IONISATION PROCESS & KOOPMANS' THEOREM

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IONISATION PROCESS

❖ Ionisation is the process by which an atom or a molecule acquires a negative or positive charge by gaining or losing electrons to form ions, often in conjunction with other chemical changes.

❖ Ionisation can result from the loss of an electron after collisions with subatomic particles , collisions with other atoms or molecules and ions, through the interaction with light.

❖ Heterolytic bond cleavage can result in the formation of ions pairs.

❖ Ionisation can occur through *radioactive decay by the internal conversion process* , in which excited nucleus transfers its energy to one of the *inner-shell electrons* causing it to be ejected.
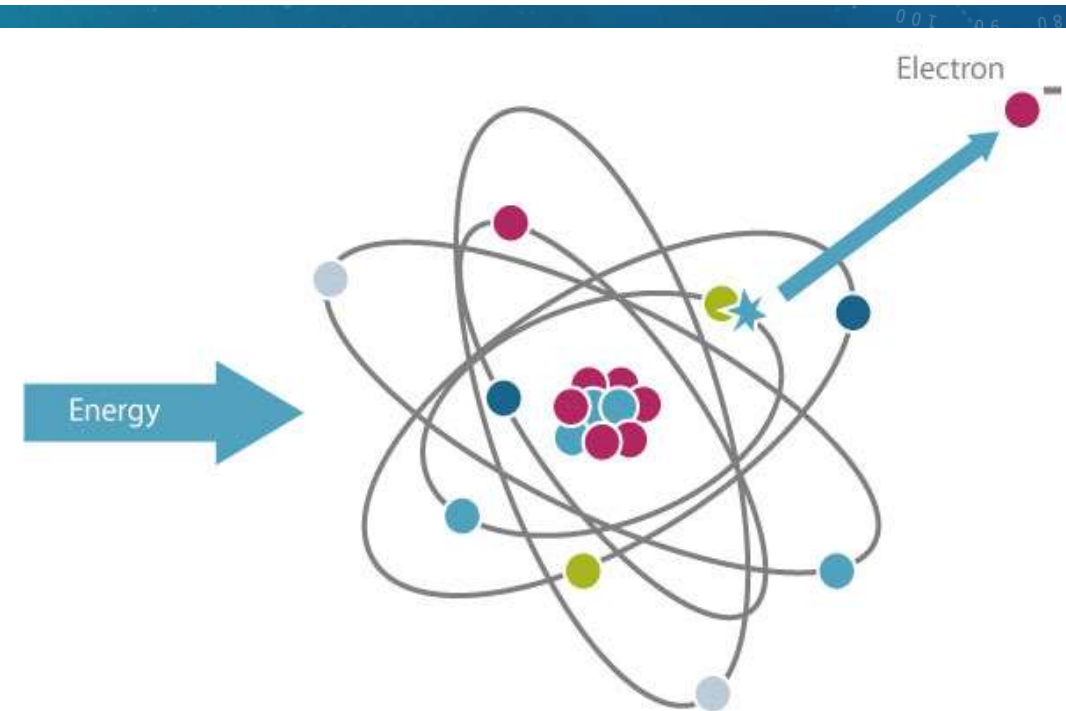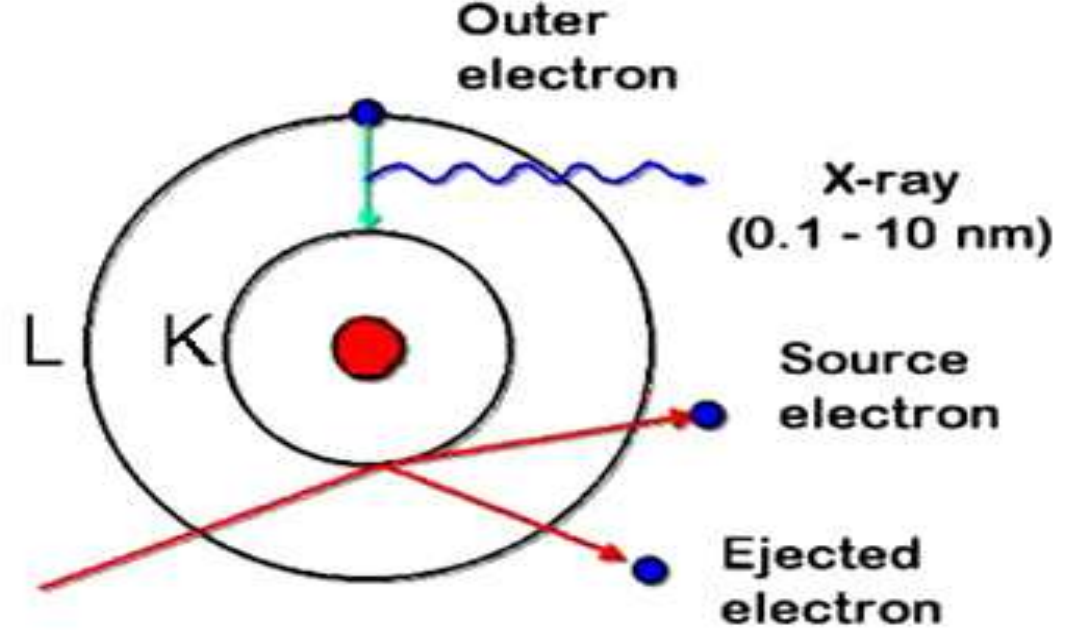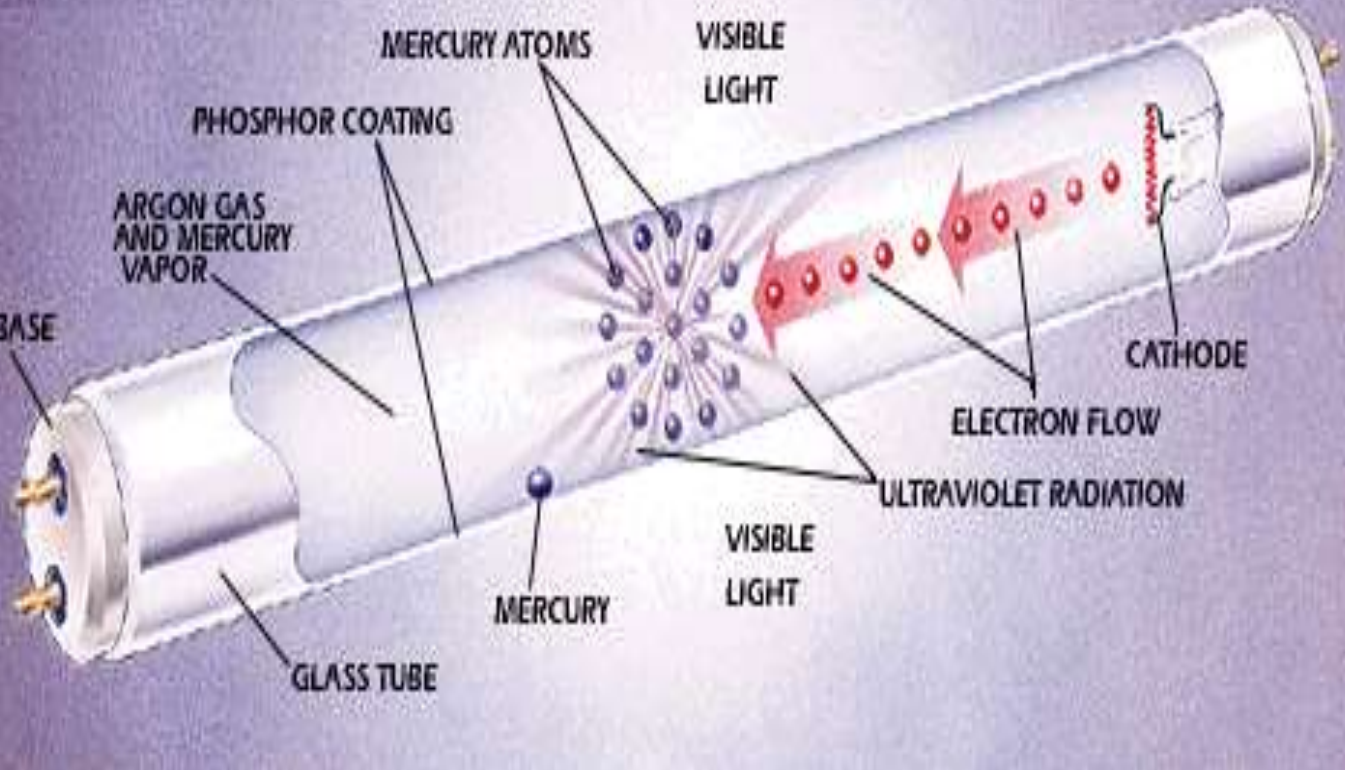
❖ THE ORBITAL MODEL OF IONISATION

