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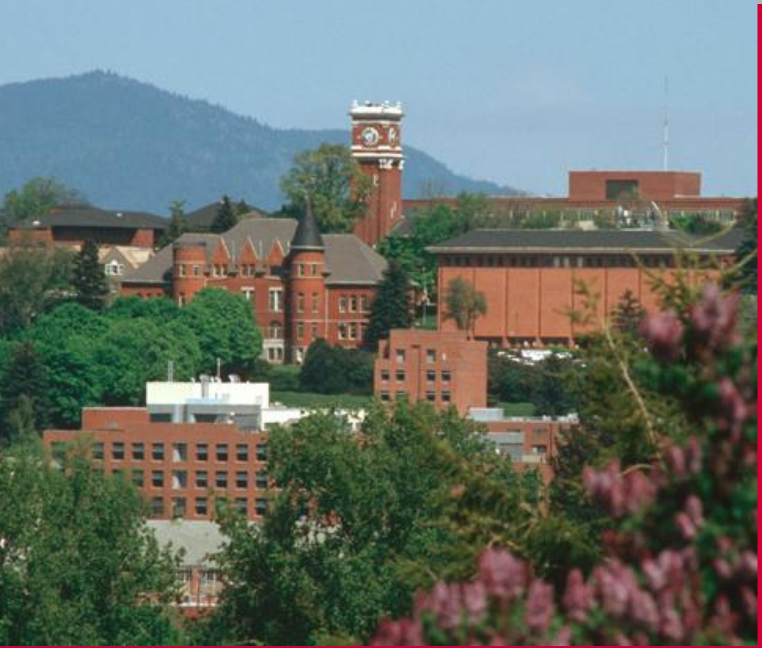

# X-Ray Photoelectron Spectroscopy (XPS)-2

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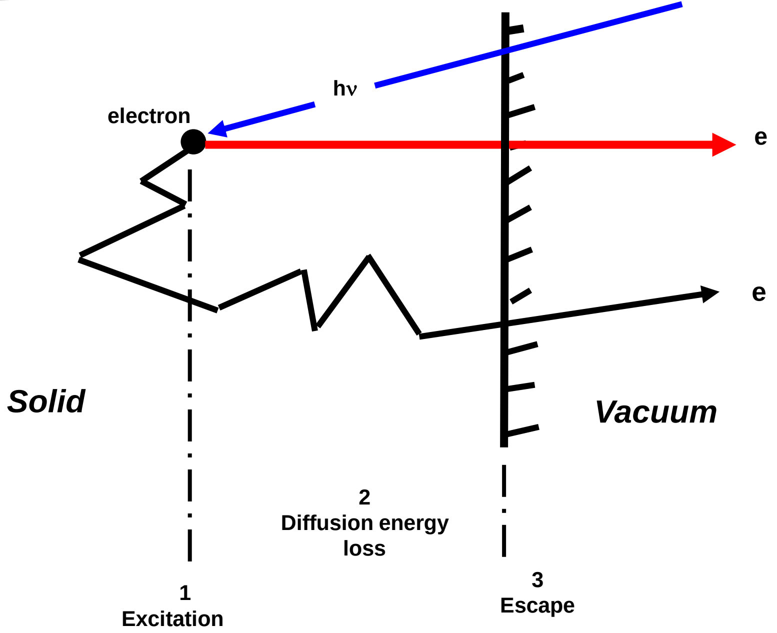
Fulmer 261A

**Electron Spectroscopy for Chemical Analysis (ESCA)**

**The 3 –step model:**

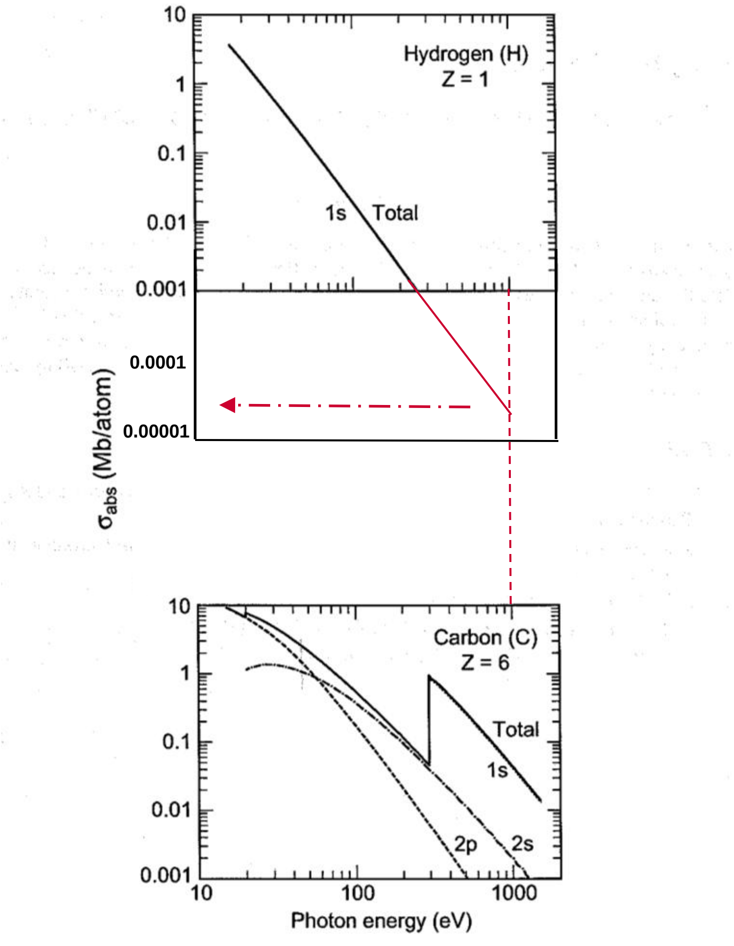
1. Optical excitation
2. Transport of electron to the surface (diffusion energy loss)
3. Escape into the vacuum



Photoemission intensity for a normal incidence $$I(\theta) \propto \frac{\sigma_{total}}{4}$$

At photon energy of 1254 eV (MgKα x-ray line), $\boldsymbol{\sigma}_H = 0.0002$ and $\boldsymbol{\sigma}_C = 1.05$
The intensity ratio is $I_H\,(90)/\,I_C\,(90) = 1.9 \times 10^{-4}$
(Based of the Scofield's calculations of the cross-sections carried out relativistically using the single potential Hartree-Slater atomic model)

Lindau’s calculations of the cross-section for isolated atoms (using the one-electron central-field frozen-core model and first –order perturbation theory)



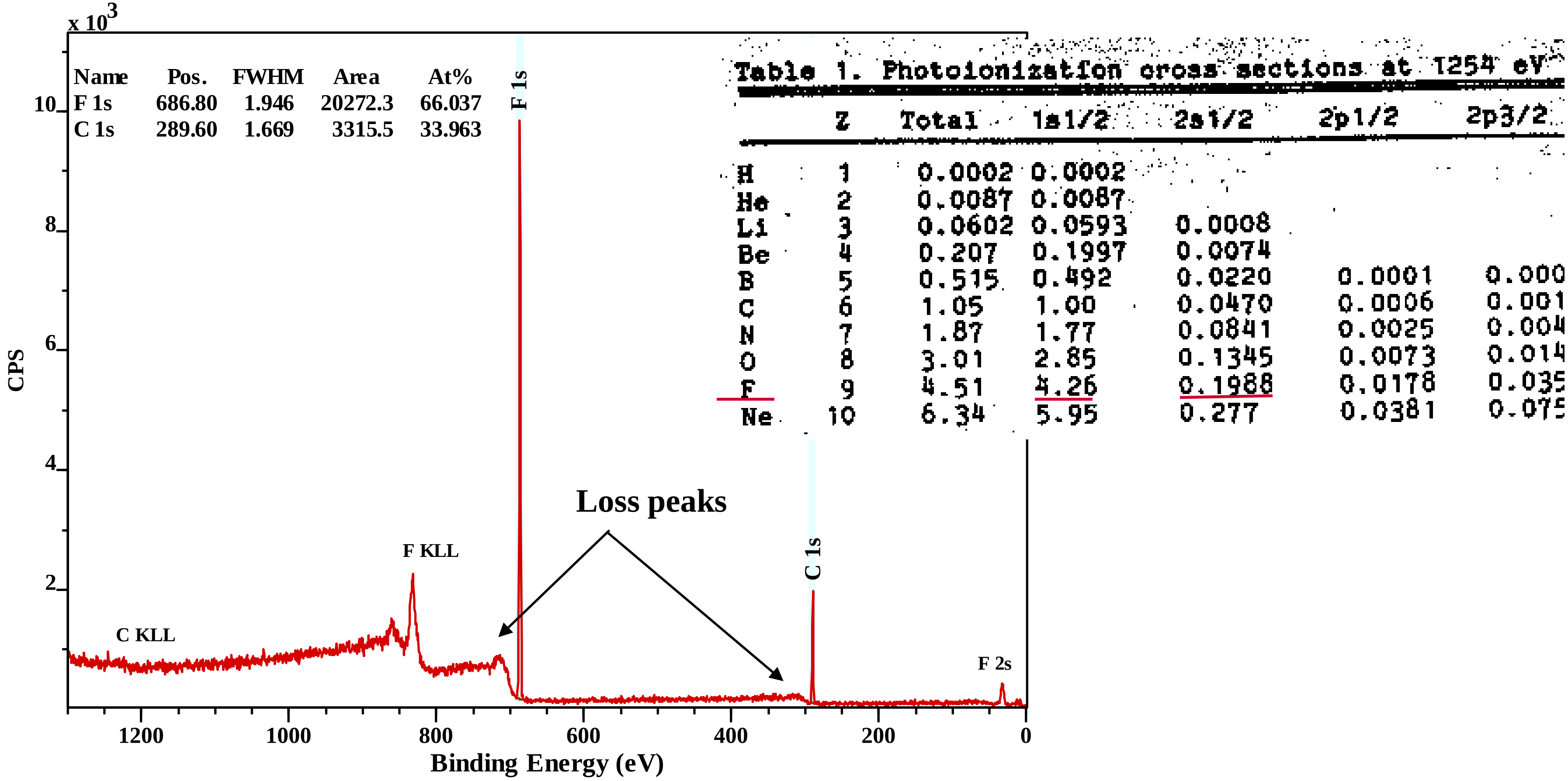
*Plots of atomic subshell photoemission cross sections, calculated for isolated atoms.*

$$I(\theta) \propto \frac{\sigma_{total}}{4}$$

For a photon energy of 1000 eV, $\sigma_H = 0.00005$ and $\sigma_C = 0.07$

The intensity ratio is $I_H(90)/ I_C(90) = 7.1 \times 10^{-3}$

# *Survey spectrum*



| Name | Pos. | FWHM | Area | At% |
|---|---|---|---|---|
| F 1s | 686.80 | 1.946 | 20272.3 | 66.037 |
| C 1s | 289.60 | 1.669 | 3315.5 | 33.963 |

