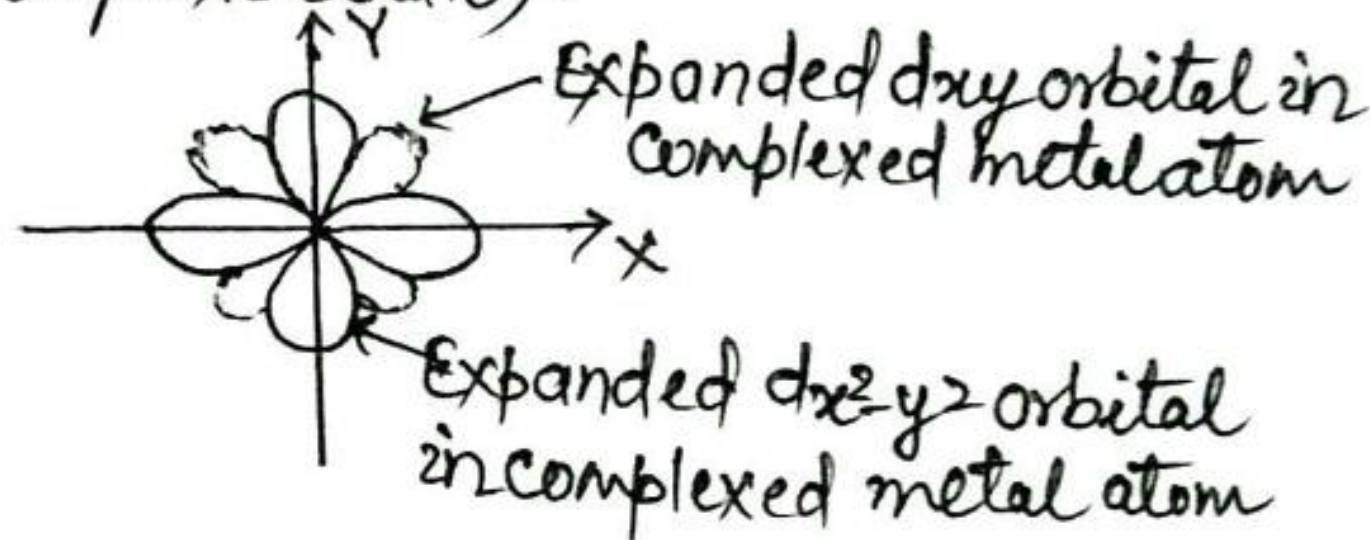
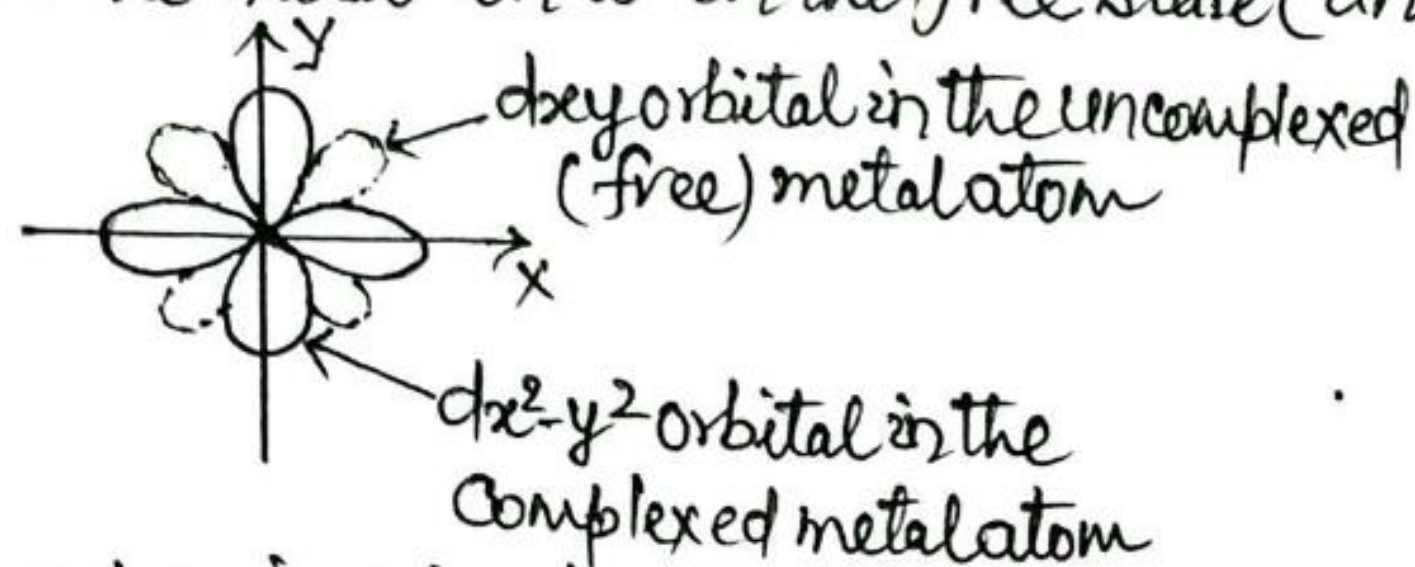


