

Surface Science September 13, 2010

Introduction to electron spectroscopy: Analyzers, electron optics

References and sources:

Woodruff and Delchar (2nd ed.), pp 105-212

<http://venables.asu.edu/grad/lectures.html>

<http://www.cem.msu.edu/~cem924sg/>

<http://www.chem.qmul.ac.uk/surfaces/scc/>

Why are spectroscopies with electrons so central in surface science?

Many possible probes:

➤ Photons

➤ Ions

➤ Electrons

Photons and ions (except at very low energy) interact weakly with the sample, so they penetrate deeply.

Electrons interact strongly, so they are very sensitive to the surface.

Different electron spectroscopies for surface analysis

- Auger electron spectroscopy
- X-ray photoelectron spectroscopy
- UV photoelectron spectroscopy
 - Inverse photoelectron spectroscopy
- Electron energy loss spectroscopy

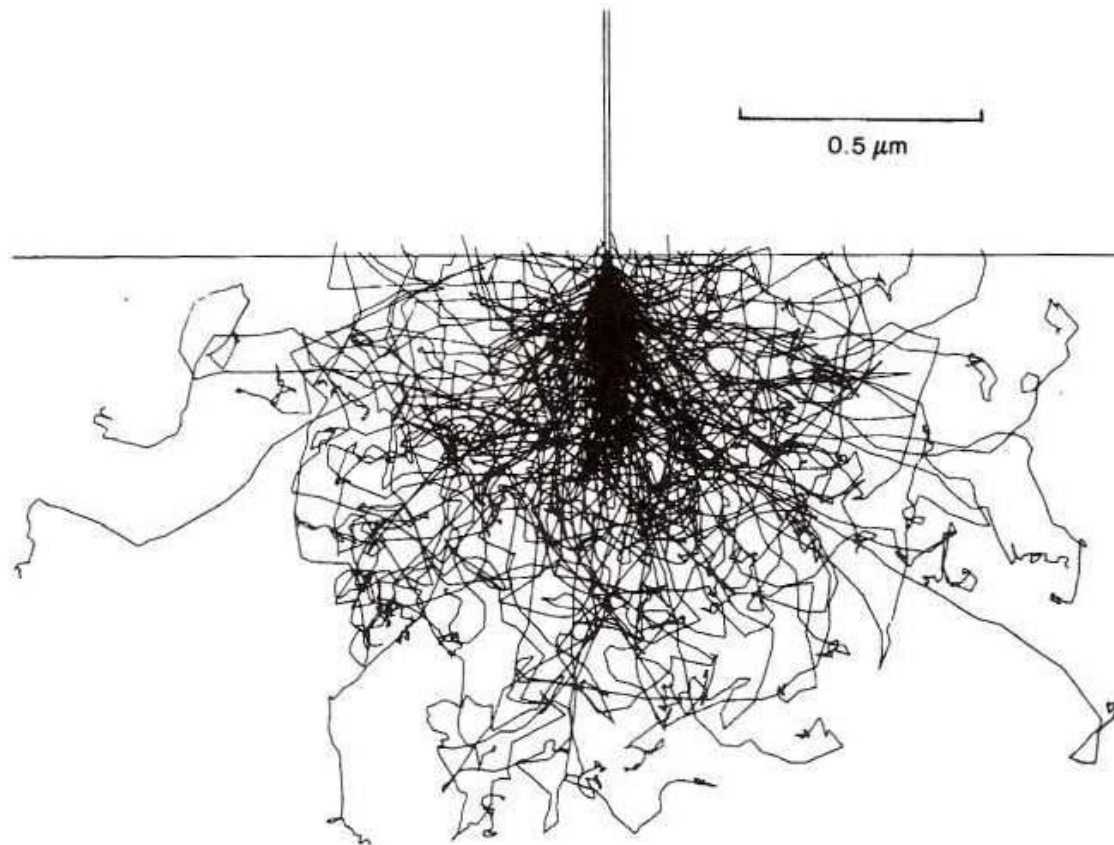
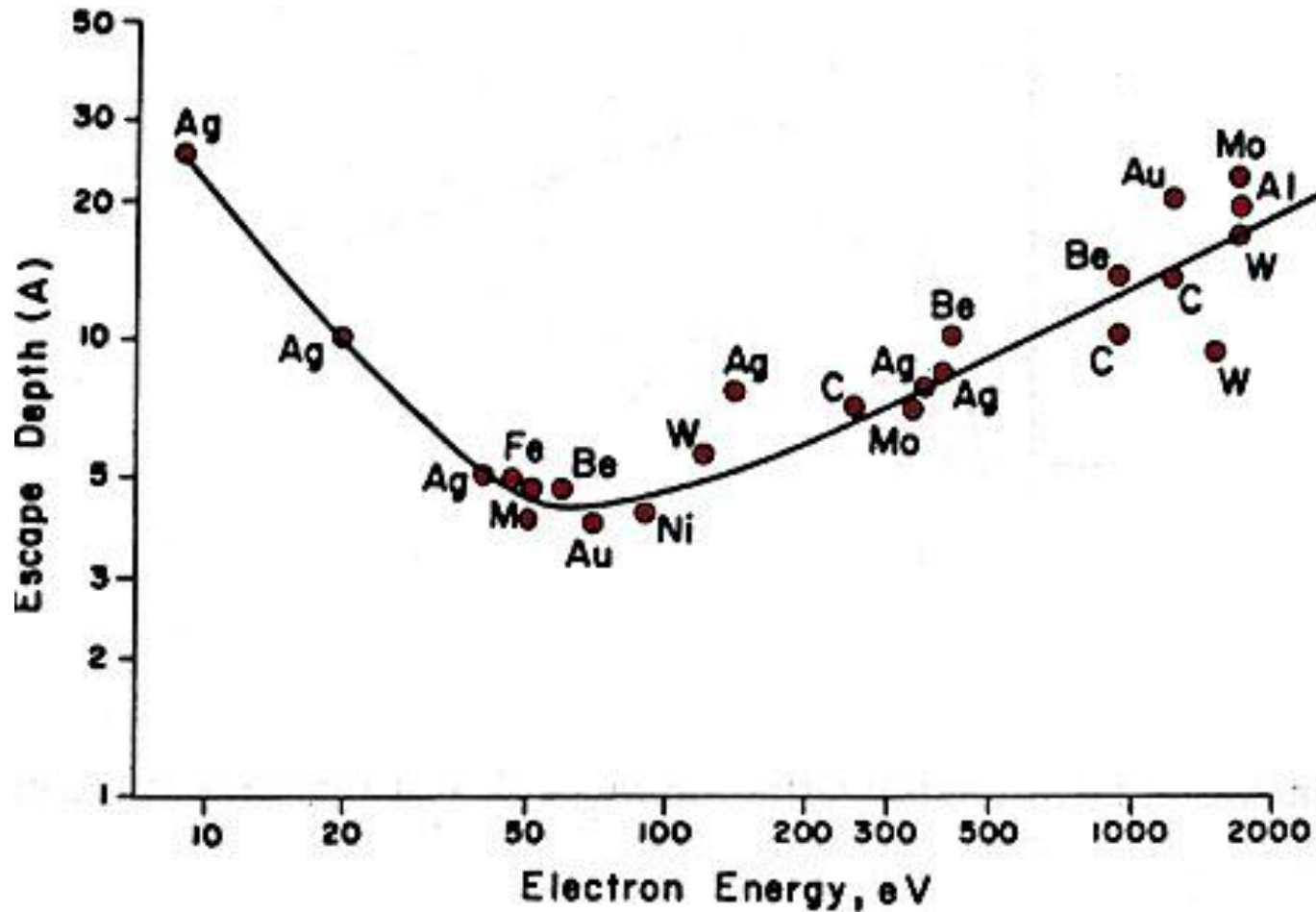


Figure 6.13 Monte Carlo electron trajectory simulation of a 20 keV beam at normal incidence on Fe. The density of trajectories gives a visual impression of the interaction volume. [From Goldstein et al. (1981).]

