Spectroscopy I: Optical and Electronic

Spectroscopy is the use of light, sound or particle emission to study matter. It originated through the study of visible light dispersed, according to its wavelength, by a prism. Later, the concept was expanded greatly to comprise any interaction with radiative energy as a function of its wavelength or frequency.

The data that is obtained from spectroscopy is called a spectrum. A spectrum can be used to obtain information about the specimen's energy states, its atomic or molecular arrangements, and related processes.

Nature of the interaction between radiation and material

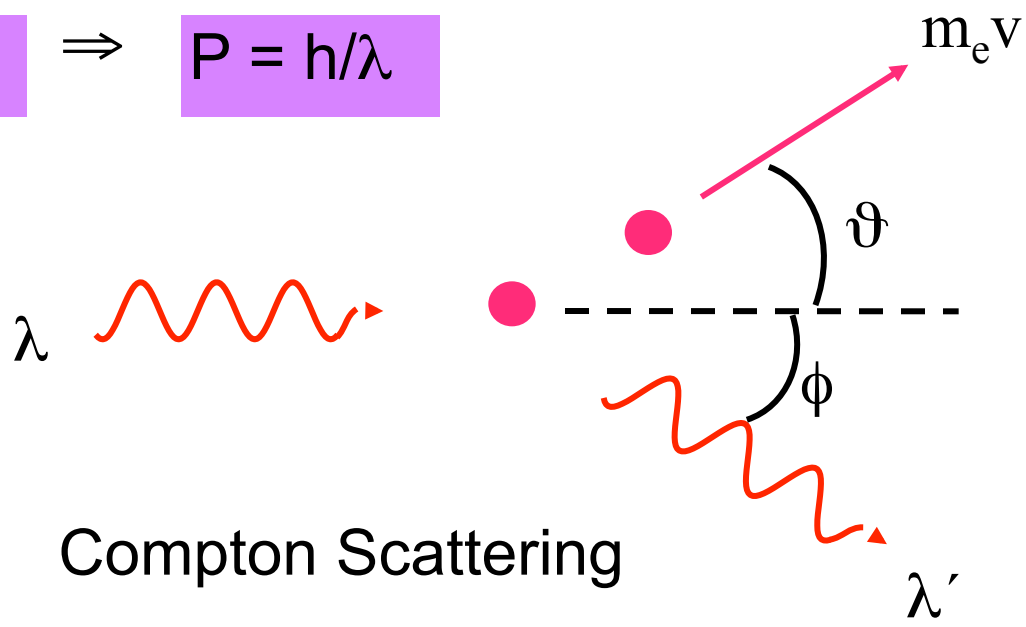
Types of spectroscopy can be distinguished by the nature of the interaction between the energy and the material.

- Absorption: measuring the fraction of incident energy transmitted through the material.
- Emission: radiative energy released by the material.
- Elastic Scattering: incident radiation reflected or transmitted by a material without energy loss.
- Inelastic Scattering: involving an exchange of energy between the radiation and the matter that shifts the wavelength of the scattered radiation.
- Refraction: the ability of a medium to impede or slow the transmittance of energy.
- Resonance: radiative energy couples two quantum states of the material in a coherent interaction.

Particle nature of photons

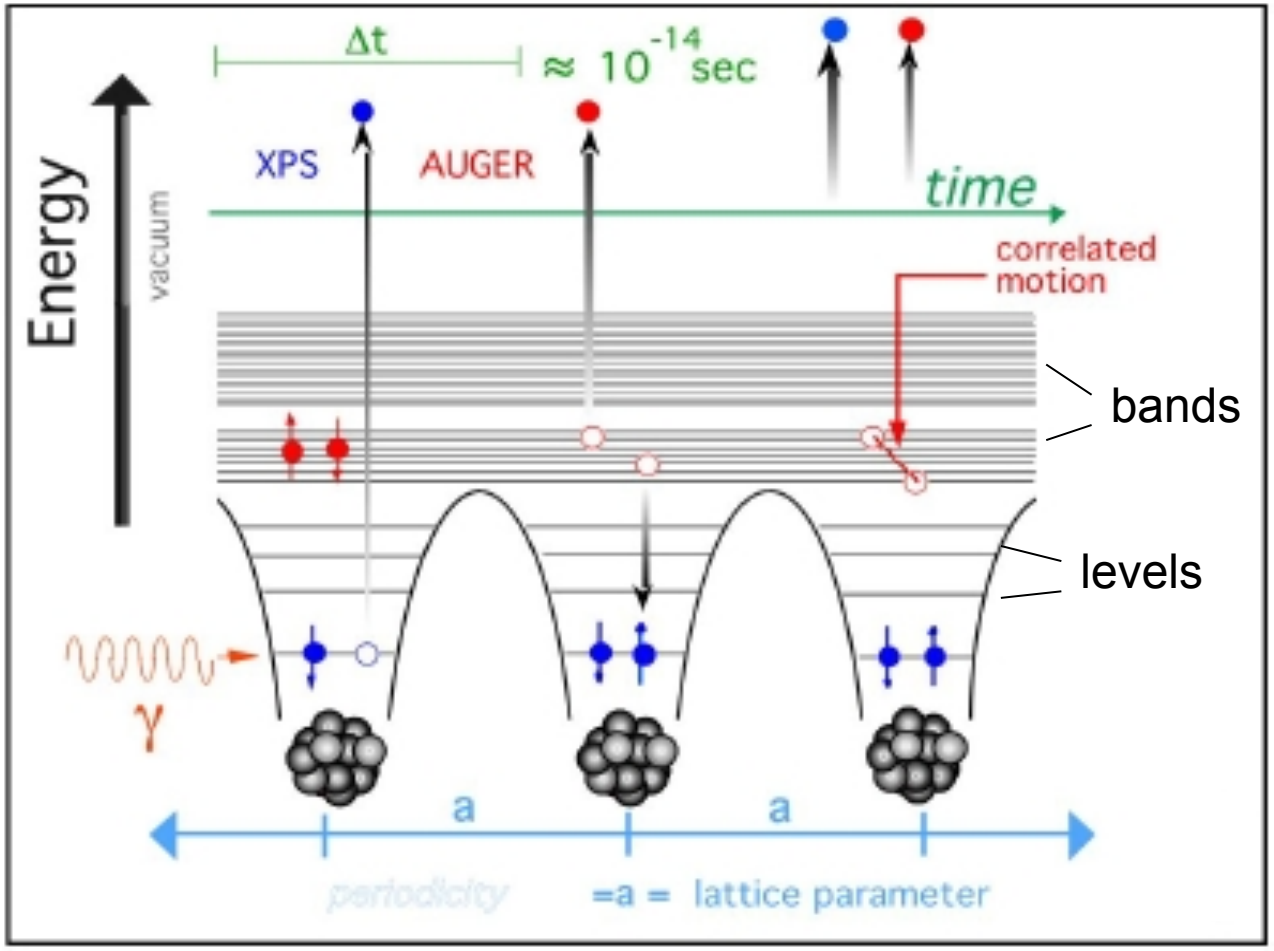
Einstein's proposal:

$E = h\nu \Rightarrow P = h/\lambda$



Compton Scattering

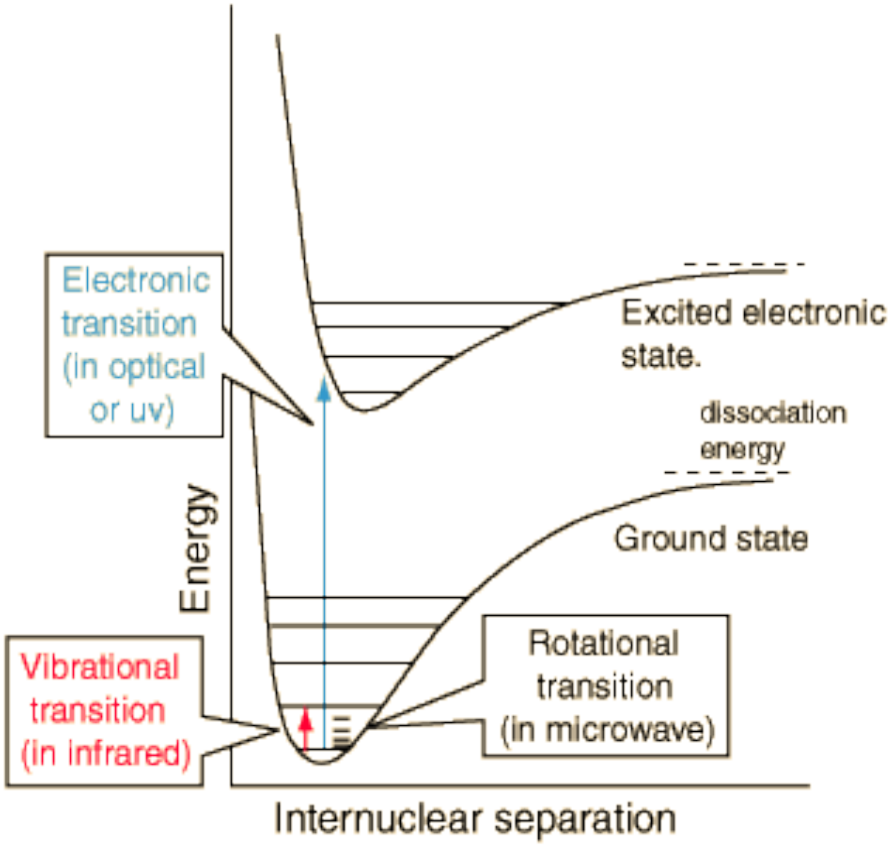
Energy levels and bands

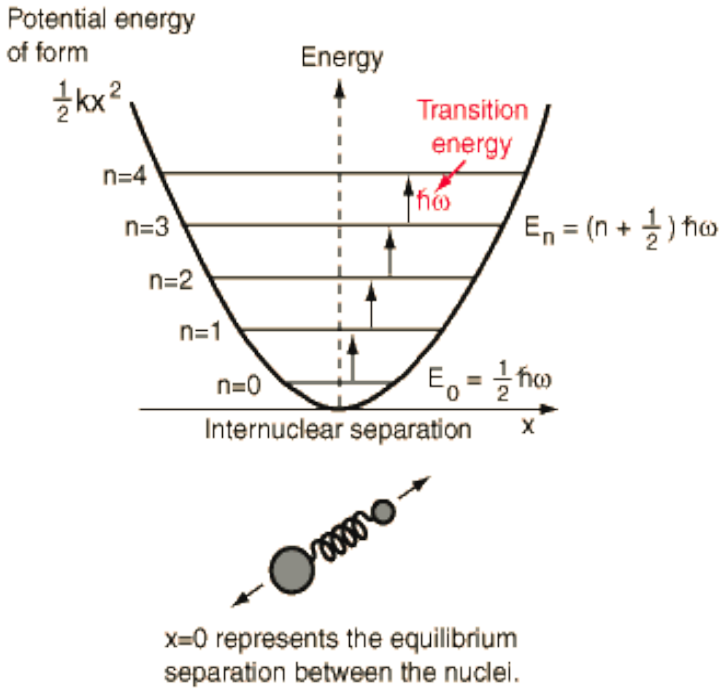


Electronic and vibrational levels

Born-Oppenheimer Approximation

$$\psi_{\text{molecule}}(\vec{r}_i, \vec{R}_j) = \psi_{\text{electrons}}(\vec{r}_i, \vec{R}_j)\psi_{\text{nuclei}}(\vec{R}_j)$$





Transition between two quantum states

Fermi's golden rule

Transition rate:

$$T_{i\to f} = \frac{2\pi}{\hbar} \left|\langle f|H'|i\rangle\right|^2 \rho,$$

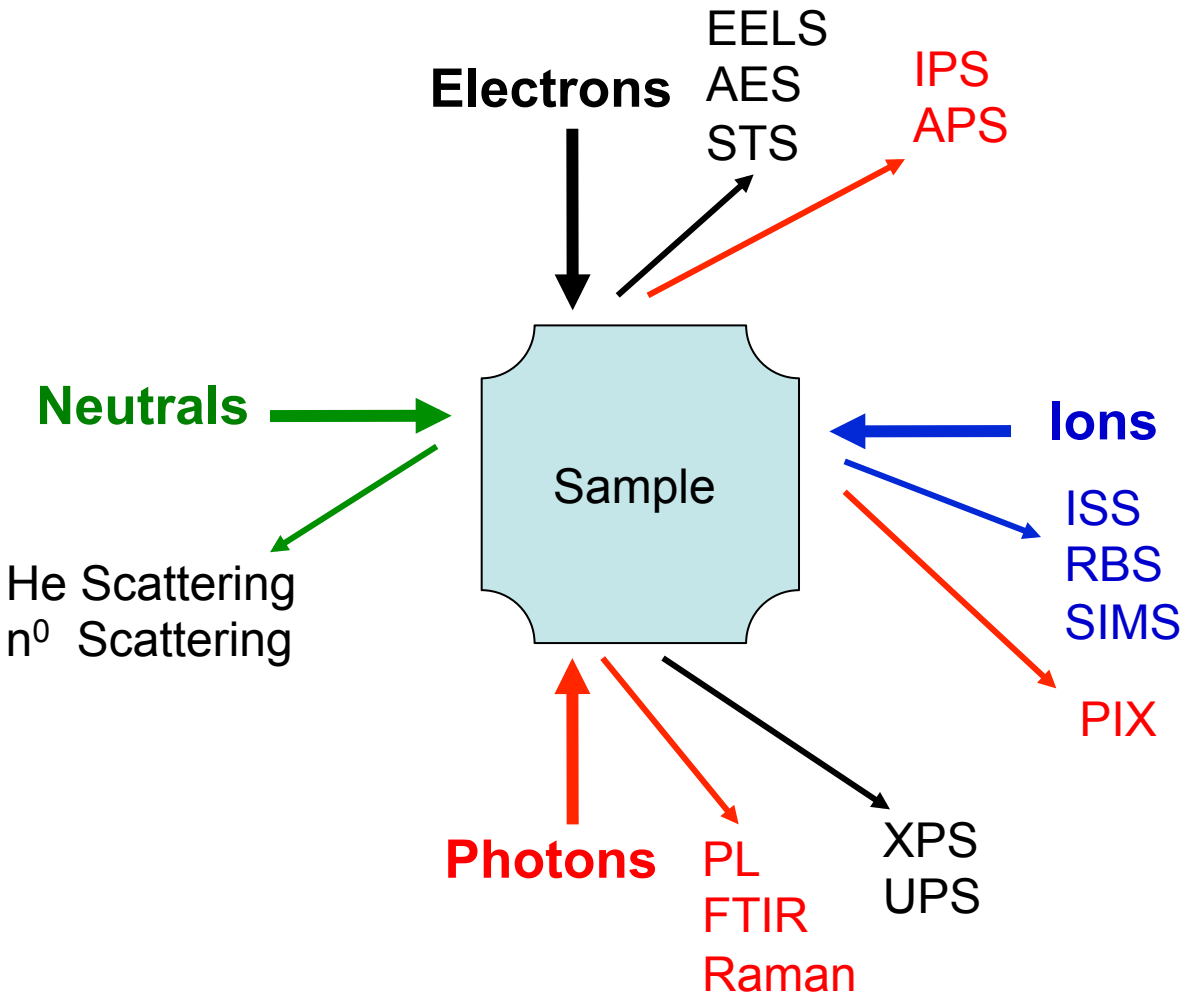
Transition probability

Density of final states

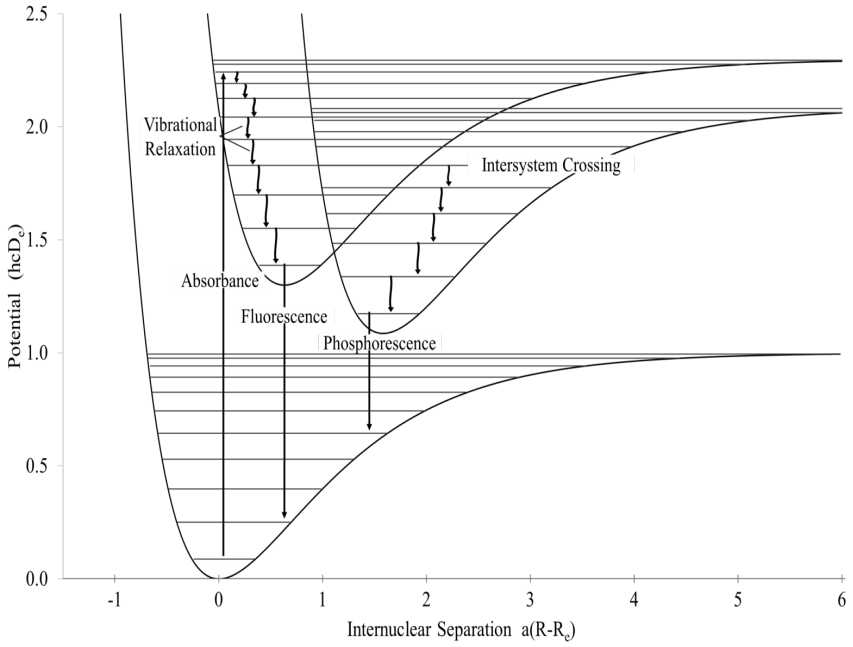
Transition probability is determined by the wavefunction overlapping of initial and final states, and dictated by the selection rules reflecting the nature of interaction *H'*.

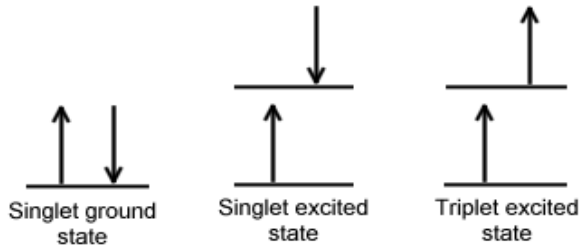
Various spectroscopic methods

Spectroscopy is the use of light, sound or particle emission to study matter.

