M.Sc Chemistry
Inorganic Chemistry
Semester-II

Course Title: Chemistry of d and f block elements

Course Code: 201-B

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Inorganic Group III and IV

REFERENCE BOOKS:

1. Electronic Spectra of Transition Metal Complexes by D. Sutton
2. Introduction to Ligand Field Theory: Figgis
3. Concise Inorganic Chemistry by J. D. Lee

Tanabe Sugano Diagram

Though it is possible to add low-spin states to an Orgel Diagram, Tanabe Sugano diagrams are commonly used instead for interpretation of spectra including both weak and strong fields.

Tanabe Sugano diagrams are similar to Orgel diagrams in that they show how energy levels change with Δo, but they differ in several ways:

1.
- **Ground State is taken as the abscissa and provides a constant reference point. The other energy states are plotted relative to this.**

2.
- **Low spin terms i.e. states where the spin multiplicity is lower than ground state are included.**

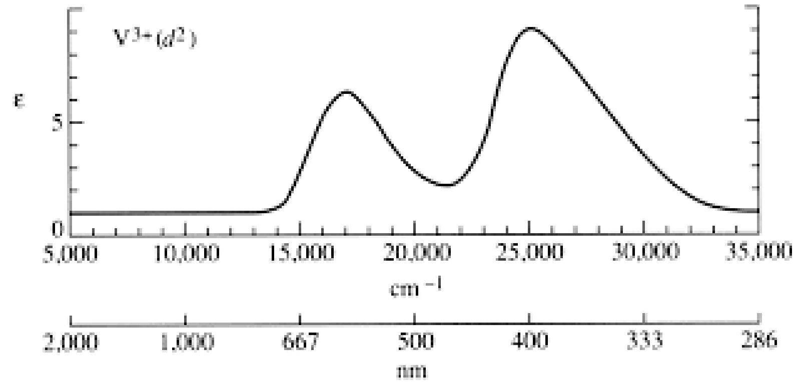
3.
- **In order to make the diagrams general for different metal ions with same electronic configuration and to allow for different ligands energy/B is plotted against $\Delta o/B$**

Difference between Orgel and Tanabe-Sugano Diagrams

Sl. No	ORGEL	TANABE-SUGANO
1	Weak Field	Weak-Strong Field
2	Spin Allowed	Spin allowed and forbidden
3	E v/s CFS	E/B vs Δ_o/B

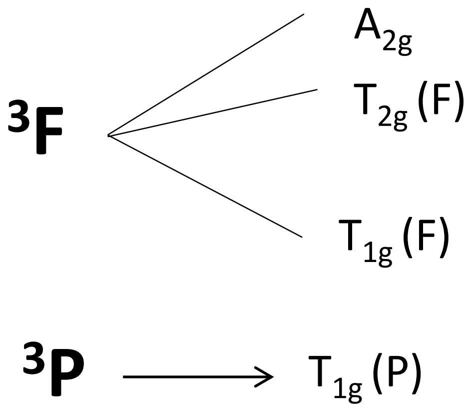
Tanabe Sugano Diagram for d^2 system

$[V(H_2O)_6]^{3+}$ Green and 2 bands: 17100 cm^{-1} and 25200 cm^{-1}



d^2 configuration:

^3F, ^3P, ^1D, ^1G, ^1S



Possible Arrangements are:

dxy^1 dyz^1 dxz^o
dxy^1 dyz^0 dxz^1
dxy^0 dyz^1 dxz^1

T_{1g} (F)

When one electron gets promoted:

$d_{xy}^1\ d_{z2}^1$
$d_{yz}^1\ d_{x^2-y^2}^1$
$d_{zx}^1\ d_{x^2-y^2}^1$

T_{2g} (F)

$d_{xy}^1\ d_{x^2-y^2}^1$
$d_{yz}^1\ d_{z2}^1$
$d_{zx}^1\ d_{z2}^1$

T_{1g} (P)

When both electrons get promoted:

$d_{x^2-y^2}^1\ d_{z2}^1$

A_{2g} (F)