Electron mean free path vs. energy

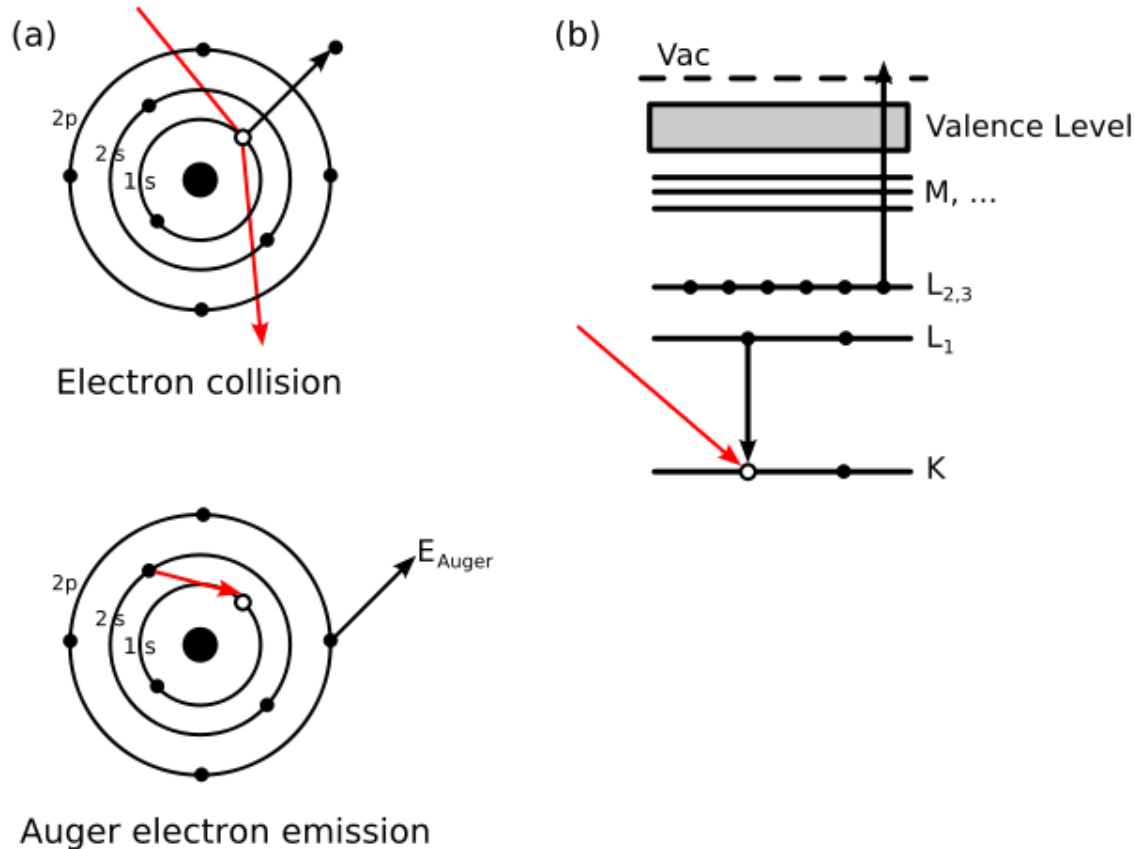


Processes that determine the mean free path: Scattering off conduction electrons, excitation of core electrons, excitation of collective modes (surface and bulk plasmons)

Electron spectroscopies for surface analysis (simplified and very schematic)

Spectroscopy	Process	What you learn	Projectile energy
Auger	Filling of core hole (radiationless process)	Sample composition, also used for depth profiling	1 – 5 keV
XPS	X-ray	Composition, chemical state	1 – 4 keV (1486 eV)
UPS	UV photon	Valence band	5 – 500 eV
ELS	e in	Electronic energy losses (interband, plasmons)	10 – 1000 eV
EELS	e in	Vibrations	1 – 5 eV
IPS	e in, photon out	Unoccupied states	8 – 20 eV

The Auger process



Two views of the Auger process. (a) illustrates sequentially the steps involved in Auger deexcitation. An incident electron creates a core hole in the 1s level. An electron from the 2s level fills in the 1s hole and the transition energy is imparted to a 2p electron which is emitted. The final atomic state thus has two holes, one in the 2s orbital and the other in the 2p orbital. (b) illustrates the same process using spectroscopic notation, $KL_1L_{2,3}$. Note: The energy of the Auger electrons do not depend on the energy of the projectile electron in (a)!

Why use derivative mode?

where I_0 contains all non-time-dependent terms. In this calculation we assumed $k \ll V$ so that terms of order k^3 and higher can be neglected in practice. Using a lock-in amplifier, for phase sensitive detection, we select the component of the signal associated with the frequency ω , which is simply the desired quantity I' or dN/dE for a cylindrical mirror Auger analyzer. To satisfy this criteria, we require that k be less than the Auger width of ~ 5 eV.

An example of the use of derivative techniques is shown in Figure 11.11 for 2 keV electrons incident on a Co sample. In the direct spectrum, $n(E)$, the main features are the peak of elastically scattered electrons and a nearly flat background. The arrows in Figure 11.11a indicate the energies of oxygen and Co Auger transitions. The derivative spectrum (Figure 11.11b) reveals the LMM Co and KLL carbon and oxygen signals.

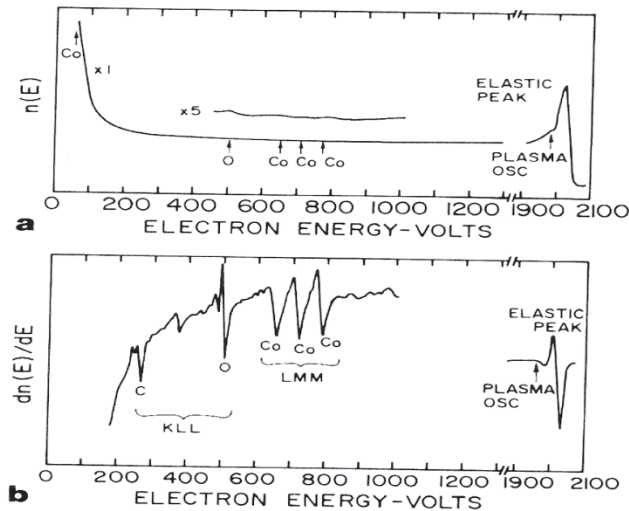
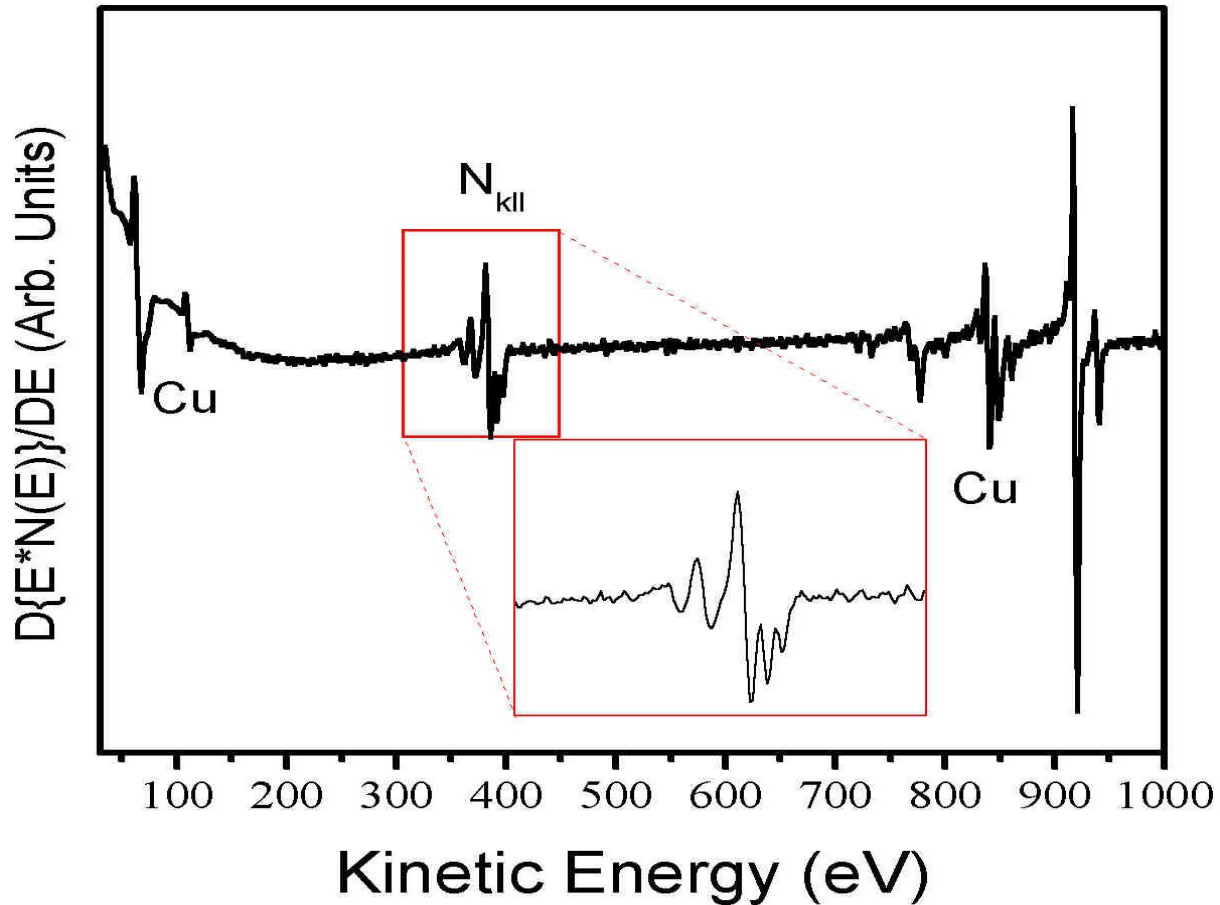


