Orgel diagrams:

Plotting of Splitting energy versus energy of the field and it is qualification for the assignments of d-d spectra of d-block complexes

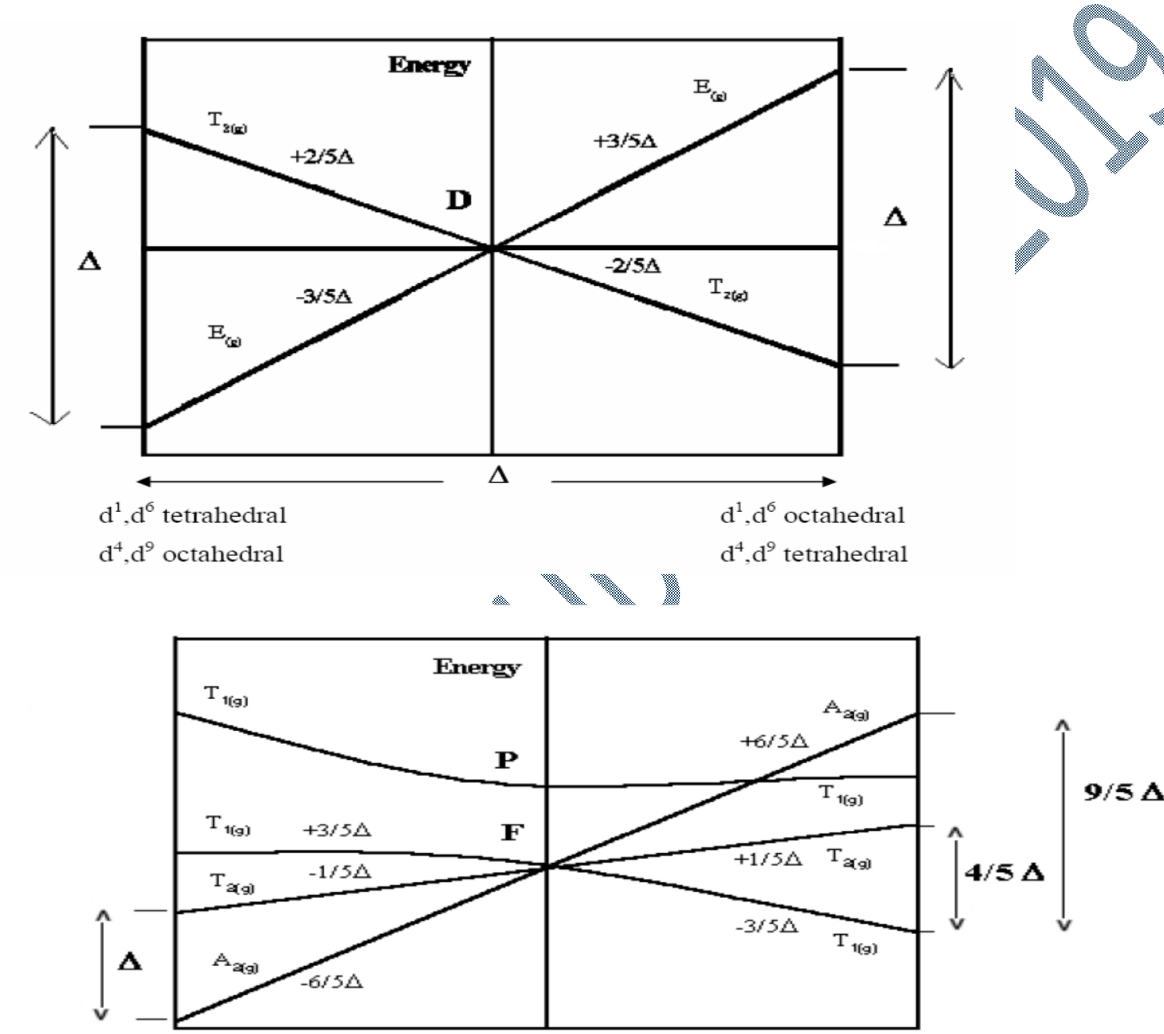

Figure 1.Orgel diagram for some states in d-block

Tanabe-Sugano diagrams:

Appear much more "busy" than Orgel diagrams because they contain all terms arising from a configuration, not just terms of highest spinmultiplicity. Appear different than Orgel diagrams because they use the ground symmetry state as a straight-line horizontal base, whereas Orgel diagrams place the parent term in a central location and direct ground symmetry states below it. Appear "split" for d^4, d^5, d^6, d^7, cases because both low and high spin symmetry states are included. Consequently, these diagrams appear to be discontinuous - having two parts separated by a vertical line. The left part pertains to the weak field /high spin condition and the right to strong field/ low spin.

