

School on
Synchrotron Light Sources
and their Applications



6 - 17 December 2021
An ICTP Virtual Meeting
Trieste, Italy

Further information:
<http://indico.ictp.it/event/9445/>
sm2019@ictp.it



SESAME

Synchrotron-light for
Experimental **S**cience and
Applications in the **M**iddle **E**ast



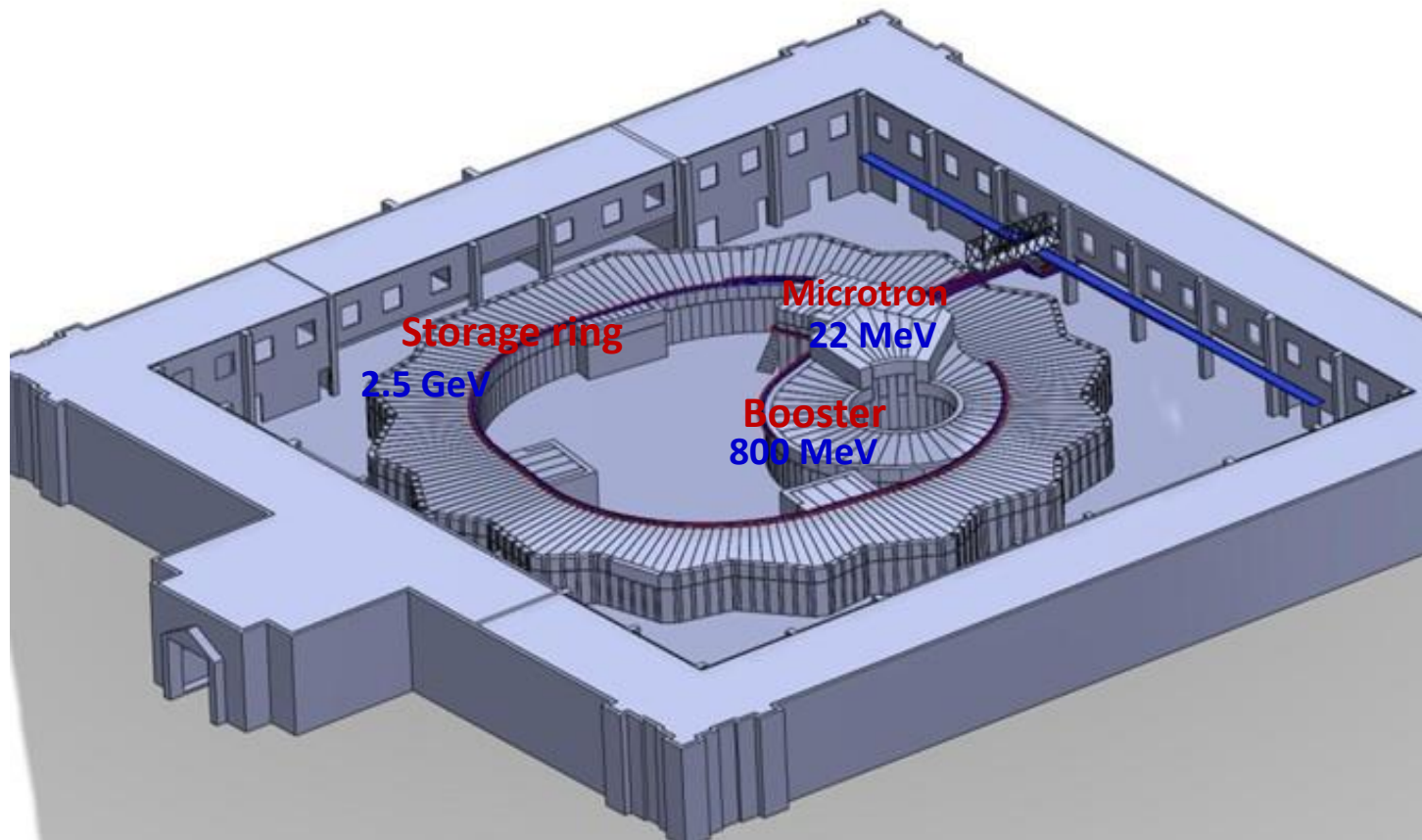
School on Synchrotron Light Sources and their Applications, 6 - 17 Dec. 2021

XAFS/XRF Beamline @ SESAME, Sample Preparation, and Data Collection

Messaoud Harfouche

Synchrotron-light for Experimental Science and Applications in the Middle East, Jordan

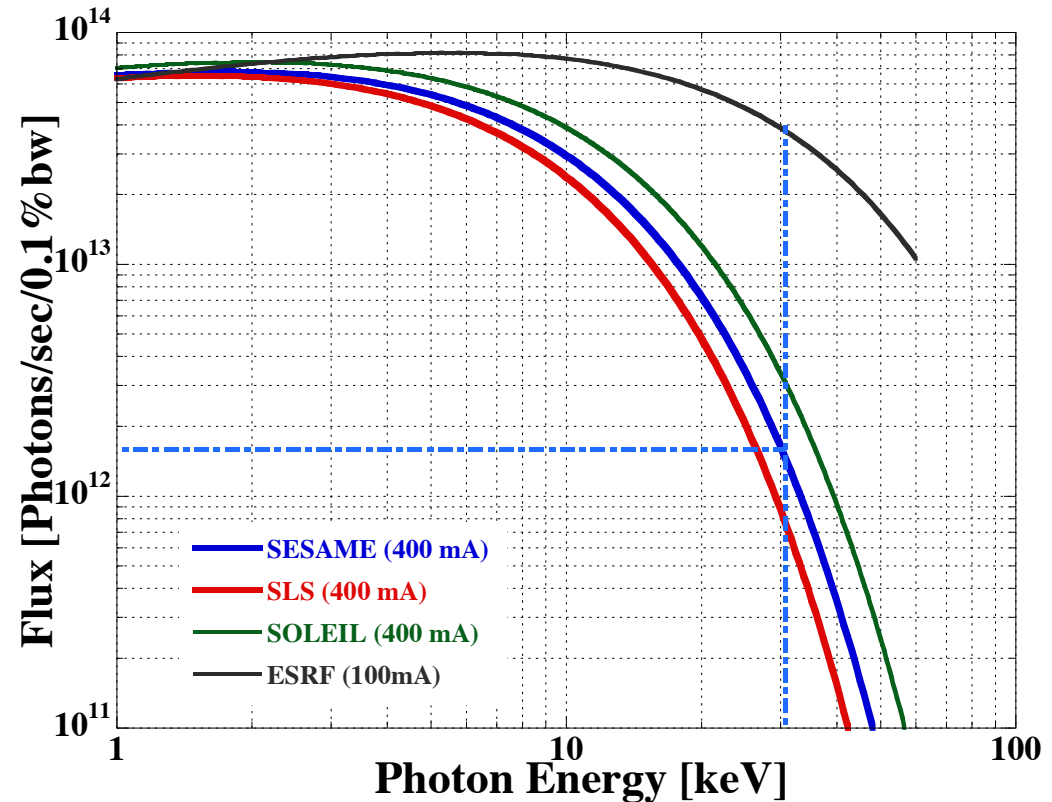
SESAME Machine



3D drawing of the SESAME Building

Machine Design Parameters

Parameter	Unit	Value
Energy	GeV	2.5
Circumference	m	133.2
Current	mA	400
Beam Lifetime	hr	21.5
Magnetic field (BM)	T	1.45
Critical energy	eV	6049.4



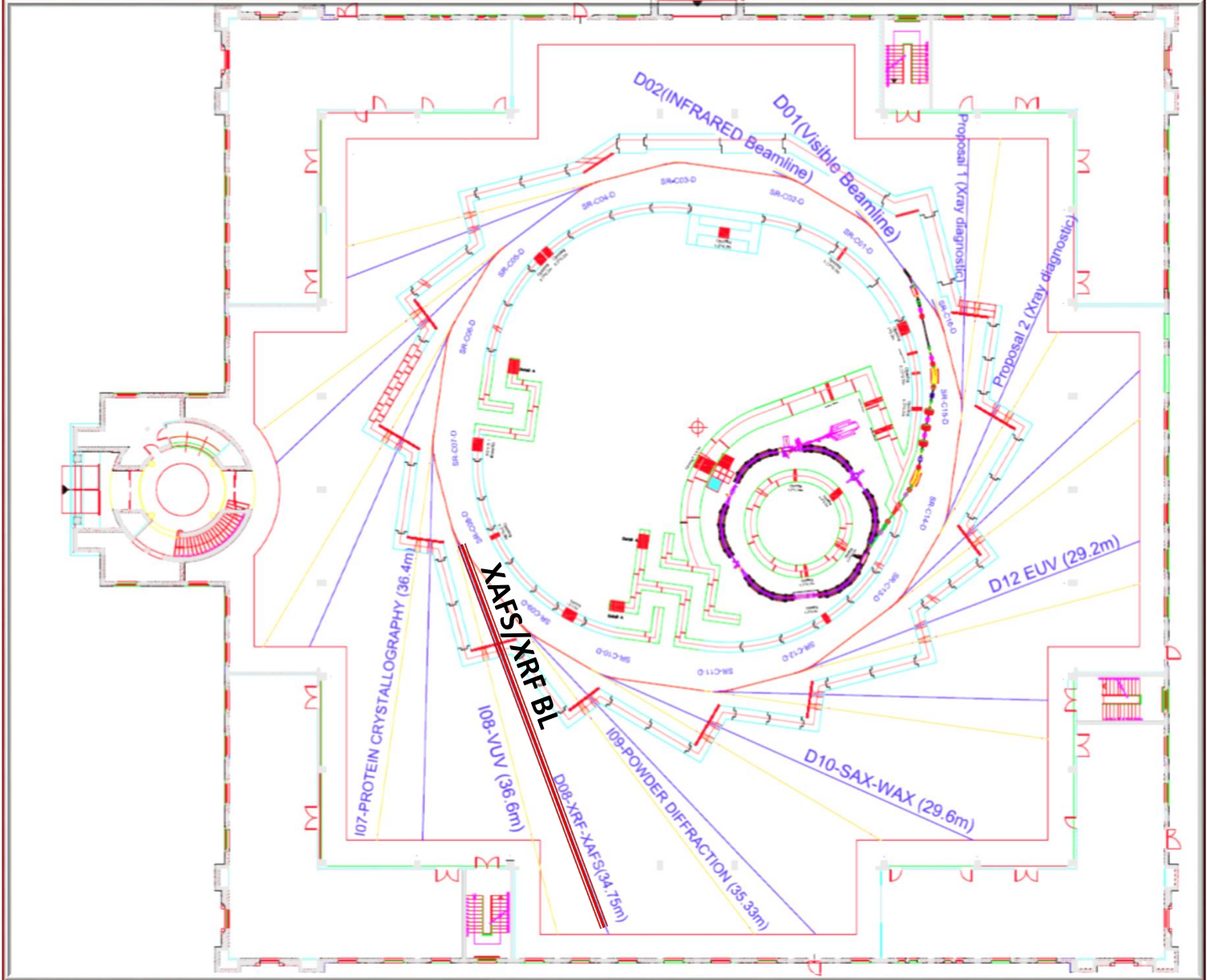
SESAME machine is comparable to world class machines
SOLEIL, France and **SLS** Switzerland



XAFS/XRF Beamline
(BASEMA)

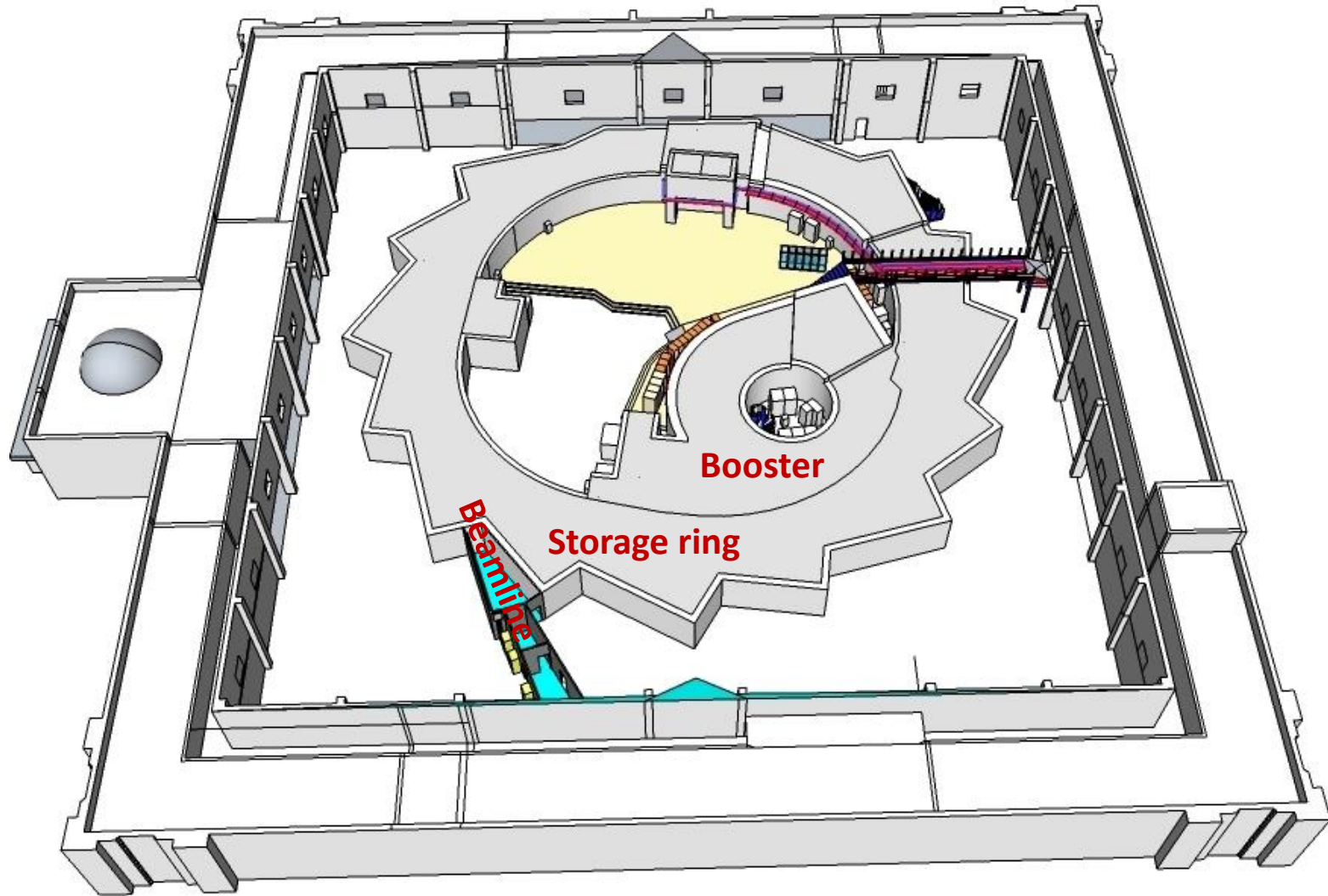
Brief History of the XAFS/XRF beamline

Task	Period
Conceptual Design Report	July 2012
Technical Design Report	October 2014
Installation (Pb Hutches, Optics)	March 2016
Control and alignment	2015-July 2017
Call for proposals (Sem-0)	March, 2017 (36 submitted, 19 accepted)
FE installation	April-September 2017
Start BL commissioning	October 2017
First Monochromatic beam	November 2017
First Scan	November 2017
End BL commissioning	July 2018 (<i>only 3 months of operation</i>)
First non-official User	April 2018
Official beamtime for Users	July 2018
Second call for proposals (Sem-1)	October 2018 (61 submitted, 36 accepted)