Lower energy band is assigned to transition:

$^3T_{1g}$ (F) $\longrightarrow$ $^3T_{2g}$ (F)

Then a rough estimate of position of

$^3T_{1g}$ (F) $\longrightarrow$ $^3A_{2g}$ (F) can be made because in strong field limit, these transitions are

$(t2g)^1(eg)^1$ $\longleftarrow$ $(t2g)^2$ (E= Δ_o) and

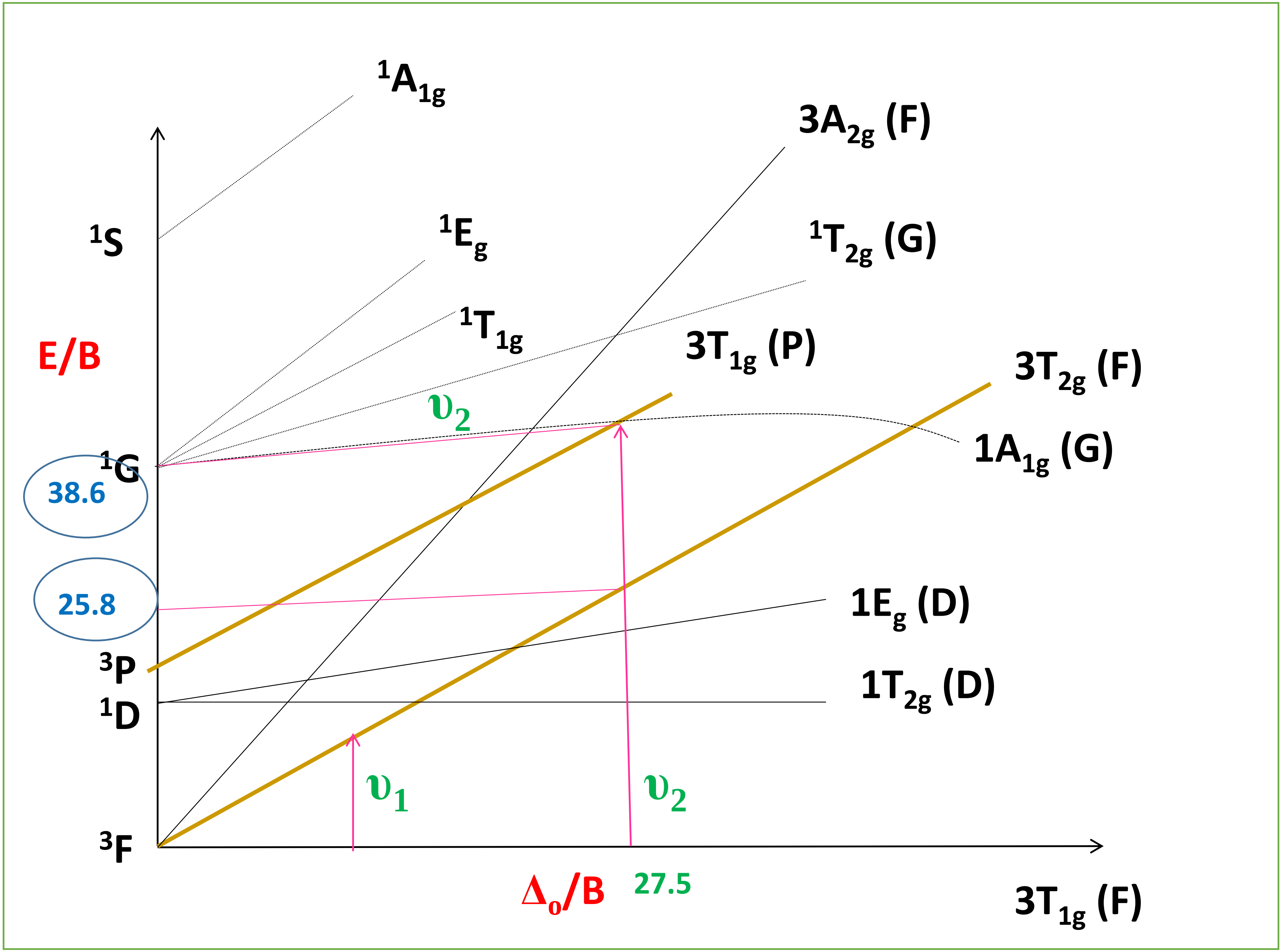
$(eg)^2$ $\longleftarrow$ $(t2g)^2$ (E= $2\Delta_o$)