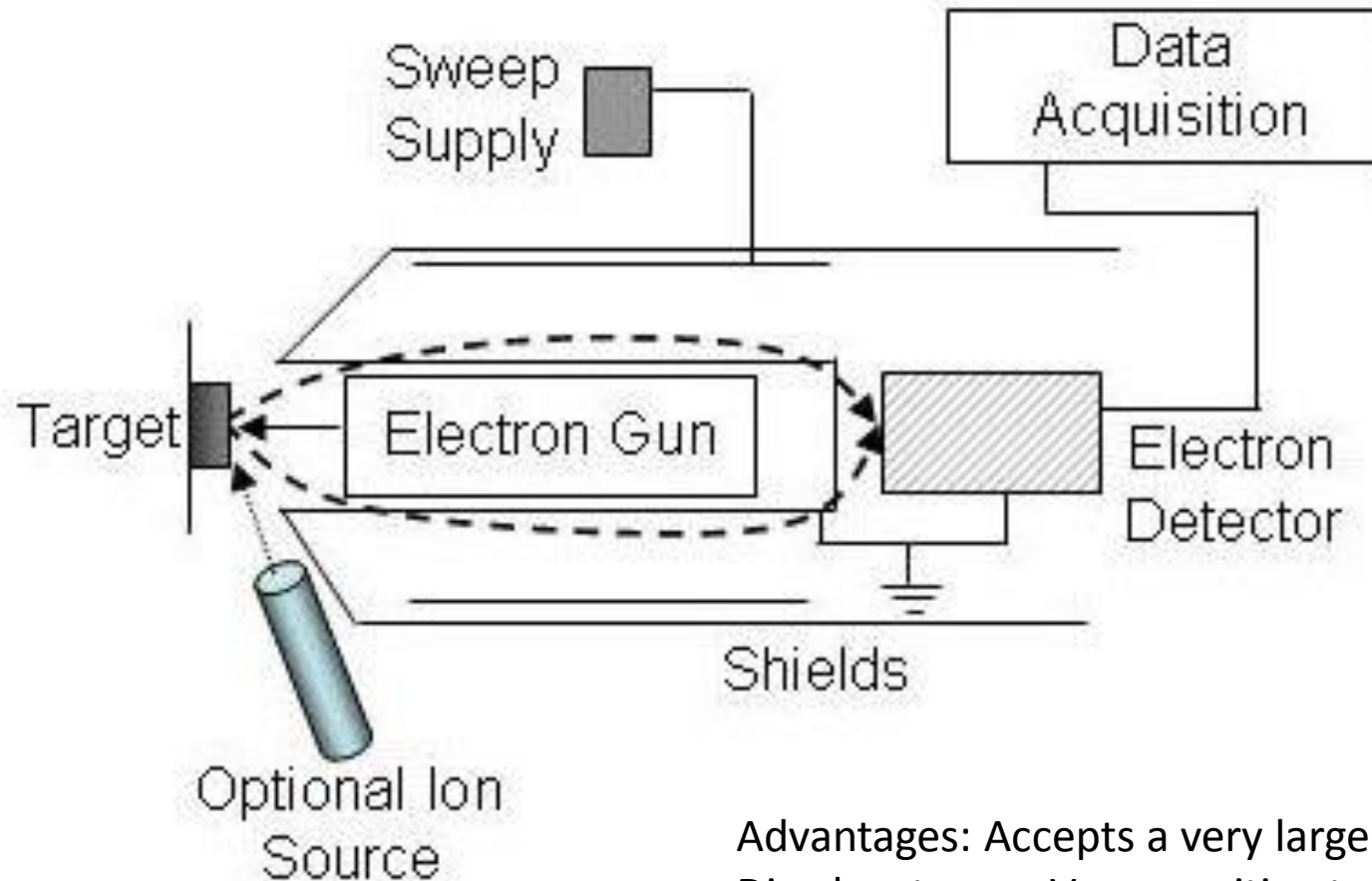
Figure 11.11 Comparison of (a) the spectrum $N(E)$ and (b) the derivative $dN(E)$ for 2 keV electrons incident on a Co sample. [From Tousset, in Thomas and Cachard, 1978.]

Auger spectrum of CuN



Auger spectrum of a copper nitride film in derivative mode plotted as a function of energy. Different peaks for Cu and N are apparent with the N KLL transition highlighted.

Instrumentation for AES



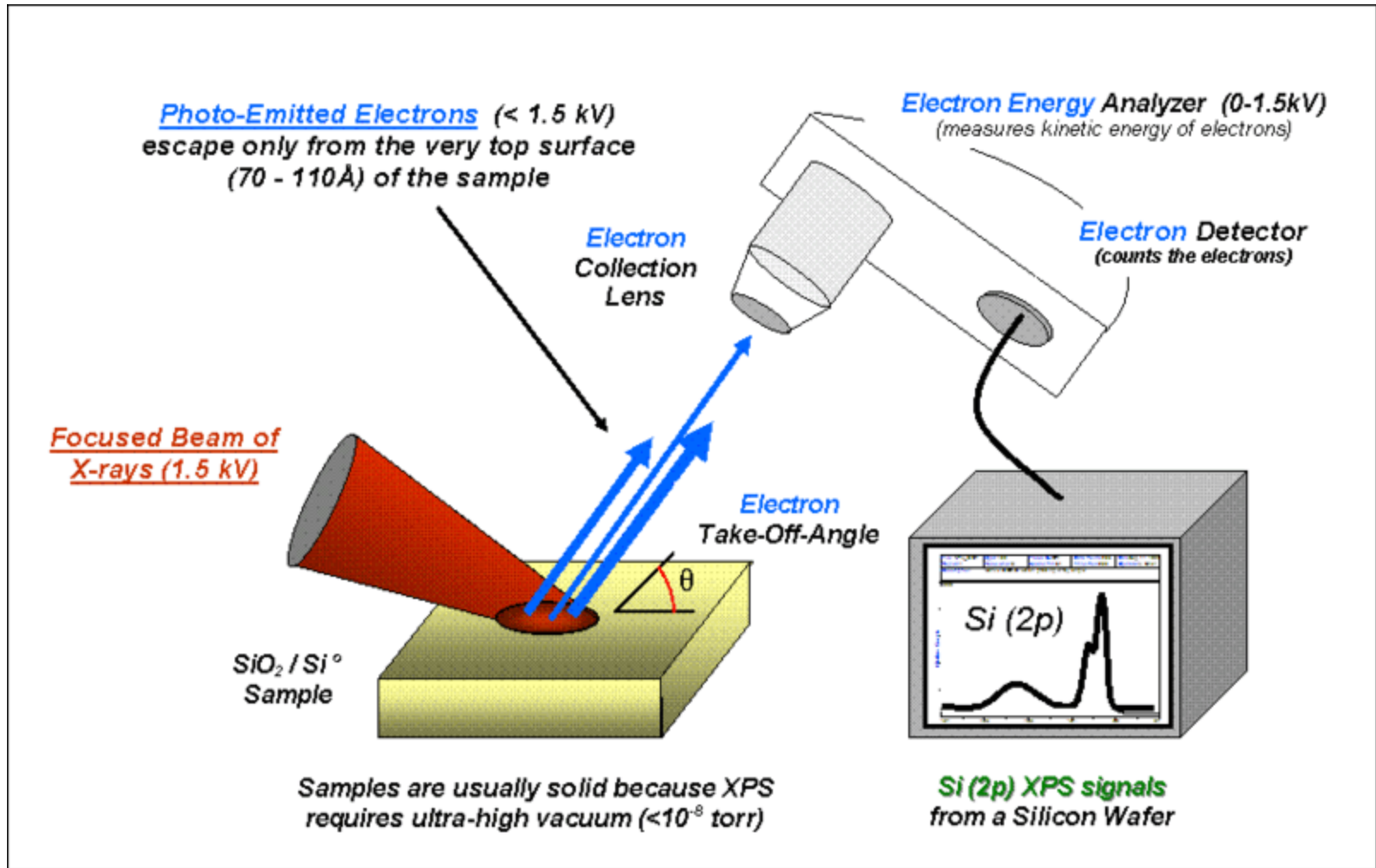
Advantages: Accepts a very large solid angle

