Minimizing Sample Damage in Hard X-ray Spectroscopy Experiments

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NSLS User-Meeting

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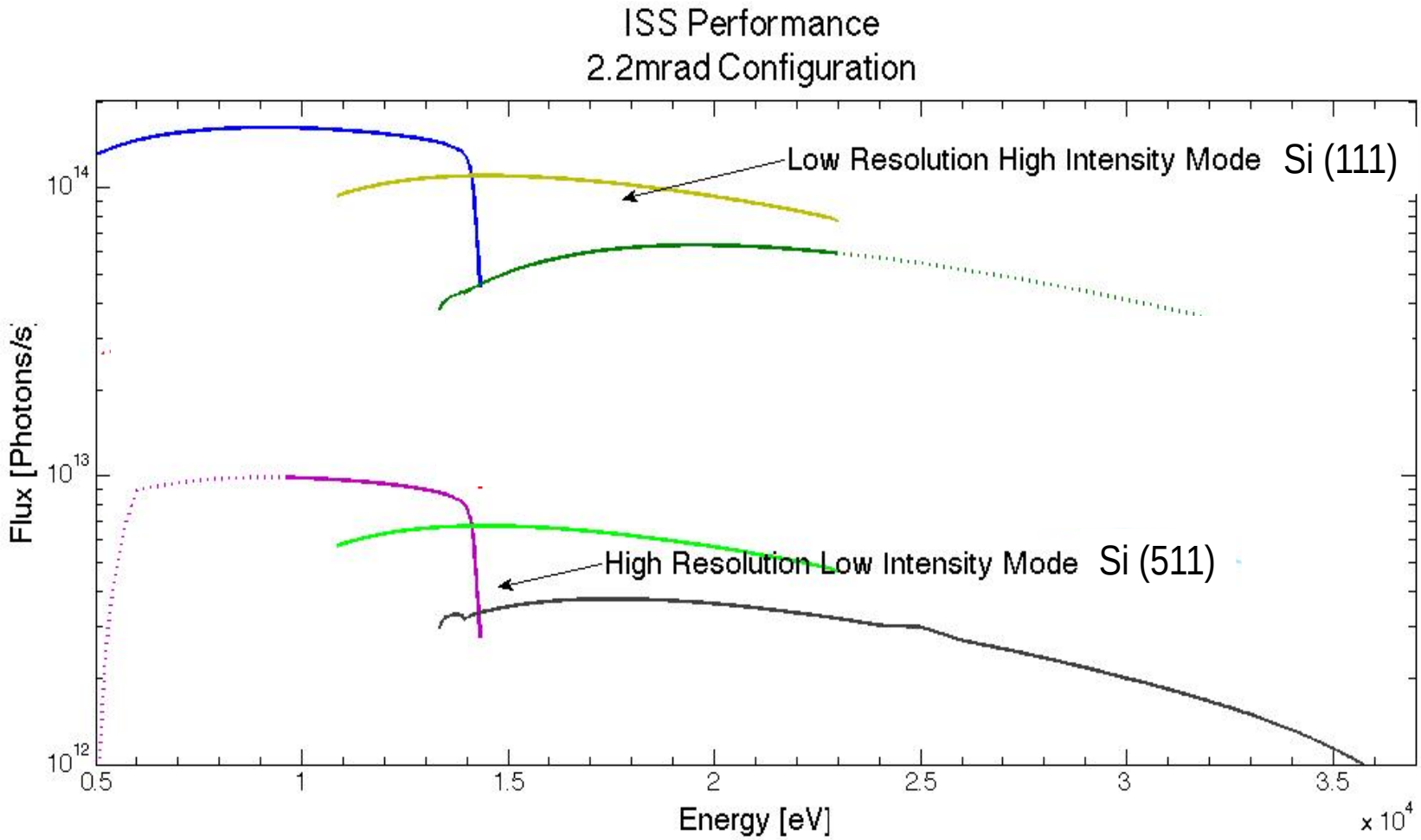
Outline

- New opportunities in hard x-ray spectroscopy
- Sample damage strategies
  - Optimized detection system
  - Optimized beam delivery system and data-acquisition
  - What data statistic is needed: Theory support
  - Optimized sample preparation and handling
- Conclusion

NEW BEAMLINE DESIGNS ALLOW HIGH FLUX BEAMLINES

Performance in full heat load mode:



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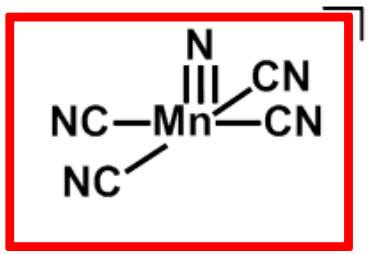
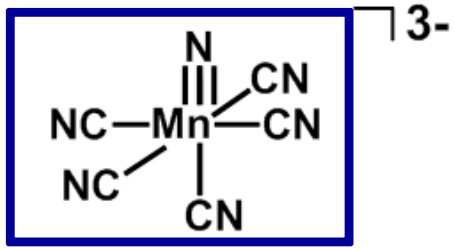
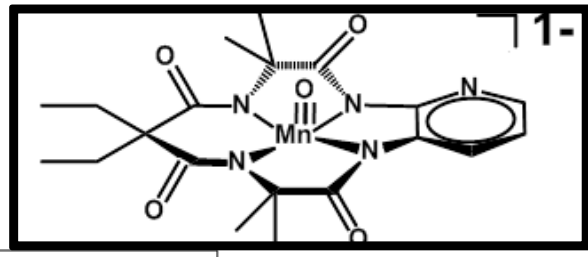
New Opportunities in Hard X-ray Spectroscopy Chemical Sensitivity Counts!

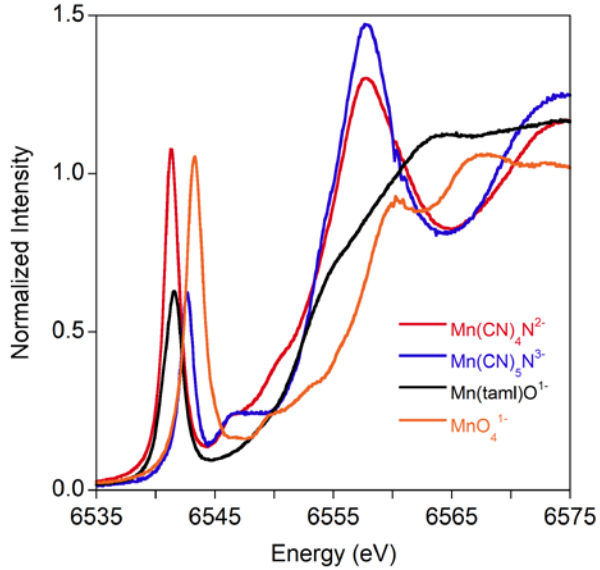
Four Mn compounds:

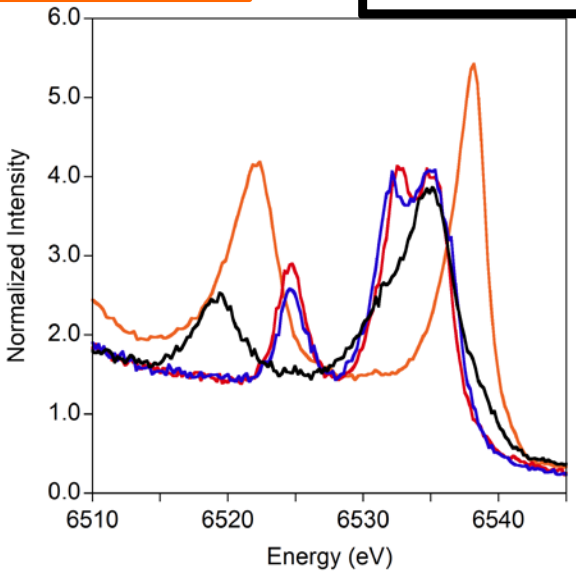






K_β-"RIXS"

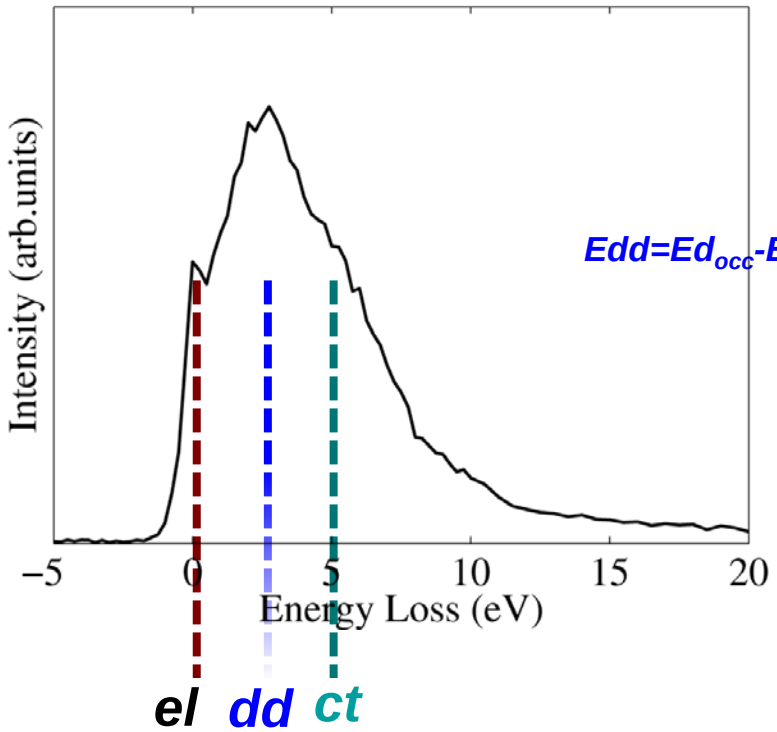


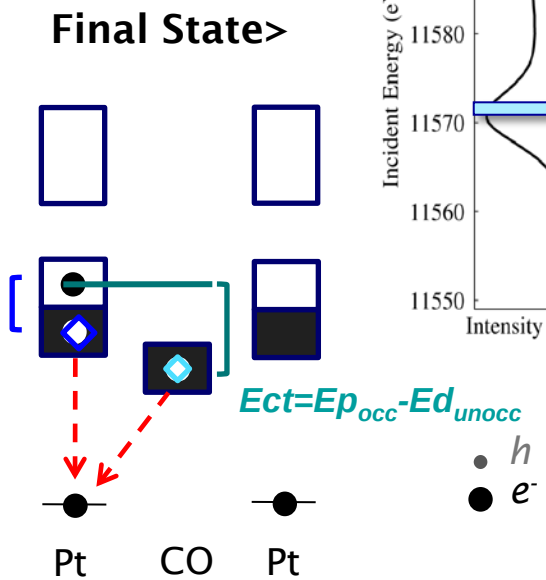


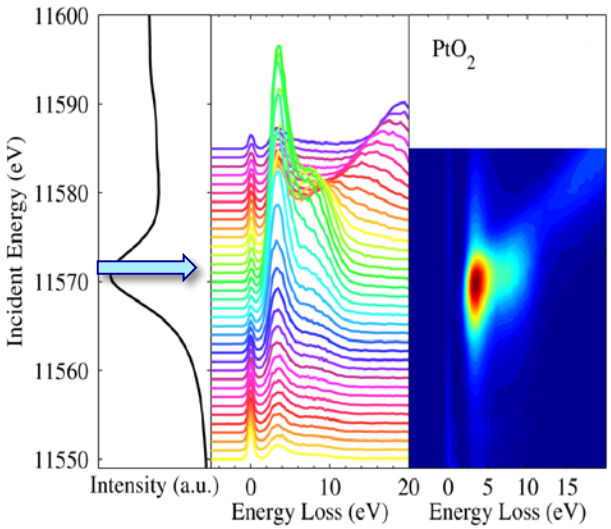
Valence band emission

1. Conventional EXAFS cannot distinguish between the 4 structures
2. Kβ-RIXS and valence band emission can answer the Mn-configuration

