XPS - XPS Notes

Chemistry (SRM Institute of Science and Technology)

X-ray photo Electron Spectroscopy (XPS) (or) Electron Spectroscopy for chemical Analysis: (ESCA)

A surface is a boundary layer between a solid and a vacuum, a gas (or) a liquid. Generally a surface is regarded as a part of a solid that differs in composition of the bulk of the solid. Hence, the surface comprises not only the top layers of atoms or molecules of a solid, but also a transition layer having uniform composition that varies continuously from that of the outerlayer to that of the bulk. Thus, the surface may be many atomic layers deep. However, the difference in composition of the surface layer generally does not affect significantly, the overall composition of the bulk.

This is due to the fact that the surface layer is genally a very very small fraction of the total solid.

In recent years, a number of methods have been developed for surface characterisation. The classical methods, already in use, provide much useful information about the physical nature of surfaces, but give much less information about their chemical nature.

Spectroscopic surface methods, now provide useful information about the chemical nature of surfaces. These methods provide both Qualitative and quantitative chemical information about the Composition a surface layer of the solid.

Various different phenomena can take place when a substance is bombarded by energetic particles or photons. The primary process is the ejection of electrons from target atoms, which leaves vacancies.

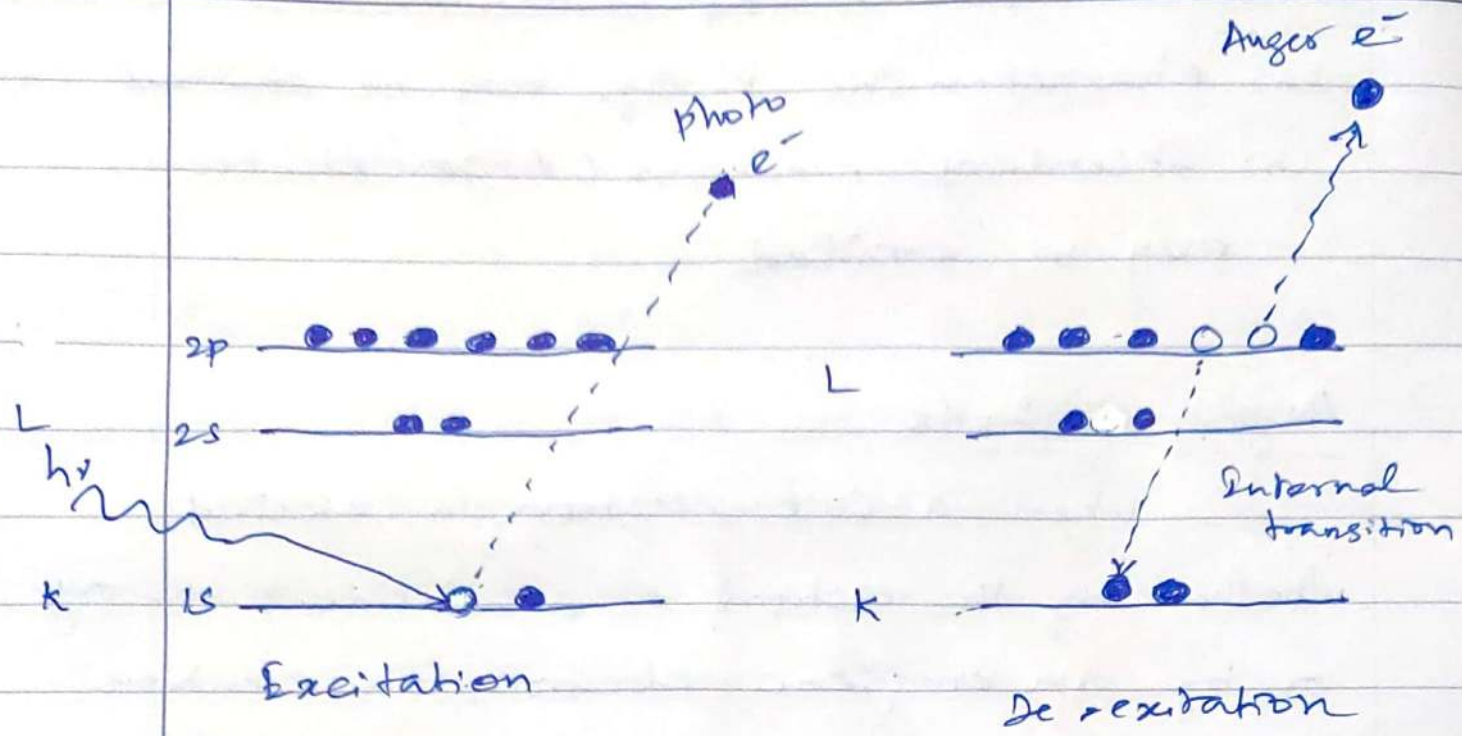
Following the process, either return to the normal Configuration (relaxation) (or)