⇒ Nephelauxetic Effect

Nephelauxetic effect is indirect evidence of the existence of covalent bonding character in metal-ligand bond in complexes. Electrons present in partially-filled d-orbital of a metal ion repel one another. This repulsion is called d-d inter electronic repulsion. It has been found experimentally that when a metal ion gets coordinated with the ligands and forms a complex, the repulsion existing between d-electrons of the complexed metal ion becomes less than when the metal ion is in the free state (uncomplexed state).



Due to the expansion of metal d-orbitals into the region of ligand orbitals, the overlap of metal d-orbitals with ligand orbital takes place and metal-ligand bonds acquire some covalent character in metal-ligand bond.

Thus, complexed metal d-electrons spend sometime on the ligands, i.e., metal d-electrons are partially delocalised into ligand orbitals. This effect of ligands in expanding metal d-electron cloud is known as Nephelauxetic (a Greek word meaning 'cloud expanding') effect. The capability of a ligand to expand metal d-electron cloud differs from one ligand to the other.

⇒ Nephelauxetic ratio (β)

Due to the overlap of metal ion d-orbitals with the ligand orbitals, delocalisation of d-electrons from the metal ion to the ligand occurs. The extent of delocalisation of d-electrons is called Nephelauxetic ratio, and expressed by symbol 'β'. It is the ratio of the inter-electronic repulsion Racah parameter of the complexed metal ion (β') to that of the free metal ion (β).

Thus, Nephelauxetic ratio (β) =
$$\frac{\text{Inter-electronic repulsion Racah parameter of the complexed metal ion}}{\text{Inter-electronic repulsion Racah parameter of the free metal ion}}$$

Or,
$$\beta = \frac{\beta'}{\beta} \quad \text{--- (1)}$$

When a metal ion gets complexed, the size of d-orbitals of the metal ion increases. Due to this increase in the size of d-orbitals of the metal ion, the interelectronic repulsion amongst d-electrons of the complexed metal ion is decreased. Therefore, the value of β' is always less than that of β. Consequently, β is always less than 1.

The approximate value of Racah parameter of a metal ion present in a complex ion (i.e., value of β') is given by
$$\beta' = \beta(1 - h_1 k_2) \times 10^3 \quad \text{--- (2)}$$

(Where β = Racah parameter for the free metal ion, h₁ = Arbitrary parameter for the free metal ion, k₂ = Arbitrary parameter for the ligands present in the complex ion.)