Identifying the Absorbent

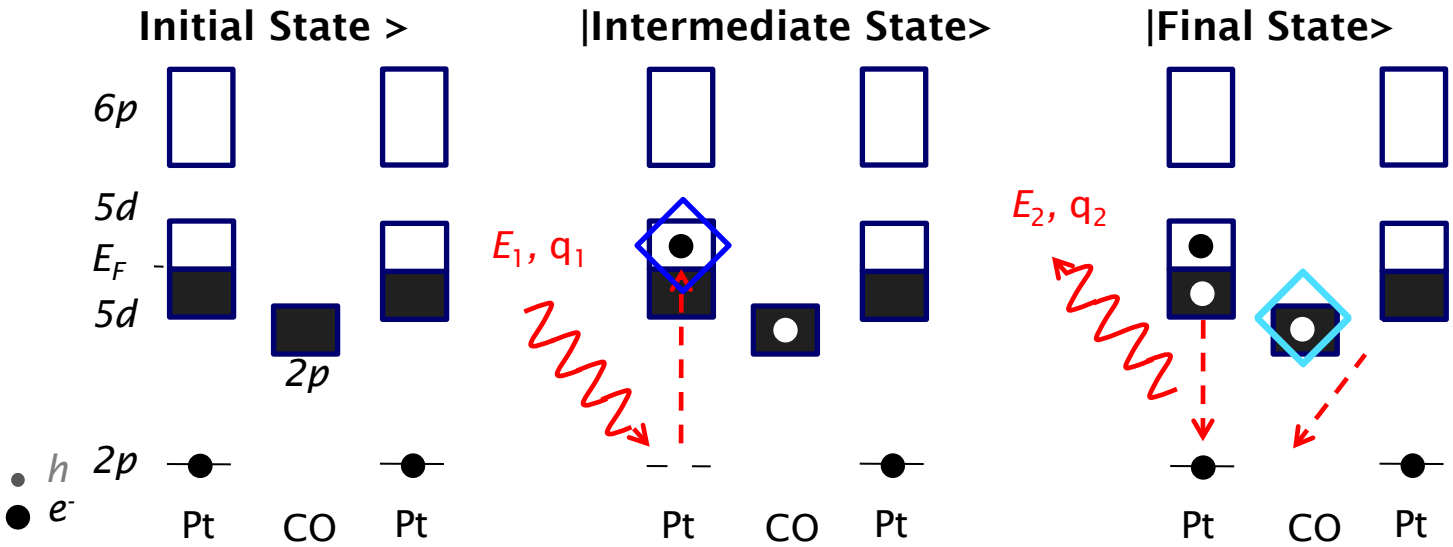


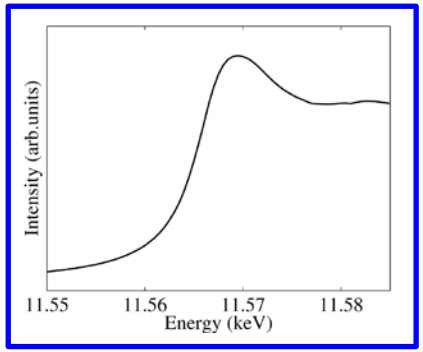


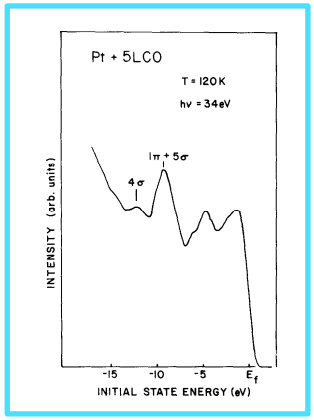


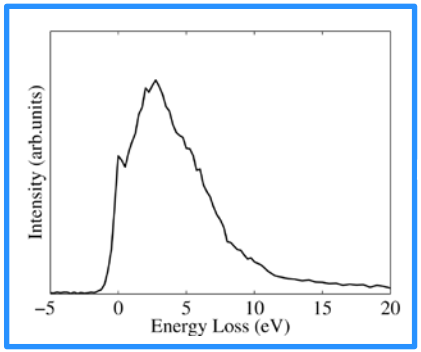
Cond. Band * Val. Band: RIXS (cst E loss)

Increasing Chemical Sensitivity









Cond. Band (XAS) * **Val. Band (XES)** = **RIXS**

- Access both **VB** and **CB**
- **Element and symmetry** selectivity
- **Bulk** sensitivity
- Detects **chemical absorbents**

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How Many Photons do we Need?

$$n = \frac{NumberOfP}{SpectroscopyEfficiency * StatisticalError^2} * \frac{1}{DetectionEfficiency}$$

Technique	Spectroscopy Efficiency	NumberOfP	Detection Efficiency	Statistical Error	n
EXAFS/XAFS (K_α–Spectroscopy)	0.9-1	500-1000	0.01-0.1	0.001-0.001	~10^{11}
RIXS (K_β–Spectroscopy)	0.1-0.12	100x100	0.001-0.01	0.01-0.05	~10^{12}
HERFD (K_β–Spectroscopy)	0.1-0.12	100	0.001-0.01	0.01-0.05	~10^{10}
Valence-to-Core	0.005-0.001	100	0.001-0.05	0.02-0.05	~10^{12}

n: Necessary number of X-ray photons absorbed by the compound (element under investigation) (with perfect background suppression)

DETECTION EFFICIENCY

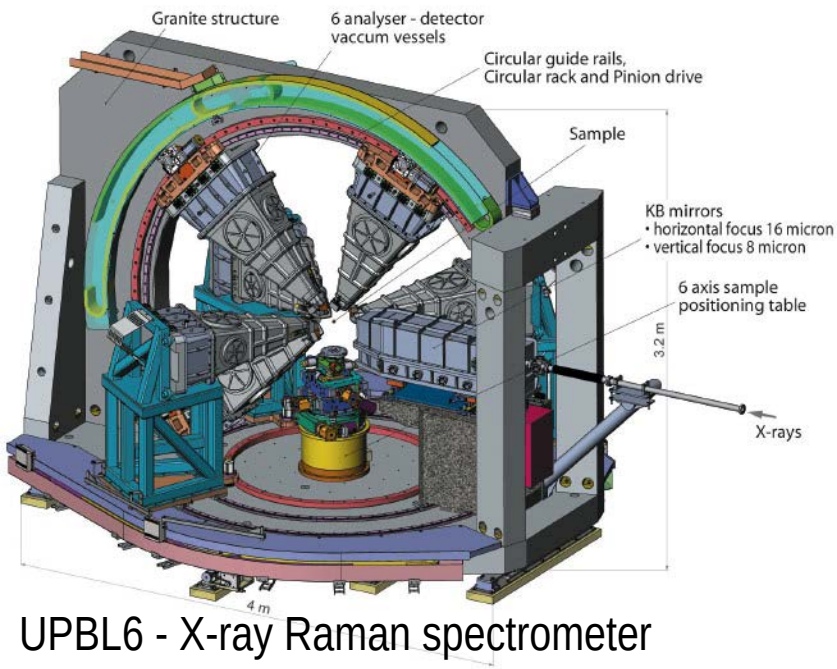
$$E^{Det} = SolidAngleRatio * E^{detection} * E^{Optics}$$

Solid Angle Ratio: Increase detection area and/or distance between detector and sample

$E^{Detection}$: Optimize sensor material to energy range (issues with high energy range)

E^{optics}: Optimize spectrometer optics and background suppression optics

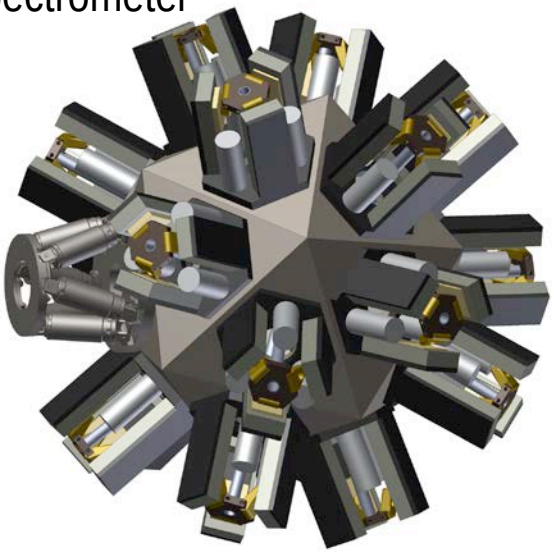
Highly integrated sample environments allow optimization:



UPBL6 - X-ray Raman spectrometer

0.5m

ISS – Spectrometer



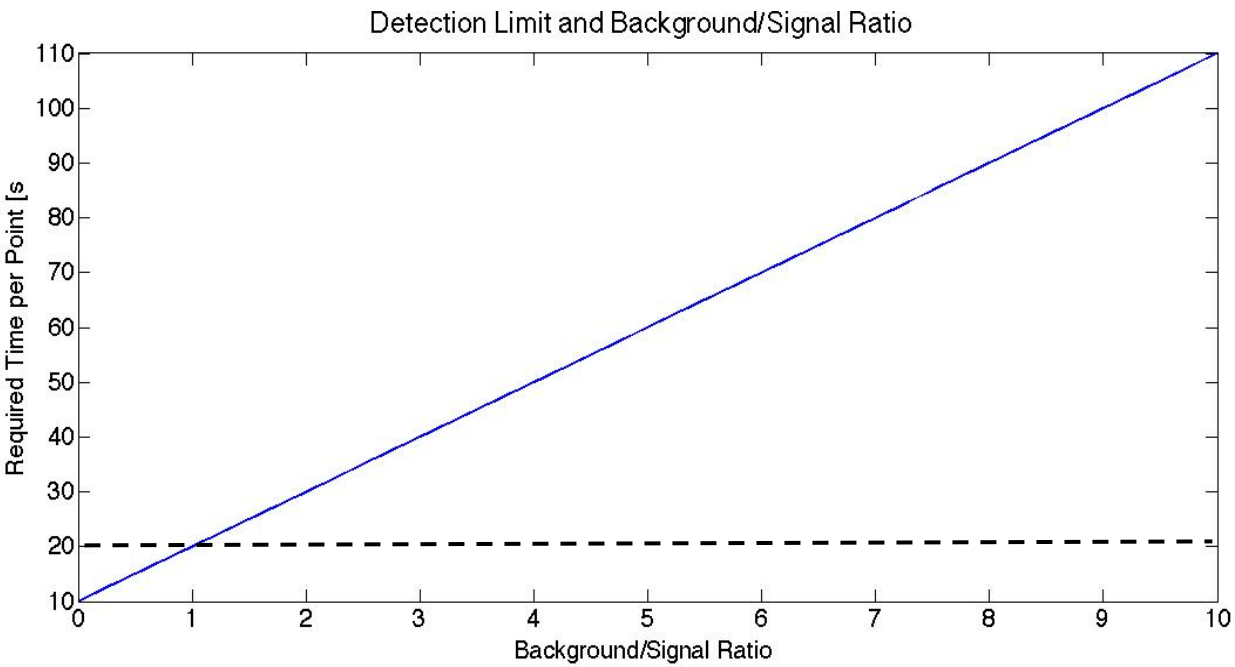
DETECTION SYSTEM
THE BACKGROUND SUPPRESSION

Model:

Property	Ultra dilute
Incoming intensity	10^{14} Photon/s
Signal (Fe K_α)	10^{7} Photons/s
Background (Thomson & Compton)	$2x10^{11}$ Photons/s

Total count-rate: $(\chi+1) * n$

Statistic noise: $\frac{1}{(\chi+1)^2} * \frac{1}{n^2}$

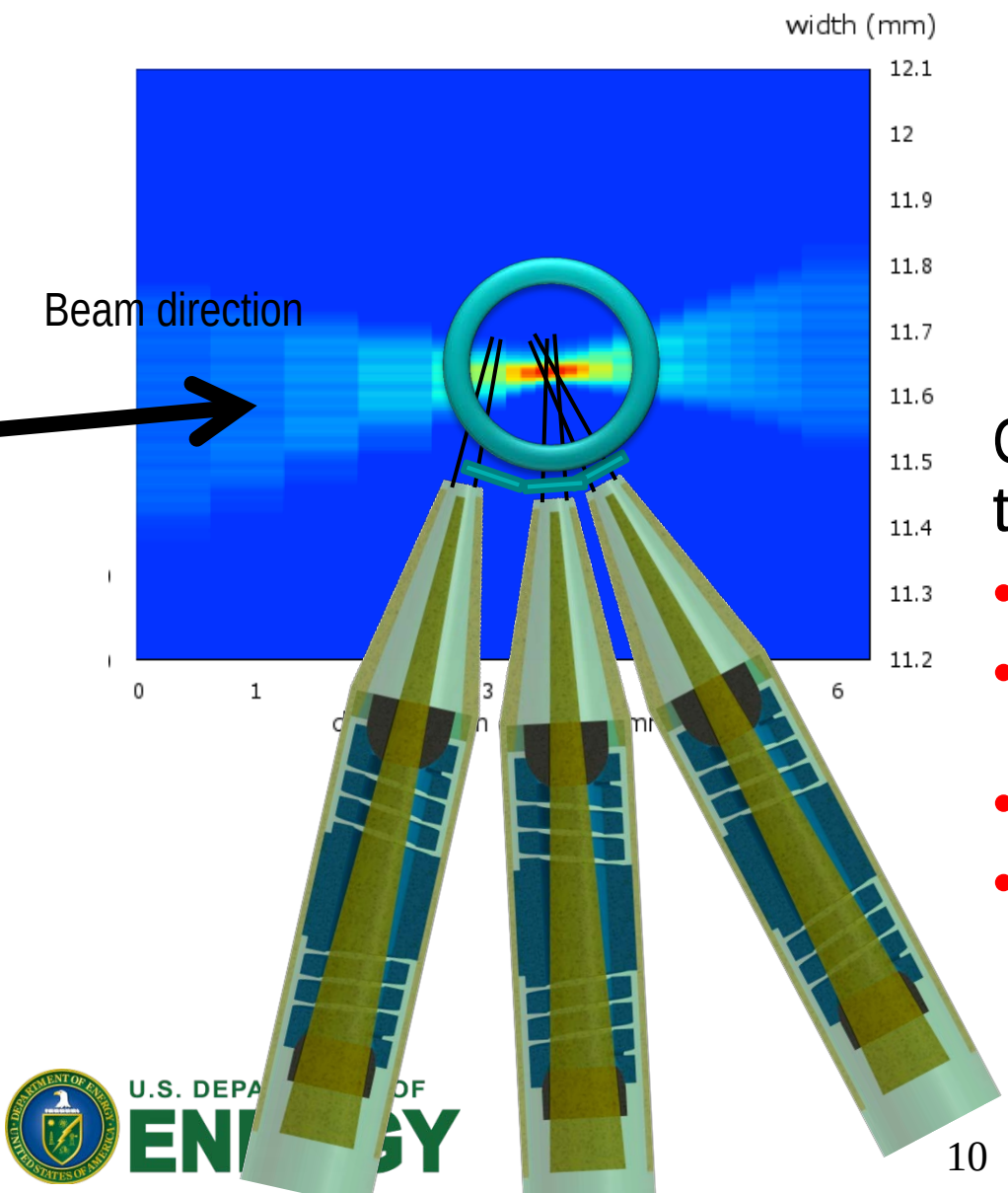


Model assumptions:

- a 1μmol/L solution of Fe in H_2O (Ultra dilute case)
- 10^{14} Photons/s on the sample
- 1% detection efficiency
- 0.1% statistical noise per point

Background to signal ratio dominates detection efficiency

THE PERFECT DETECTION SYSTEM



The Perfect Detector:

- Large solid angle
- No count rate limitation
- High background suppression
- Adjustable band-width

Confocal Detection Concept helps to reduce background

- Focusing polycapillary: ~25 μm focal spot
- Extraction polycapillary: 50 – 200 μm focal spot (exchangeable)
- Z-1 filter with 12μd
- Extraction lens alignment:
  - Angle: horizontal & vertical
  - Translation: Z-position

