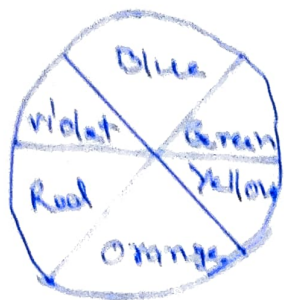


Semester - 6 (M)
Inorganic

[spectra of co-ordination compounds - (25)
Free ion terms and their splitting in octahedral
symmetry. Orgel diagram. Laport selection rule,
vibronic coupling and colour of complexes,
electronic spectra of $[M(H_2O)_6]^{n+}$ complexes.]

The colour of co-ordination complexes is
complementary colour of absorbed light.
Artist colour wheel



The colour of complexes are occurred due to
electronic transition called d-d transition
from lower energy state to higher energy
state. t_{2g} to e_g in octahedral complex and
 e to t_2 in tetrahedral complex.

If transition takes place by absorbing
UV or IR region then the complex will be
colourless.

$$\Delta E = E_2 - E_1$$

symbols $= h\nu = h \frac{c}{\lambda} = hc \bar{\nu}$ represent normal meaning.

The $\epsilon_{FS}(\Delta)$ can be measured with wavelength of light absorbed, This amount of light absorbed is called absorbance ($\log E$).

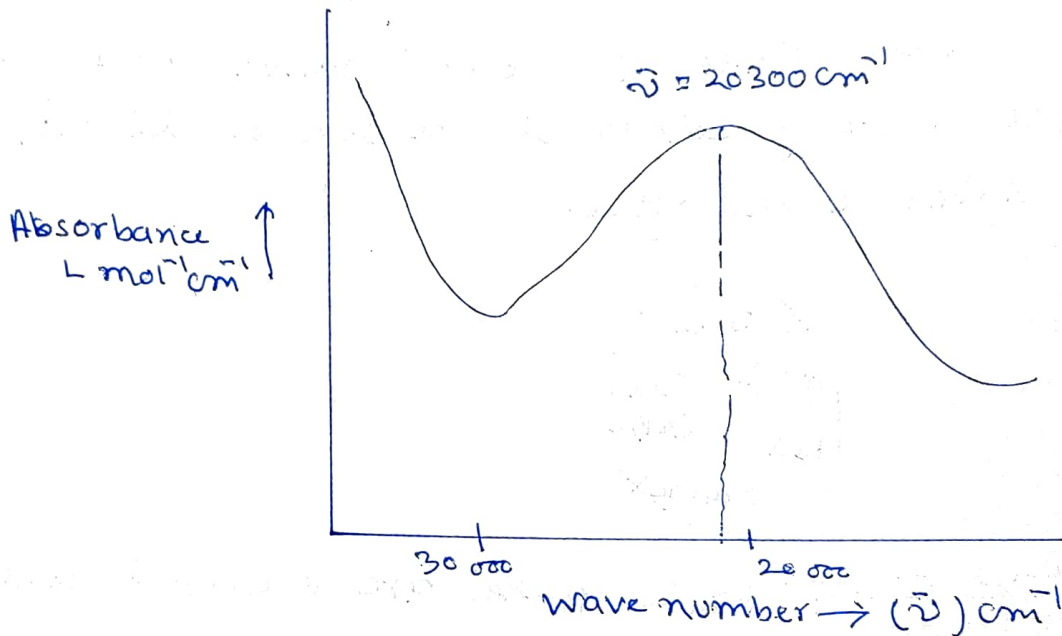
The plot of absorbance vs wavelength or wave number is called absorption spectrum.

In case of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ gives only one peak in its electronic spectrum because of d^1 configuration, The single broad peak with max^m absorption at 20300 cm^{-1}

$$1 \text{ kJ mol}^{-1} = 83.7 \text{ cm}^{-1}$$

$$\Delta_0 \text{ of } [\text{Ti}(\text{H}_2\text{O})_6]^{3+} = \frac{20300}{83.7} (= 242.53 \text{ kJ mol}^{-1})$$

but for many electronic system (d^n) more calculation are needed because of e-e interaction.



