

Chapter - 4

Introduction to Electron Spectroscopy

Photoemission from solids is one of the versatile techniques that can be advantageously used for characterization of a number of properties of the solid substrate especially catalysts and their surfaces. The phenomenon of photoemission is one of the direct proofs of the Einstein's postulate. Three parallel endeavours led to the development of photoemission as a technique for solid state chemistry. They are:

- (i) Siegbahn and his group developed improved energy resolution of the electron spectrometers and combined it with X-rays.
- (ii) Turner and his co-workers applied photoelectric effect to gases and by using ultraviolet line from helium source they could resolve vibrational fine structure of the electronic levels.
- (iii) Spicer measured photoelectron spectra from solids in vacuum irradiated with UV light but the LiF window used cut off all the photons with energies greater than 11.6 eV and hence he could only get a small part of the valence band. Eastman and Cashion extended the energy range to about 40 eV by differential pumping and windowless UV sources.

The availability of synchrotron sources has extended the photon energy range further such that all energies between the UPS and XPS regime are available. The mean free path of the electrons decides the depth to which the material can be probed. **Fig. 4.1** shows the mean free path λ , of electrons in elemental solids and it is found to depend on the kinetic energy of the electrons and it is of the order of 1-2 nm for kinetic energies in the range 15-1000 eV and this is an ideal situation for surface sensitivity.

XPS and UPS are two techniques based on photoelectric effect. When an atom absorbs a photon of energy $h\nu$, then a core or valence electron with binding energy E_b is ejected with the Kinetic energy

$$E_k = h\nu - E_b - \phi$$

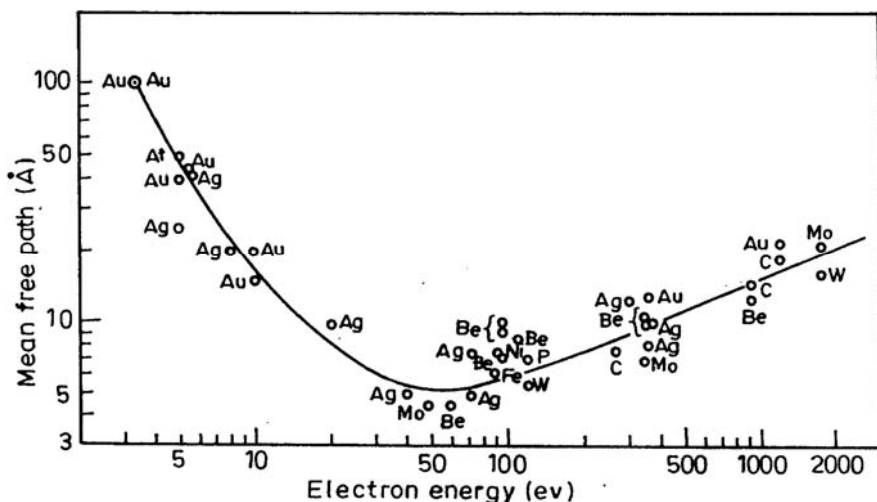


Fig. 4. 1. Universal curve for electron mean free path as a function of the electron energy. The ability of electrons to penetrate into and/or escape from materials is strongly energy dependent. At energies of ≈ 50 eV the mean free path reaches a minimum

Where E_k is the Kinetic energy of the ejected electron, h is the Planck's constant, ν is the frequency of the exciting radiation, E_b is the binding energy of the photoelectron with respect to the Fermi level of the sample and ϕ is the work function of the spectrometer. In XPS spectrum one measures the intensity of photoelectrons $N(E)$ as a function of their kinetic energy or more often in terms of binding energy. The photoelectron peak designations are based on the quantum numbers of the levels from which the photoelectron is originating. Spin orbit splitting as well as binding energies of a particular electron energy

level increase with increasing atomic number. The nomenclature used is shown in Table 4.1. The intensity ratio of the spin orbit split doublet peaks is determined by the multiplicity of the corresponding levels and is equal to $2j \pm 1$. For example the $3d_{5/2}$ and $3d_{3/2}$ peaks will have an intensity ratio of 6:4 where as the $4f_{7/2}$ and $4f_{5/2}$ peaks will have an intensity ratio of 8:6 and $2p_{3/4}$ and $2p_{1/2}$ will have intensity ratio 4:2.