Table 1. Photoionization cross sections at 1254 eV

|  | Z | Total | 1s1/2 | 2s1/2 | 2p1/2 | 2p3/2 |
|---|---|---|---|---|---|---|
| H | 1 | 0.0002 | 0.0002 |  |  |  |
| He | 2 | 0.0087 | 0.0087 |  |  |  |
| Li | 3 | 0.0602 | 0.0593 | 0.0008 |  |  |
| Be | 4 | 0.207 | 0.1997 | 0.0074 |  |  |
| B | 5 | 0.515 | 0.492 | 0.0220 | 0.0001 | 0.000 |
| C | 6 | 1.05 | 1.00 | 0.0470 | 0.0006 | 0.001 |
| N | 7 | 1.87 | 1.77 | 0.0841 | 0.0025 | 0.004 |
| O | 8 | 3.01 | 2.85 | 0.1345 | 0.0073 | 0.014 |
| F | 9 | 4.51 | 4.26 | 0.1988 | 0.0178 | 0.035 |
| Ne | 10 | 6.34 | 5.95 | 0.277 | 0.0381 | 0.075 |

# Six features seen in a typical XPS spectrum

1. Sharp peaks due to photoelectrons created within the first few atomic layers (elastically scattered).

2. Multiplet splitting (occurs when unfilled shells contain unpaired electrons).

3. A broad structure due to electrons from deeper in the solid which are ineslastically scattered (reduced KE) forms the background.

4. Satellites (shake-off and shake-up) are due to a sudden change in Coulombic potential as the photoejected electron passes through the valence band.

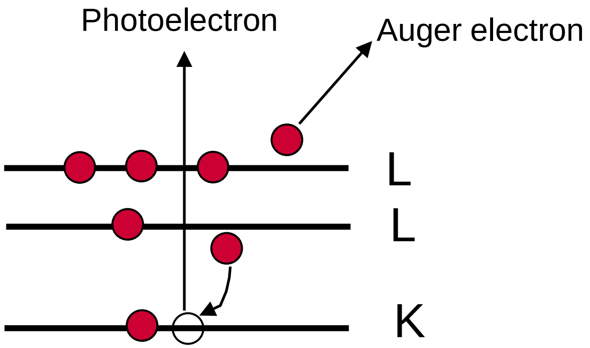
5. Plasmons which are created by collective excitations of the valence band

- Extrinsic Plasmon: excited as the energetic PE propagates through the solid after the photoelectric process.

- Intrinsic Plasmon: screening response of the solid to the sudden creation of the core hole in one of its atom

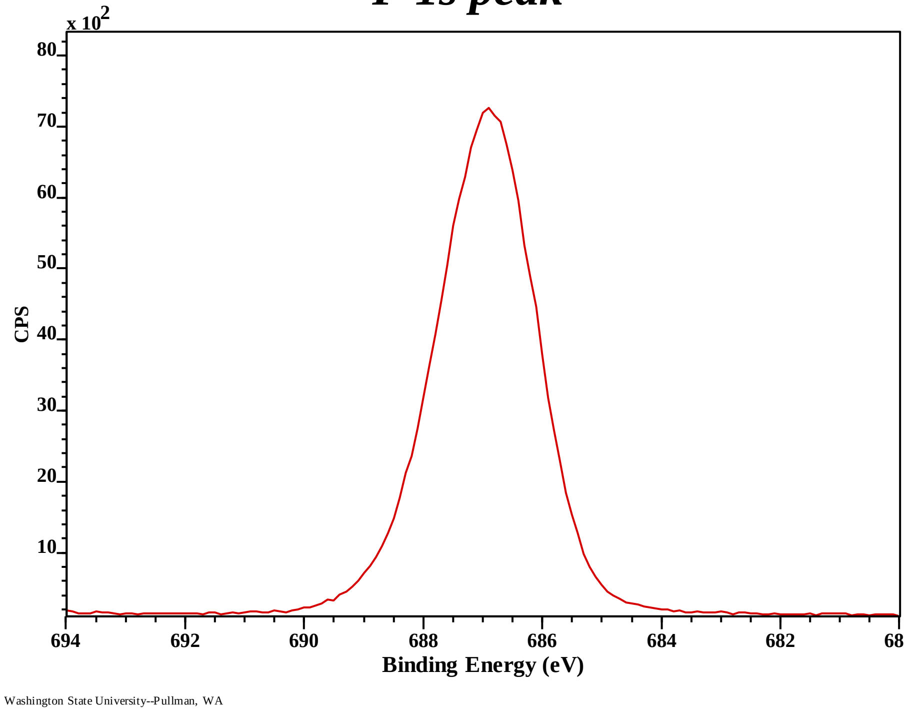
*The two kinds of Plasmon are indistinguishable.*

6. Auger peaks produced by x-rays (transitions from L to K shell: O KLL or C KLL).

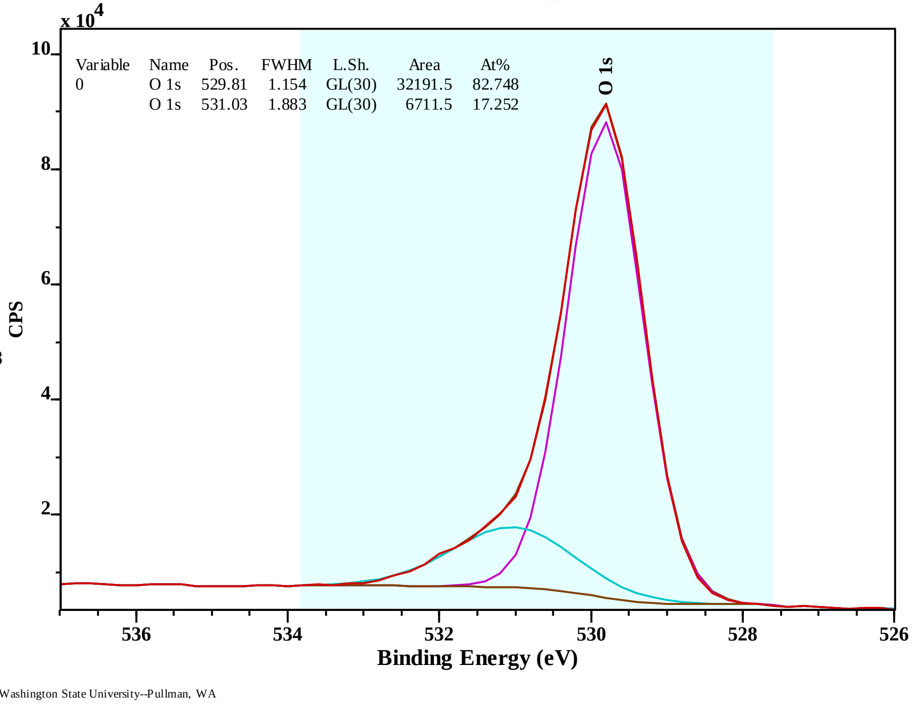


# Sharp Peak (core level)

## *F 1s peak*

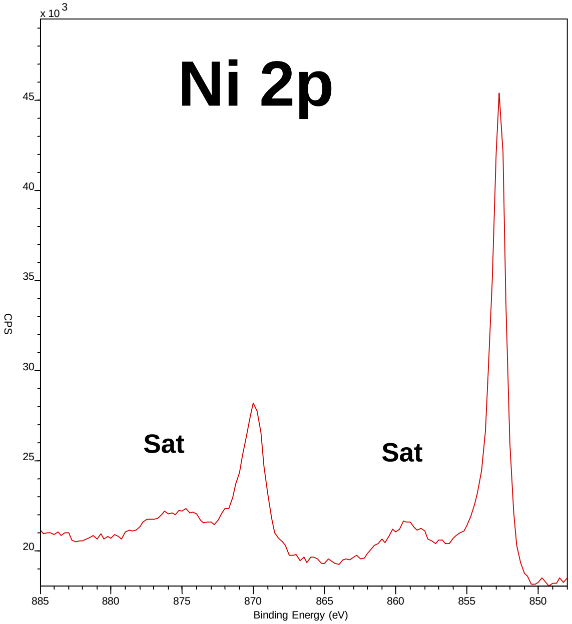


## *O 1s peak*



| Variable | Name | Pos. | FWHM | L.Sh. | Area | At% |
|---|---|---|---|---|---|---|
| 0 | O 1s | 529.81 | 1.154 | GL(30) | 32191.5 | 82.748 |
|  | O 1s | 531.03 | 1.883 | GL(30) | 6711.5 | 17.252 |

