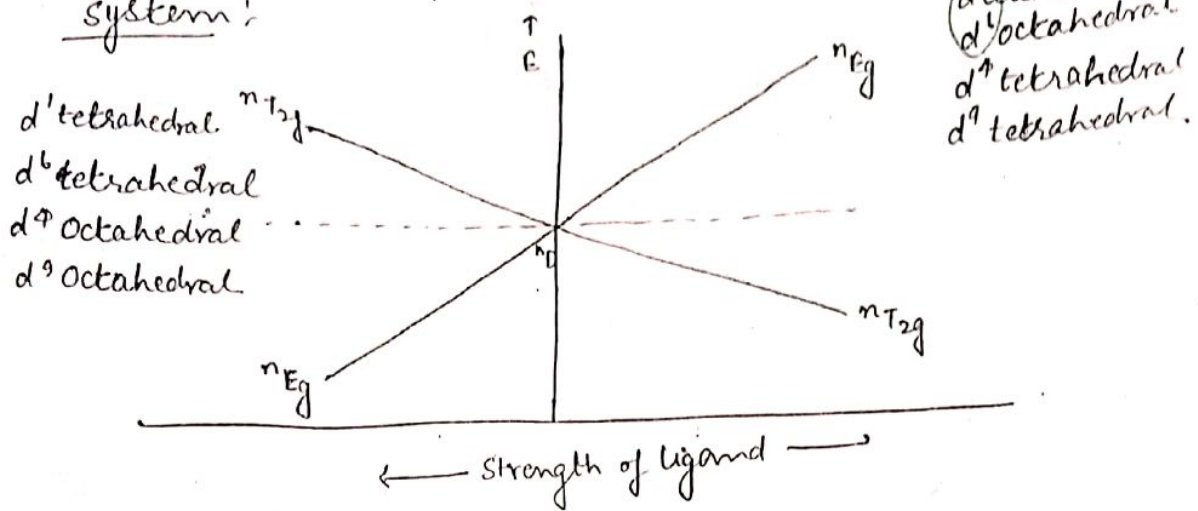


Combined ~~crystal field~~ Orgel diagram for d^1, d^4, d^6, d^9 system:



\Rightarrow d^2 system \rightarrow e.g. $[V(H_2O)_6]^{+3}$

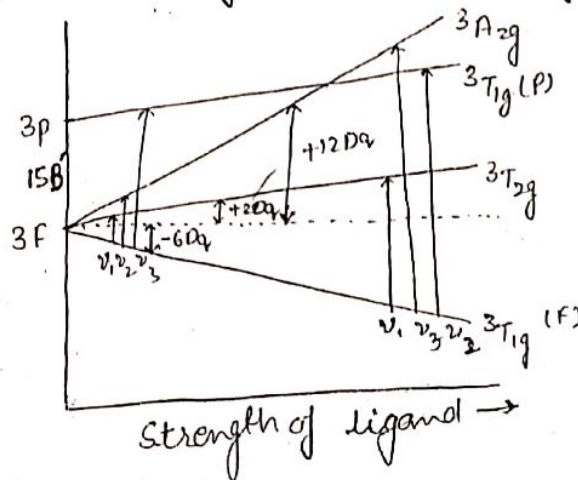
$^{23}V = 3d^3, 4s^2$
 $V^{3+} = 3d^2$

G.S. term = 3F
 other terms = $^3P, ^1D, ^1F, ^1S$

\Rightarrow 3P term splits, in oct. field into $^3A_{2g} + ^3T_{1g}(F) + ^3T_{2g}$

f-degeneracy = 7

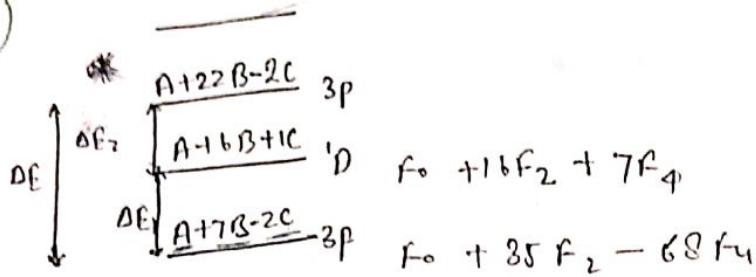
3P term transforms into $^3T_{1g}(P)$



(B') inter electronic repulsion parameter

Condon Shortley parameter. F_0, F_2, F_4
 Racah Parameter. A, B, C

(eg)



energy gap (ΔE_2) = $(A+6B+1C) - (A+7B-2C)$
 $= -B + C$

$\Delta E_2 = 16B - 3C$

$\Delta E = 15B$ transition only possible betⁿ the the ~~ground~~ terms having same multiplicity.

