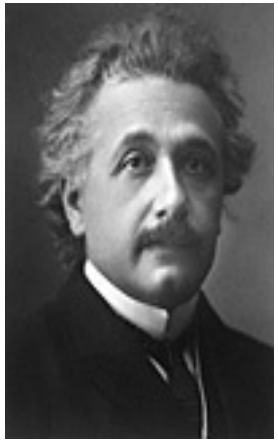
History of Photoelectron Spectroscopy

- *1. H. Hertz, Ann. Physik 31,983 (1887).*
- *2. A. Einstein, Ann. Physik 17,132 (1905).*
  - *1921 Nobel Prize in Physics*



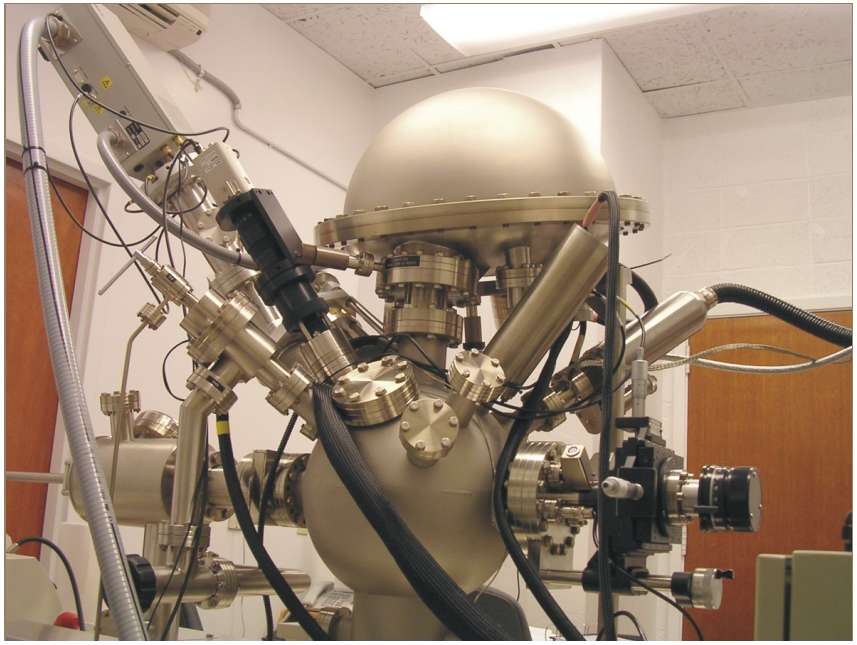
- *3. K. Siegbahn, Et. Al.,Nova Acta Regiae Soc.Sci., Ser. IV, Vol. 20 (1967).*
  - *1981 Nobel Prize in Physics.*

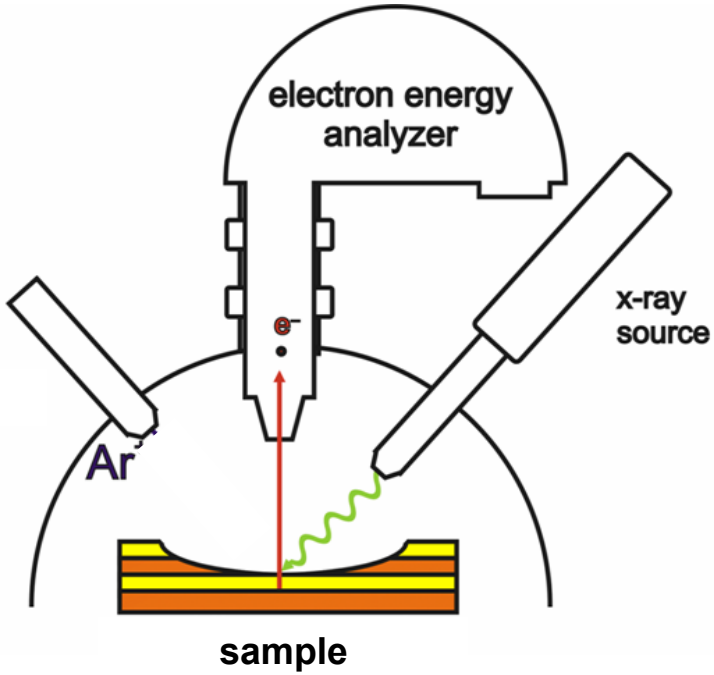
*many slides courtesy of Dr. Ted Monchesky.

Photoelectron Spectroscopies

- *X-ray photoelectron spectroscopy (XPS) – x-ray in, electron out*
  - *Atomic core levels*
  - *Binding energies 10s of eV to 1.5 keV (or more)*
  - *Elemental information*
  - *Chemical binding information*
- *Ultraviolet photoelectron spectroscopy (UPS) – UV photon in, electron out*
  - *Valence band (occupied states, HOMO, etc)*
  - *Conduction electrons*
  - *Work functions/ionization potentials*
  - *Band alignment at interfaces*
  - *k-resolved band dispersions*
- *Inverse photoelectron spectroscopy (IPES) – Electron in, photon out*
  - *Unoccupied states (conduction band, LUMO, etc)*
  - *Conduction electrons*
  - *Band alignment and dispersion*
  - *Surface band gap (combined with UPS)*

X-ray Photoelectron spectroscopy





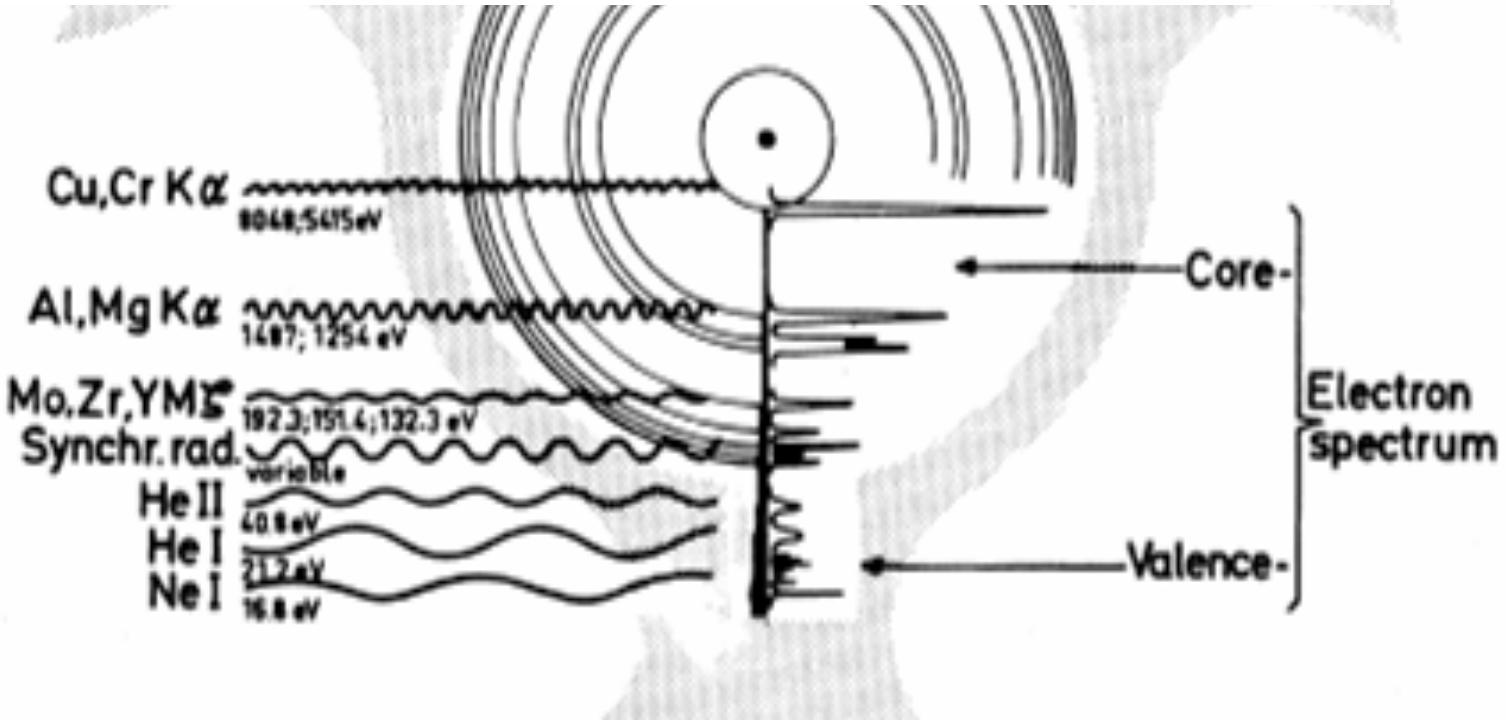
Applications of Photoelectron Spectroscopy

