X-Ray Absorption Spectroscopy

Matt Antalek
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KIPAC

Overview

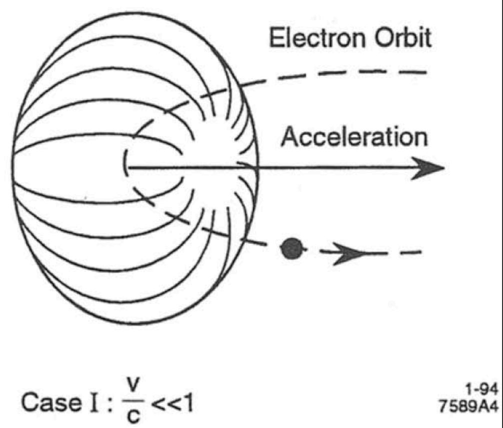
- How a beamline is set up
  - Synchrotron
  - Upstream Optics
  - Experimental Hutch
- How XAS works
  - How spectra are obtained
  - The XAS spectrum
  - Spectral components
- Data Analysis and Examples

Beamline Basics

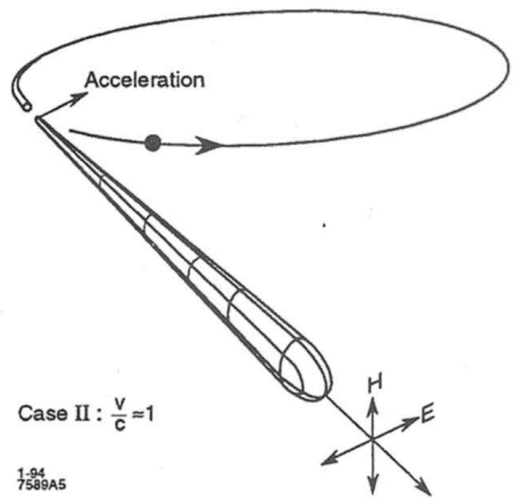
- Synchrotron
  - Accelerates electrons at relativistic speeds
  - As electrons undergo acceleration they emit photons
  - These photons are high in energy with short wavelengths, in the range of 10^{-9}m to 10^{-11} m
  - SSRL operates at 3GeV

Beamline Basics

Electrons in *circular motion* are also undergoing acceleration



When electrons are moving slowly the radiation comes out in ***doughnut pattern***

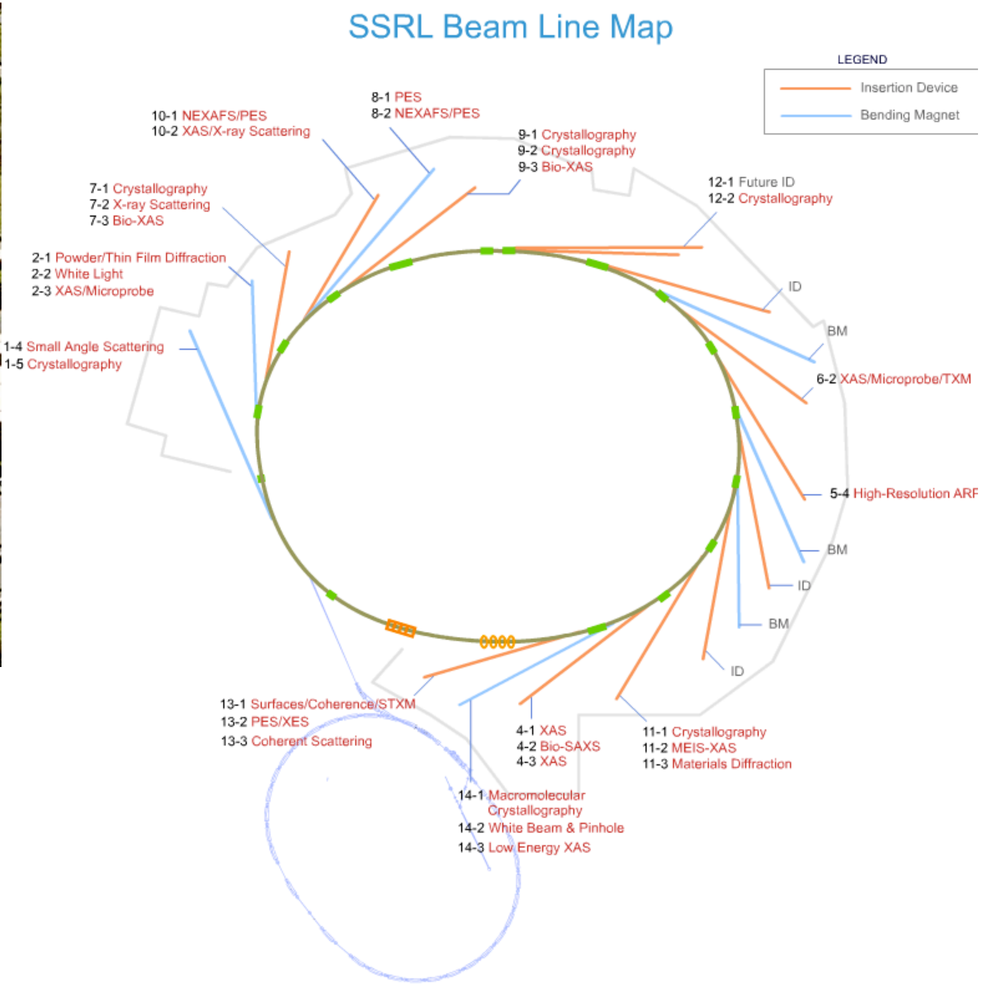


When the electron speed gets close to the speed of light, the radiation comes out only in a narrow forward cone; ***a laser-like concentrated stream***

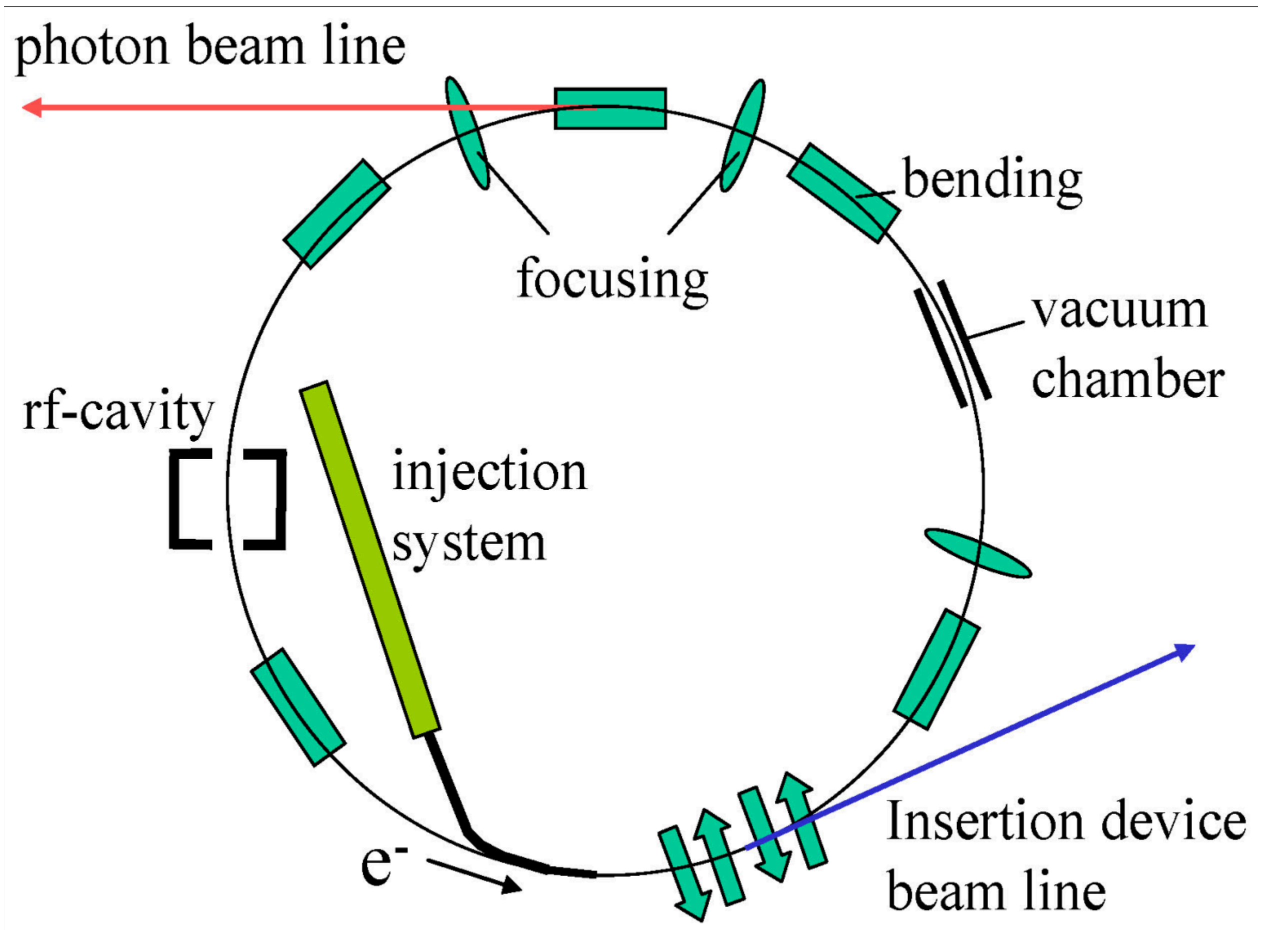
- In SPEAR electron speed is 99.999999% speed of light