# Doublet and satellites peaks for Ni 2p, Cr 2p and Au 4f



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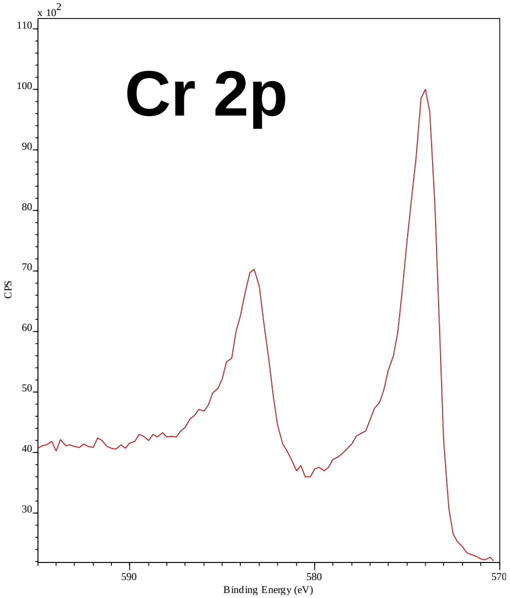

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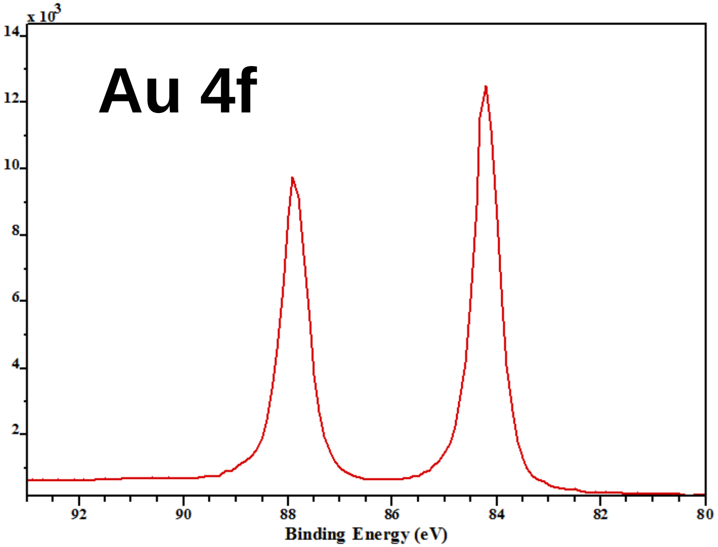


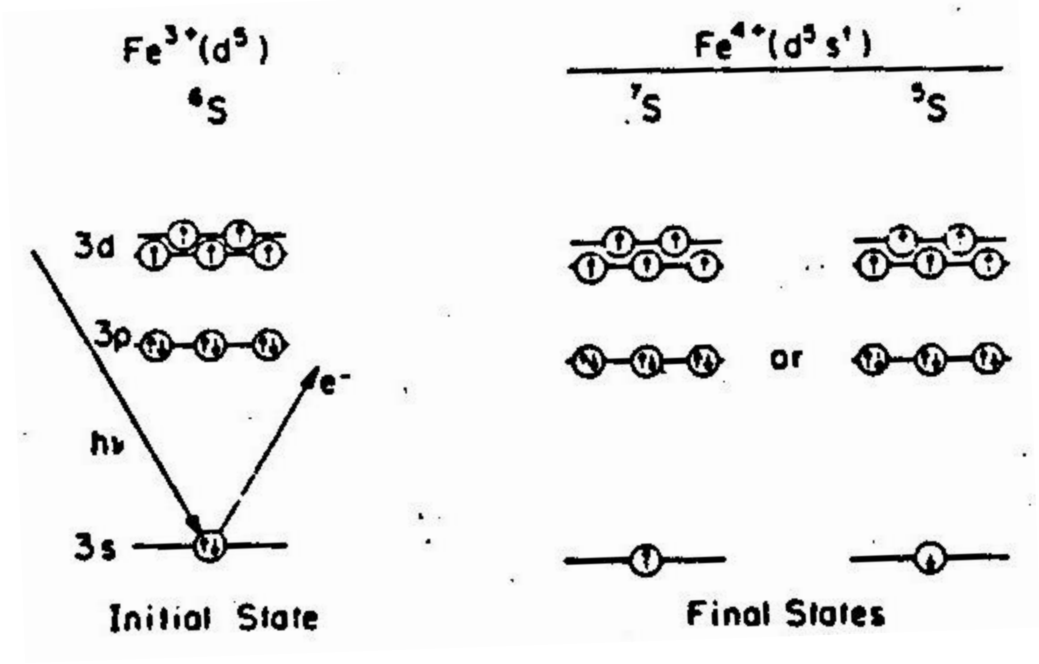
Doublet occurs in transition metals with ***p***, ***d*** and rare earth with ***f*** orbitals (not s-orbitals) due to spin-orbital interaction.

However, under certain environment conditions, elements such as Cr, Mn and Fe etc.. show presence of s orbitals (3s) splitting due to coupling between unpaired electrons (created by photoionization and the unpaired electron in the original shell).

Vacancy created by photoionization (unpaired electron left behind (after ionization)) couples with a unpaired electron in the originally incompletely filled shell can generates splitting of s orbitals and p orbitals (spin doublet separation energy).

*Example: $Fe_2O_3$ has 5 unpaired electrons in the 3d shell as shown below. Following photoionization in the 3s shell, there are 2 possible final states.*

***Schematic of Multiplet Splitting following photoionization in $Fe^{3+}$ and XPS spectrum***



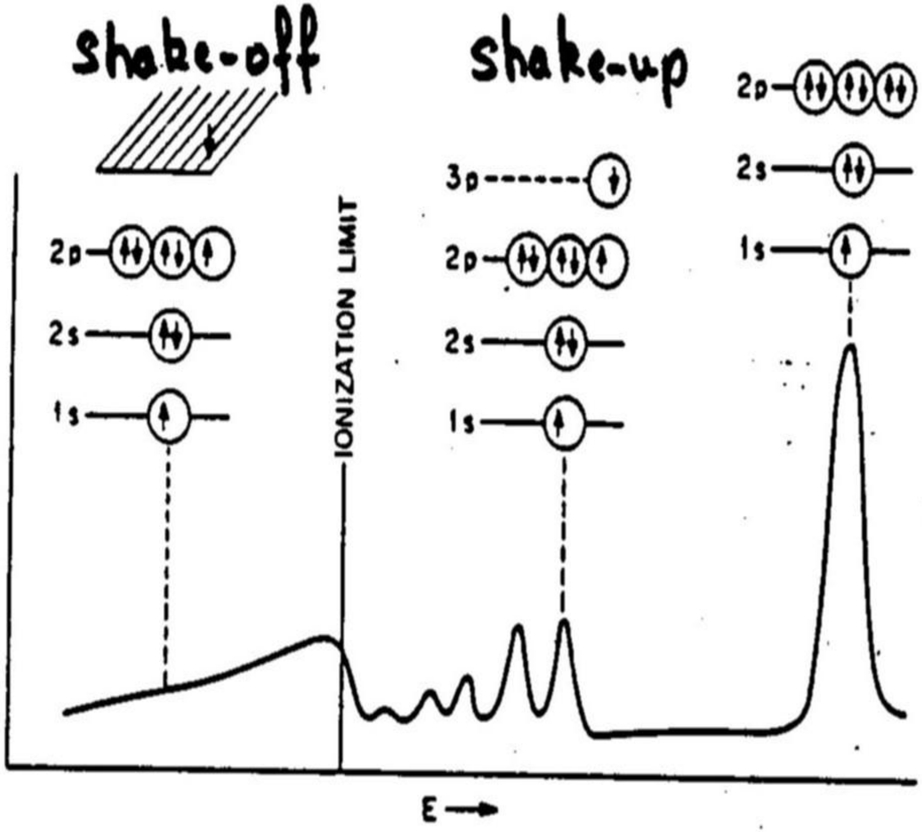
**Satellites** arise when a core electron is removed by a photoionization. There is a sudden change in the effective charge due to the loss of shielding electrons. (This perturbation induces a transition in which an electron from a bonding orbital can be transferred to an anti-bonding orbital simultaneously with core ionization).

Two types of satellite are detected.

***Shake-up:*** The outgoing electron interacts with a valence electron and excites it (shakes it up) to a higher energy level. As a consequence the energy core electron is reduced and a satellite structure appears a few eV below (KE scale) the core level position.

***Shake-off:*** The valence electron is ejected from the ion completely (to the continuum). Appears as a broadening of the core level peak or contribute to the inelastic background.