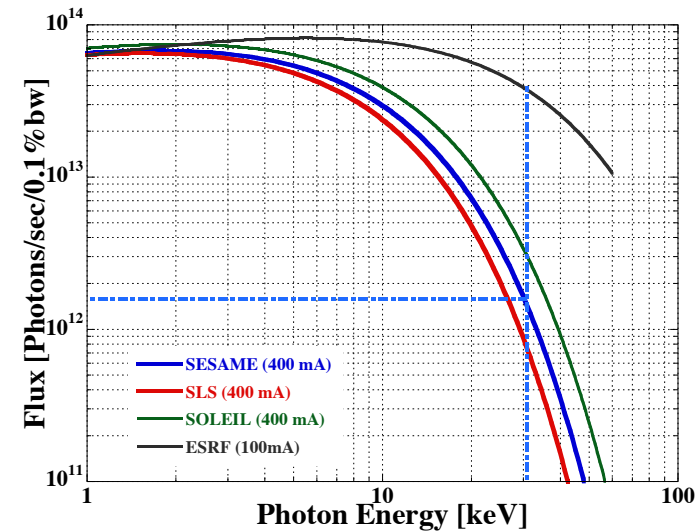
BASEMA Port D08

by Adel Amro



Beamline Design Parameters

Parameter	Unit	Value
Source (BM)	T	1.45
Hor. acceptance	mrad	3
Vert. acceptance	mrad	0.6
Energy range	keV	4 – 30
Energy resolution	-	$\sim 10^{-4}$
Photon flux (S1)	Ph/sec	2×10^{12} (8keV)
Beam size (S1)	mm ²	$\sim 0.1 \times 0.1$
Beam size (S2)	μm^2	8×10
Photon flux (S1)	Ph/sec	5×10^9 (8keV)



Energy range

- Lower limit due to **absorption of air in the EH**
- Higher limit due to **machine limitation**

XAFS/XRF beamline optics

Donation by: Helmholtz-Zentrum Dresden Rossendorf (HZDR, Germany)
ROBL (BM20) a CRG beamline at ESRF

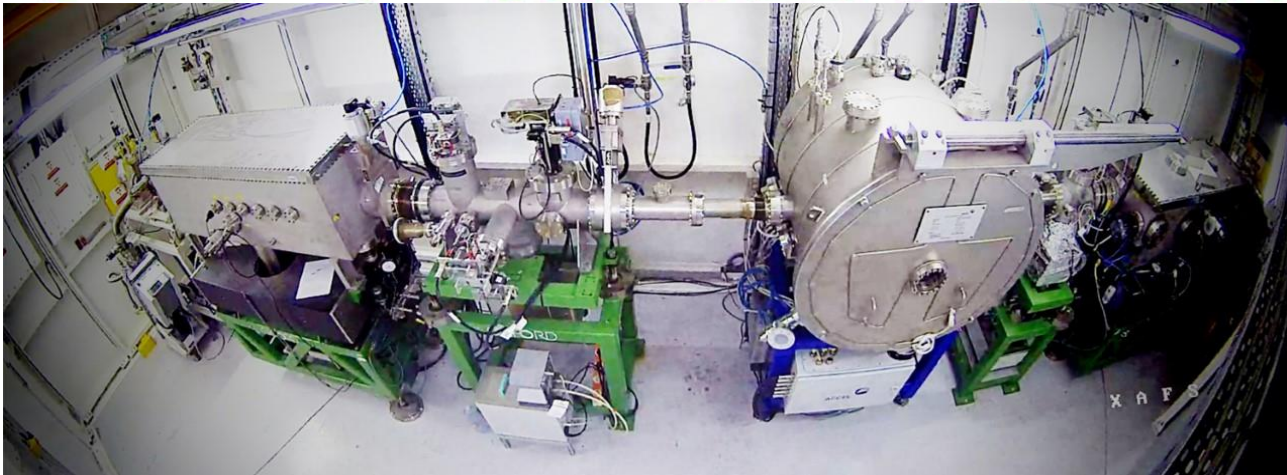
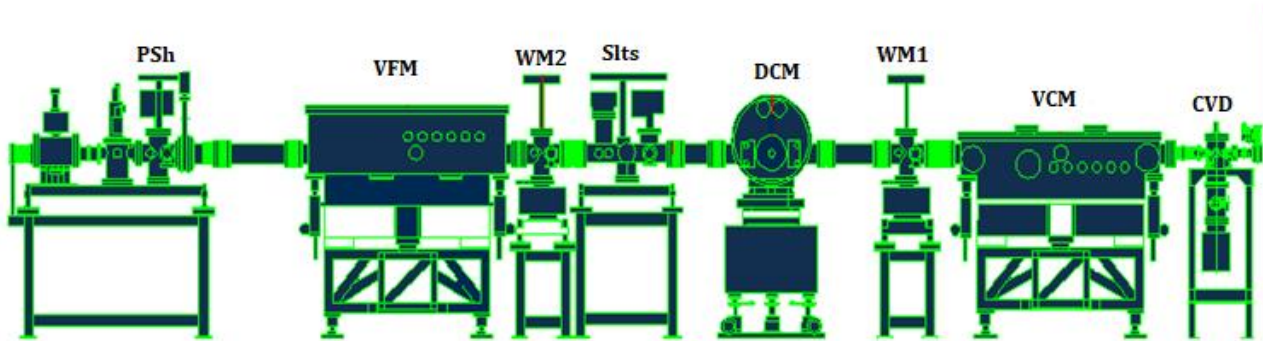


VCM: Vertical Collimating Mirror
DCM: Double crystal Monochromator
VFM : Vertical Focusing Mirror

WM: Wire Monitor
M-Slt: Monochromatic Slits

XAFS/XRF Beamline at SESAME

(operational since 2018)



Design Parameters

Parameter	Unit	Value
Source (BM)	T	1.45
Hor. acceptance	mrad	3
Vert. acceptance	mrad	0.6
Energy range	keV	4.7 – 30
Energy resolution	-	$\sim 10^{-4}$
Photon flux (S1)	Ph/sec	2×10^{12} (8keV)
Beam size (S1)	mm ²	1x1 - 5x20

XAFS/XRF beamline: "Current Situation"

**Si(111) & Si (311)
Crystals**

Beamline Characteristics

Energy range 4.5 – ~30 keV

Beam current 300 mA (decay mode)

Beam Size 2x2 mm² to 5 x 20 mm²

PERIODIC CHART OF THE ELEMENTS

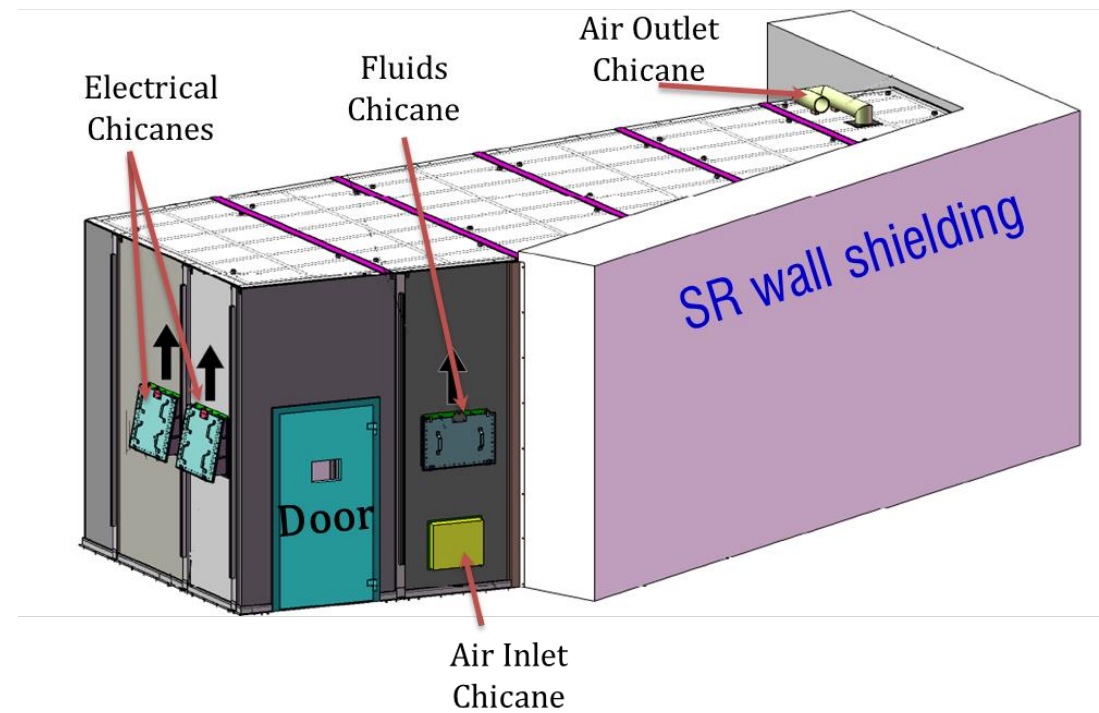
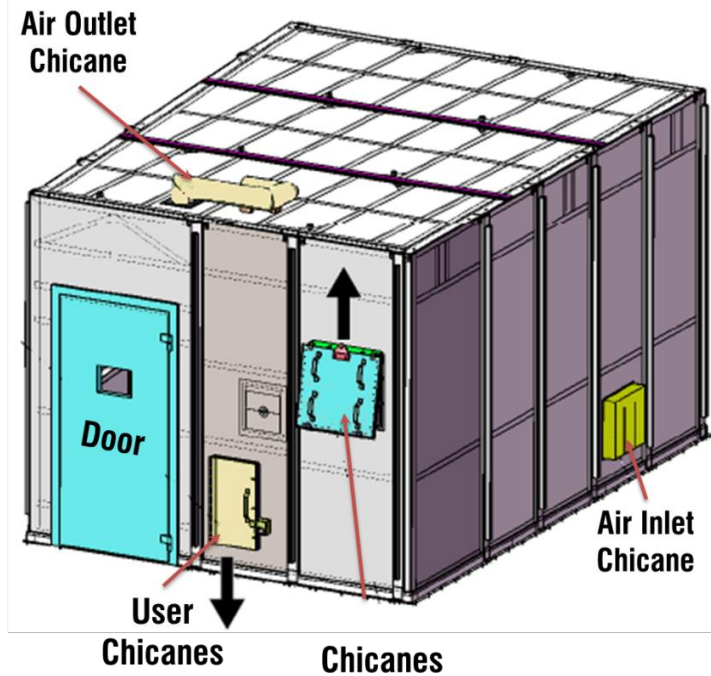
IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES				
1 H 1.00797														1 H 1.00797	2 He 4.0026				
3 Li 6.939	4 Be 9.0122													5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312													13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80		
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30		
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)		
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)								
* Lanthanide Series																			
58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97						
† Actinide Series																			
90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)						

Legend:
 : K-edge
 : L-edge
 : Difficult

Construction

Lead Hutches (OP + ES):

Constructed in May 2016 (CARATELLI)



XAFS/XRF Beamline [“Constructing the Hutches”](#)

Optical Hutch

Installation of Optics



Installing
major optics: May 2016



Installation of Optics

Installation of major optics:

May 2016



BL Installation: (*Challenges*)



Cooling of the VCM



Motors and wiring of the DCM



Alignment of the DCM
&
Other components



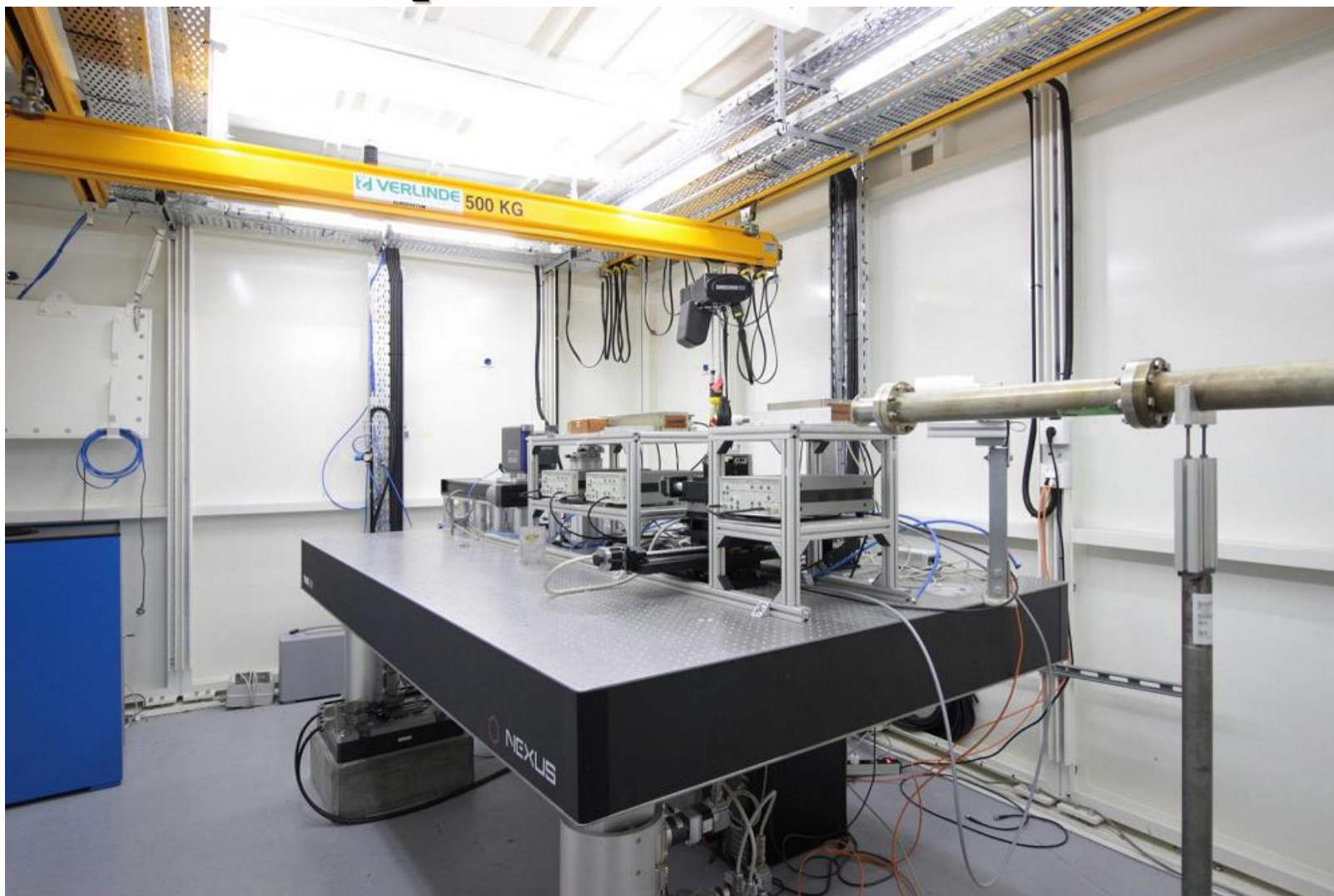
Adding a fluorescence screen
Dismantling vertical slits (alignment)