- Industry
  - R&D processing technologies
  - Quality control in manufacturing
  - Environmental issues
  - Forensic investigations
- Adhesion Science
  - Bond failure location
- Metallurgy and Mineral Sciences
  - Elemental diffusion
  - Oxide growth
  - Intergranular and transgranular studies of fracture
- Microelectronics
  - Film analysis and thickness determination
  - Chemical distribution of species
  - Chemical mapping of surface structures
  - Diffusion
  - Dopants
- Polymers, Papers and Packaging
  - Analysis of surface treatments for enhanced printability
  - Chemical state identification an mapping
  - Investigation of de-inking and recycling
- Corrosion Science
  - Interaction of metal surface with environment
  - Studies of the breakdown of protective surface coatings and treatments
  - Identification of passivation layers
- Catalysis
  - Comparison of spent and fresh catalysts
  - Identification of catalyst poisons

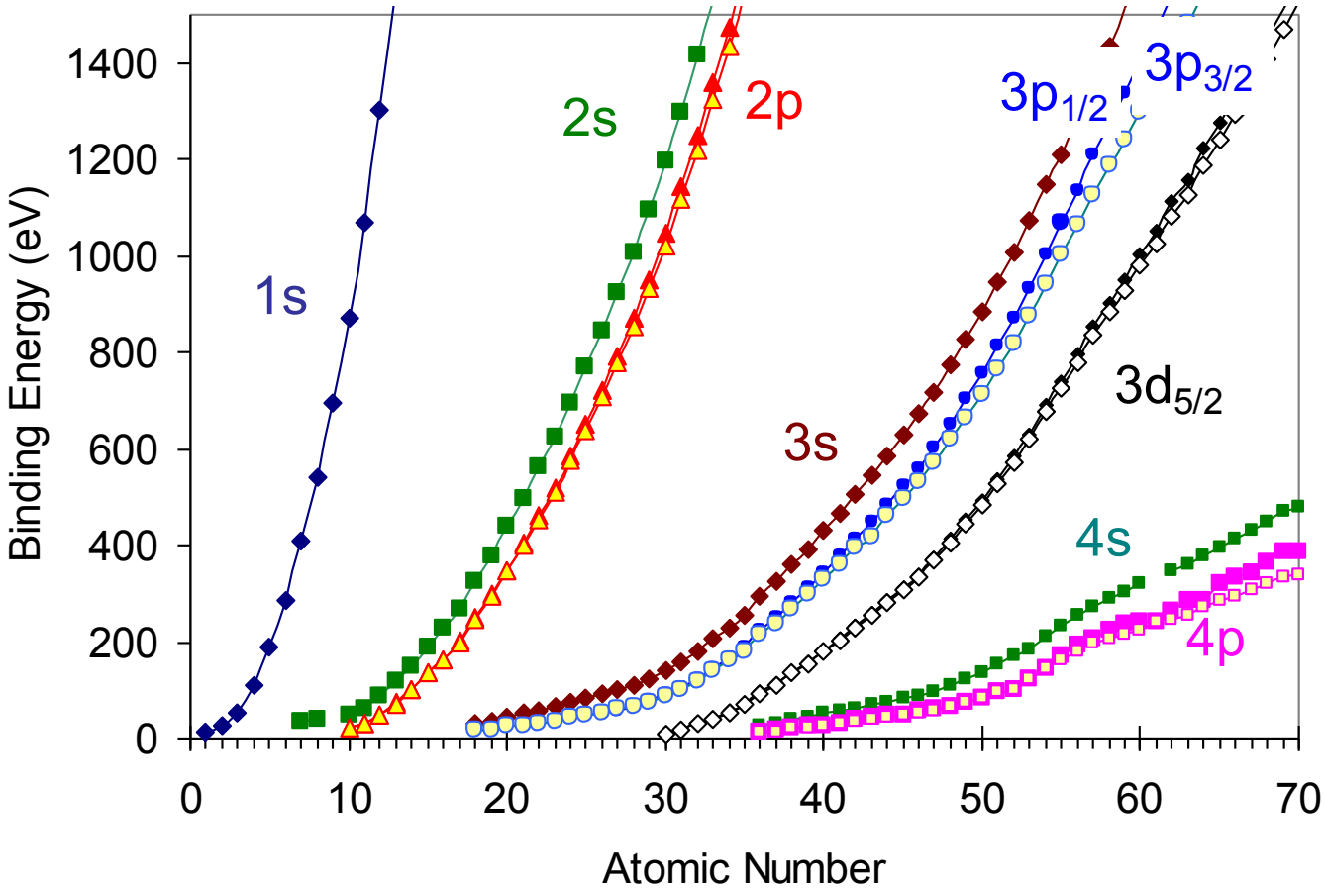
Photon sources for XPS

- Monochromatic photon sources are required:
  -by conservation of energy the BE can be inferered from the KE of the photo-electron
  -Koopman's Theorem:

KE = hν – BE

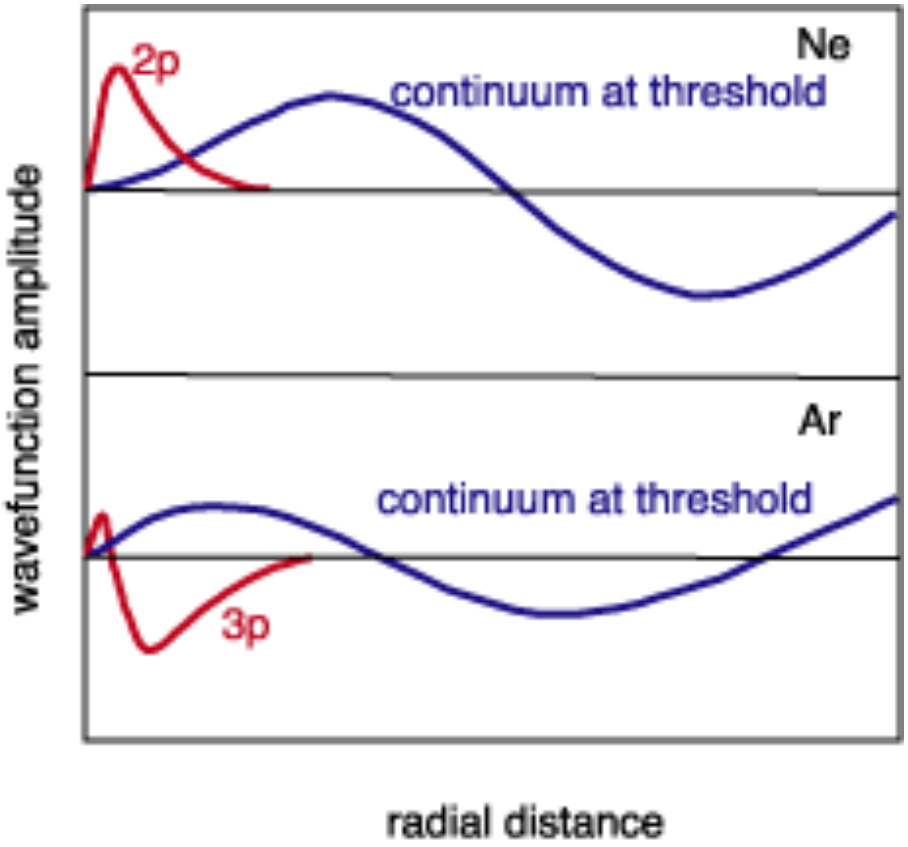


Photoelectron energies used for chemical identification



Measured binding energies for elements and compounds can be found at http://srdata.nist.gov/xps/

