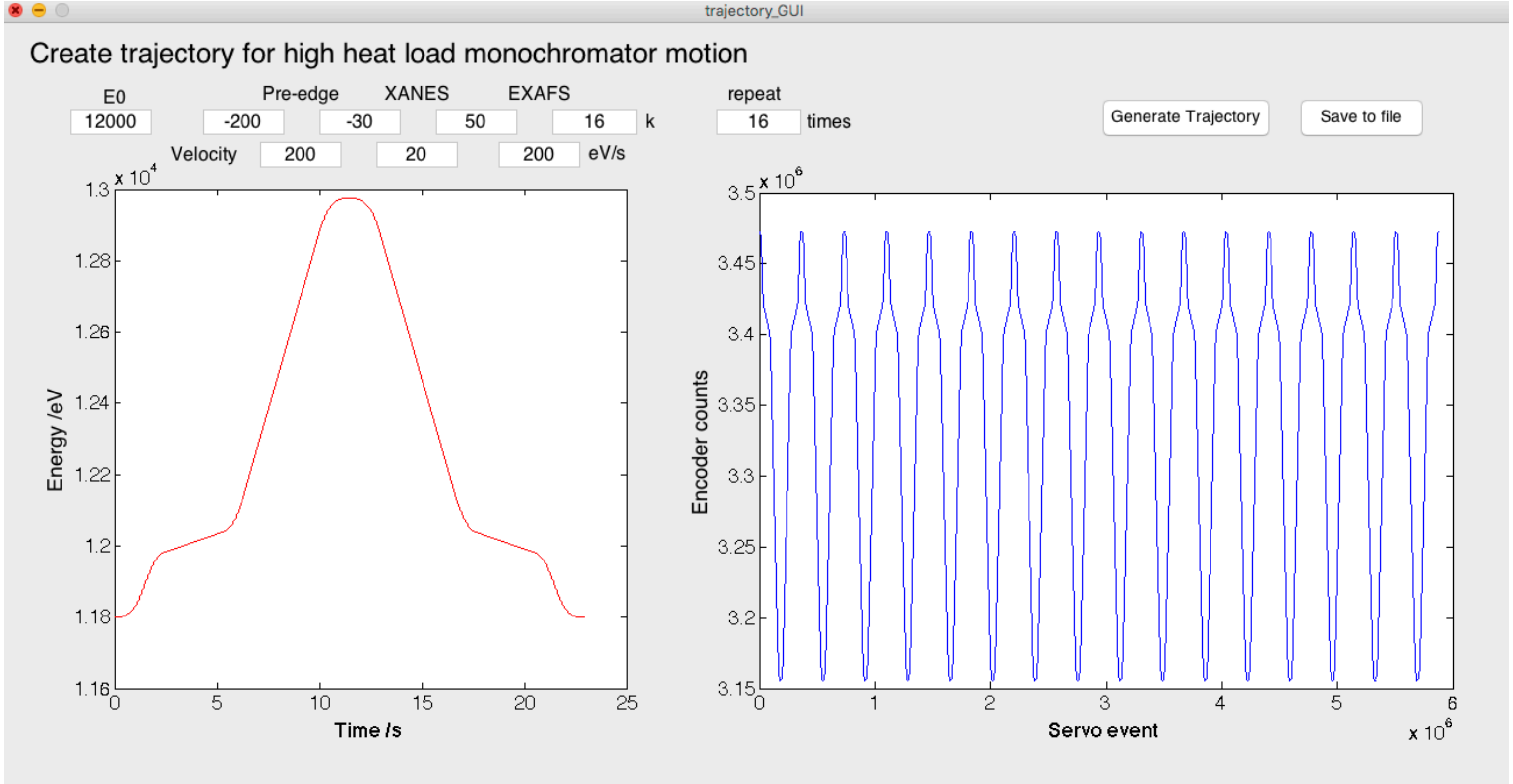
- Data is collected at points equidistant in time
- It can be binned based on the required density of information



Monochromator trajectory motion

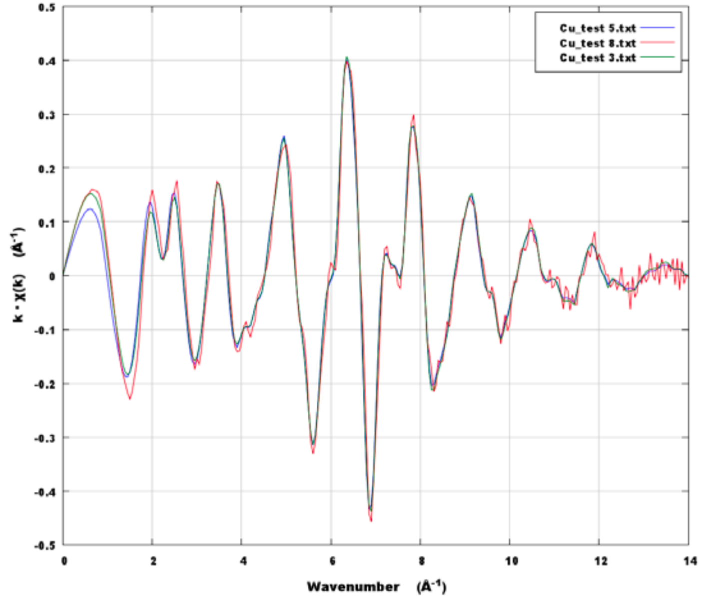
- Power PMAC controller can be programmed to execute a continuous motion trajectory
  - Refresh rates up to tens of kHz (currently 16kHz is used)

- Motion profile for a trajectory XANES+EXAFS scan uses speed instead of a “conventional” step size
  - Speed transitions are smoothed