Shake-up satellites: distinct peaks a few eV below the main line.
Shake-off satellites: broad feature at lower energy w.r.t. to main line.



$$\Delta J = \Delta L = \Delta S = 0\ ;\ \Delta \ell = \Delta s = 0$$

$$P_{n\ell j - n'\ell j} = \left| \int \psi^*_{n'\ell j}\, \psi_{n\ell j}\, d\tau \right|^2$$

$$\Psi_{nlm}(r,\theta,\psi) = Y_{lm}(\theta,\psi) R_n(r)$$

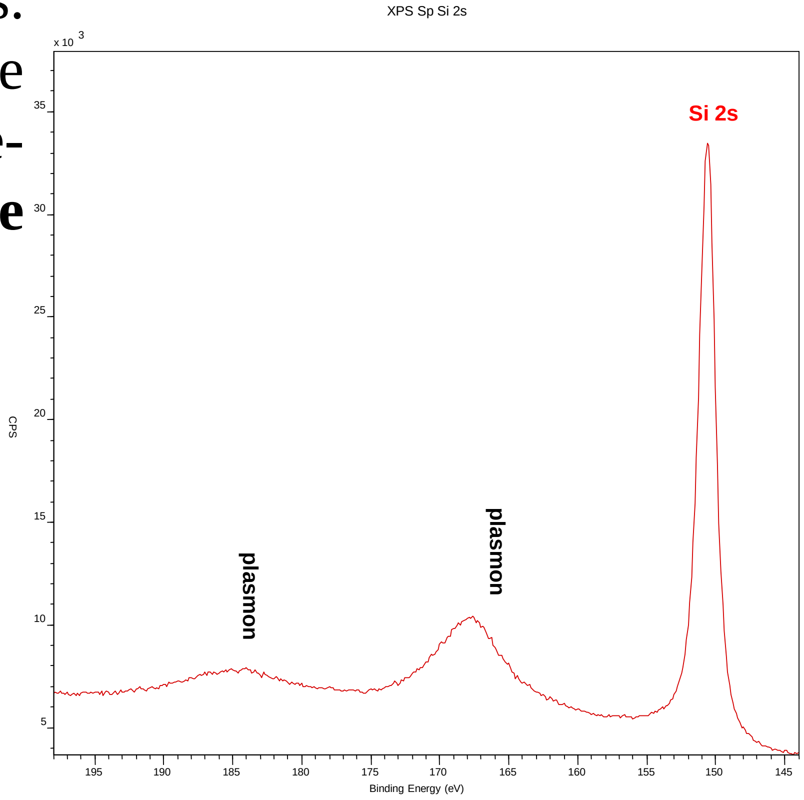
# Plasmons

This feature is specific to clean surfaces. The photoelectron excites collective oscillations in the conduction band (free-electron gas), so called Plasmons. (**discrete energy loss**).

The plasmon (bulk) energy is

$$\hbar\omega_p = \hbar\left(\frac{4\pi n e^2}{m}\right)^{1/2}$$

*n*: e density, *e*: charge of e,
*m*: mass of e electron.



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Surface plasmon: bulk plasmon / 1.414.

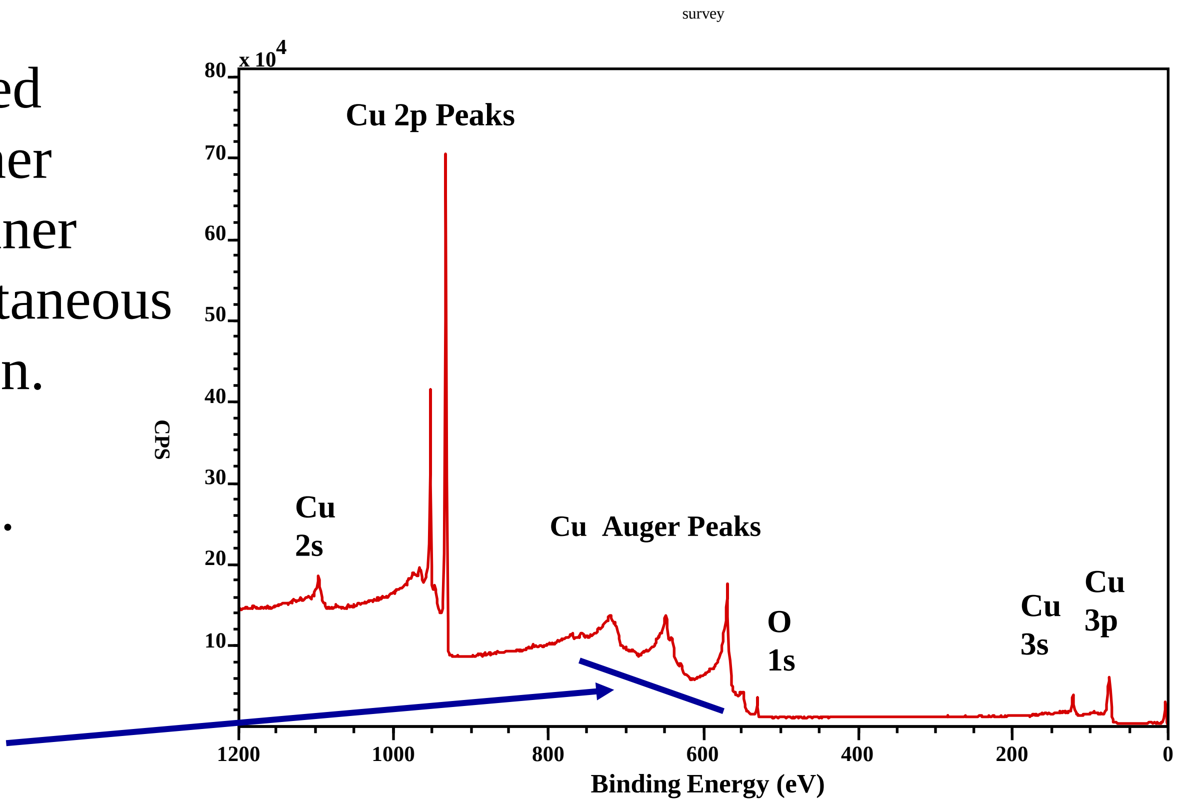
For Al, Mg, Na etc… the energies are 15.3 eV, 10.6 eV and 5.7 eV, respectively.

# *Auger features*

*Auger electron* emission occurs also when x-rays impinge a sample. Auger electron is initiated by the creation of an ion with an inner shell vacancy. Auger electrons are emitted in the relaxation of the excited ion. An electron from a higher lying energy level fills the inner shell vacancy with the simultaneous emission of an Auger electron.

It is a ***three-electron*** process.

3 Distinct Auger Peaks are seen in the data for Copper

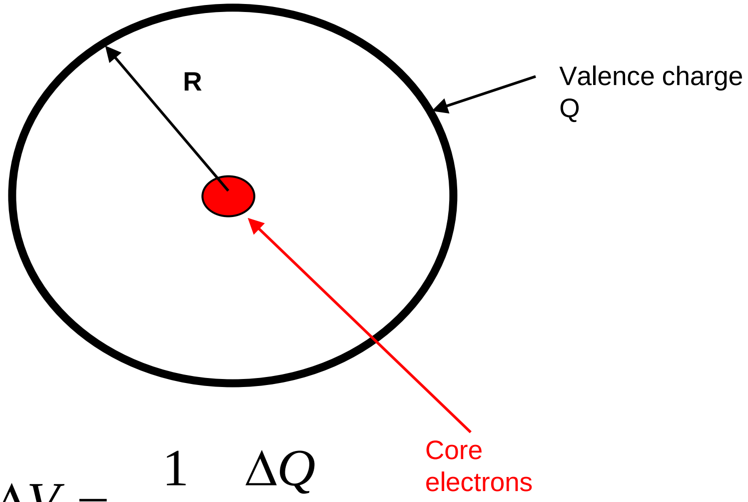


Chemical shift arises in the initial state from the displacement of the electronic charge from the atom towards its ligands, reducing the electrostatic potential at the atom. There is a final state shift due to the polarization of the ligand by the core on the central atom.

Core electron BE in molecular systems exhibits chemical shifts which are simply related to various quantitative measures of covalency. Greater the electronegativity of the ligands, the greater the BE of the core electron of the ligated atom.

Basic concept: The core electrons feel an alteration in the chemical environment when a change in the potential (charge distribution) of the valence shell occurs.

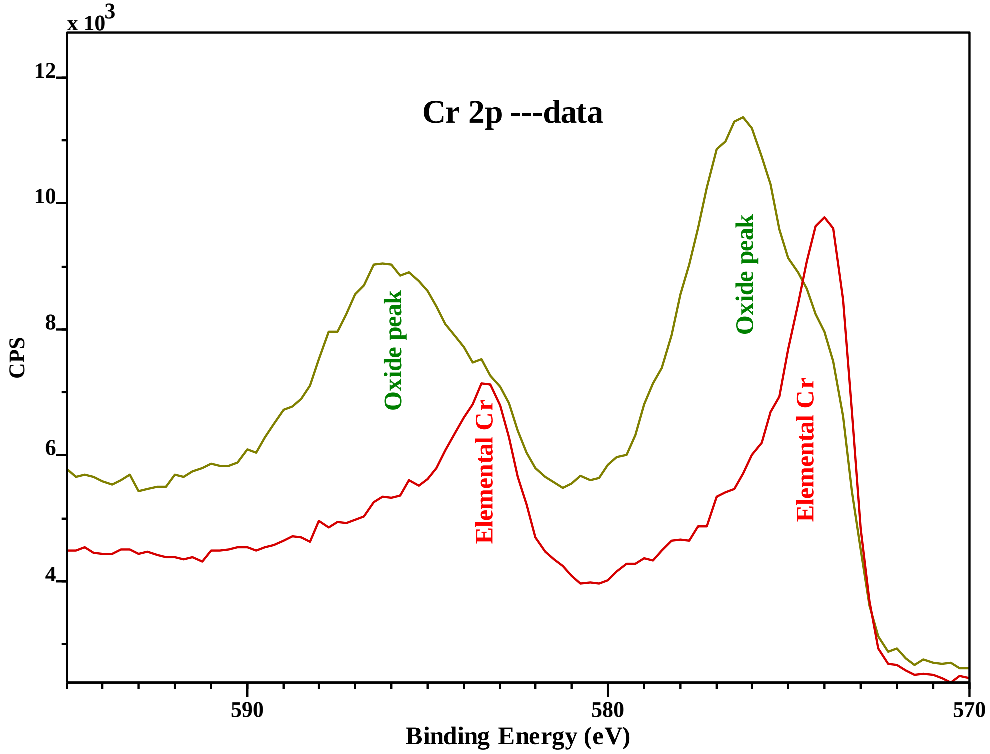
*For example:* let's assume that the core electrons are inside a hollow spherical charged shell. Each core electron then sees a potential V. A change in Q by ΔQ gives a change in V.