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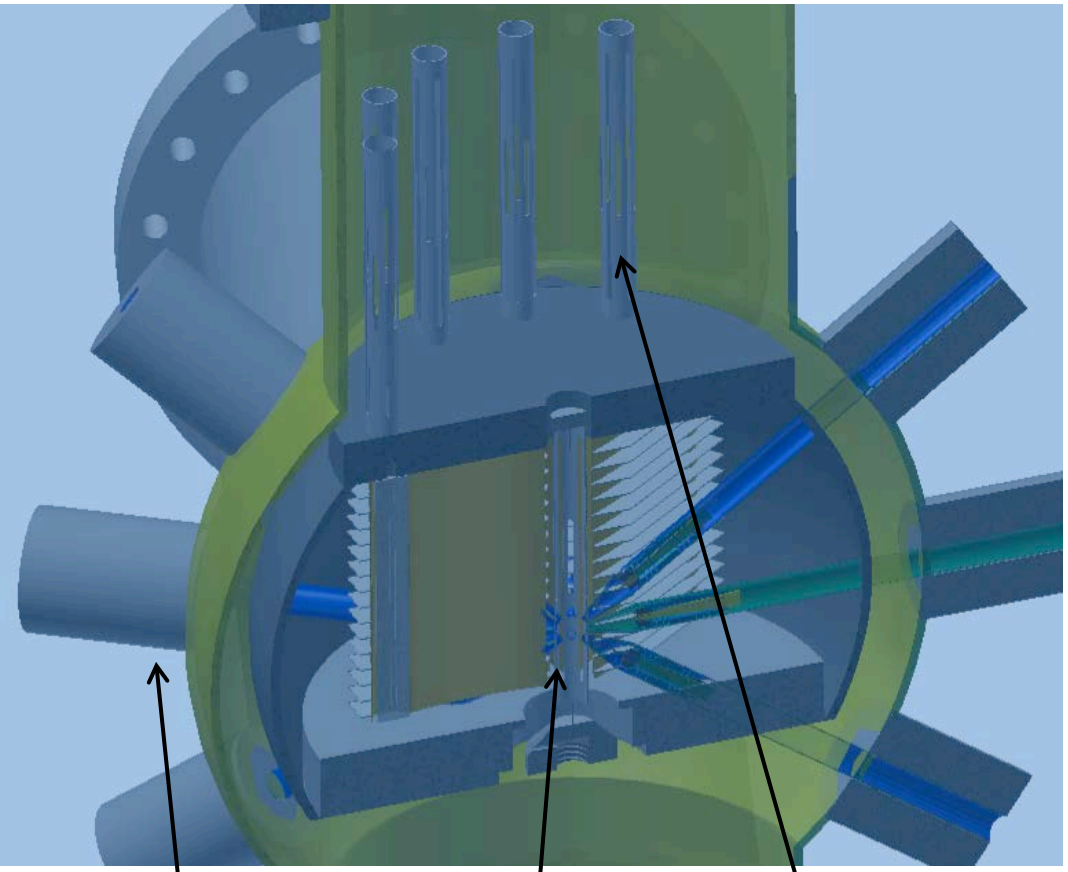
THE EXTRACTION SYSTEM:



Configurable extraction ports

Z-1 filter holder

Z-1 filter Magazine (12)

Alternative Stern-Heald Detection concept

- Polycapillaries lenses instead of Soller slit
- Covers about 22% solid angle
- Extraction ports are freely configurable
- Detector System:
  - SDD for complex materials
  - PIN diodes for high count rate application
  - 3 different kind of detectors

Performance

- Filter suppression: ~10^{-7}
- Expected fluorescence count rate per port
  - For ultra dilute sample: ~10^3 photons/s (~ 27 hours)

Significant improvement

BEAM DAMAGE BY INEFFICIENT OPERATIONS

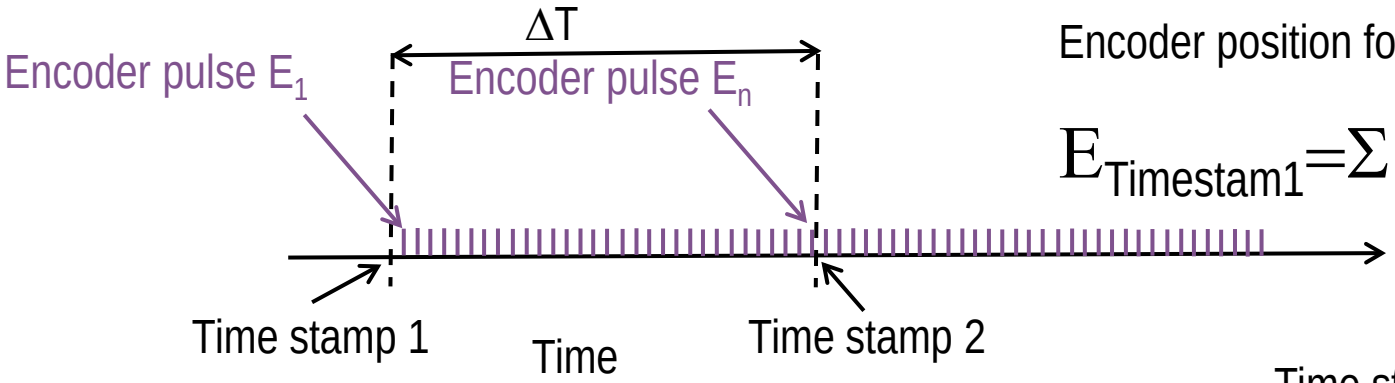
The most common inefficiencies

- Unnecessary beam exposure during motor motion
- Unnecessary beam exposure during scan preparation
- Data collection is not adjusted to the statistical needs (too long time measured at unimportant parts of the scan)
- Systematic errors after exchanging sample during a more-dimensional scan

The ISS concept:

- Continuous scans of all motors possible with
  - Programmable speed profile
  - Optimized fast motions
- Simultaneous continuous scans of multiple motors possible
  - Programmable phase correlation between motors
- Integration of fast shutter