emission process may occur. (i.e.,
(a) characteristic x-rays may be emitted. (or)
(b) secondary electrons (Auger electrons) may be emitted.

Auger Electrons:

When a core electron is ejected whether by the action of an incident x-ray or by an energetic electron, an electron from a higher level will drop in to fill the vacancy. The energy released by this transition is sufficient to remove another electron from the same shell in the atom.

Thus, if a electron (K shell) is ejected in the primary process, one L shell electron may take its place in the K shell and at the same time a second L shell electron is ejected from the atom. This is known as Auger Effect.



Principle:

Surface Analysis of XPS involved irradiation of the sample by low energy (and mono-energetic) x-rays and the subsequent analysis of the energy of emitted electrons. Typically used x-rays are Kα lines of Mg (1.2536 keV) and Al (1.4866 keV). The penetration depth of the photons in solids is limited to a few microns. Thus, the interaction takes place between the incident photons and the surface atoms leading to the photoelectric

emission of electrons.

The kinetic energy of the emitted electrons is $K.E = h\nu - B.E - \phi_s$.

$h\nu$ – energy of the photon.

B.E – Binding energy of the atomic orbital from which the electron is released.

ϕ_s – work function of spectrometer.

Instrumentation:

XPS Consists the following

(i) Source.

(ii) Sample holder

(iii) An energy Analyser

(iv) Detector

(v) A high vacuum system.

i) Source:

The simplest x-ray sources for the XPS spectrometer are x-ray tube equipped with Mg (or) Al targets and suitable filters.

Al and Mg targeted tubes are generally used without a monochromator because of the high intensity and narrow

Wave length bands of Kα lines of these light elements. It should be noted that narrow bands are desirable because they give rise to enhanced resolution.

ii) Sample holder.

Solid samples are mounted in a fixed position as done to photon or electron source and the entrance slit of the Spectrometer as possible.

iii) An Energy Analysis.

The energy analyser is placed between the sample and detector. It should be very sensitive to identify the electron beam that is coming out of the sample.

Most widely used monochromators utilise either cylindrical or Spherical electrostatic fields. Most of the electron Spectrometers are of hemispherical type

in which the electron beam is deflected by an electrostatic magnetic field in such a manner that the electrons travel in a curved path.

Energy Analyser has two concentric metal cylinders at different voltages. one of the metal cylinders will have a +ve voltage and the other will have zero voltage. This will create an electrical field between the two cylinders.

When the electrons pass through the metal cylinder they will collide with one of the cylinders or they will just pass through.

1) If the electrons velocity is too high, it will collide with the outer cylinder.

2) If the electrons velocity is too slow, then it will collide with the inner cylinder.

3) only the electron with the right velocity will go through the cylinder to reach the detector.

iv) Detectors:

The electron photomultiplier tube is used as a detector, because of its sensitivity and convenience.

v) High vacuum systems / Ultra High vacuum (UHV)

The ultra high vacuum environment will prevent the contamination of the surface and aid an accurate analysis of the sample. It will allow the photo electrons to travel from the surface of the sample to the detector without striking a gas atom.

Working:

In XPS, when the sample kept in ultra high vacuum, is illuminated by the photons of energy ($h\nu$), the surface of the sample emits core electrons called photo electrons. These electrons absorbs a photon and converts part of the energy into K.E. while leaving the atom, some energy of the electron is consumed in overcoming the coulombic attraction of nucleus thereby decreasing its kinetic energy.

At this time the outer orbitals readjusts and delivering the extra energy to the outgoing electrons. Then the XPS spectrum is obtained by determining the kinetic energy & the no. of electrons escaping from upper 0 to 10 nm of sample under investigation.