Table 4.1. Spectroscopic Notations used in XPS and also in AES

n	L	j	X-ray level	Electron level
1	0	$\frac{1}{2}$	K	1s
2	0	$\frac{1}{2}$	L_1	2s
2	1	$\frac{1}{2}$	L_2	$2p_{1/2}$
2	1	$\frac{3}{2}$	L_3	$2p_{3/2}$
3	0	$\frac{1}{2}$	M_1	3s
3	1	$\frac{1}{2}$	M_2	$3p_{1/2}$
3	1	$\frac{3}{2}$	M_3	$3p_{3/2}$
3	2	$\frac{3}{2}$	M_4	$3d_{3/2}$
3	2	$\frac{5}{2}$	M_5	$3d_{5/2}$
4	3	$\frac{5}{2}$	N_6	$4f_{5/2}$
4	3	$\frac{7}{2}$	N_7	$4f_{7/2}$

Composition analysis:

The general expression for the intensity of an XPS peak is

$$I = F_x S(E_k) \sigma(E_k) \int n(z) \exp[-z/\lambda(E_k) \cos\theta] dz$$

Where $\sigma(E_k)$ is the cross-section for emission of a photoelectron in the direction of the analyzer from the relevant inner shell per atom of X by a photon of energy $h\nu$. F_x is the flux of the X-ray line per unit area at the sample and $S(E_k)$ is a spectrometer dependent function containing the detection efficiency, $n(z)$ denotes the atomic density as function of the depth in the sample, z and the depth distribution function (DDF) is characterized by the inelastic mean free path (IMFP) $\lambda(E_k)$ of the photoelectrons.

In the case of a homogeneous concentration through out the sample the following expression will hold for the intensity of emission for each element.

$$I = F_x S(E_k) \sigma(E_k) n \lambda(E_k) \cos\theta$$

Cross section values have been tabulated by Scofield. He has tabulated extensive list of X-ray cross sections for the sub shells of electrons in the elements of the periodic chart and has specifically utilized X-ray energies of 1254 and 1487 eV to produce absorption coefficients relevant to PES measurements. These data have been normalized to a relative atomic sensitivity of 1.00 for carbon. One such compilation is available in ref 1. Typical data can be . Mean free path is a function of the material. For example the Si 2p electrons have a mean free path 3.7 nm in SiO_2 and 3.2 nm in Si. Appropriate back ground corrections have to be carried out for determining the intensity of the photoemission peak.

Binding energies and oxidation states

Binding energies can be used not only to identify the chemical element but also the oxidation state of the element since the binding energy of core electron depends on the chemical state of the element as well. Chemical shifts are in the range of 0-3 eV. In general the binding energy increases with increase in

oxidation state and for a fixed oxidation state with the electronegativity of the ligands like FeF_3 , FeCl_3 , FeBr_3 and so on. Typical data collected from literature are given in Table 5.2 and 3.

Table 4.2. Typical observed binding energy for C 1s and oxygen 1s in various organic compounds showing the chemical shifts

Functional group	Structural fragment	Binding energy, eV
Hydrocarbon	$\underline{\text{C}}\text{-H, } \underline{\text{C}}\text{-C}$	285.0
Amine	$\underline{\text{C}}\text{-N}$	286.0
Alcohol, ether	$\underline{\text{C}}\text{-O-H, } \underline{\text{C}}\text{-O-C}$	286.5
Cl bound to carbon	$\underline{\text{C}}\text{-Cl}$	286.5
F bound to carbon	$\underline{\text{C}}\text{-F}$	287.8
Carbonyl	$\underline{\text{C}}\text{=O}$	288.0
Amide	$\text{N-}\underline{\text{C}}\text{=O}$	288.2
Acid, ester	$\text{O-}\underline{\text{C}}\text{=O}$	289.0
Carbamate	$\text{N-}\underline{\text{C}}\text{=O}$	289.6
Carbonate	$\underline{\text{C}}\text{O}_3^{2-}$	290.3
2F bound to Carbon	$\text{-(CH}_2\text{-}\underline{\text{C}}\text{F}_2\text{-)}$	290.6
3F bound to carbon	$\text{-}\underline{\text{C}}\text{F}_3$	293.2
Carbonyl oxygen	$\text{C=}\underline{\text{O}}$	532.2
Alcohol, ether oxygen	$\text{C-}\underline{\text{O}}\text{-H, C-}\underline{\text{O}}\text{-C}$	532.2
Ester	$\text{C-}\underline{\text{O}}$	533.2

Table 4.3. Typical Binding energy (chemical shift) data for a set of inorganic compounds.