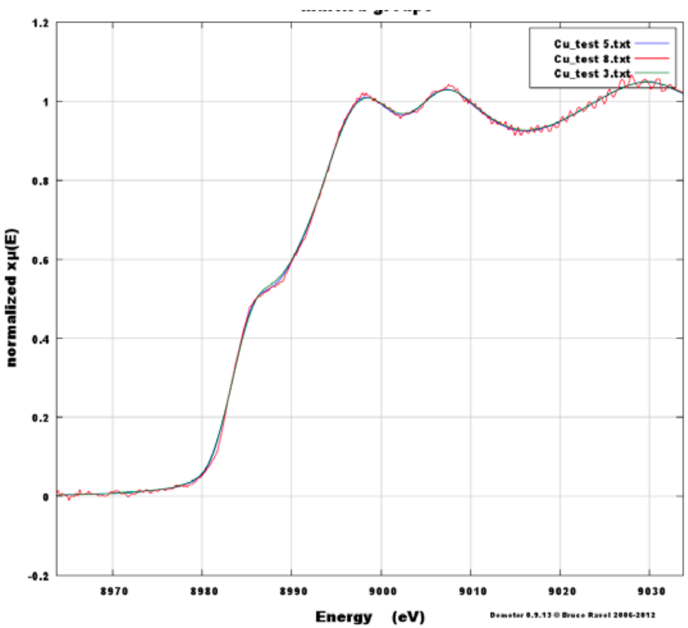


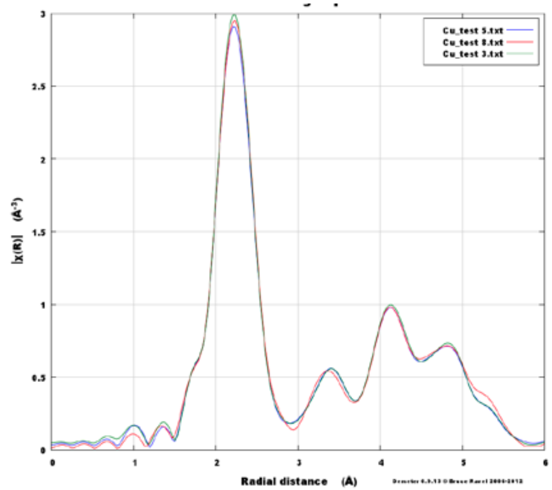
First results: speed test

- Copper foil spectra at various monochromator speeds

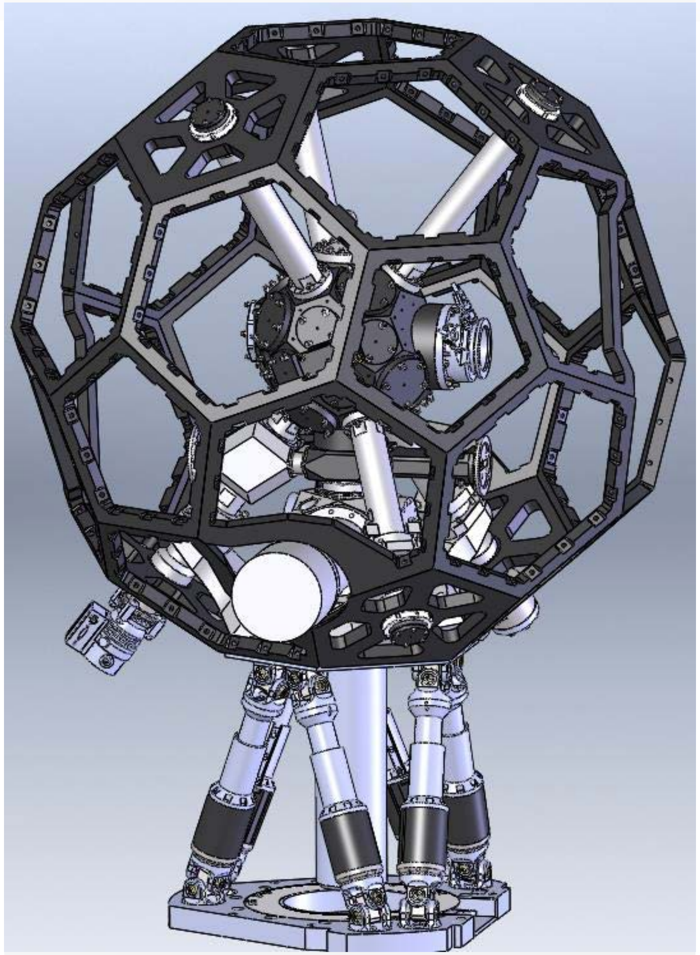


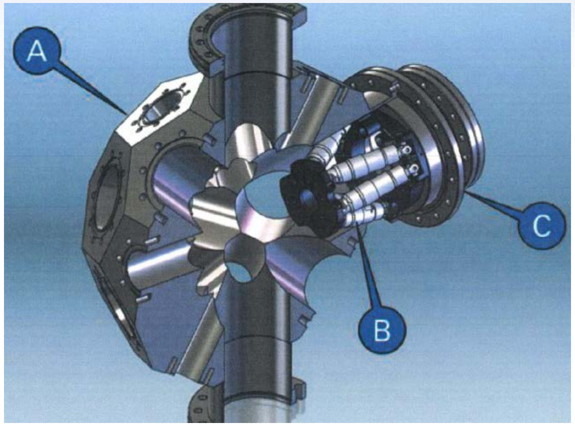
200 s
20 s
2 s

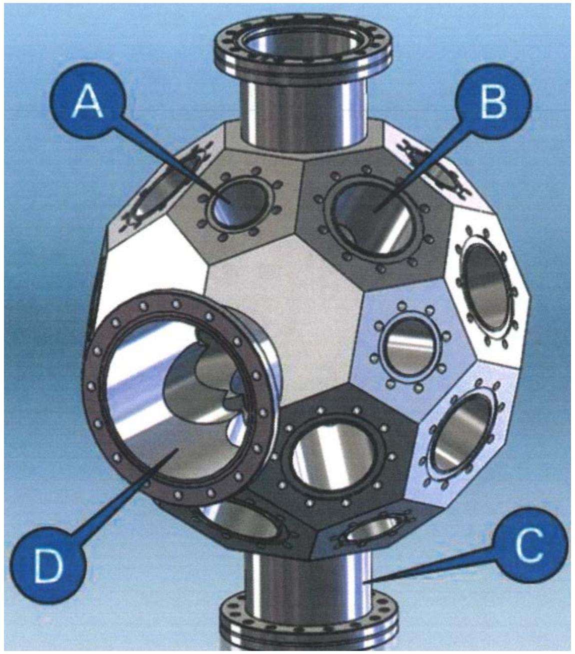




ISS Sample Chamber and Detection Scheme



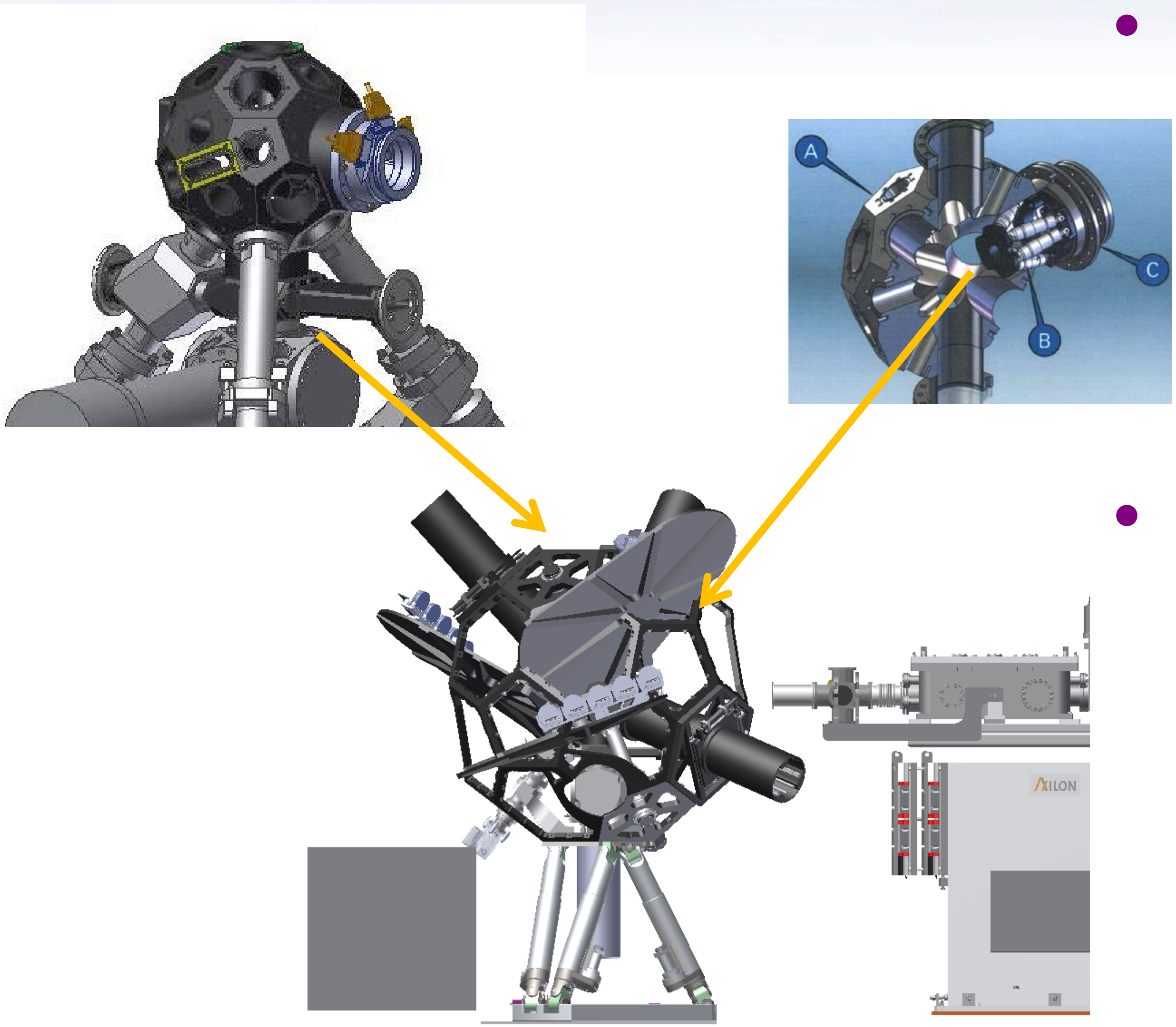




Chamber with large flexibility:

- Large number of ports available (32 facets)
  - 2 DN 100CF
  - 14 (+2) DN 75CF
  - 8 (+3) DN 50CF
- At least 20 spectrometer ports available
- Additional ports for optical characterization available
- Each port can host collection lenses and hinge system (collimation or focusing)
- Each port can be used without collection lens [2.5cm (or larger) diameter opening: 0.7% (total:30%) solid angle]