So, if electron gets excited from

T_{1g} (F) $\longrightarrow$ A_{2g} (=2 x Δ_o)

(=34200 cm^{-1})

But second absorption is 25, 200 cm^{-1} which is much less than 34, 200 cm^{-1}.

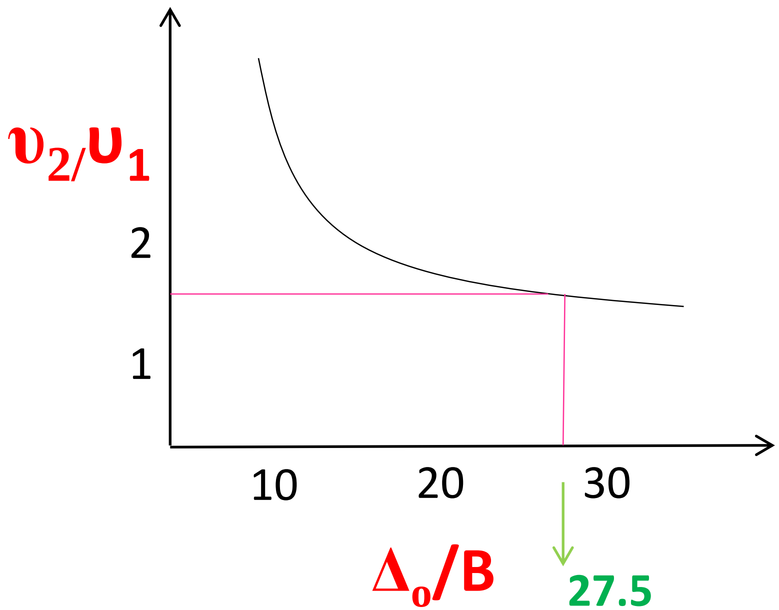


1A1g
3A2g (F)
1S
1Eg
1T2g (G)
1T1g
E/B
3T1g (P)
3T2g (F)
υ2
1A1g (G)
1G
38.6
25.8
1Eg (D)
3P
1D
1T2g (D)
υ1
υ2
3F
Δo/B
27.5
3T1g (F)

$\upsilon_{2}=$ E[$3T_{1g}(P) \leftarrow 3T_{1g}(F)$] $\upsilon_{1}=$ E[$3T_{2g}(F) \leftarrow 3T_{1g}(F)$]

Ratio

$$\frac{\upsilon_2}{\upsilon_1} = \frac{25200}{17100} = 1.47$$



For First Transition:

E/B=25.8

For second transition:

E/B=38.6

E[3T2g(F)]= 25.8 x B

= 25.8 x 860

= 22188 cm-1

E[T1g(P)]= 38.6 x 860

= 33196 cm-1

These values of υ1 and υ2 are higher as B we are using for free V^{3+}

Now to see how much υ_1 and υ_2 are varying

First Band= $E_{calculated}$/ E $_{Observed}$

= 22188/17100

= 1.3

Second Band= 33200/25200

=1.3

We have accounted for 1.3 times higher B.

