Vibronic progression: → It can be seen in the absorption & emission spectra.

→ Vibronic progression means that there is a coupling to vibrational modes in a polymer or oligomer resulting in excitation from the ground state to the excited state or emission from the excited state or emission from the excited state down to the ground state.

↳ For polyatomic molecules, progressions are most often observed when the change in bond lenghts upon electronic excitation coincides with the change due to a "totally symmetric" vibration. This is the same process that occurs in Resonance Raman spectra. As in HCHO, the $n-\pi^*$ transition involve excitation of an e^- from a nonbonding orbital to an antibonding π orbital which weakens & lengthens the C–O bond. This produces a long progression in the C–O ~~stretch~~ stretching vibration.

Vibronic spectra involve simultaneous change in the vibrational & electronic energy state of the molecules. In the gas phase vibronic transitions are accompanied by change in rotational energy also.

→ The Intensity of allowed vibronic transition is governed by Franck-Condon principal.

Photoelectron spectroscopy (PES)

↳ or photoemission

↳ Its refers to energy measurement of electron from solids, gases or liquid by the photoelectric effect, in order to determine the binding energies of electrons in a substance.

↳ It is an experimental technique that measures the relative energy of electrons in atoms and molecules.

↳ Scientists often use PES to study the elemental composition of materials or to characterize bonding in molecule.

(*) **Principle of PES** → If a molecule is excited by a high energy photon in the U.V region of the spectrum that has sufficient energy to ionize the molecule, the excited species will eject electrons.

Threshold frequency → For each metal there is a minimum frequency, called threshol frequency, of the incident light below which no electron are emitted how much intense the radiation may be.

↳ The no of e^- emitted from the metal surface in a given time depends on the intensity of radiation used. There are two imp. facts about the photoelectric emission →

(a) No of e^- librated from the metal surface $\propto$ Intensity of incident radiation.

(b) Incident radiation की frequency के increa होने पर librated e^- की velocity बढ़ जाती है।

(2) Explanation of photo electric emission

Acc to quantum theory, radiation consists of particles of energy, called quanta or photons of energy $h\nu$.

Metal surface

+

photon energy $h\nu$

→ ie metal surface पर $h\nu$ photon आने पर metal के atoms द्वारा $h\nu$ का absorption होता है।

Where $h\nu$ = photon energy

→ metal surface के atoms द्वारा absorbed photon energy, $h\nu$ is equal to the sum of,

ie $h\nu$ = Kinetic energy of emitted electron ie $\frac{1}{2}mv^2$ + energy e_1, required to release the electron from the metal surface

$$h\nu = KE + e_1$$

The ejected e^-s travel from the sample to an energy analyser where their K.E are recorded, then to a detector, which counts the no of photoelectrons at various K.E

↳ Here energy (e_1) is product of the work function of the metal & the electronic charge.

ie $$h\nu = \frac{1}{2}mu^2 + e_1 \longrightarrow (A)$$

where ν = frequency of incident radiation.

↓

photon energy = KE + work function

↳ It is clear from this equation that → $h\nu$ को e_1 से greater होना चाहिए [$h\nu > e_1$ ie <u>photon energy > work function</u>

↳ So clear है कि incident radiation की frequency, जब तक एक definite minimum value, जिसे threshold frequency कहते हैं, को exceed नहीं करती है, तब तक electron का photoelectric emission नहीं हो सकता है।

(ν_0 = Threshold frequency)

We know that, $e_1 = h\nu_0$, so from eqn (A)

$$h\nu = \frac{1}{2}mu^2 + h\nu_0$$

$$\text{or } \frac{1}{2}mu^2 = h\nu - h\nu_0$$

$$\text{or } \boxed{\frac{1}{2}mu^2 = h(\nu - \nu_0)}$$

↳ This is Einstein's photoelectric equation

(5)

Einstein's equation indicates →

(a) Incident radiation की frequency increase होने पर liberated e^- की velocity बढ़ती है

(b) No electron will be emitted when frequency of incident radiation (ν) is less than threshold frequency (ν_0)

we know that $\boxed{E_1 = h\nu_0}$ → clear that threshold frequency or threshold energy is known as work function of the metal.