ISS: Double Hexapod Concept



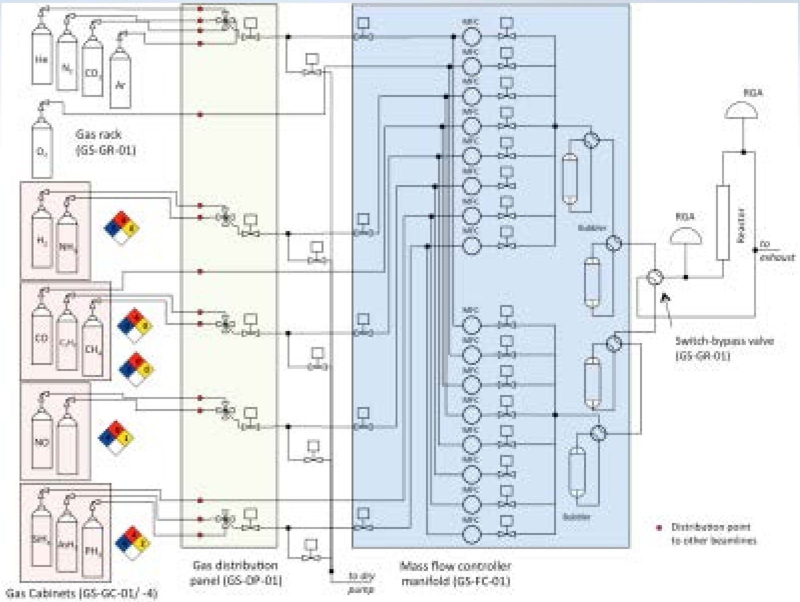
Alignment Concept

- Sample hexapod allows to align chamber:
  - Vertical alignment to allow all focusing/energy modes and through mode for beam access in B2 hutch
  - Horizontal alignment (+-15mm)
  - Theta and chi (+-7.5 degree)
- Focusing-lens hexapod is "slaved" to sample hexapod and higher harmonic rejection mirror system
  - Allowing "liquid spectrometer" geometry
  - Fast change of modes with predefined positions

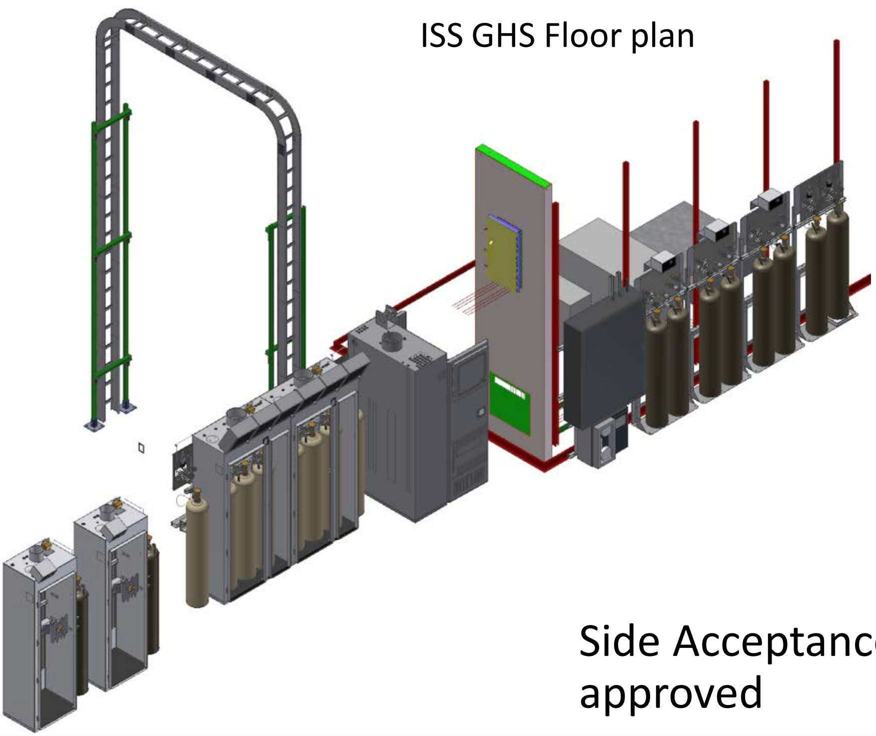
The ISS Gas Handling System

Gas handling system (GHS) will be fully integrated into the beamline controls and data acquisition systems

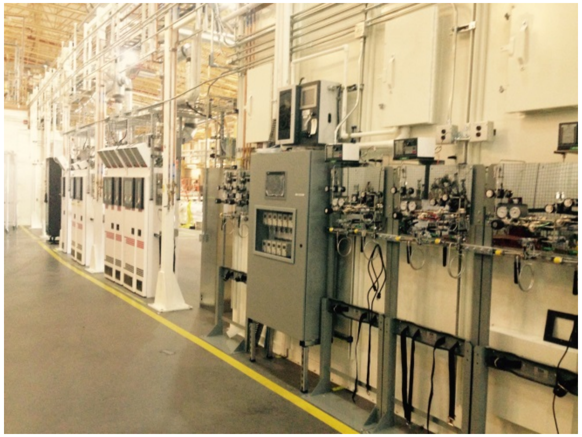
A wide range of gaseous and liquid materials, relevant for catalysis and material science will be available for the experiments



