Synchrotron Radiation and XAFS Data Collection

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Synchrotron Radiation

- What is “Synchrotron Radiation”?
  - Source of broad spectrum electromagnetic radiation extending from infrared through x-ray wavelengths
  - SR offers unique properties not attainable from laboratory sources
  - Available through dedicated national user facilities

How is it produced?

- When the velocity of a charged particle changes in time, it generates electromagnetic radiation (radio, microwave, infrared, light, ultraviolet, x-rays...)
- When the speed of the charged particle approaches the speed of light, special relativistic effects affect the spectrum as measured in the laboratory frame
  - The spectrum is shifted to much higher energies
  - Radiation pattern tilts in forward direction “headlight effect”
  - Time structure is introduced - flashes
- The phenomenon was first observed at a synchrotron. We now build dedicated electron storage rings to generate it.

Synchrotron Radiation Facilities

- These use technologies developed by particle physicists as well as new techniques and devices to produce x-ray beams for experiments.
- The major difference from other accelerators is that Synchrotron Radiation facilities are designed to enhance SR, not minimize it. They use electrons or anti-electrons (positrons) instead of protons because lighter particles create much more radiation.
- SR has broad applications in biology, chemistry, physics, engineering, environmental science, geology, soil science, and other fields…
- They are complex multi-user facilities in which 50-100 diverse experiments may be going on simultaneously with different groups. Excellent environment for cross fertilization between fields.

Properties of Synchrotron Radiation

- Broad energy (wavelength) spectrum extends from infra-red into x-ray region. Although lab XAFS facilities do exist, SR provides the best x-ray source available at present for most applications.
- Tunable (selectable) energy (or wavelength)
- Very high intensity compared to conventional sources
- Highly collimated beams (in one or two directions)
- Polarization: Linear, circular, elliptical
- Brilliance: high flux, small angular divergence, small source size

Advanced Photon Source

Figure from APS

Inside the APS

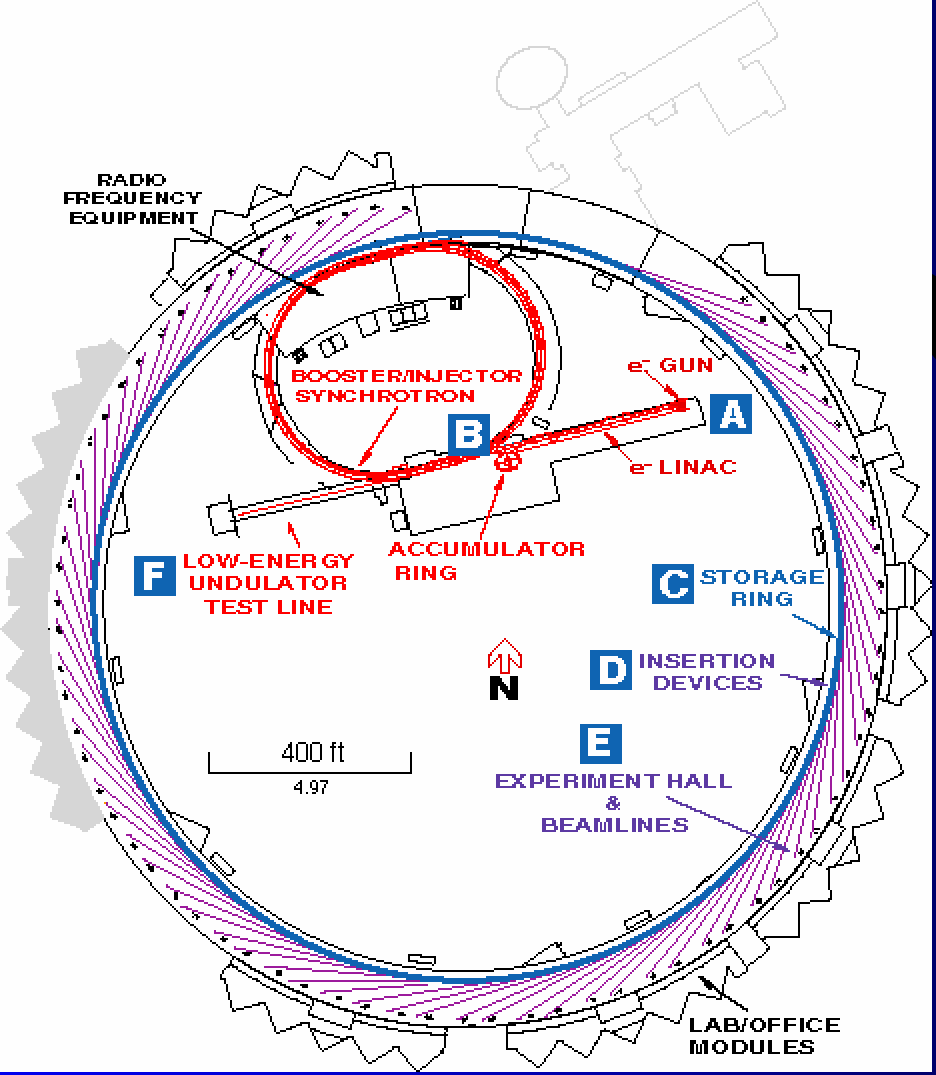


Figure from APS

Inside the ring

The electrons circulate at speeds extremely close to the speed of light within an evacuated beam pipe.