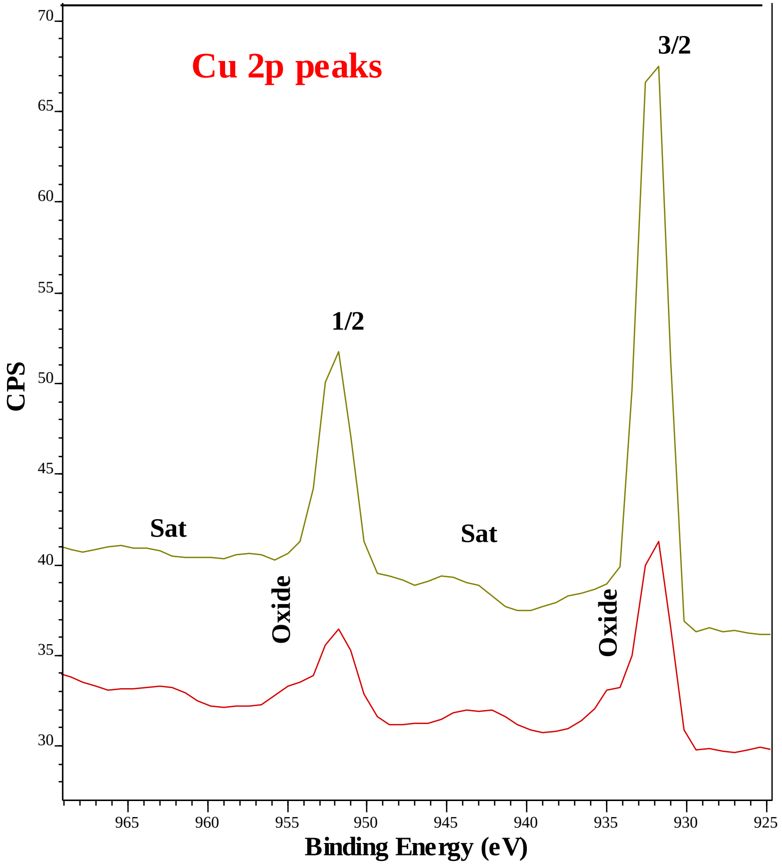


$$\Delta V = \frac{1}{4\pi\varepsilon_0}\frac{\Delta Q}{R}$$

where ΔV is the ***chemical shift***

# Oxidized surfaces



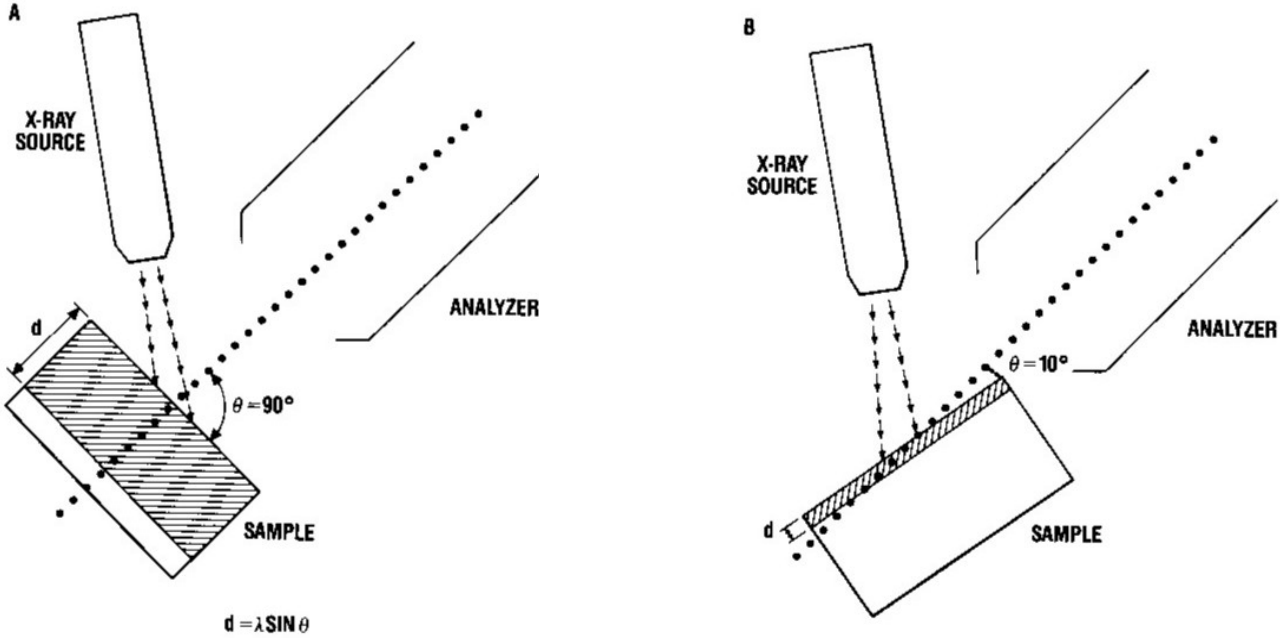


Oxidized and clean Cr 2p spectra (left). Oxidized and clean Cu 2p spectra (right). The oxide layer resulted in extra peaks (shoulder at higher BE—left of the main line). Satellites are also seen on the Cu 2p spectra.

# *Angular Distributions*

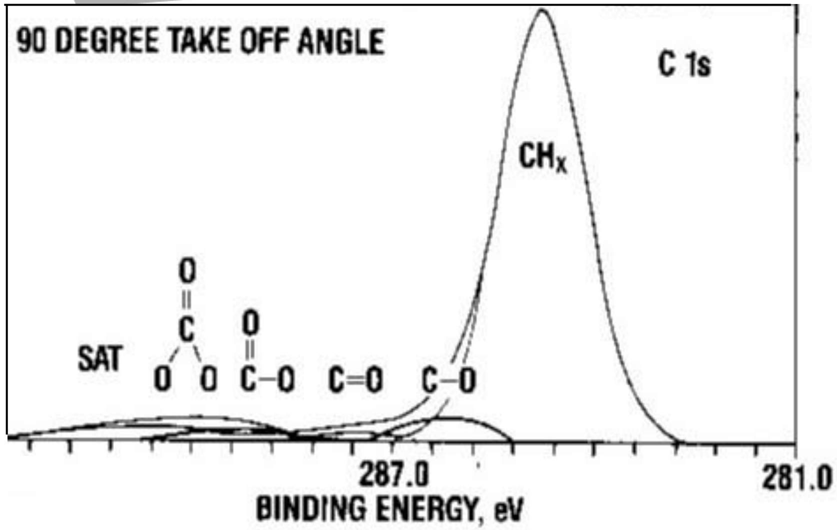
*(C.S. Fadley, J.E.S. and R.P. (1974) 5 p 725-754)*

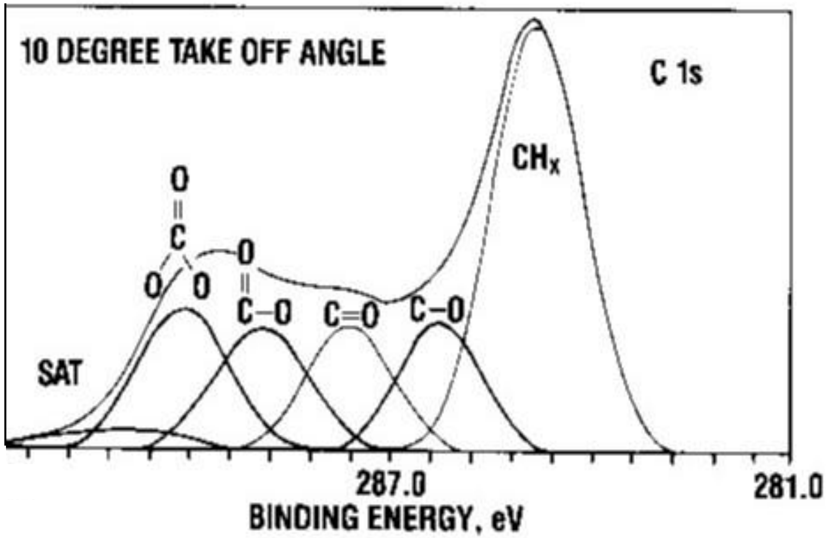
The mean free paths (IMFP) are in the range of 5 -100Å falling within 5 –40 Å for inorganic materials. To enhance the surface signal we can vary the photon energy—closer to the attenuation length minimum **or** decrease the angle of electron emission relative to a solid surface.



*For example: Au 4f IMFP is about 22Å (d) at angle of 90° using AlKα. The depth (d) probed by XPS becomes about 4-5 Å at angle of 10°.*

# *Chemical Bonding*





The curve fitting of the main hydrocarbon line ($C_xH_y$) reveals chemical shifts corresponding to

- Ether and alcohol groups (C-O at 1.55 eV higher BE),
- Carbonyl groups (C=O at 2.8 eV higher),
- Ester and acid functional at 4.2 eV
- Carbonate groups at 5.2 eV higher BE.

Finally, the $\pi$- $\pi^*$ satellite at 291.5 eV appears at the extreme left.

# *Spin-orbit and lines intensity*

**Multiplet splitting occurs when the system has unpaired electrons in the Valence levels.**

*Example:* Mn $^{2+}$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$ ($3d^5$ all unpaired and with // spins)

Also the total electronic angular momentum (j) is a combination of the orbital angular (l) and spin (s) momenta. The j-j coupling is equal to |L ± S| where L and S are the total orbital angular and spin momenta, respectively.

For angular quantum number $l \neq 0$ the line is a doublet. ($\boldsymbol{p_{1/2}}$, $\boldsymbol{p_{3/2}}$).