Aligning all the optics components

Testing:

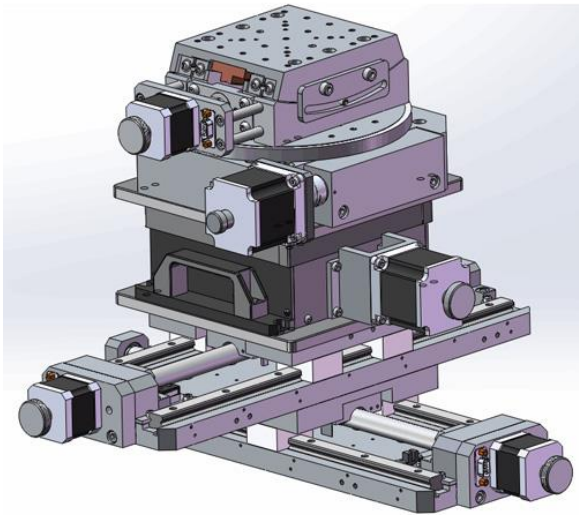
- ✓ **Motion system**
- ✓ **Cooling system**
- ✓ **Vacuum system**

Experimental Station



Experimental Station

5 Axis Motorized Positioning Stage
(Optics Focus)



PR for the Sample
Manipulator **issued**

2 short ionization chambers
1 long IC for the I_{t2} (OKEN, Japan)

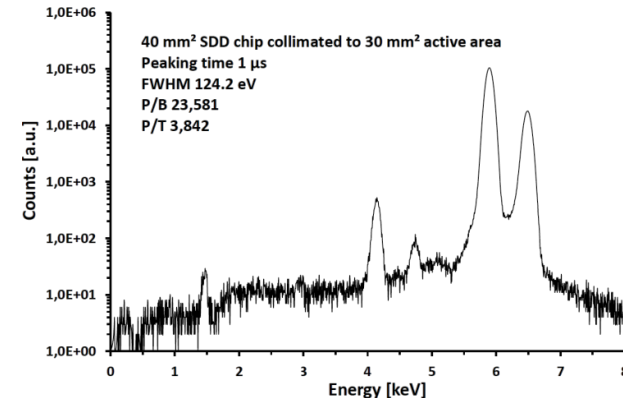


PR for the Ionization
chambers **issued**

Experimental Station: Detectors

A typical energy selective fluorescence spectrum:

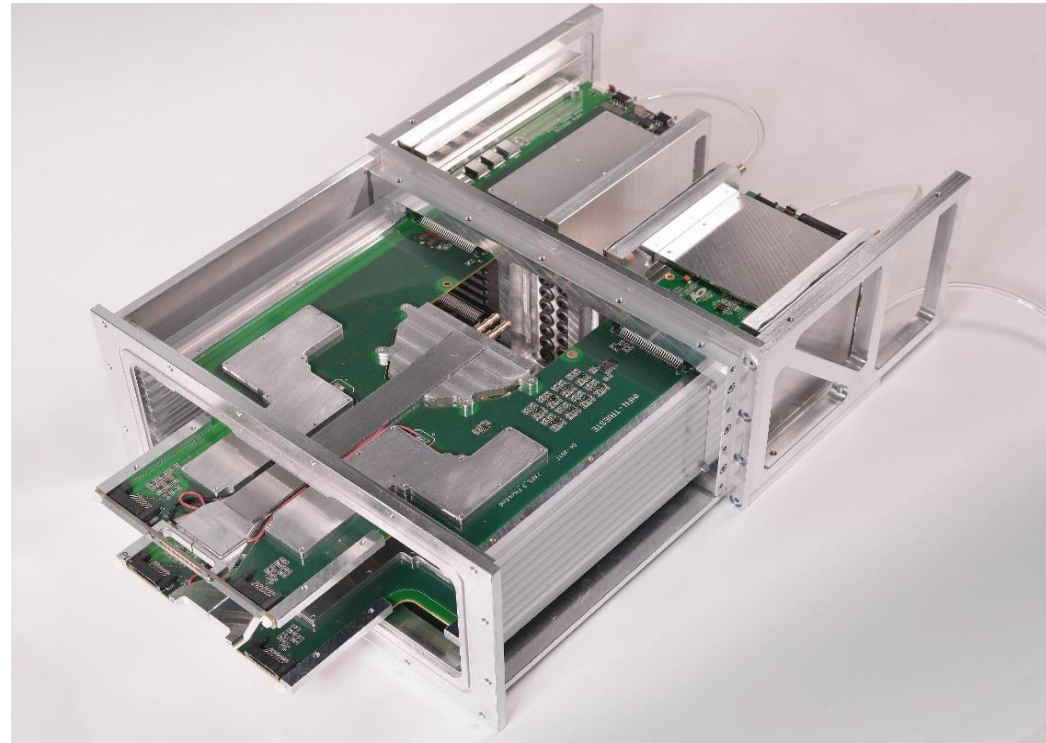
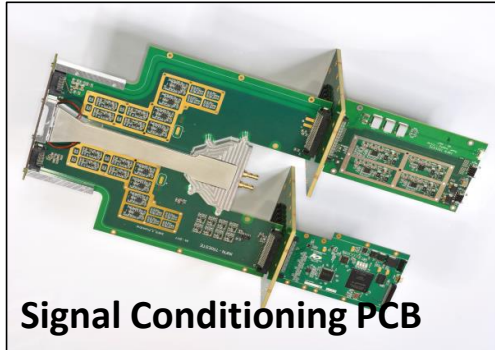
Signal output	Low noise preamplifier (XIA DXP)
Output connector (analog)	LEMO FFS.00.250
Vacuum tightness	Optional; He leakage rate $<10^{-6}$ mbar · l/s
Number of channels	max. 8192
Peaking time range	0.1 to 24 μ s in 24 steps
Software parameters	Digital gain, threshold, peaking time etc.
Signal form	Ramped reset type +1 V to -2 V; 5 mV/keV
Digital interfaces	USB 2.0, RS232 (on request)
Channel depth	24 bit
ADC	14 bit
Maximum read-out speed	1 ms (@1024 channels)
Clock frequency	40 MHz



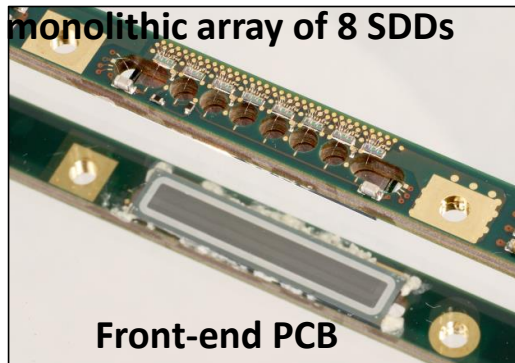
New Fluorescence Detector System: *64 Silicon Drift Detectors*



INFN (Italy), Elettra (Italy) & SESAME

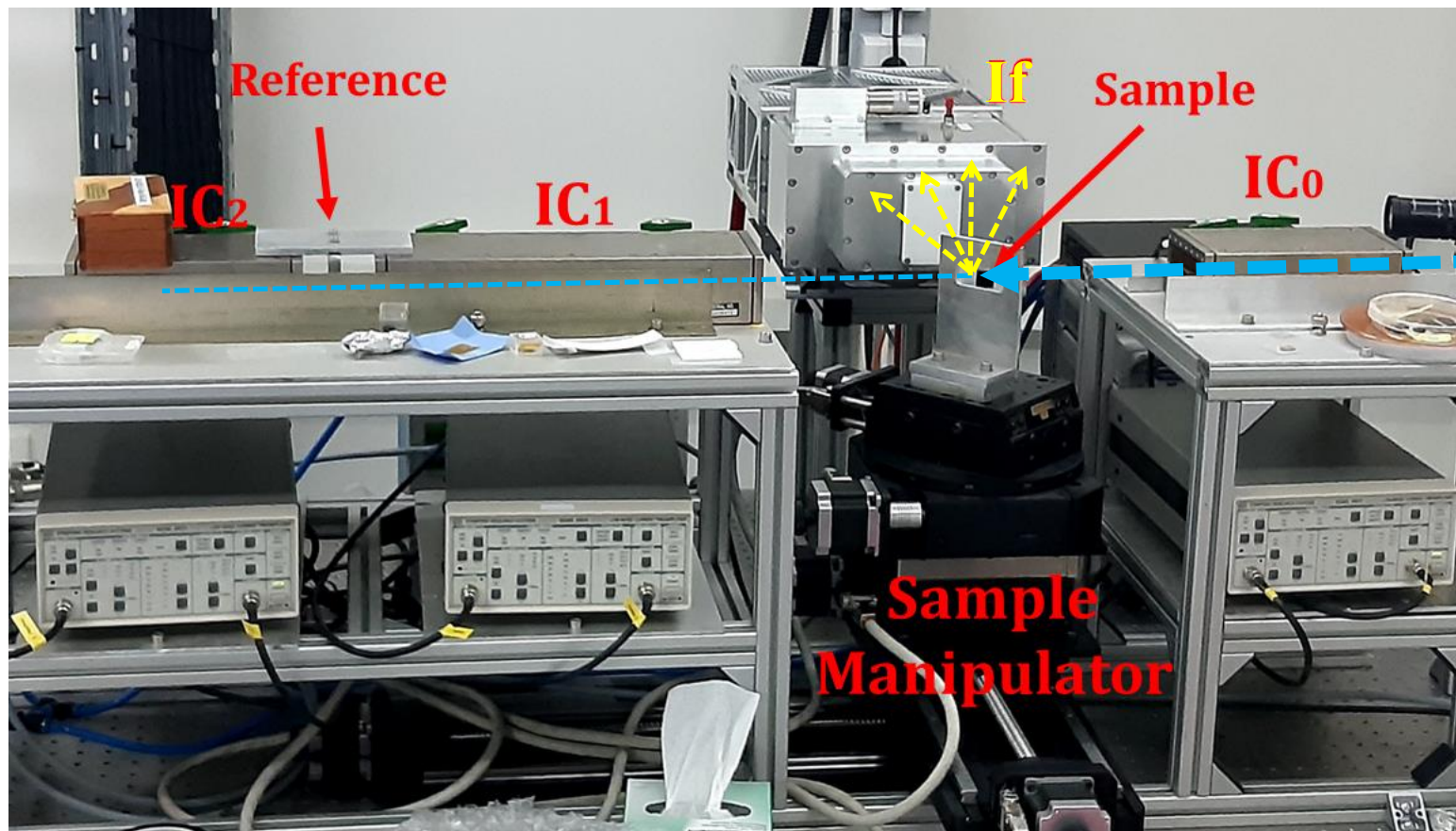


1. Front-end PCBs
2. Conditioning PCBs
3. Brass profile with cooling liquid flowing inside
4. Insertion guides at flanks of detecting heads
5. Rails for eight detection heads
6. Power supply and filters
7. Back-end PCBs
8. Inlet cooling distribution
9. Outlet cooling distribution
10. Ethernet PCBs
11. Power supply connectors