Dipole bend magnets and quadrupole, sextupole, and octupole magnets bend and focus the electron beam to maintain the proper electron beam shape as the beam continuously recirculates.

The electron beam stays in the machine producing x-rays for many hours before it is replenished. The x-ray photons produced are conveyed to beamlines for use by experimenters

Sources

- Bend Magnets
  - Needed to guide electron beam around ring
  - They also provide useful light
- Insertion Devices
  - Specifically tailor spectrum for experimental needs
  - Wigglers
  - Undulators
    - Planar
    - Helical
    - Fixed magnet
    - electromagnetic

Insertion Devices - Wigglers and Undulators

These comprise an array of fixed magnets of alternating N/S polarity. The alternating magnetic field in the vertical direction imparts an oscillating force in the horizontal plane. The electron oscillates back and forth, causing it to radiate. Relativistic effects shift the spectrum to high energies. Wiggler spectra are similar to bend magnets, except they can better adapted to experimental needs. In undulators, the electron deflection is small, and the x-rays emitted at the poles interfere with each other, causing the radiated power to be concentrated at specific x-ray energies, and to produce a pencil beam.

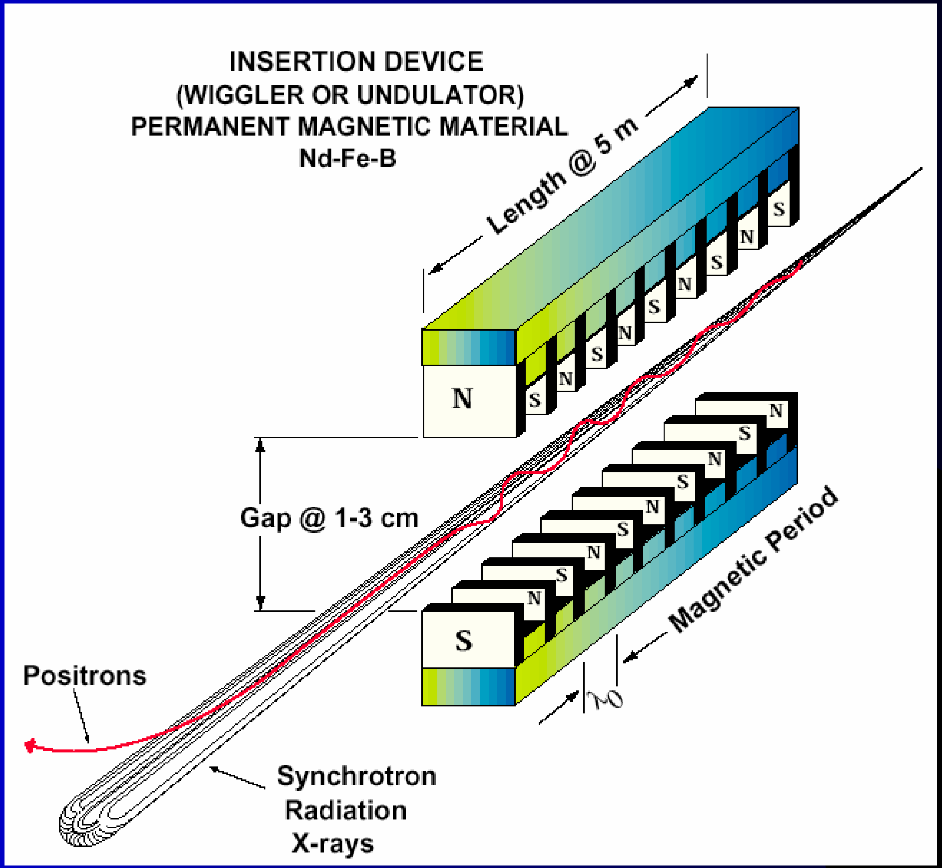


Figure from APS

Spectral Brilliance of Synchrotron Radiation Sources

The intensity from SR sources is much greater than conventional laboratory sources.

The “brilliance” is a quantity that measures the combination of flux, source size, and angular divergence of the light. Beamline optics cannot increase brilliance, only decrease it.

