

❖ Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes ($d^1 - d^9$ States)

It is a well-known fact that electronic transitions are always accompanied by vibrational as well as rotational changes which results in a considerable broadening of the bands in the UV-visible spectra of transition metal complexes too. The nature of these transitions is quite complex to understand and requires some basic knowledge of quantum mechanics and chemical applications of group theory.

The selection rules:

The selection rules governing the electronic spectra of transition metal complexes are given below.

1. There should be no change in the number of unpaired electrons. In other words, for all the multiplicity allowed transitions, $\Delta S = 0$. Hence, a triplet-triplet or singlet-singlet transitions will be multiplicity allowed while a singlet-triplet or triplet-singlet will be multiplicity forbidden.
2. If the complex possesses the center of symmetry, all the transitions which do not involve a change of ± 1 in angular momentum quantum number are Laporte forbidden. In other words, in molecular geometries with the centre of symmetry, electronic transitions with $\Delta l = \pm 1$ are Laporte allowed. Hence, are the $d-d$ transitions in free ions as well as in perfectly octahedral environment are Laporte forbidden.

Relaxation of the abovementioned rules can occur through two mechanisms. The first one is the spin-orbit coupling which gives rise to weak spin forbidden bands. The second one is the absence of perfect octahedral geometry due to the presence of a different ligand or vibronic coupling in which a perfect octahedral complex may have some allowance of $d-d$ transitions. vibrations where the molecule is asymmetric and the absorption of light at that moment is then possible. Both of these effects (vibronic coupling or six dissimilar ligands) generally mixes the d and p -orbitals of the transition metal so that the transitions are no longer purely $d-d$ in nature. For example, the tetrahedral $[\text{MnCl}_4]^{2-}$ is colored because it does not possess the centre of symmetry and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ also lacking the center of symmetry due to the presence of one Cl^- ligand, and therefore is colored. However, the perfect octahedral geometries like $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with a d^5 -electronic configuration is expected to be colorless (spin forbidden and Laporte forbidden) but does show a pale-pink color which can be explained in term of slight vibronic allowance.

The splitting of free ion terms:

It is pretty interesting to note that the degeneracy of free-ion terms like 2D or 3F can be removed not only by L-S coupling alone but can also be removed by the perturbation produced by the ligands. Moreover, the wavefunctions for S, P, D, F or G states have the same symmetry as that s , p , d , f or g orbitals sets; which means that the splitting pattern of D and F states will same as d and f -subshell, respectively.

The s -orbital is spherically symmetric in nature and is not affected by any crystal field. Hence, S state also does not get split in any type of ligand field. The p -orbitals are directional in nature and are affected by different types of crystal field differently. Hence, P state may or may not get split in the presence of ligand field. For example, P state does not get split in octahedral or tetrahedral field but does get split in square planar

crystal field. The d -orbitals are also directional in nature and are affected by different types of crystal field differently. Hence, D state does get split in the presence of the ligand field. For example, D state does get split in the octahedral or tetrahedral field with triply and doubly degenerate sets but the splitting pattern and degeneracy are totally different in pentagonal bipyramidal crystal field. The splitting profile of different electronic states in octahedral and tetrahedral crystal fields in the following tables, which will be used very frequently in the further text of this chapter.

Table 7. Splitting of free ion terms in the tetrahedral crystal field.

Electronic state	Symmetry designation in the tetrahedral field (Mulliken symbols)
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$
G	$A_1 + E + T_1 + T_2$
H	$E + T_1 + T_1 + T_2$
I	$A_1 + A_2 + E + T_1 + T_2 + T_2$

Table 8. Splitting of free ion terms in the octahedral crystal field.

Electronic state	Symmetry designation in the octahedral field (Mulliken symbols)
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

The A, E and T represent singly, doubly and triply degenerate states, respectively. The presence of "g" in symmetry designations of the octahedral field is for the gerade or centrosymmetric environment.

Terms correlation in the tetrahedral and octahedral field:

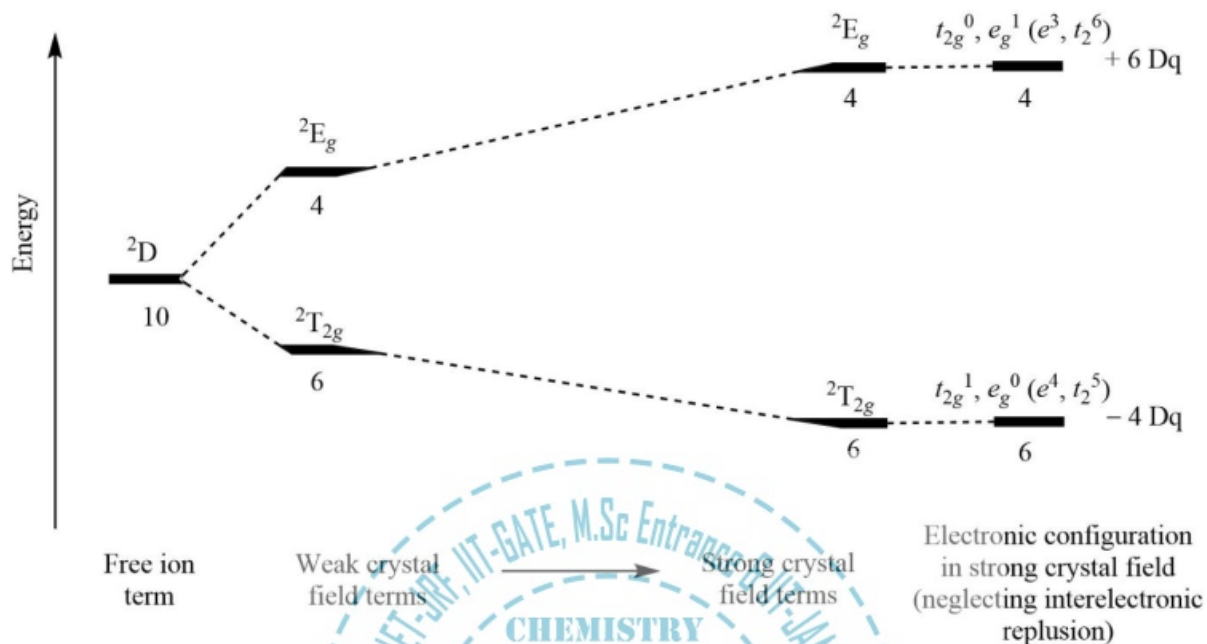
The qualitative description of different energy term for d^n and d^{10-n} configuration, from free ion to strong crystal field configurations ignoring inter-electronic repulsions, can be given as:

1. The total number of energy levels remain the same under the influence of weak and strong crystal fields.
2. The one to one correspondence of different energy levels in a strong crystal field may get stabilized or destabilized in comparison to the weak field case.
3. Energy levels of the same symmetry never cross each other and each level has a contribution in its energy from all other energy states of the same symmetry.
4. Term correlation for d^1, d^9, d^2, d^8 configuration are shown completely while for d^3, d^4, d^5, d^6, d^7 are shown partially by taking only lower energy levels.
5. According to hole formalism, the number of microstates and hence all free ion terms for d^n and d^{10-n} configuration are same. Now, as the magnitude of the crystal field experienced positive electrons is the same as what experienced by the negative electrons, but is of opposite sign. Therefore, the splitting pattern for d^n and d^{10-n} configurations are opposite of each other.
6. Owing to the hole formalism in quantum mechanics, strong field configuration of $t_{2g}^4, t_{2g}^5, e_g^3$ give rise to the same terms as given by the strong field configuration of $t_{2g}^2, t_{2g}^1, e_g^1$. However, weaker inter-electronic repulsion is considered as the perturbation over stronger V_o .
7. The splitting pattern of d^n tetrahedral is just the opposite of what is for d^n octahedral. However, no g or u are used in the tetrahedral case because there is no center of symmetry in a tetrahedral geometry.