Most of transition metal complexes give broad spectrum (absorption bands) extending over several thousands wave number. M-L bond is not rigid. When light is absorbed then electronic transition and vibration both are happened,

Called vibronic transitions. Due to vibration of ligands energy of electron is changed. If the ligand moves towards metal atom the value of Δ_0 increases and if go away then decreases. So in a vibration, a large no. of electronic transitions over several thousand wave numbers occurs.

There are two other factors for broad bands - spin-orbit coupling and Jahn-Teller coupling distortion.

Sharp peaks are observed where Δ_0 does not change, or the energy of ground state and excited state are changed equally.

* Lanthanoid complexes gives sharp-bands because f orbitals are buried in deep, no interaction of ligands on f orbitals. So the vibration of ligands or change of nature of ligand does not change the energy of f orbitals. Hence Δ_0 value remain same.

Beer-Lambert's Law.

$$A = \log \frac{I_0}{I}$$

$$= \epsilon \lambda c l$$

A → absorbance

I_0 → Intensity of incident light

I → Intensity of transmitted light

ϵ → molar absorptivity ($L \text{ mol}^{-1} \text{ cm}^{-1}$)

l → Path length

c → concⁿ (mol L^{-1})

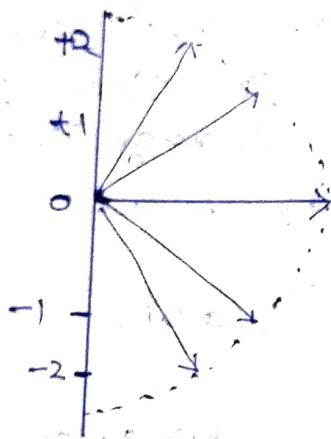
Angular momentum of an electron.

- (a) orbital angular momentum (l) —
An electron moving in its orbital round the nucleus possesses an angular momentum called orbital angular momentum (l)

$$l = \sqrt{l(l+1)} \frac{h}{2\pi}$$

$l \rightarrow$ orbital angular momentum quantum number
 l is vector quantity, its value is ≥ 0 . It has $2l+1$ orientations in space about reference direction, generally Z axis. All the components are whole number multiple of $\frac{h}{2\pi}$

$\therefore l_z = l_z \frac{h}{2\pi}$, l_z is magnetic quantum number, may call m_l , value ranges from $+l$ to $-l$



- (b) Electron spin angular momentum (s) \rightarrow
spinning of electron around its own axis generates an angular momentum known as spin angular momentum (s) it is also a vector quantity.

$$s = \sqrt{s(s+1)} \frac{h}{2\pi} \quad s \rightarrow \text{spin quantum number}$$

it has two orientations with reference to chosen axis generally Z axis. each component will be half integral multiple of $\frac{h}{2\pi}$, represented s_z or m_s values are $+\frac{1}{2}$ or $-\frac{1}{2}$.

② Spin-orbit coupling

Interaction of orbital angular momentum and spin angular momentum is spin-orbit coupling. Its effect on energy levels depends on orientation of orbitals and spin angular momentum.

④ Total angular momentum (j'): \rightarrow

It is the vector sum of orbital angular momentum and spin angular momentum.

$$j' = l + s$$

If two angular momentum are parallel then

$$j' = l + \frac{1}{2} \text{ and if opposite}$$

$$j' = l - \frac{1}{2}$$

$$\therefore j' = \sqrt{j'(j'+1)} \frac{h}{2\pi}$$

Total angular momentum of many electron atoms \rightarrow

When two or more electrons are present in a subshell of an atom, their individual orbital angular momenta may add together, or oppose each other. The total orbital angular momentum

$$L = \sqrt{L(L+1)} \frac{h}{2\pi}$$

$L \rightarrow$ total orbital angular momentum quantum no. (≥ 0)

If there are two electrons in a subshell with orbital angular momentum quantum no. l_1 and l_2 , the value of L is obtained by coupling as

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$$

if two electrons are parallel then L is \max^m and if oppose then it is $\min^m(l_1 - l_2)$

for d^2 electrons $l_1 = l_2 = 2$
 $\therefore L = 2+2, 2+2-1, \dots, (2-2)1$
 $= 4, 3, 2, 1, 0$

For quantum number $L = 0, 1, 2, 3$ etc. The terms are S, P, D, F... are used which are parallel to l values.

orbital angular momentum has $2L+1$ orientations ~~rep~~ represented by M_L .

