Introduction to XAFS Experiments

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In this talk …

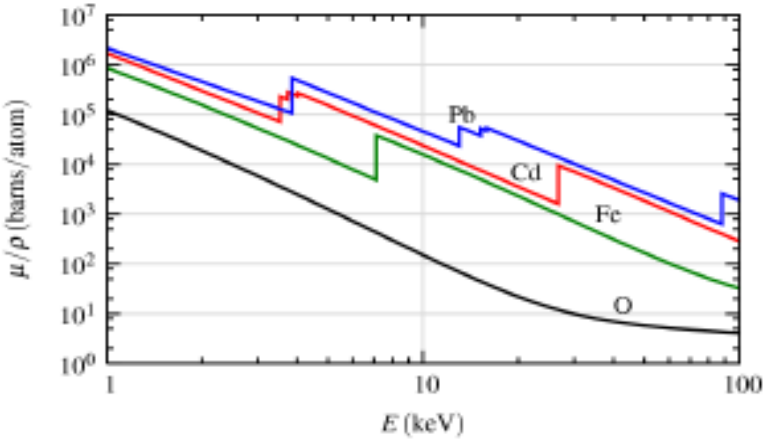
- Reminder about x-ray techniques
- Experiment “modalities”
- X-ray sources
- X-ray beamlines
- “In-hutch” instrumentation
- Sample considerations

X-ray Techniques

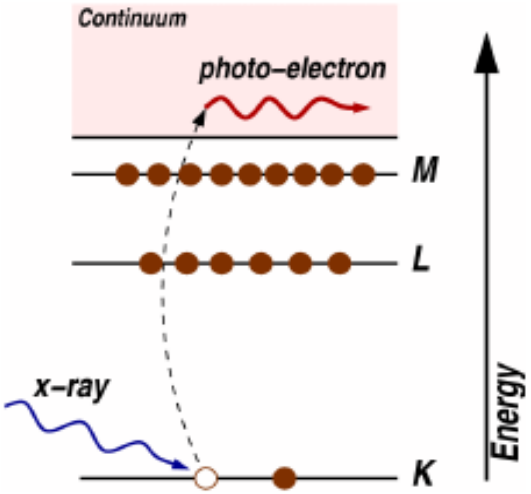
- X-ray diffraction (look at diffraction peaks)
  - **Long-range crystalline order**
- X-ray diffuse scattering (also look between peaks)
  - **Short range order**, info on alloys, vibrations, etc.
  - Sees all possible atom pairs, this can be good or bad
- X-ray reflectivity (or reflectometry)
  - Measure specular-reflected beam intensity as function of incidence angle
  - Reveals **electron density as function of depth** near surface or interface
- X-ray absorption spectroscopy
  - **Short range order**, vibrations, etc. about **particular atomic species**

X-ray Absorption

Many contributions to absorption, but largest in x-ray region is the **photoelectric effect: Ionization of inner-shell atomic electrons**



Absorption Edge:
High enough energy for excitation of **atomic core electrons** to **unoccupied states** (either bound or continuum)



Figures courtesy Matt Newville, University of Chicago / CARS

If monatomic gas, generally smooth spectrum above edge.
If molecules, liquid, or solid, see oscillatory structure.