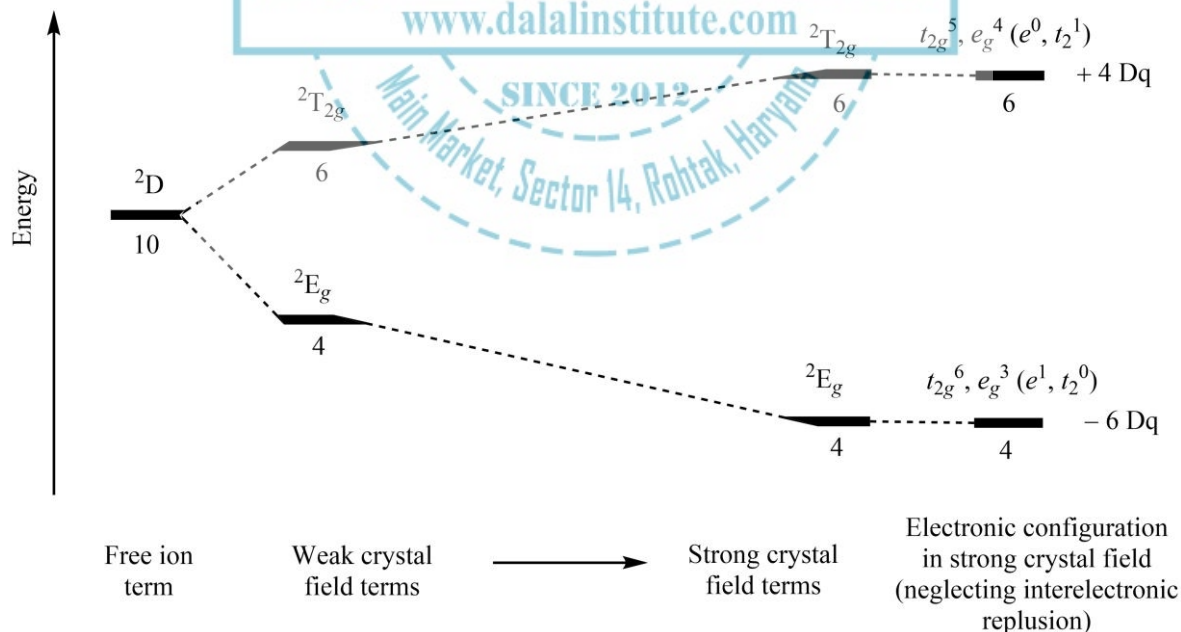
It has already been discussed that the total number of microstates for electronic configuration without inter-electronic repulsion or with inter-electronic repulsion (free ion terms) remains the same. Furthermore, the number of microstates also remains same even in the presence of weak or strong crystal field; and when the inter-electronic repulsion is completely neglected in comparison to the ligand field strength, the calculation of microstates is carried out individually for t_{2g} and e_g set and multiplied afterward to give the total.

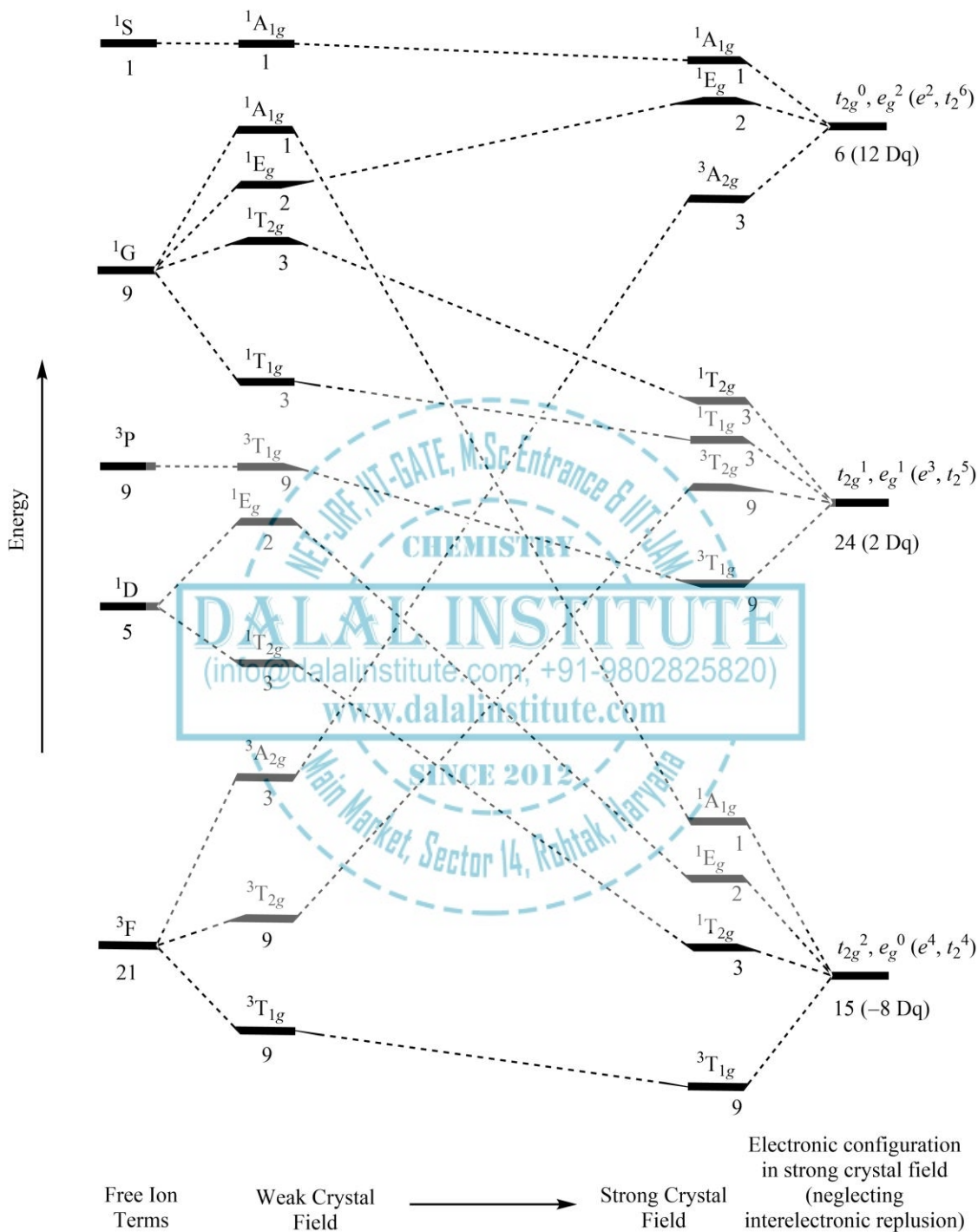
Furthermore, the strength of the crystal field does not alter the ground state Mulliken symbol in the case of d^1, d^9 -octahedral or tetrahedral complexes. However, in the case of d^2 - d^8 electronic configurations, the splitting pattern of free ion term at weak and strong crystal fields is quite different. Generally, the energy of some irreducible component of low multiplicity free ion term decreases so rapidly with the increase in the strength of the crystal field that it becomes the ground state symbol. In other words, the ground state term symbol of metal complexes with d^2 - d^8 electronic configurations is different in weak and strong crystal fields. For example, the ground state term symbol for d^5 -configuration with small ligand field is ${}^6A_{1g}$ (from 6S) but as the magnitude of crystal field increases, the ${}^2T_{2g}$ Mulliken state (from 2I) becomes highly stable and also make up the ground electronic state.