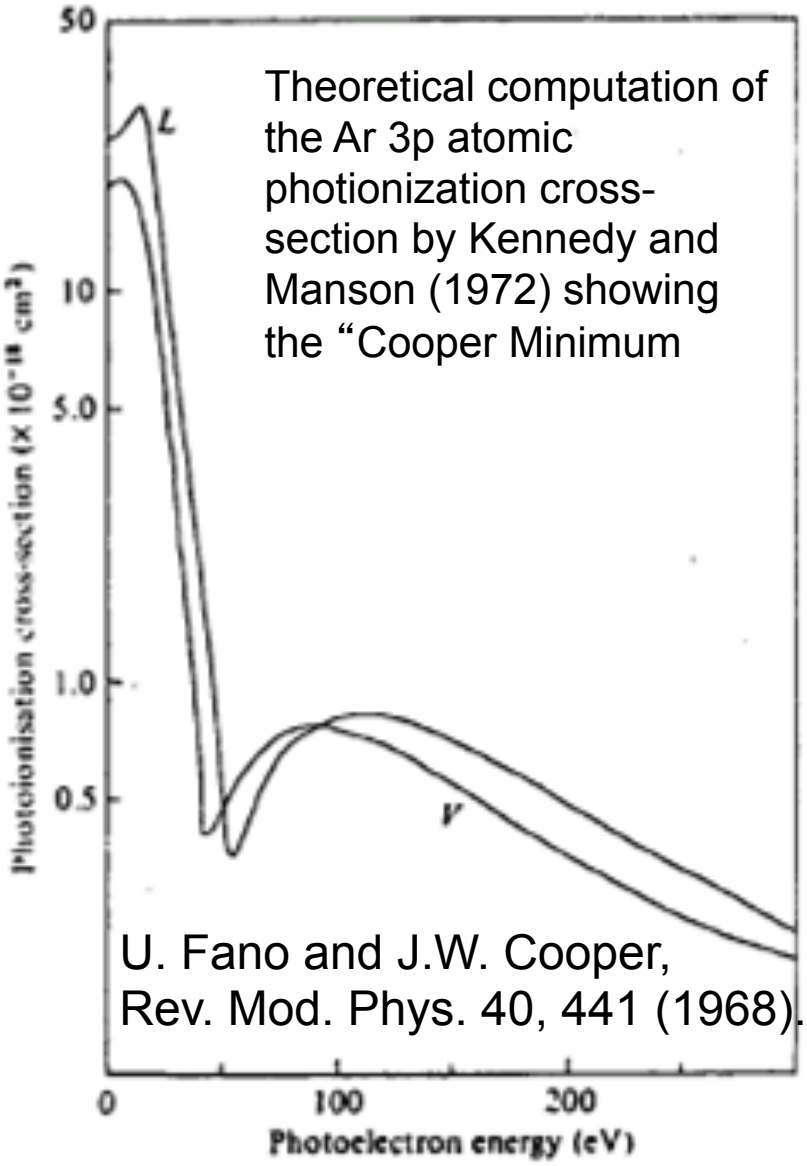
Photoelectron Cross-section



Probability per unit time of exciting a photoelectron is

$$R \sim (\hbar\omega)^2 \left|\langle \psi_f | r | \psi_{core} \rangle\right|^2 \delta\left(E_f - E_{core} - h\nu\right)$$

(dipole approximation)

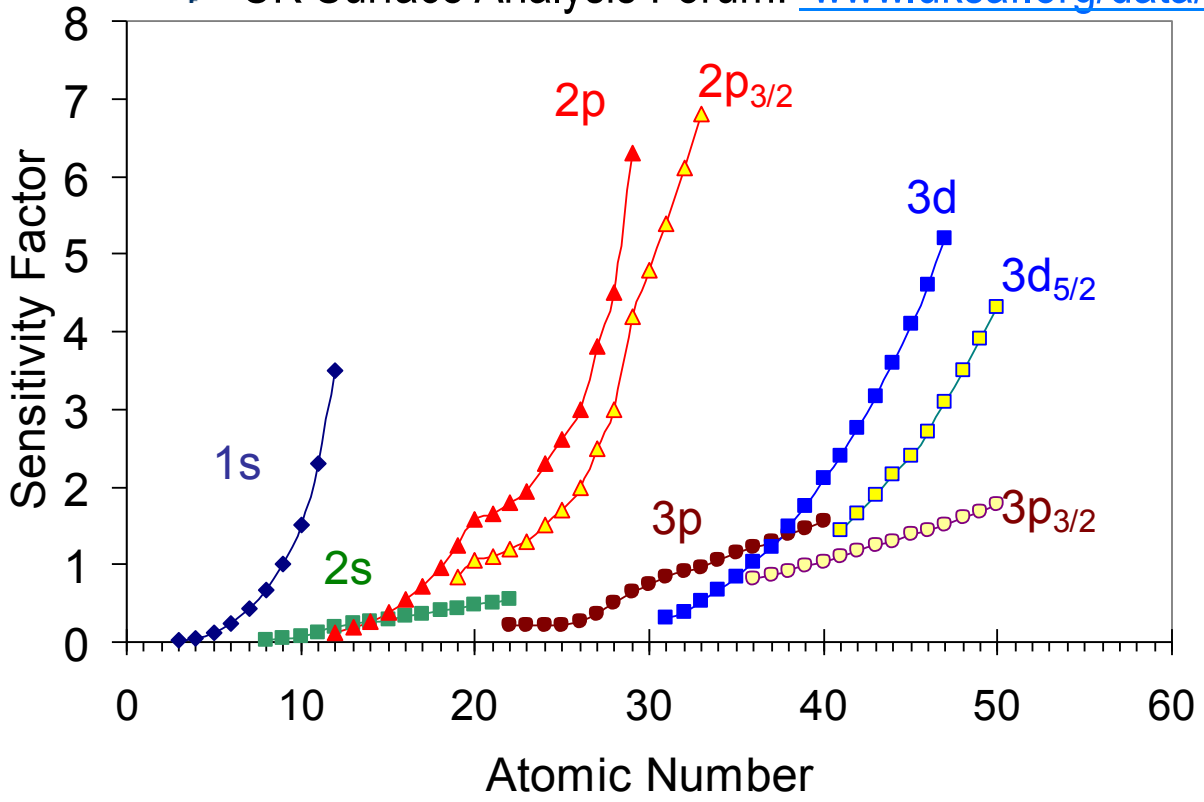


Theoretical computation of the Ar 3p atomic photionization cross-section by Kennedy and Manson (1972) showing the "Cooper Minimum

U. Fano and J.W. Cooper, Rev. Mod. Phys. 40, 441 (1968).

Sensitivity Factors

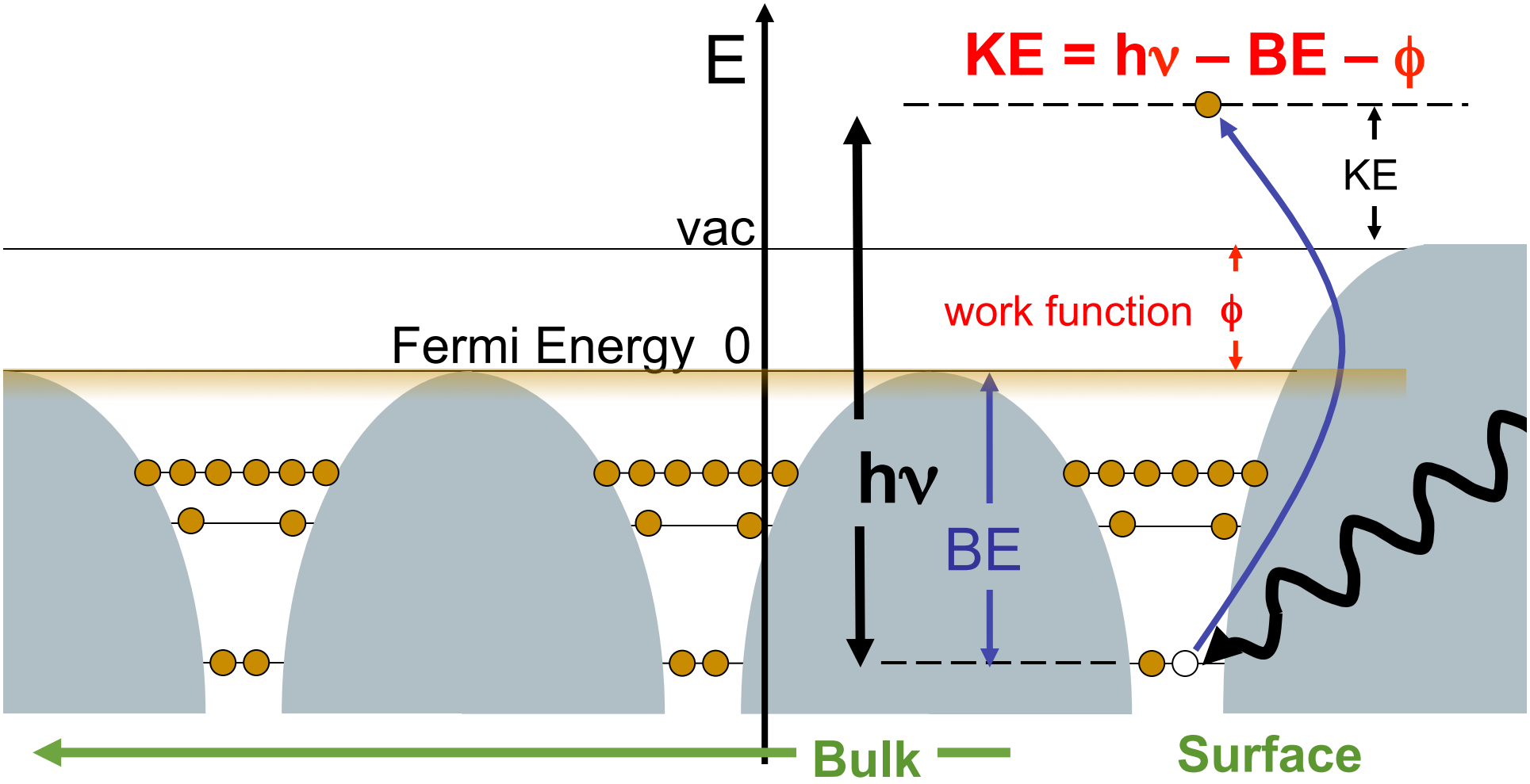
- Calculated photoelectron cross-sections for Al Kα radiation (Schofield 1976)
- Empirically Derived cross-sections
  - Appendix 6 of *"Practical Surface Analysis", Vol. 1., 2nd Edition, by C. D. Wagner, eds. D. Briggs and M. P. Seah,*
  - UK Surface Analysis Forum: www.uksaf.org/data/sfactors.html