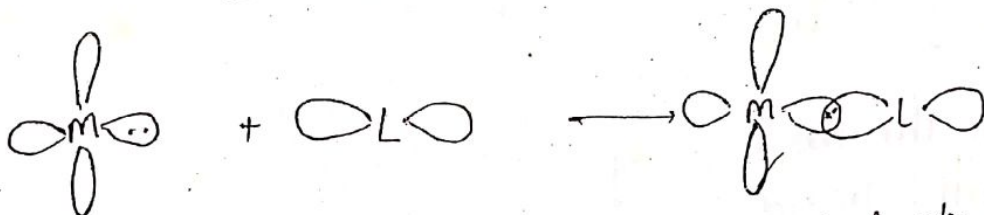
$\Rightarrow B =$ Inter electronic repulsion parameter in a free metal ion.

$B' =$ Inter electronic repulsion parameter in a complex.

$\therefore \beta = \frac{B'}{B}$

where, $\beta =$ nephelauxetic ratio
or covalency parameter

$B' < B$



free metal ion
 B'

B metal atom
 in complex

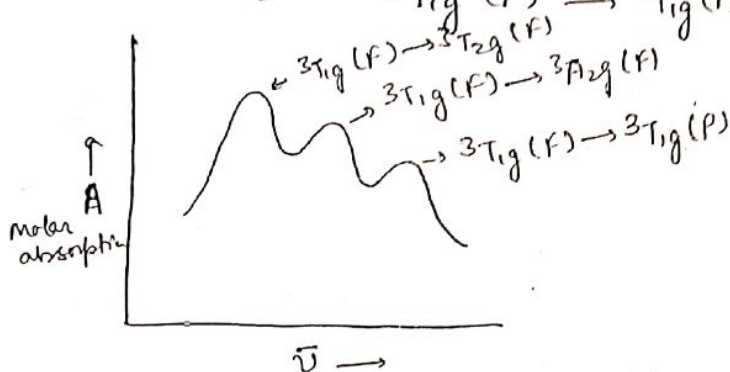
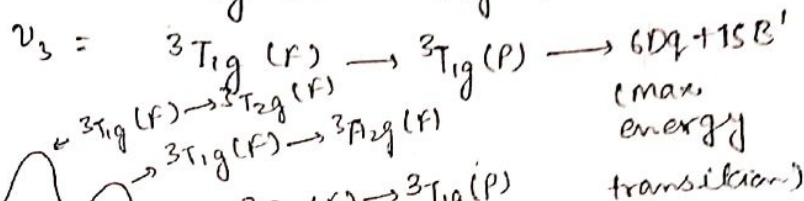
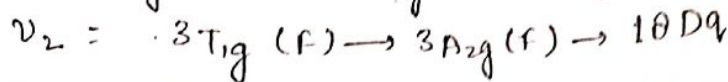
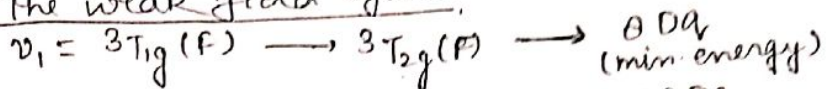
In this case of complex the molecular orbitals are formed which provided greater space to travel.

* β is always less than 1.

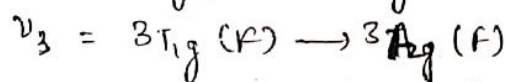
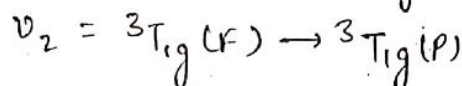
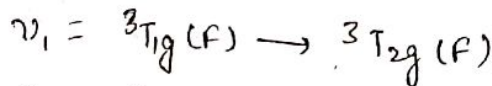
* Smaller the value of β greater is the covalent character.