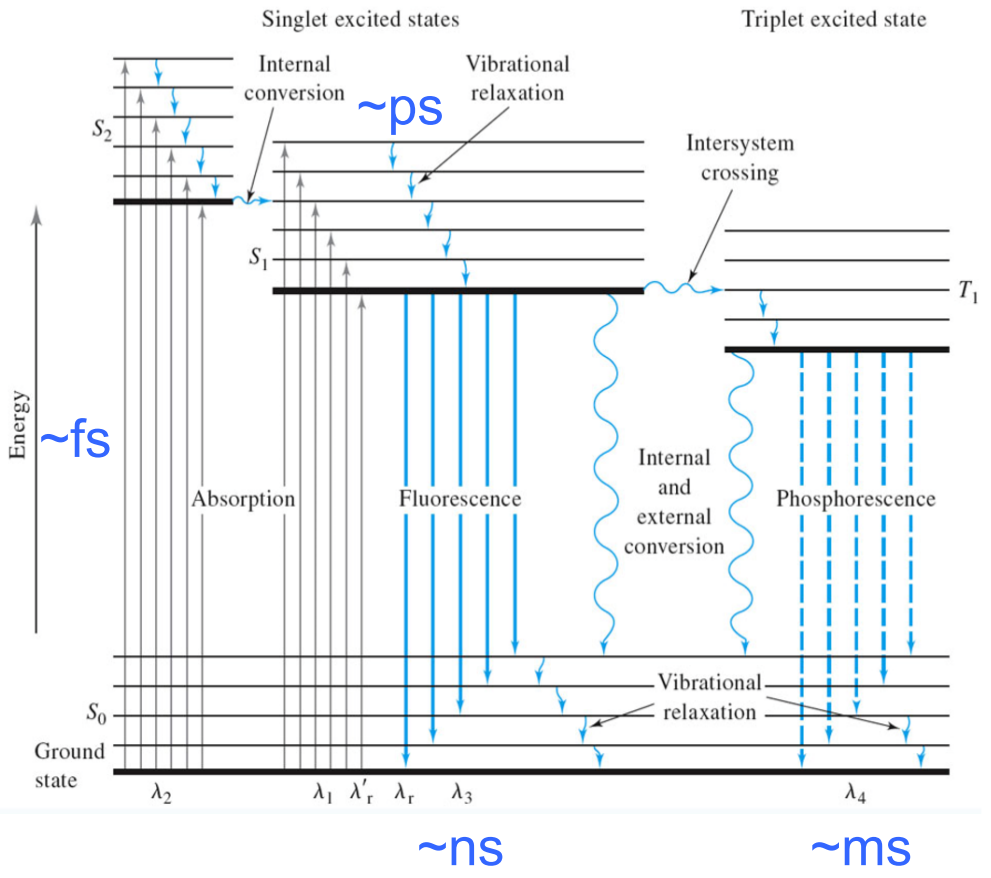


Fluorescence Spectroscopy

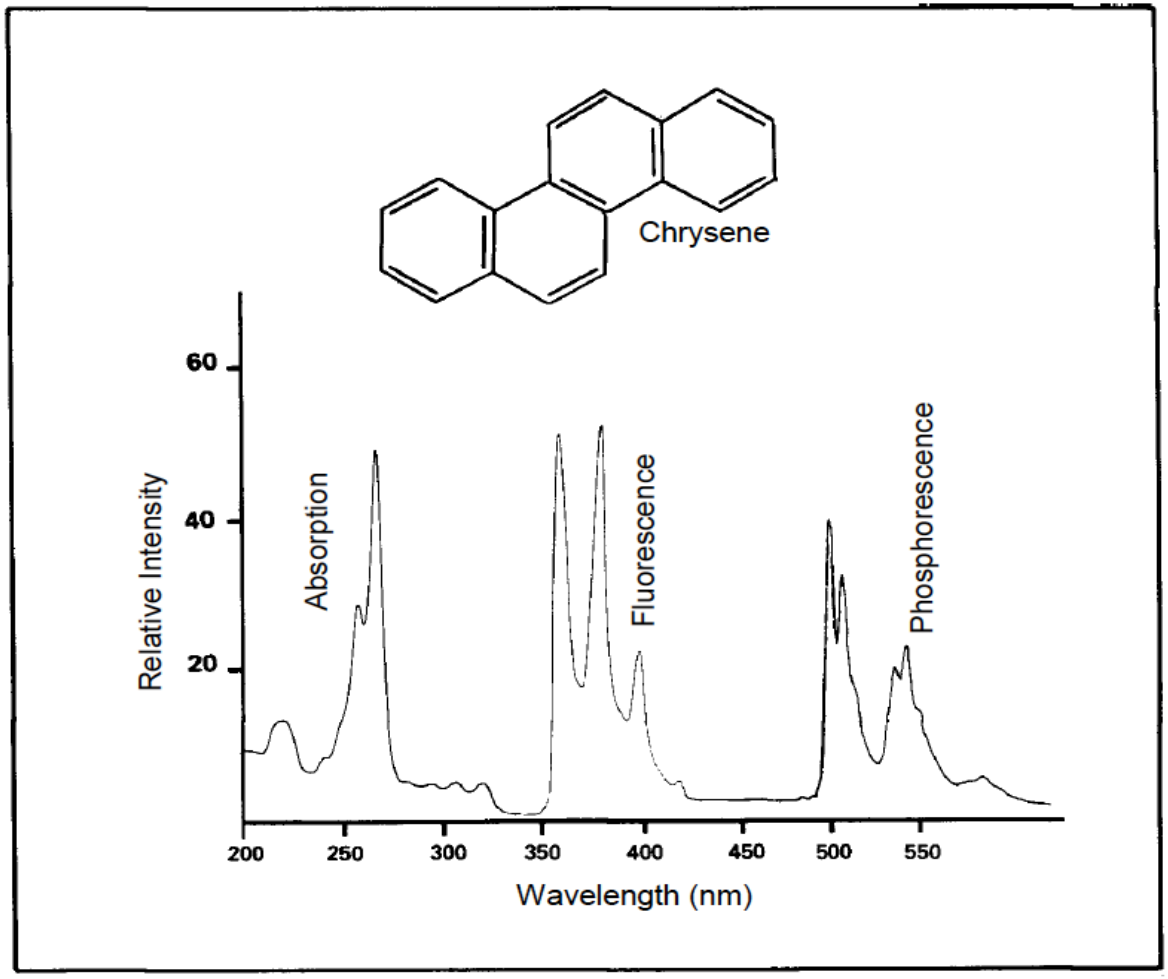




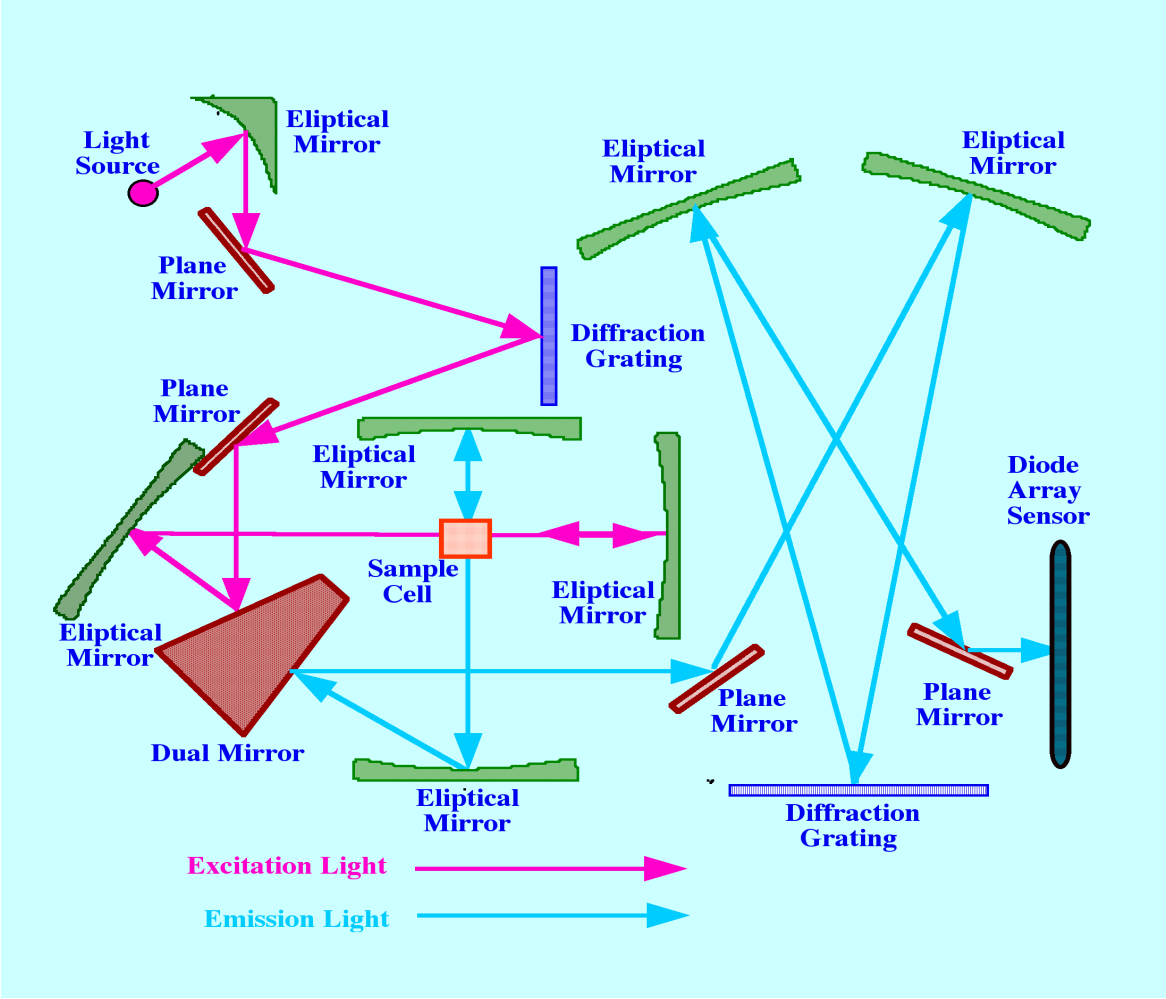
Jablonski Energy Diagram



Various Lasers



Instrumentation



Infrared Spectroscopy

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher-energy near-IR, approximately 14000–4000 cm^{-1} (0.8–2.5 μm wavelength) can excite harmonic vibrations. The mid-infrared, approximately 4000–400 cm^{-1} (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400–10 cm^{-1} (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