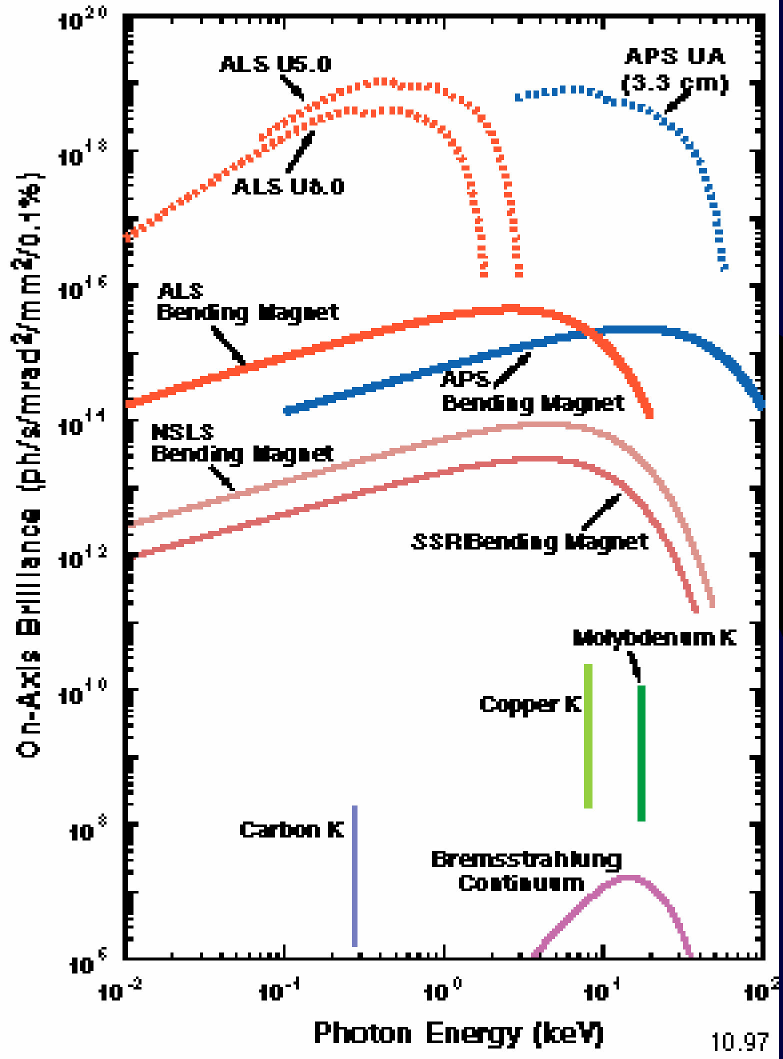
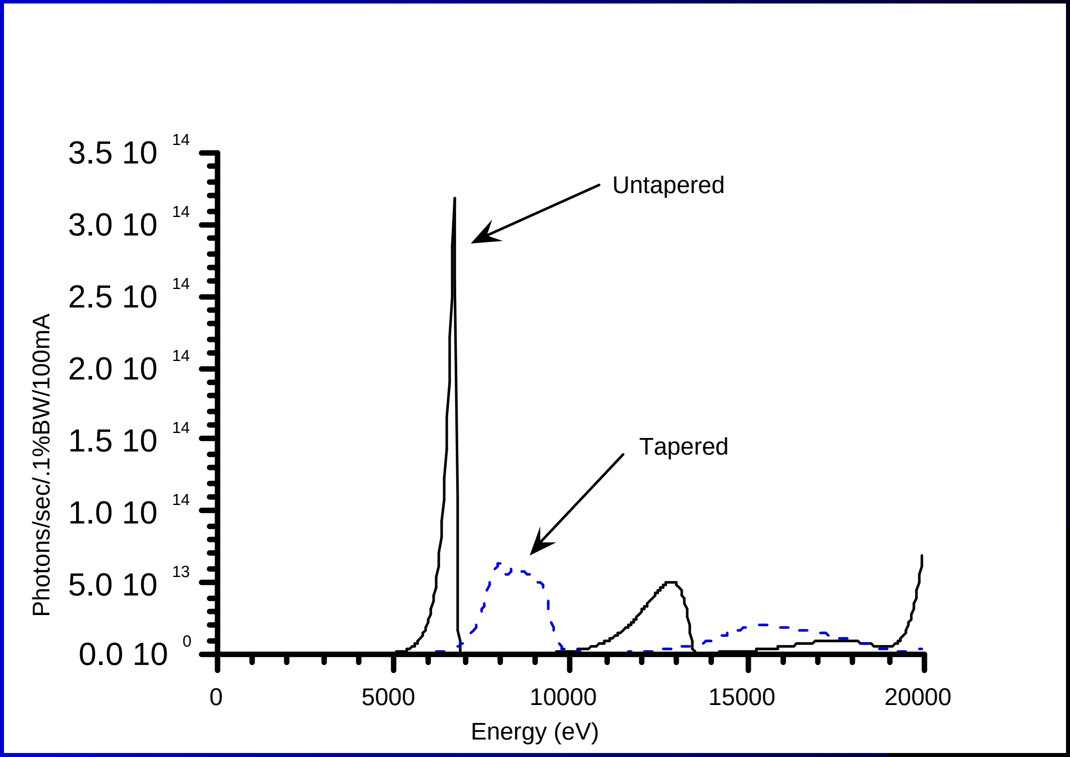


Figure from APS

Calculated flux from APS Undulator A

The position of undulator peaks can be tuned by adjusting the undulator gap, which varies the strength of the magnetic field felt by the electrons.