Conceptual piping and instrumentation diagram layout

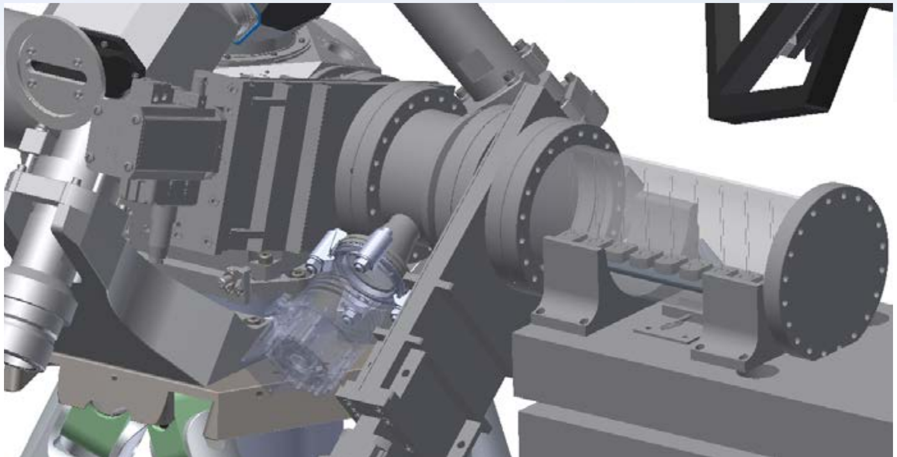


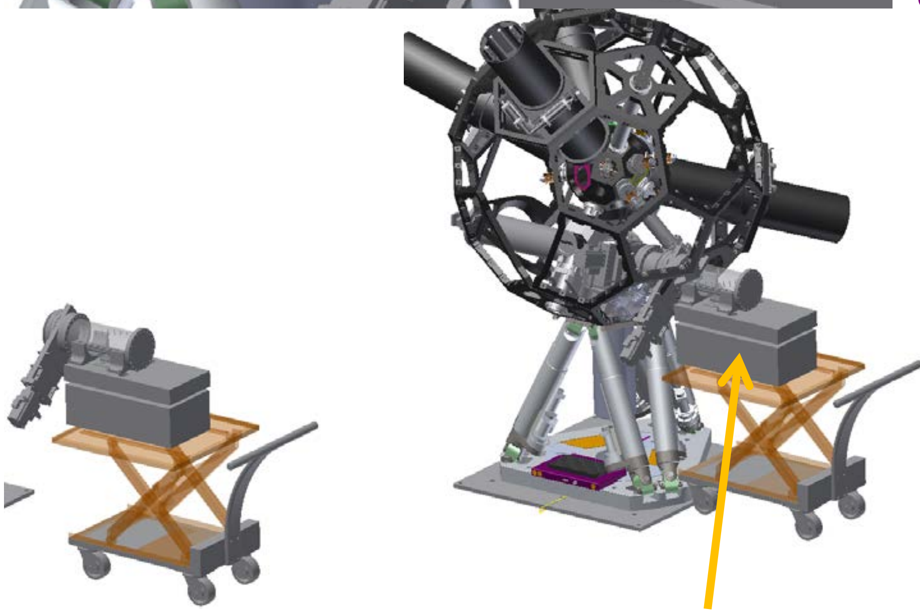
ISS GHS Floor plan



Side Acceptance Test (SAT) approved

A Novel Sample Handling System



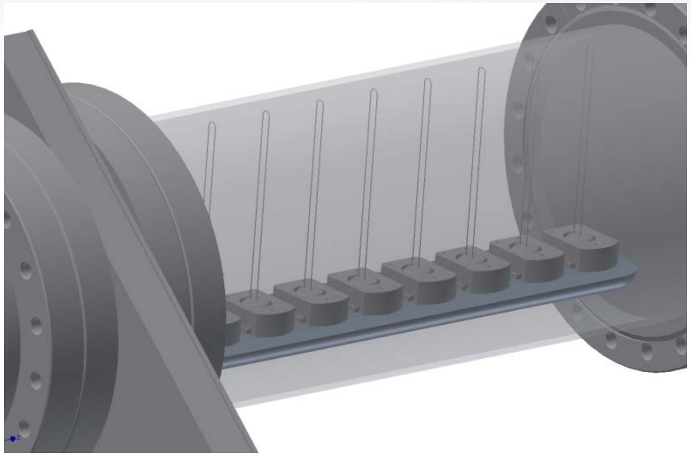


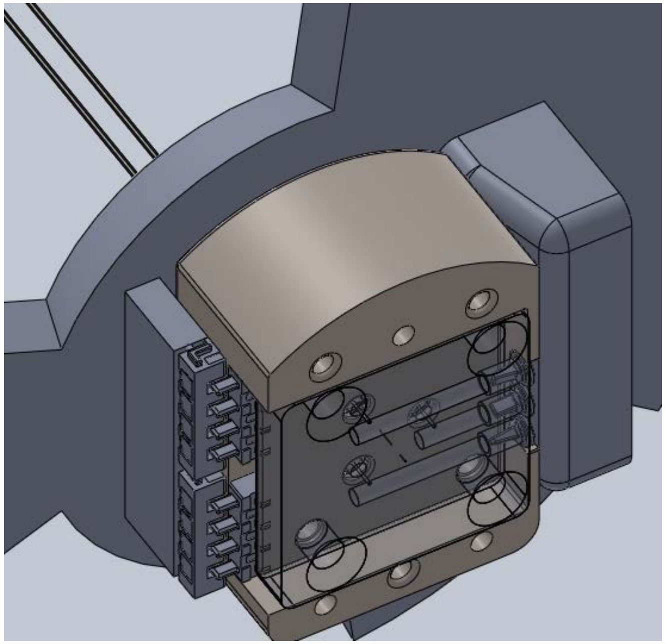
Transport cart

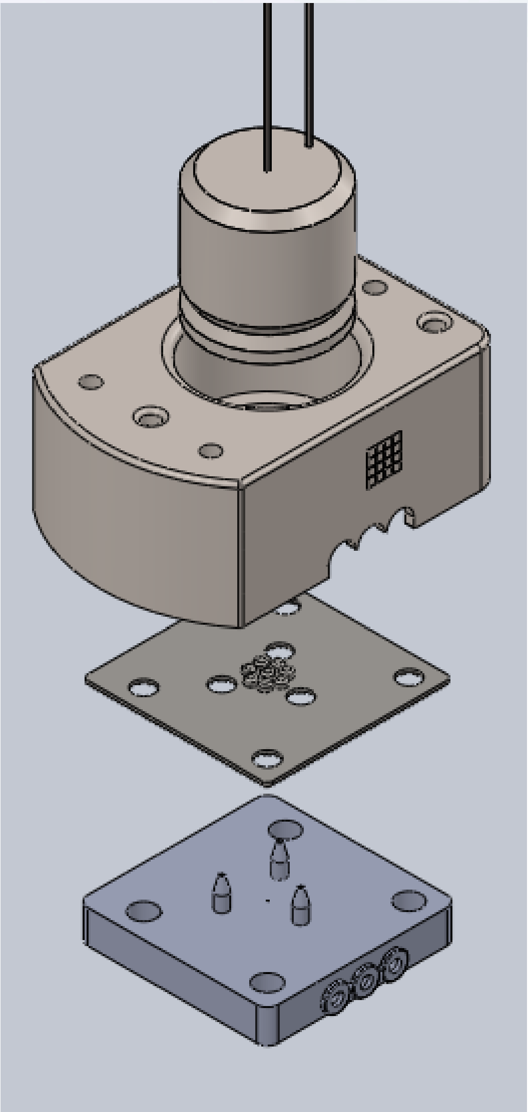
Sample transport and mounting

- Sample transfer system with
  - Vacuum/inert gas compatible transfer box containing 10 samples
  - Containment can be shipped between facilities
  - Double containment concept
- Automatic sample transfer
  - Samples are not exposed to air
  - Allows mail-in/remote access and high throughput
  - System includes barcodes and readers for sample and sample holder identification