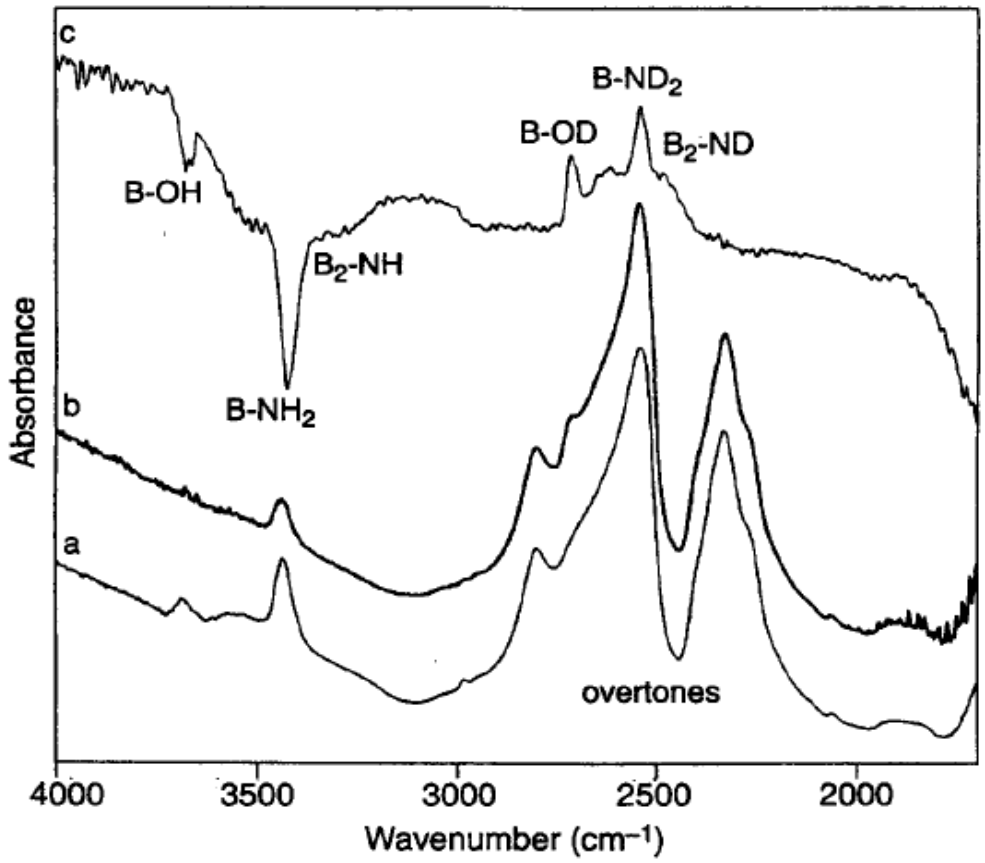
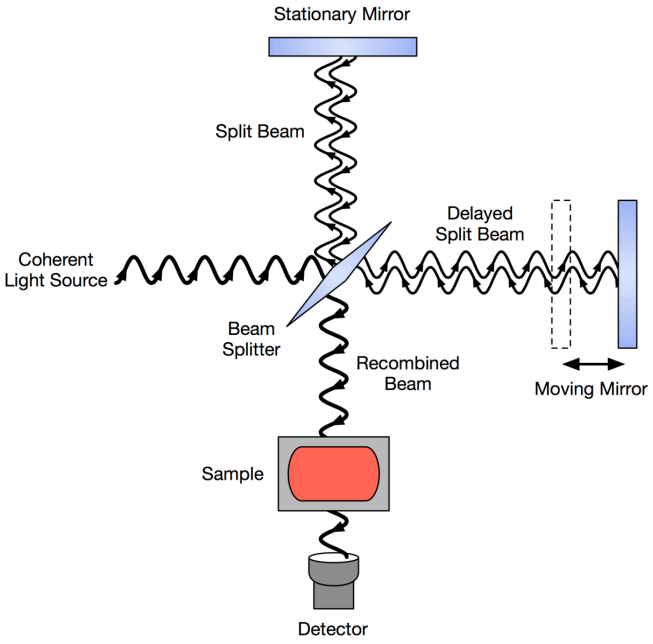


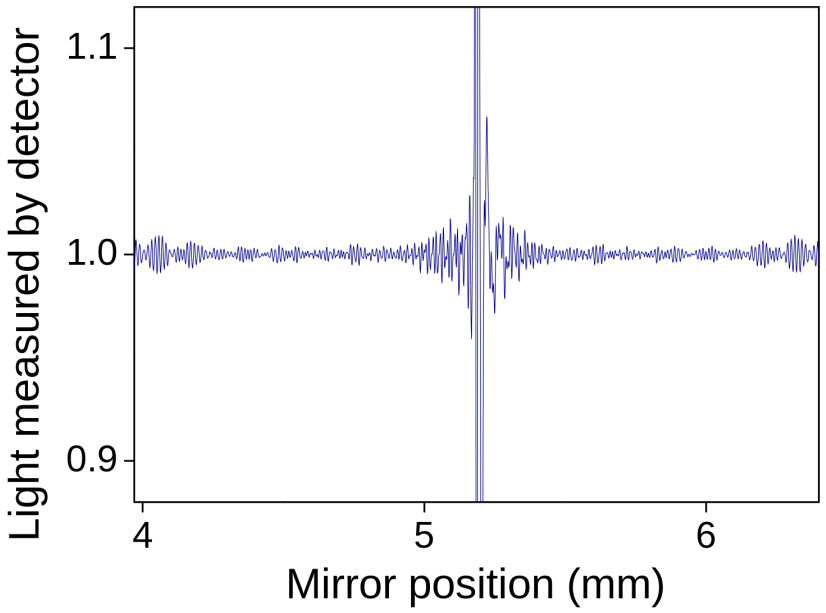
Figure 8.5. FTIR spectra of boron nitride nanopowder surfaces after activation at 875 K (tracing a), after subsequent deuteration (tracing b), and (c) difference spectrum of *a* subtracted from *b* (tracing c). [From M.-I. Baraton and L. Merhari, P. Quintard, V. Lorezenvilli, *Langmuir*, **9**, 1486 (1993).]