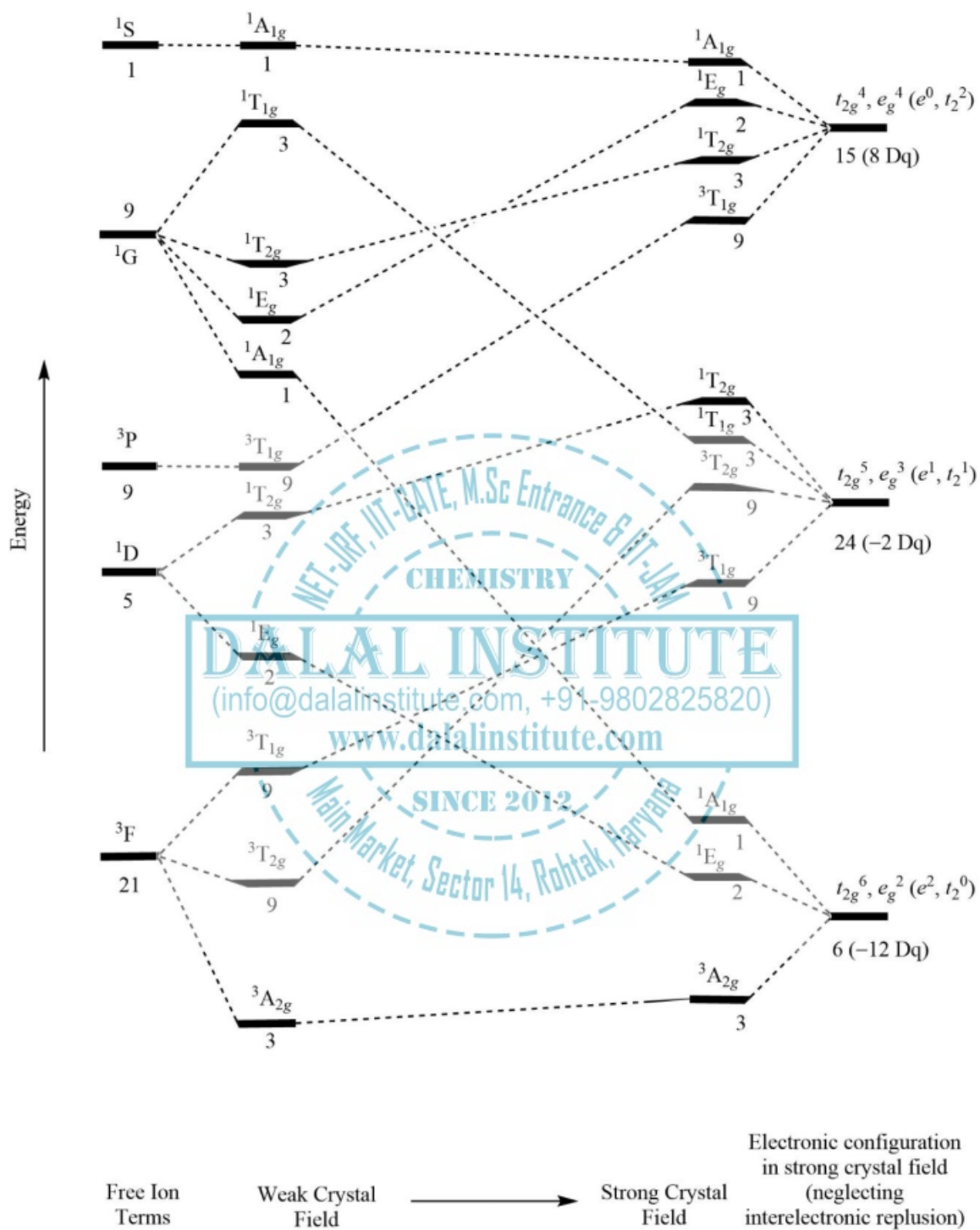
The correlation diagrams (with the corresponding microstates shown below each level) for different electronic configurations in transition metal complexes with four-coordinated tetrahedral and six-coordinated octahedral symmetry are given below.

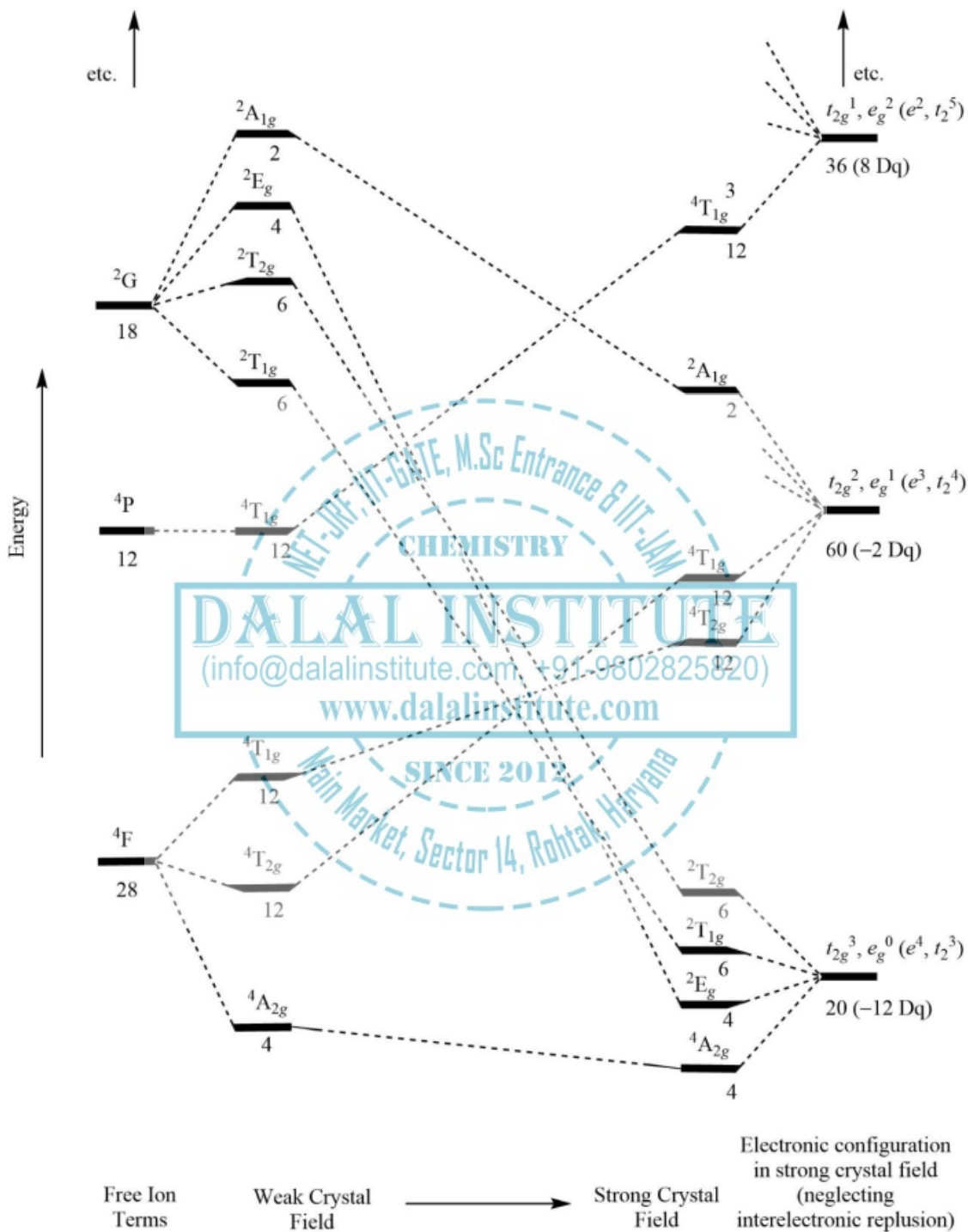
1. d^1, d^9 systems:

 Figure 7. Qualitative correlation diagram for d^1 octahedral and d^9 tetrahedral complexes.

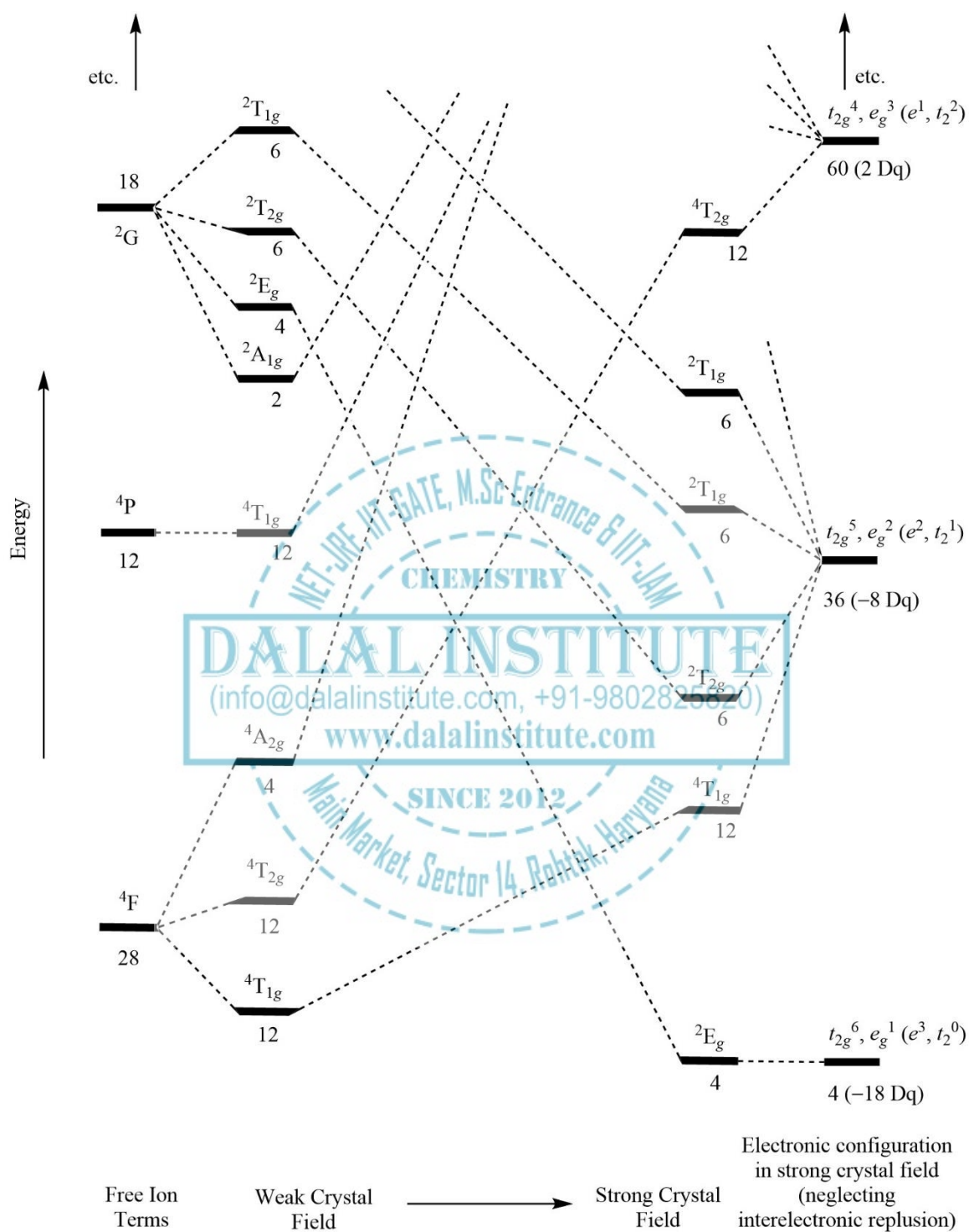
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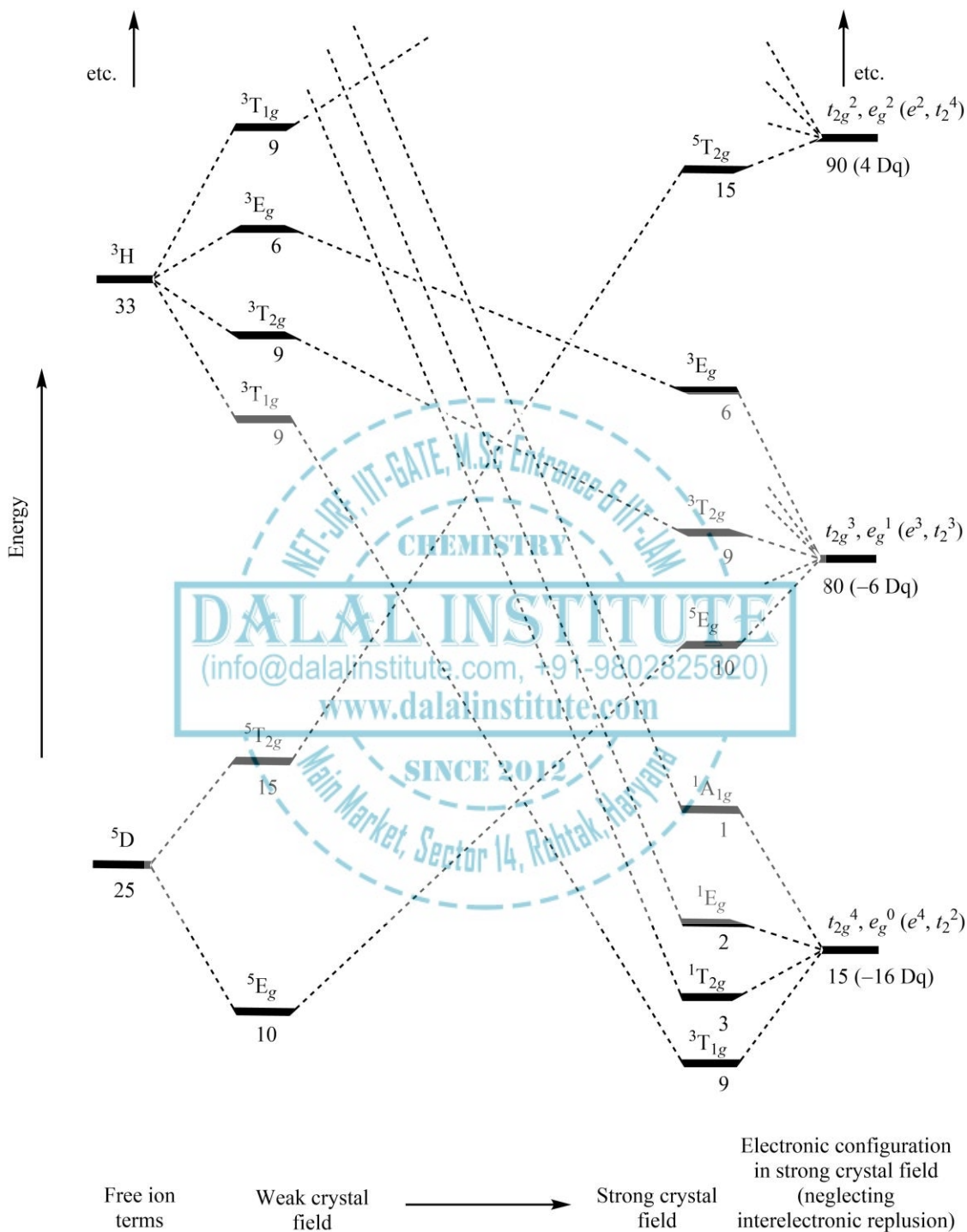