Applications:

i) Qualitative determination

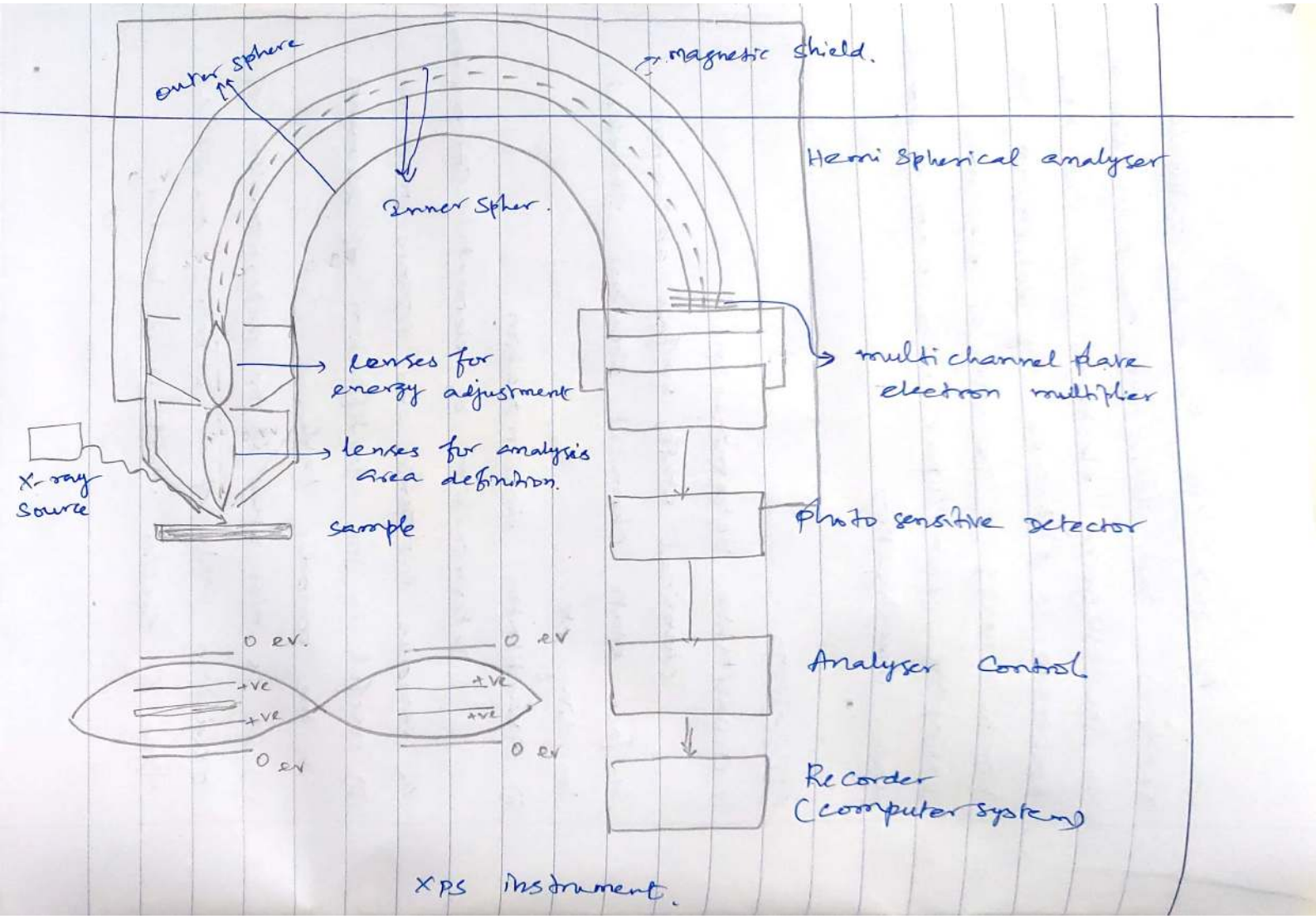
Chemical state, surface adsorption, surface state, chemical structure, chemical bonding etc.

ii) Quantitative determination

Determination of elemental composition of various inorganic and organic materials.

iii) useful in the identification of elements in the periodic table.

iv) It is also used in the determination of oxidation state of an element as well as type of species which it is bonded.



XPS instrument.