Fourier transform infrared spectroscopy (FTIR)

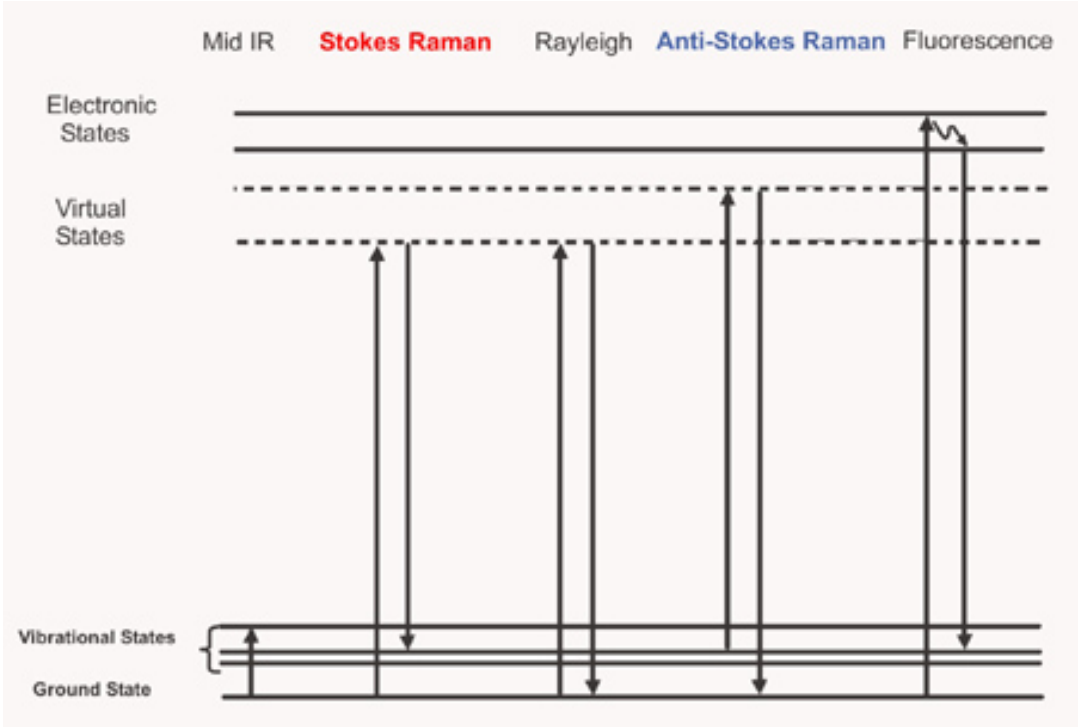
FTIR is a technique which a spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR has made dispersive infrared spectrometers all but obsolete.