Species	Level probed	Binding Energy, eV
Li	1s	55.1
Li_2O	1s	55.6
LiF	1s	55.7
Be	1s	111.6
BeF_2	1s	115.3
BeO	1s	113.7
B	1s	186.5
B_2O_3	1s	193.3
C	1s	284.5
CO_2	1s	291.9
CF_4	1s	296.7
N	1s	
NH_3	1s	398.8
O_2/Mo	1s	530.2
Al_2O_3	1s	531.6
F	1s	
LiF	1s	685
Na	1s	1070.8
NaF	1s	1071.3
Mg	1s	1303.2
MgO	1s	1303.9
Mg	2p	49.6
MgO	2p	50.3
Al	2p	72.8
Al_2O_3	2p	74.6
Si	$2p_{3/2}$	99.5
SiO_2	$2p_{3/2}$	103.3

K	2p _{3/2}	294.7
KF	2p _{3/2}	293.1
Ca	2p _{3/2}	345.9
CaF ₂	2p _{3/2}	347.9
Ti	2p _{3/2}	454.0
TiO ₂	2p _{3/2}	459.0
V	2p _{3/2}	512.4
V ₂ O ₅	2p _{3/2}	517.4
Cr	2p _{3/2}	574.6
Cr ₂ O ₃	2p _{3/2}	576.6
Mn	2p _{3/2}	638.8
MnF ₃	2p _{3/2}	6426
Mn ₂ O ₃	2p _{3/2}	641.5
Fe	2p _{3/2}	706.8
Fe ₂ O ₃	2p _{3/2}	711.0
FeO	2p _{3/2}	709.6
Co	2p _{3/2}	778.1
CoF ₂	2p _{3/2}	783
Co ₃ O ₄	2p _{3/2}	780.2
Ni	2p _{3/2}	852.5
NiO	2p _{3/2}	854.4
Cu	2p _{3/2}	933.1
CuO	2p _{3/2}	934.1
Zn	2p _{3/2}	1021.6
ZnO	2p _{3/2}	1021.8
Ga	3d	18.5
Ga ₂ O ₃	3d	19.7
Ge	3d	29.4
GeO ₂	3d	33.2
As	3d	42.05
As ₂ O ₃	3d	45.8
Ag	3d	374
Ag ₂ So ₄	3d	374.2
Cd	3d	411.5
CdO	3d	411.7
In	3d	451.8
In ₂ O ₃	3d	452.3
Sn	3d	492.9
SnO ₂	3d	494.6
Sb	3d	537.3
Sb ₂ O ₃	3d	539.2
Te	3d	583.7
TeO ₂	3d	587.2
Mo	3d _{5/2}	227.8
MoO ₃	3d _{5/2}	232.4
Pd	3d _{5/2}	335
PdO	3d _{5/2}	337
Ta	4f _{7/2}	21.7
Ta ₂ O ₅	4f _{7/2}	26.0
Pt	4f _{7/2}	71.2
PtO	4f _{7/2}	74.6

Data compiled from http://srdata.nist.gov/xps/Bind_E.asp

Final state effects

Consider an element with N electrons, with a total energy E_N^i in the initial state. The atom absorbs a photon of energy $h\nu$; the absorption event takes less than 10^{-17} s. Some 10^{-14} s later, the atom has emitted the photoelectron with kinetic energy E_k and is itself in the final state with one electron less and a hole in one of the core levels.

$$E_N^i + h\nu = E_{n-1,1}^f + E_k$$

E_N^i is the initial total energy of the atom with N electrons in the initial state i.e., before the photoemission, $h\nu$ is the energy of the photon,

$E_{n-1,1}^f$ is the total energy of the atom with N-1 electrons and a hole in the core level 1 in the final state, E_k is the Kinetic energy of the photo ejected electron.