 Figure 8. Qualitative correlation diagram for d^9 octahedral and d^1 tetrahedral complexes.

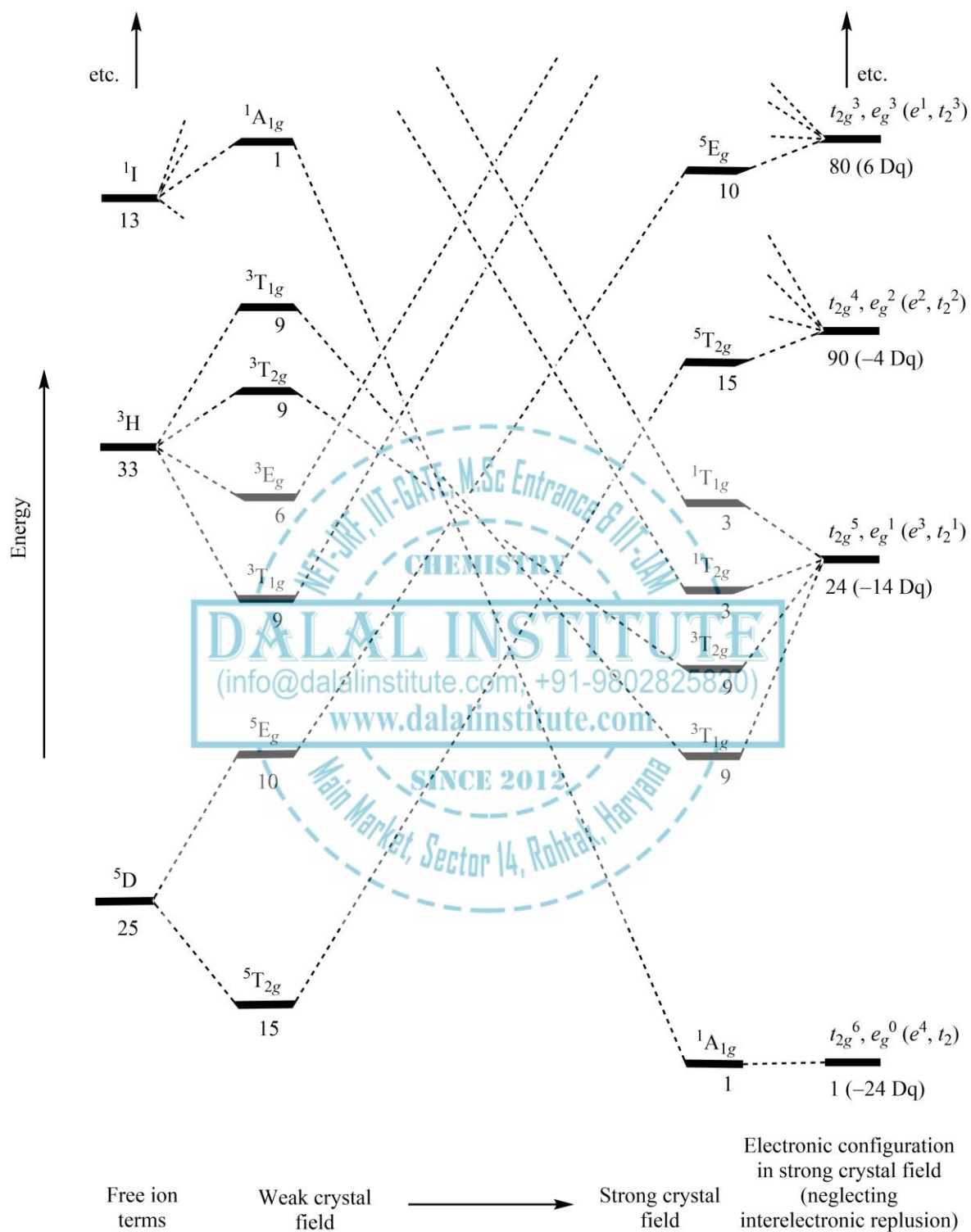
2. d^2, d^8 systems:Figure 9. Qualitative correlation diagram for d^2 octahedral and d^8 tetrahedral complexes.