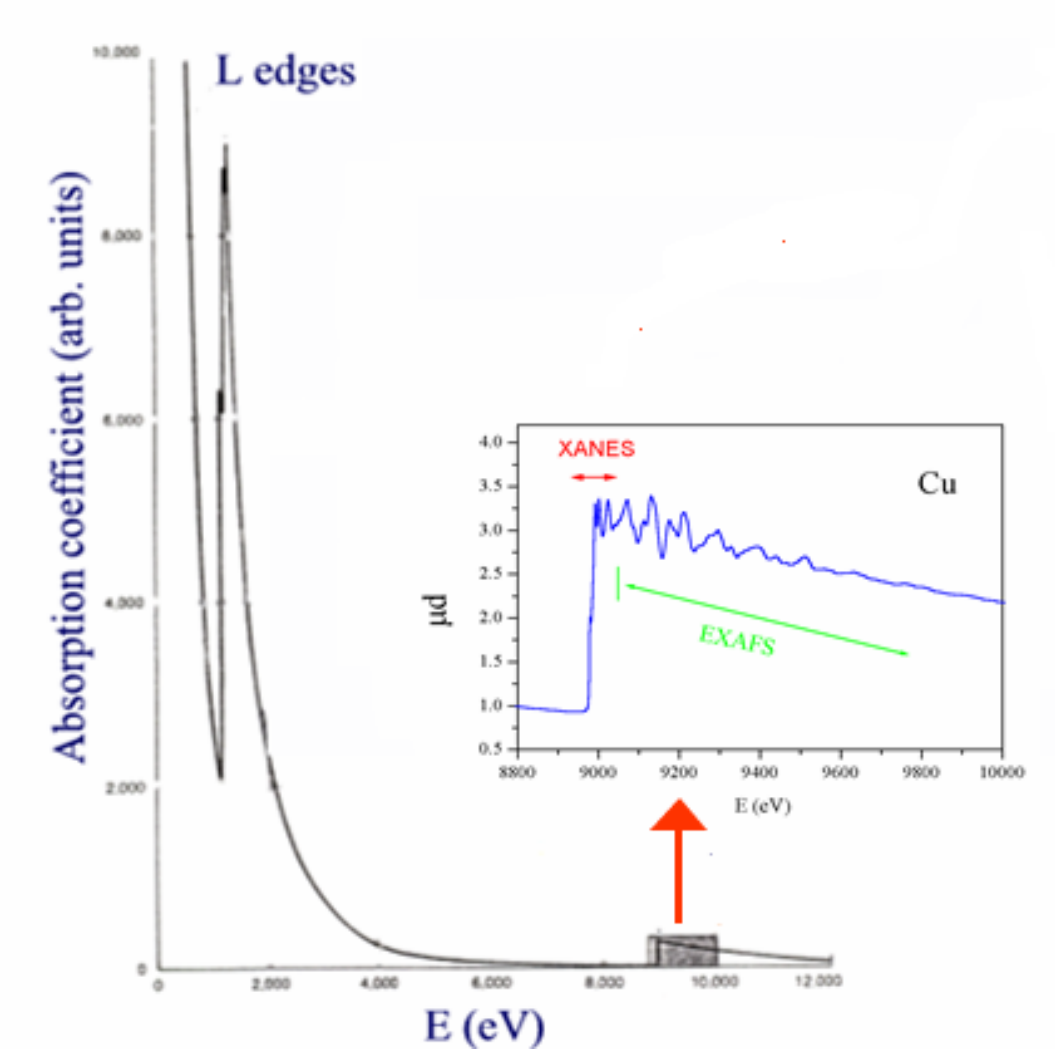


Figure courtesy Matt Newville, University of Chicago / CARS

The x-ray spectroscopy acronym game

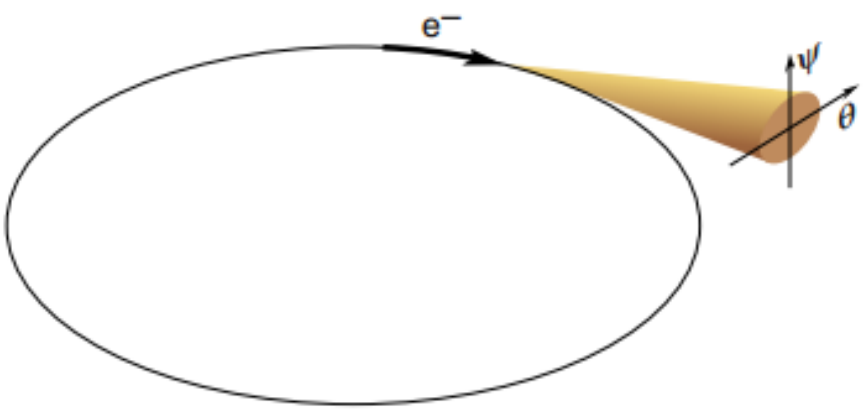
- X-ray Absorption Spectroscopy (**XAS**)
  - X-ray Absorption Fine-structure Spectroscopy **(XAFS)**
  - **Extended** X-ray Absorption Fine-structure Spectroscopy (**EXAFS**)
  - X-ray Absorption **Near-Edge** Spectroscopy (**XANES**) or
  - **Near-Edge** X-ray Absorption Fine Structure (**NEXAFS**)
  - And many more variations of techniques
- In all cases, variations in x-ray absorption coefficient as function of energy related to **structural or electronic properties** of sample

Back to extraction of structural information in a minute, first…

- These experiments require x-ray beam that is
  - **extremely intense**
  - **well-collimated** (for some experiments)
  - **broad-spectrum** so that we can tune x-ray energy
- By far best source for most experiments is **synchrotron radiation**

Synchrotron Radiation and Storage Rings

- Accelerated charged particles (e.g. electrons) radiate electromagnetic radiation
- If highly relativistic electrons, radiation in x-ray region, strongly focused in forward direction

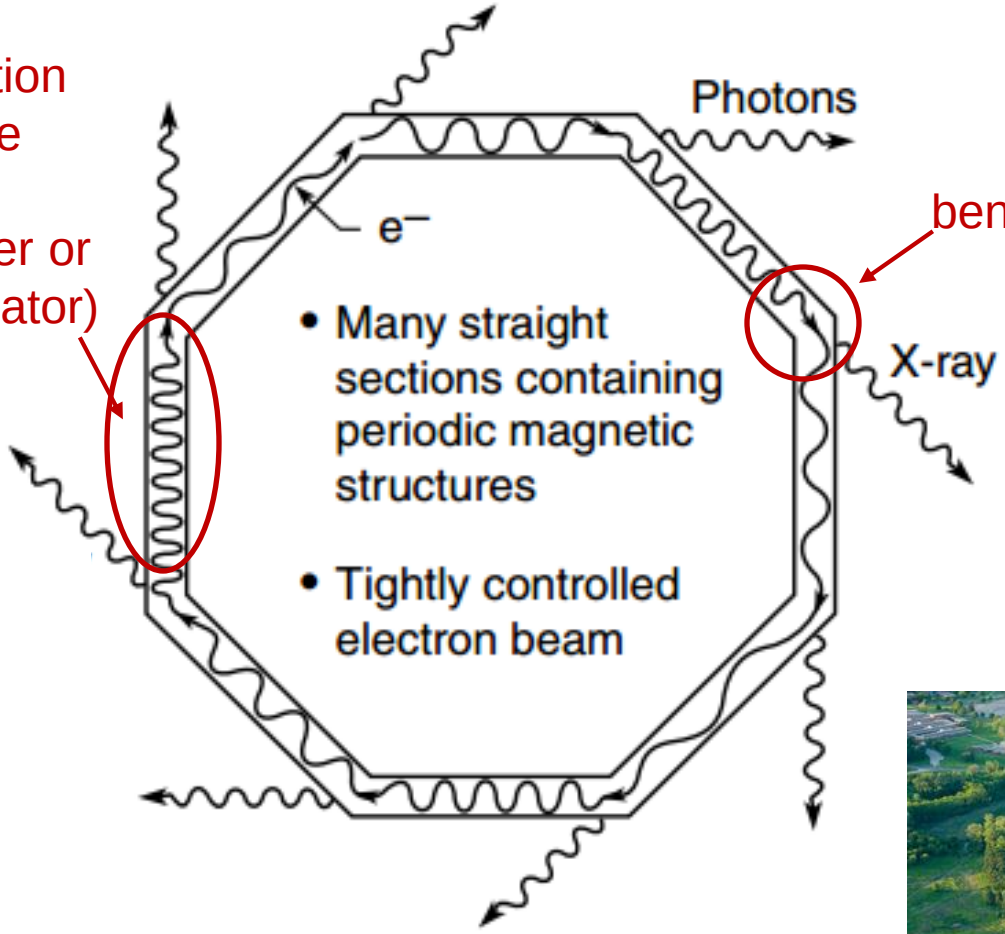


Synchrotron radiation

- 10^{10} brighter than the most powerful (compact) laboratory source
- An x-ray "light bulb" in that it radiates all "colors" (wavelengths, photons energies)