Decreasing the gap increases the field, causing a larger deflection, and slightly slowing down the electron's average speed through the undulator. This shifts the spectrum to lower energy.



The x-ray frequency of the fundamental is given approximately by $2\gamma^2 \Omega_w /(1+K^2/2 + \gamma^2 \theta_0^2)$. Here $K=\gamma\delta_w$, where $\delta_w=\lambda_0/2\pi\rho_0$, λ_0 is the undulator period, and ρ_0 is the bend radius corresponding to the peak magnetic field.

Beamlines

- Beamlines prepare the beam for experiments, and protect the users against radiation exposure. They combine x-ray optics, detector systems, computer interface electronics, and computer hardware and software.
- Typical functions
  - Radiation shielding and safety interlocks
  - Select specific energies/wavelengths ($E=hc/\lambda$) using *monochromators*
  - Focus the beams with *x-ray mirrors*, *bent crystals*, or *fresnel zone plates*
  - Define the beams with *x-ray slits*
  - *Detectors* measure beam intensity as function of energy
  - Electronics amplify signal and interface to the computers
  - Computer control and data acquisition system orchestrates motion of the monochromator and other optics, and reads detectors, and helps remote control alignment of samples.
  - Comprises other specialized instrumentation as needed

Generic computer interface

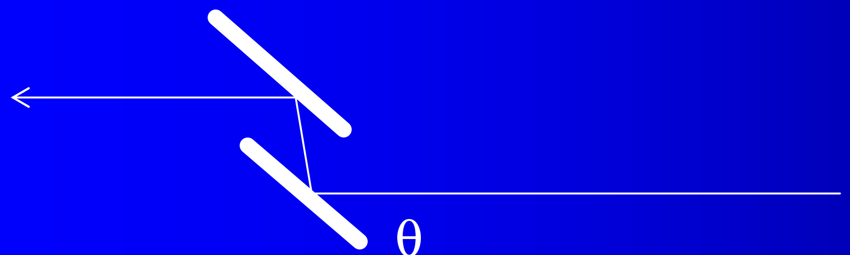
- Ion chambers produce low level currents (typically between nanoamps and microamps)
- These are amplified with a current amplifier to produce voltage output on the order of a volt, that depends linearly on the current.
- The voltage is fed into a voltage to frequency converter, producing a pulse train whose frequency is proportional to the voltage
- The pulses are counted in a scaler (counter) for a fixed time (precisely the same time interval for all channels). The number of pulses counted in a specific time is proportional to the ion chamber current.
- Direct analog to digital readout is also feasible but not widely used.
- Pulse-counting detectors typically integrate the charge produced by each photon, which is proportional to the photon energy. That is converted to a voltage pulse with a height proportional to the charge, and discriminators are used to pick out the right energy pulses. These are counted in the same manner as above.

Panorama of BioCAT Beamline

ID-18 APS

Silicon crystal monochromators

The "white" x-ray beam impinges on a perfect single crystal of silicon at a specified orientation. Those X-ray photons that are of the correct wavelength and angle of incidence θ to meet the Bragg diffraction condition $n\lambda=2\, d_{hkl} \sin(\theta)$ are diffracted through an angle 2θ; the rest are absorbed by the crystal. Here λ is the x-ray wavelength; the photon energy $\varepsilon=hc/\lambda$; and n is the harmonic number.
The spacing between diffracting atomic planes in the crystal for "reflection" hkl is $d_{hkl} =a_0/(h^2+k^2+l^2)^{1/2}$, where a_0 is the lattice constant (0.5431 nm for Si).



Si double crystal monochromator

The second crystal simply redirects the diffracted beam parallel to the incident beam. If bent, it can be used for horizontal "sagittal" focussing.