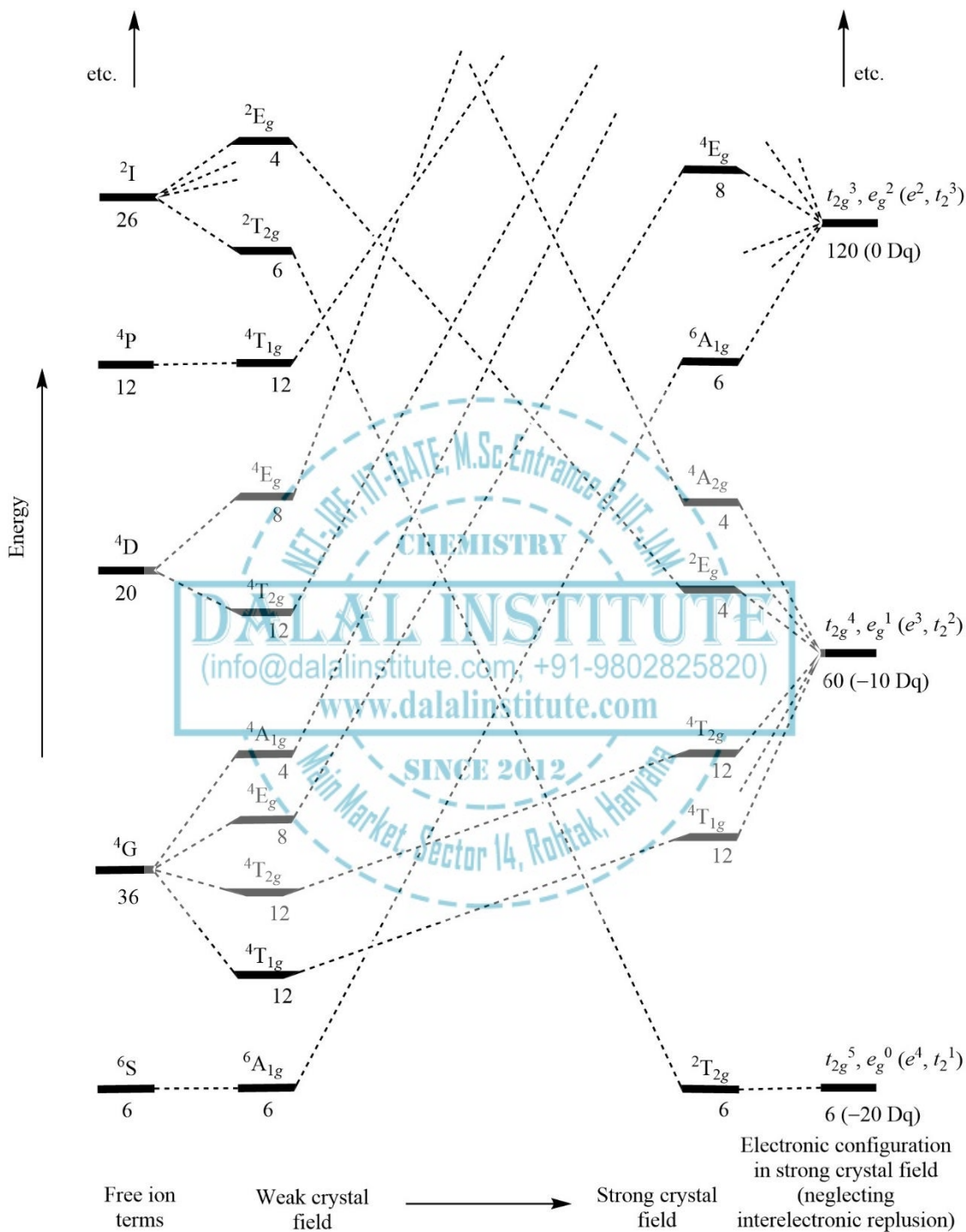
Figure 10. Qualitative correlation diagram for d^8 octahedral and d^2 tetrahedral complexes.

3. d^3, d^7 systems:Figure 11. Qualitative correlation diagram for d^3 octahedral and d^7 tetrahedral complexes.


 Figure 12. Qualitative correlation diagram for d^7 octahedral and d^3 tetrahedral complexes.

4. d^4, d^6 systems:Figure 13. Qualitative correlation diagram for d^4 octahedral and d^6 tetrahedral complexes.


 Figure 14. Qualitative correlation diagram for d^6 octahedral and d^4 tetrahedral complexes.

5. d^5 systems:Figure 15. Qualitative correlation diagram for d^5 octahedral and tetrahedral complexes.

➤ Orgel Diagrams

Orgel diagrams are the oversimplified version of correlation diagrams that show the relative energies of electronic terms in transition metal complexes. They are named after their inventor, Leslie Orgel. These diagrams are restricted only to show weak field cases and offer no information about strong field cases. Because Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams. Moreover, Orgel diagrams only show the symmetry states of the highest spin multiplicity instead of all possible terms, unlike a general correlation diagram. Thus, Orgel diagrams include only those transitions which are spin-allowed in nature, along with corresponding symmetry designations.

In an Orgel diagram, the parent term (P, D, or F) in the presence of no ligand field is located in the center of the diagram; and the Mulliken terms arising from different electronic configurations in a ligand field are represented at each side. There are two Orgel diagrams, one for d^1 , d^4 , d^6 , and d^9 configurations and the other with d^2 , d^3 , d^7 , and d^8 configurations. An Orgel diagram for d^5 has also been very popular which includes spin-forbidden transitions too. In the Orgel diagram, lines with the same Russell-Saunders terms will diverge due to the non-crossing rule, but all other lines will be linear.

1. d^1 , d^9 , d^4 , d^6 systems:

For the “D” Orgel diagram, the left side contains d^1 and d^6 octahedral, and d^4 and d^9 tetrahedral complexes. The right side contains d^4 and d^9 octahedral, and d^1 and d^6 tetrahedral complexes. The lowest energy absorption band on the left side of the spectrum is $T_{2g} \rightarrow E_g$ while on the right side of the spectrum it is $E_g \rightarrow T_{2g}$ transition.

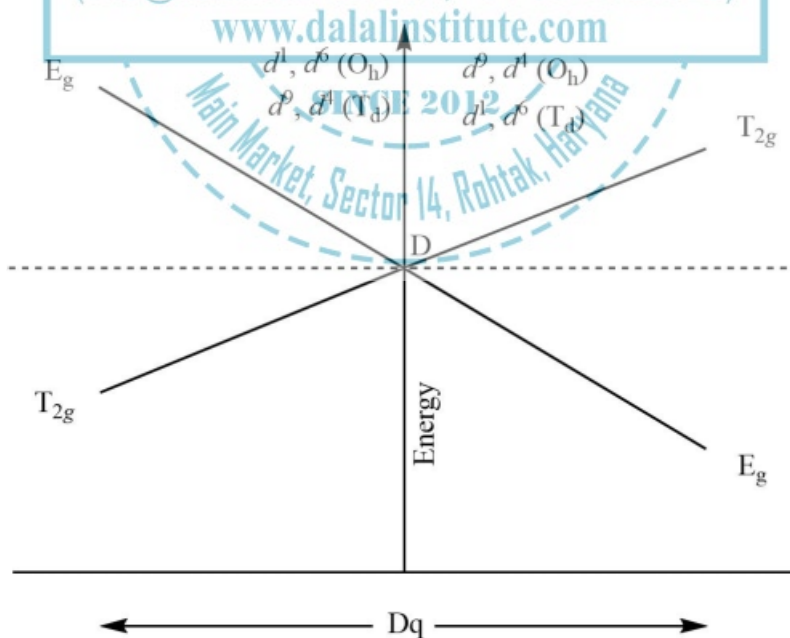


Figure 16. Orgel diagram for d^1 , d^9 , d^4 , d^6 complexes in octahedral (O_h) and tetrahedral (T_d) crystal fields.

i) Spectra of d^1 and d^9 octahedral complexes:

The ground state term symbol for d^1 and d^9 complexes is 2D ; but the splitting pattern of their 2D states is just the opposite of each other, which can be attributed to the electron-hole inverse relationship or simply the hole-formalism. In other words, a d^9 metal has an electron vacancy or “hole” in its d -subshell and thus can be considered as the inverse of the d^1 arrangement. Therefore, despite having identical ground state term symbol 2D (split into ${}^2T_{2g}$ and 2E_g in the octahedral field), the energy order of Mulliken states in d^9 -configuration complexes will be just the inverse of what is in d^1 system.