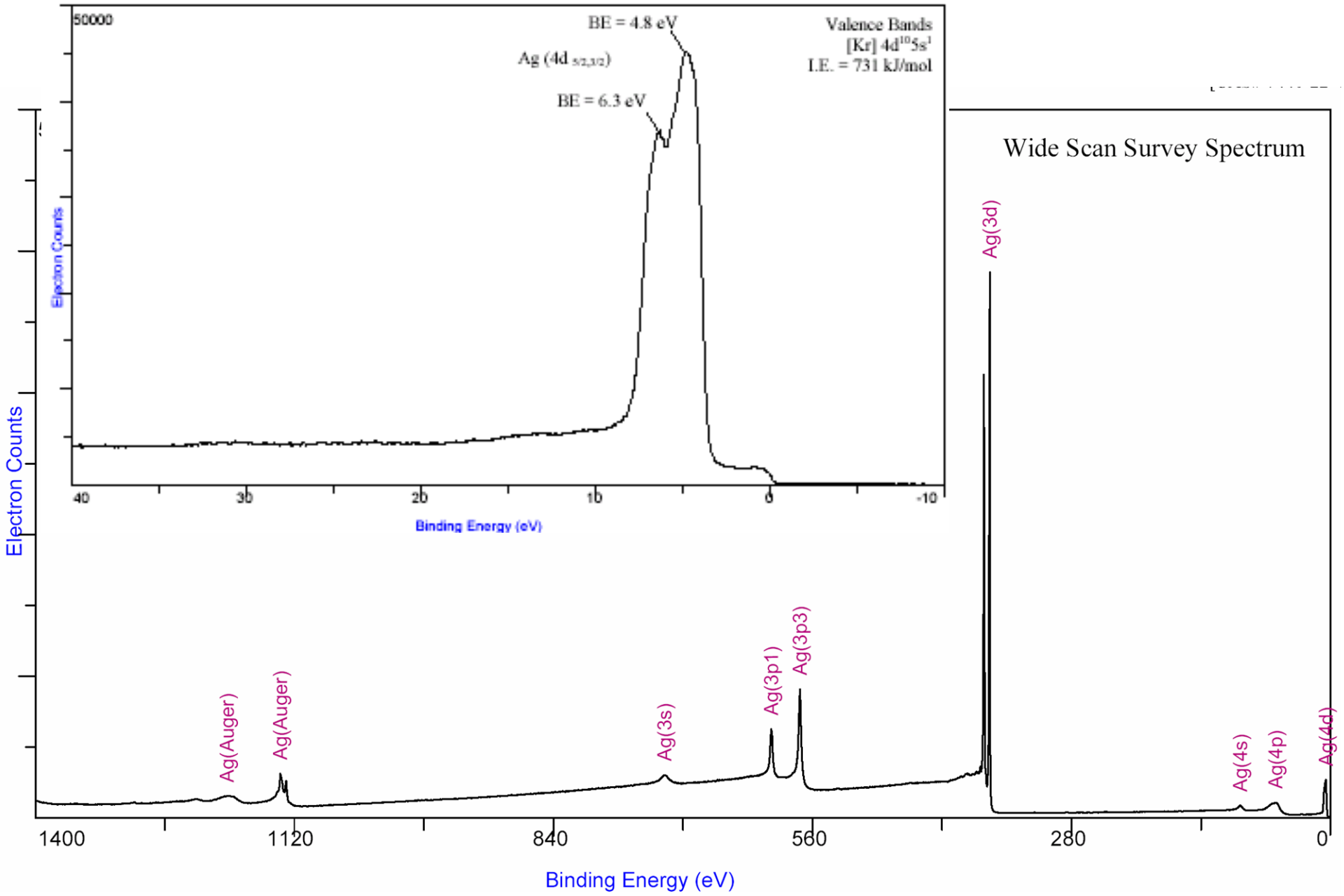
Strong lines insensitive to radiation source (Mg or Al).

Factors for secondary lines (2s,3p) are dependent to an extent upon the photon energy. For more accurate results, multiply the factors by 0.9 when Mg Kα used and by 1.1 when Al Kα used.