Graphic obtained from Tom Rabedeau

SSRL


SSRL Beam Line Map
LEGEND
Insertion Device
Bending Magnet
8-1 PES
8-2 NEXAFS/PES
10-1 NEXAFS/PES
10-2 XAS/X-ray Scattering
9-1 Crystallography
9-2 Crystallography
9-3 Bio-XAS
12-1 Future ID
12-2 Crystallography
7-1 Crystallography
7-2 X-ray Scattering
7-3 Bio-XAS
2-1 Powder/Thin Film Diffraction
2-2 White Light
2-3 XAS/Microprobe
ID
BM
1-4 Small Angle Scattering
1-5 Crystallography
6-2 XAS/Microprobe/TXM
5-4 High-Resolution ARF
BM
ID
BM
ID
13-1 Surfaces/Coherence/STXM
13-2 PES/XES
13-3 Coherent Scattering
4-1 XAS
4-2 Bio-SAXS
4-3 XAS
11-1 Crystallography
11-2 MEIS-XAS
11-3 Materials Diffraction
14-1 Macromolecular Crystallography
14-2 White Beam & Pinhole
14-3 Low Energy XAS

Beamline Basics

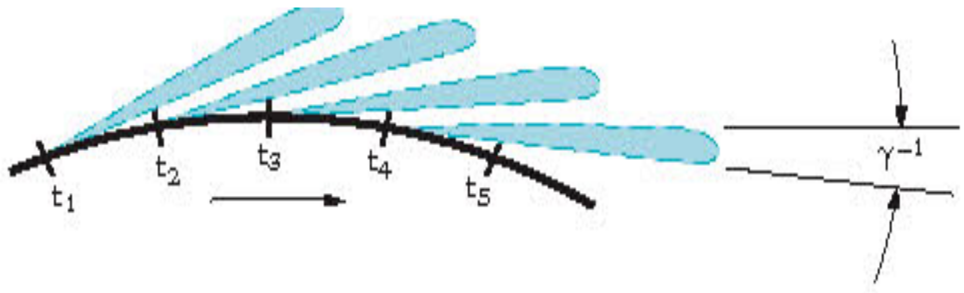


Graphics obtained from Tom Rabedeau

Beamline Basics

- Synchrotrons may contain extra devices
- These include bending magnets, wigglers and undulators
- Bending Magnets
  - Used to keep electron beam in circular motion
  - This is the most fundamental component of the synchrotron
  - Emits radiation in a sweeping arc

Beamline Basics



bending magnets - a "sweeping searchlight", BLs 1, 2, 8, 14 e_c= 7.78 keV

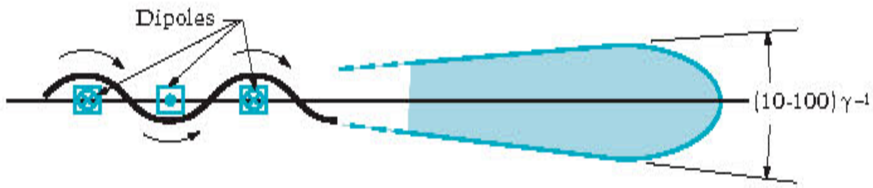
•Bend magnets can produce intense x-rays, but what if your experiment requires more keVs?

Graphic from Tom Rabedeau

Beamline Basics

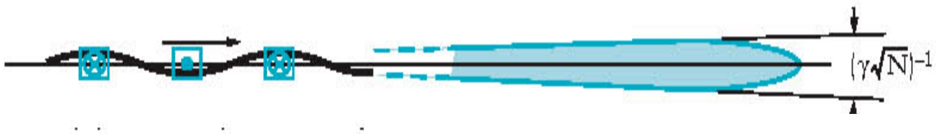
- Wigglers and Undulators
- Consist of an array if magnets arranged to “wiggle” or move the electron beam back and forth
- Wigglers produce incoherent radiation with a broad emission cone, emits continuous spectrum
- In undulators, magnets are appropriately spaced to produce coherent beam of radiation

Beamline Basics



- intensity ~ N_{poles}
- broad horizontal fan

wiggler - incoherent superposition of radiation from an array of magnet poles
BL6 ε_c= 5.39 keV,   BL7 ε_c= 12.2 keV



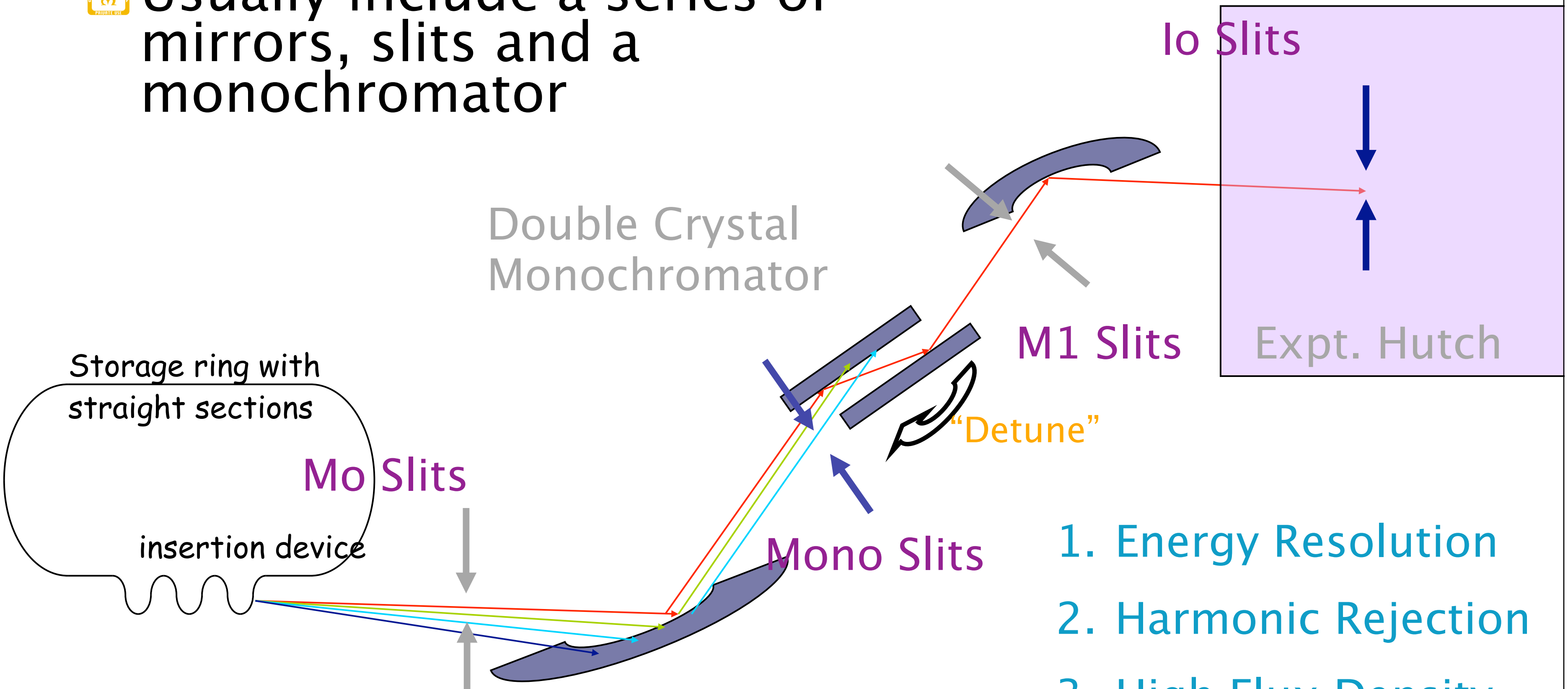
- intensity ~ $(N_{poles})^2$
- narrow horizontal emission cone

undulator - coherent interference of radiation from an array of magnet poles

Graphics obtained from Tom Rabedeau

Beamline Basics

- Upstream Optics
- Usually include a series of mirrors, slits and a monochromator