Empirical values of h₁ for different metal ions/cations are given below:

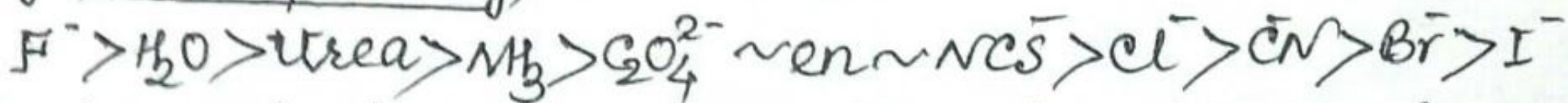
Metal ion	Co ²⁺	Co ³⁺	Cr ³⁺	Fe ³⁺	Mn ³⁺	Ni ²⁺
h ₁ value	0.23	0.35	0.21	0.24	0.07	0.12

k_L values (empirical) for different ligands are given below:

Ligand	6CN	6Br ⁻	6Cl ⁻	6OH	3en	6H ₂ O
k_L value	-	2.3	2.0	2.0	1.5	1.4

⇒ Nephelauxetic Series

A series of ligands in the decreasing order of β -values/in the increasing order of their ability to expand metal d-electron cloud is called Nephelauxetic (Greek word, meaning cloud expanding) Series. The series is as follows:



The above order is independent of the nature of the metal ion. In this series as we move from left to right (i.e., F⁻ to I⁻), the ability of the ligands to expand metal d-electron cloud in the region of ligand orbitals increases and hence delocalisation of metal d-electrons into ligand orbitals also increases, which increases covalent character of metal-ligand bond in complexes. Thus, covalent character in M-I bond in iodo complex of a given metal (M) is more than that of M-F bond in fluoro complex of the same metal.

This series is valid for most of the metal ions. The decreasing order of β values from left to right in the series indicates that the complexes having low value of β are covalent in nature.

⇒ Calculation of Δ_o , Dq , Racah parameter (B') & Nephelauxetic ratio (β): Consider ^{Complex ion,} $[Ni(H_2O)_6]^{2+}$

$$\text{Racah parameter of a metal ion in a complex ion } (B') = B(1 - h_M k_L) \times 10^3$$

For Ni²⁺, B = Racah parameter of free Ni²⁺ ion = 1080 cm⁻¹, $h_M = 0.12$, $k_L = 1.4$

$$\therefore B' = 1080(1 - 0.12 \times 1.4) \times 10^3 = 1080(1 - 0.168) \times 10^3 = 1080 \times 0.832 \times 10^3 = 898.56 \times 10^3 \text{ cm}^{-1}$$

$$\text{Nephelauxetic ratio } (\beta) = \frac{B'}{B} \quad \therefore \beta = \frac{898.56 \times 10^3}{1080} = 0.832 \times 10^3 = 832.$$

* Crystal field stabilization energy for Octahedral complexes, $(CFSE)_{oct} = \Delta_o = +0.6n_{eg} - 0.4n_{t_{2g}}$
(where n_{eg} = number of electrons in e_g set, $n_{t_{2g}}$ = number of electrons in t_{2g} set of d orbitals)

$$\Delta_o = 10Dq \quad \& \quad \Delta_t = 4/9 \Delta_o \text{ or } 4.5 Dq.$$

$[Ni(H_2O)_6]^{2+}$ has Ni²⁺ ion (d⁸-system)

Ele. Conf of Ni²⁺ in the complex ion: $t_{2g}^6 e_g^2$

Here $n_{t_{2g}} = 6$, $n_{eg} = 2$

$$(CFSE)_{oct} \Delta_o = +0.6n_{eg} - 0.4n_{t_{2g}}$$

$$\therefore \text{Change of energy in } \Delta_o = +0.6 \times 6 - 0.4 \times 2 = 3.6 - 0.8 = 2.8.$$

$$\text{Change of energy in } Dq = 2.8 \times 10 = 28.$$

⇒ Assignments for students:-

1. Calculate CFSE in Δ_o & Dq for $[Co(NH_3)_6]^{3+}$ ion.
2. Calculate the value of Racah parameter (B') & Nephelauxetic ratio (β) for $[Fe(en)_3]^{3+}$.
Given: Racah parameter of the free Fe³⁺ ion = cm⁻¹, $h_M = 0.24$, $k_L = 1.5$.