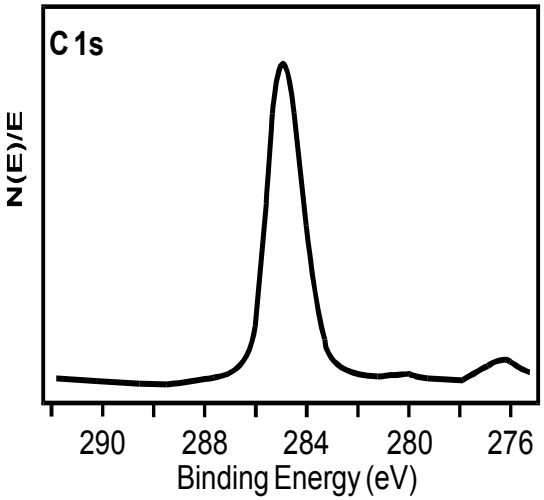
Photoemission from a solid



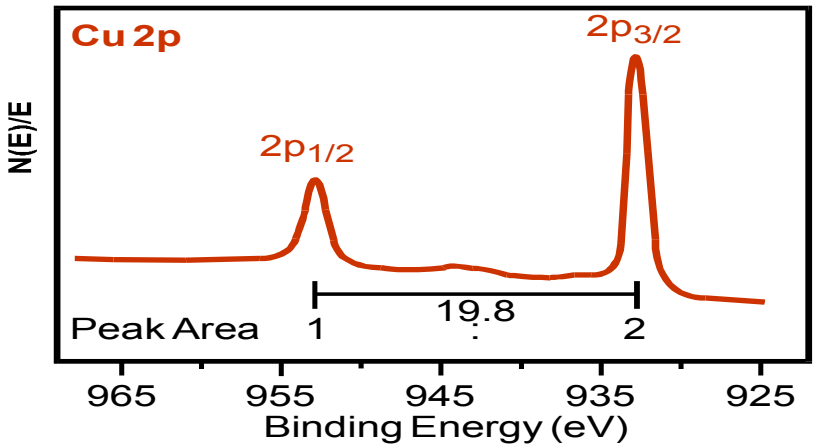
Example: XPS of Ag



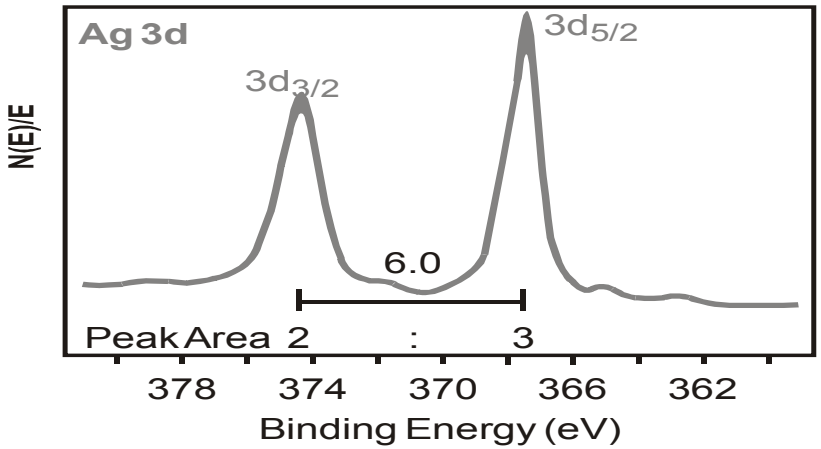
Spin-Orbit Coupling



L = 0
S = ½
J = ½



L = 1
S = ½
J = 3/2 or 1/2



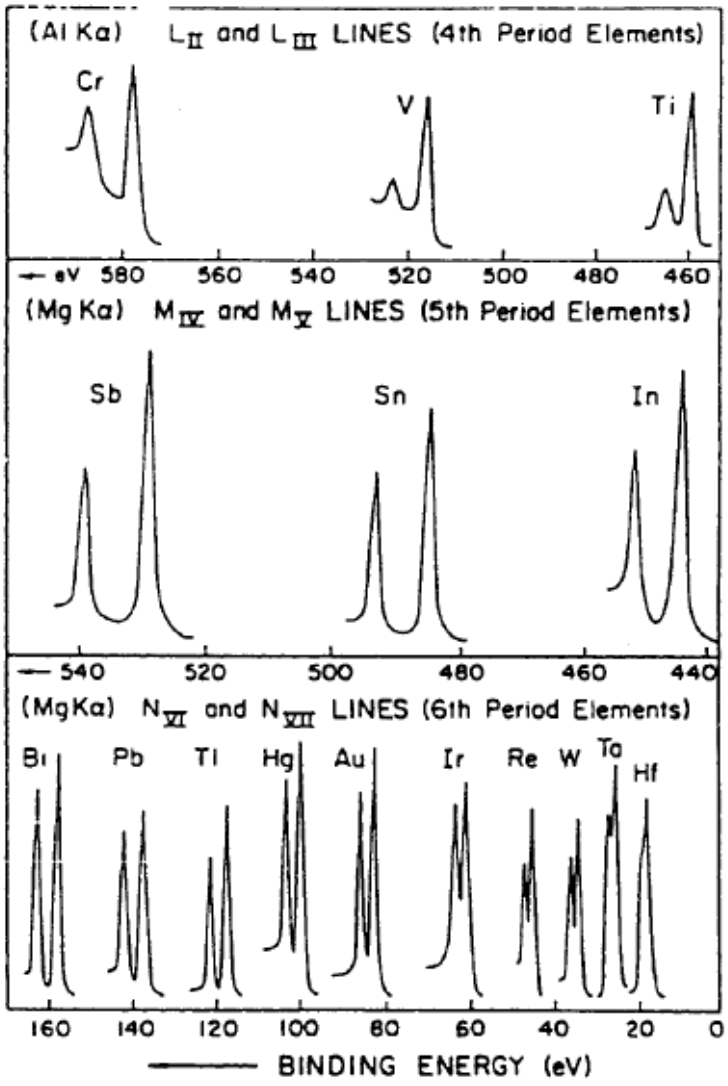
L = 2
S = ½
J = 5/2 or 3/2

Spin-Orbit Coupling

2p

3d

4f

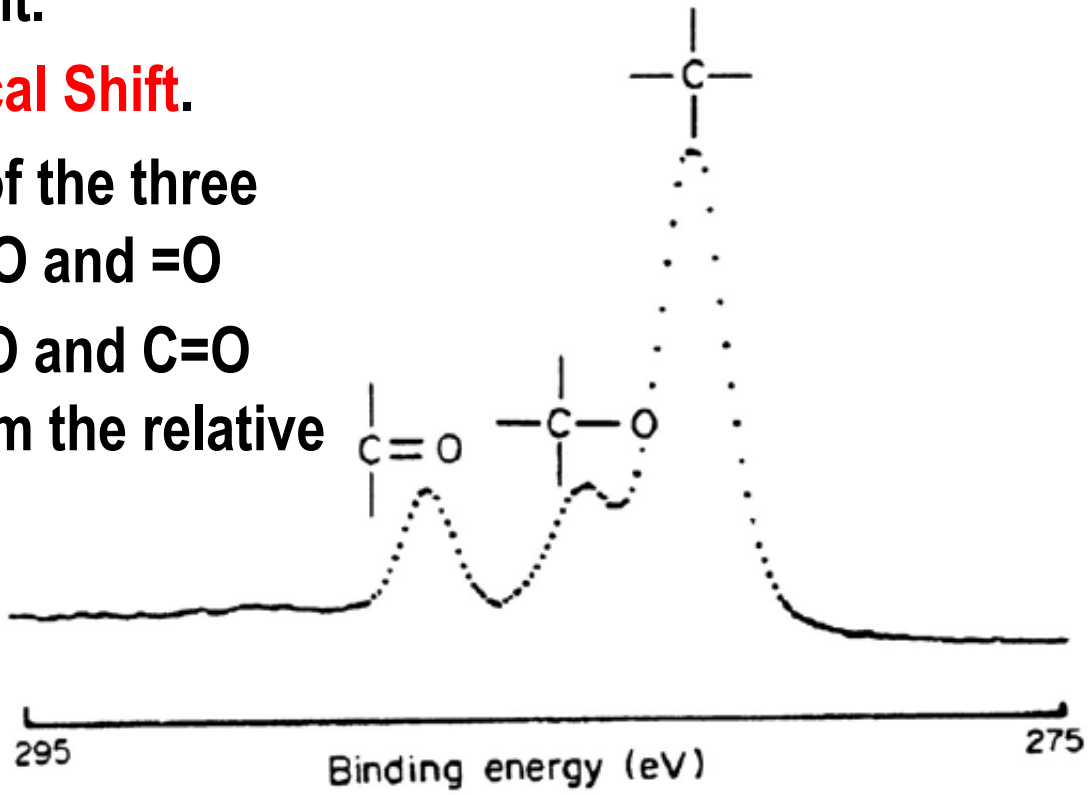


$$E_{so} = g\hbar\left(\frac{e}{mc}\right)^2\left(\frac{Z}{r^3}\right)\vec{S}\cdot\vec{L}$$

Spin orbit splitting increases from left to right along periodic table due to decreasing radius of atom

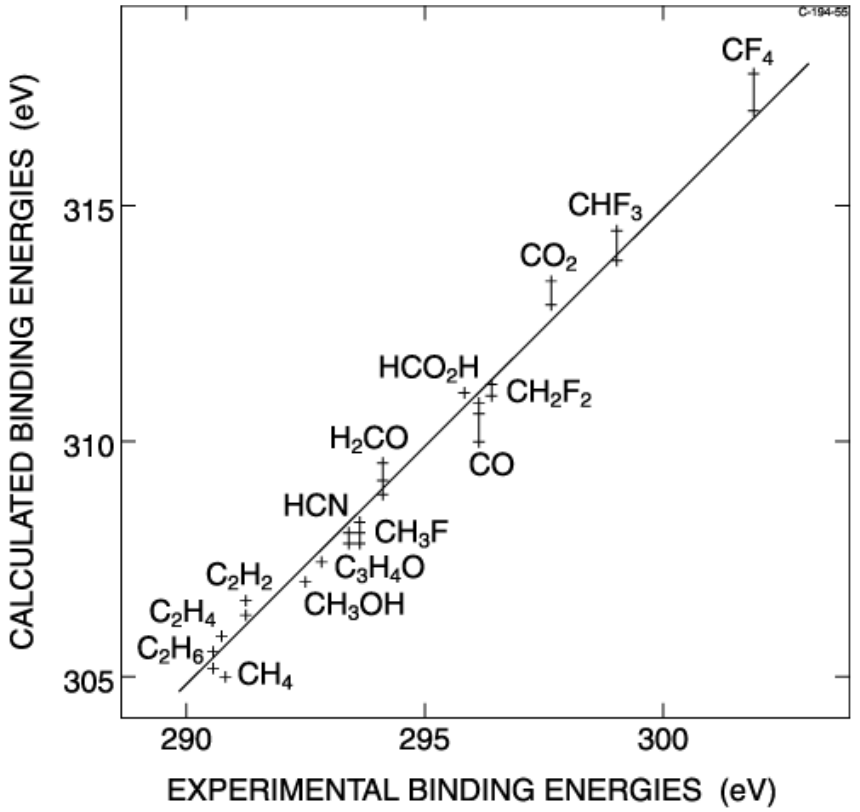
Chemical Shifts

- One of the most valuable features of XPS is its ability to distinguish different chemical bonding configurations
- The bonding energies of electrons in an atom are affected by the atom's chemical environment.
  - This is called the Chemical Shift.
- For example, the positions of the three peaks reflect the effects of -O and =O
- the ratio of C-C bonds to C-O and C=O bonds can be calculated from the relative areas of the peaks.