1. Energy Resolution
2. Harmonic Rejection
3. High Flux Density

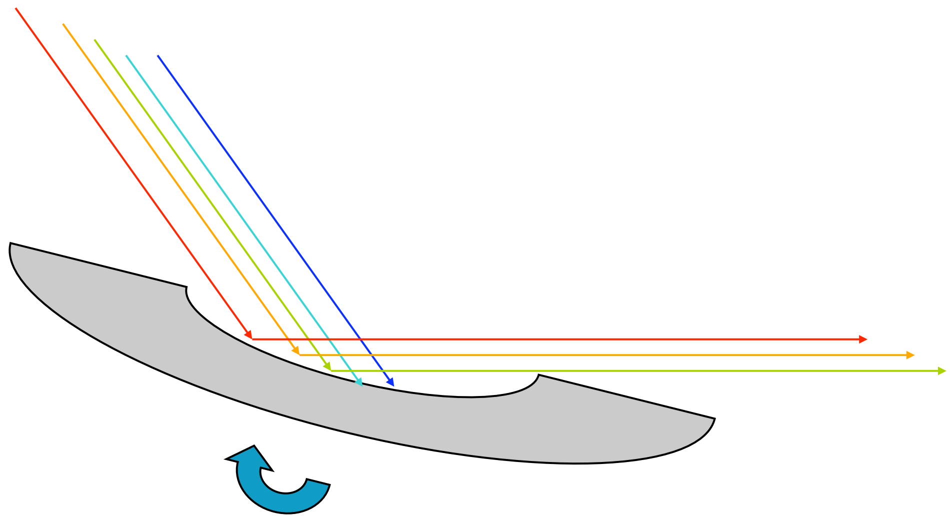
Graphic Obtained from Apurva Mehta

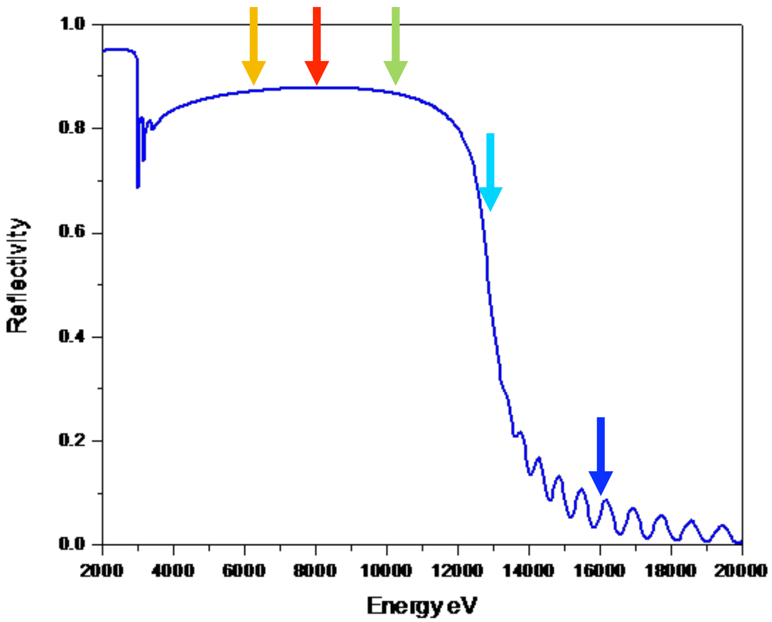
Beamline Basics

- Collimating/Harmonic rejection mirror
- Used to focus beam both vertically and horizontally
- Harmonic rejection mirrors are used to throw away photons at higher harmonics
  - Also done by de-tuning the monochromator, however this is generally not advised

Beamline Basics

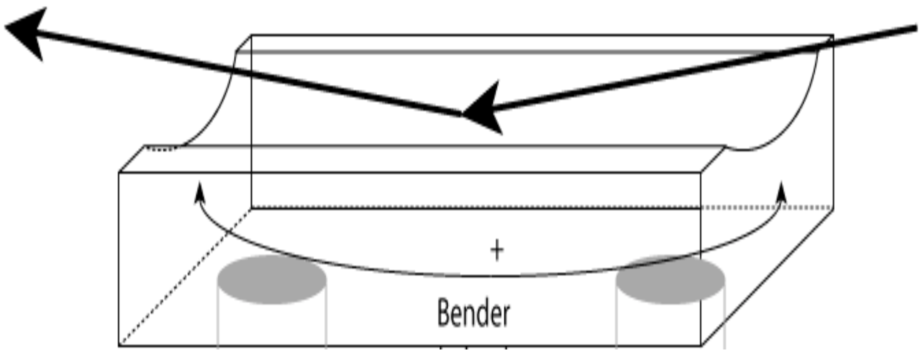
- Harmonic Rejection Mirror



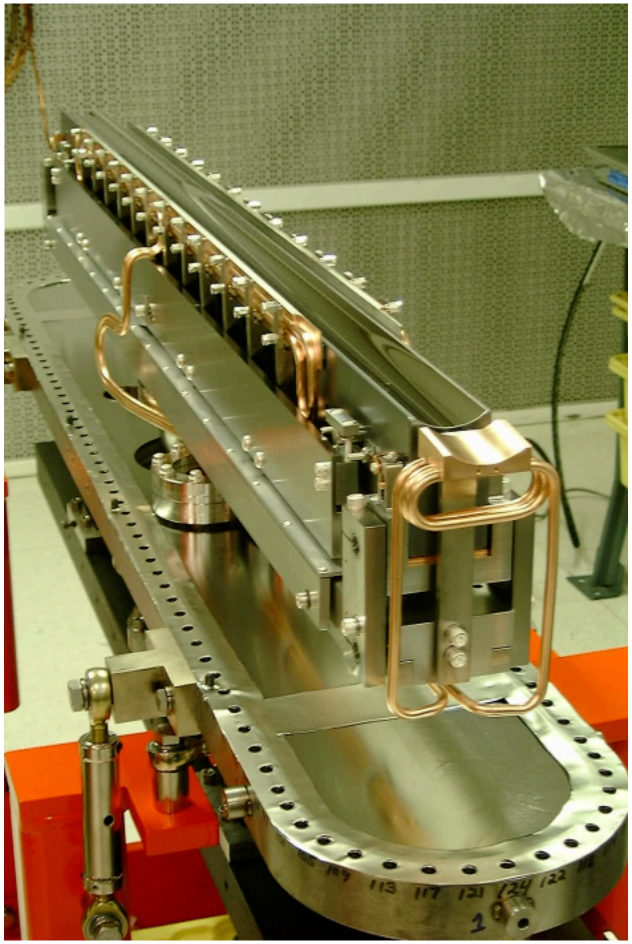


Graphic obtained from Apurva Mehta

Beamline Basics



•Focusing Mirrors

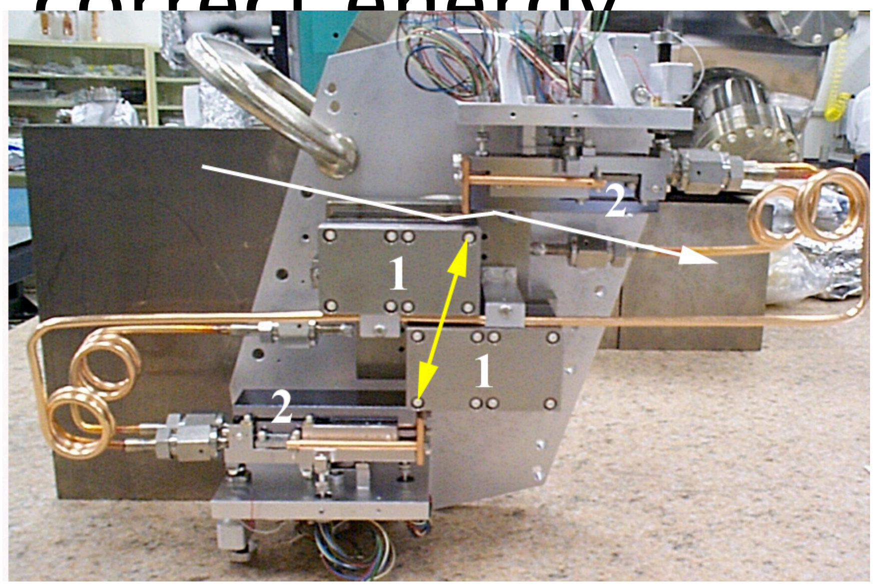


Beamline Basics

- Monochromator
- Essential to any beamline
- Allows for the selection of photons of a very specific energy
- Works on the principle of Bragg Diffraction
- Change energy by changing angle

Beamline Basics

- Can also be used with a series of slits before and after the monochromator to select for the correct energy



Beamline Basics

- Experimental Hutch
- Vary widely depending on type of experiment
- All contain ion chambers, and a detector
- Ion chambers used for sample calibration
  - Sample calibration can occur continuously or before and after scans depending on