$M_L = L, L-1, L-2 \dots 0 \dots -L$
 closed shell has zero orbital angular momentum.

Total spin angular momentum:-

When two or more electrons are present in a subshell of an atom then the total spin angular momentum is given by

$$S' = \sqrt{S(S+1)} \frac{h}{2\pi}$$

$S \rightarrow$ total spin angular momentum quantum number
 it ≥ 0 if no. of electrons is even.

and $\frac{1}{2}$ half integer is no. of electrons is odd

If for two electrons s_1 and s_2 are the spin quantum no. Then

$$S = s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|$$

for each electron $s = \frac{1}{2}$

$\therefore S = 1, 0$ for two electrons

$S = \frac{N}{2}, \frac{N}{2} - 1, \dots, \frac{1}{2}$ if N is odd, $N \rightarrow$ no. of electrons

$S = \frac{N}{2}, \frac{N}{2} - 1, \dots, 0$ if N is even.

Spin multiplicity is $2S'+1$

Spin-orbit coupling:

If there are two or more electrons in a subshell then coupling of all the spin and orbital angular momenta is to be taken. There are two ways for coupling

(i) L-S coupling or R-S coupling

(ii) j-j coupling.

In atoms of low atomic nos L-S coupling is performed, because in these atoms spin-orbit coupling is weak. For that first sum the orbital angular momentum \vec{l} to give L and then spin angular momentum to give total S separately and then add these two momenta for total angular momentum J

$$\therefore L = \sum l_i \quad S = \sum s_i$$

$$\therefore J = L + S$$

$$\text{and } J' = \sqrt{J(J+1)} \frac{h}{2\pi}$$

J is total angular momentum quantum no.
 > 0 or positive half integer

$$J = L+S, L+S-1, \dots, |L-S|$$

if there is a single electron then $J = j$
and $j = l + \frac{1}{2}$ or $l - \frac{1}{2}$

j-j coupling occurs in heavy atoms where spin-orbit coupling is large. But for strong coupling each electron is considered as a particle.

$$j_i = l_i + s_i$$

$$\text{and } J = \sum j_i$$

L-S coupling is more important in case of transition metals.

Microstates:

The different ways in which the electrons are arranged in the orbitals of a subshell is called microstates or atomic states. It can be calculated from electronic configuration with the following formula

$$\text{Number of microstates} = \frac{N!}{x!(N-x)!}$$

$N \rightarrow 2(2l+1)$ i.e. twice the number of orbitals

$x \rightarrow$ number of electrons

eg. for p^2 configuration

$$\begin{aligned} \text{microstate} &= \frac{6!}{2!(6-2)!} \\ &= \frac{6 \times 5 \times 4!}{2 \times 1 \times 4!} \end{aligned}$$

for p^2

$$= 15$$

	$m_l \rightarrow$	+1	0	-1	M_s	M_L
1	$\uparrow\downarrow$	$\uparrow\downarrow$			0	+2
2			$\uparrow\downarrow$		0	0
3				$\uparrow\downarrow$	0	-1
4		\uparrow	\downarrow		0	+1
5		\downarrow	\uparrow		0	+1
6		\uparrow		\downarrow	0	0
7		\downarrow		\uparrow	0	0
8			\uparrow	\downarrow	0	-1
9			\downarrow	\uparrow	0	-1
10		\uparrow	\uparrow		+1	+1
11		\uparrow		\downarrow	+1	0
12			\uparrow	\uparrow	+1	-1
13		\downarrow	\downarrow		-1	+1
14		\downarrow		\downarrow	-1	0
15			\downarrow	\downarrow	-1	-1

Total = 15