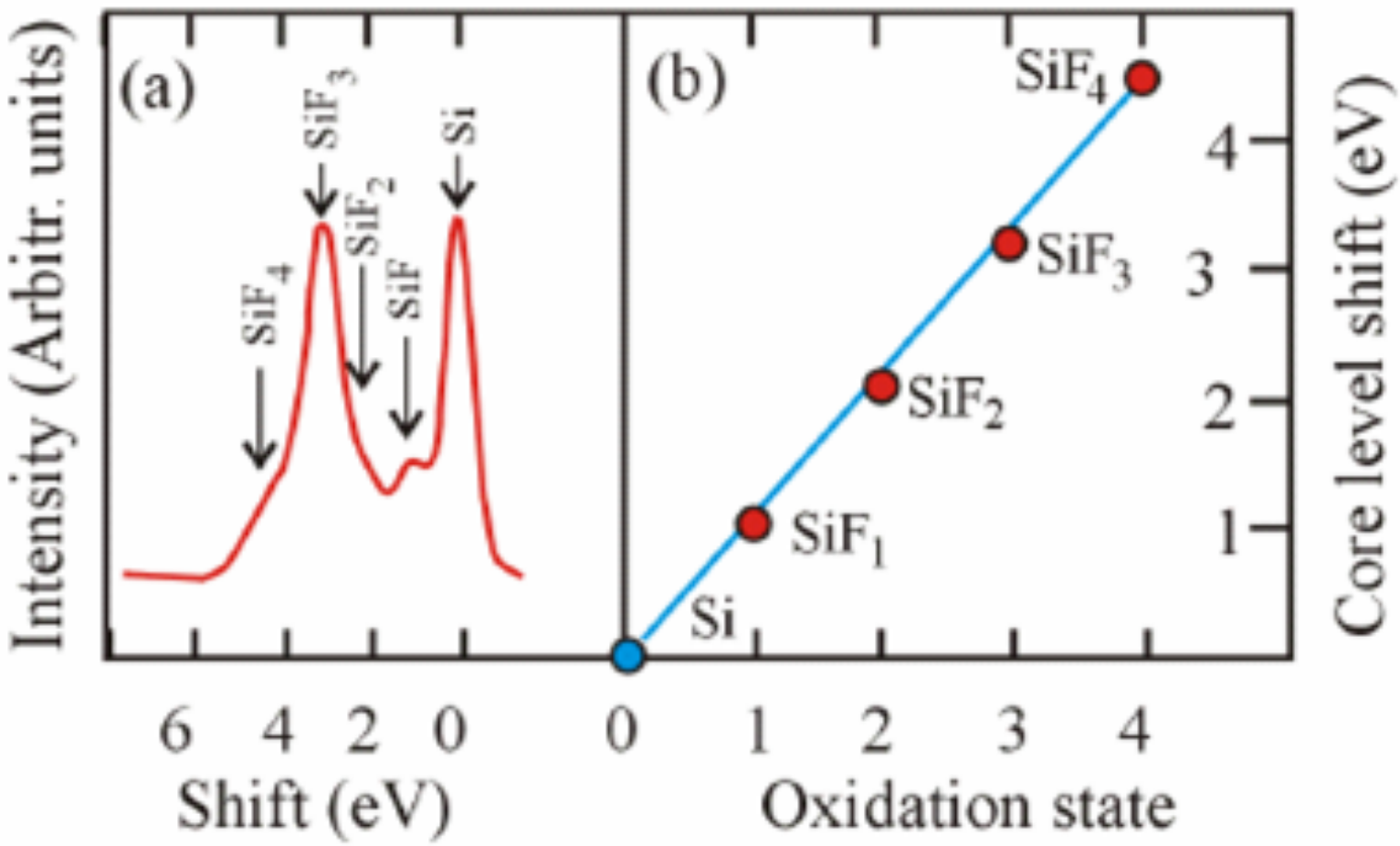


Examples of Chemical Shifts in Hydrocarbons

Functional Group		*Binding Energy (eV)*
hydrocarbon	C-H, C-C	285.0
amine	C-N	286.0
alcohol, ether	C-O-H, C-O-C	286.5
Cl bound to C	C-Cl	286.5
F bound to C	C-F	287.8
carbonyl	C=O	288.0

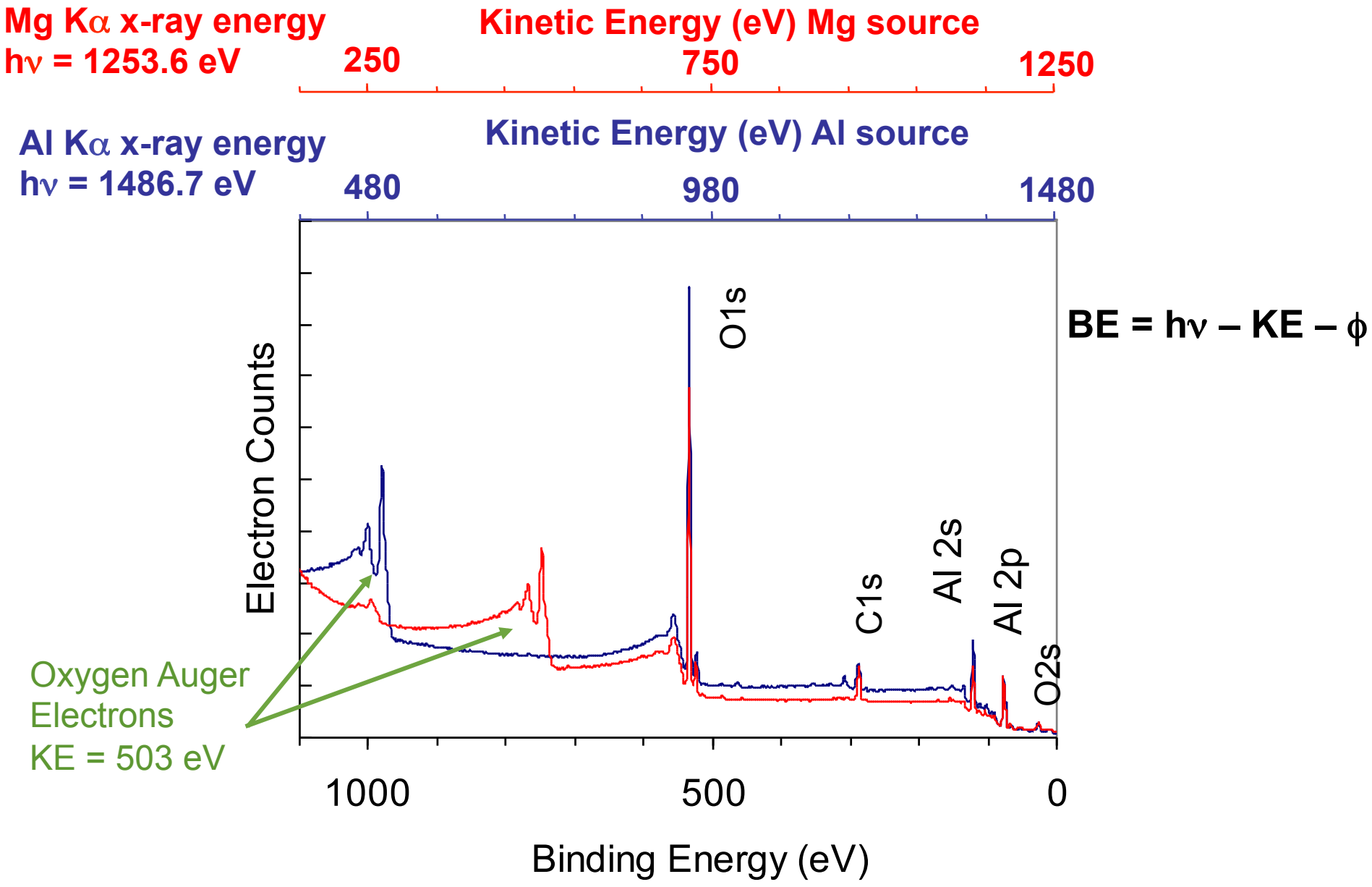


Comparison between experimental and calculated (from Koopman's theorem) C1*s* binding energies. Note that the agreement is very good if one of the axes is shifted by 15 eV. The good agreement is underlined by the line of slope 1



Taken from :
www.**uwo**.ca/ssw/services//**xps**/ **xps**grad**course**_resources/**xps**_grad_**course**.pdf