→ Three peaks are obtained in the electronic spectra.

for the weak field ligand:



for strong field ligand:

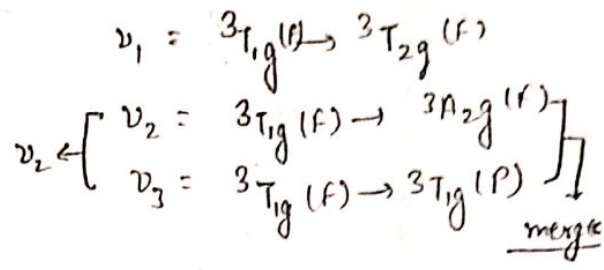
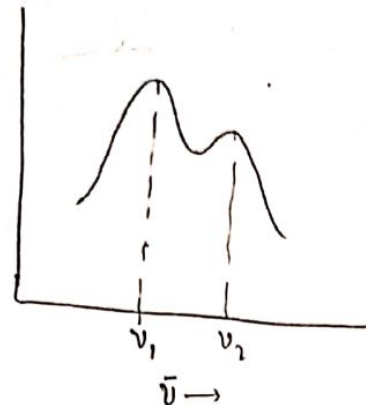
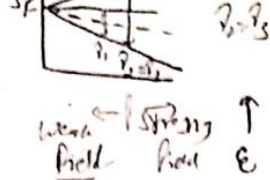


* As the strength of the ligand increases the band assignment are changed.

Net 2mc8

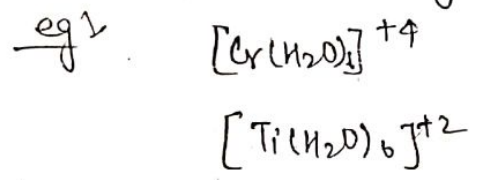
Que: Why the complex $[V(H_2O)_6]^{+3}$ show only two peaks?

Ans solⁿ: The water ligand has strength near or approximately equal to the crossover point i.e. the energy difference is very small, then for the two peaks of higher frequency are merged & we have only two peaks.



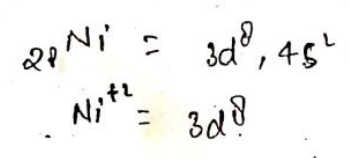
$\rightarrow \frac{e g h}{[V F_6]^{3-}} \rightarrow 3 \text{ bands (weak field ligand)}$
 $[V(NH_3)_6]^{3-} \rightarrow 3 \text{ bands (strong field ligand)}$

* But if we keep the water ligand as such but if we change metal atom then in that case we also get ~~the~~ 3-bands.