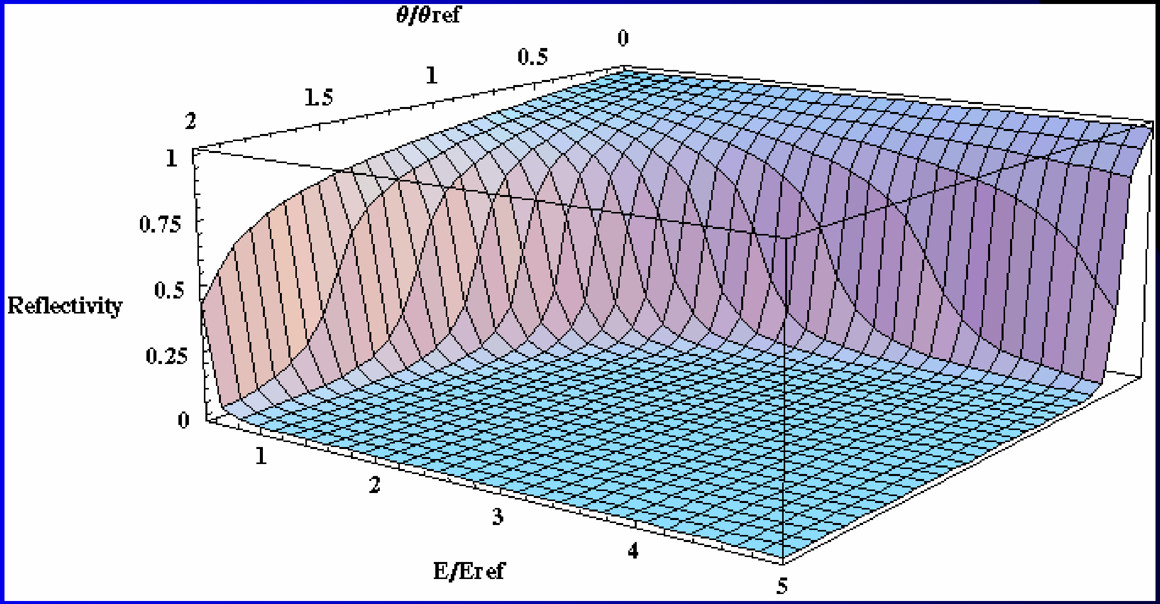
Monochromators (BioCAT ID-18)

Design by Gerd Rosenbaum and Larry Rock Automation.

Grazing incidence X-ray mirrors

For most materials, the index of refraction at x-ray energies is a complex number $n=1-\delta - i\beta$. The real and imaginary parts describe dispersion and absorption. Total external reflection occurs at angles $\theta < \theta_c$, where the "critical angle" $\theta_c = (2\delta)^{1/2}$, which is typically 5-10 milliradians, i.e. grazing incidence. Higher atomic number coatings (e.g. Pt, Pd, Rh) allow the mirror to reflect at greater angles and higher energies, at the cost of higher absorption. To a good approximation $E_c \theta_c$ = constant for a given coating. For ULE ~30 KeV mrad; Pd, Rh ~ 60 KeV mrad; Pt ~ 80 KeV mrad.

Surface plot of reflectivity vs angle and photon energy



Harmonic rejection

- Monochromators transmit not only the desired fundamental energy, but also some harmonics of that energy. Allowed harmonics for Si(111) include 333, 444, 555, 777…
- These can be reduced by slightly misaligning "detuning" the second crystal using a piezoelectric transducer ("piezo"). Detuning reduces the harmonic content much more than the fundamental.
- If a mirror follows the monochromator, its angle can be adjusted so that it reflects the fundamental, but does not reflect the harmonics.
- We have developed a device called a "beam cleaner" that is a band-pass filter to isolate a particular reflection.

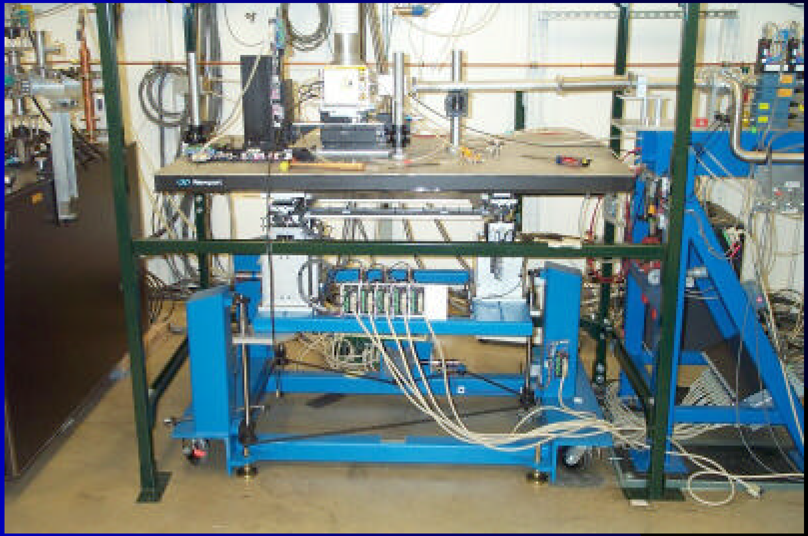
Glancing incidence X-ray Mirror
BioCAT ID-18 APS

This is a one meter long ULE titanium silicate. It is polished to ~ 2Å RMS roughness; it was measured at ~1 microradian RMS slope error befored bending. It is has Pt, Rh, and uncoated stripes to allow the user to choose the coating.

The mirror is dynamically bent and positioned.
Design by Gerd Rosenbaum and Larry Rock Automation.