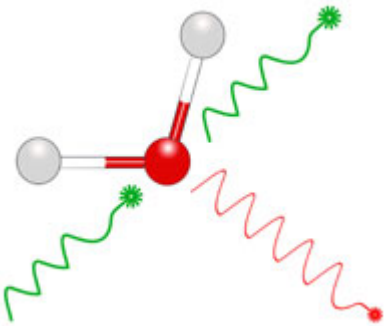


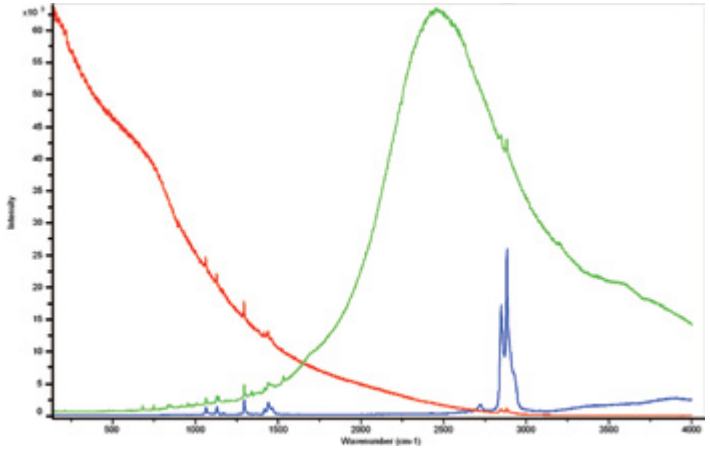
Michelson interferometer



The Theory of Raman Spectroscopy







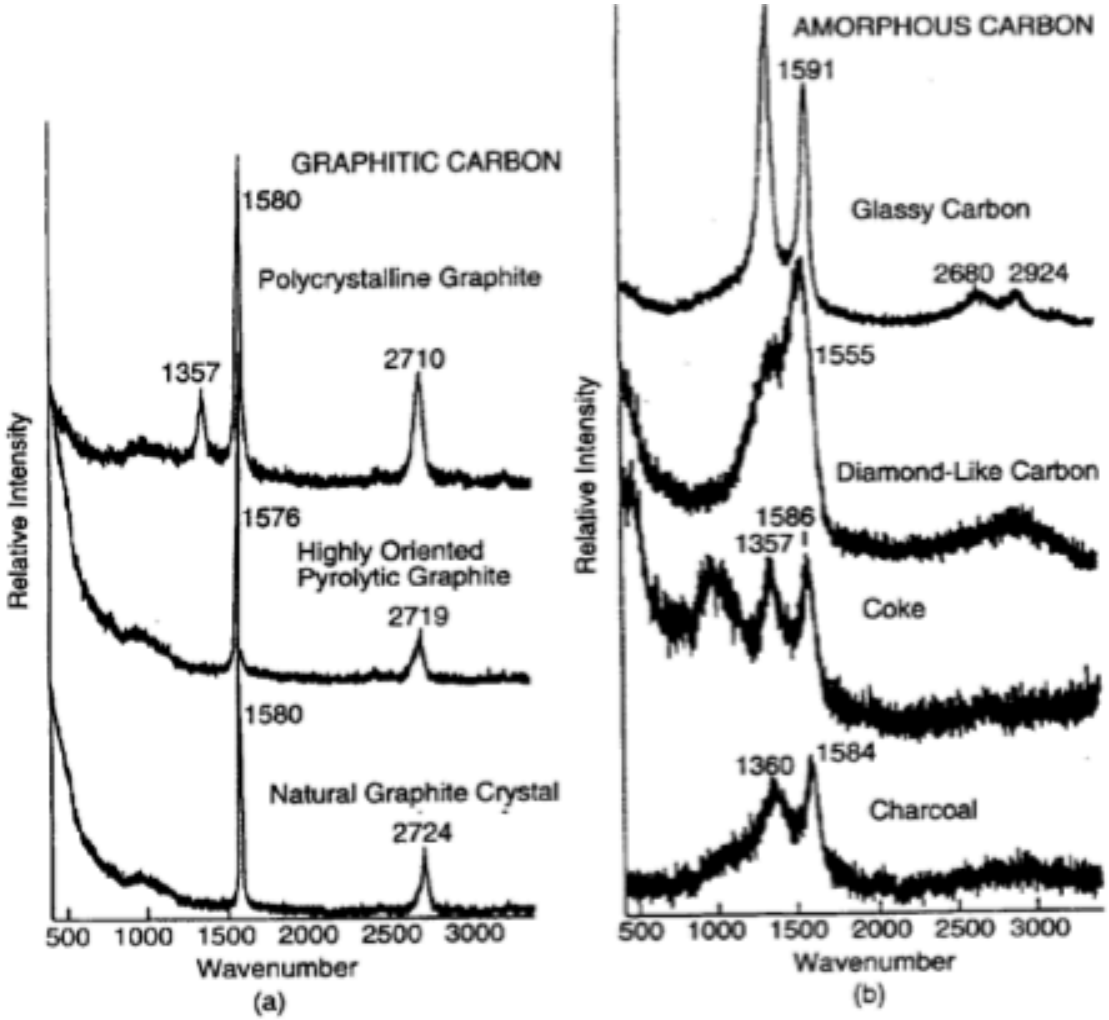
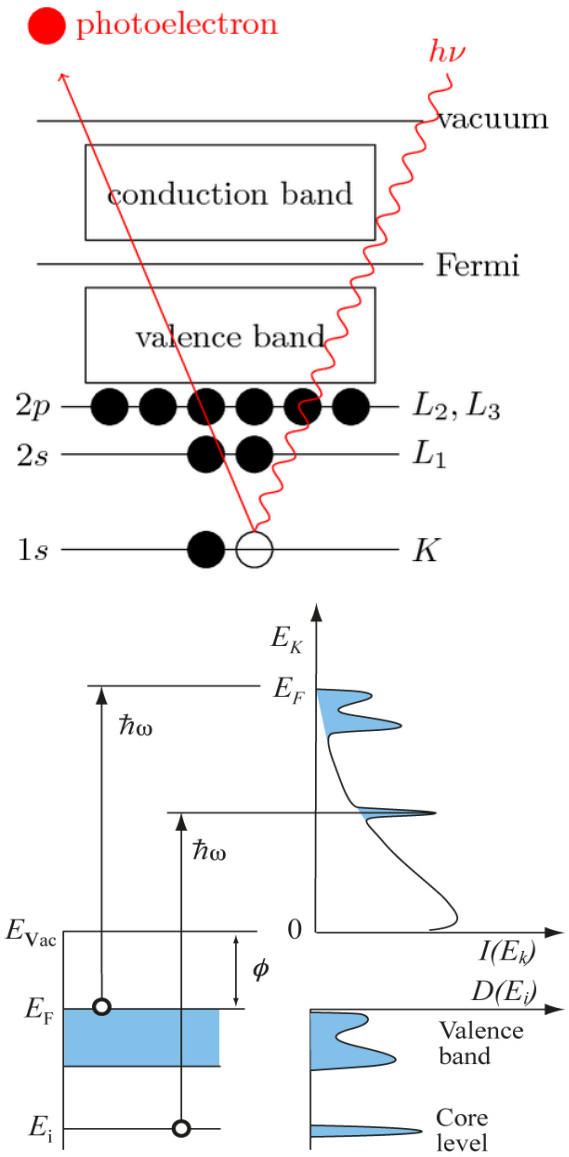
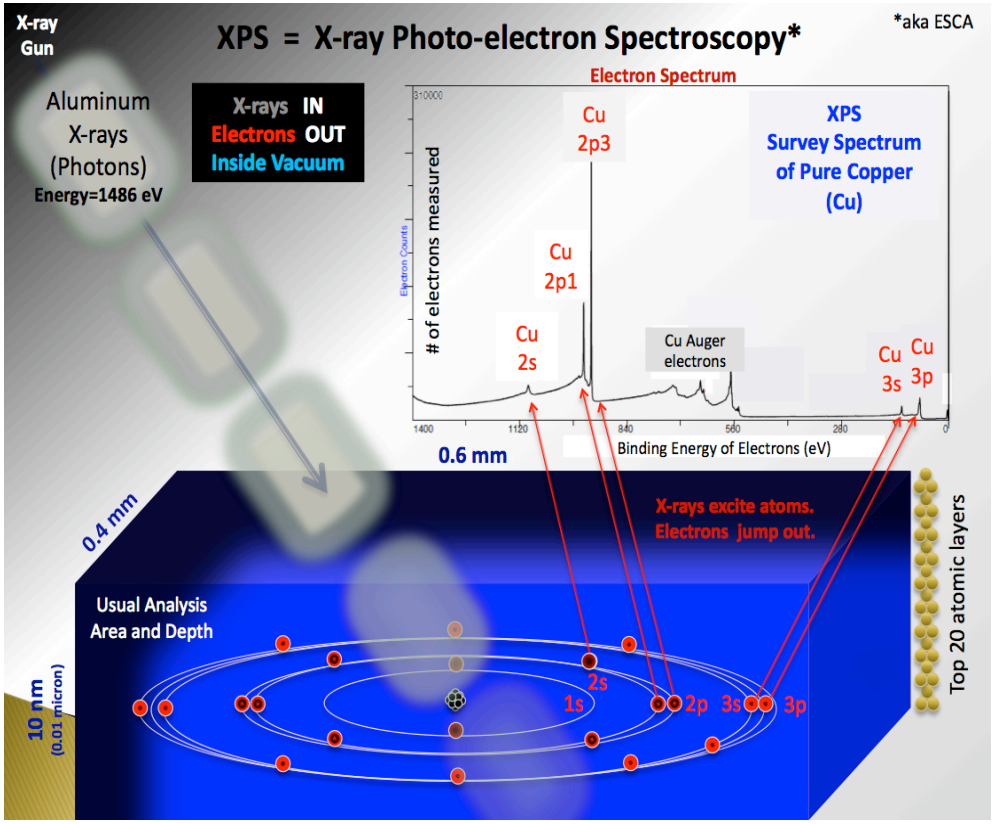


Figure 8.19. Raman spectra of (a) crystalline graphites and (b) noncrystalline, mainly graphitic, carbons. The *D* band appears near 1355 cm^{-1} and the *G* band, near 1580 cm^{-1}. [From D. S. Knight and W. B. White, *J. Mater. Sci.* **4**, 385 (1989).]

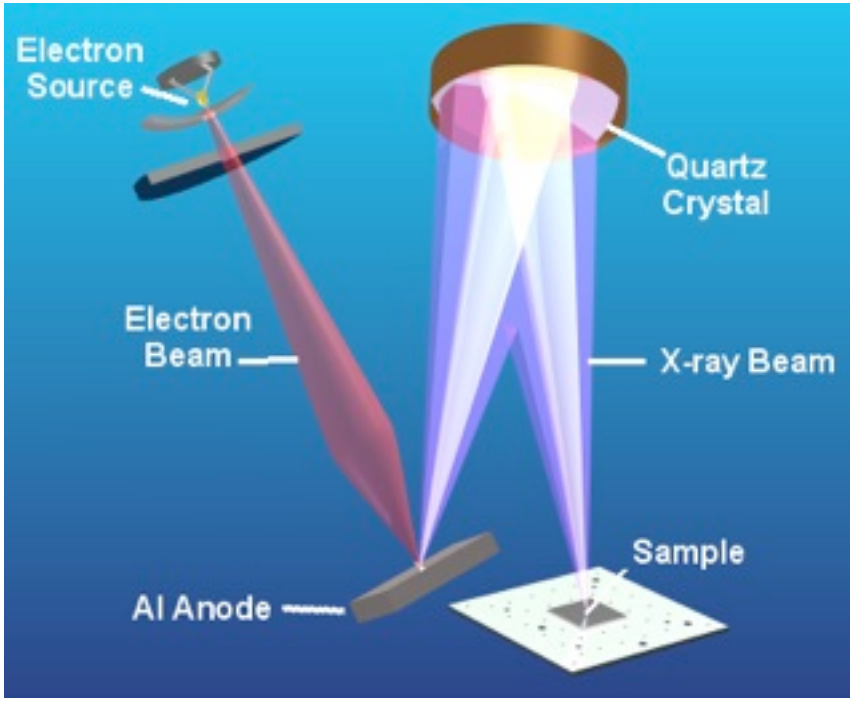
X-ray Photoelectron Spectroscopy (XPS)