Rearranging one gets

$$E_b = h\nu - E_k - \phi = E_{n-1,k}^f - E_N^i - \phi$$

The remaining N-1 electrons in the final state as well as the electrons in the neighbouring atoms feel the existence of a core hole. This results in lowering the total energy of the atom by an amount ΔE_{relax} . This relaxation energy has intra and extra atomic contributions and is included in the kinetic energy of the photoelectron. Thus the binding energy is not equal to the orbital from which the photoelectron is emitted; the difference is caused by the reorganization of the remaining electrons when an electron is removed from an inner shell.

Therefore the binding energy has both the information, that is the state of the atom before the photo ionization (**initial state**) and on the core ionized atom left behind, after the emission of an electron (**final state**).

In most cases it is possible to consider the initial state effects alone. The charge potential model explains the physics behind such binding energy shifts by means of the formula

$$E_b^i = kq_i + \sum q_j / r_{ij} + E_b^{\text{ref}}$$

E_b^i is the binding energy of an electron from an atom I, q_i is the charge on the atom, K is a constant, q_j is the charge on a neighbouring atom j,

r_{ij} is the distance between atom i and atom j, E_b^{ref} is the suitable energy reference.

The first term indicates that the binding energy increases with increase of positive charge on the atom from which the photoelectron originates. In ionic solids, the second term counteracts the first term because the charge on a neighbouring atom will have the opposite sign. Because of its similarity to the lattice potential in ionic solids, the second term is referred as the Madelung sum.

Reference:

Normally the sample and the spectrometer are in electrical contact if the sample is conducting. The Fermi levels of these two systems will be the same. If an electron were to be ejected from the substance say a metal from its Fermi level, it is still bound to the metal and these electrons have an ionization potential equal to the work function of the metal. However the electrons coming from the Fermi level of the sample are detected with a Kinetic energy equal to $h\nu - \phi_{\text{sp}}$ where ϕ_{sp} is the work function of spectrometer and not that of the sample. The removal of an electron from the Fermi level of the sample will require ϕ the work function of the sample. The liberated electron is now at the potential outside the sample but not yet at the absolute vacuum level. Thus on its way to the analyzer the electron is accelerated or decelerated by the work function difference which is the contact potential between the sample and the spectrometer.

The description given has assumed that the photoemission event occurs sufficiently slowly to ensure that the escaping electron feels the relaxation of the core-ionized atom. This is what is called the adiabatic limit. All the relaxation effects of the energetic ground state of the core-ionized atom are accounted for in the kinetic energy of the photoelectron. In other extreme, the 'sudden limit', the photoelectron is emitted immediately after the absorption of the photon before the core ionized atom relaxes. This often is

accompanied by shake-up, shake-off and plasmon loss processes, which give additional peaks in the spectrum.

Shake-up, shake-off losses are final state effects which arise when the photoelectron imparts energy to another electron of the atom. This electron ends up in a higher unoccupied state (shake-up) or in an unbound state (shake-off). As a consequence, the photoelectron loses kinetic energy and appears at a higher binding energy in the spectrum. Discrete shake-up losses are prominently present in the spectra of oxides and many other compounds. They have diagnostic value as the precise loss structure depends on the environment of the atom. In metals shake-up of electrons in the valence band to empty states at the Fermi level gives a continuous range of energy losses from zero to the energy of the bottom of the band. The result is that the XPS peaks of the metals such as Rh and Pt are asymmetrically broadened towards higher binding energies. As the probability of valence band shake-up depends on the density of states at or just above the Fermi level the effect is most pronounced in d-metals, but hardly of significance for s-metals such as Cu, Ag and Au which all give sharp symmetric peaks. In fact the narrow Ag 3d lines are often used to demonstrate the energy resolution of the spectrometer.