Beamline Basics

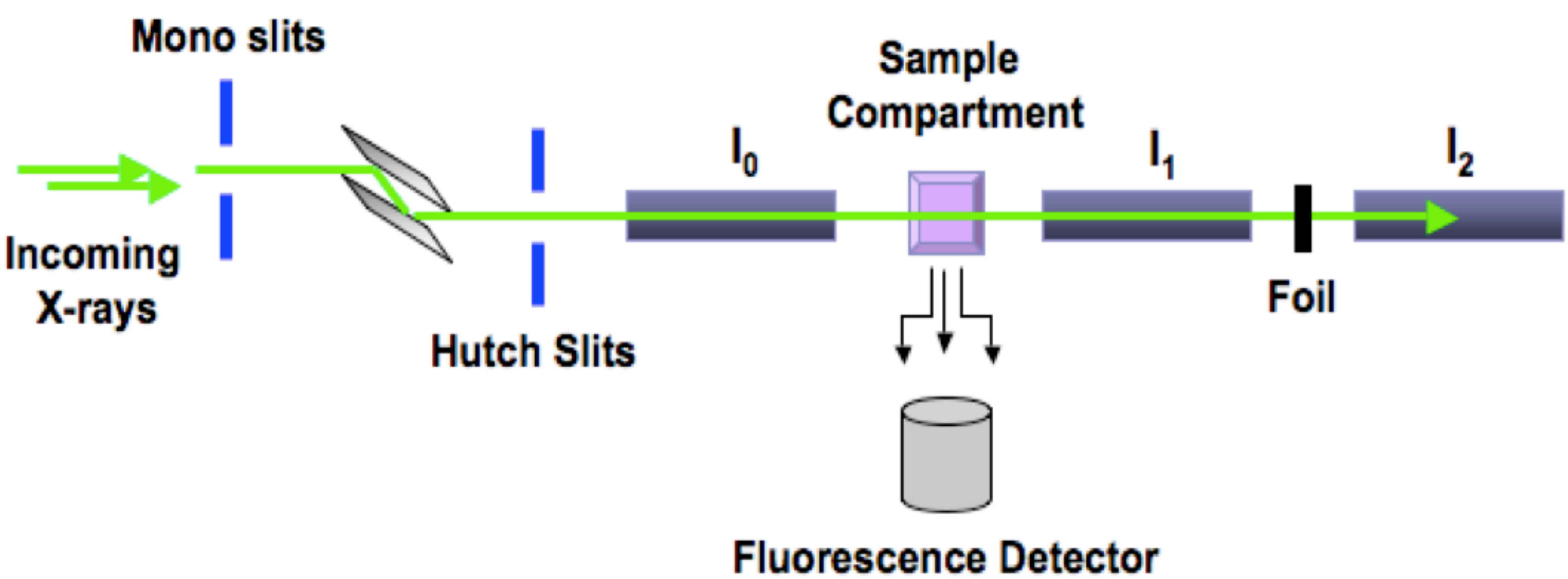
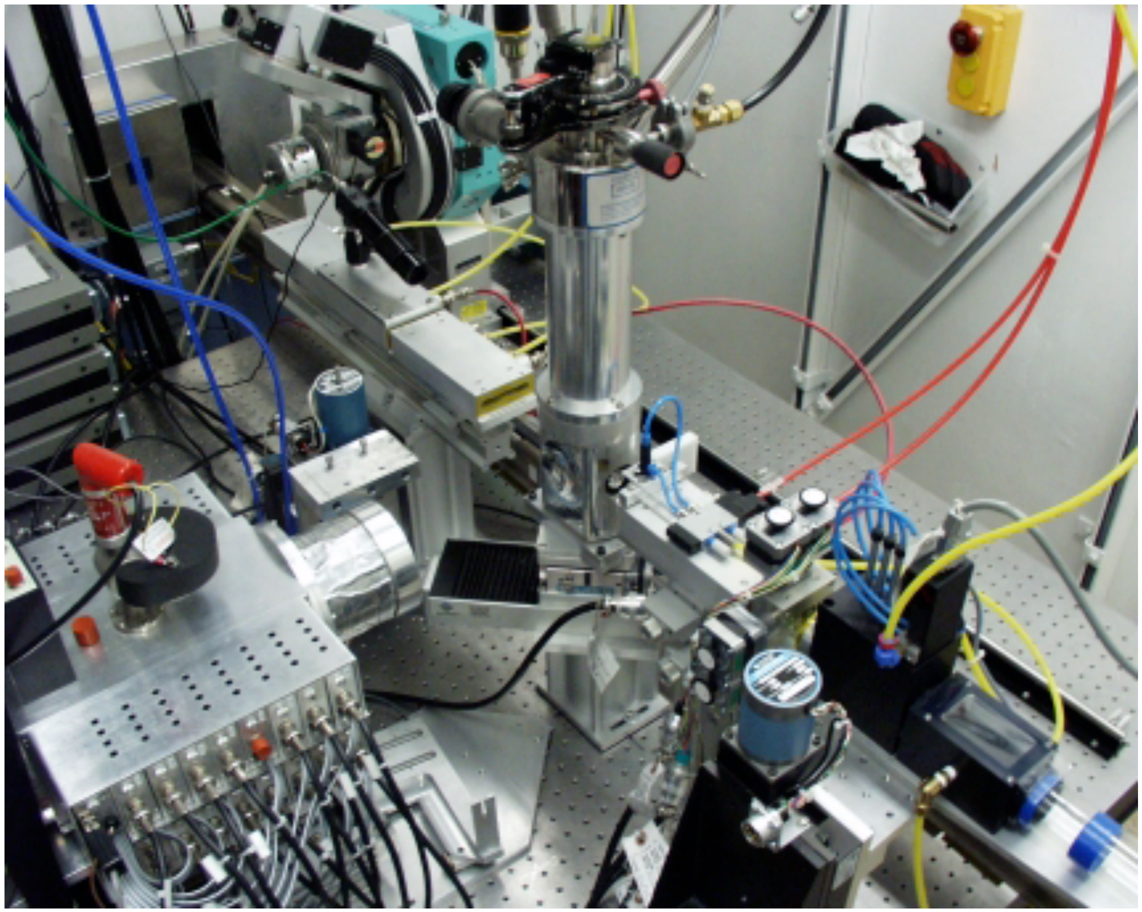