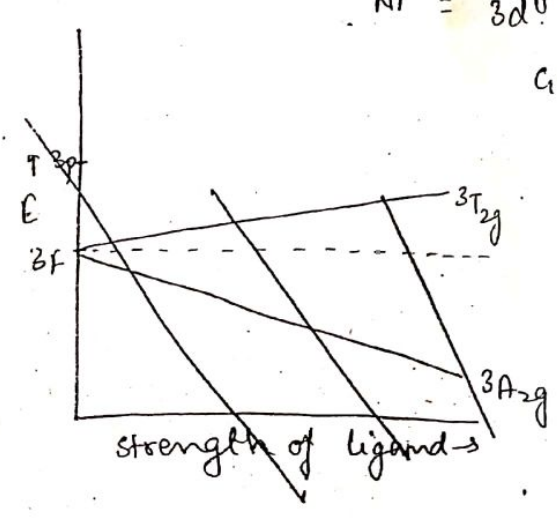


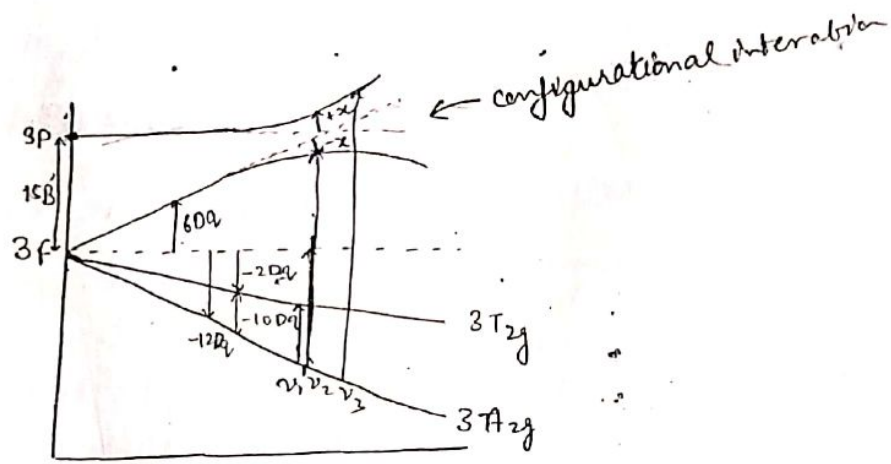
Due to change of oxidation state the spectrum is also changed because in every case the energy is changed

\rightarrow d^8 system:-



C.S. term = $3F$
 other terms = $3P, 1D, 1F, 1G, 1S$



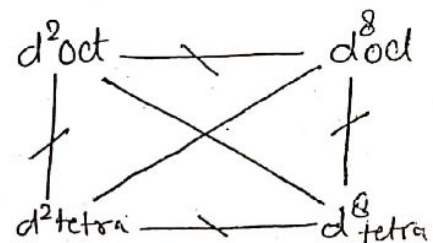
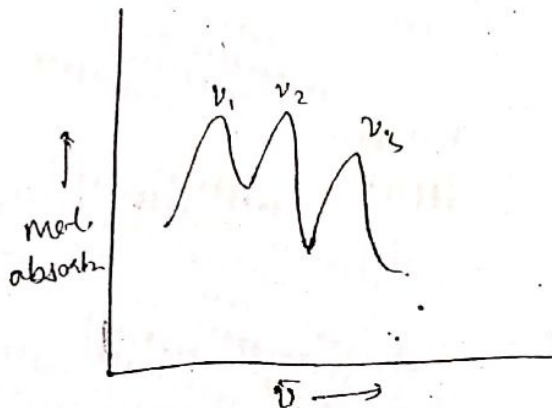


\Rightarrow Configurational Interaction or non crossing rule
 When the two terms having same configuration when come close to each other then they interact in such a way that energy of one term is decreased (i.e. stabilised) & other term is increased (or destabilised). This is called configurational interaction. Due to which this two state does not cross each other this is called the non crossing rule.

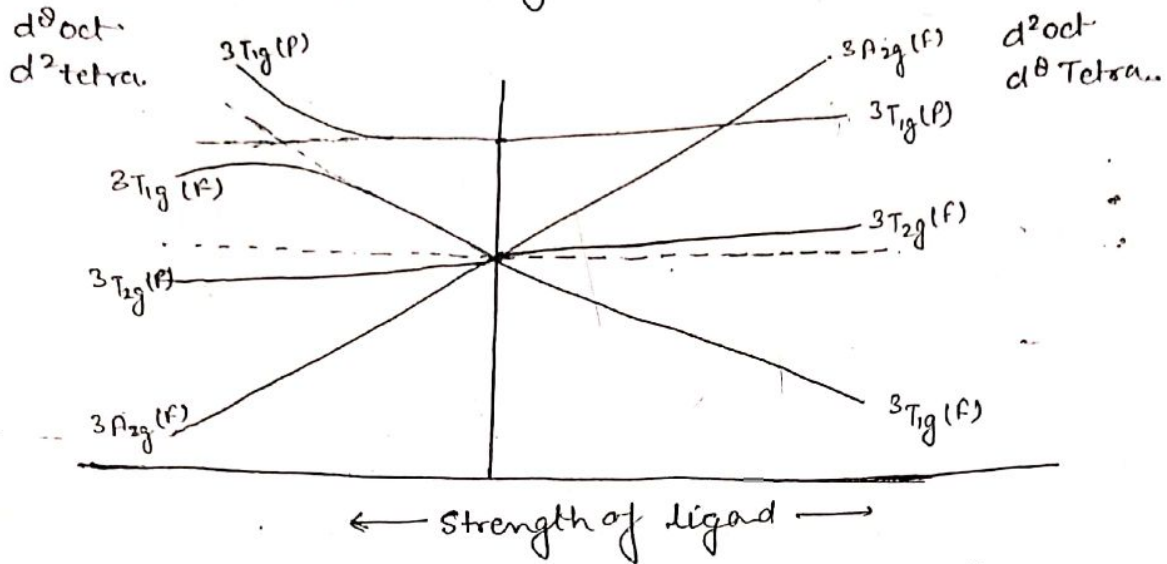
$$v_1 = 3A_{2g} \rightarrow 3T_{2g} = 10Dq$$