❑ Ionisation is explicitly defined in term of *transitions between the ground state of a molecule and ion states.*

❑ Ionisation of electrons occur from bonding molecular orbitals , lone pairs , anti bonding molecular orbitals or atomic cores.

❑ This description reflects *the relationship of ionisation energies to the molecular orbital model of electronic structure*.

❑ Ionisation energies are directly related to *the energies of molecular orbitals* by Koopmans' theorem.

❑ The ionisation energies can be considered as measures of orbital stabilities and shifts can be interpreted in terms of orbital *stabilisation or destabilisation due to electron distributions and bonding.*
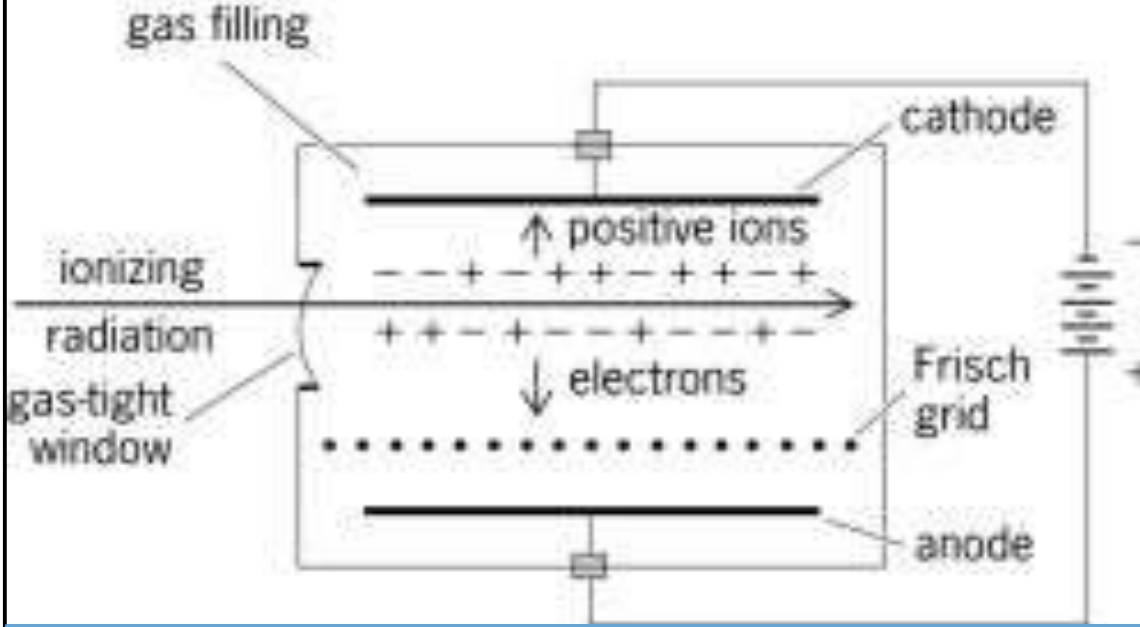
❖ IONISATION INTENSITY

❑ *The probability of ionisation is dependent upon the energy of ionizing photon, the atomic character of the orbitals ionized , the angle at which photoelectrons are collected and the polarized nature of photon.*

❑ The general trend that have been observed *for photoionization behaviour* often lead to a clear and convenient differentiation between ionisation from metal –based and ligand-based orbital in *Photoelectron Spectroscopy*.
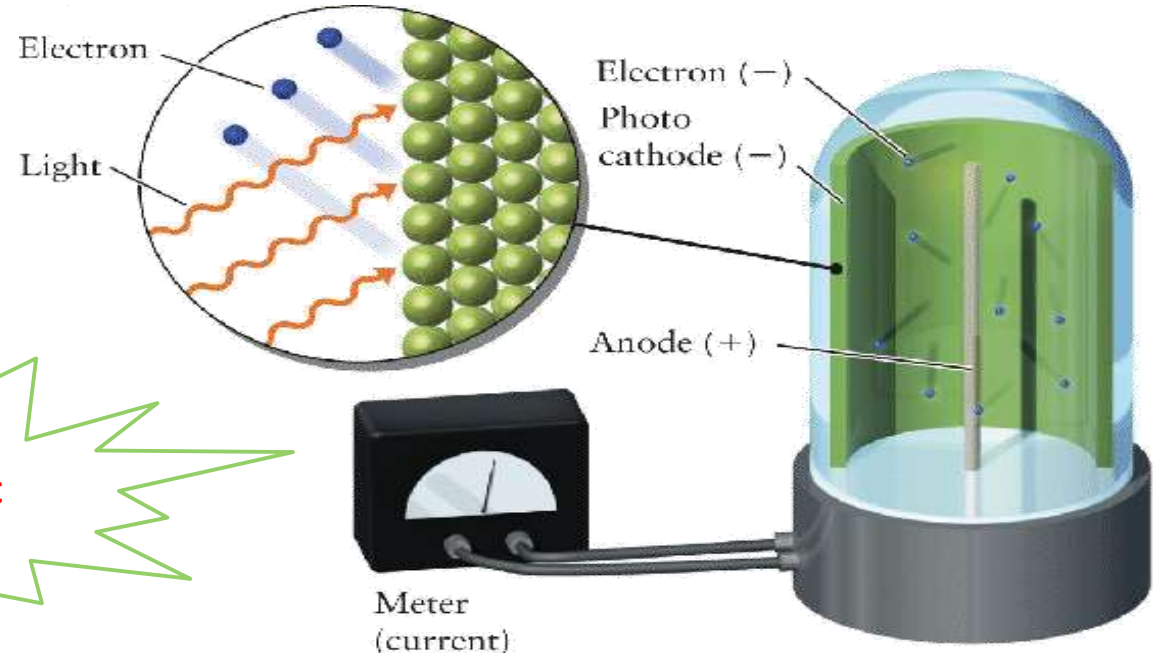
❖ USES OF IONISATION