Diagram of hutch setup

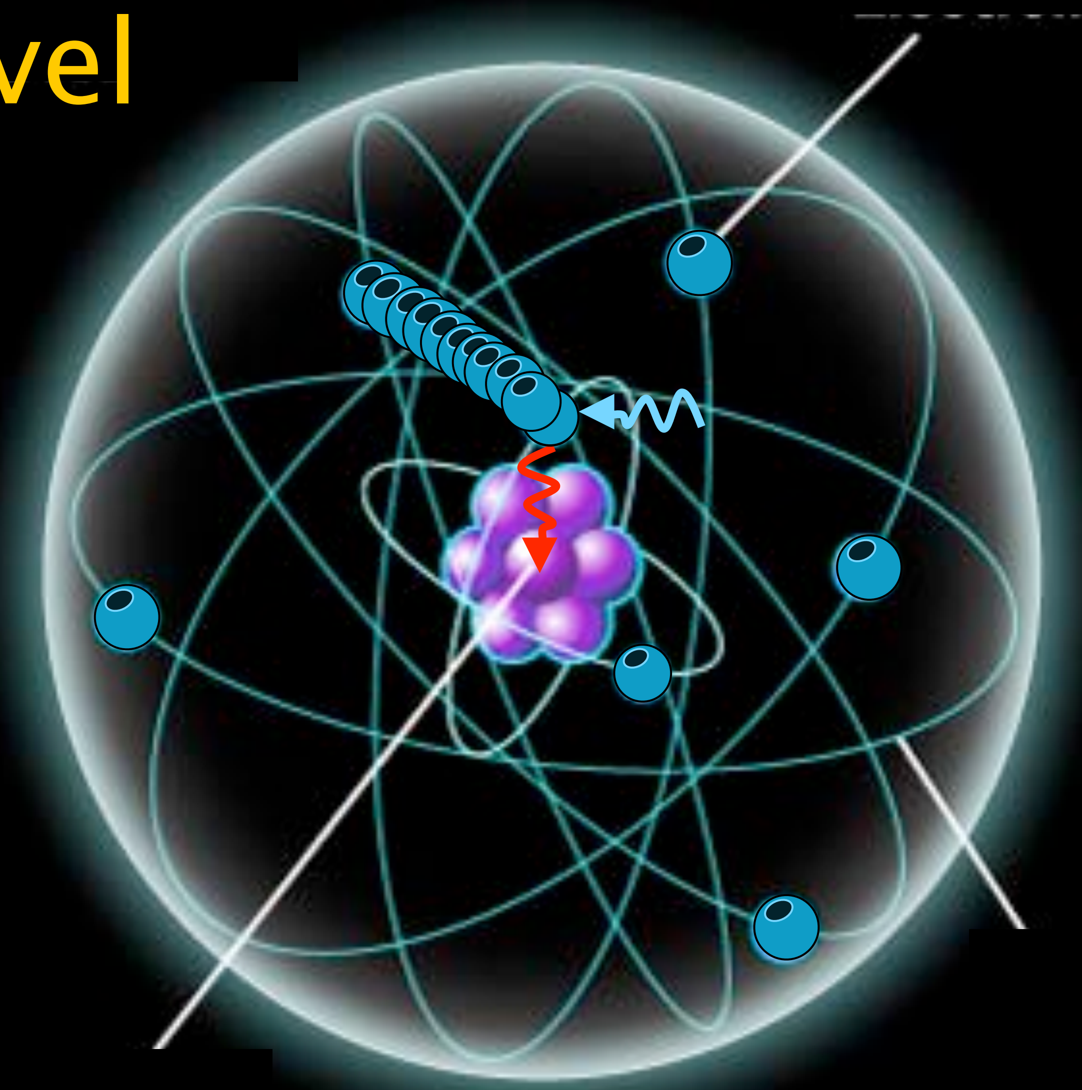
Beamline Basics



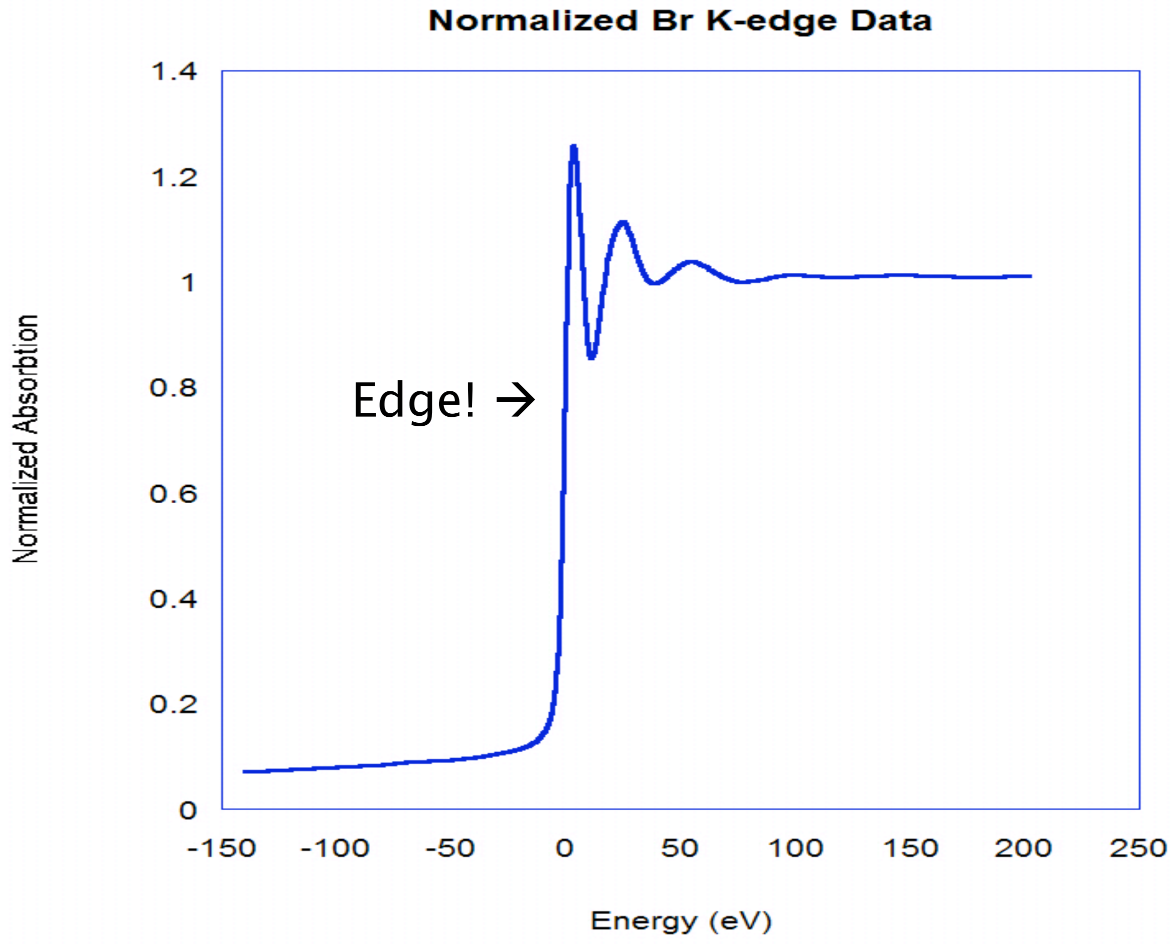
XAS

- What happens when we hit a chemical sample with x-rays?
- X-rays are absorbed by electrons, causing the electron to enter an excited state
- Eventually electron ejected
  - This property makes XAS an element specific technique, each element has different binding energies

emission from core level

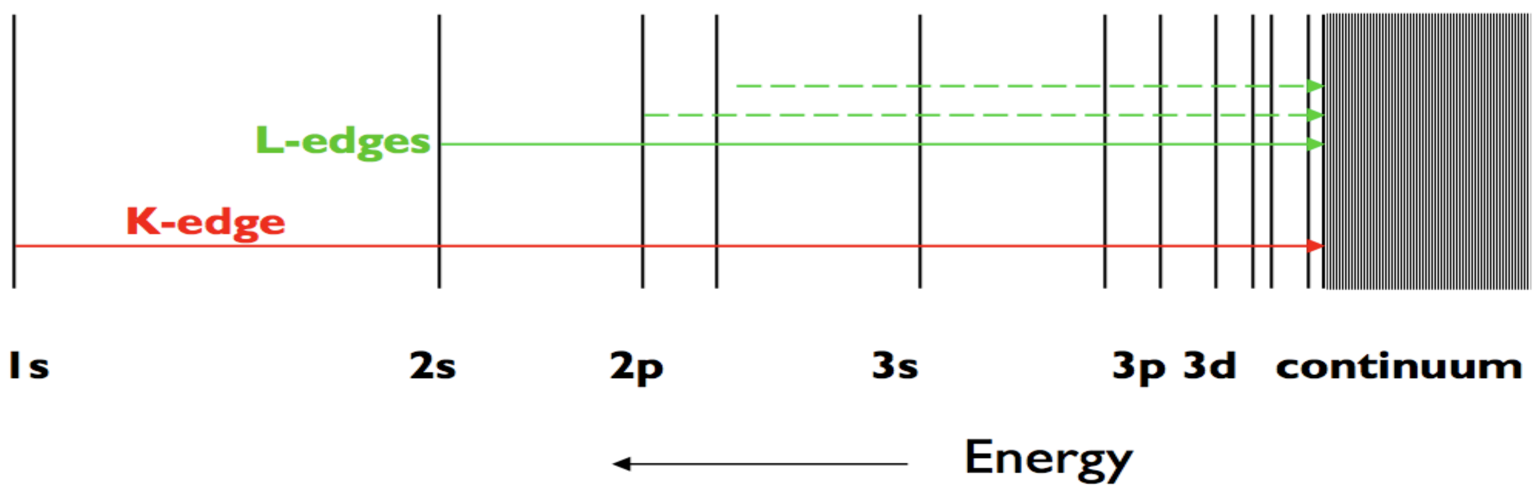


XAS


Normalized Br K-edge Data
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-150
-100
-50
0
50
100
150
200
250
Energy (eV)
Normalized Absorbtion
Edge! →