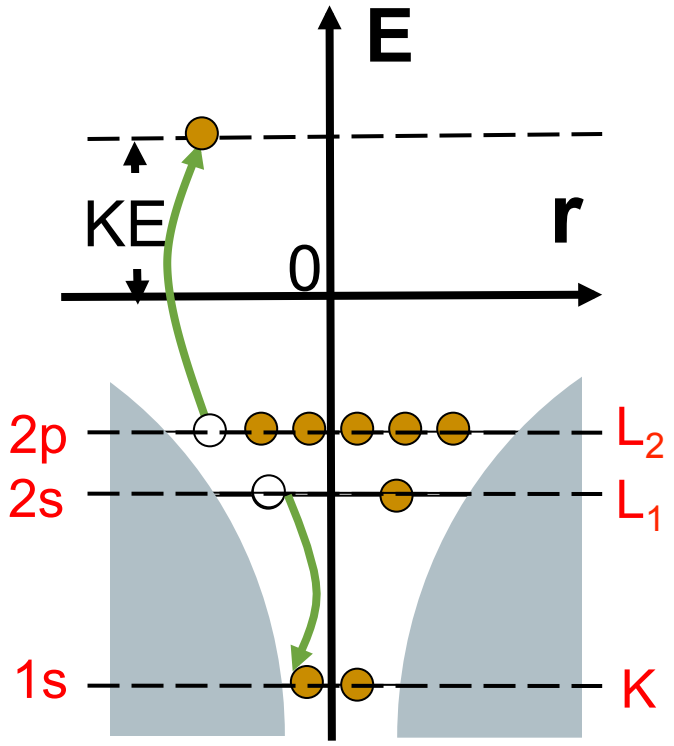
XPS example: Al foil



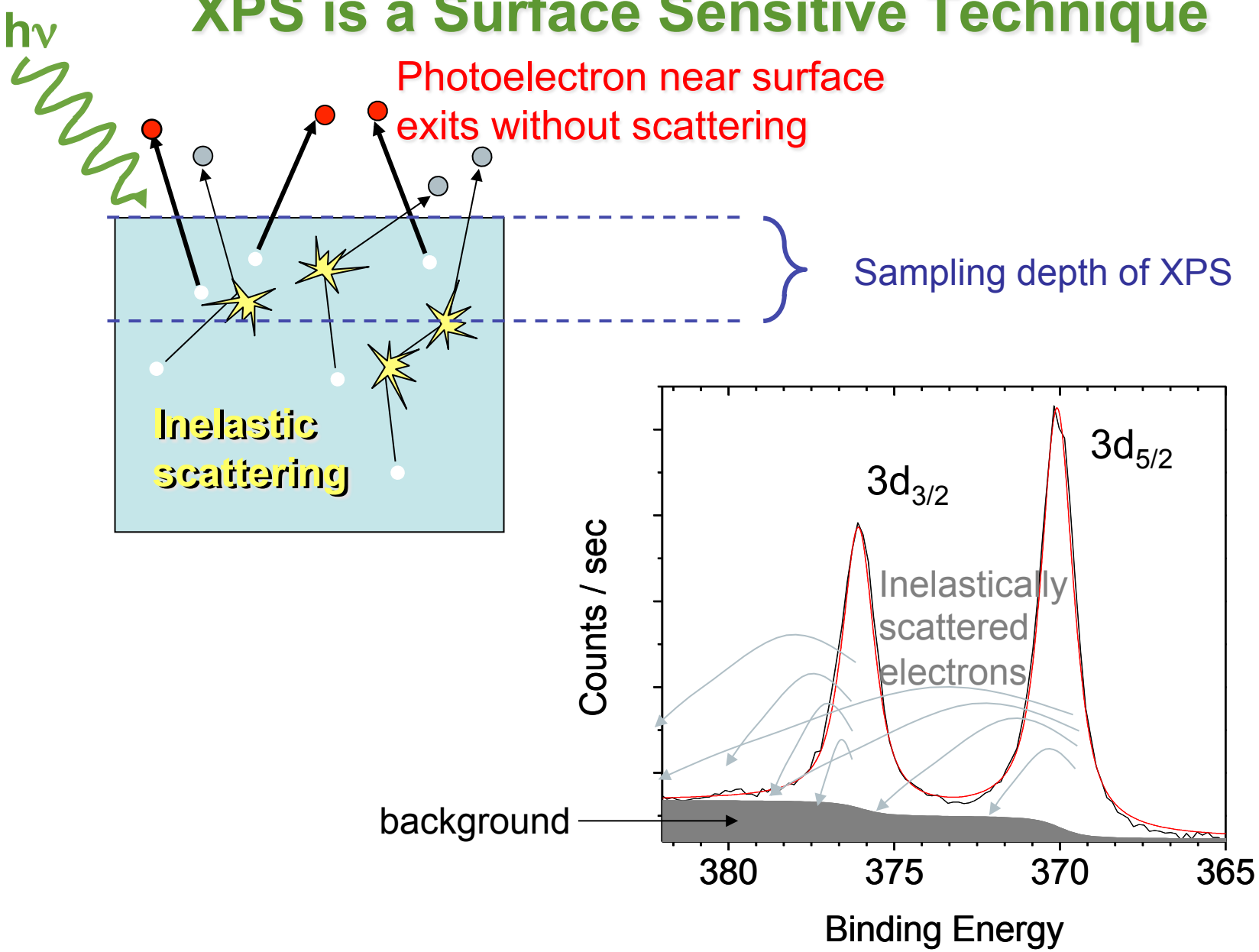
Auger Nomenclature

Quantum numbers				Atomic Notation	X-ray Notation
n	l	s	j	nl_j	
1	0	±1/2	1/2	1s	K_1
2	0	±1/2	1/2	2s	L_1
2	1	-1/2	1/2	$2p_{1/2}$	L_2
2	1	+1/2	3/2	$2p_{3/2}$	L_3
3	0	±1/2	1/2	3s	M_1
3	1	-1/2	1/2	$3p_{1/2}$	M_2
3	1	+1/2	3/2	$3p_{3/2}$	M_3
3	2	-1/2	3/2	$3d_{3/2}$	M_4
3	2	+1/2	5/2	$3d_{5/2}$	M_5

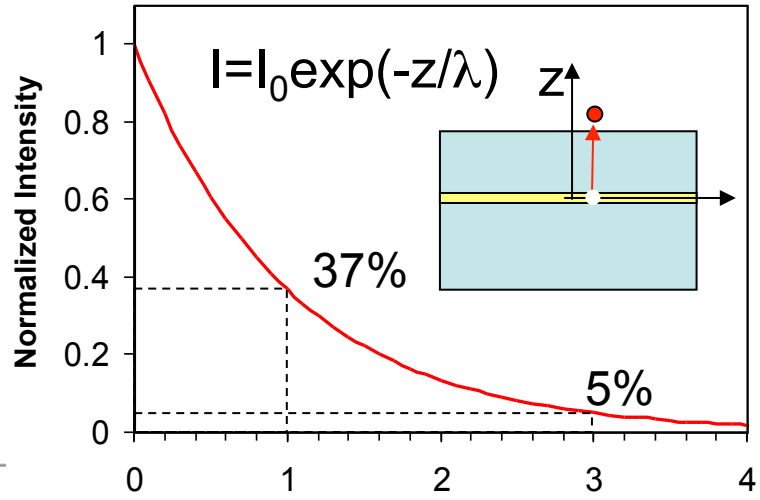
KLL Auger transition

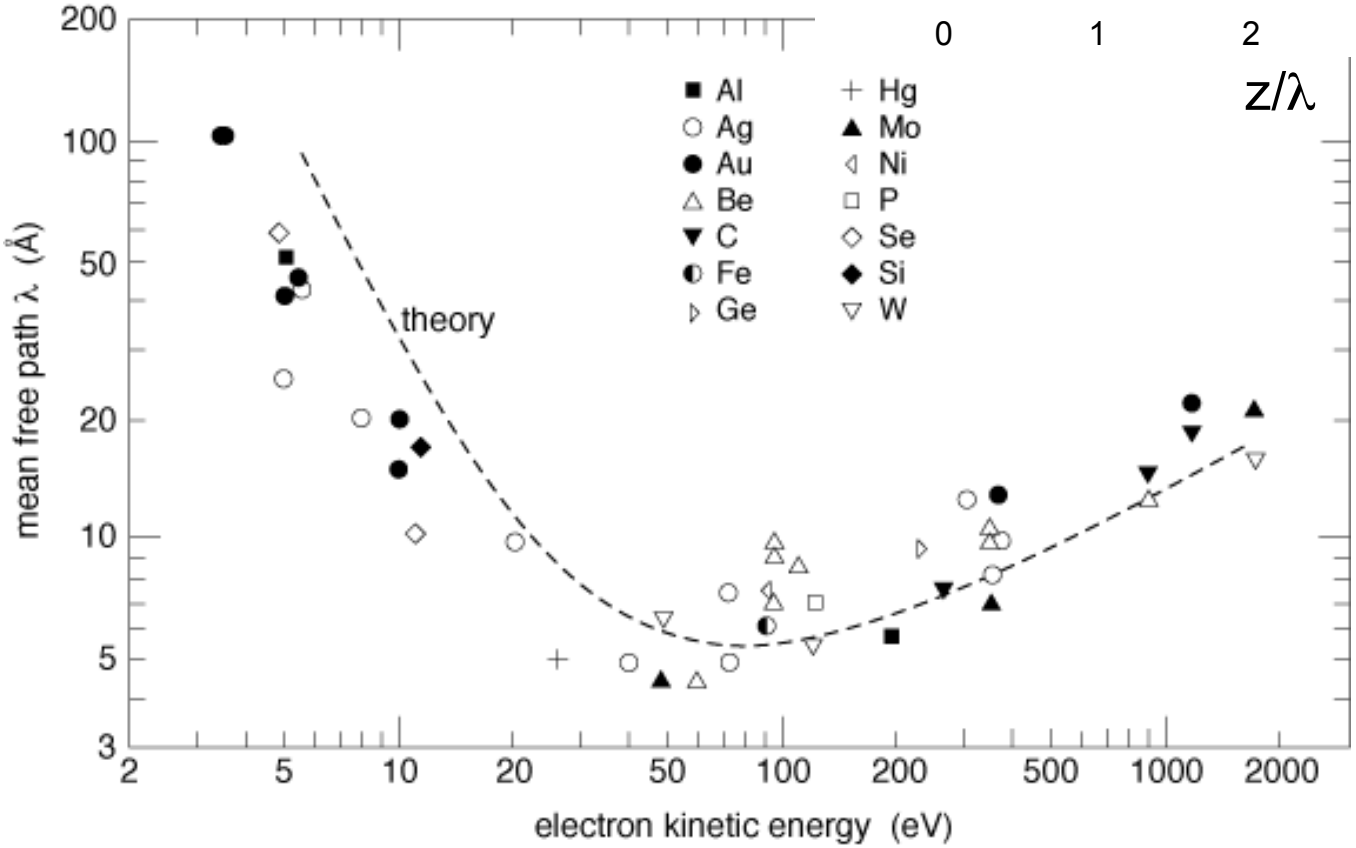


XPS is a Surface Sensitive Technique



Mean Free Path Determines Sampling Depth





Surface Sensitive Technique

Sampling depth 3λ

Signal comes from top 15 Å – 60 Å

Where to Get Inelastic Electron Mean Free Path Data

- **Seah and Dench Estimates of Inelastic Mean Free Path**
  - Seah and Dench, Surf. Interface Anal. 1, 1 (1979).
  - $\lambda(KE) = 538\ a\ (KE)^{-2} + 0.41\ (a^3\ KE)^{1/2}$ elements
  - $\lambda(KE) = 2170\ a\ (KE)^{-2} + 0.72\ (a^3\ KE)^{1/2}$ inorganic compounds
  - $\lambda(KE) = 103/\rho\ (49\ (KE)^{-2} + 0.11\ (KE)^{1/2})$ organic compounds