B’= B/1.3 =860/3= 662 cm^{-1}

Δ_o/B’= 27.5

Δ_o = 27.5 x B’

=27.5 x 662 = 18192 cm^{-1}

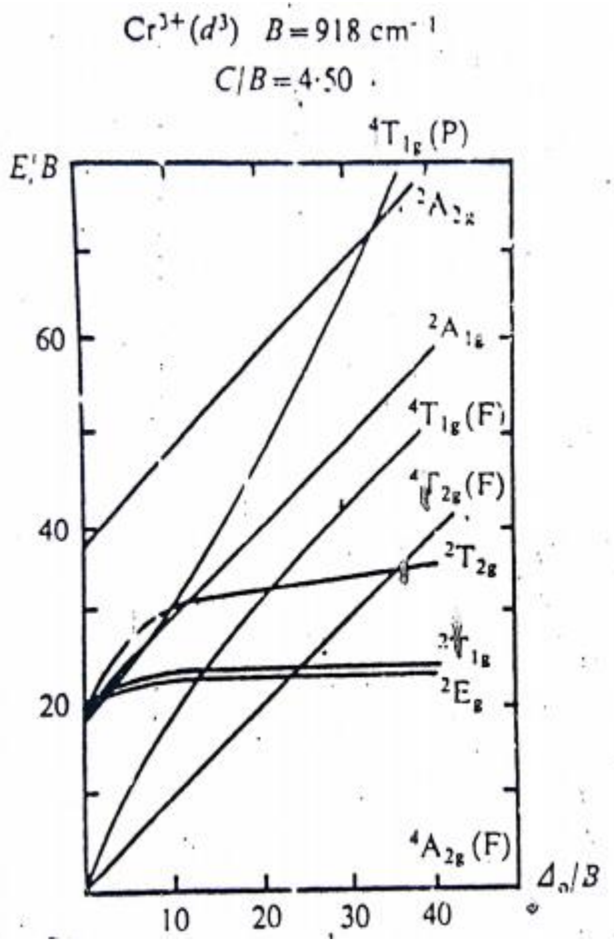
β = B’/ B = 662/860 = 0.77

Q. $[Cr(H_2O)_6]^{3+}$

d^3 configuration

υ_1 = 17400 cm-1, υ_2 = 24600 cm-1, υ_3 = 37800 cm-1

Find Δo, B' and β (B for Cr^{3+} = 918 cm^{-1})



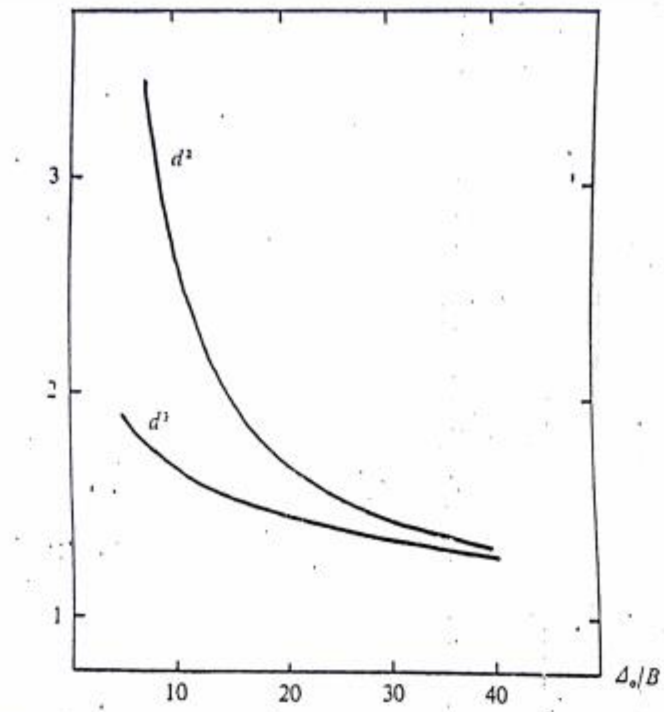


Fig. 4.17. Plot of the energy ratios $[^3T_{1g}(P) - {}^3T_{1g}(F)]/[^3T_{2g}(F) - {}^3T_{1g}(F)]$ for d^2 and $[^4T_{2g}(F) - {}^4A_{2g}(F)]/[^4T_{1g}(F) - {}^4A_{2g}(F)]$ for d^3 against Δ_o/B, taken from the Tanabe-Sugano diagrams