Disadvantages: Very sensitive to specimen placement, somewhat awkward geometry

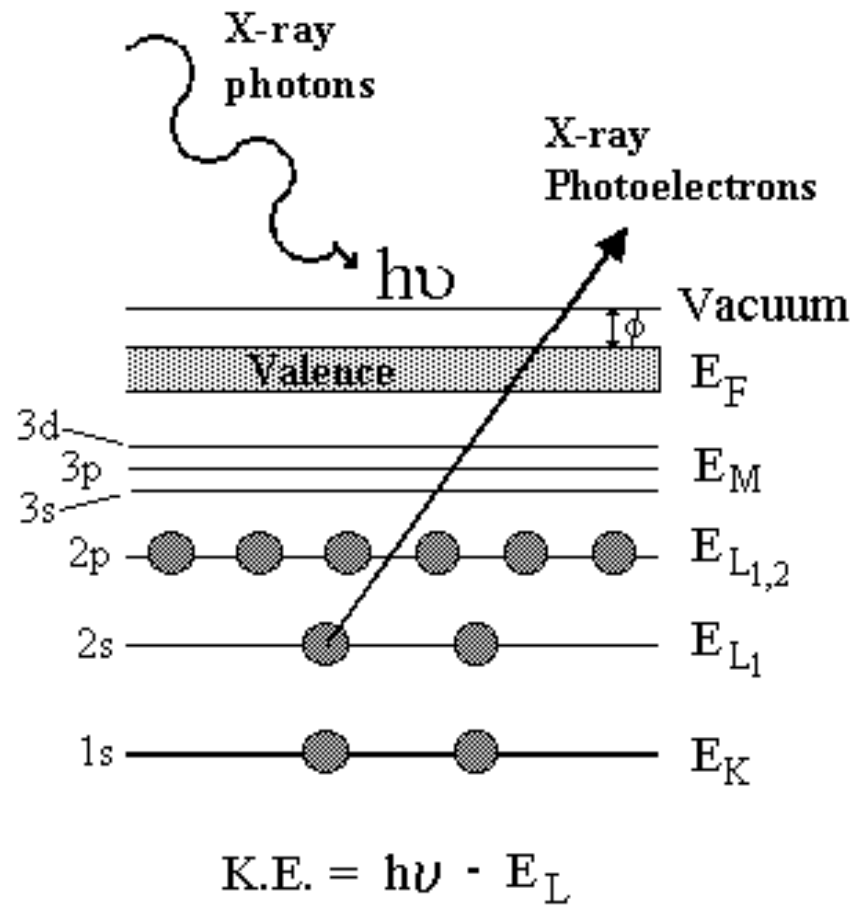
Features of AES

- High sensitivity (typically ca. 1% monolayer) for all elements except H and He.
- A means of monitoring surface cleanliness of samples
- Quantitative compositional analysis of the surface region of specimens, by comparison with standard samples of known composition.
- The basic technique has also been adapted for use in :
 - Auger Depth Profiling : providing quantitative compositional information as a function of depth below the surface (through sputtering)
 - Scanning Auger Microscopy (SAM) : providing spatially-resolved compositional information on heterogeneous samples (by scanning the electron beam over the sample)