  - One modified glove box will be available
  - Fully automatic load-lock system
  - In future:
    - Sample can be processed in sample transfer system
    - Two additional glove boxes are available and can be adapted to the sample transfer concept

ISS: The Modular Sample Holder



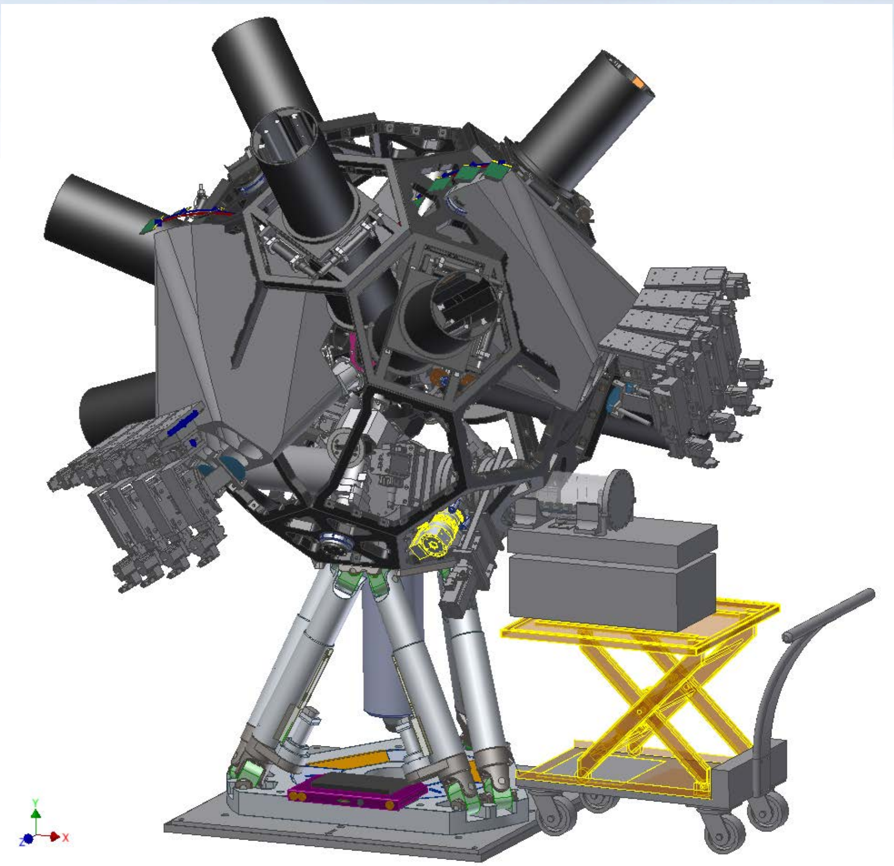


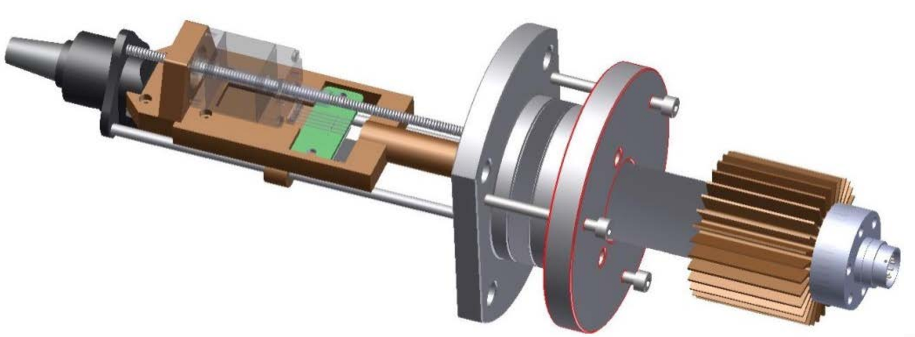


Modular sample holder

- Sample holder base
  - 8 electrical contacts
  - 3 gas ports
  - Connects ports at sample position
  - Includes bar-code for automatic registration
  - Modular design allows future integration of “intelligence”
- Sample module
  - Can be easily replaced
  - Allows large variety of experiments
  - Catalysis reactor is part of the scope
  - IR heating is provided (150W)