8 Modules x **8** SDDs with a Total collimated sensitive area of 499 mm²

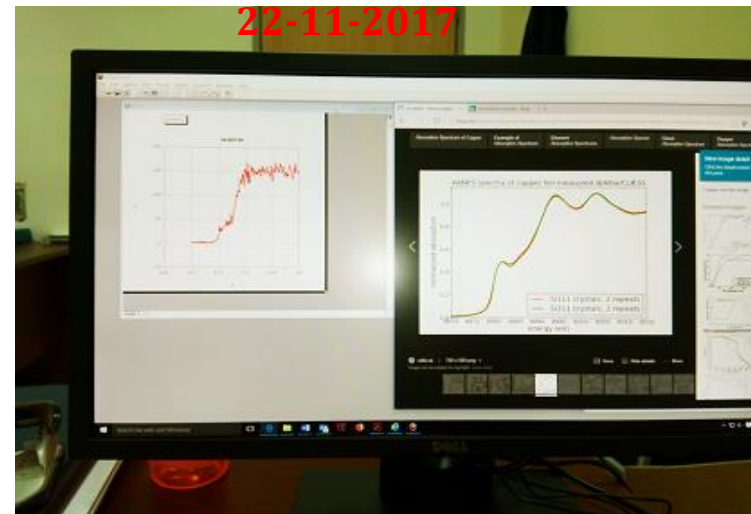
Beamline Experimental Setup



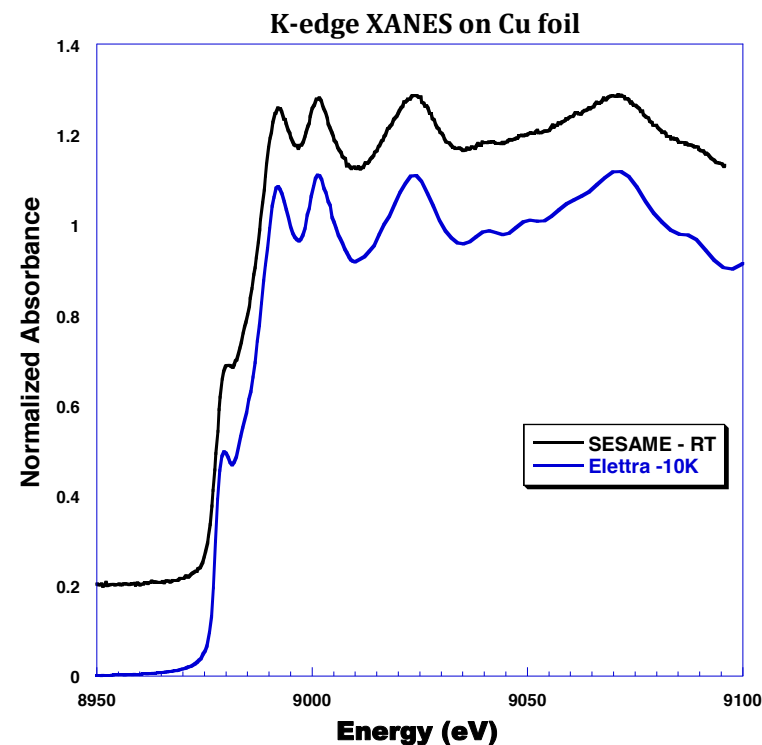
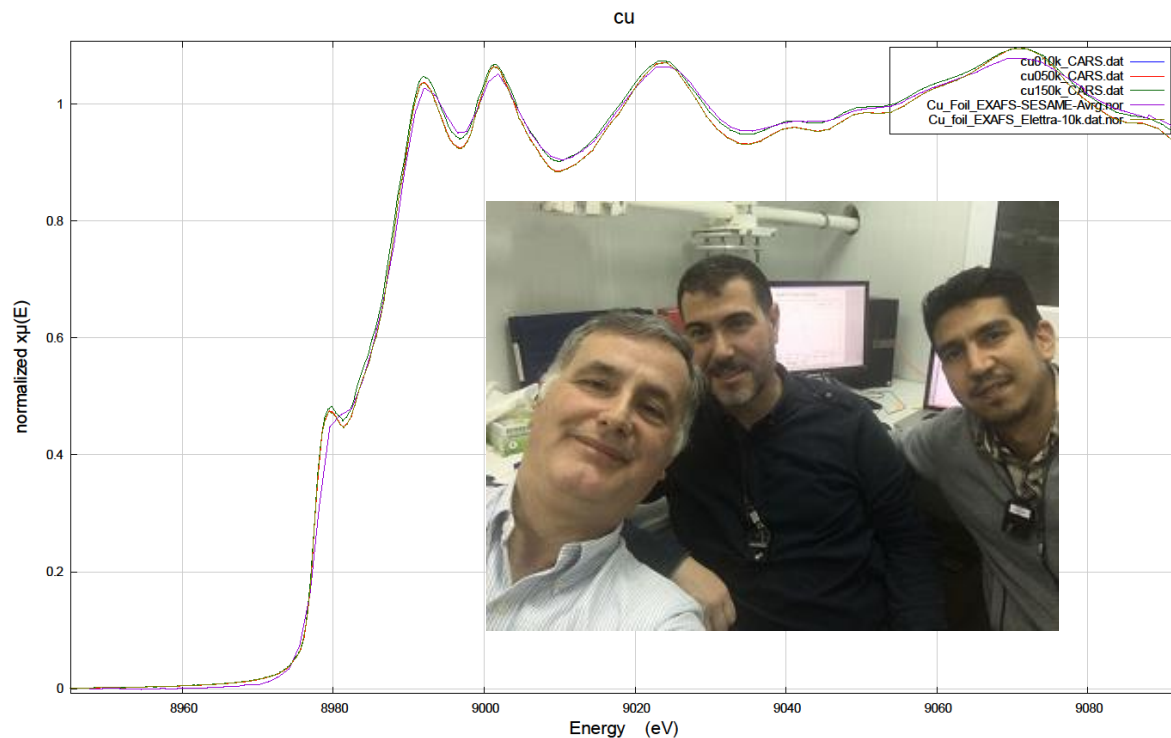
Commissioning of the beamline: (*searching for Mono beam*)



Pink Beam



First spectrum collected on the XAFS/XRF beamline at SESAME



□ XANES data collected at the K-edge of a Cu metal foil (Cu^{+0})

➤ Binding Energy: **8.979 keV**

➤ Good resolution compared to other beamlines

First user of the XAFS/XRF beamline was in July 2018

XAFS Experiment

Summary XAFS

XAFS spectroscopy give access to the modulations in the x-ray absorption coefficient (μ) as a function of incoming photon energy (**E**) related to the ion probed in the sample.

- selective chemically,
- available for almost all elements,
- efficient as low as ppm level,
- sensitive to redox-, and coordination,
- sensitive to medium range environment,
- work in aperiodic-, and other structurally complex structures such as liquids, soils, glasses, alloys...
- highly used nowadays in biochemistry, environmental sciences, geochemistry, archaeology, catalysis...

XAFS study: from experiment to results

Data collection

Suitable samples

There are good reviews on sample preparation, for example:

- Matt Newville, Anatomy of an XAFS Measurement
- Rob Scarrow, Sample Preparation for EXAFS Spectroscopy

google for them

- **General requirements**

- uniform on a scale of the absorption length of the material (typ. $\sim 10 \mu\text{m}$)
- prepared without pinholes

- **Shape, aggregative state**

- Solids: powders, foils etc.; single crystals and thin foils can utilize polarization properties of SR.
- Liquids
- Gases

- **Concentrations**

- for transmission: typ. $> 1 \text{ wt}\%$ (depending on the stoichiometry of the sample matrix)
- for fluorescence: typ. $> 100 \text{ ppm}$ and 1 mM

Before arriving at the beamline

Which detection mode to use:

- concentrated samples, transparent to x-rays – **transmission**
- dilute samples – **fluorescence**
- not transparent samples (low- E or thick) – **total electron yield** or **fluorescence** (with self-absorption correction)

Probing depth:

- **transmission**: the full sample thickness (bulk sensitivity)
- **fluorescence**: $\sim(\text{absorption length}) * \sin(\varphi)$, 0.1 – 10 μm
- **total electron yield**: \sim electron mean free path, 10 – 100 \AA

Make your plan ahead before starting the measurements

Should I measure Transmission or Fluorescence?

The choice of Transmission v. Fluorescence depends solely on the sample, and particularly the concentration of the element of interest.

Transmission Samples Concentrated samples – element of interest is above ~ 10 wt. %, and a thin enough sample can be made.

Sample preparation is more stringent for transmission measurements than fluorescence measurements.

Fluorescence Samples Dilute samples – element of interest is below ~ 10 wt. %.

For concentrated samples that cannot be made thin enough for transmission, use fluorescence, but pay attention to self-absorption effects and consider using grazing-exit geometry.

Also consider **Electron Yield**: Like fluorescence, but measures electron current emitted from the sample surface. This works best for metallic samples.

Because the electrons are emitted from a few 100\AA from the surface, this is very *surface sensitive*, but is always in the *Thin Sample* limit, so there are no self-absorption effects.

Preparing samples for Transmission Mode

Program XAFSmass: (see its web-page for detailed description):

powder:

The screenshot shows the 'powder' configuration in the XAFSmass software. The sample type is 'Powder'. The formula is $v = (\mu_T d) S (\sum_i N_i N_i 2r_i \lambda_i^3)^{-1}$; $m = M v$. The compound is 'Cu₂SiO₂' with a molar mass $M = 62.5883$ g/mol. The total absorption $\mu_T d$ is 2.6, and the scattering cross-section S is 0.72 cm². The energy E is 8979 eV. The data table is 'Henke'. The calculated volume v is 8.53016e-4 mol and the mass m is 53.389 mg. The absorption step is 'Cu(m=2.136): 0.734'. The density ρ and thickness d are currently blank.

foil:

The screenshot shows the 'foil' configuration in the XAFSmass software. The sample type is 'Foil, Film, Glas etc.'. The formula is $d = (\mu_T d) M (\rho \sum_i N_i N_i 2r_i \lambda_i^3)^{-1}$. The compound is 'Cu' with a molar mass $M = 63.5460$ g/mol. The total absorption $\mu_T d$ is 2.6, and the density ρ is 8.96 g/cm³. The energy E is 8979 eV. The data table is 'Henke'. The calculated thickness d is 10.212 μm. The absorption step is 'Cu: 2.266'.

gas:

The screenshot shows the 'gas' configuration in the XAFSmass software. The sample type is 'Gas'. The formula is $p = -\ln(1 - \text{obs.level}) / kT (d \sum_i N_i N_i 2r_i \lambda_i^3)^{-1}$. The compound is 'Ar' with a molar mass $M = 39.9480$ g/mol. The absorption level is 0.22, and the thickness d is 10 cm. The energy E is 9500 eV. The data table is 'Henke'. The calculated pressure p is 203.391 mbar.

A typical value for total absorption is about 2 for an edge jump of 1.
It can be as twice as smaller or bigger without significant change in spectrum quality.
More important is the sample uniformity (particle size).



Ø5 mm pellets	Ø13 mm pellets
weights 2–20 mg, less consumption but more difficult to handle	weight 10–100 mg
easier to remove from dies	
more samples in the holder	

Dilute your powder with a supporting agent: BN (boron nitride), polyethylene, cellulose, sugar etc.

Probably, the mostly used one is BN. To my experience, it gives fragile pellets strongly adhesive to dies.

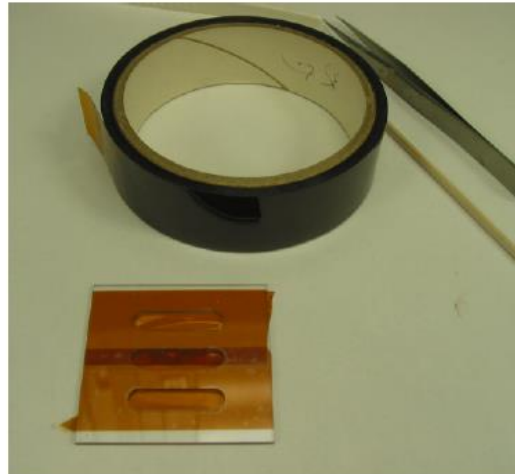
With PE and cellulose the pellets are more durable and easier to press. We will provide cellulose.

Do not put more than 1 ton! By pressing stronger you destroy the pellets rather than make them firmer. For \varnothing 5 mm dies 0.5 ton is enough.



Sample Preparation: Diluted Powder

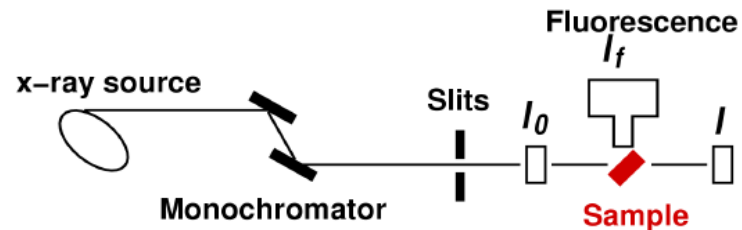
We start with a blank sample holder with known dimensions, and cover one side with tape.



We calculate the necessary mass of material (from absorption thickness, sample holder cross-section, and sample density).

The powder should be ground to give very fine particle size ($< 1/\Delta\mu!!$). Many people use a sieve to separate particle sizes. A 400-mesh sieve has wires $\sim 37 \mu\text{m}$ apart. That's a good start, but not fine enough for most transmission XAFS samples.

X-ray Absorption Measurements



XAS measures the energy dependence of the x-ray absorption coefficient $\mu(E)$ at and above the absorption edge of a selected element. $\mu(E)$ can be measured in two ways:

Transmission: The absorption is measured directly by measuring what is transmitted through the sample:

$$I = I_0 e^{-\mu(E)t}$$
$$\mu(E)t = -\ln(I/I_0)$$

Fluorescence: The re-filling the deep core hole is detected. Typically the fluorescent x-ray is measured, but sometimes emitted electrons are measured. Either way,

$$\mu(E) \propto I_f/I_0$$

X-ray Absorption Measurements: Experimental Design

Important items for an XAFS measurement:

Monochromatic x-rays: Need x-rays with a small energy spread or bandwidth:
 $\Delta E \approx 1 \text{ eV}$ at 10keV.

Linear Detectors: The XAFS $\chi(k) \sim 10^{-2}$ or smaller, so we need a lot of photons and detectors that are very linear in x-ray intensity (ion chambers). These usually means using a synchrotron source.

Well-aligned Beam: The x-ray beam hitting the detectors has to be the same beam hitting the sample.

Homogeneous sample: For transmission measurements, we need a sample that is of uniform and appropriate sample thickness of ~ 2 absorption lengths. It should be free from pinholes. If a powder, the grains should be very fine-grained (absorption length) and uniform.

Counting Statistics: For good data $\mu(E)$ should have a noise level of about 10^{-3} . That means we need to collect at least 10^6 photons.

Transmission: Fluxes at synchrotrons are $> 10^8$ photons/sec.
Count rate is not much of an issue.

Fluorescence: May be a concern, especially when concentrations are very low.

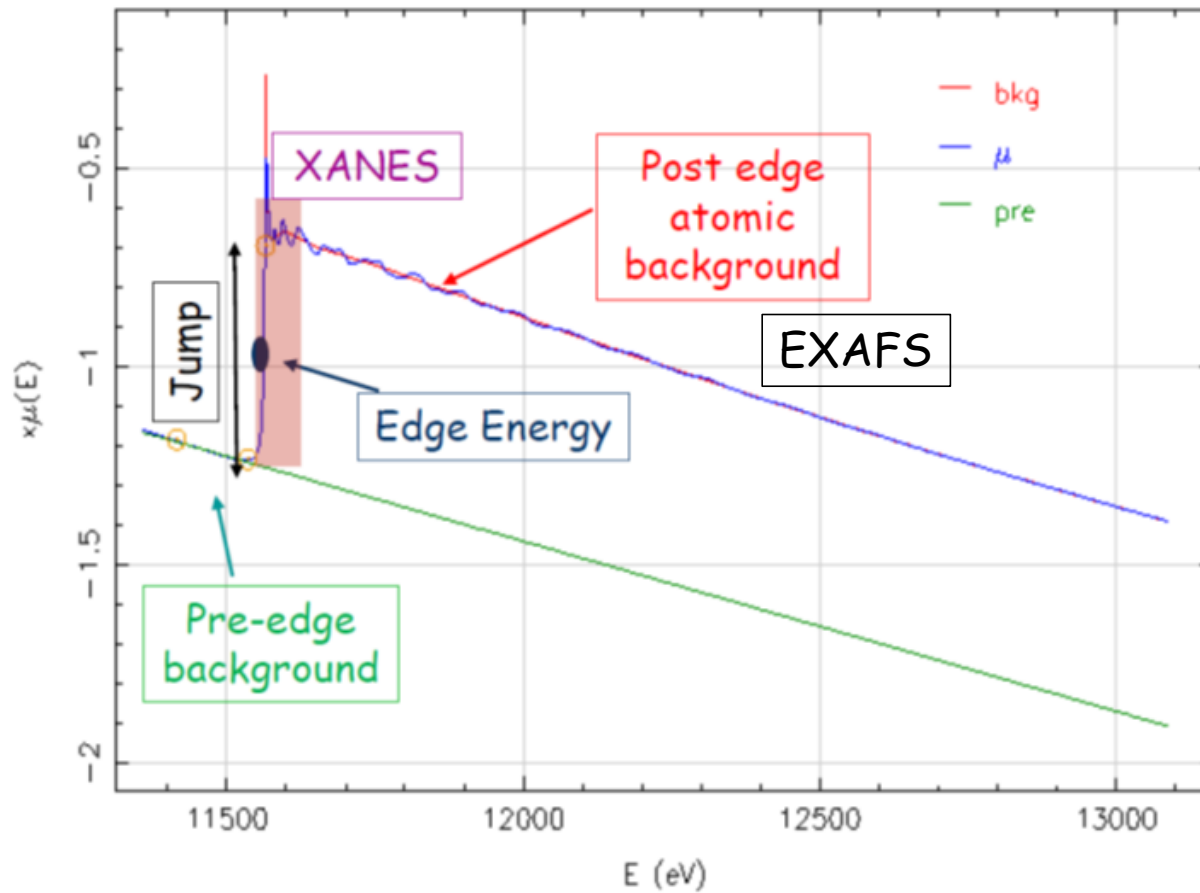
X-ray Absorption Measurements: The Experiment

Energy Scanning The monochromator gives an energy-tunable x-ray source, so we can scan energy across the absorption edge. We'll scan from ~ 200 eV below to ~ 800 eV above the selected edge energy E_0 , like this:

Region	Starting Energy (eV)	Ending Energy (eV)	Step Size (eV)
Pre-edge	$E_0 - 200$	$E_0 - 20$	5.0 – 10
XANES	$E_0 - 20$	$E_0 + 30$	0.25 – 1.0
EXAFS	$E_0 + 30$	$E_0 + \sim 800$	0.05 \AA^{-1}

- In the EXAFS region, it's common to step in k rather than energy.
- Typical count times are 1 to 15 seconds per point, so that a spectrum is collected in 10 minutes to several hours (dilute samples take longer than concentrated samples!). Multiple sweeps is common.
- Very fast measurements (1 second for the whole spectra) can be made at specialized beamlines.