FLOURESCENT TUBE

MERCURY ATOMS
VISIBLE LIGHT
PHOSPHOR COATING
ARGON GAS AND MERCURY VAPOR
BASE
MERCURY
GLASS TUBE
CATHODE
ELECTRON FLOW
ULTRAVIOLET RADIATION
VISIBLE LIGHT

1.Fluorescent tube / lamp

gas filling
cathode
↑ positive ions
ionizing radiation
− − + − + + − + + − +
gas-tight window
+ + − + − − + − − + −
↓ electrons
Frisch grid
anode

2.Ionisation Chamber

Electron
Light
Electron (−)
Photo cathode (−)
Anode (+)
Meter (current)

3.Photoelectric effect

❖ *WHO WAS KOOPMANS?*

TJALLING C. KOOPMANS WAS A DUTCH AMERICAN MATHEMATICAN AND ECONOMIST, THE JOINT WINNER WITH *LEONID KANTOROVICH* OF THE 1975(NOBEL MEMORIAL PRIZE IN ECONOMICS SCIENCE),

August 28,1910 – February 26,1985

KOOPMANS' THEOREM

❖ STATEMENT:- According to this theorem,*"The first ionisation energy of a molecule is equal to the negative of energy of highest occupied molecular orbital (HOMO)."*

INTRODUCTION:-

1.It is uses theHartree-Fock method *for the approximation of orbital energy ($\in i$) which is derived from the wave function of the spin orbital and the kinetic and nuclear attraction energies.*

2.This theorem *applies when an electron is removed from molecular orbita*l in the order to form a positive ion.

3.It is originally *only used for ionisation energies in a closed shell system but has been generalized to be used to calculate energy changes when electrons are added or removed from a system.*

4.Based on this generalization *, it is possible to use the same method to approximate the electron affinity .* In this case, *molecular orbital would be one associated with the orbital to which the electron being added.*

"Koopmans' theorem is useful because the use of this approximation mean that it is not necessary to calculate the two separate energies of the original molecule and its ion in order to find the ionisation energy and electron affinity."

BASIC DISCRIPTION :-

In order to understand Koopmans' theorem , we must first understand its background , which *is based in the Hartree-Fock method is used to approximate the wave function and energy of multi electron system .*

➤This method starts by expressing the wave function of the system as a Slater determinant of the wave function of each single particle orbital.

➤*The Slater determinant for a system with n electrons is*

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \equiv |\chi_1 \quad \chi_2 \quad \cdots \quad \chi_N|,$$

➤By breaking up the electrons into *individual wave functions* , we can create a *single – particle* Hartree – Fock equations, *which can be used as an operator whose eigenvalue is the energy of a particular orbital*.

➢ By breaking up the electrons into individual wave functions , we can create a single – particle Hartree – Fock equations, which can be used as an operator whose eigenvalue is the energy of a particular orbital.

$$\hat{F} \, | \, \phi_i \; = \; \epsilon_i \, | \, \phi_i$$

where $\hat{F}$ ▬ Operator corresponding to the Hartree – Fock equation
,

ϕ_i ▬ Wave function of the particle

ϵ_i ▬ The energy of the particle in the orbital

Using Koopmans' theorem , the equation from above and the wave function of the HOMO , we can approximate the first order ionisation energy of a molecule.

Advanced description

The Hartree-Fock equation for a particle takes the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\mathbf{r}) + V_{nucleus}(\mathbf{r})\psi_i(\mathbf{r}) + V_{electron}(\mathbf{r})\psi_i(\mathbf{r}) - \sum_j \int d\mathbf{r}' \frac{\psi_j(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r})}{\left|\mathbf{r}-\mathbf{r}'\right|} = \epsilon_i\psi_i(\mathbf{r})$$

So, the Fock operator derived from this is

$$\hat{F} = \hat{H}^0 + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \sum_{j=1}^{N}(2\hat{J}_j - \hat{K}_j)$$

❖ *CONCLUSION*

- *It is a simple spectroscopy interaction which correlate with the tool of science (QUANTUM MECHANICS,CLASSICAL MECHANICS,ATOMIC etc.) how we can applied these tools.*

- *Spectroscopy is the application part of these sciences and concepts which are sum up together make different technology.*

- *Photoelectron spectroscopy is based on concept of ionisation.*