First note why d^1 and d^9 cases have no T-S diagrams. A term description for an atom/ion is more informative than its electron configuration because terms account for e-e repulsion energies. However there is no e-e repulsion for one "d" electron so the d^1 configuration gives rise to a single term, ^2D. In Oh and Td ligand fields this single term is split into T_{2g}, E_g, or E, T_2 symmetry states respectively. Only one absorption band is expected and energy of the observed band gives the Δ_o or Δ_{Td} value directly. No calculations are necessary, so no T-S diagram for d^1 (and d^9).

Table(1). Splitting of terms for d^n configuration.

Configuration Free	G,.S	Energy level	Predicted

ion		Diag	assignments
d^3	F^4	Reverted b	ν_1=10 Dq ν_2=18Dq-x ν_3=12Dq+15B`+x
d^7	F^4	(b)	ν_1=8Dq ν_2=18Dq ν_3=6Dq+15B`
d^8	F^3	Reverted (b)	ν_1=10 Dq ν_2=18Dq-x ν_3=12Dq+15B`+x
d^9	D^2	Inverted (a)	ν_1=10Dq

Also to measure the tendency of metal ion to form a complex Jorgenson rule have been used, the *g* factors provide an estimate of the value of 10Dq for an octahedral complex when combined with the *f* value for the appropriate ligands:

10Dq = *f* ligand × *g* ion ………………………………………………(1)

Table(1). Splitting of terms for d^n configuration.

Transition element	Value of *g*	Ligands	Value of *f*
Cr^{3+}	17.7	Cl^-	0.78
Co^{2+}	9.00	Tartaric acid	1.14
Ni^{2+}	8.7	H_2O	1.00
Cu^{2+}	12.5		

In units of k (k=1000 cm-1).

If all three transitions are observed, it is a simple matter to assign a value to B`, since the following equation must hold; (B` is in cm-1 units).

15B`= ν3+ ν2–3 ν1 ……………………………………………(2)

The *nephelauxetic* ratio *β* is given by:

β= B`/B. ……………………………………..…..(3) Where ‘B’ is Racah parameter.

Example calculation for chromium(III) complexes:

Two bands are observed within the range of measurement. They have maxima at 17605 and 23419 cm-1. these are spin- allowed laporteforbidden d-d transfers. Chromium is in the +3 oxidation state, so this is a d3 system. Reference to Orgel diagram Figure (4-2) informs that three bands are expected and they can be assigned as:

ν 1 = 4A2g (F) $\rightarrow$ 4T2g (F)

ν 2 = 4A2g (F) $\rightarrow$ 4T1g (F)

ν3 = 4A2g (F) $\rightarrow$ 4T1g (P)

Δo is taken to equal the absorption energy of 17605 cm-1, and the intersect on the x-axis of Tanabe-Sugano diagram equal Δo/B. and by drawing a vertical line from this point it will intersect with other allowing electronic state of Tanabe-Sugano diagram for d3 .

There are several goals sought in analyzing spectra using Tanabe-Sugano diagram:

1- To make correct band assignments. The two bands observed could be the first and second, or the second and third. Their assignment cannot be made by inspection.

2- To determine the magnitude of the ligand field splitting parameter, Δo

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3- To determine the magnitude of the e-e repulsion parameter (called a *Racah **B** parameter*).

Assumes bands are the first and second (so third band is not observed). Compare the two results. Tanabe-Sugano diagrams are unit less graphs showing energy ratios. The abscissa shows values for the ratio Δo/B (i.e., ligand field splitting parameter / e-e repulsion parameter).

Step (1): the calculated ratio of experimental band energy is: E (υ2), E (υ1),

Δ/B intersection with 4T2g at (E/B) = 32

Δ/B intersection with 4T1g at (E/B) = 42.53

B via ν1 =17605 cm-1 /32.00 = 550 cm-1.

B via ν2 =23419 cm-1 /42.53 = 550.6 cm-1.

Then B = 550.3 cm-1.

B free-ion =918 cm-1.

To determine the ν3; Δ/B intersection with 4T1g (P) at (E/B) = 86.47

ν3 = 86.47$\times$ 550 cm-1

= 37702.7 cm-1

= 265.23 nm

And by using the equations of splitting of term for d3 in Table (A-2), we can determine the B` and β as following:

ν1=10 Dq.

17605 cm-1= 10 Dq
Dq = 1760.5 cm^{-1}