Courtesy David Atwood, UC Berkeley

Modern Synchrotron Radiation Facility



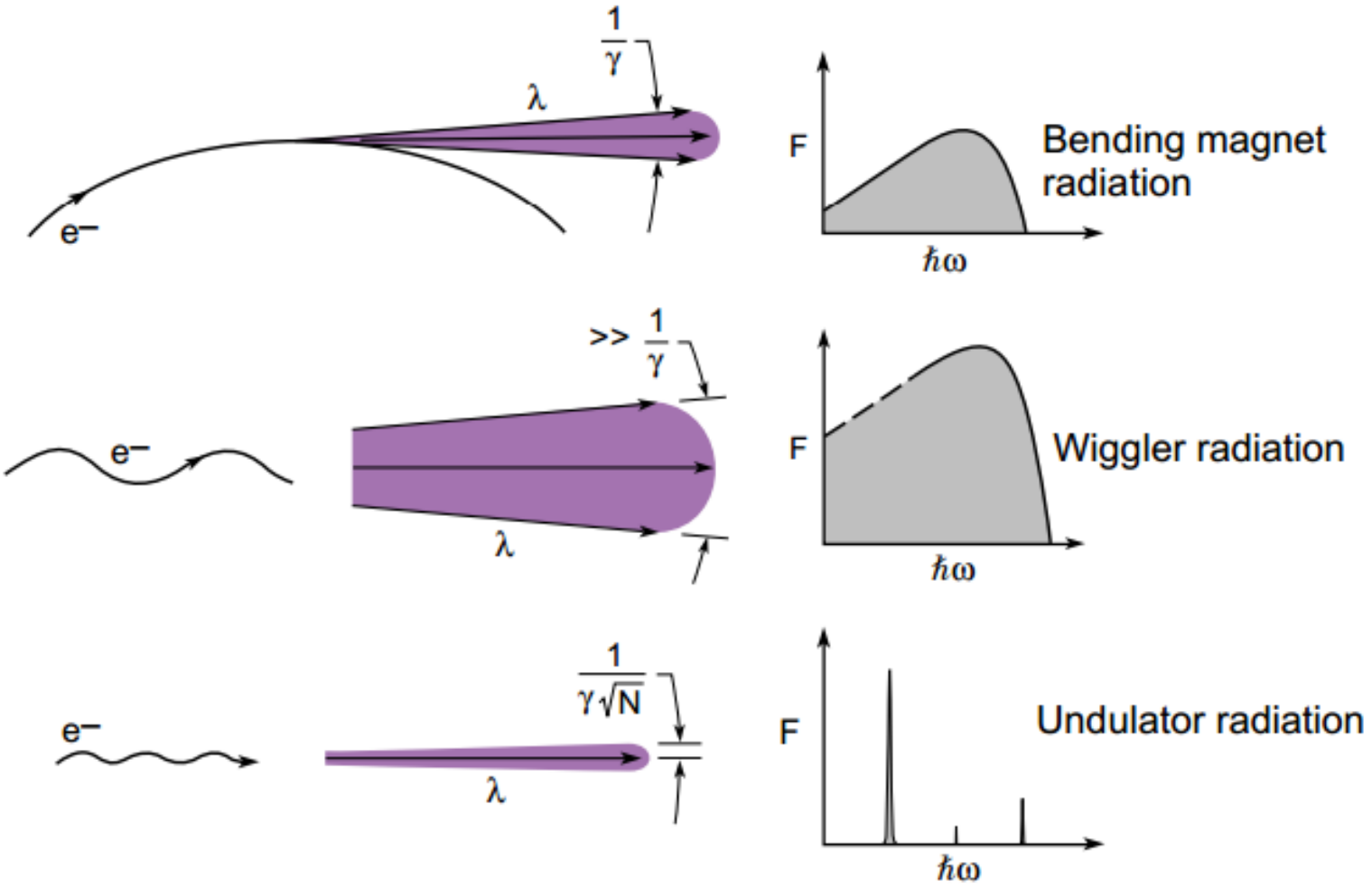
Insertion device (e.g. wiggler or undulator)

bending magnet

Advanced Photon Source

Courtesy David Atwood, UC Berkeley

Three Common Sources of Synchrotron Radiation



Courtesy David Atwood, UC Berkeley

Undulator Magnets

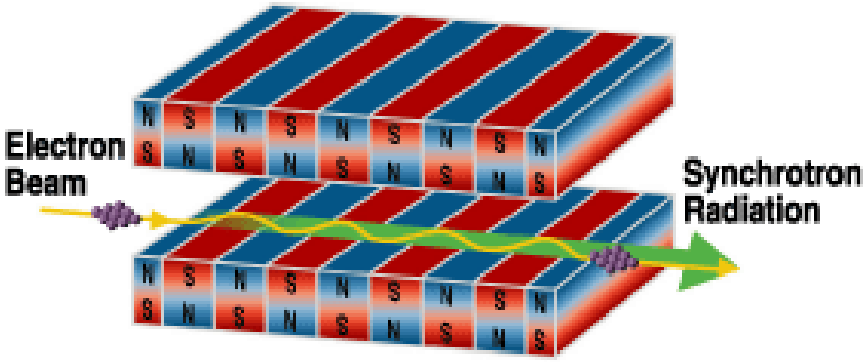


Image courtesy SPRing8

Extremely “bright” beam (small source size, small divergence)

Great for spatial resolution, angular resolution, etc.