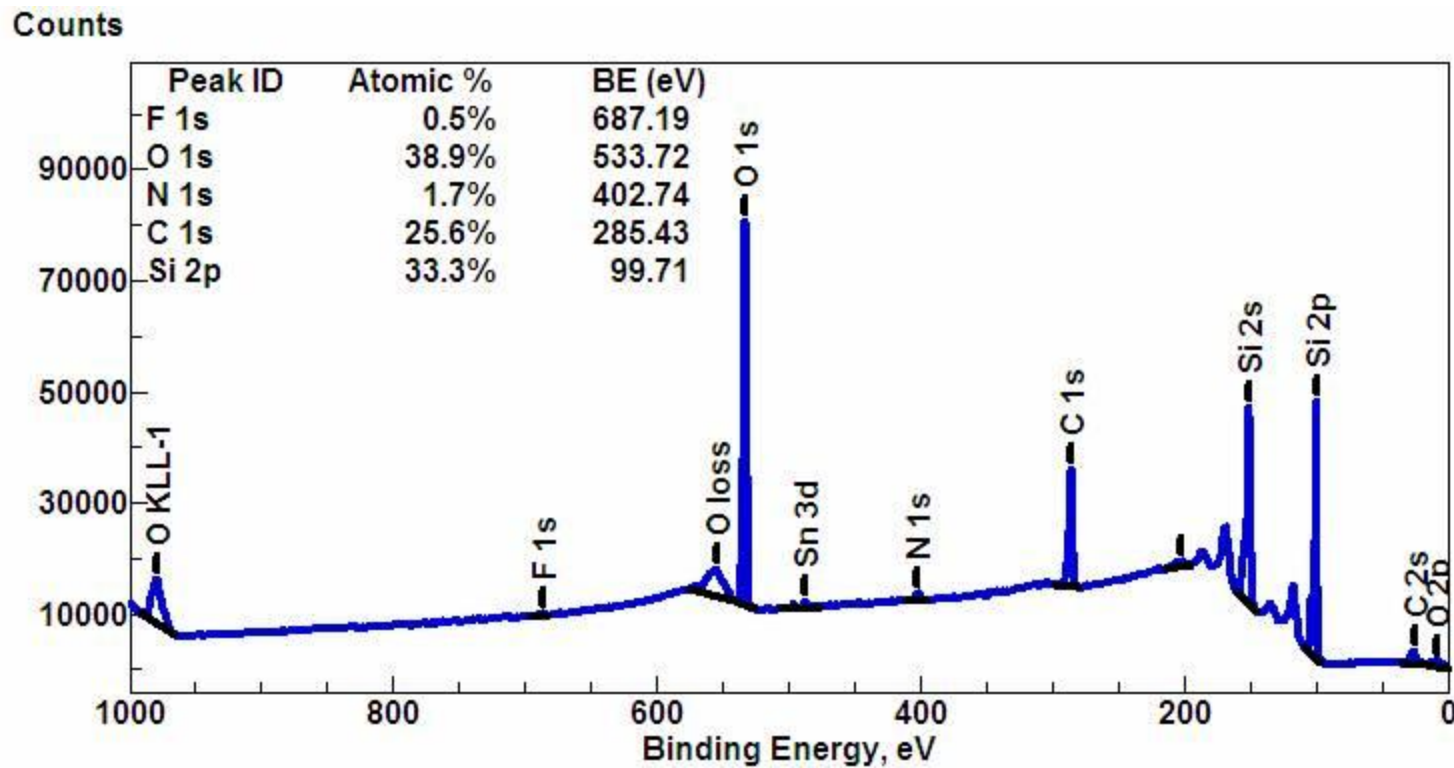
X-ray Photoelectron Spectroscopy



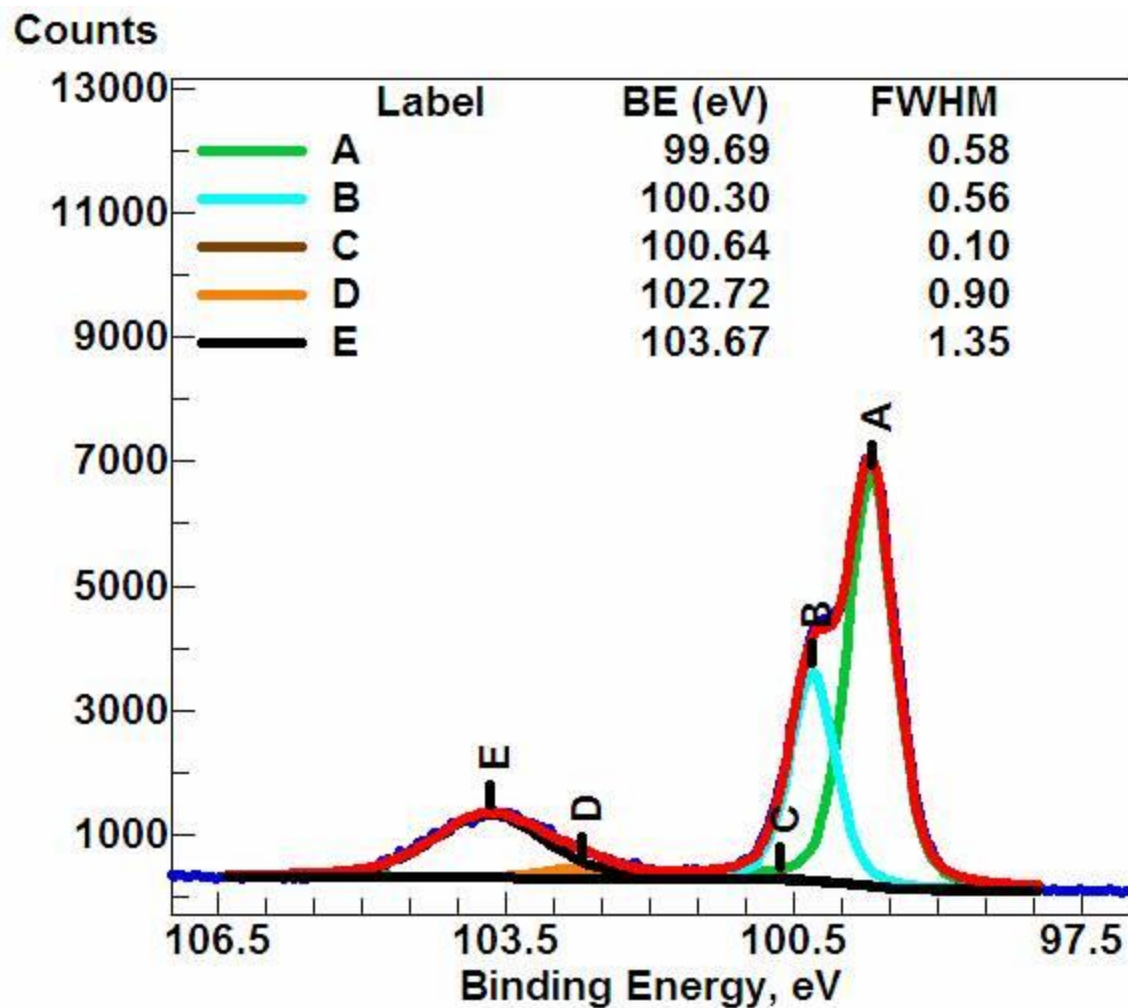
The basic process in XPS



Wide-scan survey spectrum – identification of elements



High resolution spectrum of the Si 2p region – different oxidation states (chemical shifts)



Chemical shifts (cont.)

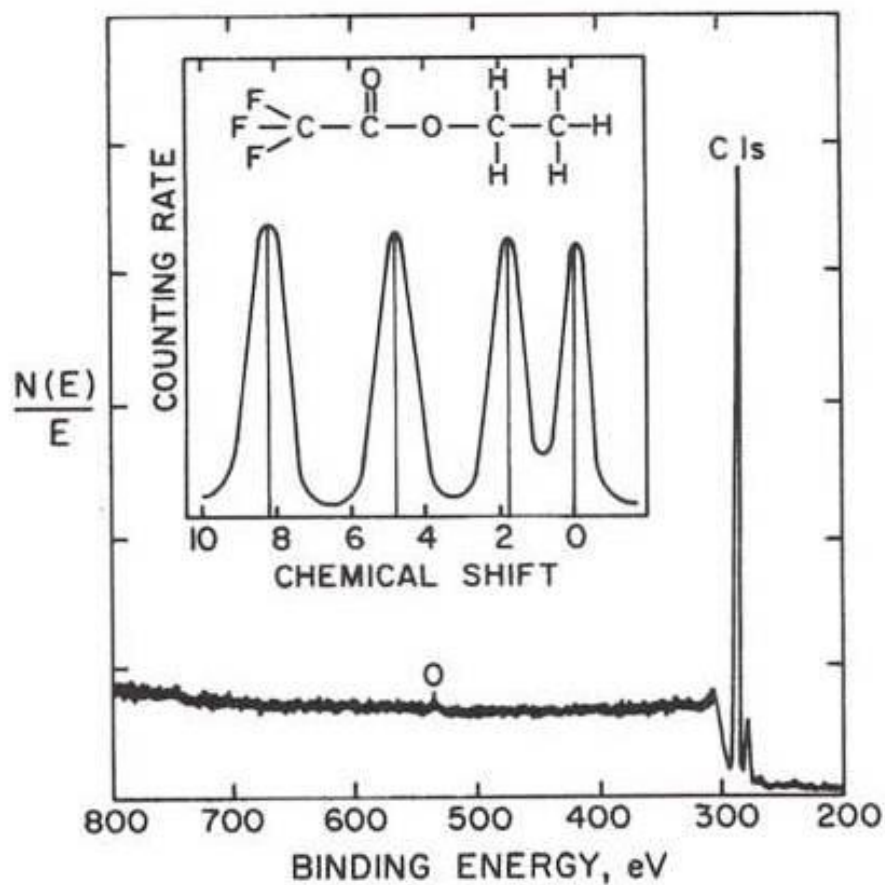


Figure 9.12 Carbon 1s chemical shifts in ethyl trifluoroacetate. The four carbon lines correspond to the four carbon atoms within the molecule. [Adapted from Ghosh, 1983.]

K_{α} radiation from an Al source – $h\nu = 1486.7 \text{ eV}$ (8.3386 \AA)

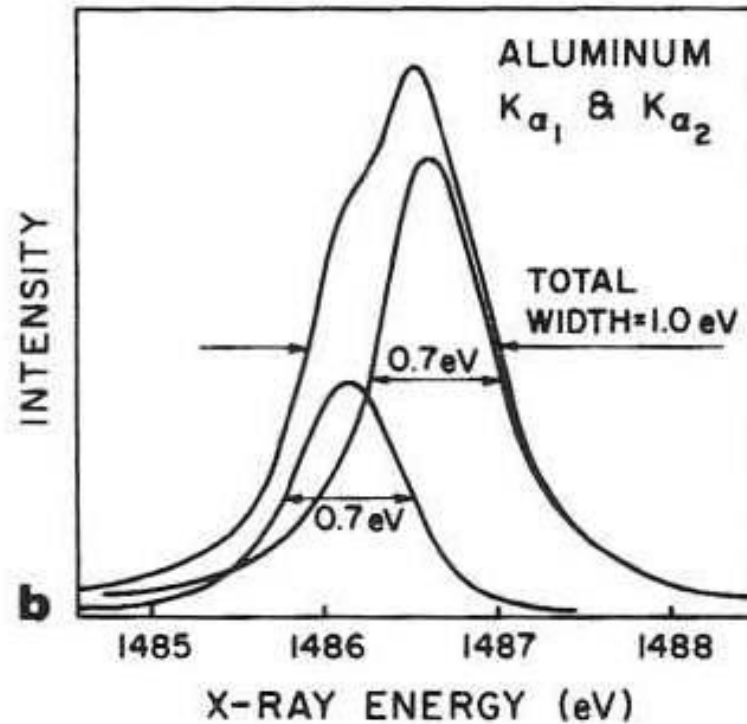
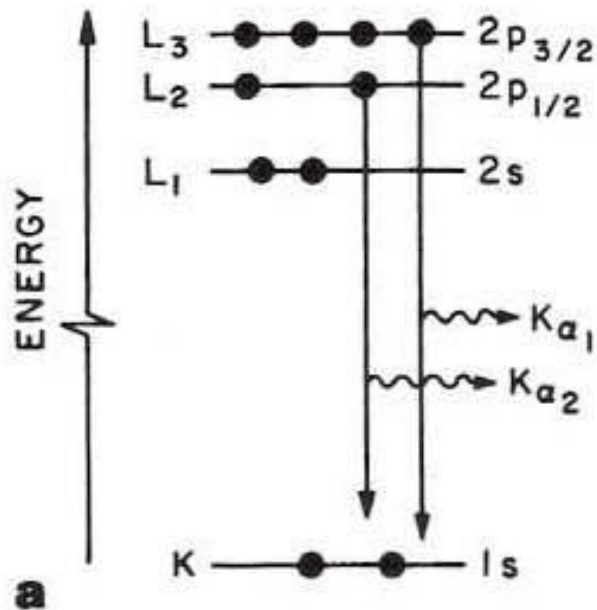


Figure 9.3 The two components of the K_{α} spectrum ($K_{\alpha_1} + K_{\alpha_2}$) which comprise the K_{α} spectrum of Al. [Spectrum from Siegbahn et al., 1967].]