  Where the kinetic energy of the electron is in [eV], the imfp λ is in [nm], the atomic volume a^3 is in [nm^3] and the density ρ is in [$g\ cm^{-3}$]
- **Inelastic Electron Mean Free Paths or specific materials**
  - S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. 17, 911 (1991)
  - S. Tanuma, , C. J. Powell, and D. R. Penn, Surf. Interface Anal. 20, 77 (1993)
  - S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. 17, 927 (1993)
  - Software to calculate IMFPs: http://www.quases.com (free download)

Instrumentation

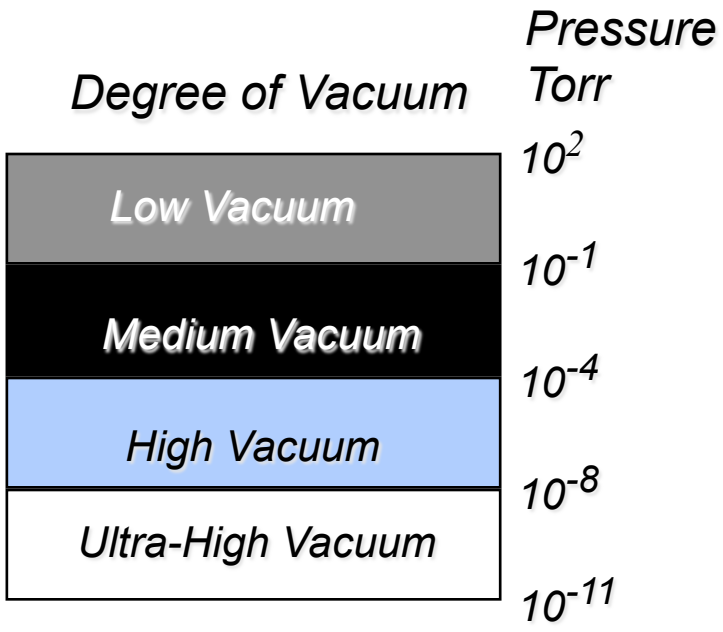
References for Vacuum Technology

- H. Luth "Surfaces and Interfaces of Solids"
- S. Dushman, "Scientific Foundations of Vacuum Technology"
- A. Roth, "Vacuum Technology"
- J.F. O'Hanlon, "A Users Guide to Vacuum Technology"
- Leybold Inc.'s Catalog "Vacuum Technology: Its Foundations, Formulae and Tables"

References for Electron Spectrometer Design

- C. E. Kuyatt and J. A. Simpson "Electron Monochromator Design" Rev. Sci. Instr. 38,103 (1967).

Why UHV for Surface Analysis?



- *Remove adsorbed gases from the sample.*
- *Eliminate adsorption of contaminants on the sample.*
- *Increase the mean free path for electrons, ions and photons.*

Vacuum Characteristics

Degree of Vacuum	Pressure (Torr)	Gas Density (molecules m^{-3})	Mean Free Path (m)	Time / ML (s)
Atmospheric	760	2×10^{25}	7×10^{-8}	$2.9\ 10^{-9}$
Low	1	3×10^{22}	5×10^{-5}	2.2×10^{-6}
Medium	10^{-3}	3×10^{19}	5×10^{-2}	2.2×10^{-3}
High	10^{-6}	3×10^{16}	50	2.2
UltraHigh	10^{-10}	3×10^{12}	5×10^{5}	2.2×10^{4}

Material Selection for UHV

- Low carbon steel has low permiation rates
  - Example : 304 stainless steel
- Polymers are permiable to all gases
  - can't use viton o-rings
- Copper : use oxygen free high conductivity Cu (OFHC)
- Aluminum: 6061 alloy commonly used
- Brass: avoid in UHV

Average outgassing rates*

Outgassing rates in torr.liter/sec cm^2

	Exposure to vacuum			Surface Condition			
	1 hour	10 hours	>24 hrs	untreated	degreased	polished	baked
Aluminum (anodized)	$3x10^{-5}$	$3x10^{-7}$	$8x10^{-8}$	$3x10^{-5}$	$3x10^{-5}$	N/A	$5x10^{-10}$
Aluminum	$8x10^{-7}$	$5x10^{-8}$	$1x10^{-10}$	$8x10^{-7}$	$1x10^{-8}$	$1x10^{-8}$	$5x10^{-13}$
Brass	$2x10^{-6}$	$6x10^{-7}$	$1x10^{-7}$	$1x10^{-6}$	$1x10^{-6}$	$8x10^{-6}$	N/A
Beryllium	$1x10^{-6}$	$5x10^{-7}$	$1x10^{-9}$	$1x10^{-6}$	$5x10^{-7}$	$1x10^{-6}$	N/A
Copper	$1x10^{-7}$	$5x10^{-9}$	$1x10^{-10}$	$1x10^{-7}$	$1x10^{-8}$	$1x10^{-9}$	$1x10^{-12}$
Copper (OFHC)	$8x10^{-9}$	$2x10^{-9}$	$3x10^{-11}$	$8x10^{-9}$	$8x10^{-9}$	$5x10^{-7}$	$1x10^{-12}$
Delrin	$6x10^{-6}$	$1x10^{-7}$	$7x10^{-7}$	$6x10^{-6}$	not available	not available	$8x10^{-7}$
Lead	$1x10^{-7}$	$2x10^{-8}$	$4x10^{-8}$	$1x10^{-8}$	$5x10^{-8}$	$1x10^{-8}$	N/A
Mild Steel	$2x10^{-6}$	$2x10^{-7}$	3x108	$2x10^{-6}$	$5x10^{-7}$	$5x10^{-8}$	$5x10^{-10}$
1018 Steel (Ni plated)	$2x10^{-6}$	$5x10^{-7}$	$1x10^{-8}$	not available	not available	not available	not available
Gold Sheet	$8x10^{-8}$	not available	5x10-9	$8x10^{-8}$	$1x10^{-8}$	not available	not available
Titanium	$1x10^{-9}$	not available	$5x10^{-10}$	$1x10^{-9}$	not available	not available	$2x10^{-12}$
Stainless steel	$5x10^{-8}$	$1x10^{-8}$	$1x10^{-10}$	$7x10^{-8}$	$1x10^{-9}$	$5x10^{-9}$	$3x10^{-13}$

*Rates can vary significantly, depending on pre-cleaning and preparation methods, and system history.

Average outgassing rates*

Outgassing rates in torr.liter/sec cm^2

	Exposure to vacuum			Surface Condition			
	1 hour	10 hours	>24 hrs	untreated	degreased	polished	baked
Epoxy (Shell Epon)	$2x10^{-5}$	$1x10^{-6}$	not available	not available	not available	N/A	$8x10^{-8}$
Buna N	$8x10^{-6}$	$2x10^{-6}$	$8x10^{-7}$	$8x10^{-6}$	$8x10^{-7}$	N/A	$4x10^{-8}$
Neoprene	$3x10^{-6}$	$8x10^{-7}$	$4x10^{-8}$	$3x10^{-6}$	$6x10^{-7}$	N/A	$2x10^{-9}$
Mylar	$8x10^{-7}$	$1x10^{-7}$	$7x10^{-9}$	$8x10^{-7}$	N/A	N/A	$2x10^{-9}$
Acrylic	$2x10^{-6}$	$1x10^{-6}$	$5x10^{-7}$	$2x10^{-6}$	$8x10^{-7}$	N/A	$1x10^{-8}$
Teflon (poly'fluoro'lene)	$2x10^{-7}$	$8x10^{-8}$	$2x10^{-8}$	$2x10^{-7}$	N/A	N/A	$8x10^{-9}$
Nylon (polyamide)	$5x10^{-6}$	$3x10^{-7}$	$4x10^{-8}$	$5x10^{-6}$	N/A	N/A	$6x10^{-9}$
Lexan (polycarbonate)	$7x10^{-7}$	$2x10^{-7}$	$6x10^{-8}$	$1x10^{-7}$	N/A	N/A	$8x10^{-9}$
PVC	$5x10^{-7}$	$3x10^{-7}$	$1x10^{-7}$	$5x10^{-7}$	N/A	N/A	$8x10^{-8}$
Silicon rubber	$7x10^{-6}$	$8x10^{-7}$	$6x10^{-8}$	$7x10^{-7}$	$2x10^{-7}$	N/A	$6x10^{-10}$
Silastic (sealant)	$5x10^{-5}$	$3x10^{-6}$	$6x10^{-7}$	$8x10^{-5}$	N/A	N/A	$5x10^{-8}$
Viton	$8x10^{-7}$	$5x10^{-8}$	$2x10^{-8}$	$8x10^{-7}$	$1x10^{-7}$	N/A	$5x10^{-10}$
Steatite (ceramic)	$5x10^{-8}$	$1x10^{-8}$	$7x10^{-9}$	N/A	N/A	N/A	N/A
Pyrex (7740)	$1x10^{-7}$	$2x10^{-8}$	$5x10^{-9}$	not available	not available	N/A	$2x10^{-9}$

*Rates can vary significantly, depending on pre-cleaning and preparation methods, and system history.