Nutshell

metal surface + $h\nu$

↓

metal surface से e^- का निकलना

↓

Called photoelectric effect, & metal surface से निकले e^- को photo electrons कहते है

K.E of photoelectron = K.E of light − Threshold energy

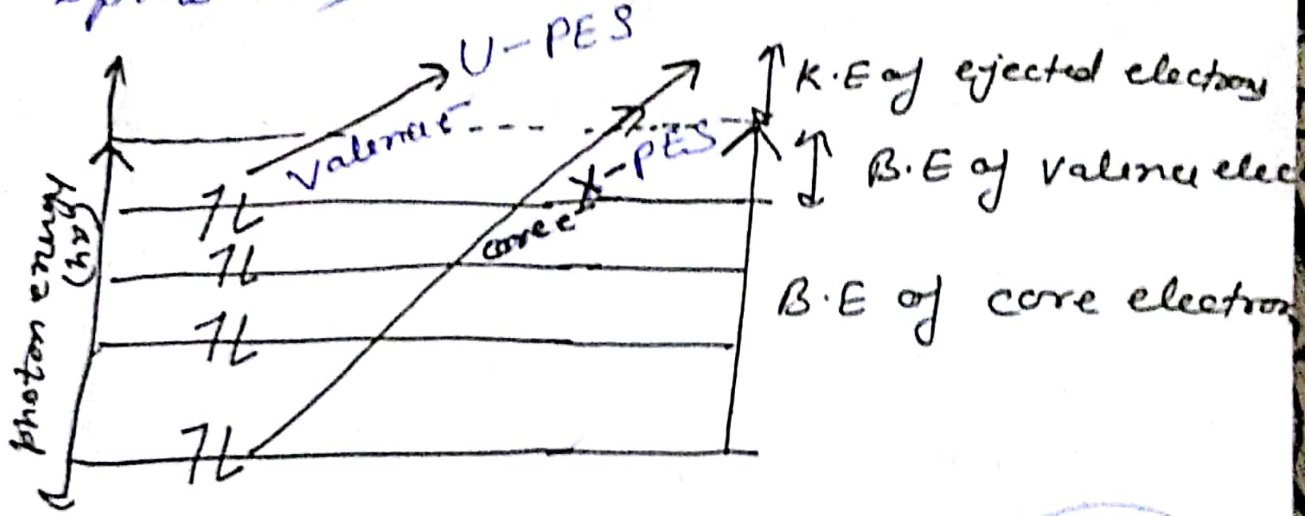
or K.E of " = light energy − Threshold energy

(7) **Principles**

→ A techniques for determining the atomic energy levels & hence the Ionization energy or binding energies of atoms or molecules

This spectroscopy observed the ionization energies of electrons from different molecular orbitals.

↳ So consider some energy levels of an atom containing electrons with paired spins →



↳ The electron are classified as → Valency e⁻ / → core e⁻

Atom or molecule
+
U.V radiation (high frequency or low energy)
↓ Here photoionization occurs
ejection of valence e⁻

↳ called photo electron spectroscopy (PES) or U.V-PES

→ & K.E of these photoelectrons are measured & this technique is called PES or UV-PES

(8) X-ray sources → It can remove core e^- from the inner shells.

Atom or molecule
+
X-ray source (give high energy photons)
↓
They can remove e^-s from the inner shells.

↓
called X-PES or ESCA (electron spectroscopy for chemical analysis)