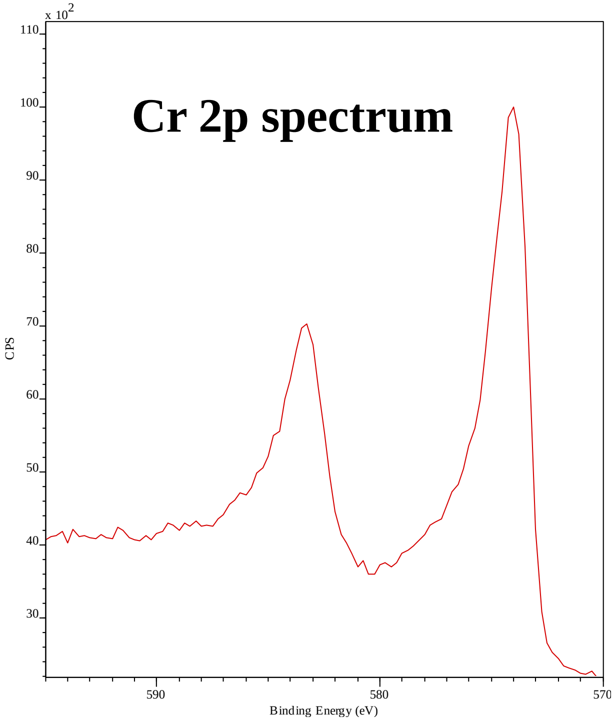
***Splitting:*** Final states are given by: $\mathbf{j_+ = l + s}$ and $\mathbf{j_- = l - s}$

*Examples*: For p orbitals the doublet will be $\boldsymbol{p_{1/2}}$ and $\boldsymbol{p_{3/2}}$ because $l = 1$ and $s = \pm 1/2$ therefore $j_- = 1/2$ and $j_+ = 3/2$.

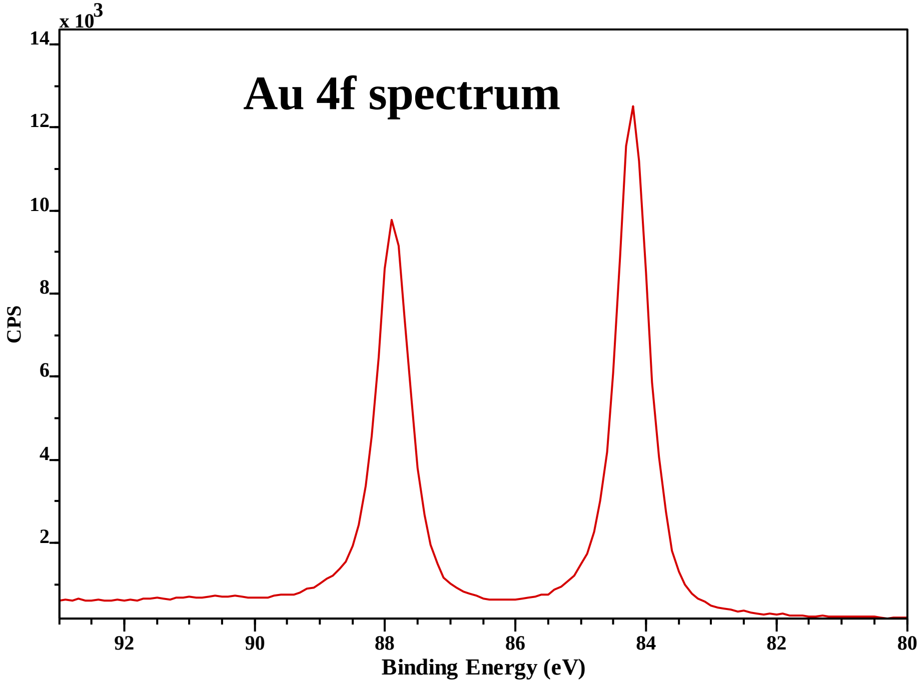
For d orbitals, the doublet will be $d_{x1}$ and $d_{x2}$ because l = and $s = \pm 1/2$ therefore $j_- =$ x1 and $j_+ =$ x2 .

***Intensity ratio*** is given by **$(2j_{-} +1) / (2j_{+} +1)$**

For p orbitals the ratio is given by $2 \times 1/2 + 1 = 2$ ($p_{1/2}$) and $2 \times 3/2 + 1 = 4$ ($p_{3/2}$). Therefore the ratios for *p* orbitals doublet is *1/2*, for *d* orbitals doublet is *4/6 = 2/3*



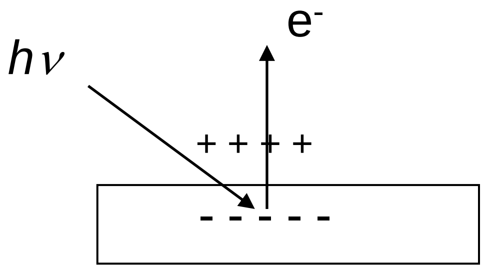
**Ratio = 1/2**



**Ratio = ??**

# *Static Charging*

***XPS:*** It arises as a consequence of the build-up of a positive charge at the surface of non-conducting specimens. The rate of photo-electron loss is greater than that of their replacement from within the specimen.
It produces a retarding field at the surface that will shift the peaks (reduce the KE of the ejected electrons).



Suggestions:

1) Use of the adventitious Carbon line to correct any shift (most materials exhibit a C 1s line).

2) Deposition of a very thin layer of gold (as use in SEM).

3) Use of a “flood gun” low energy electrons (0-5 eV).

# Linewidths (*Γ*)

**The irreducible width Γ in XPS is due to the *lifetime* of the core hole state**

$$\boxed{\Gamma = \frac{2\hbar}{\tau}}$$

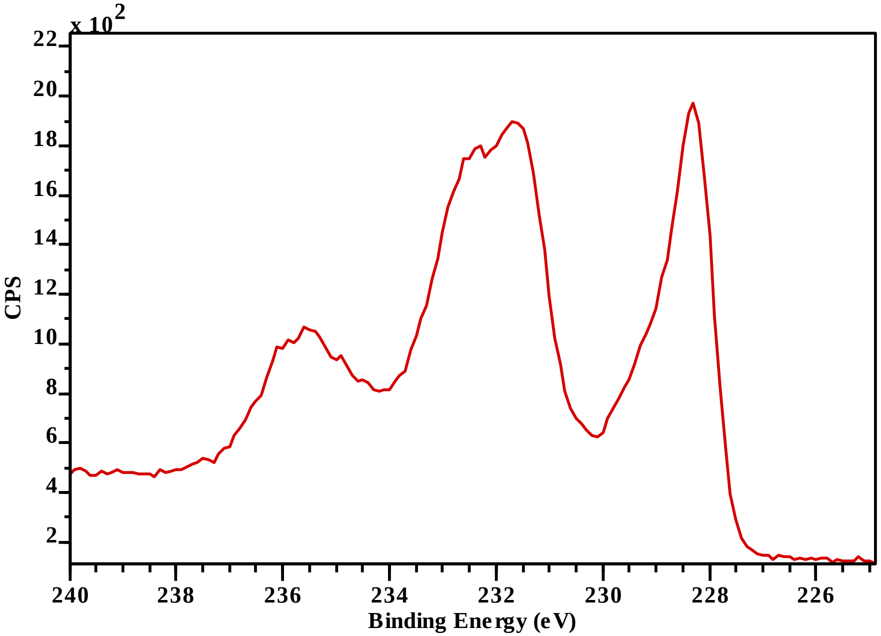
*(Ag 3d core level $\tau = 10^{-14}$ -$10^{-15}$ s)*

The resulting line shape is Lorenzian. *A core level has a number of decay channels that contribute to the width of the line.*

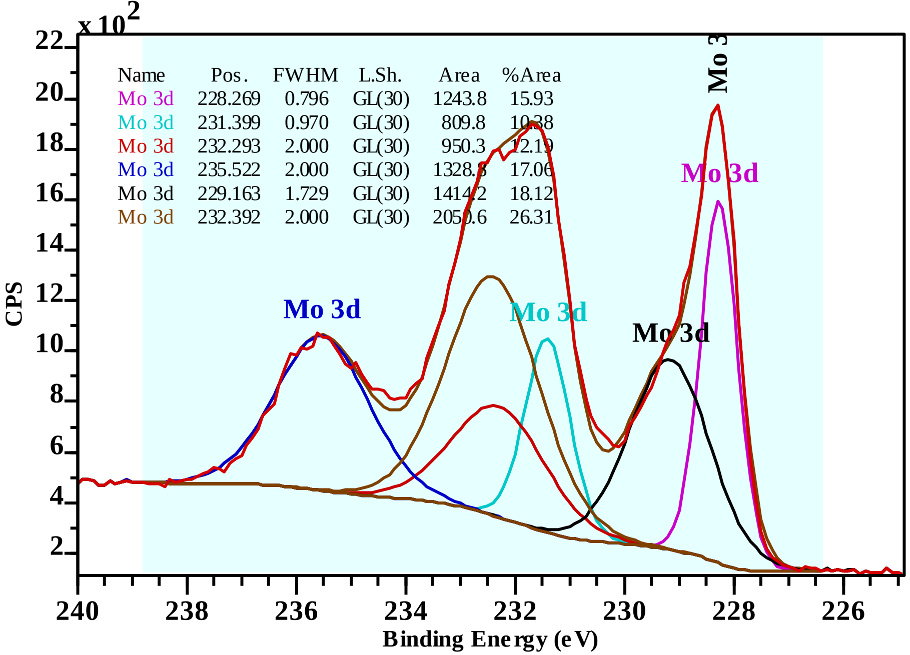
*Measurement of the lifetime width of a core hole state is complicated by the existence of:*

1. *Resolution of the instrument: dual anode long tail due to the lifetime width of the K-shell hole.*
2. *Phonon broadening (excitation of the lattice vibrations)*
3. *Inhomogeneous broadening (superposition of lines with different chemical shifts).*

# Peak Deconvolution (curve fitting)



CasaXPS (Washington State University, Pullman, Wa)



| Name | Pos. | FWHM | L.Sh. | Area | %Area |
|---|---|---|---|---|---|
| Mo 3d | 228.269 | 0.796 | GL(30) | 1243.8 | 15.93 |
| Mo 3d | 231.399 | 0.970 | GL(30) | 809.8 | 10.38 |
| Mo 3d | 232.293 | 2.000 | GL(30) | 950.3 | 12.19 |
| Mo 3d | 235.522 | 2.000 | GL(30) | 1328.8 | 17.06 |
| Mo 3d | 229.163 | 1.729 | GL(30) | 1414.2 | 18.12 |
| Mo 3d | 232.392 | 2.000 | GL(30) | 2050.6 | 26.31 |

CasaXPS (Washington State University, Pullman, Wa)

Photoelectron lines have a **Lorenzian shape** corresponding to the lifetime of the core hole that is created. Gaussian or Gaussian Lorentzian shape GL(30) curves are often used for curve fitting purposes.