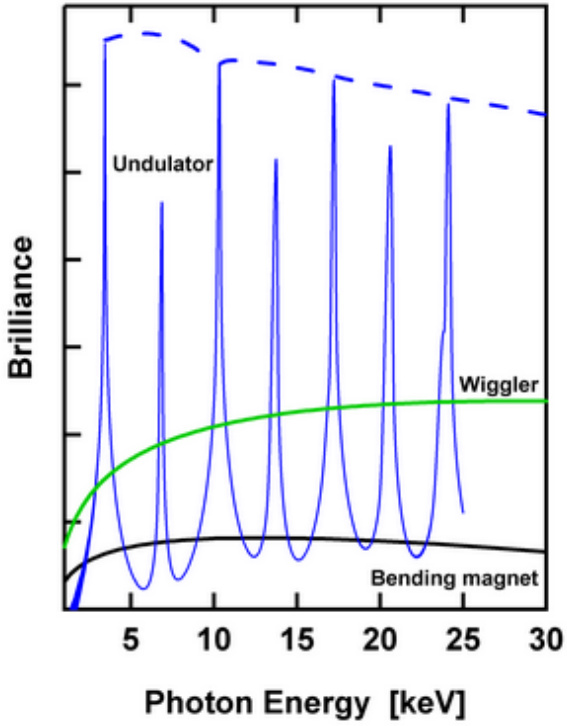
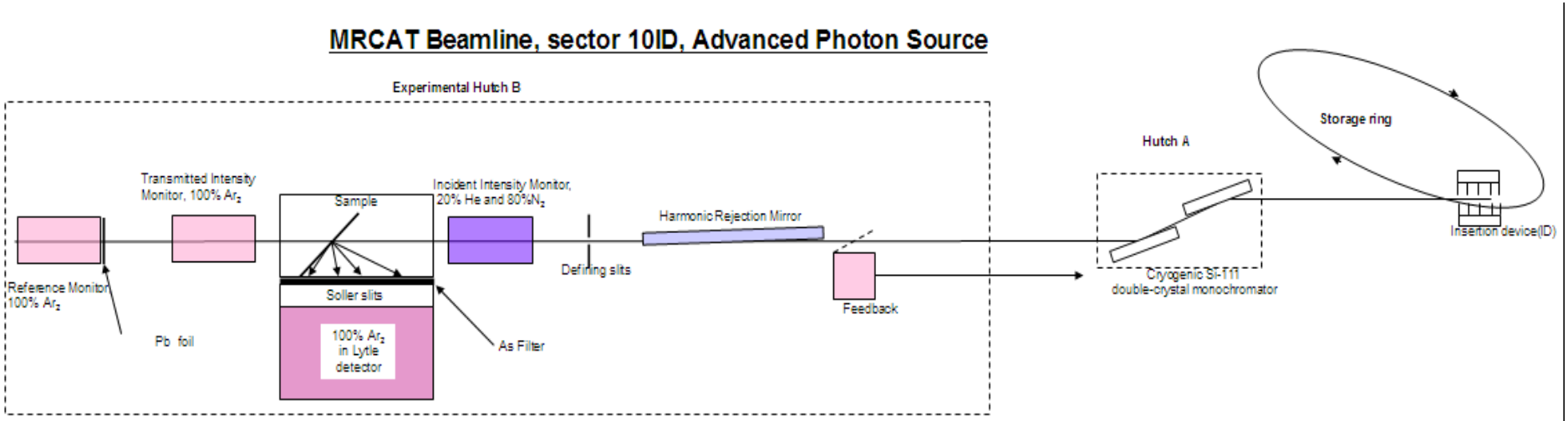


Image courtesy DESY

Undulators have sharp peaks in spectrum that can be tuned by changing gap
Wigglers have stronger field, broad spectrum (and lots of heat!)

Schematic of beamline Instrumentation



X-ray beamline components include…

- "Front-end" components (cooled slits, etc.)
- Bragg crystal **monochromator** (two Si crystals, first cooled with liquid nitrogen)
- **Harmonic-rejection** mirror (monochromator lets through not only energy of interest, but harmonics, e.g. $3E_0$)
  - Alternative: **detune monochromator**
- Detectors (several different types)
- Goniometers, etc., for sample positioning

Now, have monoenergetic x-ray beam

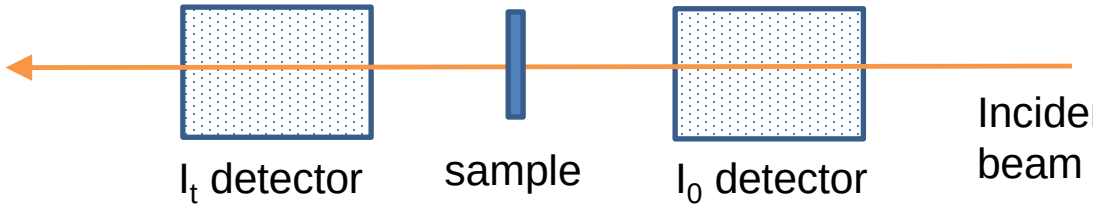
- What do we do with it?
- Obviously want to measure x-ray absorption as a function of energy, but can do it as simple **transmission** experiment or **indirectly**

- Start out with the simplest …

Experimental Techniques

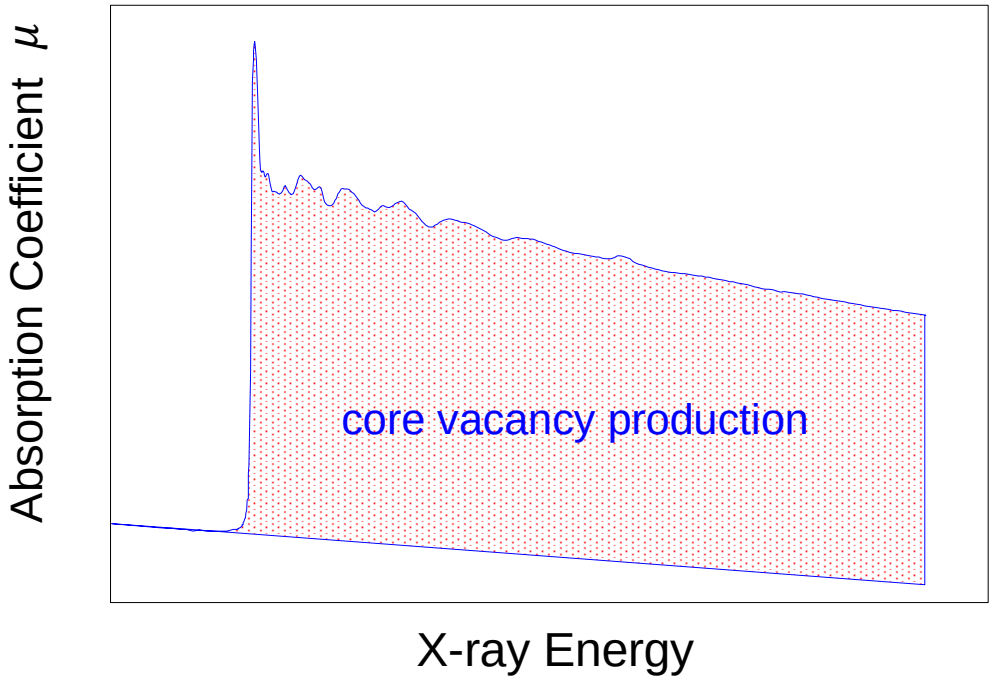
Simplest: Transmission
directly measure absorption as function of incident energy (x=sample thickness)

Note: Extra absorption above edge due to creation of atomic "core vacancies" that later decay, giving off fluorescence x-rays, etc.