•Ratio of energies of the first two excited states $^4t_{2g}$(F) and $^4T_{1g}$(F) above the gr0und state $^4A_{2g}$(F) is plotted against Δo/B

• Three main d-d bands located (with assignments) at:

	υ (cm^{-1})	ε	Assignment
A	17,400	13.3	$^4T_{2g}$(F) ⟵ $^4A_{2g}$(F)
B	24, 600	15.3	$^4T_{1g}$(F) ⟵ $^4A_{2g}$(F)
C	37, 800	4	$^4T_{1g}$(P) ⟵ $^4A_{2g}$(F)

The ratio of two energy bands A and B is 1.42. This ratio fits with Δo/B=25.0.
From figure, this corresponds to:

E ($^4T_{2g}$(F))= 25.0 B'……………………….(1)

E ($^4T_{1g}$(F))= 35.5 B'……………………….(2)

E ($^4T_{1g}$(P))= 55.5 B'……………………….(3)

$E(^4T_{2g}(F)) = 25.0 \times 918$

$= 22950\ cm^{-1}$

$E(^4T_{1g}(F)) = 35.5 \times 918$

$= 32589\ cm^{-1}$

$\upsilon_1 = E_{calculated}/E_{observed}$

$= 22950/\ 17400$

$= 1.3189$

$\upsilon_2 = E_{calculated}/E_{observed}$

$= 32589/24600$

$= 1.3247$

$B' = B/1.3$

$= 918/1.3$

$= 706\ cm^{-1}$