SCANNING AND HOW MANY POINTS PER SCAN



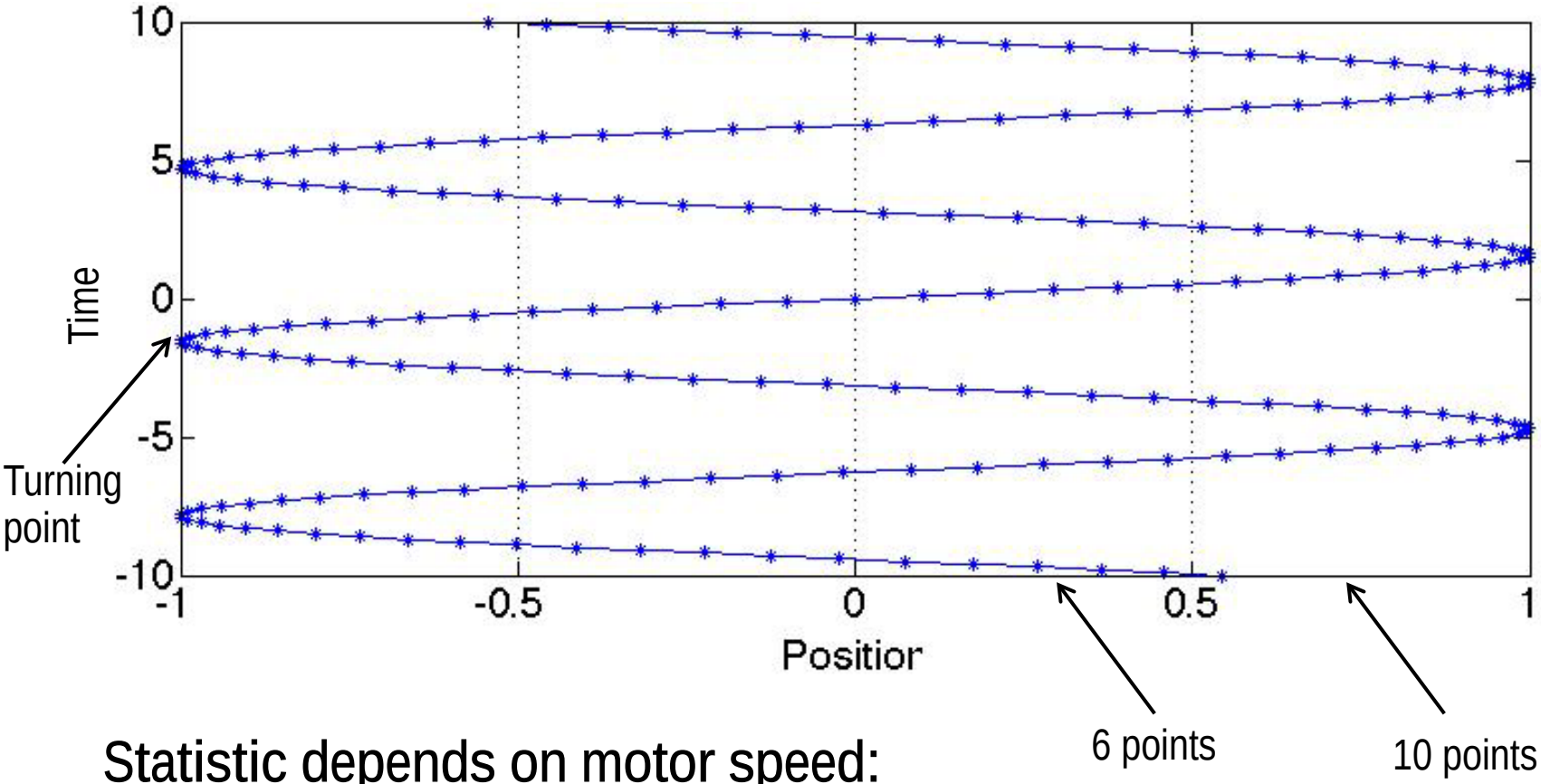
Encoder position for time stamp 1:

$$E_{Timestam1} = \Sigma\ E_i/i$$

Time stamp resolution: 100μs

Scanning type	Time Scale [ms]	Points for Normal time stamp	"Encoder" resolution	Moench	Pilatus	Eiger
Mono	10	100	~100μdeg (~0.1eV @10keV)	1mdeg (~1eV @10keV)	33mdeg	0.1-1mdeg
Analyzer	20-100	200-1000	0.25-0.05eV	2.5-0.5eV	50-12eV	2,5-0.05eV
Typical motor (1mm/s 1degree/s)	100-1000	1000-10^4	0.1-1μm/s 0.1-1mdeg/s	10μm/s 10mdeg/s	300μm/s 300mdeg/s	0.1-10μm/s 0.1-10mdeg/s

DATA STATISTIC AND SPEED PROFILE IN A CONTINUOUS SCAN

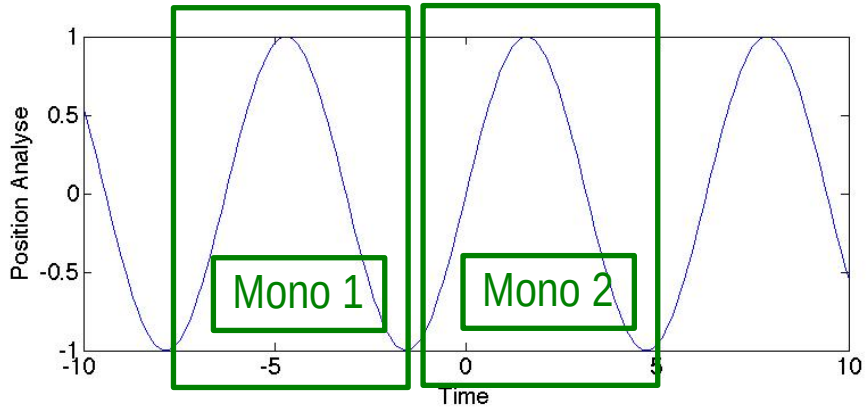


Statistic depends on motor speed: slow motion –high data quality

Best statistics on turning points (for sin-motion)

ONE DIMENSIONAL SCAN VERSUS MULTIDIMENSIONAL SCANS

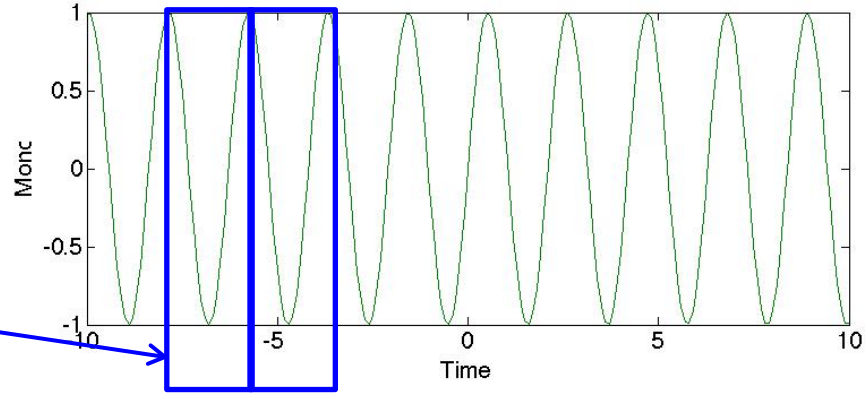
Analyzer scan



Dominating time scale (systematic error):