$$v_2 = 3A_{2g} \rightarrow 3T_{1g}(F) = 10Dq - x$$

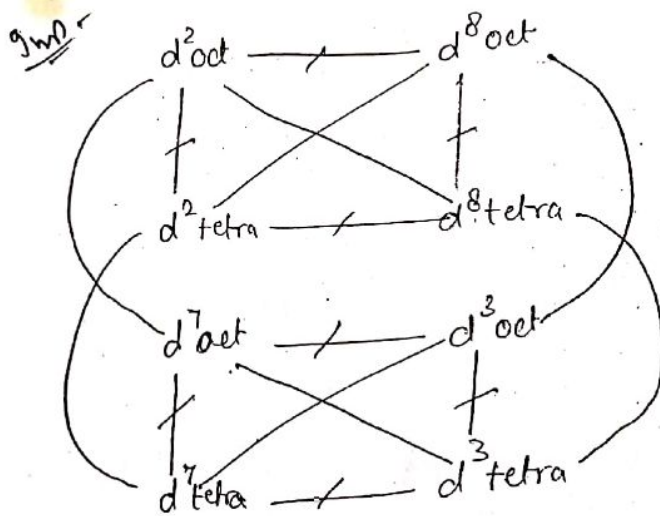
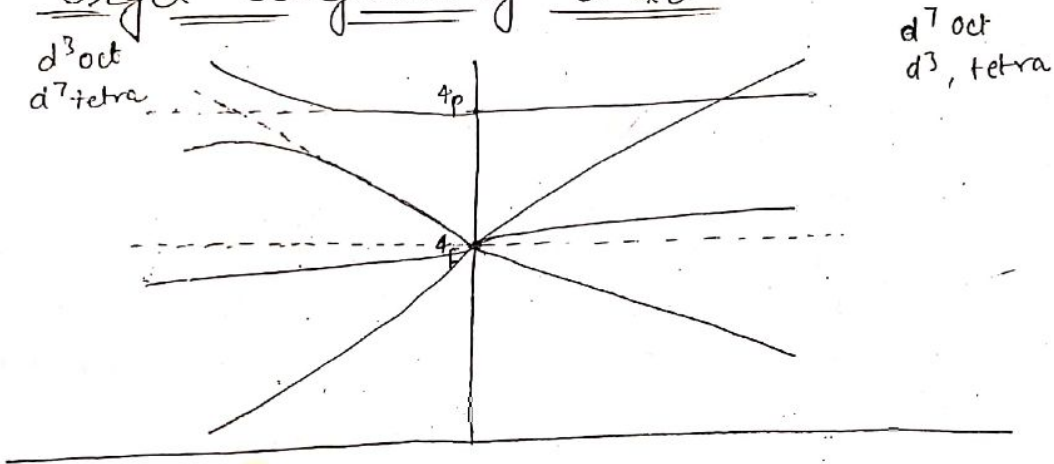
$$v_3 = 3A_{2g} \rightarrow 3T_{1g}(P) = 10Dq + 15B' + x$$