Characteristics of a XAFS spectrum





School on Synchrotron Light Sources and their Applications, 6 - 17 Dec. 2021

Data Pre-Processing and XANES Analysis and Interpretation

Messaoud Harfouche

Synchrotron-light for Experimental Science and Applications in the Middle East, Jordan

XAFS study: from experiment to results

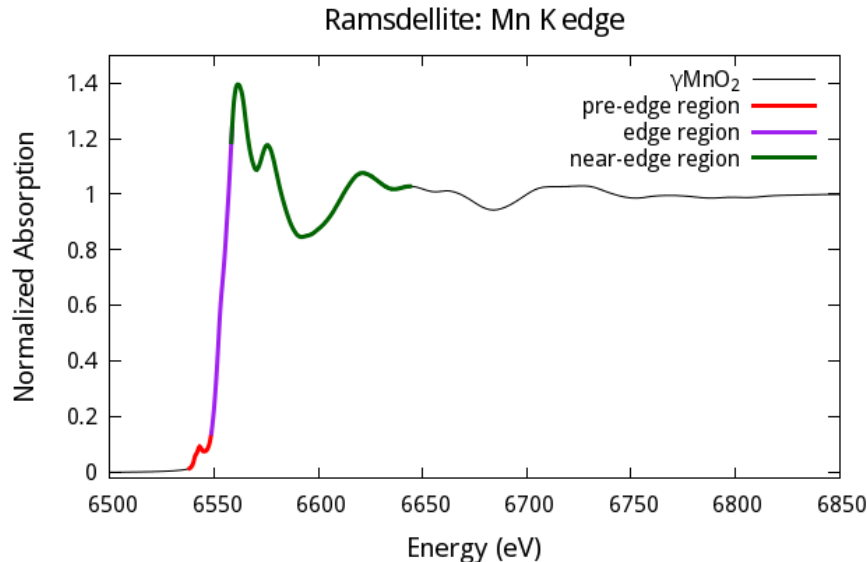
Data collection

```
graph TD; A[Data collection] --> B[Preliminary data treatment];
```

Preliminary data
treatment

Some vocabulary

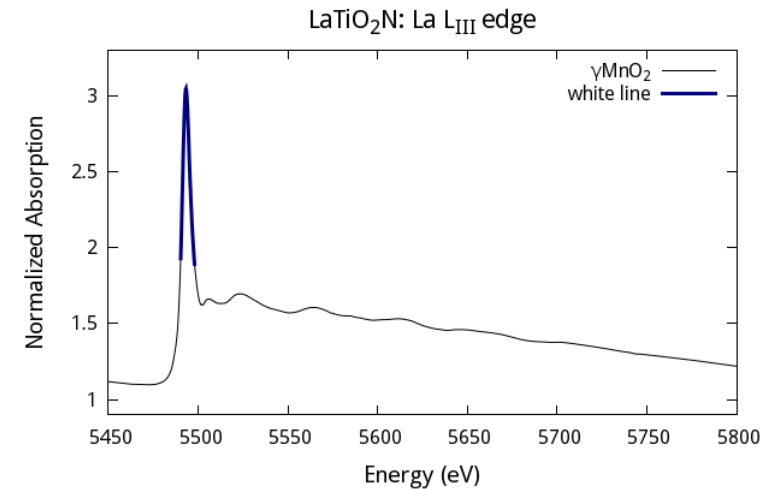
Words commonly used to describe specific parts of the XANES spectrum.



pre-edge Small (possibly large, certainly meaningful!) features between the Fermi energy and the threshold

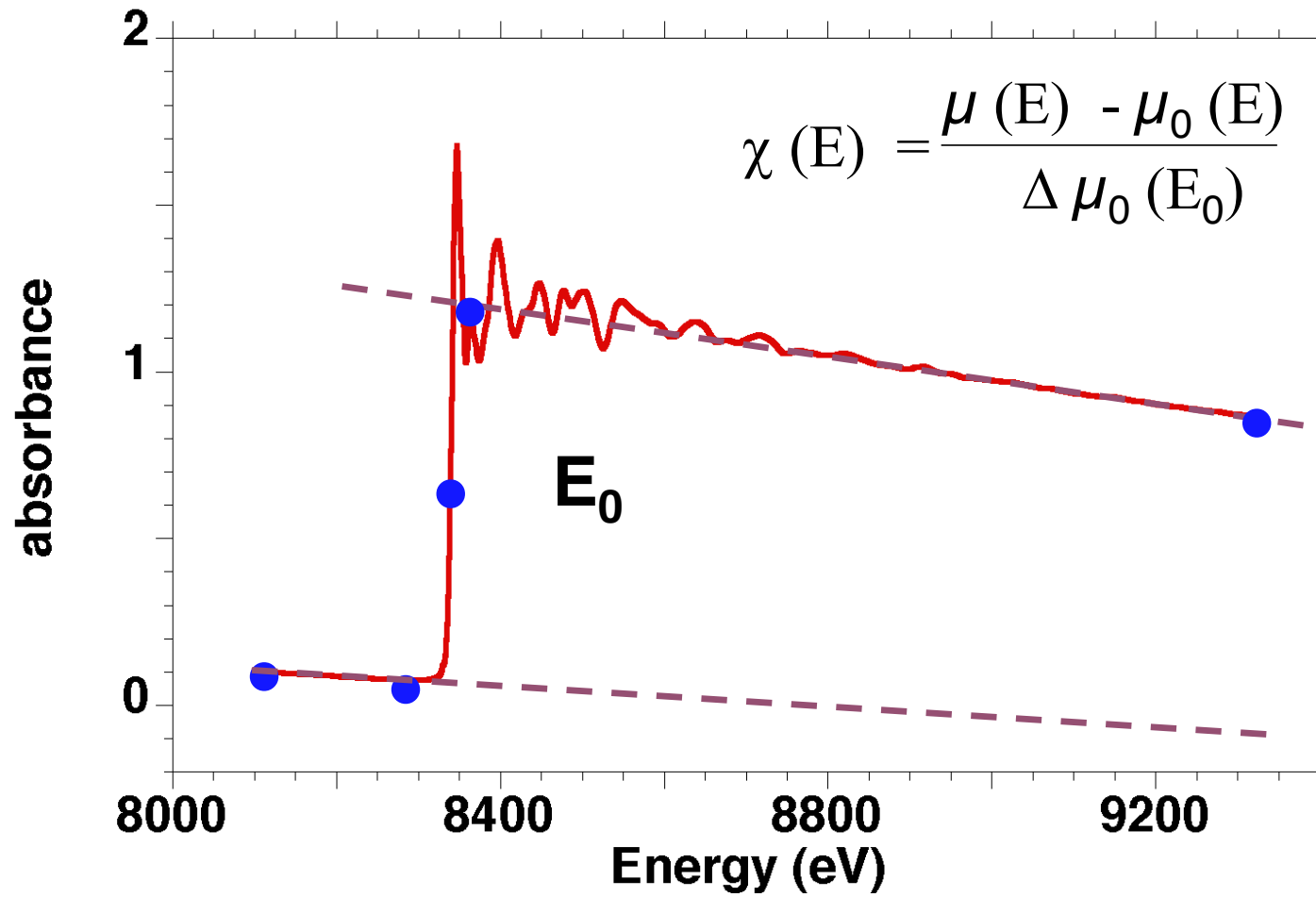
edge The main rising part of XAS spectrum

near-edge Characteristic features above the edge

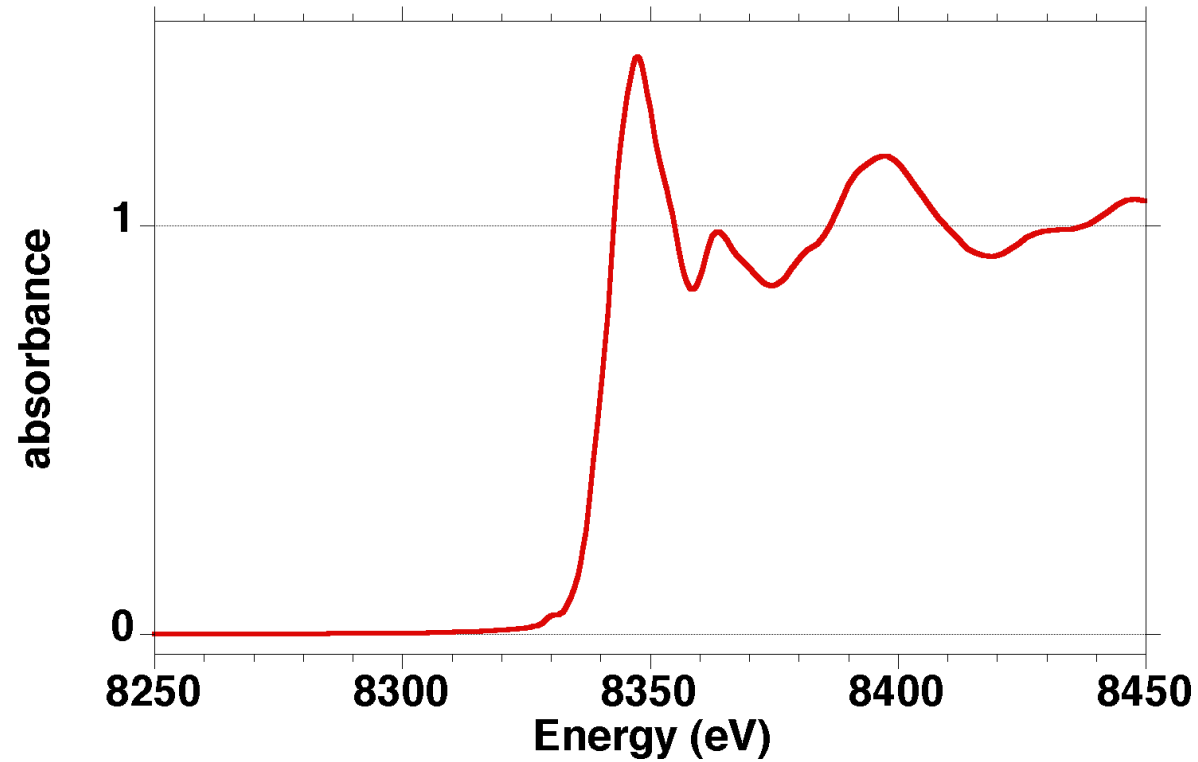


white line Large, prominent peak just above the edge, particularly in L or M edge spectra

- normalizing the spectra at zero before and at 1 after the edge :

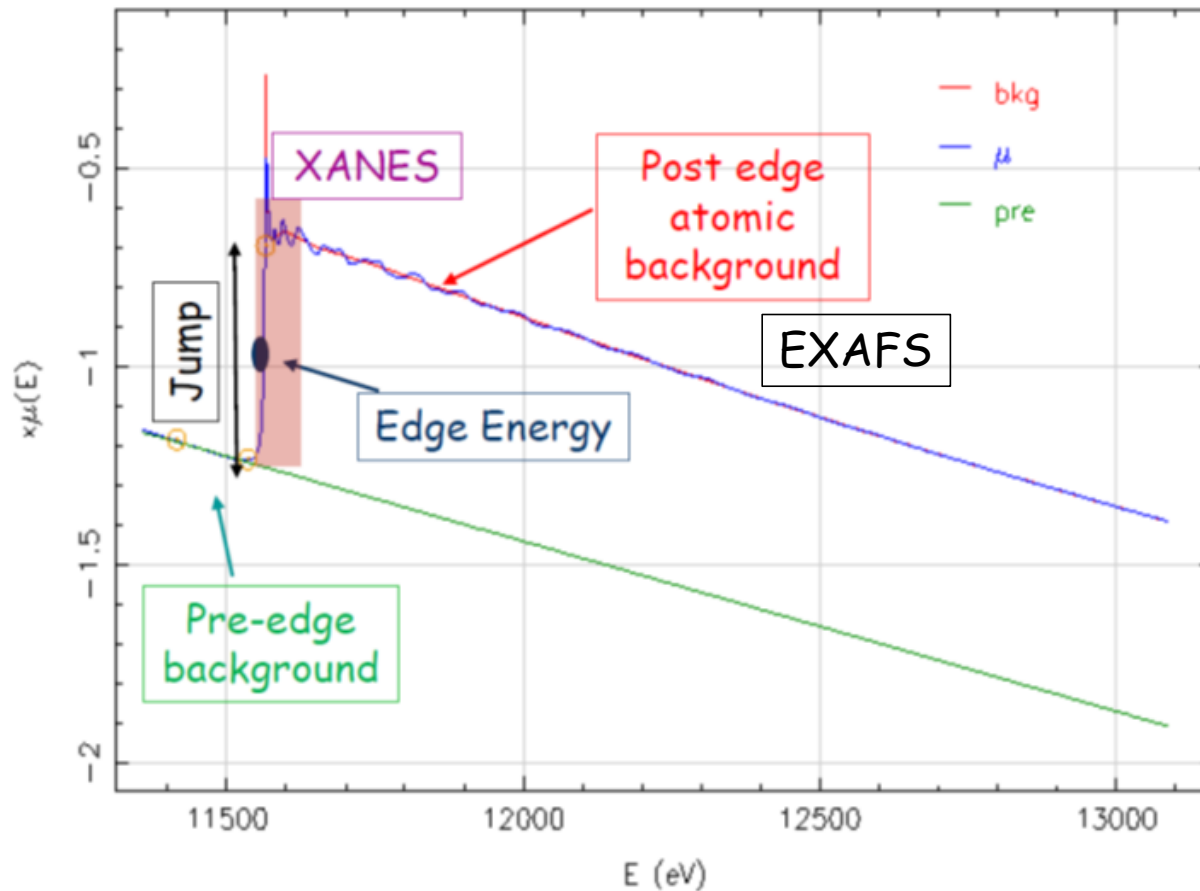


- normalizing the XANES region at zero before the edge and at 1 after the edge :



**their pre-edge studies are now possible
on these normalized XANES spectra...**

Peeling the XAFS spectrum Step by Step



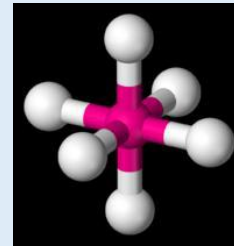


Transition metals K pre-edge peaks

Transition with a quadrupolar character

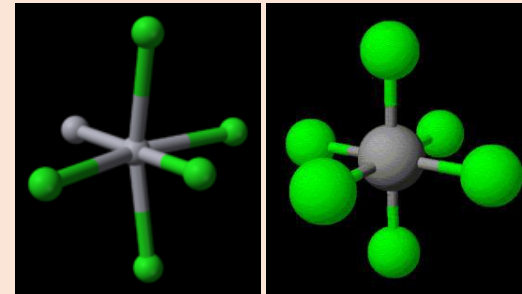
Pure octahedron

Centro-symmetry: no p-d mixing allowed
only (weak) quadrupolar transitions
No, or very low intensity prepeak