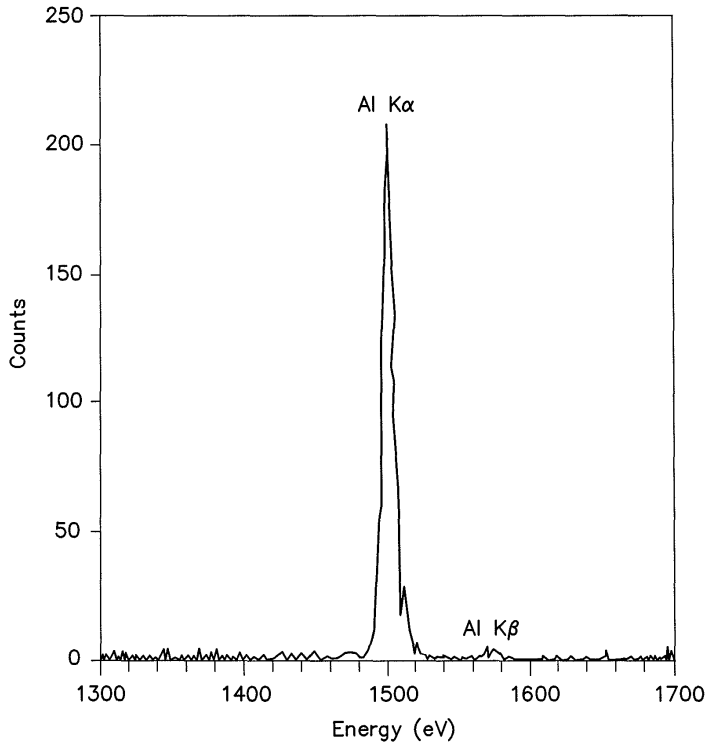




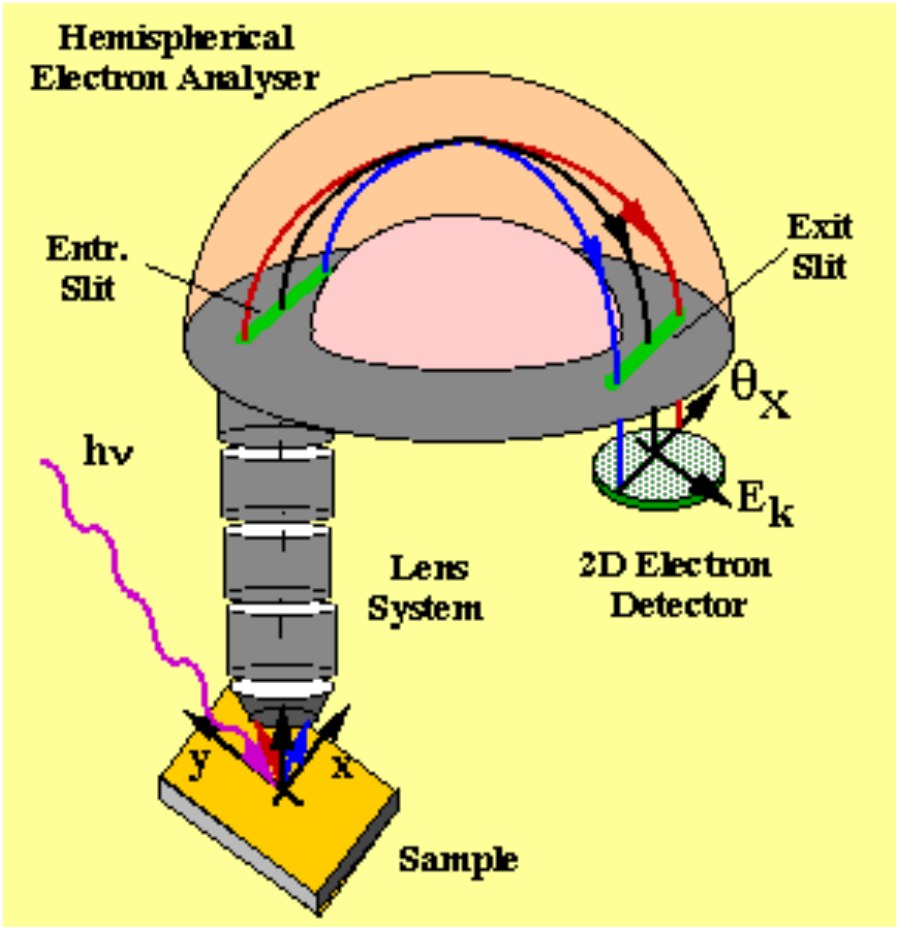
$$E_i = E_{hv} - (E_k + \phi)$$

X-ray source


Electron
Source
Quartz
Crystal
Electron
Beam
X-ray Beam
Sample
Al Anode


250
200
150
100
50
0
Counts
Al Kα
Al Kβ
1300
1400
1500
1600
1700
Energy (eV)

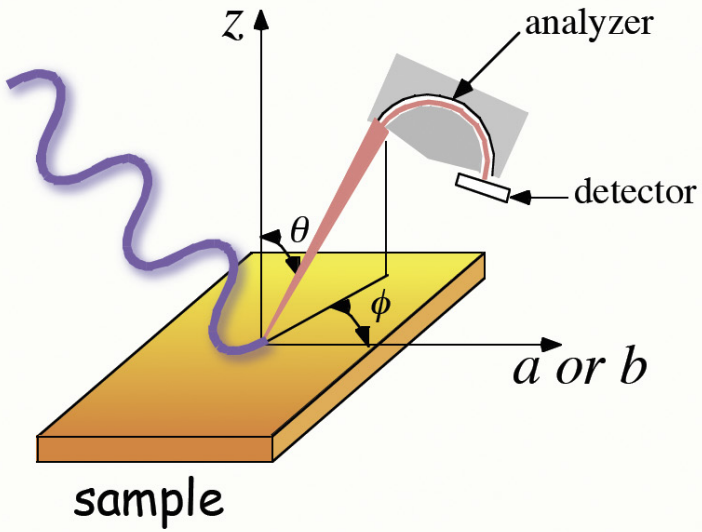
Concentric Hemispherical Analyzer (CHA)



$\Delta E/E_0 = s/ R_0$

s: mean slit width; R_0: mean radius

Angle-resolved photoemission spectroscopy (ARPES)



We need:

binding energy - E_b

initial momentum - k^i

$E_b = E - h\nu + W$

$k^i_{||} = k^f_{||} = \sqrt{2mE/\hbar^2}\sin\theta$

$k^i_{\perp} = k^f_{\perp} - G = \sqrt{2mE/\hbar^2}\cos\theta - G$