ISS: Detection capability

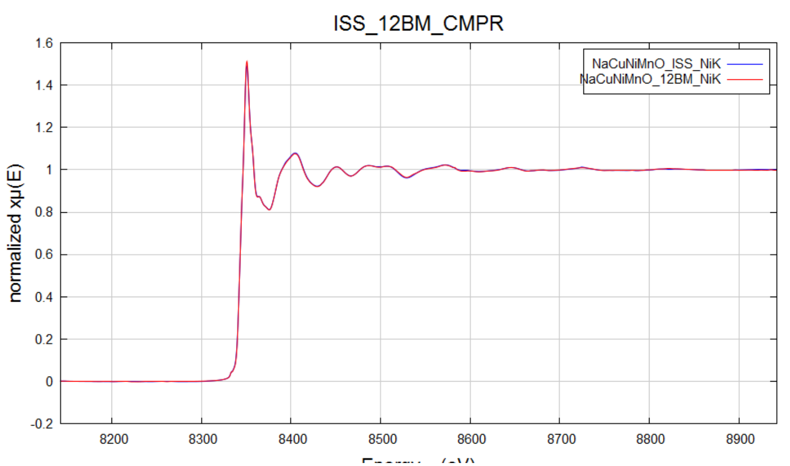


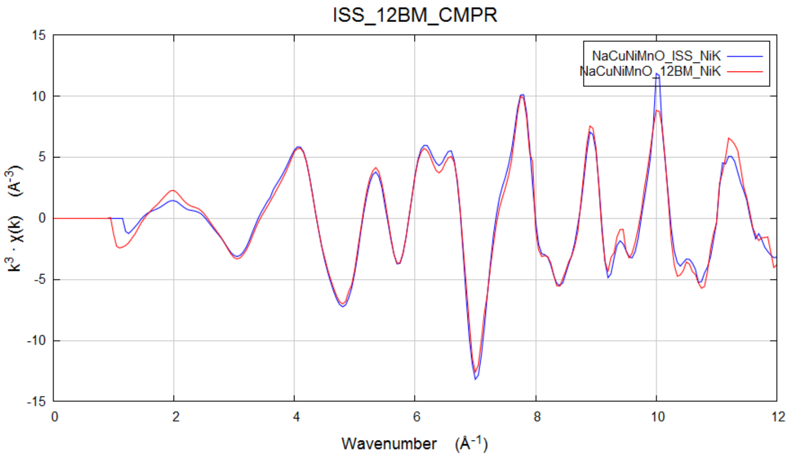


The Detection units

- Von Hamos (2 systems)
  - Wide energy range system (Si(111))
  - Angular stabilization system allows energy change without realignment
  - Double Mythen detector system allows large solid angle
  - Collection lens allows confocal detection
  - Spectrometer can be scanned along beam axis
- SDD system (20)
  - 50mm^2 SDD for high resolution and count rate
  - Digital processing
  - Adjustable distance from sample (minimum 4cm)
  - Solar slit included
  - In future: collection lens can be implemented
- Design of 4 element SBA is included

A Few Data: Comparison between BM12 (APS) and ISS





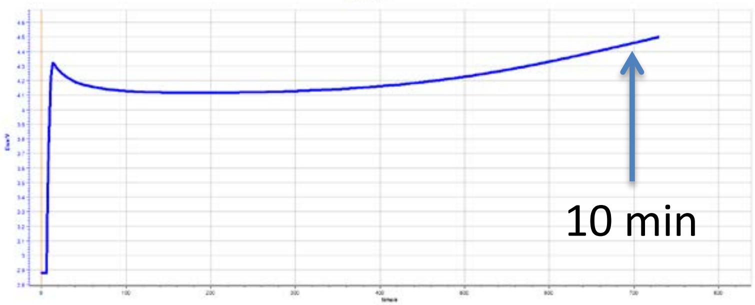
First measurements from battery materials (Xiao-Qing Yang group)

- Measurements:
  - Transmission measurement of cathode material.
  - Comparison between established bending magnet beamline BM12 from APS and ISS
    - APS measurement 30min-45min
    - ISS measurement <2min
  - ISS detection system is not optimized (10s scans are feasible if necessary)

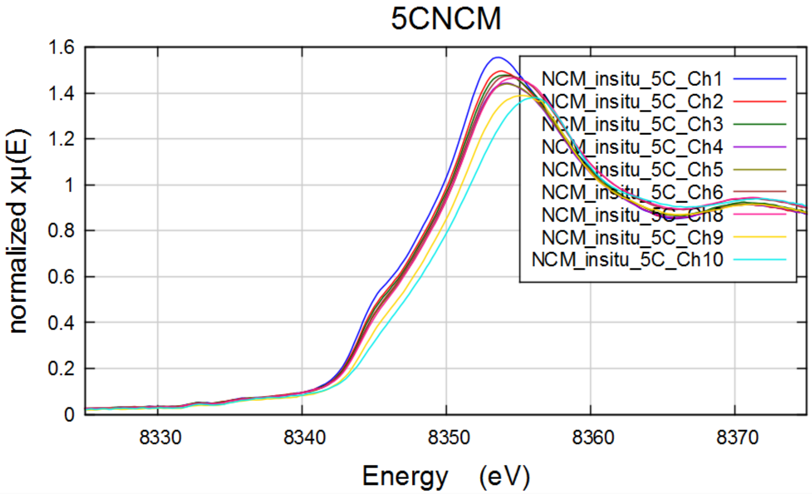
A Few Data: Cathode Oxidation State during Charging Cycle