Multiplet splitting occurs if the initial state atom contains unpaired electrons. Upon photoemission this electron may interact through its spin moment with the spin of the additional unpaired electron in the core level from which the photoelectron left. Parallel and anti-parallel spins give final states, which differs 1-2 eV in energy. A well known example is the splitting of the N 1s and oxygen 1s peaks normally single lines – in the spectrum of gas phase NO due to an unpaired spin in the 2π level in the NO molecule.

Note that multiple splitting is a final state effect, whereas the spin-orbit splitting of p, d and f levels is an initial state effect.

The line width is determined by the line width of the X-ray source, the broadening due to the analyzer and the natural line width of the level under study. These three factors

$$(\Delta E)^2 = (\Delta E_x)^2 + (\Delta E_{an})^2 + (\Delta E_{nat})^2$$

(ΔE) is the width of a photoemission peak at half maximum, (ΔE_x) is the line width of the X-ray source, (ΔE_{an}) is the broadening due to the analyzer, and (ΔE_{nat}) is the natural line width.

ΔE_x , the line width of the X-ray source is of the order of 1 eV for Al or MgK $_{\alpha}$ sources, but can be better than about 0.3 eV with the use of monochromator.

The monochromator narrows the line significantly and focuses it onto the sample. It also cuts out all unwanted X-ray satellites and background radiation. Important advantage of using a monochromator is that heat and secondary electrons generated by the X-ray source cannot reach the sample.

The broadening due to the analyzer depends on the energy at which the electrons travel through the analyzer and the width of the slits between the energy filter and the actual detector. The analyzer contribution to the line width becomes irrelevant at low pass energies however at the cost of intensity.

Heisenberg's uncertainty relation determines the natural line width

$$\Delta E_{nat} \cdot \Delta t = h/2\pi$$

The lifetime of the core-ionized atom is measured from the moment it emits a photoelectron until it decays by Auger processes or X-ray fluorescence. As the number of decay possibilities for an ion with a core hole in a deep level (e.g. 3s level) is greater than that for an ion with core hole in a shallow level (e.g. 3d level) a 3s peak is broader than a 3d peak.

Charging and sample damage:

Samples that eject photoelectrons give rise to accumulation of charge. The potential the sample acquires is determined by the photoelectric current of electrons leaving the sample, the current through the sample holder towards the sample and the flow of Auger and secondary electrons from the source window onto the sample. Due to the accumulation of the positive charge on the sample, all XPS peaks in the spectrum shifts by the same amount to higher binding energies. Normally calibration is done using the binding energy of a known compound for example Si 2p in SiO $_2$ is taken as 103.4 eV or Carbon 1s binding energy is considered as 284.4 eV. There are other substances which can be added and also used for calibration.

In addition to the shifting of the peaks the peaks can also broaden and thus decreasing the resolution with a low signal to noise ratio. Charging in supported catalysts is usually limited to a few eV in normal mode of operation but when monochromatic XPS is used it can be considerably more. These effects can be minimized by using a flood gun which showers low energy electrons on the sample or mounting the sample like powders in indium foils. It is also possible that the electrons generated by the source and heat produced can sometimes decompose the complex i.e., the organometallic complexes used as precursors for catalysts. In such cases one has to interpret the spectra obtained taking all these secondary effects that can occur inside the spectrometer like reduction of the sample in the vacuum, the charging, the decomposition of the species due to heat and electrons and all other side effects due to operating conditions.

In supported catalysts, depending on the dispersion and the particle size of the supported phase, the intensity ratio of I_p/I_s due to the emission from the supported phase and the support, can be small when the support is exposed and the dispersion is small or can be large if the dispersion is good and the support phase is not exposed and covered by the supported phase.

This simple explanation will not hold well if the supported phase were to occupy and spread inside the pores of the support or the particles were to take different geometries, or if the support were to function as a stratified layer.