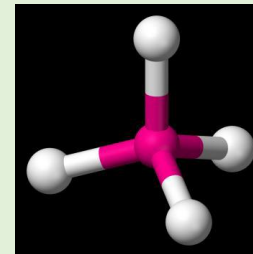
Distorted octahedron

Centro-symmetry broken: p-d mixing allowed
dipole transition in the edge
moderate intensity prepeak



Tetrahedron

No Centro-symmetry : p-d mixing allowed dipole
transition in the edge high intensity prepeak



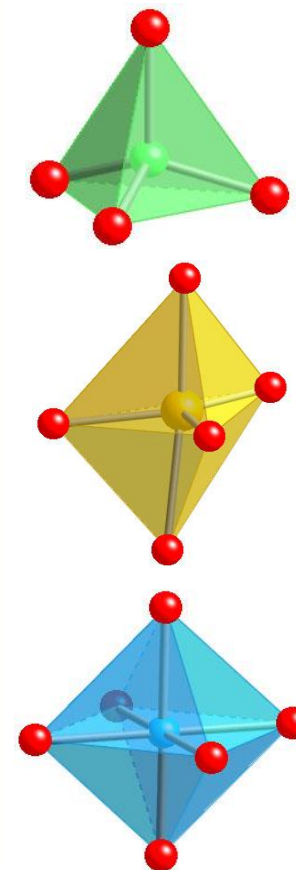
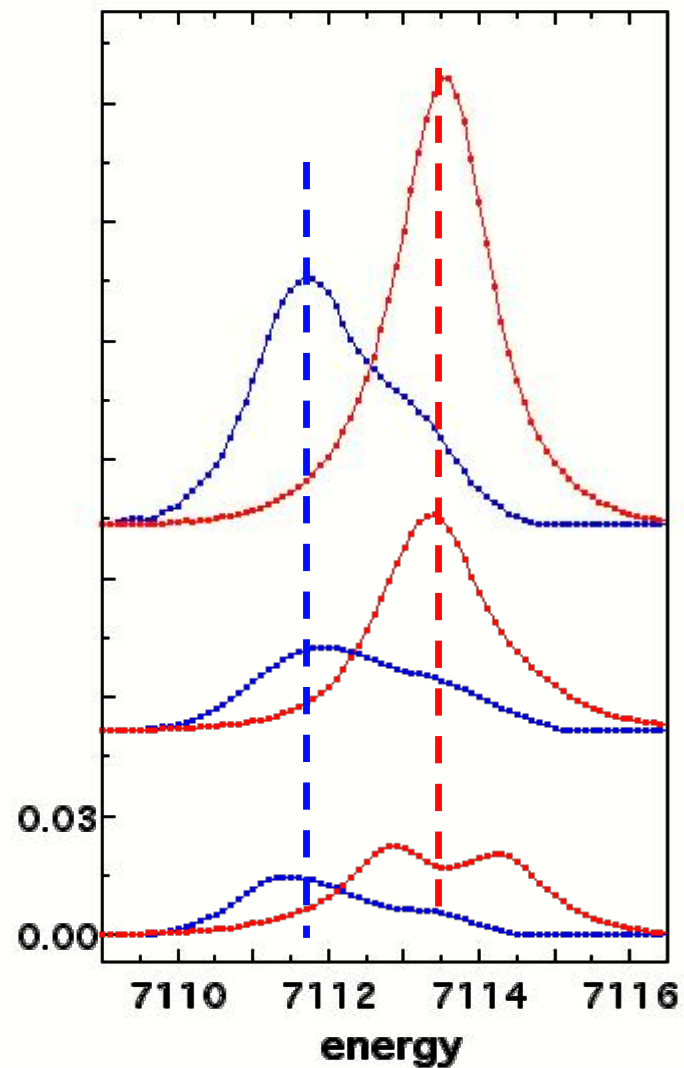


FUNDAMENTALS OF X-RAY ABSORPTION FINE STRUCTURE: XANES

XANES Pre-edge Analysis

- redox

- symmetry





XANES Interpretation

The EXAFS Equation breaks down at low-k, and the mean-free-path goes up. This complicates XANES interpretation:

There is no simple equation for XANES

XANES can be described **qualitatively** (and nearly **quantitatively**) in terms of

coordination chemistry	regular, distorted octahedral, tetrahedral, . . .
molecular orbitals	p-d orbital hybridization, crystal-field theory, . . .
band-structure	the density of available electronic states
multiple-scattering	multiple bounces of the photoelectron

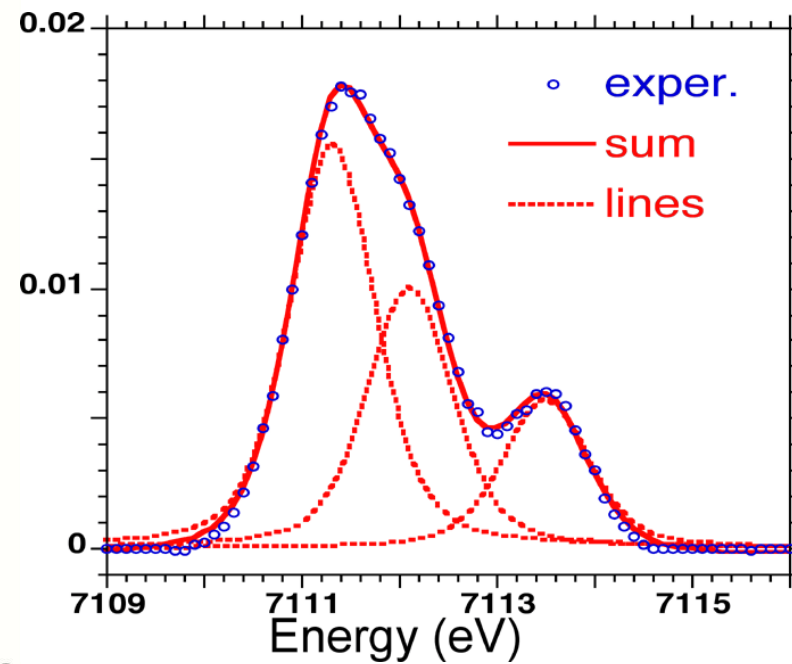
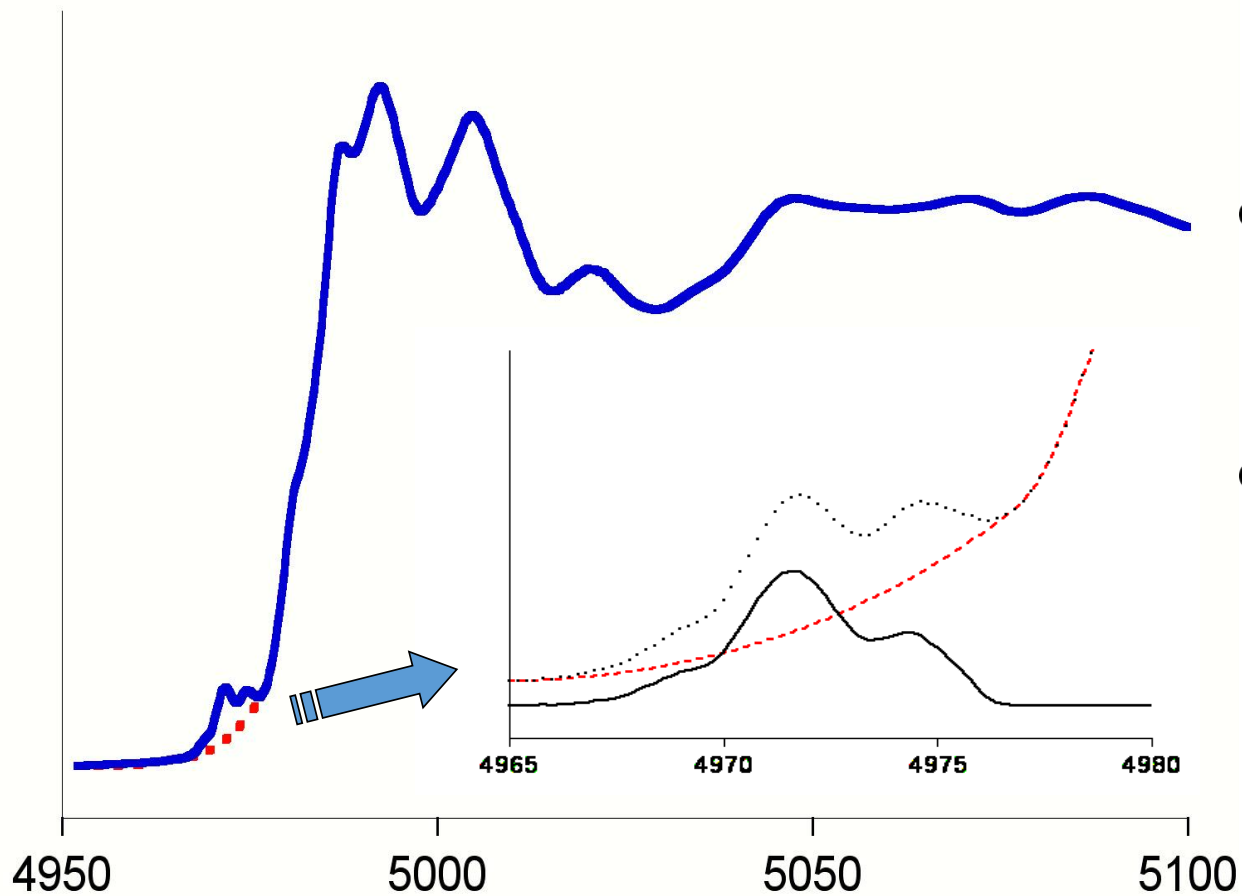
These chemical and physical interpretations are all related, of course:

XANES calculations are becoming reasonably accurate and simple. These can help explain what **bonding orbitals** and/or **structural characteristics** give rise to certain spectral features.

Quantitative XANES analysis using first-principles calculations are still rare, but becoming possible...

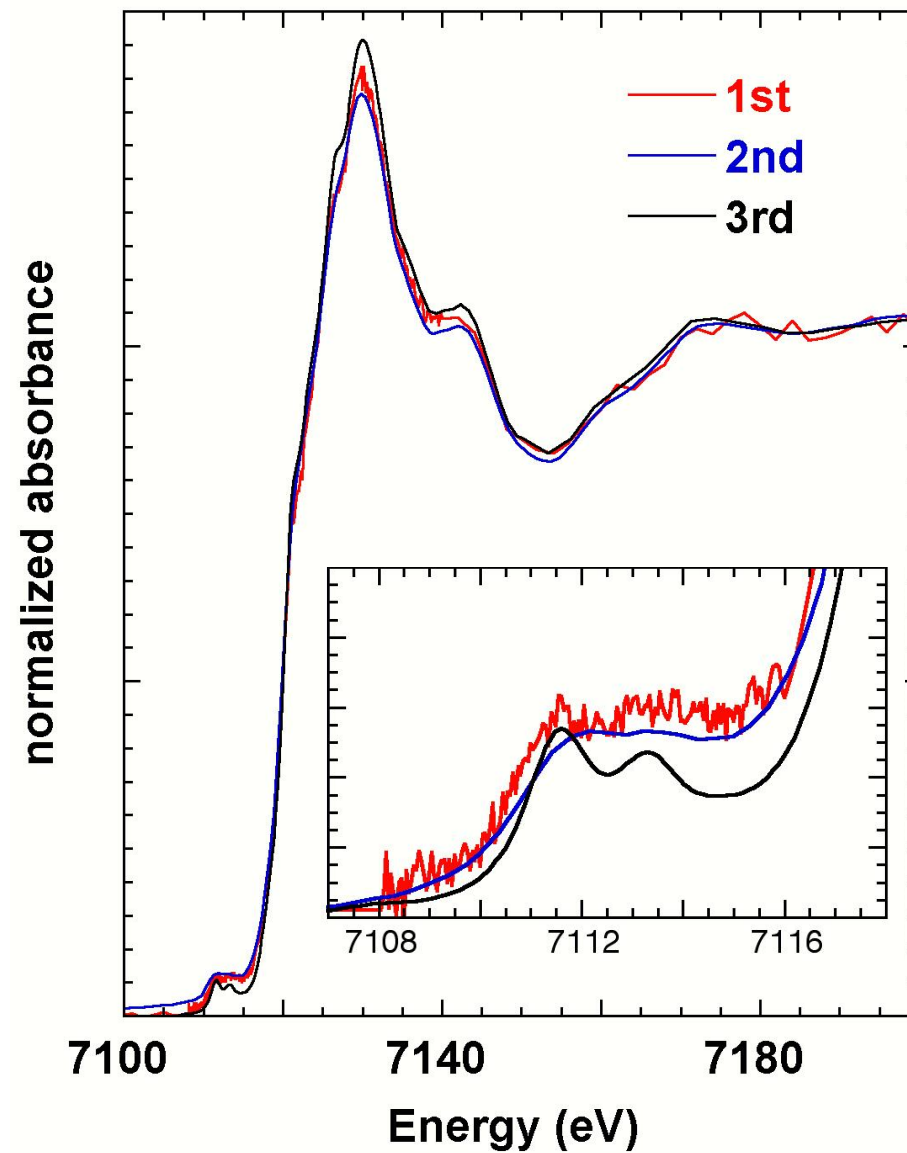
Pre-edge

- rutile (TiO_2) at the Ti K-edge



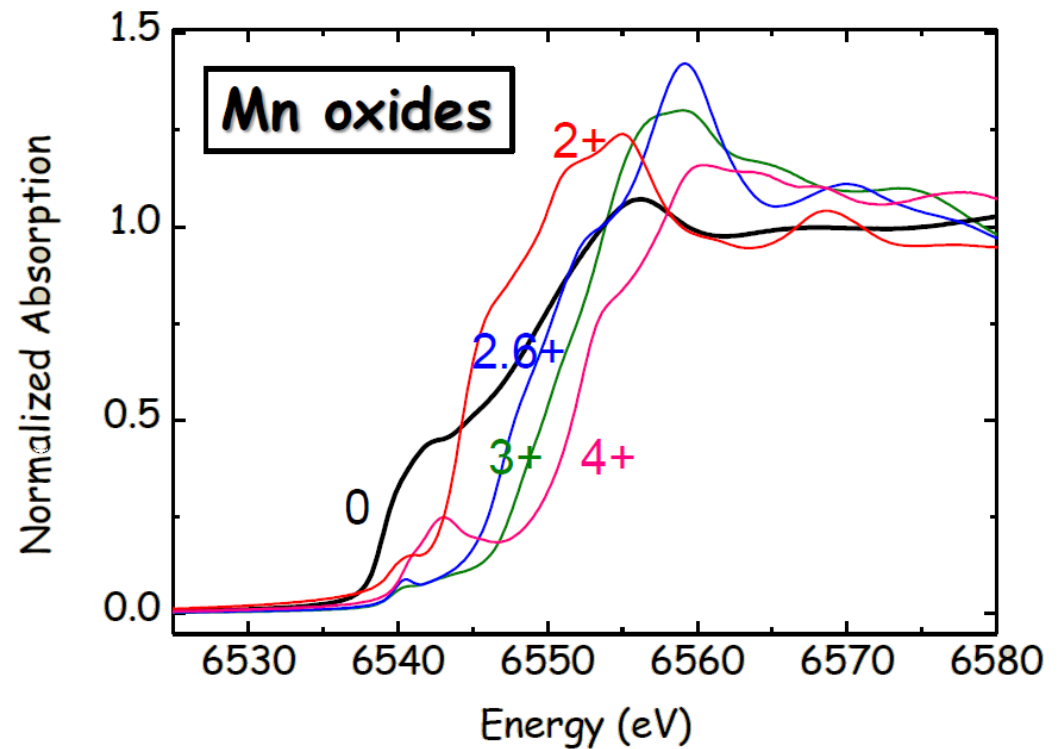
caveats :