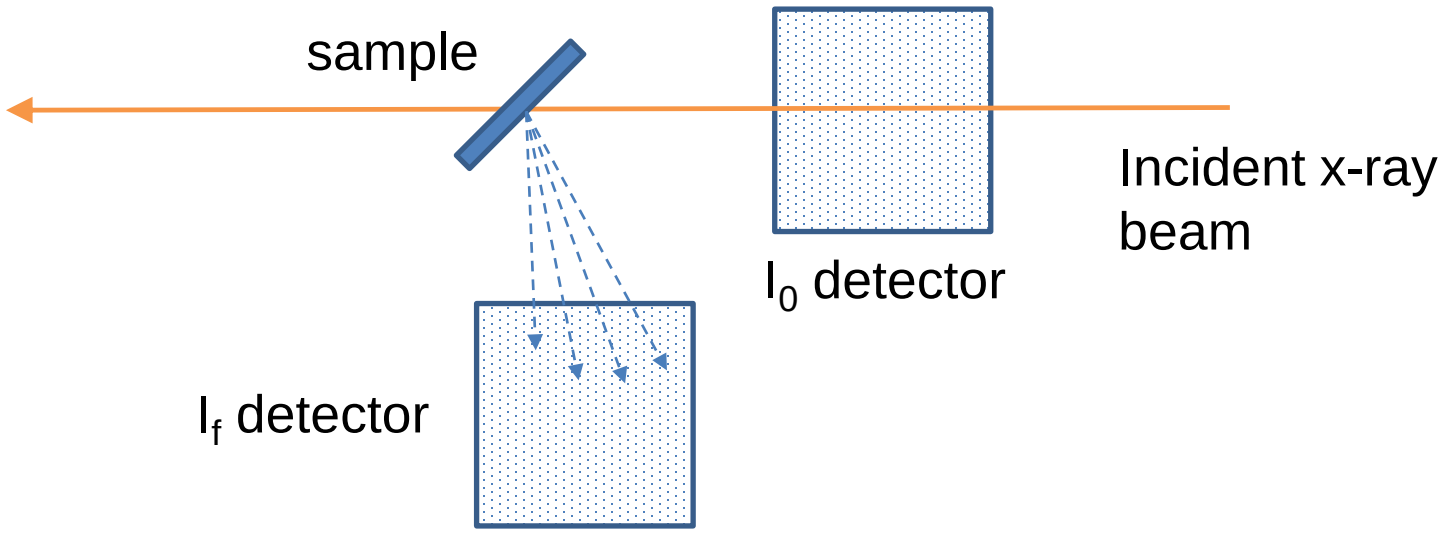
$$I_t = I_0\, e^{-\mu x} \qquad \mu x = -\ln(I_t/I_0)$$

Note: Single μ, t



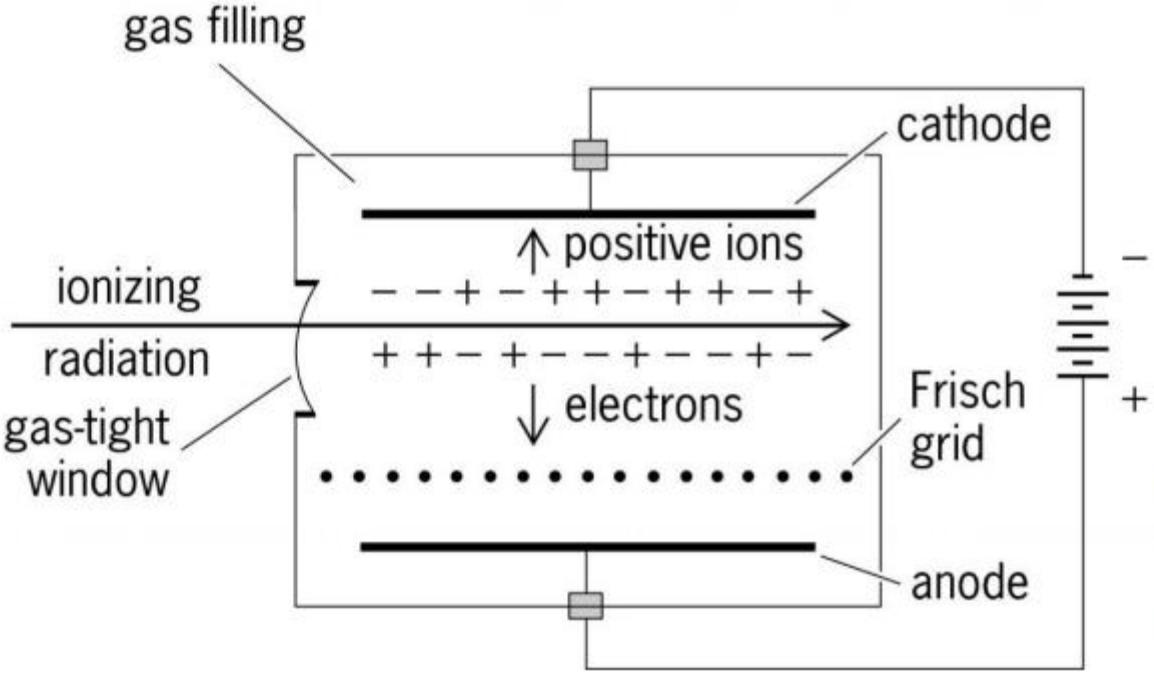
“Indirect” XAFS Detection Methods: (proportional to absorption)

- x-ray fluorescence, or
- emitted electrons (total or partial “electron yield”)