↳ we know that, $h\nu = B.E + KE$

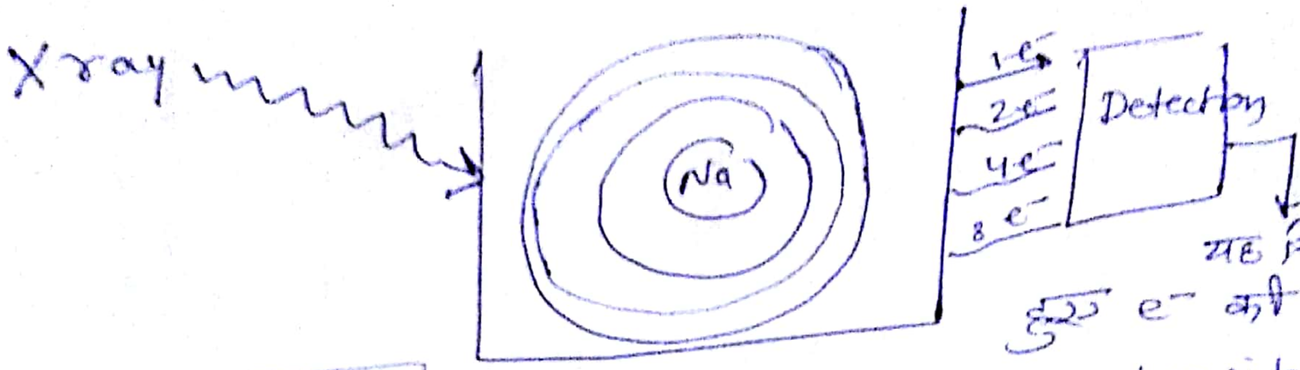
so $B.E = h\nu - K.E$

So work function of the metal is the energy required to remove the bulk electrons from to the surface of the metal.
→ It is analogue of the ionization energy of the atom or the molecule in photoelectron spectroscopy (PES)

PES → tell the atomic & molecular orbitals
- To surface study
- To study the M.OT

(B)

As $_{11}Na^{23} \rightarrow 1s^2, 2s^2p^6, 3s^1$



यह निकले हुए e^- की energy & Intensity को measured करेंगे।

photo e^- की intensity ही signal को बताता है

यह indicate करता है कि यदि 4 differed type के e^- निकल कर आये, तो It means, It consist of 4 type of energy levels & intensity ratio है

(A) X-ray PES is also known as electron spectro-scopy for chemical analysis (ESPA). It can be used to identify the chemical composition of sample in surface

↓

It depend on mosely. Rule

↓

elements & its %age
(core e^- की Binding energy से)

Auger electron spectroscopy

↳ a common analytical technique used mainly in the study of surface & more generally in the area of material science.

↳ Based on the analysis of energetic electron emitted from an excited atom after a series of internal relaxation events.

↳ It is characterization technique for probing chemical & compositional surface environments & has found application in metallurgy etc.

↳ (AES) → two step phenomenon.

(Ist step) → formation of an electronically excited ion A^{*+} by exposing a beam of electrons / or sometimes X-ray. Ionization occurs as →

(1) $A + h\nu \rightarrow A^{+*} + e^-$ → (यह X rays के साथ होता है)

(2) with an electron beam, excitation is indicated as —

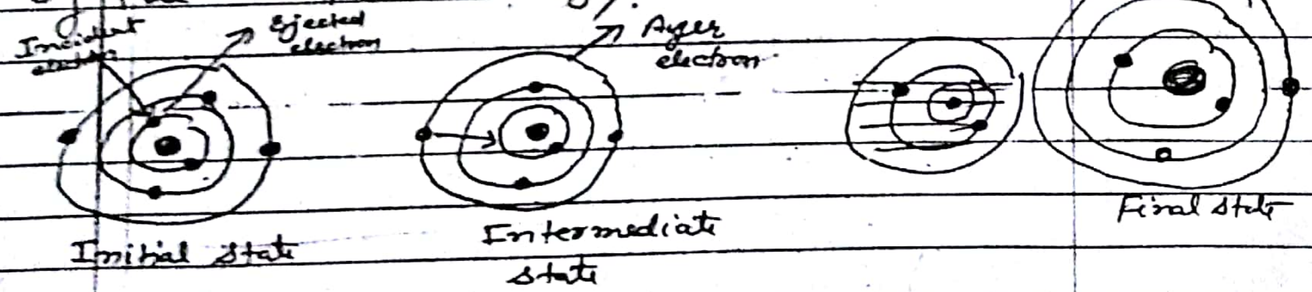
A + (Incident electron from the source → e_i^-) → A^{+*} + (same electron after it has interacted with A & has lost some of its energy — indicated by $e_i'^-$) + (ejected electron from one of the inner orbital of A → e_A^-)

(3) The relaxation of the excited ion A^{+*} occur in two ways

$A^{+*} \rightarrow A^{2+} + e_A^-$ Auger electron

or $A^{+*} \rightarrow A^{+} + h\nu_f$ X-ray fluorescent

($h\nu_f$) → It is energy of fluorescence radiation & independent of the excitation energy.



↳ Agar effects occurs when the X-ray fluorescence get consumed for the ejection of outer shell electron of lower binding energy. Due to agar effect unwanted signals appears in the photoelectron spectrum.

Koopman's theorem → applies to the removal of an electron from any occupied molecular orbital to form a positive ion. Removal of the electron from different occupied molecular orbitals leads to the ion in different Electronic states. In this Excited state ionization energies can be measured by photoelectron spectroscopy