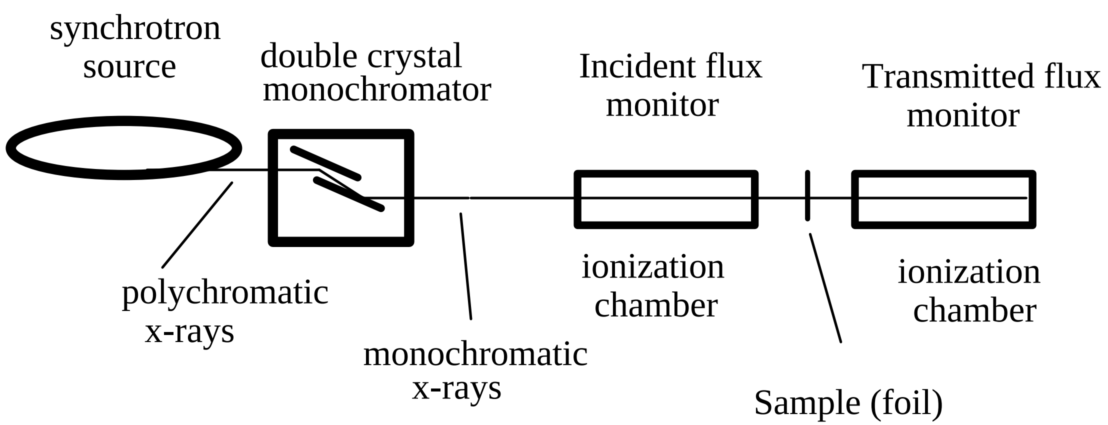
BioCAT Experimental Station

Optical table for scattering Experiments.



Positioning table and Low vibration displex System for XAFS

Generic experimental schematic for XAFS



SR X-rays are used in many ways

- Single Crystal Diffraction
- Powder Diffraction
- Fiber Diffraction
- Small angle scattering
- Wide angle scattering
- Diffuse Scattering
- Inelastic Scattering/Compton
- X-ray Absorption Fine Structure
- X-ray Magnetic Circular Dichroism (XMCD)
- Tomography/micro
- DEI Imaging
- Intensity Fluctuation Spectroscopy
- Coherent techniques/holography
- Mössbauer Spectroscopy
- Other…

New Opportunities

- Third generation synchrotron radiation sources offer unprecedented flux into small spots.
- Time resolved and spatially resolved studies
- Pump-probe, kinetics, in-situ, high pressure/temperature…
- Great opportunities for new science

Planning XAFS experiments

- First work out absorption lengths of the material at the relevant energies.
  - Check for beamlines with needed energy range and focal properties
  - Can you get x-rays through the sample with only a few absorption lengths of attenuation?
  - Is the edge step large enough for a transmission measurement?
  - If the sample is dilute or inhomogeneous, use fluorescence
  - If the energy is too low, absorption from air and windows can be a problem.

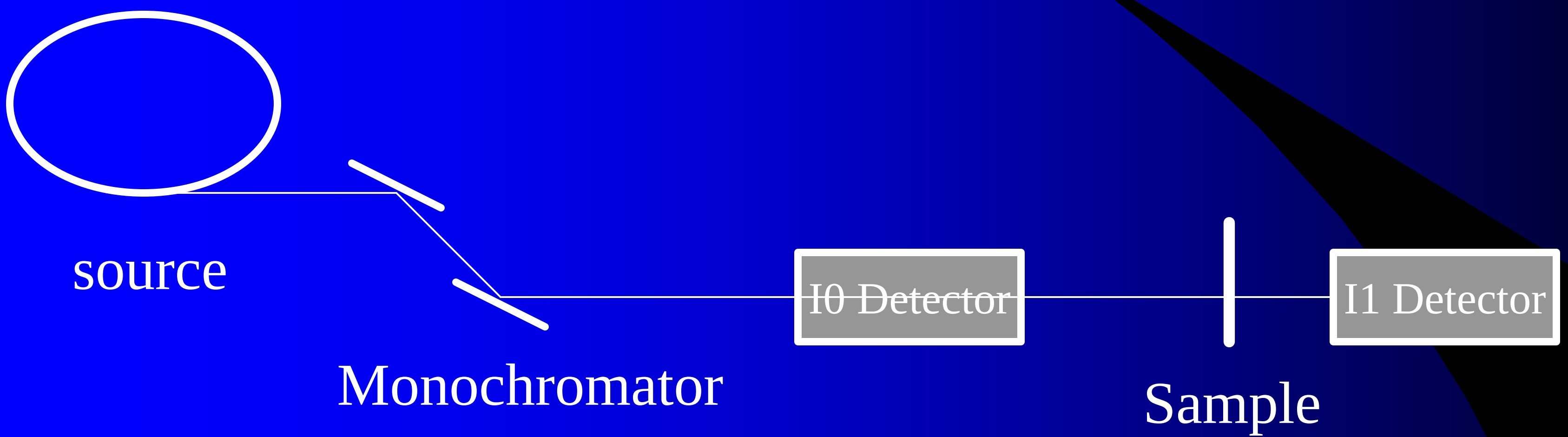
$$m = \sum_i r_i s_i = r \sum_i \frac{m_i}{M} s_i$$