$\Delta_o/B' = 25.0$

$\Delta_o = 25.0 \times 706$

$= 17653\ cm^{-1}$

$\beta = B'/B$

$= 706/918$

$= 0.7690$

Q. $[CoF_6]^{3-}$ and $[Co(en)_3]^{3+}$ → $\upsilon_1 = 16500\ cm^{-1}$, $\upsilon_2 = 24950\ cm^{-1}$

Strong Field

$[CoF_6]^{3-}$ ↓ $\upsilon_1 = 13000\ cm^{-1}$

Weak Field

d^6 configuration

^5D: Ground state

^1I, ^1F……: Excited states

$^5D \rightarrow {}^5T_{2g}, {}^5E_g$

$^1I \rightarrow {}^1A_{1g}, {}^1T_{1g}, {}^1T_{2g}, {}^1E_g, {}^1A_{2g}$

$^1F \rightarrow {}^1A_{2g}, {}^1T_{2g}, {}^1T_{1g}$

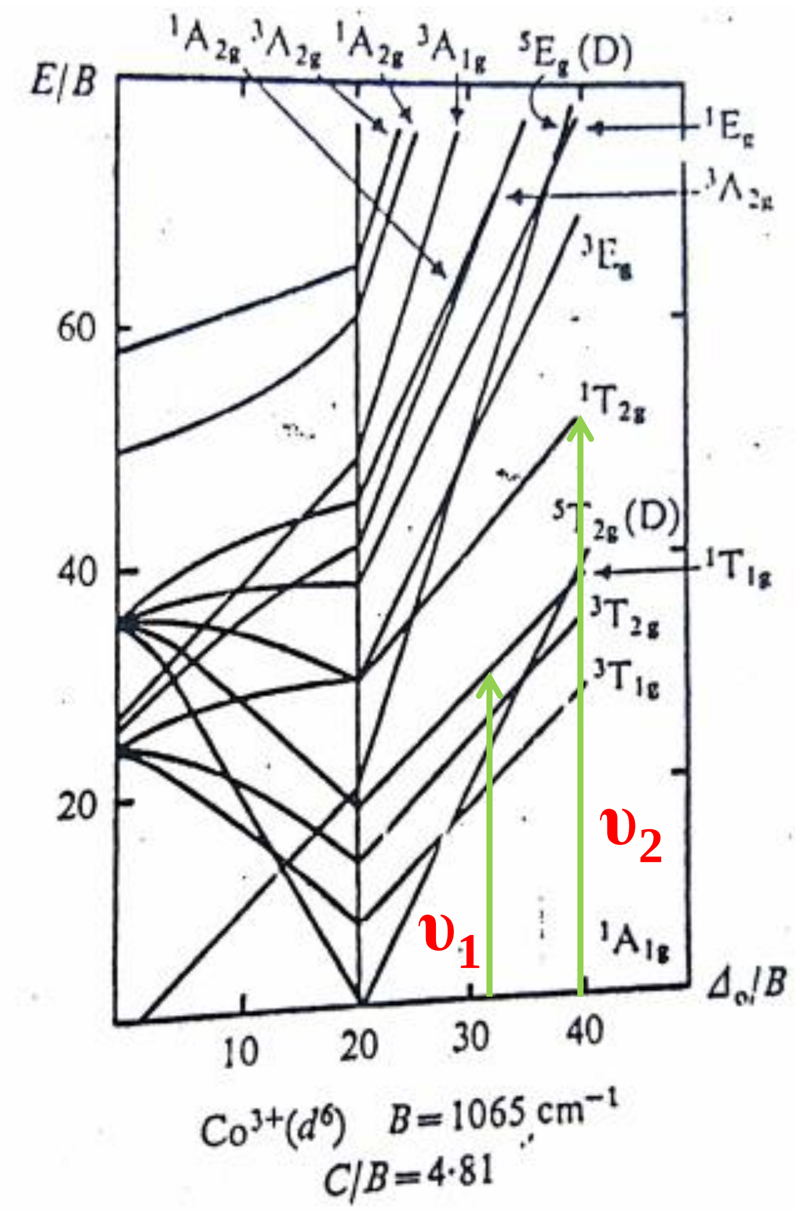
The state of highest multiplicity for d^6 is ^5D and for weak field, there is only 1 spin allowed transition:

$^5T_{2g} \longrightarrow {}^5E_g$

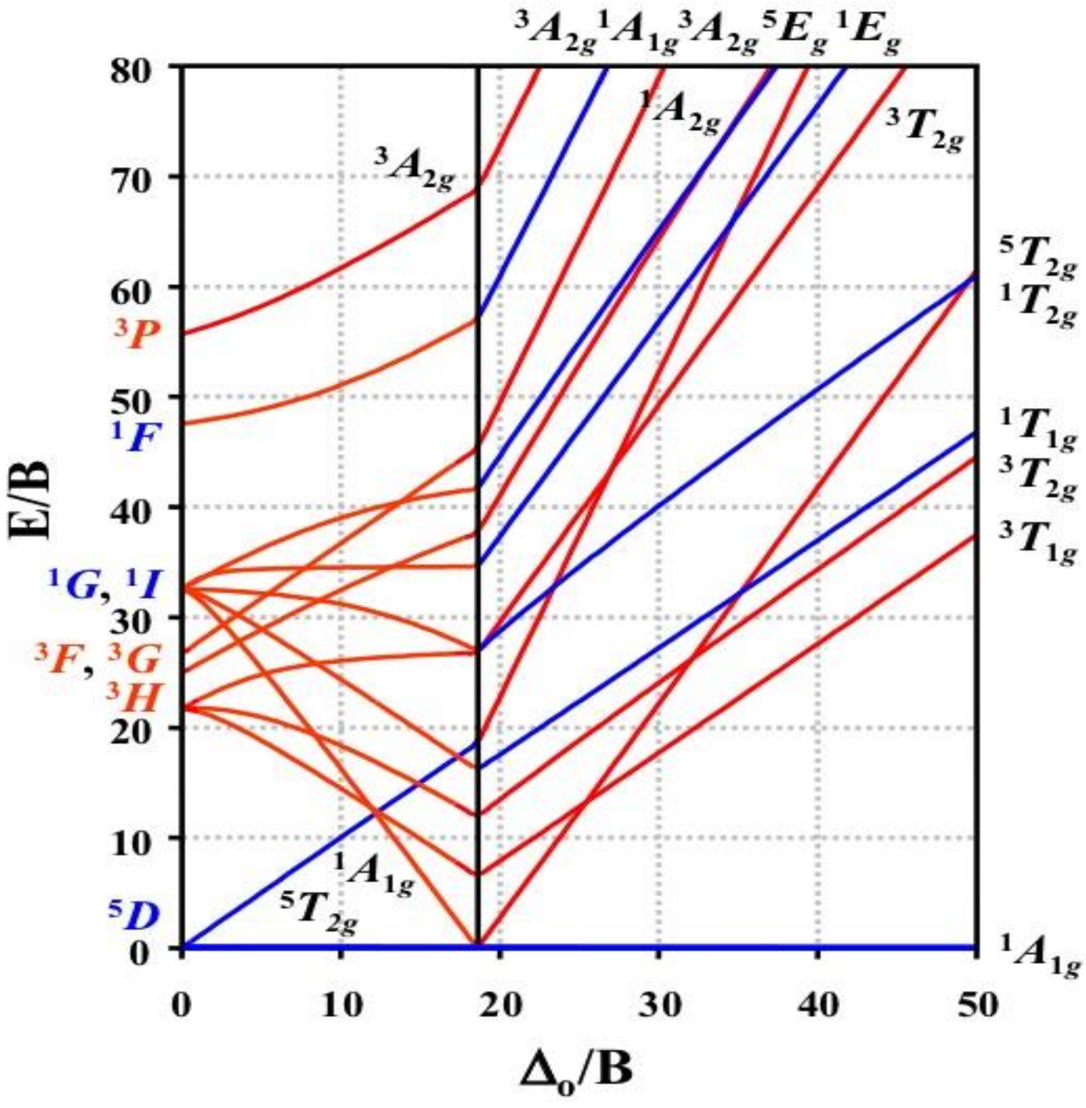
Low spin d^6 complexes possess the orbital singlet ground state $^1A_{1g}$ arising from strong field configuration $(t_{2g})^6$