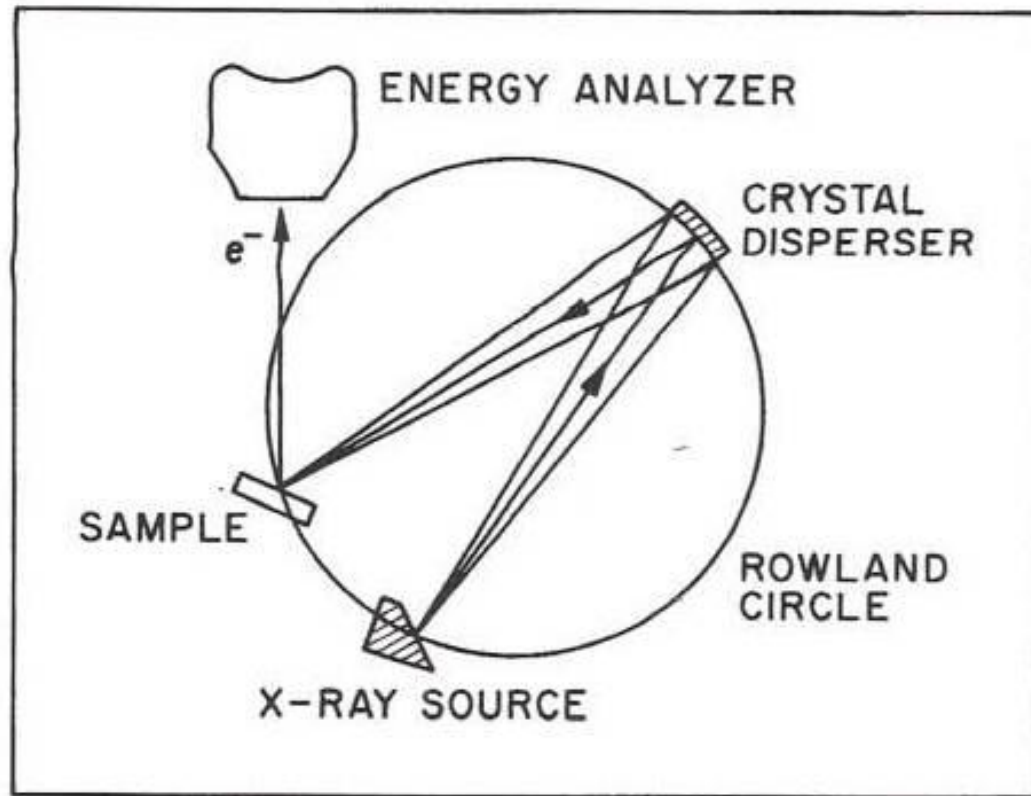
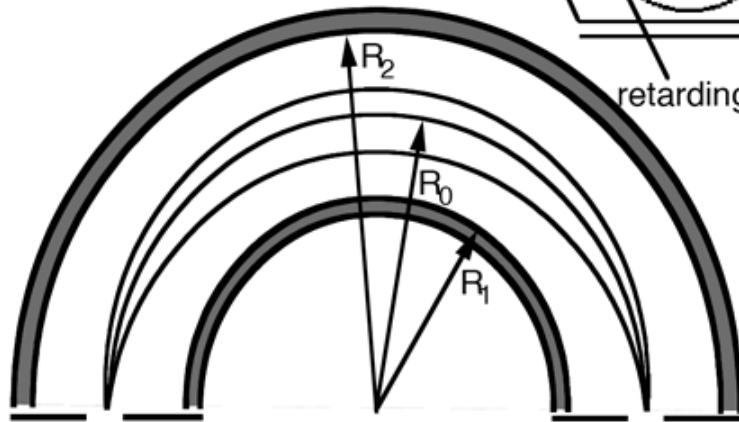
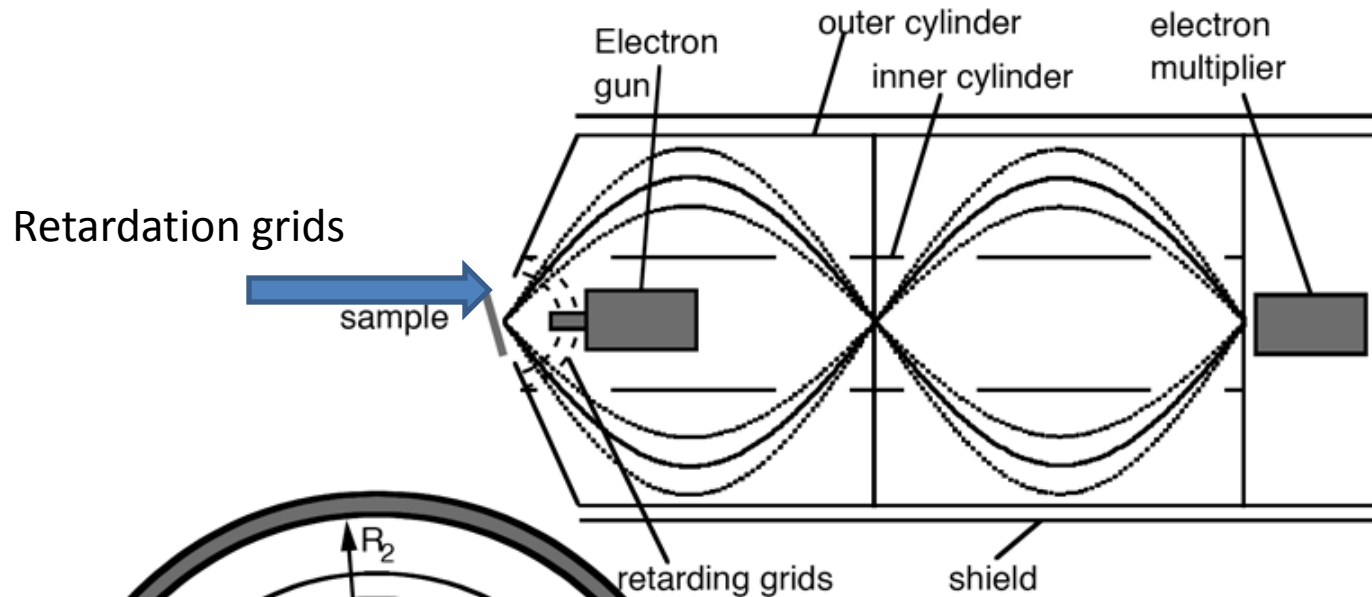


Figure 9.4 Schematic of an X-ray monochromation system.

Different electron energy analyzers:

(a) Concentric Hemispherical Analyzer (CHA) and (b) (Double pass) Cylindrical Mirror Analyzer (CMA)



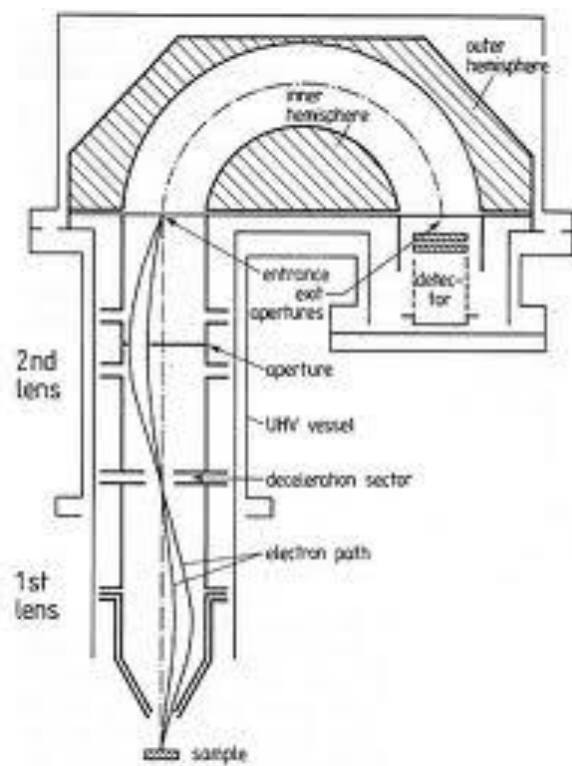
(a.)