X-ray absorption cross sections are σi, densities ρi. The mass fractions are mi/M. To calculate absorption cross sections, see for example: http://www.csrri.iit.edu/periodic-table.html

XAFS scans

- Step-scan, continuous scan ("QXAFS"), or dispersive XAFS
- Typical scan parameters
  - Sample pre-edge to get background trend
    - (Range ~ -100eV to -20eV, 5 eV sampling)
  - EXAFS region
    - Uniform in k-space (to > 12 Å^-1, sampling .07 Å^-1)
    - Prefer increased integration time per point at high k
  - Sample edge region
    - (-20eV to +40 eV, 1 eV)

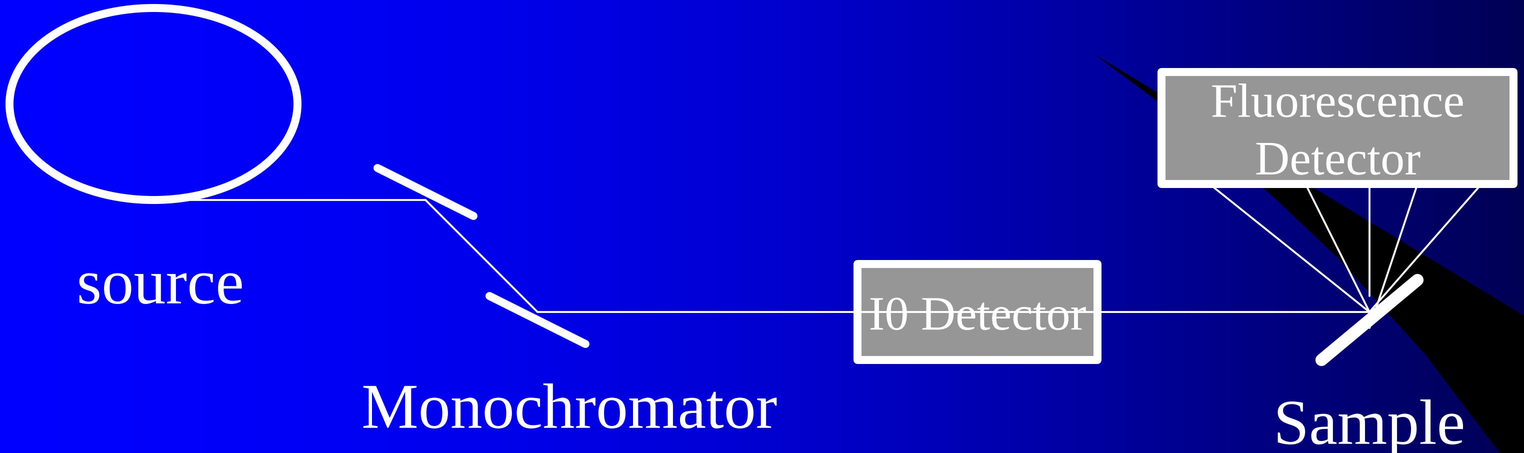
Transmission Mode



$$I = I_0 \exp(-m(E)x)$$

X is the sample thickness, μ(E) is the absorption coefficient. Transmission is best when the sample is not more than a few absorption lengths thick, and the edge step is > 0.1

Fluorescence Mode



$$I \propto I_0 \mu_s(E)\left(\frac{1-\exp(-\alpha)}{\alpha}\right)$$

$$\alpha = (\mu_t(E)/\sin\theta + \mu_t(E_f)/\sin\phi)x$$

Fluorescence detection is preferred for dilute samples (say, < 0.1 absorption length). The detector center is positioned along the x-ray polarization vector because scattered radiation is minimum there.