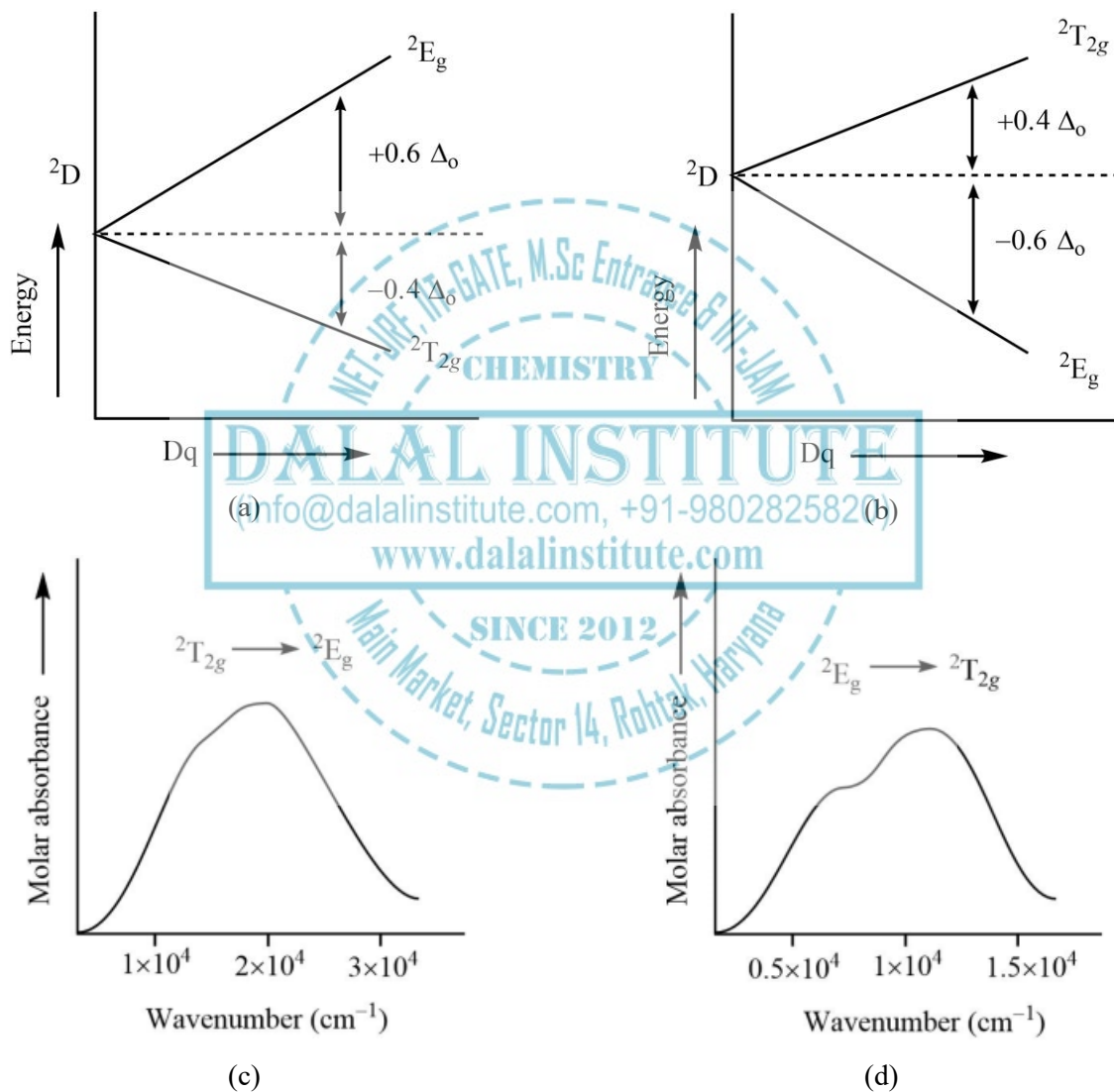


Figure 17. The splitting pattern of 2D state in octahedral complexes with (a) d^1 -configuration and (b) d^9 -configuration; and the corresponding electronic spectra of (c) $[Ti(H_2O)_6]^{3+}$ and (d) $[Cu(H_2O)_6]^{2+}$.

ii) Spectra of d^1 and d^9 tetrahedral complexes:

In addition to the electron-hole inverse relationship for d^1 and d^9 octahedral complexes, an inverse relationship for octahedral-tetrahedral crystal field symmetries also exists. This is simply because the crystal fields of these two symmetries produce the inverse splitting patterns of the d -subshell. Therefore, despite having identical ground state term symbol 2D (split into 2T_2 and 2E in the tetrahedral field), the energy order of Mulliken states in the tetrahedral field will be just the inverse of what is in octahedral systems. However, it is worthy to note that the subscript “g” or “u” cannot be used due to the lack of the center of symmetry.