- need resolution
- need high S/N
- some other transitions (rare) quadrupolar or metal/metal

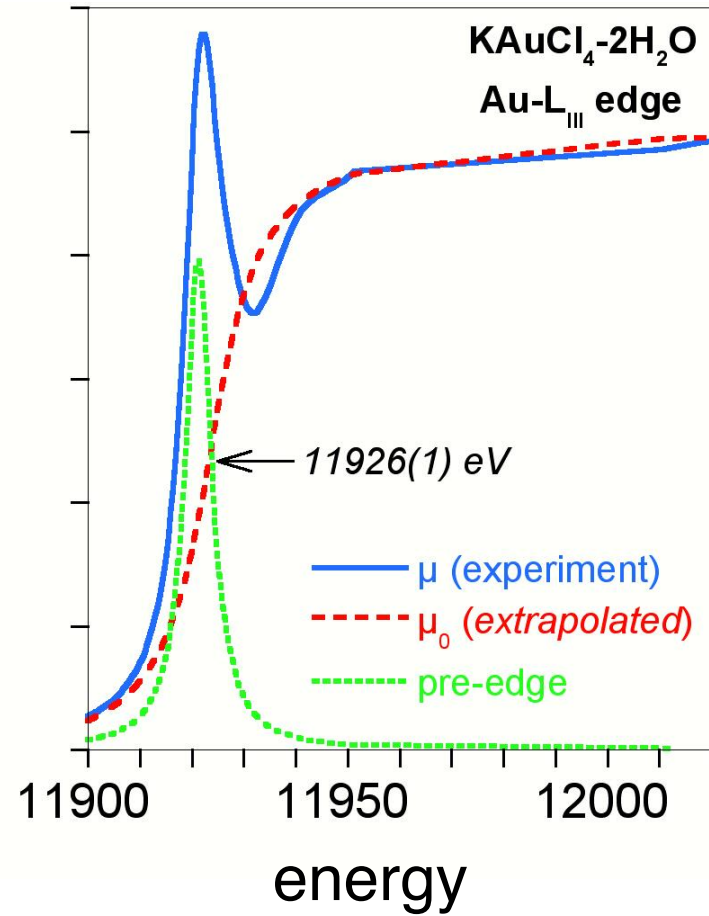
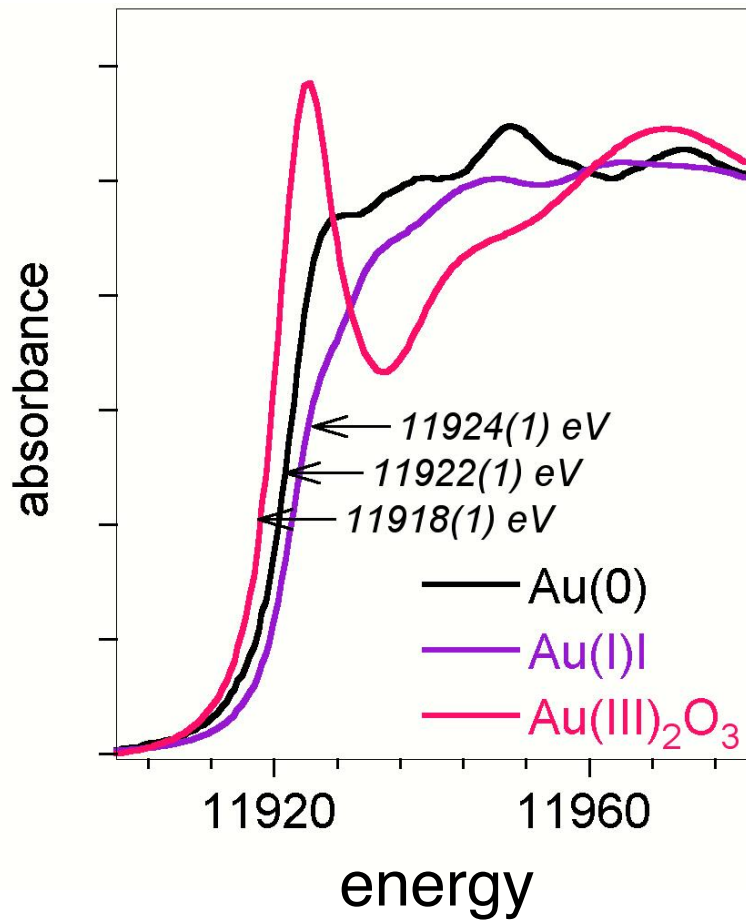


Edge position:

Many edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.



caveat: interferences from pre-edge and scattering



edge for Au(III) before that for the metal !!

because the edge is a gigantic pre-edge !

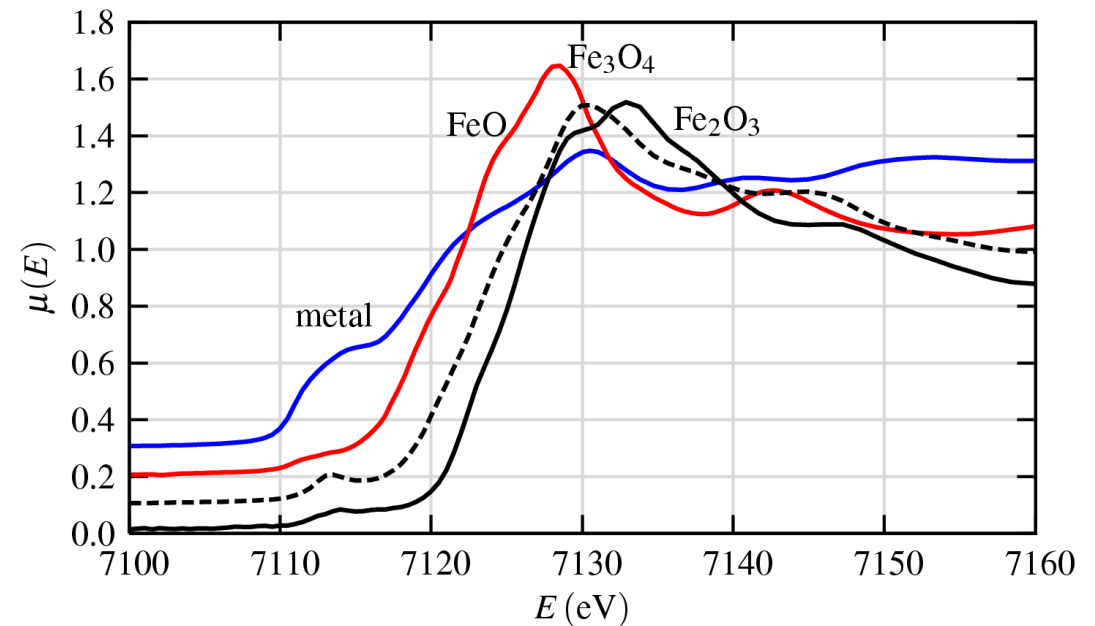
Edge position:

Finger print

The simplest way of using XAS is to simply identify chemical species in a sample of unknown composition.

Compare the signal from your with the standards to identify the dominant species.

Qualitative



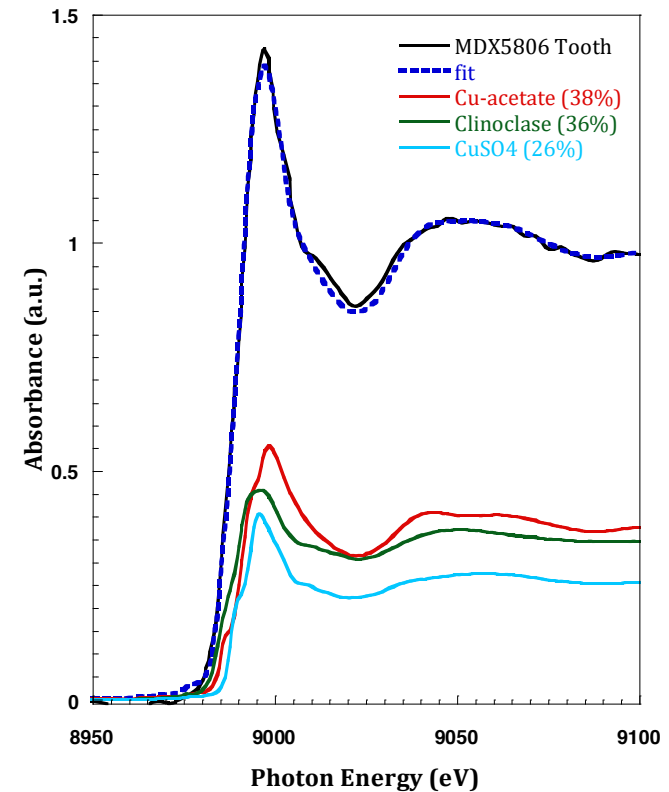
There are a variety of quantitative tools available for interpreting XANES data.

XANES: Linear Combination Fitting

- Can be used in heterogeneous/Natural samples
- Bulk XAFS

Determine the percentage of each oxidation state
(quantitative)

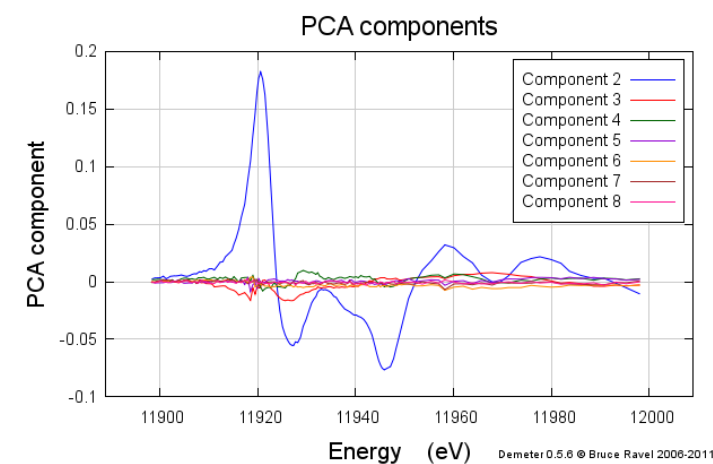
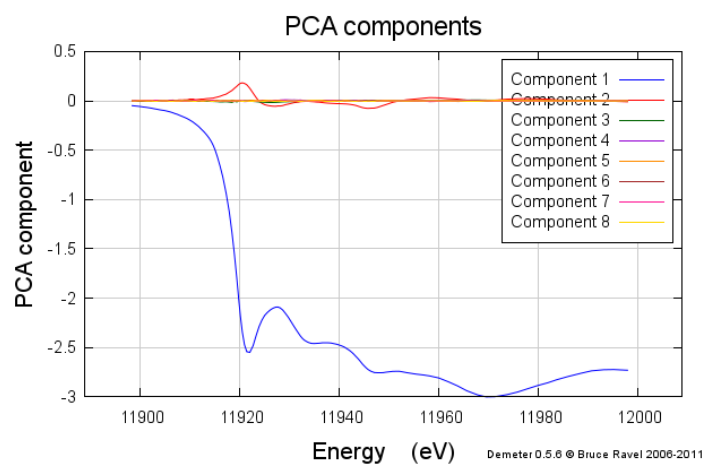
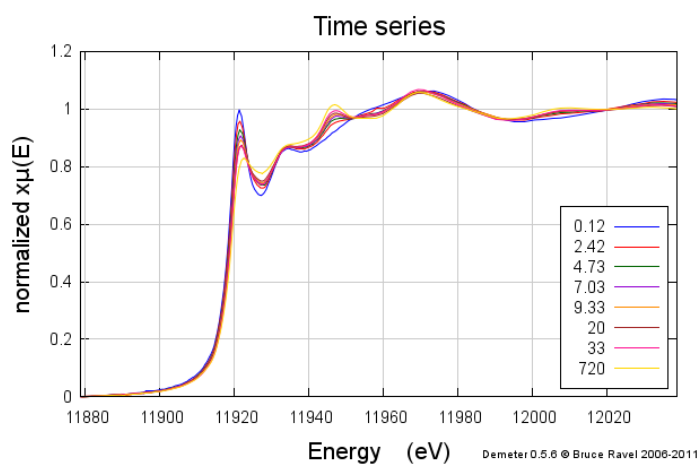
Identify the possible species
(semi quantitative)



Need to measure model compounds and references (not always available)

XANES: Principle Components Analysis

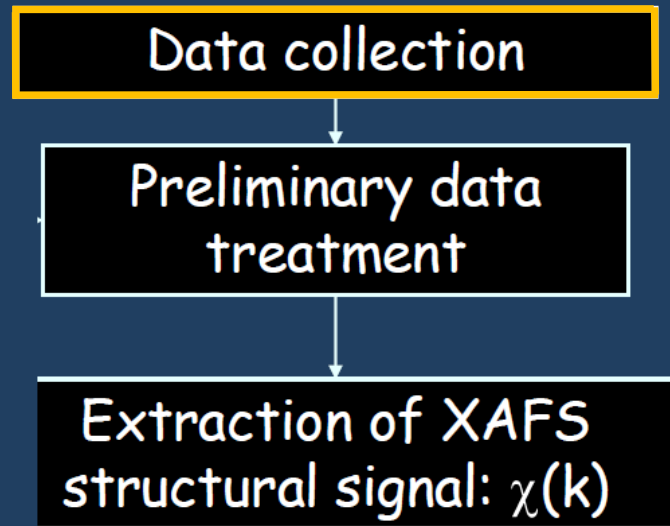
PCA is a bit of linear algebra which breaks down an ensemble of related data into abstract components.



The components can then be used to try to construct a standard as a test to see whether that standard is present in the ensemble.

The number of species represented in the ensemble is related to the number of statistically significant components.