Period time of Analyzer

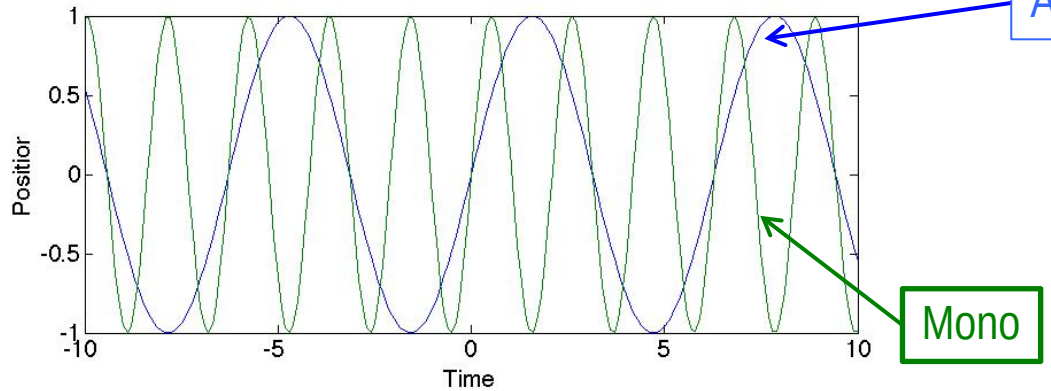
Mono scan



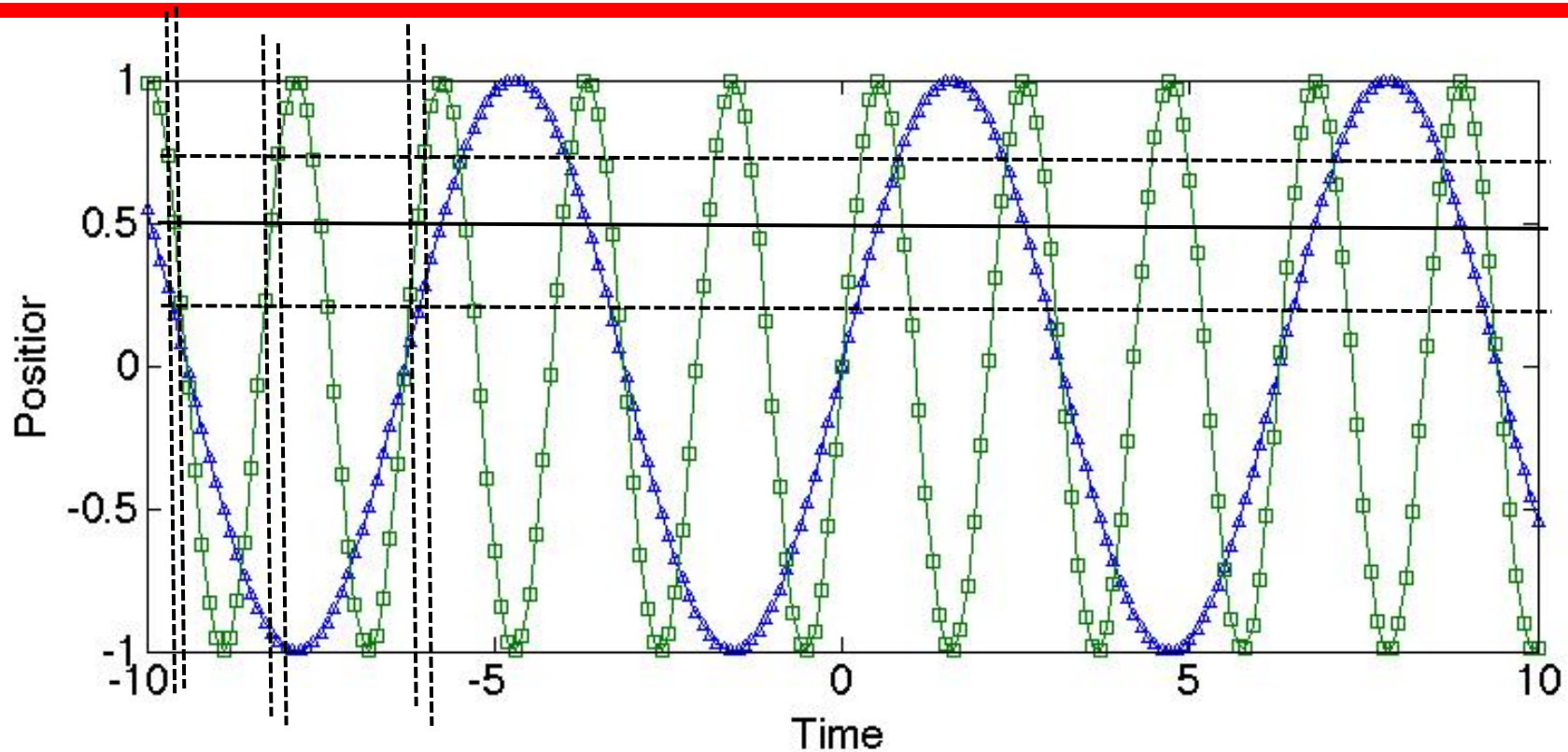
Dominating time scale (systematic error):

Period time of Mono

2-D scan



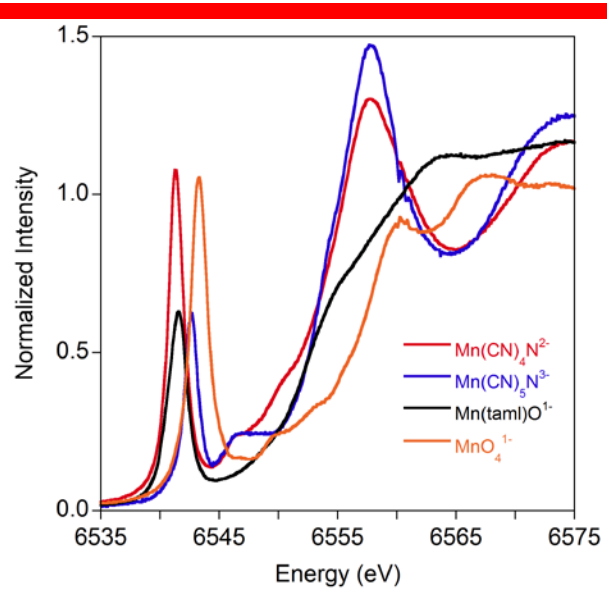
POINT DENSITY, OVERSAMPLING: MULTIDIMENSIONAL SCANS

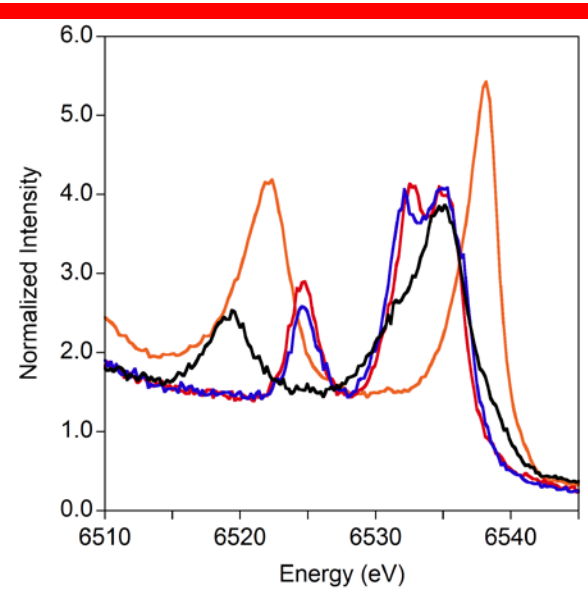


- Complex statistics build up: Speed profile can be optimized to collect statistics at the "important" parts of the spectrum
- Statistics is build up "simultaneously" for the full phase-space
  - sample change can be done at any time
  - Data acquisition can be stopped at any time

THE REQUIRED DATA STATISTICS

K_β-"RIXS"





Valence band emission

- Required statistics depends on significance of differences in spectra
- Theoretical simulations of spectra (based on models which have to be available) may help to
  - choose the optimum detection method (spectra with maximal differences0
  - Choose a minimized energy range
  - Tells which parts of the spectrum needs "most attention"
- Applying statistical methods like "test statistic" may help
  - To determine if statistic is enough
  - May use data base spectra and simulations to reduce required data

SAMPLE HANDLING AND PREPARATION

Preparation:

- Degassing of all solutions
- Freezing of samples (ice crystal formation is not an issue)
- Exploration of chemical scavengers