Angle dependent XPS:

The intensity ratio of an over layer to the substrate is given by

$$I_0/I_s = \{(\sigma_0 n_0 \lambda_0(E_0)) / (\sigma_s n_s \lambda_s(E_s))\} [1 / \exp(-d / [\lambda_0(E_0) \cos \theta]) / \exp(-d / [\lambda_0(E_s) \cos \theta])]$$

Where I_0 and I_s are the XPS intensities of over layer and substrate, n is the atomic densities in mol/cm^3 , σ is the XPS cross section, usually taken from the tables of Scofield $\lambda(E)$ is the inelastic mean free path at the prevalent kinetic energy E through the over layer (λ_0) or the substrate (λ_s), θ is the take off angle with respect to the surface normal and d is the thickness of the over layers. Note that $\lambda_0(E_s)$ is the mean free path of electrons formed in the substrate traveling through the over layer. In the case that the over layers formed is a film of SiO_2 on a silicon single crystal the expression reduces to

$$I_{\text{SiO}_2}/I_{\text{Si}} = [n_{\text{SiO}_2} \lambda_{\text{SiO}_2} - 1 - \exp(-d / \lambda_{\text{SiO}_2} \cos \theta)] / [n_{\text{Si}} \lambda_{\text{Si}} \exp(-d / \lambda_{\text{SiO}_2} \cos \theta)]$$

The intensity ratio of Si^{4+}/Si is a function of take-off angle. The agreement up to take-off angles of about 60° is good. At higher angles elastic scattering phenomenon reduces the intensity of the substrate electrons traveling at shallow angles from deeper regions.

Ultraviolet photoelectron spectroscopy:

The commonly used sources are He I at 21.2 eV and He II light at 40.8 eV. Since at these low energies only valence electrons can be ejected this spectroscopy is restricted to probing bonding in metals and molecules and in adsorbed states.

In **Fig.4.2** a schematic representation of a UP spectrum of a d-metal along with the density of states of its electrons is given. The onset of the UP spectrum is clearly seen at the Fermi level where the density of states is high and this provides a convenient zero for the binding energy. Most of the intensity at higher binding energies is due to secondary electrons. These are inelastically scattered photoelectrons from the valence band which have suffered energy loss while traveling through the solid. The shape of this secondary electron emission depends on the structure and composition of the material, the orientation of the sample with respect to the analyzer and the presence of other fields in the spectrometer.

It is clear that the electron coming from the Fermi level has a kinetic energy $E_k = h\nu - \phi$ and the slowest electrons with $E_k = 0$ with the highest binding energy since the kinetic energy of the electrons in UPS is low between 5 to 15 eV and since the final state of the photoelectron is still in the region of the unoccupied part of the density of states of the metal this spectrum can be considered at Joint Density of states of both occupied and unoccupied states. If the photon energy were to increase then the final states will be in the range corresponding to entirely free electrons in vacuum. If the photon energy increases then one can probe the true density of states of metals and in XPS also one probes the true density of states of metals but it is at a lower resolution due to broader line width of the X-ray source.

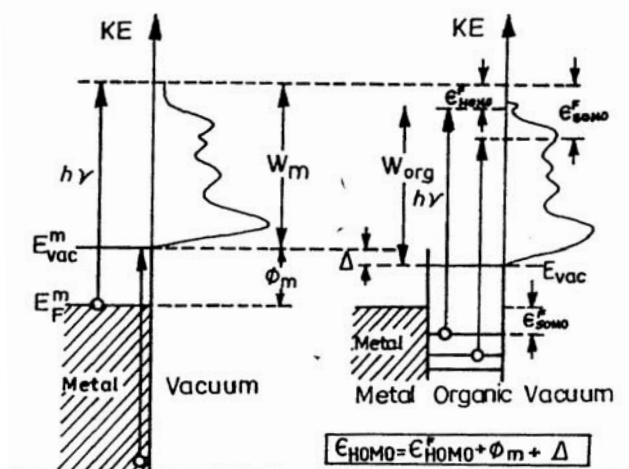


Fig. 4.2 . Schematic representation of the photoelectron spectrum of Au (on the left) and with organic layer deposited on the metal substrate (in the right). It is seen that the density of state (DOS) of metal is probed by the photoelectron spectroscopy. (reproduced from Seki, Trans on Electron devices, 44 (1997) 1295)

UPS is most often used to study single crystals and to probe the molecular orbitals of chemisorbed molecules.

