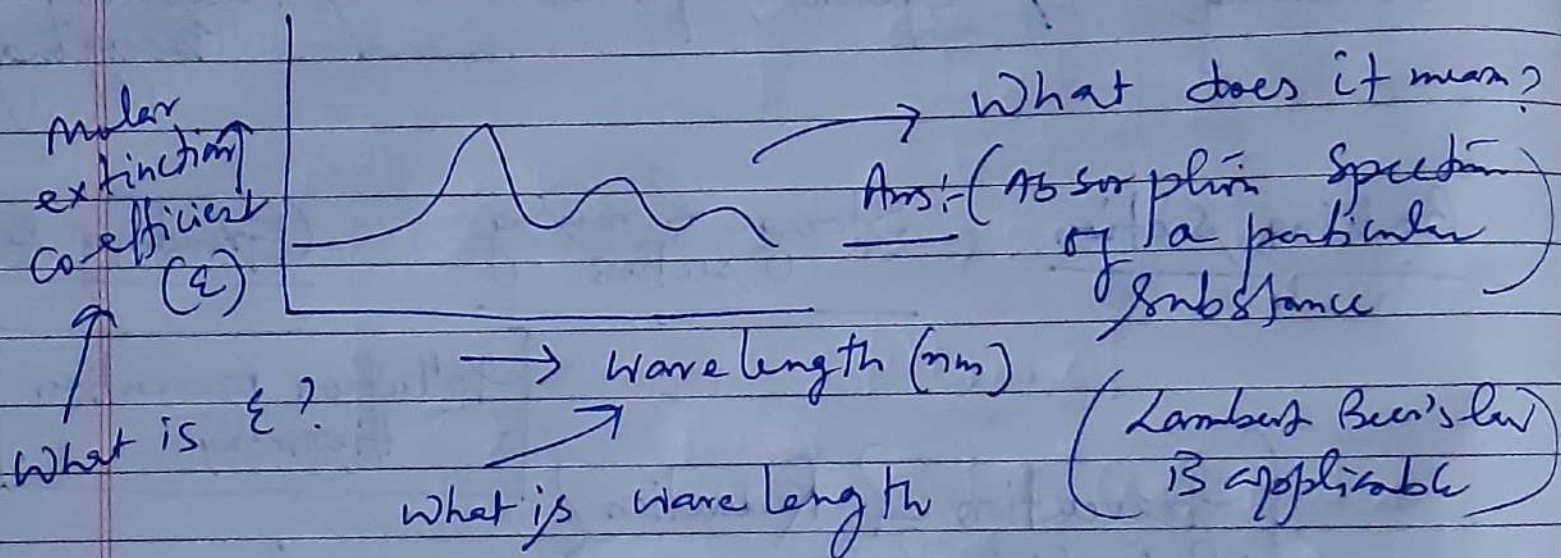


Electronic Spectra (Introduction)



Types of electronic spectra:-

- 1) Ligand field spectra (d-d spectra)
- 2) Charge transfer spectra (CT)
- 3) Ligand spectra ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ etc)
- 4) Counter ion spectra

We will focus more about d-d spectra.

Selection rules for the electronic transition

Laporte or orbital selection rule

$$\Delta l = \pm 1 \quad (\text{allowed})$$

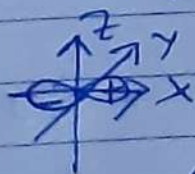
$$\left. \begin{array}{l} s \rightarrow s \\ p \rightarrow p \\ \textcircled{d \rightarrow d} \end{array} \right\} \times \text{forbidden } \Delta l = 0$$

orbital $\left\{ \begin{array}{l} s \rightarrow \text{gerade} \rightarrow 'g' \\ p \rightarrow \text{ungerade} \rightarrow 'u' \end{array} \right.$

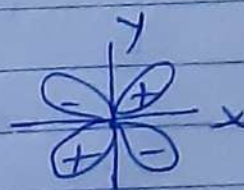
d and f $\rightarrow ?$ (Home tasks)

$$\left. \begin{array}{l} g \rightarrow g \\ u \rightarrow u \end{array} \right\} \times \text{forbidden transition}$$

$$\left. \begin{array}{l} g \rightarrow u \\ u \rightarrow g \end{array} \right\} \checkmark \text{Allowed transition}$$

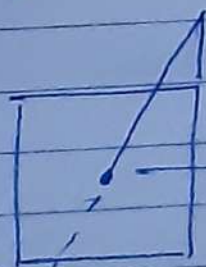


p_x (u-symmetric)



d_{xy} (g-symmetric)

(gerade and ungerade \rightarrow denotes in terms of inversion symmetry)



\rightarrow inversion center.

$$\left. \begin{array}{l} \checkmark s \rightarrow p \\ \checkmark p \rightarrow d \\ \checkmark d \rightarrow f \end{array} \right\} \text{allowed transition}$$

So, d-d transition is a Laporte forbidden transition.

From quantum mechanics:-

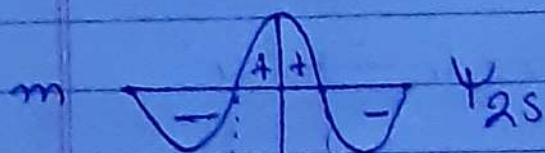
$$|M_{mn}|^2 = \left[\int_{-\alpha}^{+\alpha} \psi_m^* \hat{\mu}_{mn} \psi_n d\tau \right]^2 \neq 0$$

Transition moment integral

$\mu_{mn} \rightarrow$ dipole moment operator

$S =$ even function
 $P =$ odd function

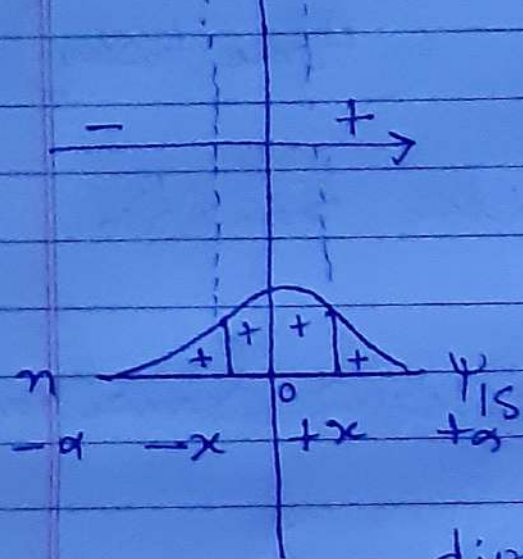
1s \rightarrow 2s



1s \rightarrow 2s

odd function changes sign for $+x$ to $-x$.

(Considering x direction)



$$|M_{nmx}| = \int_{-\alpha}^{+\alpha} \psi_{1s}^* (ex) \psi_{2s} dx$$

(Photon Considered to be negligible)

$$= \int_{-\alpha}^{-x} (+) (-) (-) + \int_{-x}^{+x} (+) (-) (+) + \int_{+x}^{+\alpha} (+) (+) (+) + \int_{+\alpha}^{+\alpha} (+) (+) (-)$$

dipole moment vector is always odd.

$$= (+) + (-) + (+) + (-)$$

$$= 0$$

As the integral is 0 zero. Then the transition is forbidden.

Selection rule:- odd function and even function.