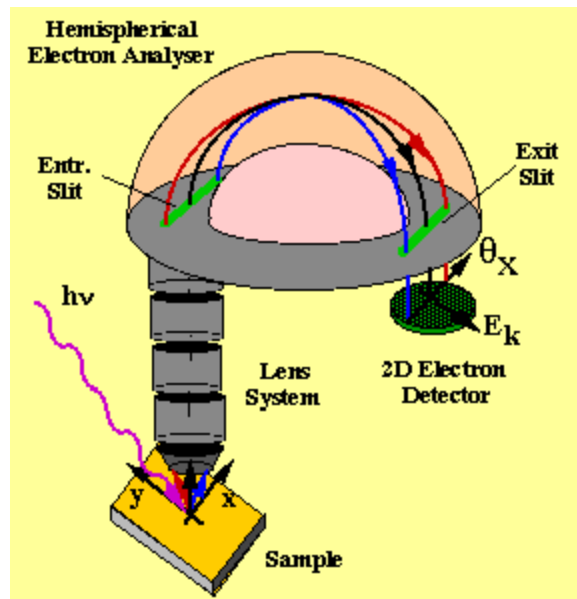
Advantages of CMA: Very large solid angle, defines its own beam spot
Disadvantages: Somewhat awkward geometry

(b.)

Advantages of CHA: Higher resolution than CMA, convenient geometry
Disadvantages: Small solid angle

Electron energy analyzer with lens system





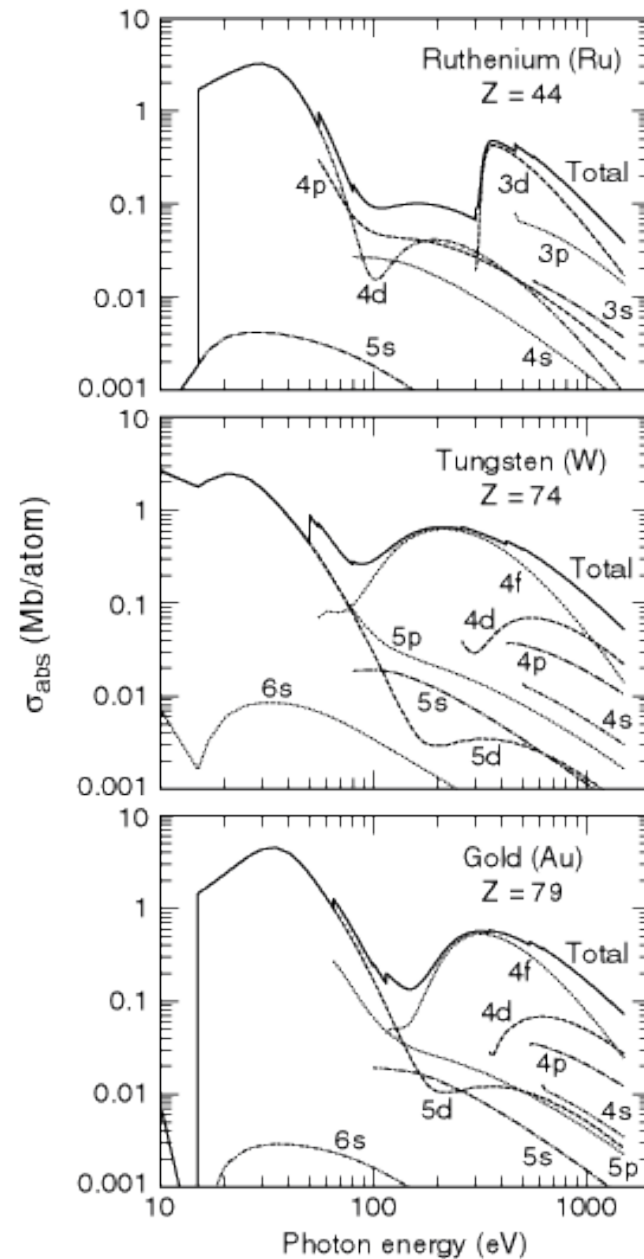
Studies with XPS

- Elemental composition
- Chemical shifts

Difficulty: Photoionization cross sections vary widely and are difficult to determine

- Angle Dependent Studies – by varying the angle of electron emission you can do depth profiling
- Imaging

Some atomic photoionization cross sections, solids have additional complications



UV photoemission

Light sources:

Lab sources:

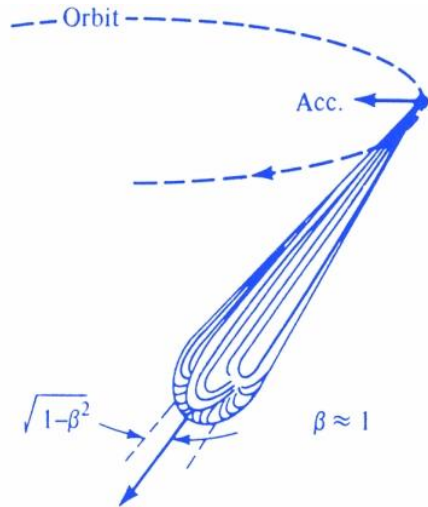
Discharges in He ($h\nu = 21.2 \text{ eV}$ and 40.8 eV)

Advantages: Very narrow lines – high resolution

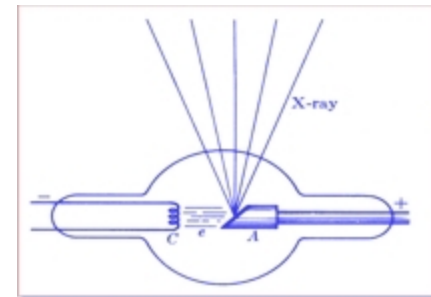
Synchrotron radiation sources:

Now widely available, require a monochromator

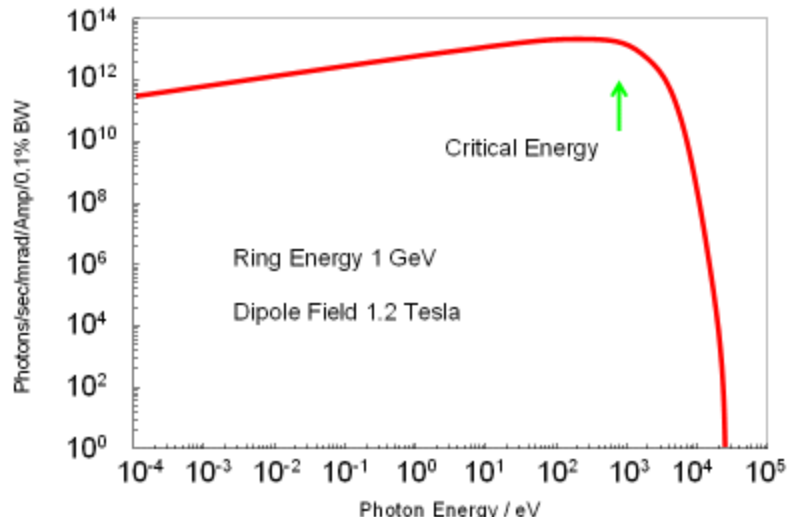
Advantages: Continuously variable photon energy, can be made very narrow, highly collimated, very intense



VS.



Typical SR output curve



ESRF, Grenoble, France



Studies with UV Photoemission

- The electronic structure of solids - detailed angle resolved studies permit the complete band structure to be mapped out in k -space.
- The adsorption of molecules on solids- by comparison of the molecular orbitals of the adsorbed species with those of both the isolated molecule and with calculations.

The distinction between UPS and XPS is becoming less and less well defined due to the important role now played by synchrotron radiation.