The UP spectrum of silver layers deposited on ruthenium shows that the high density of d-state of Ru is seen till 5 eV below the Fermi level. However on deposition of silver these bands are attenuated while the d band of silver develops progressively between 1-4 monolayers until the energy distribution characteristic of silver is obtained for film thickness of about 10 monolayers. The effect of work function on the width of the spectra is also seen. Silver has a lower work function (4.72 eV) than ruthenium (5.52 eV) and the width of the spectra increases from 15.7 eV for Ru to 16.7 eV for a thick Ag film.

The adsorption of gases on single crystal metallic surfaces can be probed by UPS. One of the examples is the adsorption of CO on metallic surfaces. The MO level diagram and the corresponding UPS spectrum for gas phase CO is shown in the top of Fig. 4.3. On adsorption of CO on nickel surfaces, the molecular levels of are rearranged such that the 1π and 5σ levels overlap thus showing the orbitals involved in bonding with the metallic surfaces. Details of applications of Ultraviolet photoelectron spectroscopy will be dealt with in a separate chapter.

Xenon adsorption on Ru surface and Ag deposited ruthenium surface was studied. It was seen that the Xe 5p doublet at low coverages is at 6.7 eV for $5p_{1/2}$ which is characteristic of Xe on Ru (001). At higher coverages the Xe $5p_{1/2}$ peak occurs at 7.6 eV characteristic adsorption of Xe on Ag. The sequential adsorption on Ru and silver surfaces probably reflects that the adsorption energy of Xe on Ru is higher.

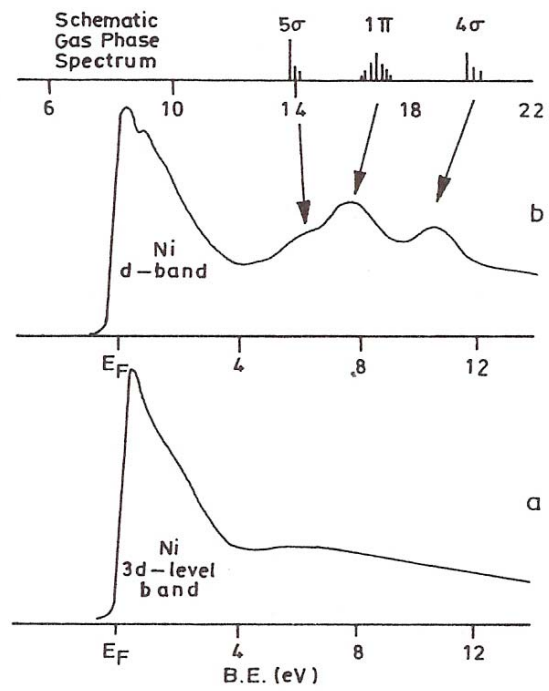
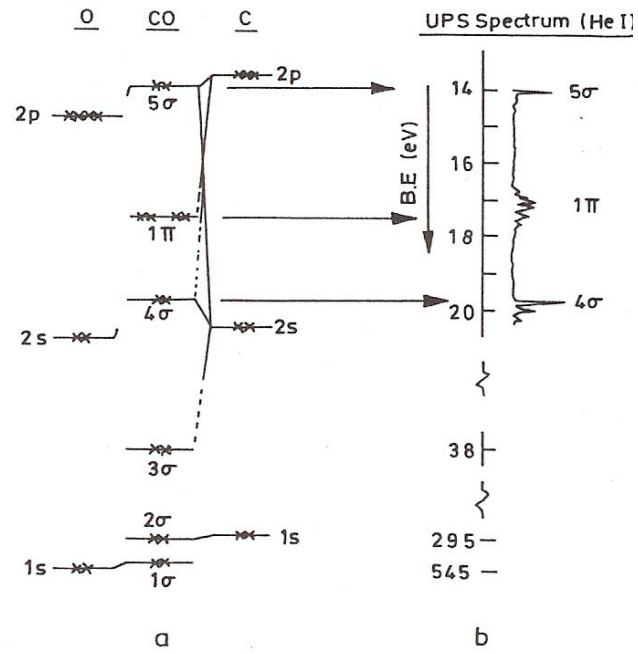


Fig. 4.3. The molecular energy diagram for CO and the corresponding ultraviolet photo electron spectrum (top half) and the UPS spectrum of CO adsorbed on nickel surface shown in the bottom half.