Deconvolution of the XPS Mo samples reveals the existence of several Mo species ($Mo^0$, Mo4+, Mo6+ but others could also be detected: Mo3+ and Mo5+).

# *Peak Widths and Intensities*

***Peak widths***: it is a convolution of the natural width of the core level, the width of the x-ray line and the analyzer resolution:

$$\Delta E = (\Delta E_n^2 + \Delta E_p^2 + \Delta E_a^2)^{1/2}$$

***Intensities:*** Only the ratio of area of lines has some meaning (relative concentration).

$$\frac{[A]}{[B]} = \frac{\sigma_b \zeta_b \lambda_b \eta_b I_a}{\sigma_a \zeta_a \lambda_a \eta_a I_b}$$

$\sigma$: *cross-section;* $\zeta$: *fraction of PE events (w/o intrinsic plasmon excitation);* $\lambda$: *mean free path;* $\eta$: *KE dependent spectrometer transmission and I : area of the line*

# *Quantitative Analysis*

1. Use of standards:

$I_x$ is the amplitude of the element X in your sample,
$I_{x,std}$ is the amplitude of the element X in pure material

The concentration of X in your sample is THEN given by $C_x = I_x / I_{x,std}$
PROBLEM with this approach is that you need a large No of Standards.

2. Modify Method:

It introduces the relative sensitivity factor, $S_x$ based upon one pure element standard (usually Ag, silver standard). So, if we want to calculate $S_x$ : sensitivity for element X from a compound $X_aY_b$ we could do it by using:

$$S_x = \frac{(A+B)}{A}\frac{I_x}{I_{Ag(pure)}}$$

# Quantitative Analysis (cont.)

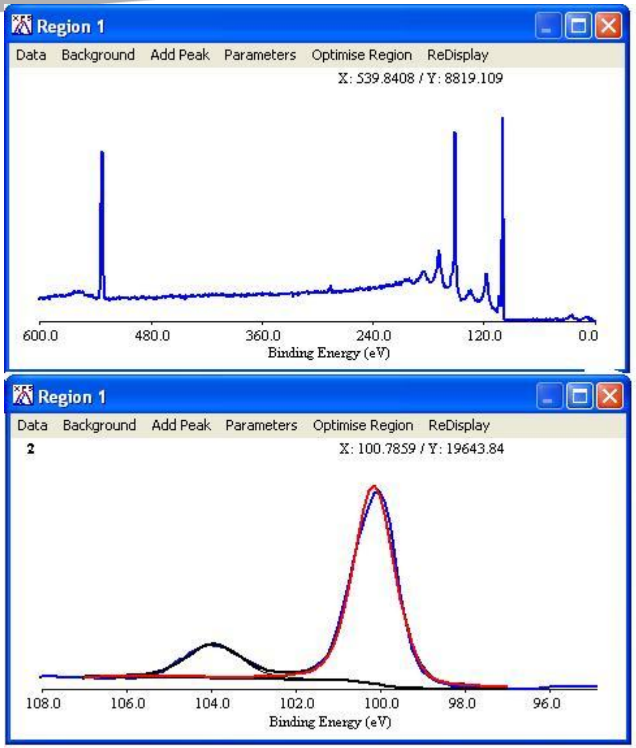
$$S_x = \frac{(A+B)}{A} \frac{I_x}{I_{Ag(pure)}}$$

Where $I_x$ is the amplitude of the known compound, (A+B)/A is the 1 / fraction of X atoms and $I_x / I_{Ag}$ the ratio of peak to peak amplitudes. THEN from an unknown sample: $C_x = I_x / I_{Ag} \,.\, S_x$ = concentration

OR to make it self consistent $\boxed{C_x = (I_x / S_x) / \sum_a (I_a / S_a)}$

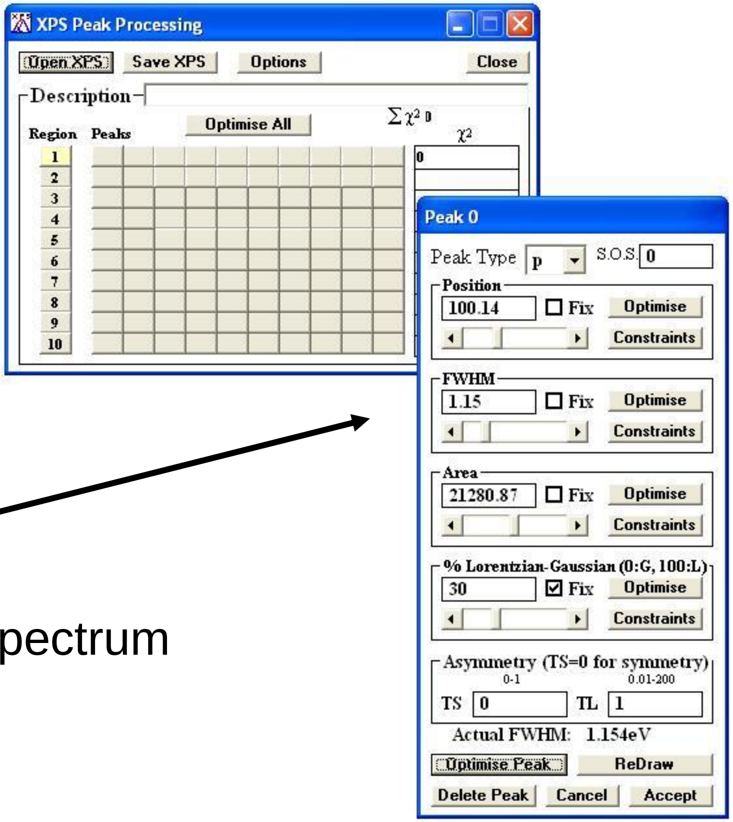
where $I_x$ and $I_a$ are measured and $S_x$ and $S_a$ are obtained from standards as mentioned above

# XPSPeak41 (free software)



X: 539.8408 / Y: 8819.109

X: 100.7859 / Y: 19643.84



Peak Type: p
S.O.S: 0

Position: 100.14 ☐ Fix

FWHM: 1.15 ☐ Fix

Area: 21280.87 ☐ Fix

% Lorentzian-Gaussian (0:G, 100:L): 30 ☑ Fix

Asymmetry (TS=0 for symmetry)
TS (0-1): 0
TL (0.01-200): 1

Actual FWHM: 1.154eV

Deconvolution of Si 2p spectrum

# Auger parameter

Difference in BE between 2 chemical states.
Depends on the change in core electron level energy and the change in intra and extra-atomic relaxation energies.

For a 1s (K) electron:

$\Delta BE(K) = \Delta\varepsilon(K) - \Delta R(K^+)$ {Δ *in relaxation E for singly ionized state*}

For KLL Auger process, the Δ KE between chemical states is given by:

$\Delta E(KLL) = \Delta\varepsilon(K) - \Delta R(K^+) - 2\Delta\varepsilon(LL) - \Delta R(L^+L^+)$ *{Doubly ionized state}*