Measure **emitted flux** as function of **incident beam energy**

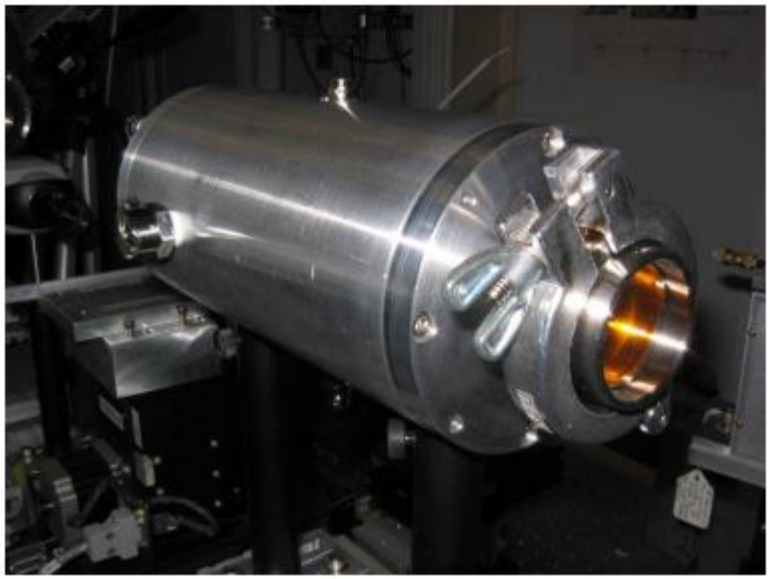
Ionization chamber -Principle



Note: frequent spike noise comes from a discharge
Low voltage is recommended

Two types of ionization chamber

@PF

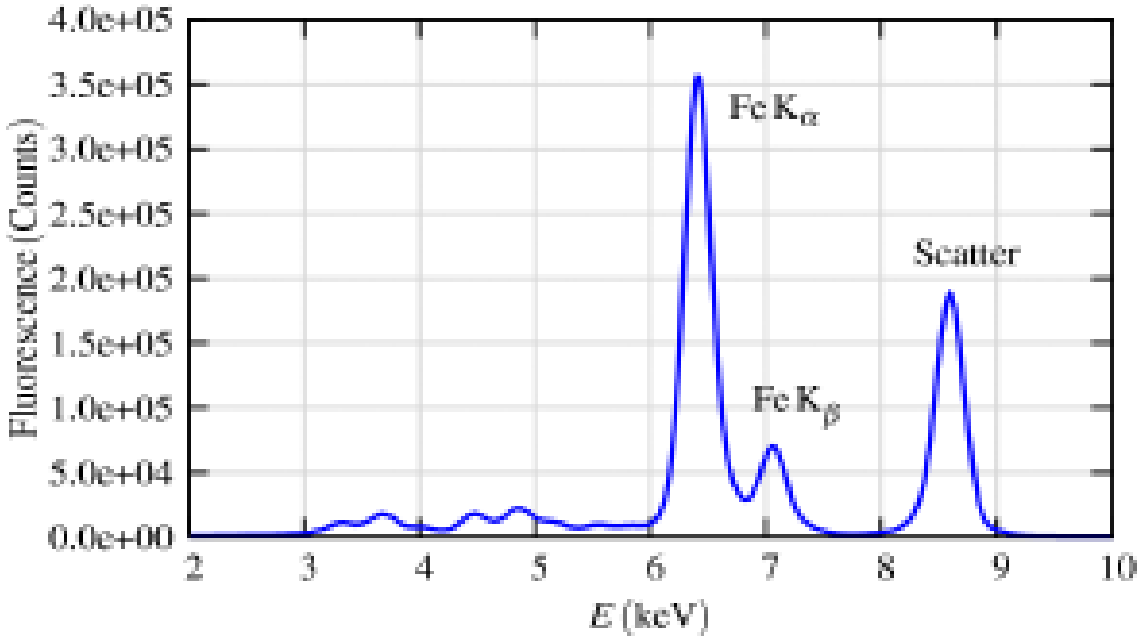


@CLS

Courtesy Hiroyoki Oyanagi

More on Fluorescence Measurements

- X-rays from sample include not only fluorescence signal, but also background:
  - Elastic and Compton scattered x-rays
  - Fluorescence from other atomic species



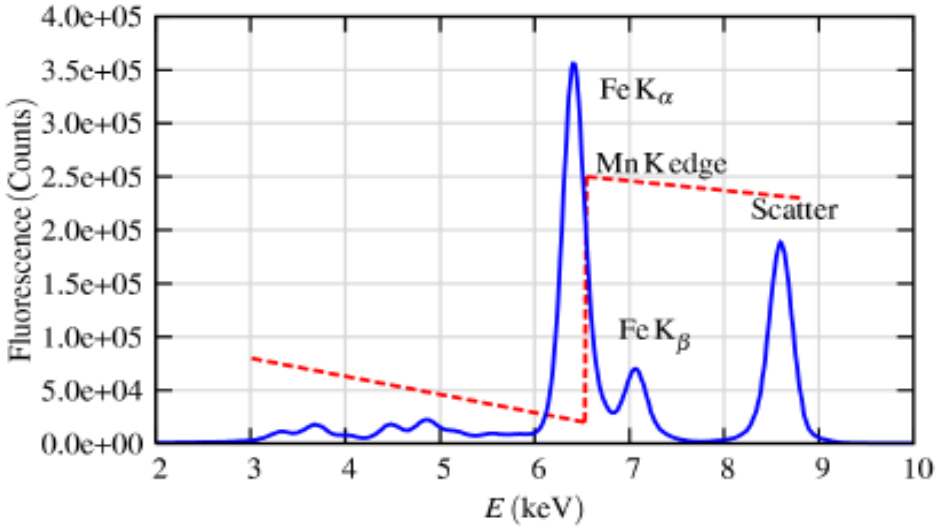
For many systems, background can be 10-100 times larger than desired fluorescence