Auger Electron Spectroscopy:

Auger spectroscopy normally is carried out using electrons as the source in the energy of 1 KeV to 10 KeV . These electrons create core holes in the atoms of the sample. The excited atom relaxes by filling the core hole with an electron from a higher shell. The energy is either liberated as an X-ray photon (X-ray fluorescence) or in an Auger transition by the emission of a second electron, the Auger electron. As indicated in the **Fig. 4.4** The kinetic energy of the Auger electron is determined by the electron levels involved in the Auger process and not by the energy of the primary electrons used. Three letter notations like KL₁L₂ for Auger transition denote that primary ionization takes place in the K shell and the core hole is filled from L₁ shell while the Auger electron is emitted from L₂ shell. Valence levels are indicated by the letter V as in KVV.

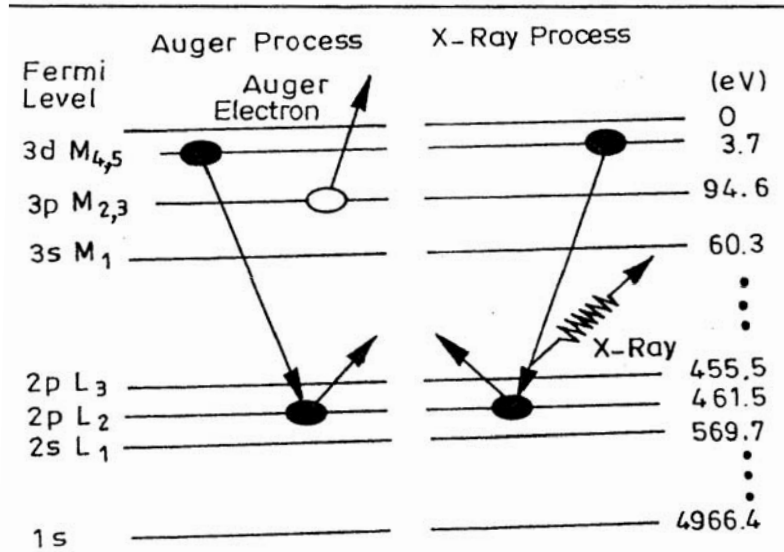


Fig. 4.4. Pictorial representation of Auger and X-ray processes

In the conventional electron excited spectrum the Auger signal will be small against the background of secondary electrons originating from the primary beam. However, the spectra are usually shown in the derivative form.

The energy of Auger transition, for example for a KLM transition at a first approximation is given by

$$E_{KLM} \approx E_K - E_L - E_M - \delta E - \phi$$

E_{KLM} is the kinetic energy of the Auger electron E_K is the binding energy of the electron in K-shell; E_L that of L shell and E_M that of M shell electron is the work function and E is the energy shift caused by relaxation effects due to relaxation taking place in the heavily excited doubly ionized atom.

Though chemical identity of the elements can be easily seen from Auger transitions, it is difficult to identify the oxidation states from Auger peaks as chemical shifts in XPS since relaxation processes are more complicated in Auger spectroscopy. It is only at times possible to get finger print data on the chemical nature of species.

Inverse photoemission spectroscopy:

Inverse photoemission spectroscopy (IPES) is spectroscopy that measures the energy of photons ($h\nu$) emitted when electrons incident on a substance using an electron beam with a constant energy (E_i) relax to a lower energy unoccupied state (E_f). In this process, the energy conservation law is given by:

$$E_i = E_f + h\nu$$

By measuring E_i and $h\nu$, the unoccupied state (E_f) of the surface can be found.

Two modes are used for this measurement. One is the isochromat mode, which scans the incident electron energy and keeps the detected photon energy constant. The other is the tunable photon energy mode, which keeps the incident electron energy constant and measures the distribution of the detected photon energy. The latter can also measure the resonant inverse Photoemission spectrum. This is the only technique which probes the unoccupied states while all other electron spectroscopies only probe the occupied states.

Reference:

1.A.W.Czanderna, Methods of Surface Analysis, Elsevier Scientific Publishing Company, 1975 pp.110-113.