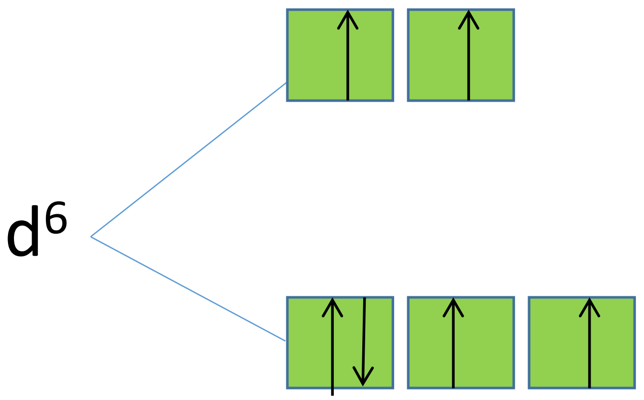
At certain point $^5T_{2g}$ goes higher and $^1A_{1g}$ becomes ground state term.

- Discontinuity is TS diagram indicates that electron starts pairing

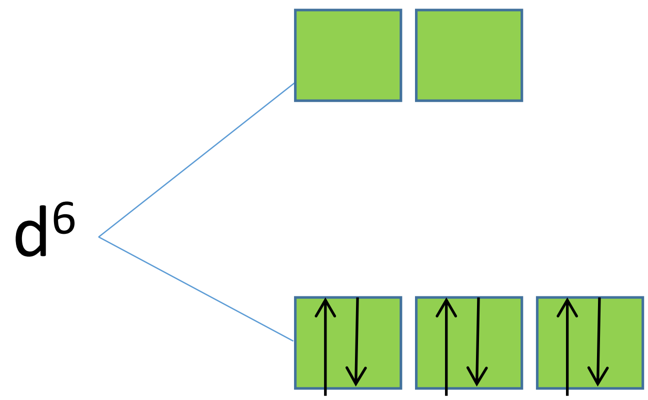


d^6 Tanabe-Sugano Diagram





Weak Field
(same as d^1)



Strong Field
S=0
Singly degenerate
Here G.S term is A_{1g}