~~Complex~~
Combined Orgel Diagram for d^2 & d^8 system



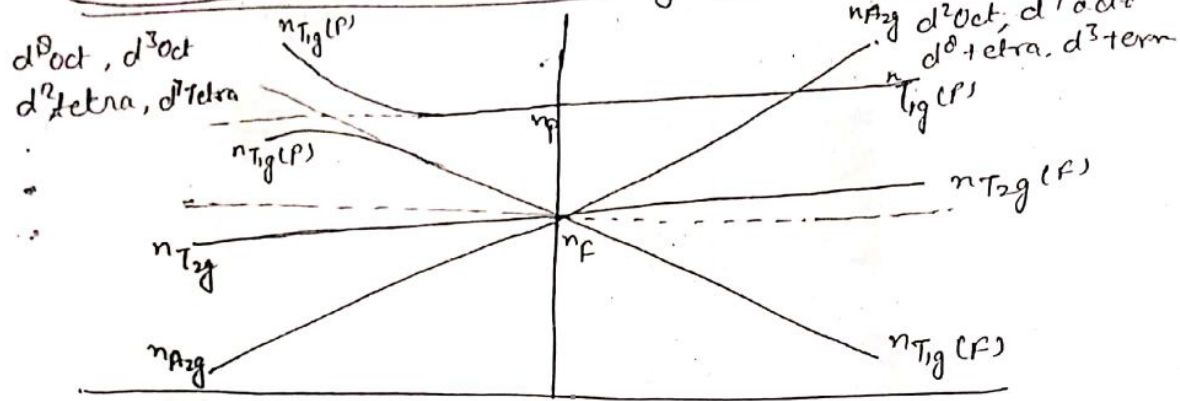
\Rightarrow Orgel diagram of d^3 & d^7 \Rightarrow



d^2 T
 d^7 T
 8T
 8D

d^3 O
 d^7 T
 8S
 2T

→ combined Octahedral diagram of d^2, d^3, d^7, d^8 :



→ $[CrF_6]^{-3}$ It shows three transitions at 14900cm^{-1} , 22700cm^{-1} & 34400cm^{-1}

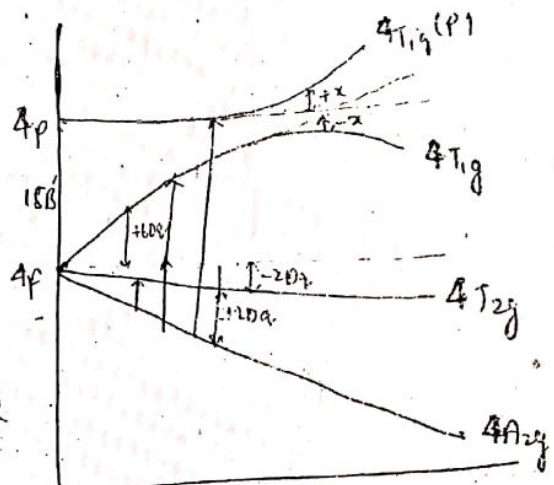
- (i) Calculate the value of Δ_o or $10Dq$ for this complex
- (ii) Calculate CFSE
- (iii) Calculate interelectronic repulsion parameters (e^2, f^2)
- (iv) β
- (v) covalency parameter.
- (vi) Bending constt.

Solⁿ → $Cr = 3d^5, 4s^1$
 $Cr^{3+} = 3d^3$
 G.S. term = $4F$

$$v_1 = {}^4A_{2g} \rightarrow {}^4T_{2g} = 10Dq$$

$$v_2 = {}^4A_{2g} \rightarrow {}^4T_{1g} = 18Dq - x$$

$$v_3 = {}^4A_{2g} \rightarrow {}^4T_{1g}(P) = 15B' + 12Dq - x$$



(i) $10Dq = 14900 \text{ cm}^{-1}$

(ii) \therefore for d^3 system CFSE = $-12Dq$

$\therefore 10Dq = 14900 \text{ cm}^{-1}$

$\therefore -12Dq = \frac{14900}{10} \times (-12)$

$= -17880 \text{ cm}^{-1}$

$$\begin{array}{r} - - - \\ \hline + + + \end{array}$$

(iii) $\therefore 10Dq = 14900 \text{ cm}^{-1}$

$\therefore 10Dq = \frac{14900}{10} \times 10 = 26820 \text{ cm}^{-1}$

If there is no configurational interaction the value of $\nu_2 = 26820 \text{ cm}^{-1}$

But we have a lower value of $\nu_2 = 18000$
This means there is configurational interaction