Fluorescence Detection

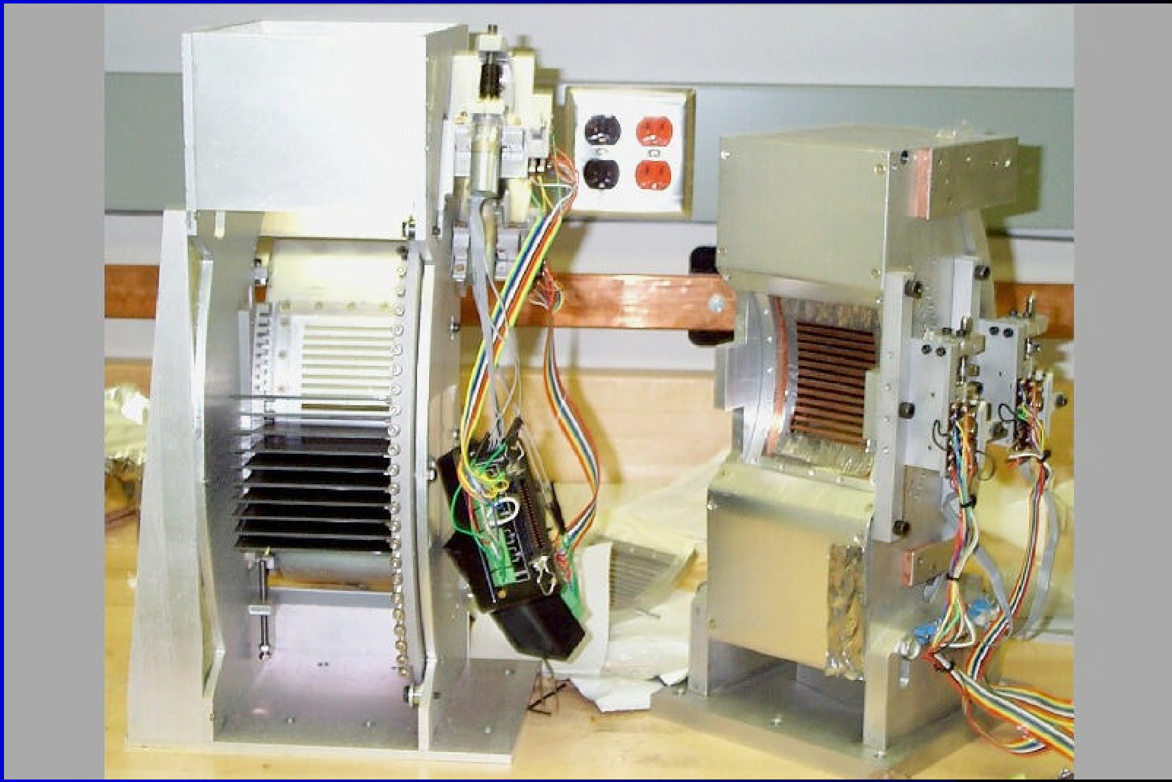
- Integrating detectors
  - Stern-Heald ion chambers (“Lytle detectors”)
  - PIN diodes
  - Scintillator/PMT in current mode
- Pulse-counting detectors - count rate limits
  - Scintillator/PMT in pulse counting mode
  - Solid state detectors and arrays
    - NSLS detector project
  - Proportional counters
  - Avalanche photodiodes
  - Silicon Drift Detectors look promising

Eliminating Background in Fluorescence

- Rejecting scattered x-rays and undesired fluorescence
  - Solid state detector array: determine the energy of each photon and throw out the bad ones. These suffer from saturation problems at high rates/nonlinearity. Can use with filters. Good on bend magnet lines.
  - Suppress the high energy photons with a well optimized filter, and suppress the filter fluorescence with slits. Limited background rejection at high dilution. Useless if background fluorescence is below the filter edge.
  - If you can prepare a beam ~ 0.1 mm, use a good bandpass analyzer system which have only recently become available.
    - Multilayer analyzer
    - Log spiral bent Laue analyzer
  - Be sure to shield the detector from air scatter and ambient fluorescence

Multilayer Array Analyzers

These devices use Bragg diffraction from arrays of graded index synthetic multilayers to select the desired fluorescence. They are tunable over a wide range and effectively eliminate detector saturation.



Bent Laue analyzers use silicon crystals bent to logarithmic spiral shape to reject background. These devices are optimized for particular energy ranges.

Experimental problems to avoid

- Particle size effects - particles should be less than one absorption length to get accurate spectra in transmission and fluorescence. The relevant length scale must be calculated before preparing samples.
- Thickness effects - For transmission, homogeneous sample of uniform thickness on scale of an absorption length.
- Self absorption effects - in fluorescence, for a thick sample, distortions of spectra will occur if the absorption from the species of interest is not small compared to the total absorption coefficient. This problem will occur if there are large particles, even if they are in a sample matrix that is dilute on average.
- Use thin sample in this case, if possible.
- If not possible, consider electron yield detection

Experimental Precautions

- "HALO"
  - Harmonics: they must be eliminated from the beam by use of a mirror, detuning, or other means.
  - Alignment: beam should see *only* a uniform sample, same beam in both detectors
  - Linearity: Detectors and electronics must be operated in their linear ranges
  - Offsets: dark currents and amplifier offsets must be subtracted out or intensity fluctuations won't normalize out.

Conclusion

- There has been considerable progress in experimental methods in recent years
- Better sources, beamlines, and detectors are now available, and there are more to come.
- Coupled with improvements in data analysis and modeling, XAFS experiments can now be done that were previously impossible.
- Attention to basic experimental design and sample preparation will help to ensure correct conclusions.