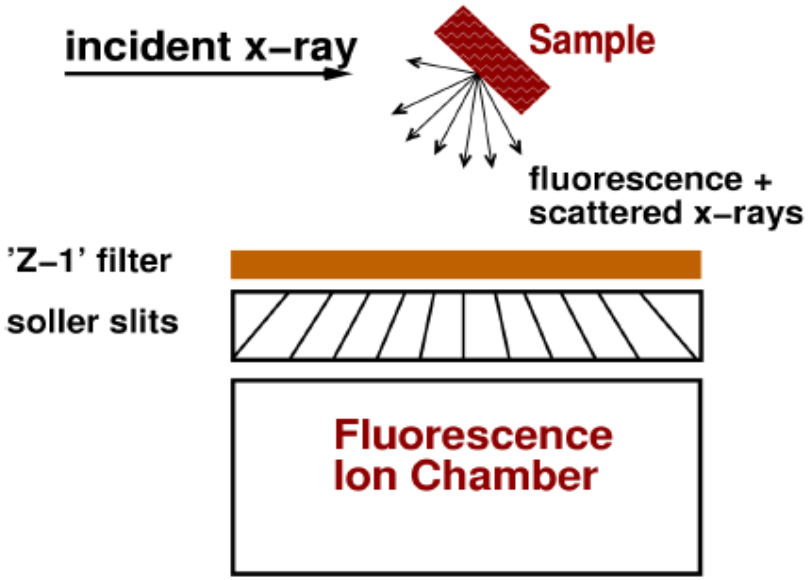
Figure courtesy Matt Newville, University of Chicago / CARS

Minimization of X-ray Background

- Note that scattered x-ray background is higher energy than fluorescence
- Two common methods:
  - Can use x-ray “filters” that have higher absorption for background than fluorescence signal
  - Use energy-resolving detector to choose just desired energy
  - For the most dilute systems (or to remove close undesired fluorescence lines) can use focusing crystal analyzer to choose desired energy

For high fluorescence flux: X-ray Filters

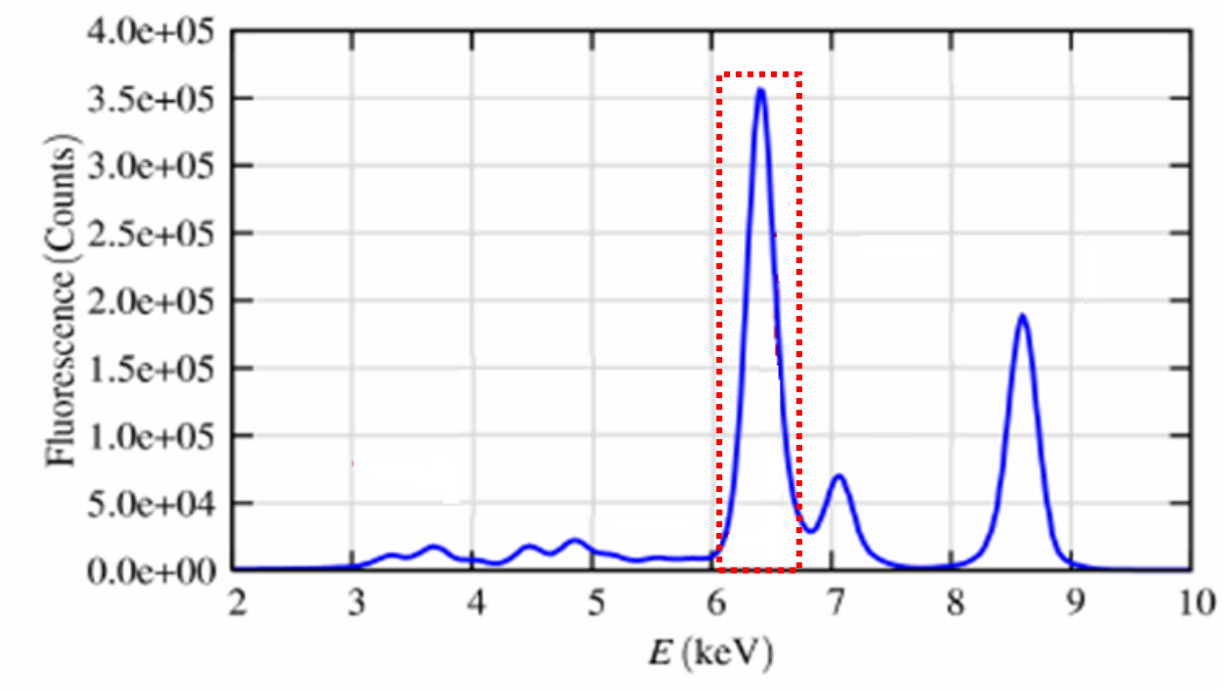




This technique works well for relatively concentrated samples as long as no other fluorescence emission close to desired energy

Figure courtesy Matt Newville, University of Chicago / CARS

Energy-discriminating solid-state detectors (usually either Ge or Si)



- Select just energy region of interest
- Problems: Relatively low count rate, possible non-linearity from “dead time”
- Almost always use multi-element detectors

Figure courtesy Matt Newville, University of Chicago / CARS

Samples for XAFS Measurements

- **Transmission** measurements:
  - Need thin samples, typically on order of x-ray penetration depth
  - If too thick or heterogeneous, signal distorted by “thickness effects”, where most signal coming from thinner parts of sample
    - Signal “compressed” causing distortion, incorrect amplitudes
    - Similar distortion if grain size too large in polycrystalline samples

Samples for XAFS Measurements

- **Fluorescence** measurements:
  - Useful for (1) dilute systems (e.g. biological) or (2) thick samples with too little transmitted beam (e.g. single crystals)
  - For (2), some complications:
    - X-ray diffraction peaks
    - X-ray penetration depth varies with XAFS oscillations, get distortion of XAFS signal
    - Tricks to deal with both problems

Angular dependence (K edges)

- With lower-symmetry samples (single crystals, clays, etc.) can generalize using θ_i, the angle between x-ray electric field polarization vector and direction to scattering angle, get

$$\left\langle S_0^2 \sum_i \frac{3\cos^2\theta_i}{kr_i^2} |f_i(k,r)| e^{-\frac{2r_i}{\lambda(k)}} \sin(2kr_i + \delta_i(k,r)) \right\rangle$$

where $\langle \quad \rangle$ represents average over all sites in sample.