Vibrational spectroscopy

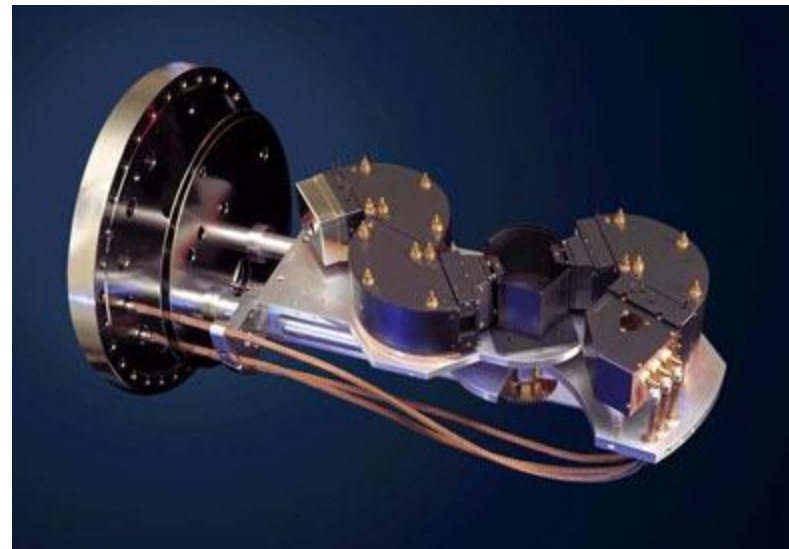
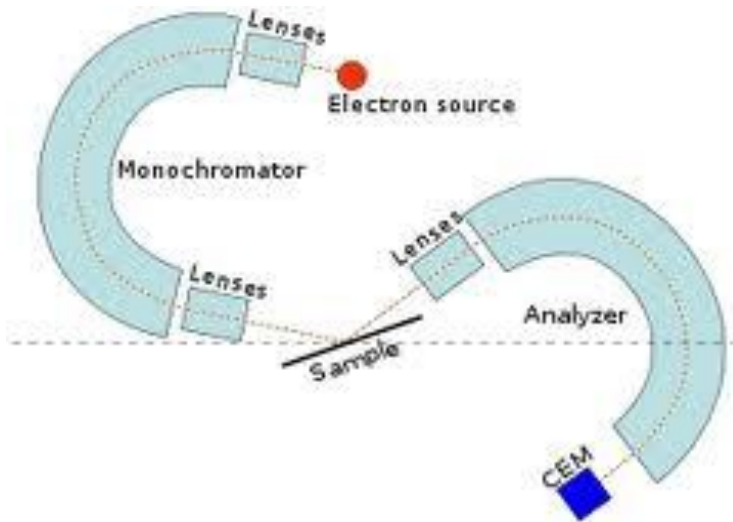
By determining the vibrations of adsorbed species, their identities can be determined, just as for bulk species. You can fingerprint adsorbed species and use selection rules to deduce bonding orientation.

Two techniques for vibrational studies of molecules on surfaces:

[IR Spectroscopy (later in the course ?)]

Electron Energy Loss Spectroscopy (EELS, ~ 1 eV primary E)

Need very well defined electron energy (~ 1 meV) \rightarrow monochromator



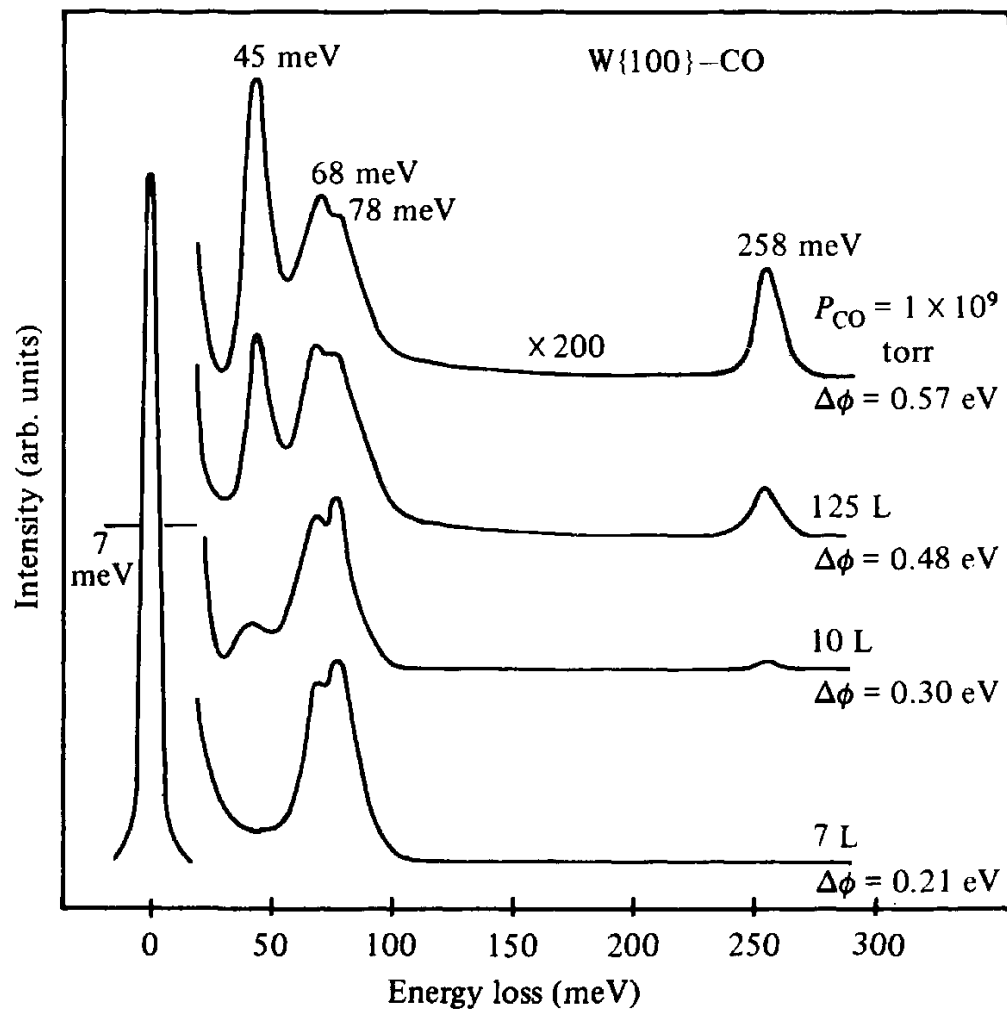


Fig. 9.13 Electron energy loss spectra of CO on $W\{100\}$ at 300 K. The spectra are recorded with a primary electron beam energy of 5 eV incident at an angle of 75° ; $\Delta\phi$ is the measured increase in work function (Froitzheim *et al.*, 1976).

Electron Energy Loss Spectroscopy

Probes electronic energy losses: Interband, core excitations and collective excitations (surface and bulk plasmons, $\sim 10 - 1000$ eV primary E for surface analysis)

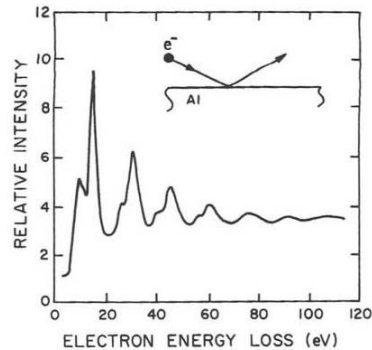
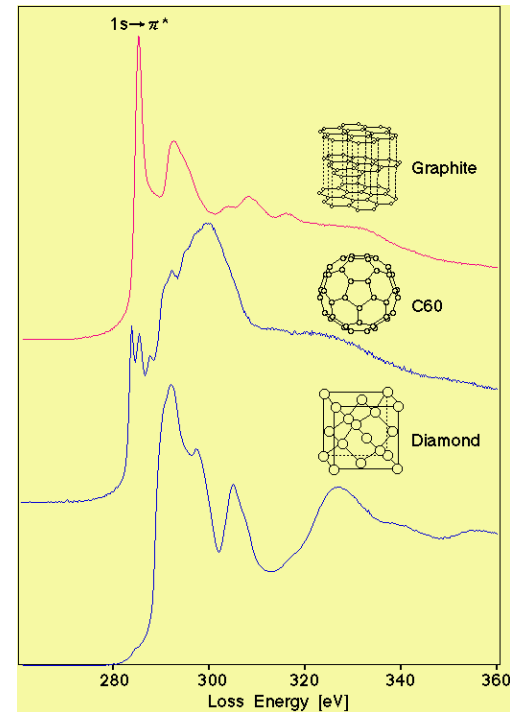
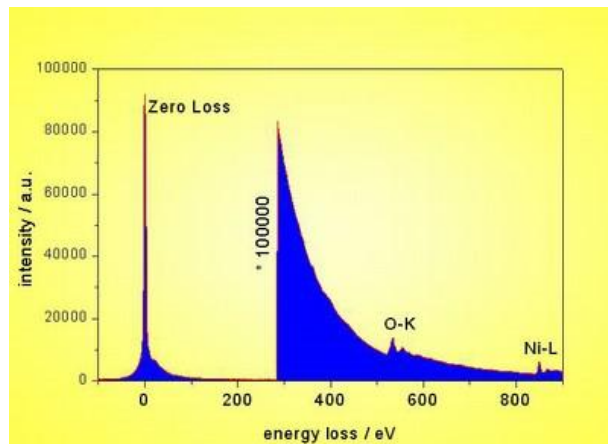


Figure 6.9 Energy loss spectrum for electrons reflected from Al for incident primary electron energy of 2 keV. The loss peaks are made up of a combination of surface and bulk plasmon losses.



This technique is used (at higher primary E) in electron microscopy (later in this course)