\therefore the value of $\beta = 26820 - 22700$
 $= 4120 \text{ cm}^{-1}$

\therefore from eqⁿ

$12Dq + 15\beta' + x = 34400$

$\Rightarrow 17880 + 15\beta' + 4120 = 34400$

2) $15\beta' = 34400 - 22000$

2) $15\beta' = 12400$

2) $\beta' = 826.66 \text{ cm}^{-1}$

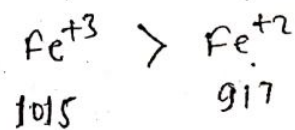
(iv) $\beta = \frac{\beta'}{B}$

2) $\beta = \frac{826.66}{918}$

2) $\beta = 0.90$

($\because B = 918$ for Cr^{+3})

As the oxidation state increases value of B also increases



(V) Covalency parameter.

$$\begin{aligned} &= (1-\beta) \times 100 \\ &= (1-0.9) \times 100 \\ &= 10\% \end{aligned}$$

(VI)

Bending constt. $x = 4120 \text{ cm}^{-1}$

$$\div \boxed{15 B' = \nu_3 + \nu_2 - 3\nu_1}$$

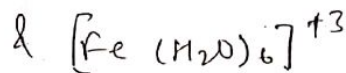
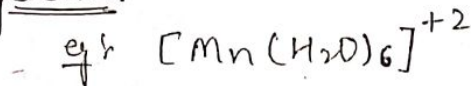
$$= 34400 + 22700 - 3(14900)$$

$$= 57100 - 44700$$

$$= 12400$$

$$\boxed{B' = 827 \text{ cm}^{-1}}$$

\div d^5 system:



g.s. Term \div $6s$ ——— $6A_{1g}$

other terms $\xrightarrow{\text{multip}}$ $4 \rightarrow 4I, 4H, 4P, 4G, 4D, 4F$

$2 \rightarrow 2p$

↓

d-d transition for d^5 system

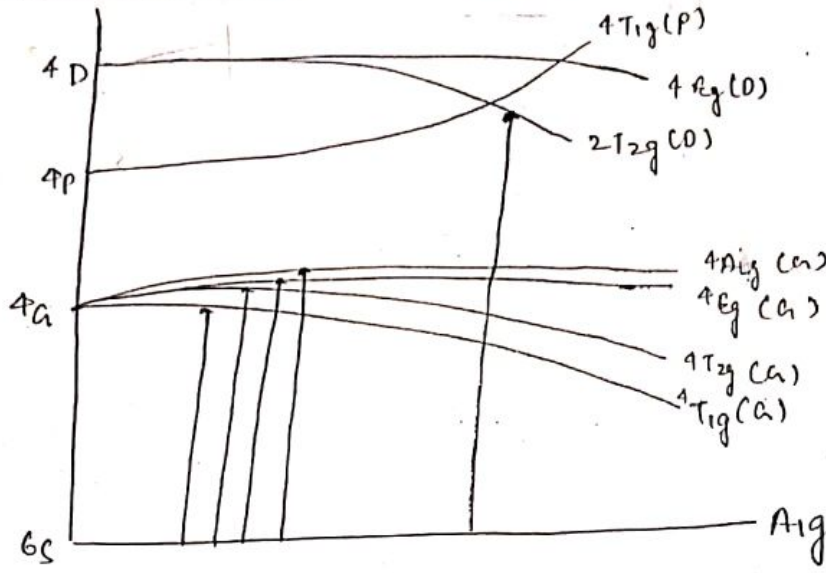
↓

Laporte forbidden Transition

Spin forbidden Transition

Therefore, allowed transition in d^5 system = 0

\div But there is some forbidden transition due to which we obtained the pinkish colour of $[\text{Mn}(\text{H}_2\text{O})_6]^{+2}$.



- 6A_{1g} → 4T_{1g}(G) 18900 cm⁻¹
- 4T_{2g}(G) 23900 cm⁻¹
- 4E_g(G) 24970 cm⁻¹
- 4A_{1g}(G) 25300 cm⁻¹
- 4T_{2g}(D) 28000 cm⁻¹
- 4E_g(D) 29700 cm⁻¹
- T_{1g}(P)

These all are not allowed.