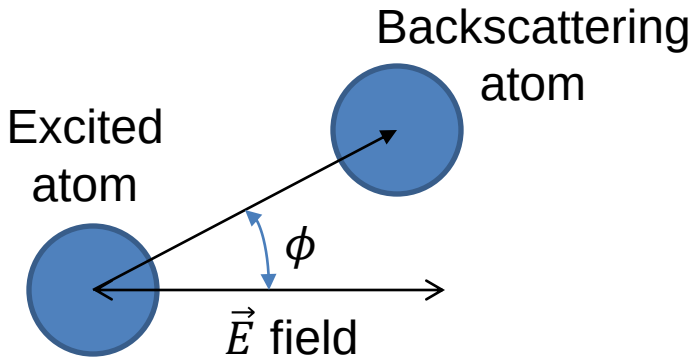
- Angular dependence useful for single-crystal, surface, interface studies (more later)

Polarization Dependence in XAFS

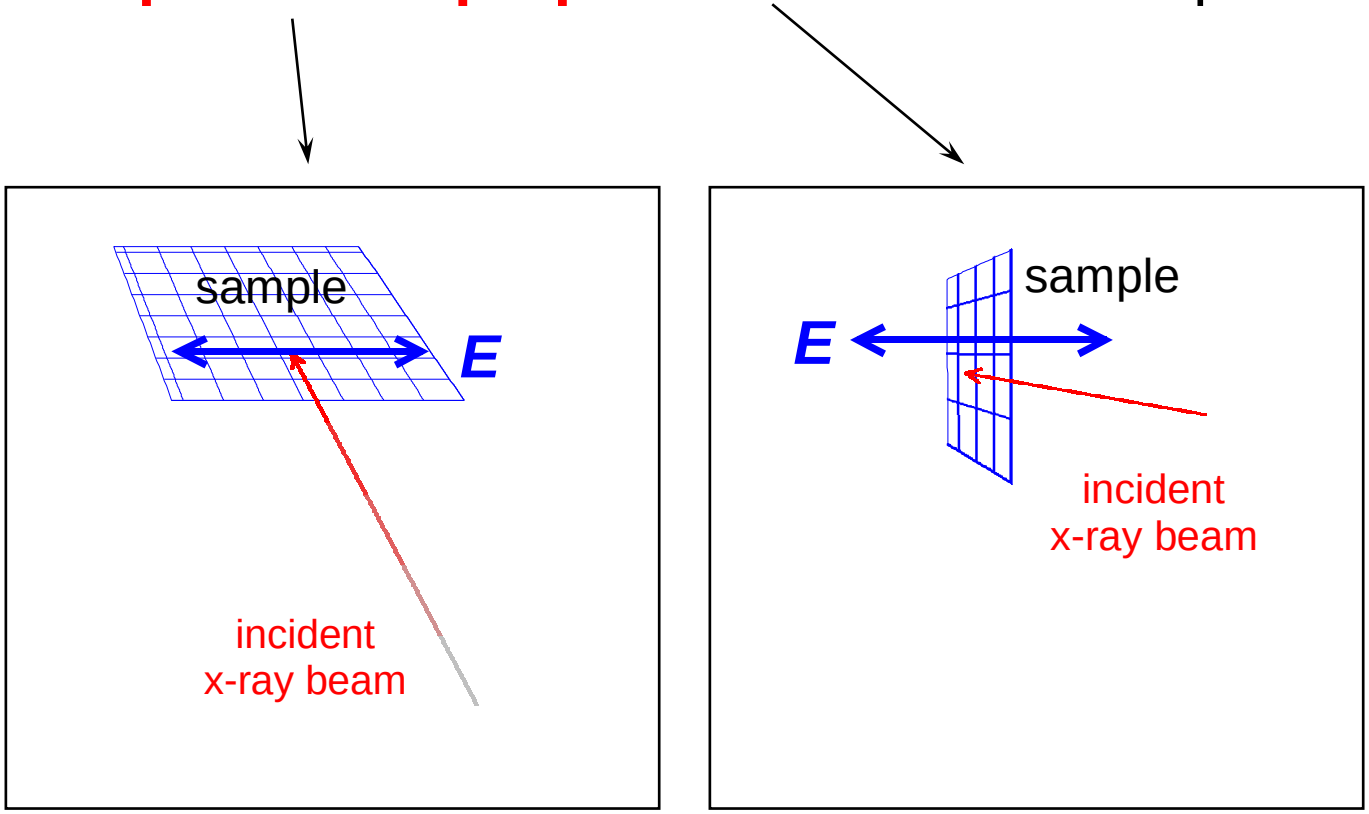
- X-rays from synchrotron source (usually) polarized in **horizontal** plane (this direction of x-ray electric field)
- For ***s*** initial electron state (e.g. K or L_1 edge), final electron state will have ***p*** symmetry

  $\rightarrow$ dipole pattern for emitted electron wave

Atoms in direction of $\vec{E}$ will be emphasized in XAFS spectrum, weighted by $\cos^2 \phi$



Can use polarization of x-rays to emphasize atoms **parallel** or **perpendicular** to surface plane



Makes no difference for isotropic samples, but can be very useful for studying surfaces, interfaces, layered materials, etc.

When performing experiments, need to keep track of (depending on beamline)

- If **undulator** line, set gap to optimize for your energy region: choose taper and/or scanning parameters
- **Monochromator** (optimize scanning, feedback stabilization, glitches)
- **Harmonic rejection mirror** (optimize for your energy range) (or **detune monochromator**)
- **Detectors** (I_0, I_t, fluorescence; optimize gases if ion chambers, set regions of interest if counting detectors)
- **Samples** (design for optimum thickness, uniformity, etc. During measurements need to monitor temperature, radiation damage, etc.)
- **Sample environment** (temperature, gas-handling, high pressure, etc.

Not covered here (but wish I could)

- Techniques for extreme environments, e.g. diamond pressure cells
- Micro- and nano-focusing using mirrors, Fresnel zone plates, capillaries, etc.
- Time-resolved techniques
  - Quick/slew scanning
  - Energy dispersive techniques
  - Pump/probe measurements using laser excitation
- Spin-resolved measurements: Magnetic circular dichroism
- X-ray emission spectroscopy

Next…

- Specifics for different types of applications (e.g. materials science, biological systems, etc.)
- Different approaches to data analysis and interpretation
- Stick around!