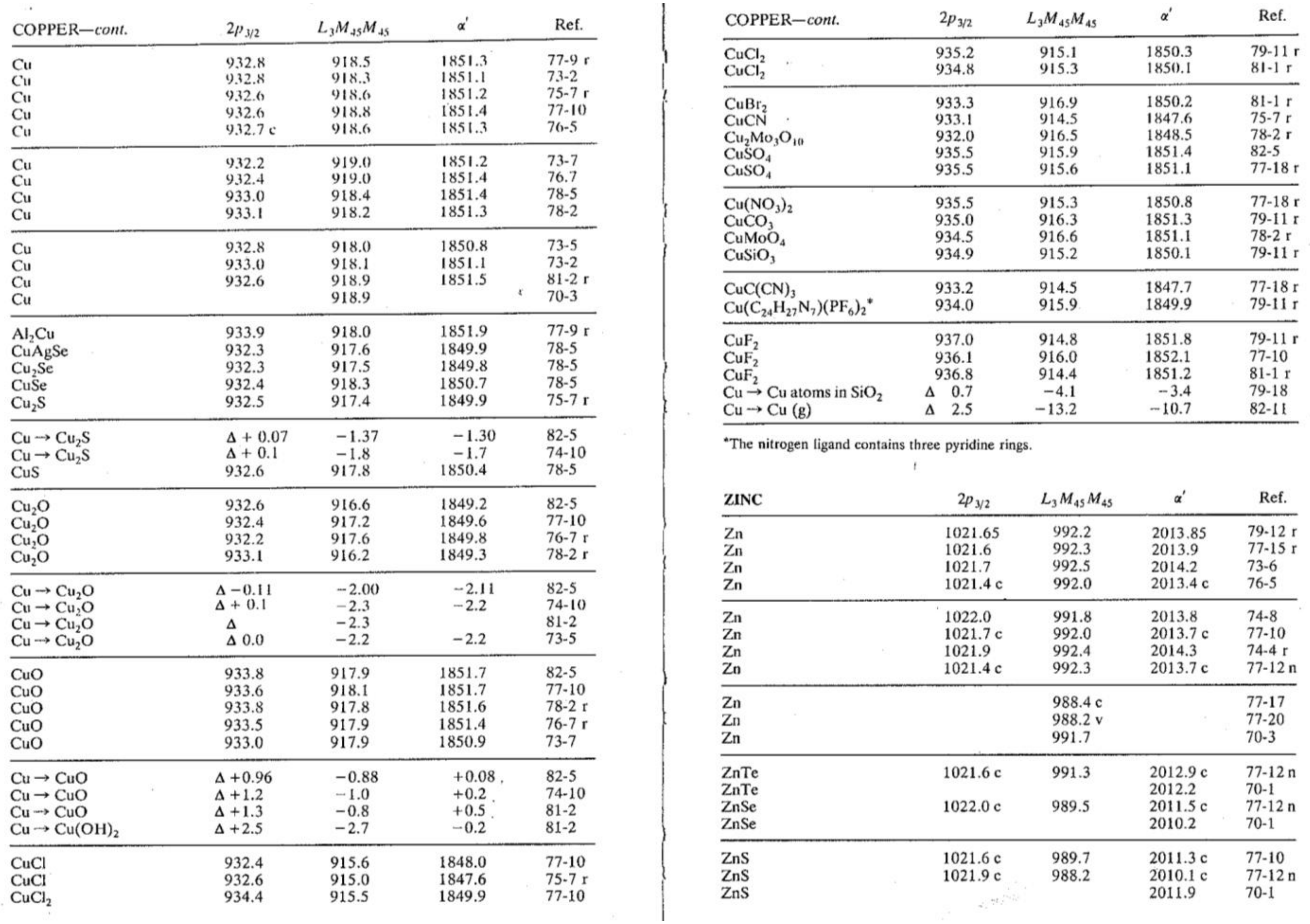
The Auger parameter (α) is defined as follows:

$\alpha = E(KLL) - E(K)$ {difficult to use-not practical} $E(K) = h\nu - BE(K)$

“Modified” $\alpha' = \alpha + h\nu = E(KLL) + BE(K)$

E(KLL) is {Auger peak in KE} and BE(K) is {core level peak in BE)

***For insulator α is independent of any static charging and is a parameter characteristic of a particular chemical state measured with greater accuracy than core-level BE or Auger peak KE.***



| COPPER—*cont.* | $2p_{3/2}$ | $L_3M_{45}M_{45}$ | $\alpha'$ | Ref. |
|---|---|---|---|---|
| Cu | 932.8 | 918.5 | 1851.3 | 77-9 r |
| Cu | 932.8 | 918.3 | 1851.1 | 73-2 |
| Cu | 932.6 | 918.6 | 1851.2 | 75-7 r |
| Cu | 932.6 | 918.8 | 1851.4 | 77-10 |
| Cu | 932.7 c | 918.6 | 1851.3 | 76-5 |
| Cu | 932.2 | 919.0 | 1851.2 | 73-7 |
| Cu | 932.4 | 919.0 | 1851.4 | 76.7 |
| Cu | 933.0 | 918.4 | 1851.4 | 78-5 |
| Cu | 933.1 | 918.2 | 1851.3 | 78-2 |
| Cu | 932.8 | 918.0 | 1850.8 | 73-5 |
| Cu | 933.0 | 918.1 | 1851.1 | 73-2 |
| Cu | 932.6 | 918.9 | 1851.5 | 81-2 r |
| Cu |  | 918.9 |  | 70-3 |
| $Al_2Cu$ | 933.9 | 918.0 | 1851.9 | 77-9 r |
| CuAgSe | 932.3 | 917.6 | 1849.9 | 78-5 |
| $Cu_2Se$ | 932.3 | 917.5 | 1849.8 | 78-5 |
| CuSe | 932.4 | 918.3 | 1850.7 | 78-5 |
| $Cu_2S$ | 932.5 | 917.4 | 1849.9 | 75-7 r |
| $Cu \rightarrow Cu_2S$ | Δ + 0.07 | −1.37 | −1.30 | 82-5 |
| $Cu \rightarrow Cu_2S$ | Δ + 0.1 | −1.8 | −1.7 | 74-10 |
| CuS | 932.6 | 917.8 | 1850.4 | 78-5 |
| $Cu_2O$ | 932.6 | 916.6 | 1849.2 | 82-5 |
| $Cu_2O$ | 932.4 | 917.2 | 1849.6 | 77-10 |
| $Cu_2O$ | 932.2 | 917.6 | 1849.8 | 76-7 r |
| $Cu_2O$ | 933.1 | 916.2 | 1849.3 | 78-2 r |
| $Cu \rightarrow Cu_2O$ | Δ −0.11 | −2.00 | −2.11 | 82-5 |
| $Cu \rightarrow Cu_2O$ | Δ + 0.1 | −2.3 | −2.2 | 74-10 |
| $Cu \rightarrow Cu_2O$ | Δ | −2.3 |  | 81-2 |
| $Cu \rightarrow Cu_2O$ | Δ 0.0 | −2.2 | −2.2 | 73-5 |
| CuO | 933.8 | 917.9 | 1851.7 | 82-5 |
| CuO | 933.6 | 918.1 | 1851.7 | 77-10 |
| CuO | 933.8 | 917.8 | 1851.6 | 78-2 r |
| CuO | 933.5 | 917.9 | 1851.4 | 76-7 r |
| CuO | 933.0 | 917.9 | 1850.9 | 73-7 |
| $Cu \rightarrow CuO$ | Δ +0.96 | −0.88 | +0.08 | 82-5 |
| $Cu \rightarrow CuO$ | Δ +1.2 | −1.0 | +0.2 | 74-10 |
| $Cu \rightarrow CuO$ | Δ +1.3 | −0.8 | +0.5 | 81-2 |
| $Cu \rightarrow Cu(OH)_2$ | Δ +2.5 | −2.7 | −0.2 | 81-2 |
| CuCl | 932.4 | 915.6 | 1848.0 | 77-10 |
| CuCl | 932.6 | 915.0 | 1847.6 | 75-7 r |
| $CuCl_2$ | 934.4 | 915.5 | 1849.9 | 77-10 |
| $CuCl_2$ | 935.2 | 915.1 | 1850.3 | 79-11 r |
| $CuCl_2$ | 934.8 | 915.3 | 1850.1 | 81-1 r |
| $CuBr_2$ | 933.3 | 916.9 | 1850.2 | 81-1 r |
| CuCN | 933.1 | 914.5 | 1847.6 | 75-7 r |
| $Cu_2Mo_3O_{10}$ | 932.0 | 916.5 | 1848.5 | 78-2 r |
| $CuSO_4$ | 935.5 | 915.9 | 1851.4 | 82-5 |
| $CuSO_4$ | 935.5 | 915.6 | 1851.1 | 77-18 r |
| $Cu(NO_3)_2$ | 935.5 | 915.3 | 1850.8 | 77-18 r |
| $CuCO_3$ | 935.0 | 916.3 | 1851.3 | 79-11 r |
| $CuMoO_4$ | 934.5 | 916.6 | 1851.1 | 78-2 r |
| $CuSiO_3$ | 934.9 | 915.2 | 1850.1 | 79-11 r |
| $CuC(CN)_3$ | 933.2 | 914.5 | 1847.7 | 77-18 r |
| $Cu(C_{24}H_{27}N_7)(PF_6)_2$* | 934.0 | 915.9 | 1849.9 | 79-11 r |
| $CuF_2$ | 937.0 | 914.8 | 1851.8 | 79-11 r |
| $CuF_2$ | 936.1 | 916.0 | 1852.1 | 77-10 |
| $CuF_2$ | 936.8 | 914.4 | 1851.2 | 81-1 r |
| $Cu \rightarrow$ Cu atoms in $SiO_2$ | Δ 0.7 | −4.1 | −3.4 | 79-18 |
| $Cu \rightarrow$ Cu (g) | Δ 2.5 | −13.2 | −10.7 | 82-11 |

*The nitrogen ligand contains three pyridine rings.

| **ZINC** | $2p_{3/2}$ | $L_3M_{45}M_{45}$ | $\alpha'$ | Ref. |
|---|---|---|---|---|
| Zn | 1021.65 | 992.2 | 2013.85 | 79-12 r |
| Zn | 1021.6 | 992.3 | 2013.9 | 77-15 r |
| Zn | 1021.7 | 992.5 | 2014.2 | 73-6 |
| Zn | 1021.4 c | 992.0 | 2013.4 c | 76-5 |
| Zn | 1022.0 | 991.8 | 2013.8 | 74-8 |
| Zn | 1021.7 c | 992.0 | 2013.7 c | 77-10 |
| Zn | 1021.9 | 992.4 | 2014.3 | 74-4 r |
| Zn | 1021.4 c | 992.3 | 2013.7 c | 77-12 n |
| Zn |  | 988.4 c |  | 77-17 |
| Zn |  | 988.2 v |  | 77-20 |
| Zn |  | 991.7 |  | 70-3 |
| ZnTe | 1021.6 c | 991.3 | 2012.9 c | 77-12 n |
| ZnTe |  |  | 2012.2 | 70-1 |
| ZnSe | 1022.0 c | 989.5 | 2011.5 c | 77-12 n |
| ZnSe |  |  | 2010.2 | 70-1 |
| ZnS | 1021.6 c | 989.7 | 2011.3 c | 77-10 |
| ZnS | 1021.9 c | 988.2 | 2010.1 c | 77-12 n |
| ZnS |  |  | 2011.9 | 70-1 |
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