Sample environment

- Liquid flow cells
- Stop-flow cells
- Freezing-thawing

Controlled environment

- temperature
- Gas
- Automated handling

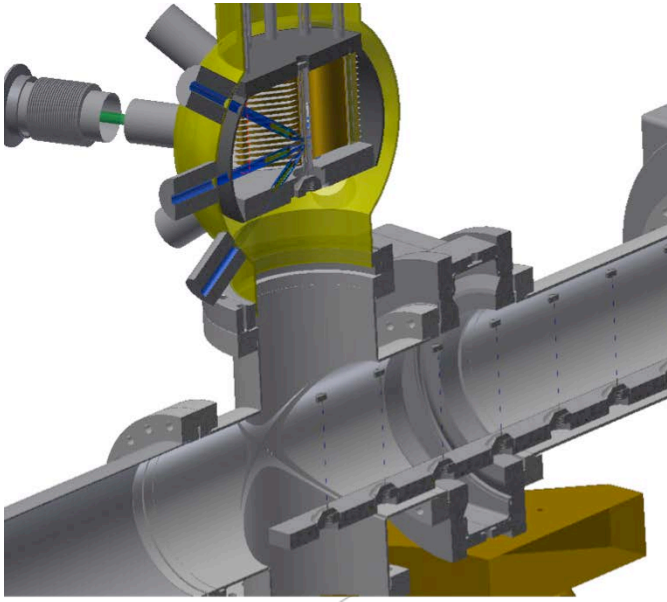
SAMPLE HOLDER AND FLOW-CELL DESIGNS

General:

- All sample sample holders can be optimized for specific conditions
- Auxiliary contacts (DC, RF ….) possible
- Gas atmosphere can be chosen (pressure, gas, vapor)
- Gas atmosphere can be changed during data acquisition
- High pressure (up to 700 bar) planned

Capillary Geometry

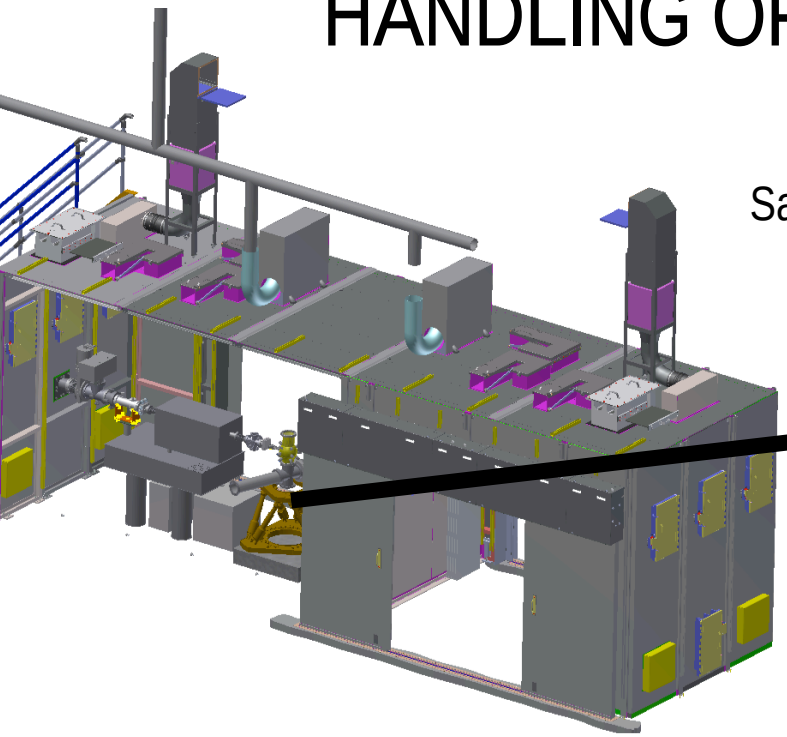
- Variable diameter between 100μm and 3000μm
- Feed and return line
- External pump possible (synchronized with data acquisition?)
- Freezing-thawing is possible without changing sample

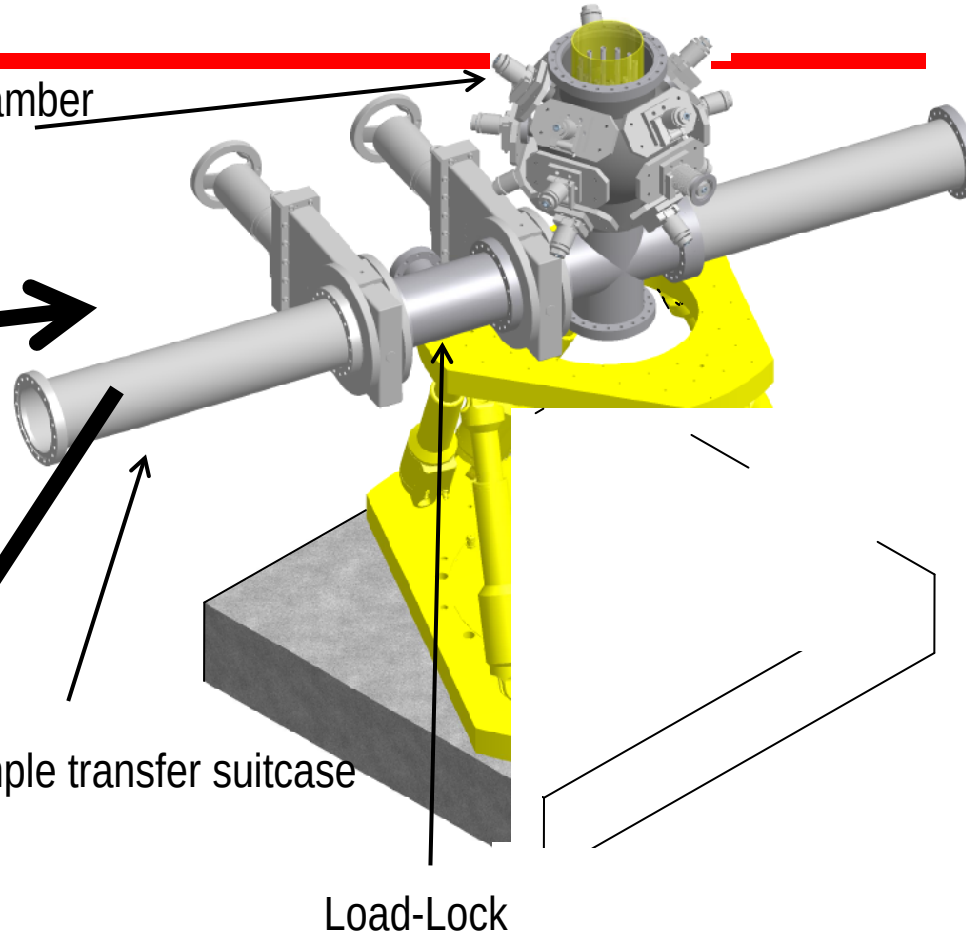


Tube Geometry

- Maximal diameter of tube is 9mm
- Anything what fit can be build

HANDLING OF SENSITIVE SAMPLES





Transport of sample suitcase: Trolley

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SUMMARY

Sample damage depends not on flux but on efficiency:

- The right detection method needs to be selected
- The detection system has to be optimized for
  - Large solid angle acceptance
  - Background suppression
  - Flexibility to change between detection modes
- Data acquisition has to be optimized to
  - Avoid unnecessary beam exposure
  - Require the necessary statistics in the various parts of the spectrum
- Sample handling has to be integrated and provide
  - Controlled preparation and handling environment
  - Flexibility between freeze- and liquid experiments (also in between)

ISS will provide these conditions starting in 2016