XAS

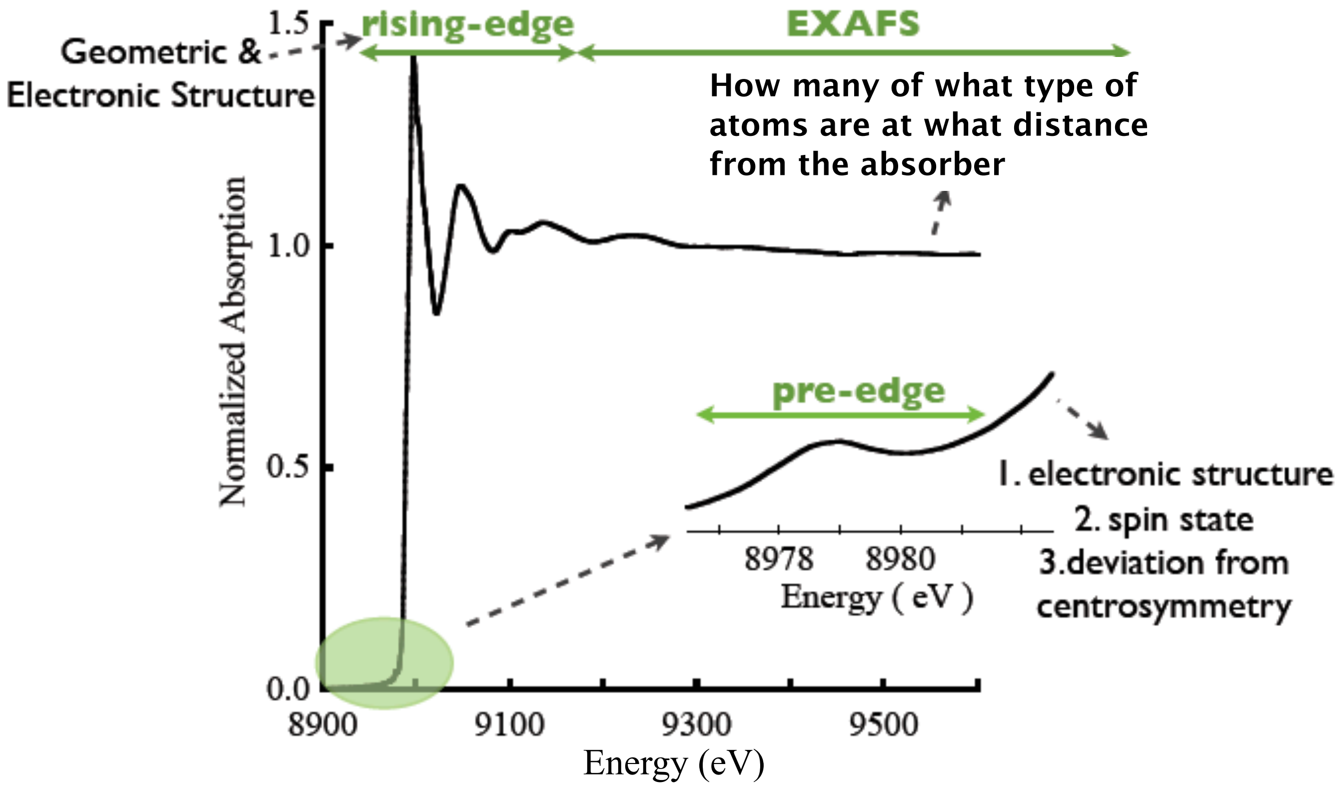
- Cu K-edge ~9000 eV
- Cu L-edges ~930 eV
- Fe K-edge ~7000 eV
- Fe L-edges ~720 eV
- Br L-edges~1600 eV
- I K-edge~33160 eV
- I L-edges~5000 eV



XAS

- The XAS spectrum
- Consists of three components, the near edge region (X-ray Absorption Near Edge Spectrum, XANES), the edge, and the post edge region (Extended X-ray Absorption Fine Structure, EXAFS)

XAS



Geometric &
Electronic Structure
rising-edge
EXAFS
How many of what type of
atoms are at what distance
from the absorber
pre-edge
1. electronic structure
2. spin state
3.deviation from
centrosymmetry
1.5
1.0
0.5
0.0
Normalized Absorption
8978
8980
Energy (eV)
8900
9100
9300
9500
Energy (eV)

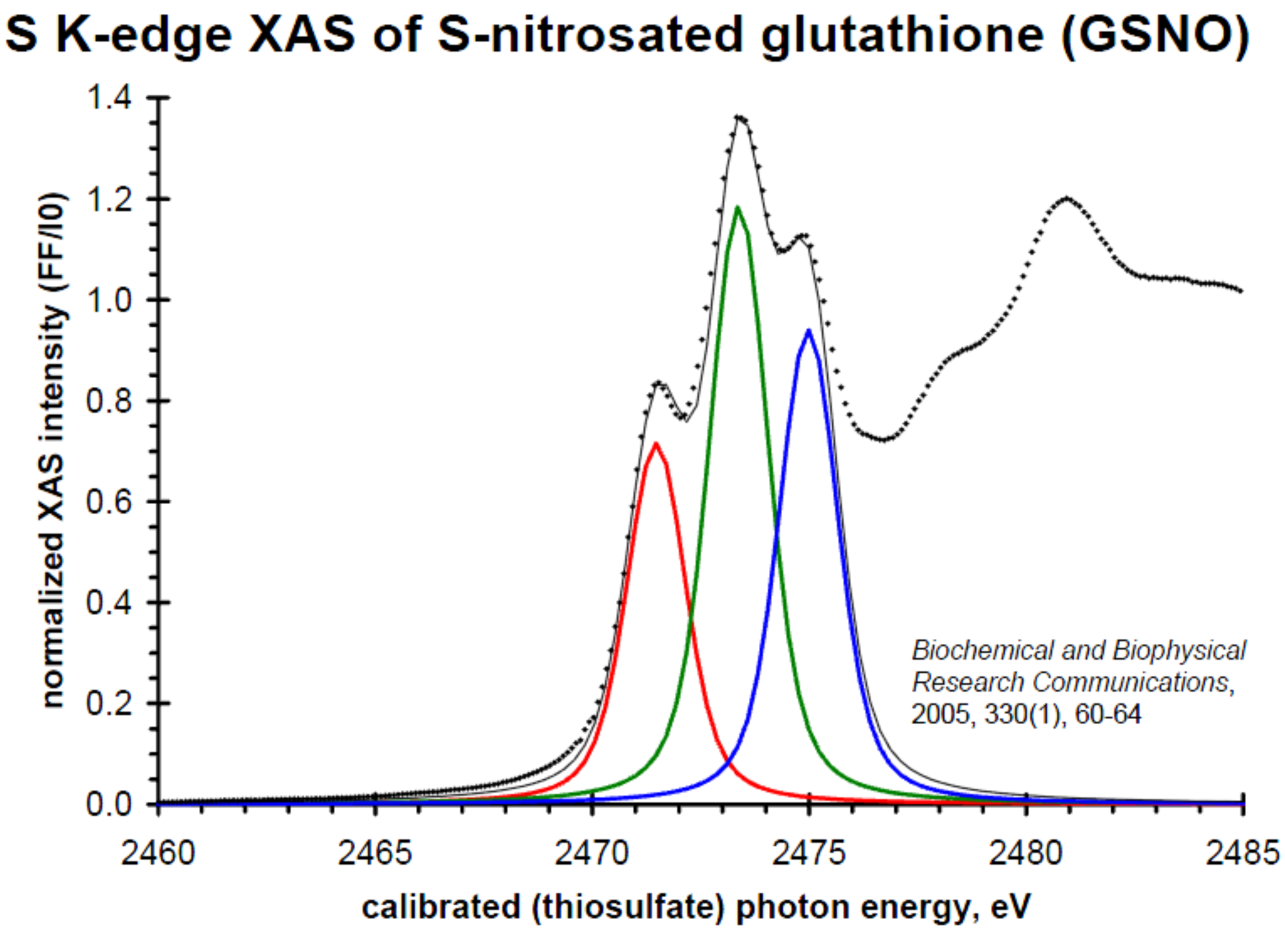
Data

- Once data is collected what can we do with it?
- There are a wide variety of data analysis techniques
  - Principle Component analysis (PCA)
  - EXAFS analysis
  - XANES analysis

PCA

- In principle component analysis, the goal is to essentially “fingerprint” your sample
- Not only allows you to determine what is in the sample but in what ratios

PCA

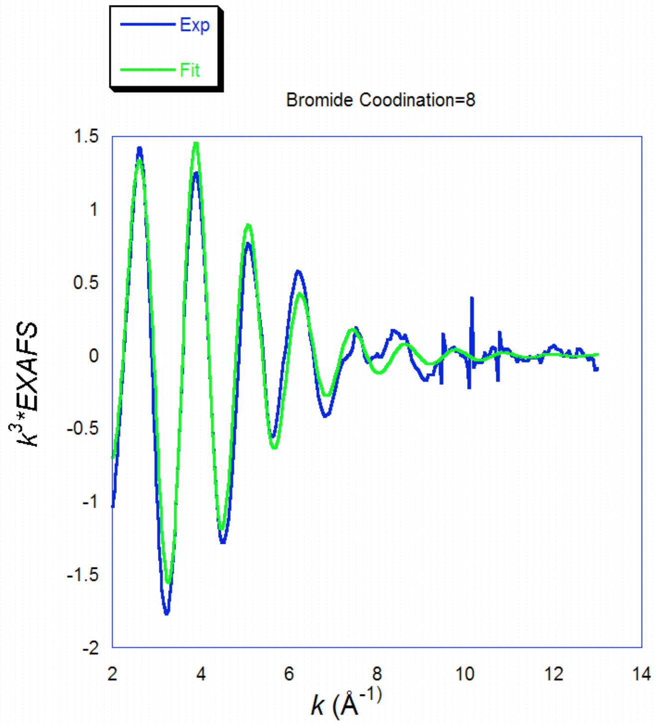


Graphic Obtained from Robert K. Szilagyi

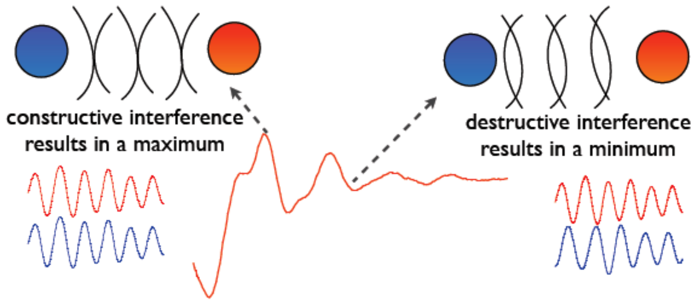
EXAFS

- Extended X-ray Absorption Fine Structure
- Composed of small fluctuations in absorption
- Useful for determining how many and what type of atoms are from the absorbing atom
  - Photoelectrons are continuously being ejected from the absorbing atom