XAFS study: from experiment to results



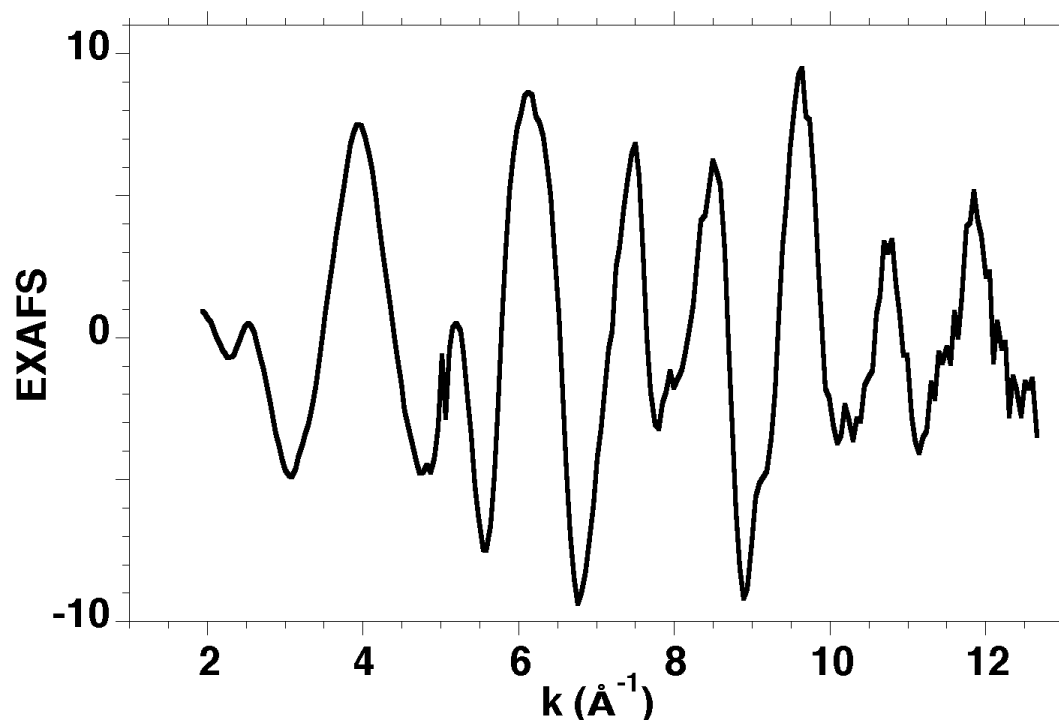
EXAFS: Data Processing

energies are recalculated
into the photo-electron
momentum, k :

$$k = \sqrt{2m / \hbar^2 \cdot (E - E_0)}$$

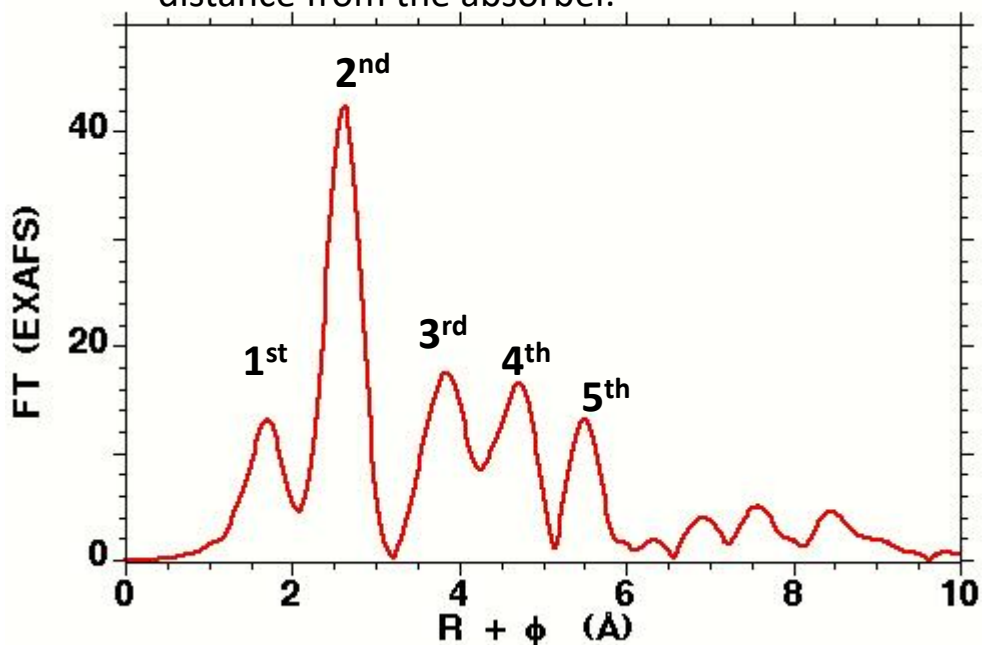
with E_0 is the edge energy, h is Plank constant and m is the electron's mass

EXAFS spectra are
weighted by k^2/k^3 to
enhance high- k signals

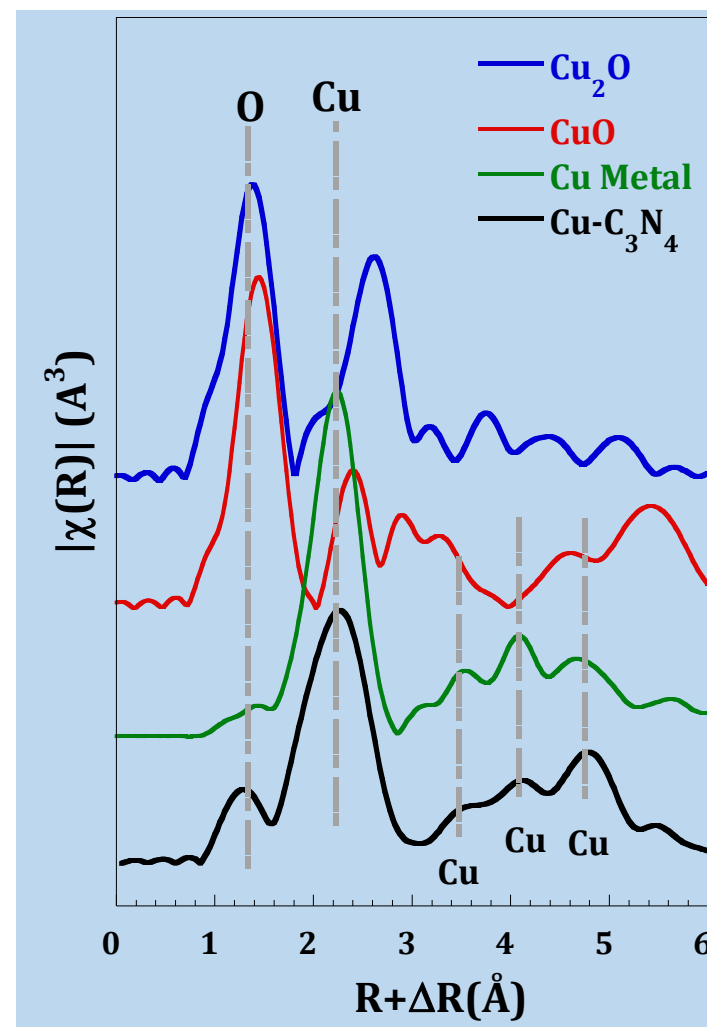


EXAFS: Data interpreting

Fourier Transform of EXAFS signal provides a photoelectron scattering profile as a function of the radial distance from the absorber.



Fourier Transforms are used to visualize the various contributions to the EXAFS arising from the shells of neighbors

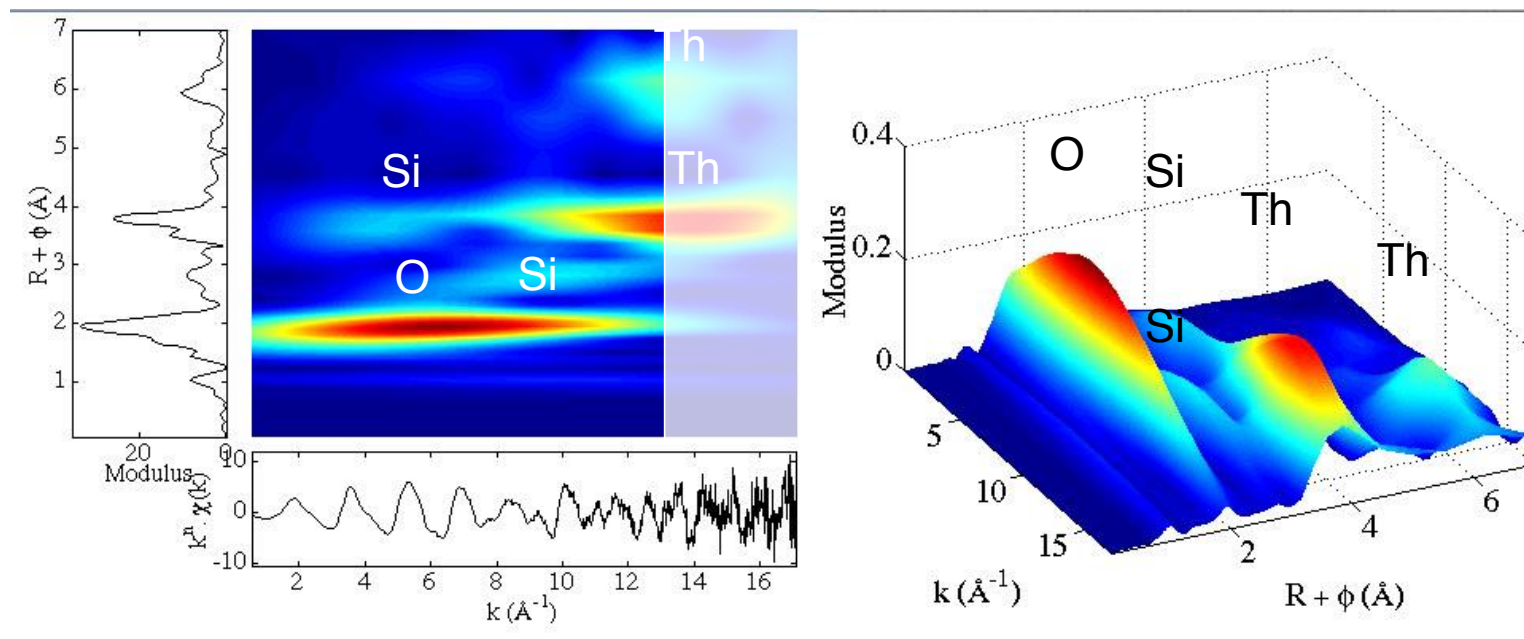


Similar to XANES

Compare the signal from your with the standards to identify the possible similarities with references

EXAFS: Data interpreting

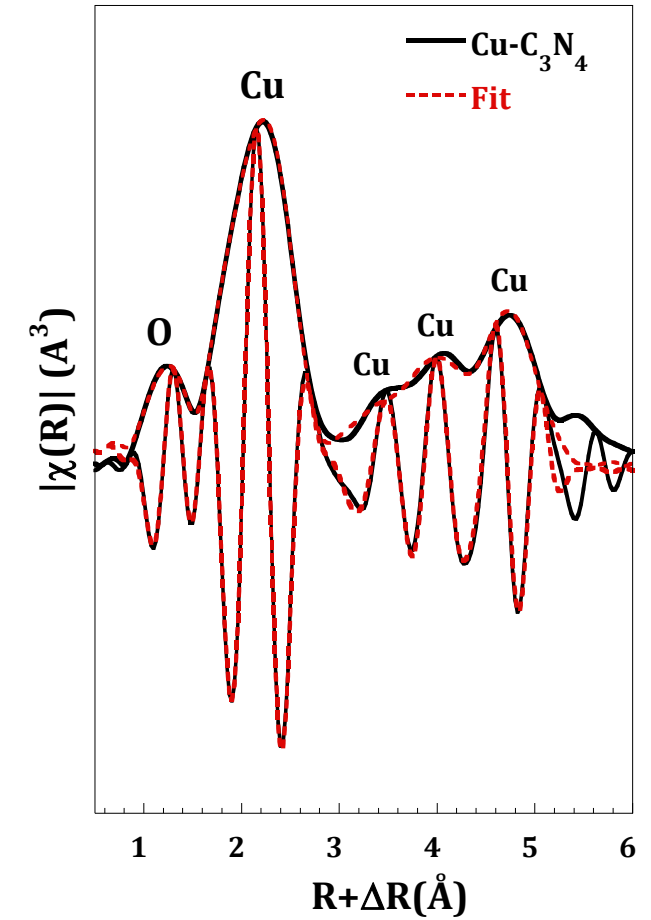
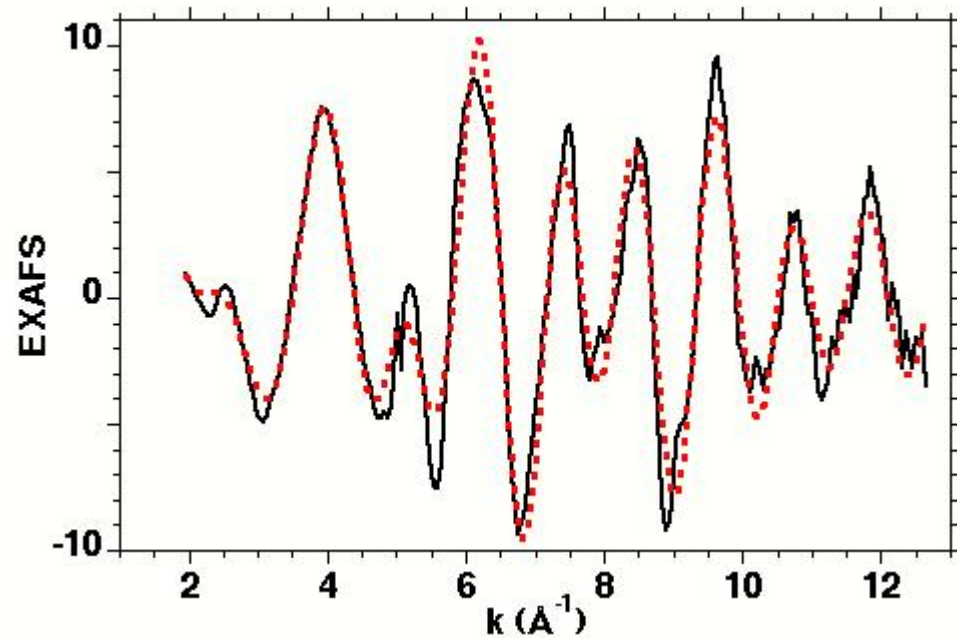
- wavelet studies of EXAFS provides a clearer view on the k-R dependencies :



- Si near 3 and 4 \AA are detected but not near 6 \AA
- also, cutting data at $k=13 \text{\AA}^{-1}$ is fine for O but not OK for Th

EXAFS: Data analysing (fitting)

- EXAFS are modelled to derive structural parameters



Acknowledgment

Some slides are derived from other presentations by:

Bruce Ravel → Lead Beamline Scientist for beamline 6-BM, NSLSII, USA

François Farges → Professeur des universités 1ère classe
au Muséum national d'Histoire naturelle, Paris, France

Giuliana Aquilati → Head of XAFS and XRF beamlines, Elettra, Italy

Data we will use for the demonstration are from *XAFS beamline* at Elettra, Italy

Demonstration

XANES

NEXT 