Fast charging of a battery

Electrochemical profile:



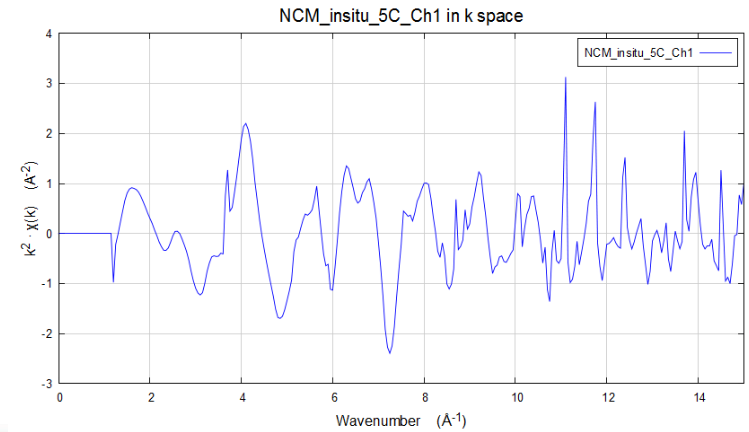
XANES data:



First operando measurements from battery materials (Xiao-Qing Yang group)

Measurements:

- Fast charging battery material (10min cycle).
- Data acquisition time and operando cycle matches well.
- After optimization, operando cycles of 1min will be feasible.
- Issues with glitches in exafs rang: importance of optimization.



Issues of Transmission Experiments:

$I_1 = I_0 x \exp^{(-\mu d)}$ Measurement: $Ln(I_0/I_1) = \mu d$

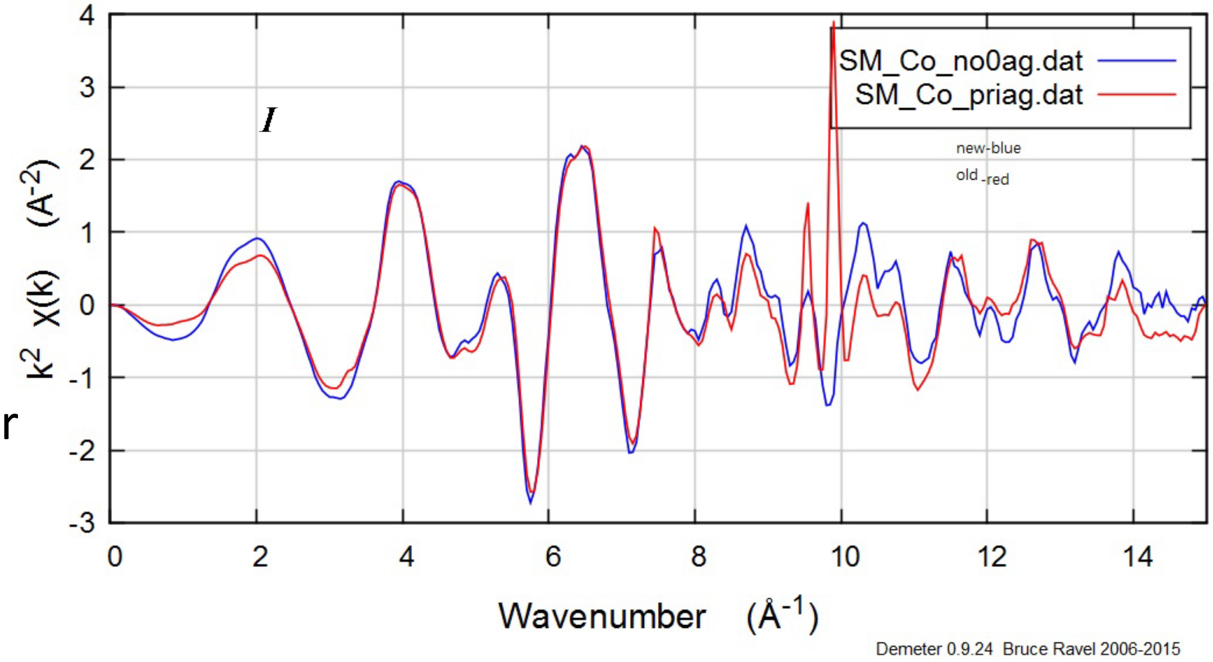
However measured signals are:

$$\mathit{I}_0 = I_0 + I_0^{Offset}$$

$$\mathit{I}_1 = I_1 + I_1^{Offset}$$

I_i^{Offset} may be:

- Offset current of amplifier
- Higher harmonics contribution in incoming beam
- Sample inhomogeneity



The Spectroscopy Program at NSLS-II

- Access and availability
  - 3 program areas are involved
    - Hard x-ray spectroscopy
    - Soft x-ray scattering & spectroscopy
    - Imaging and spectroscopy
  - Status
    - 5 beamlines will be operating in January 2017 in GU mode
    - 12 beamlines will be available within the next 18 month
  - Techniques
    - All standard techniques will be available within the next 18 month
    - In addition there are also inelastic techniques (energy loss, RIXS, HRXAFS, emission spectroscopy) available
    - Spatial resolution is ranging from 1mm to 10nm
- Targeted Science
  - In-situ and operando community
  - Focus on energy research, bio, and geo
  - Program is build to support new users (collaboration with consortia)