EXAFS



Exp
Fit
Bromide Coodination=8
1.5
1
0.5
0
-0.5
-1
-1.5
-2
2
4
6
8
10
12
14
k^3*EXAFS
k (Å^-1)

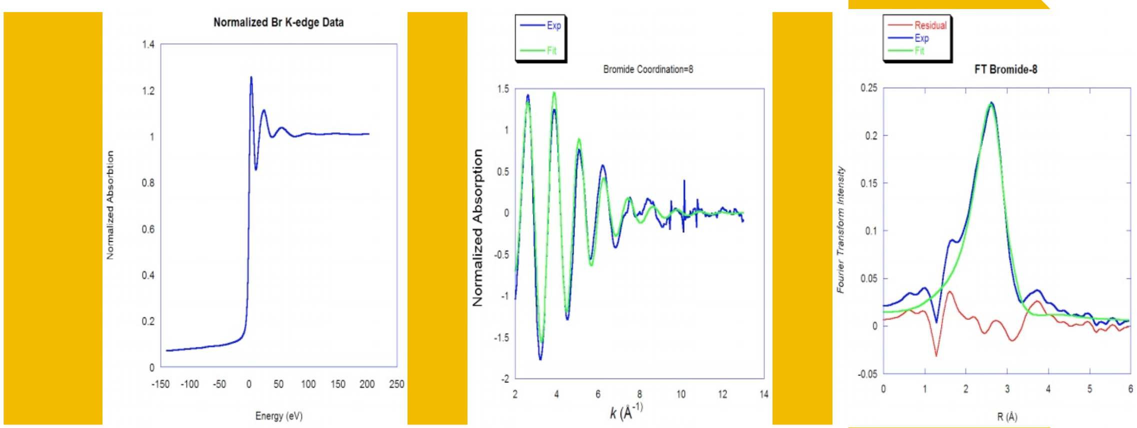


constructive interference results in a maximum
destructive interference results in a minimum

multiple scattering - photoelectron may be scattered by more than one atom before returning to the absorber

EXAFS

- Data is normalized and splined, then cubed, then Fourier transformed



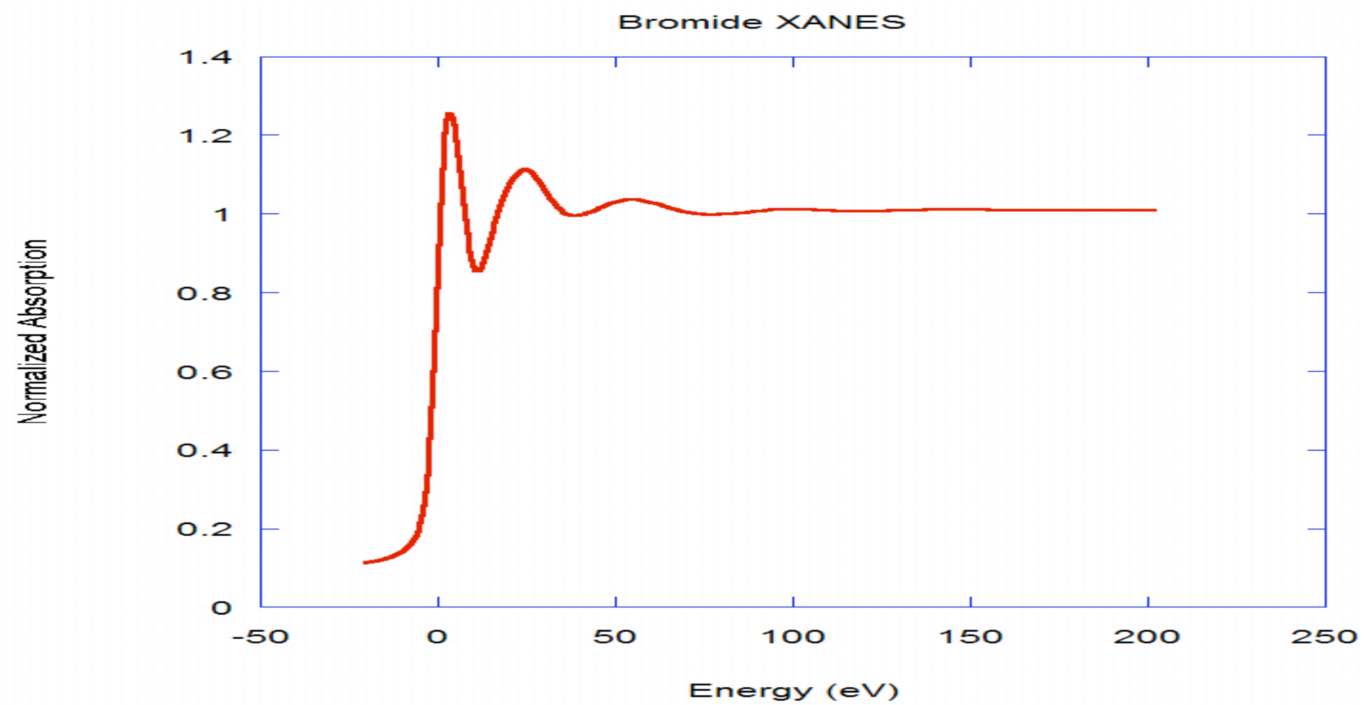
•Peaks on the Fourier transform correspond to a particular scattering atom at a specific distance from the absorbing atom
•The intensity of the peak corresponds to the relative concentration of a particular scattering atom

EXAFS

- Pros:
  - Good for determining bond distances, coordination numbers
- Cons:
  - Not sensitive to geometric structure
  - About 25% error (this comes from cubing the normalized data, which has ~3% error)
  - Hard to differentiate models

XANES

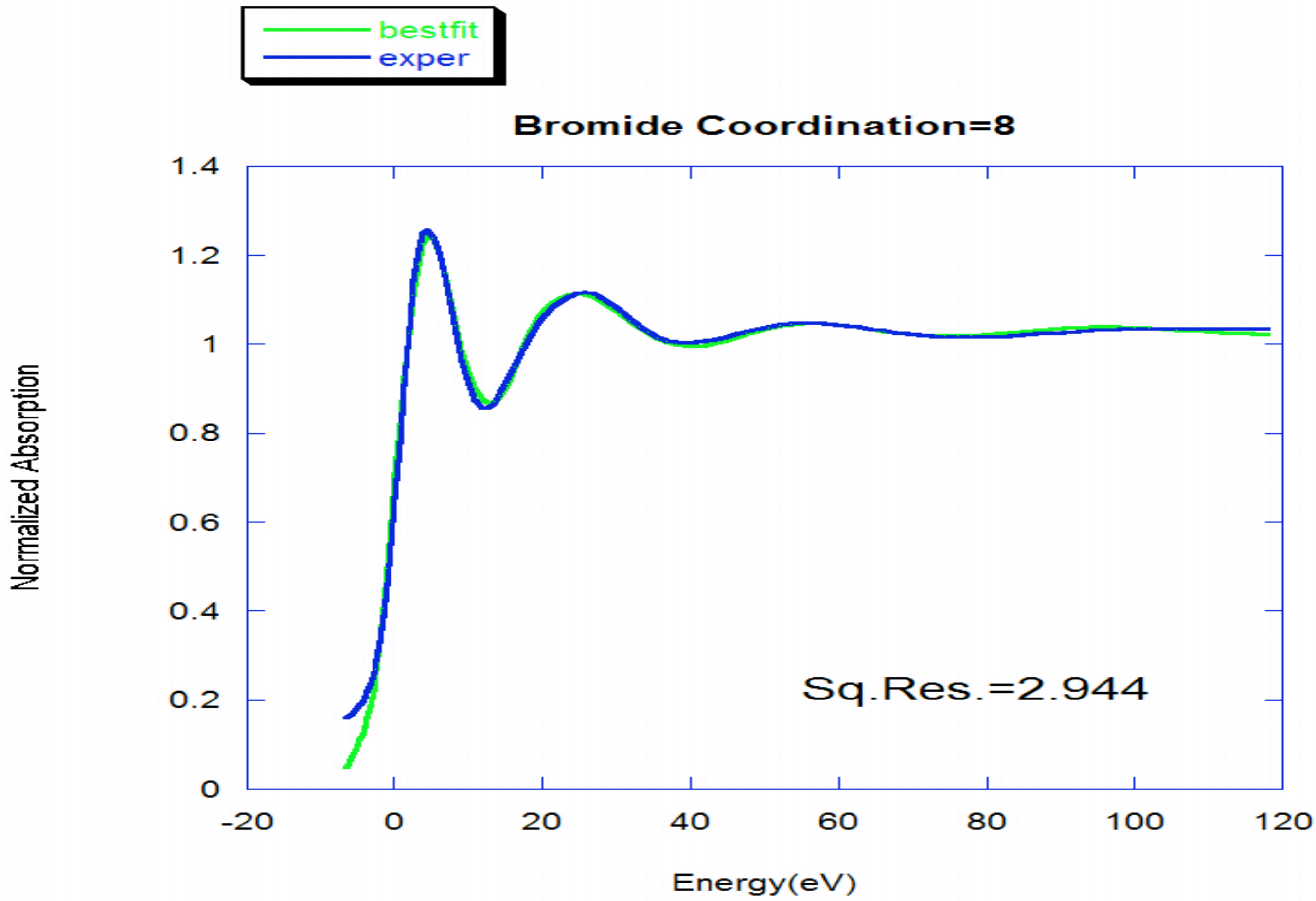
- X-ray Absorption Near Edge Spectrum
- Part of the spectrum which includes the pre-edge, edge, near post-edge



XANES

- XANES analysis fits the normalized spectrum according to MS theory
- In some cases we can reproduce experimental spectra nearly perfectly!
  - This is exciting because we can create models with more precision and rigor
  - In XANES analysis, differences in models are usually more evident

XANES



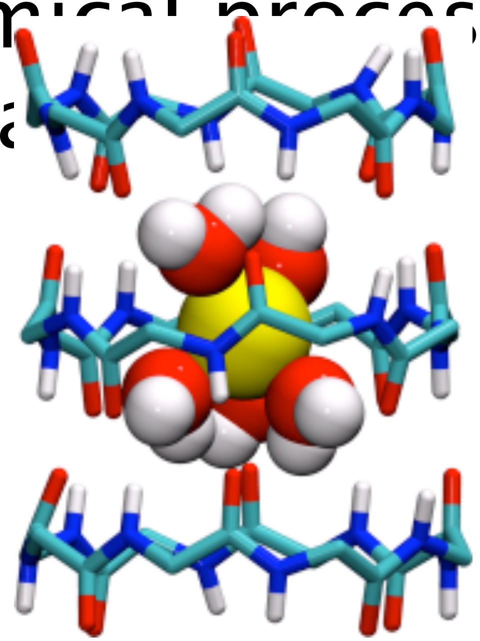
bestfit
exper
Bromide Coordination=8
Normalized Absorption
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-20
0
20
40
60
80
100
120
Energy(eV)
Sq.Res.=2.944

XANES-MXAN

- Pros:
  - Reproduces experimental data with precision and rigor according to non-structural and structural parameters
- Cons:
  - Calculations can take hours, even days

Summer Work

- This summer I have been studying the solvation shell of Bromide and Iodide in water
- Important in bio-chemical processes, such as ionic equilibria

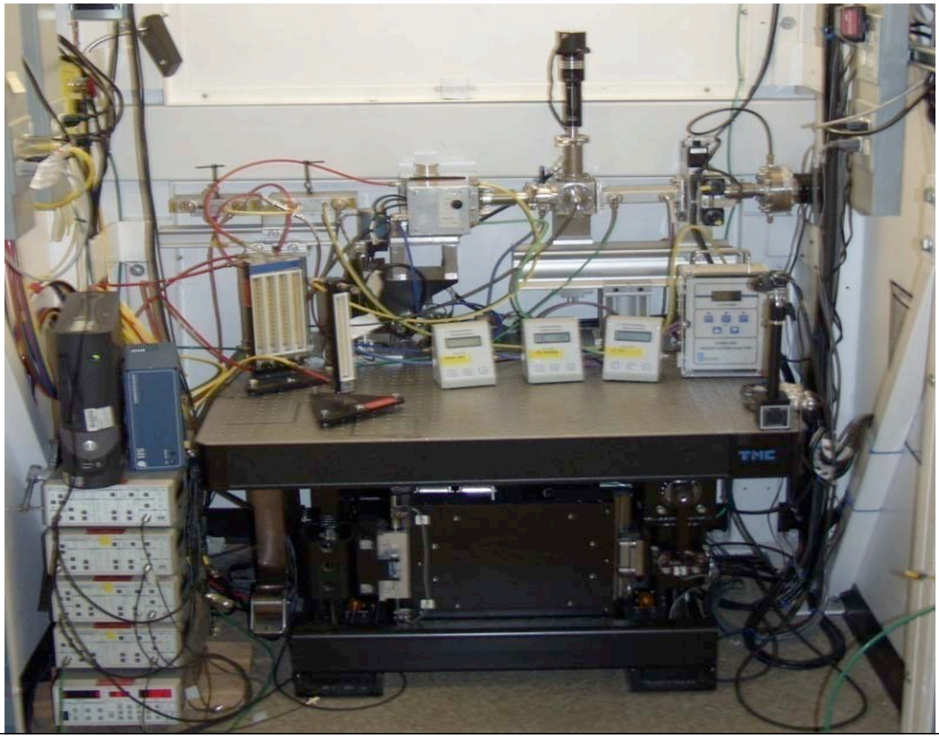


Summer Work

- So why haven't we figured this out yet?
- Difficult to probe such structure
  - In liquid solution, there is lots of thermal noise
  - These solvation shells are dynamic

Summer Work

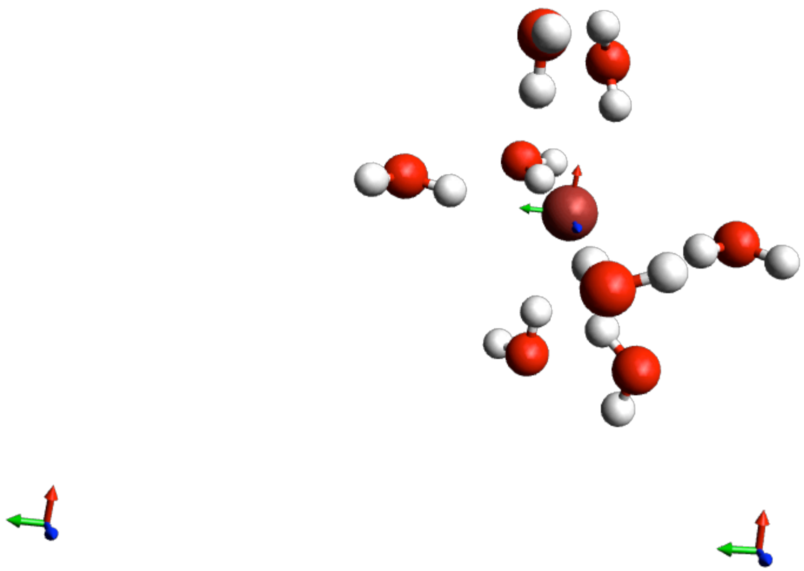
- What we have done:
  - Took XAS data on KBr and KI
  - Performed EXAFS and XANES analysis



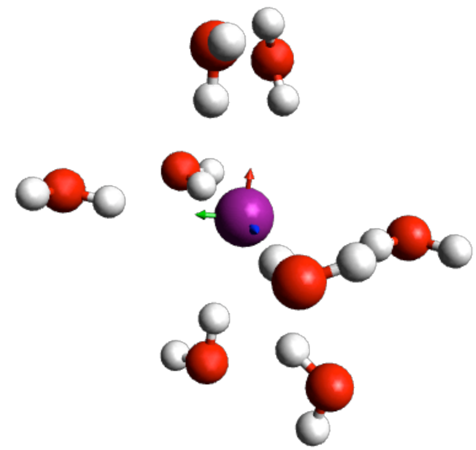
Summer Work

- What we found:
  - Br- and I- have similar shells, both have asymmetric coordination with 8 water molecules
  - The Br- shell is more “compact” i.e. the Br–O distances are about .3 Å shorter than the I–O distances

Summer Work



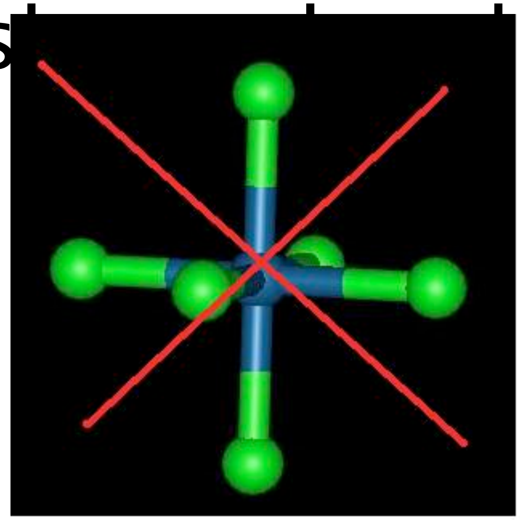
Bromide Solvation Shell



Iodide Solvation Shell

Summer Work

- Why interesting?
- Classical chemical theory says that the bigger the ion, bigger the hydration sphere
- We have s the case!



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- Dr. Apurva Mehta
- Dr. Maurizio Benfatto
- SULI Organization

The End

Thank you for your attention!

Questions?

Comments?

Have a nice Wednesda