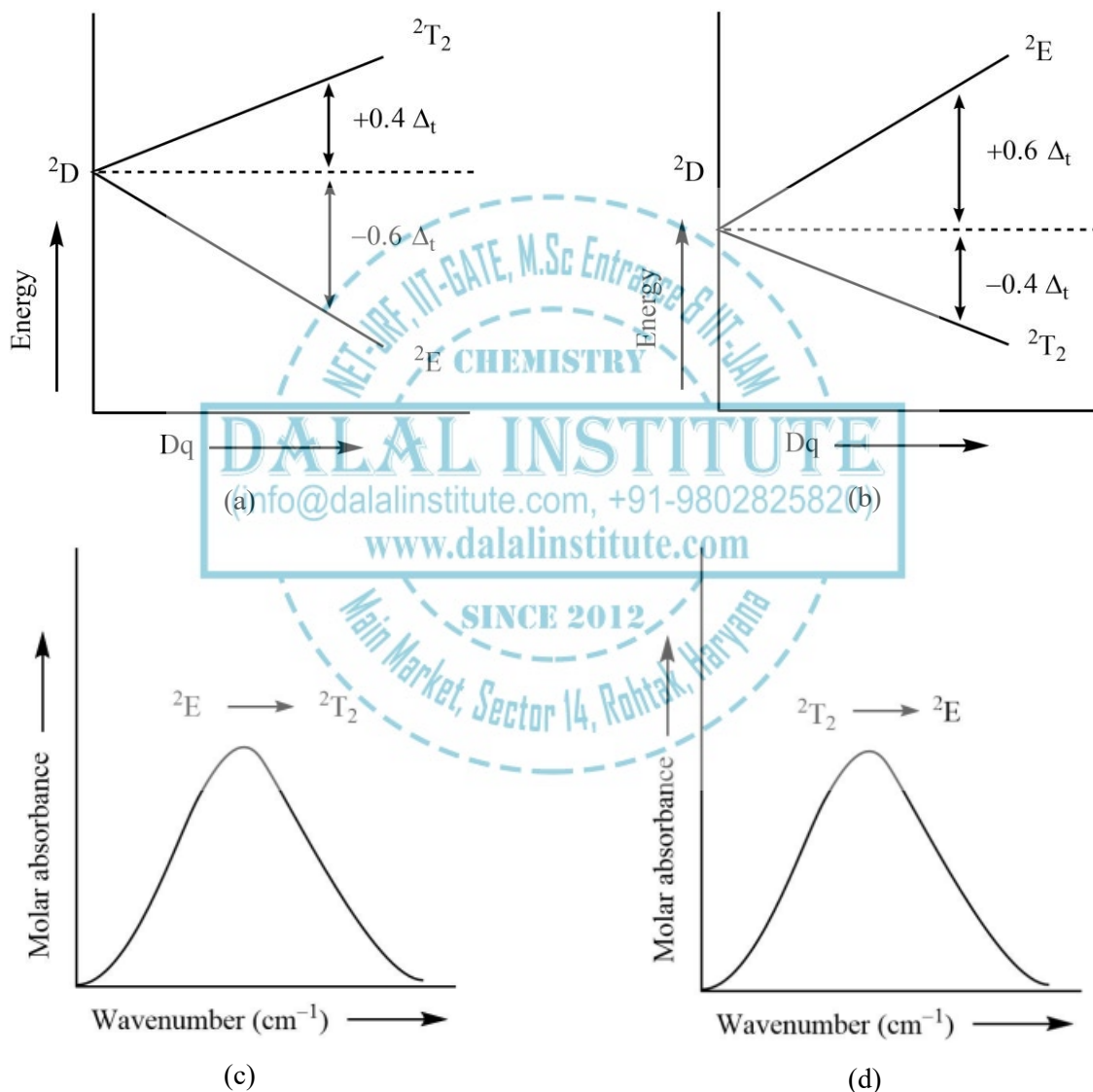


Figure 18. The splitting pattern of 2D state in tetrahedral complexes with (a) d^1 -configuration and (b) d^9 -configuration; and the corresponding electronic spectra of (c) ML_4 (d^1) and (d) ML_4 (d^9).

iii) Spectra of d^4 and d^6 octahedral complexes:

The ground state term symbol for d^4 and d^6 complexes is 5D ; but the splitting pattern of their 5D states is just the opposite of each other, which can be attributed to the electron-hole inverse relationship or simply the hole formalism. In other words, a d^6 metal has an electron vacancy or “hole” in its d -subshell and thus can be considered as the inverse of the d^4 arrangement. Therefore, despite having identical ground state term symbol 5D (split into ${}^5T_{2g}$ and 5E_g in the octahedral field), the energy order of Mulliken states in d^6 configuration will be just the inverse of what is in d^4 system.

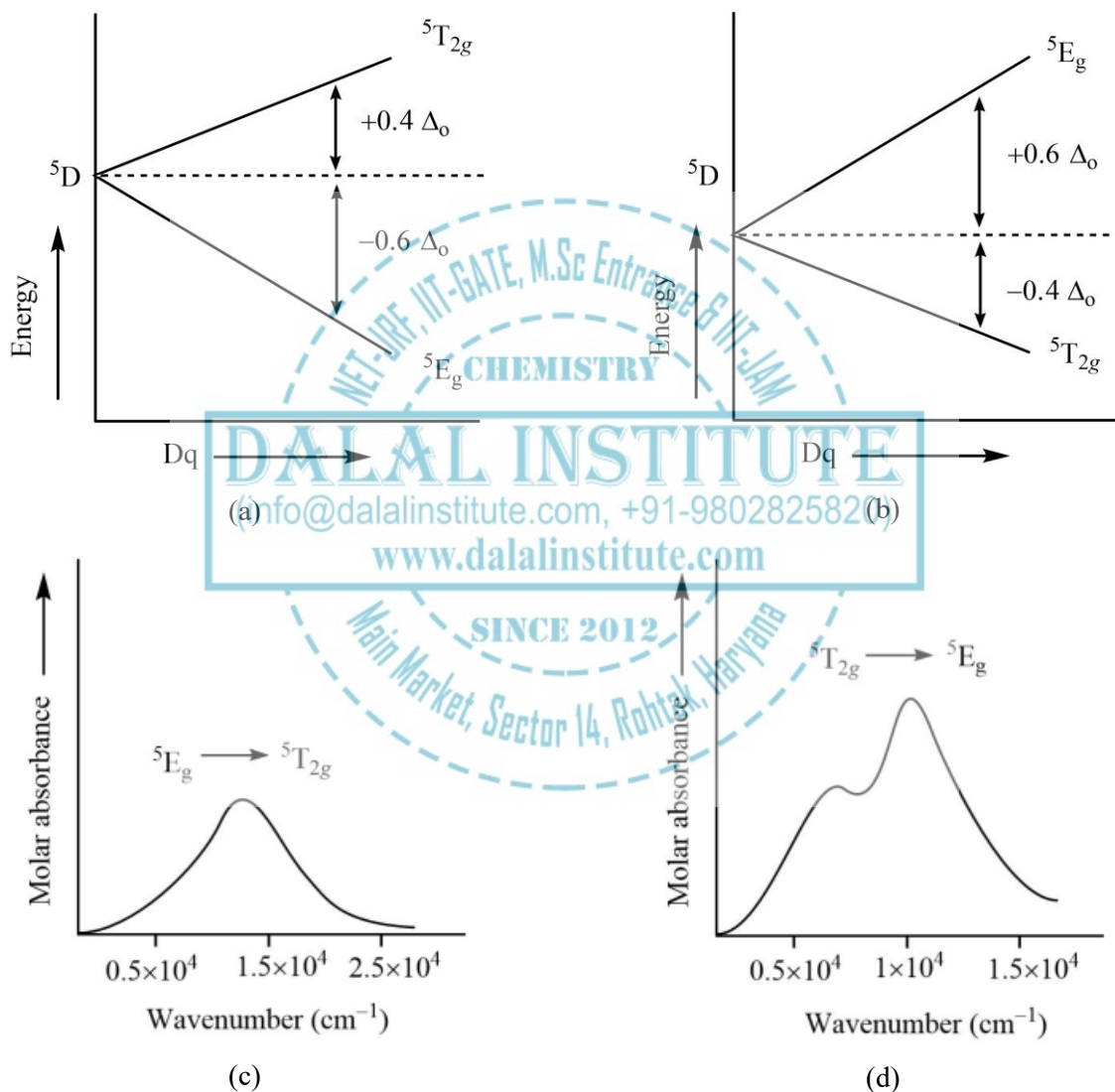


Figure 19. The splitting pattern of 5D state in octahedral complexes with (a) d^4 -configuration and (b) d^6 -configuration; and the corresponding electronic spectra of (c) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and (d) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.

iv) Spectra of d^4 and d^6 tetrahedral complexes:

In addition to the electron-hole inverse relationship for d^4 and d^6 octahedral complexes, an inverse relationship for octahedral-tetrahedral crystal field symmetries also exists. This is simply because the crystal fields of these two symmetries produce the inverse splitting pattern of the d -subshell. Therefore, despite having identical ground state term symbol 5D (split into 5T_2 and 5E in the tetrahedral field), the energy order of Mulliken states in the tetrahedral field will be just the inverse of what is in octahedral systems. However, it is worthy to note that the subscript “g” or “u” cannot be used due to the lack of the center of symmetry.

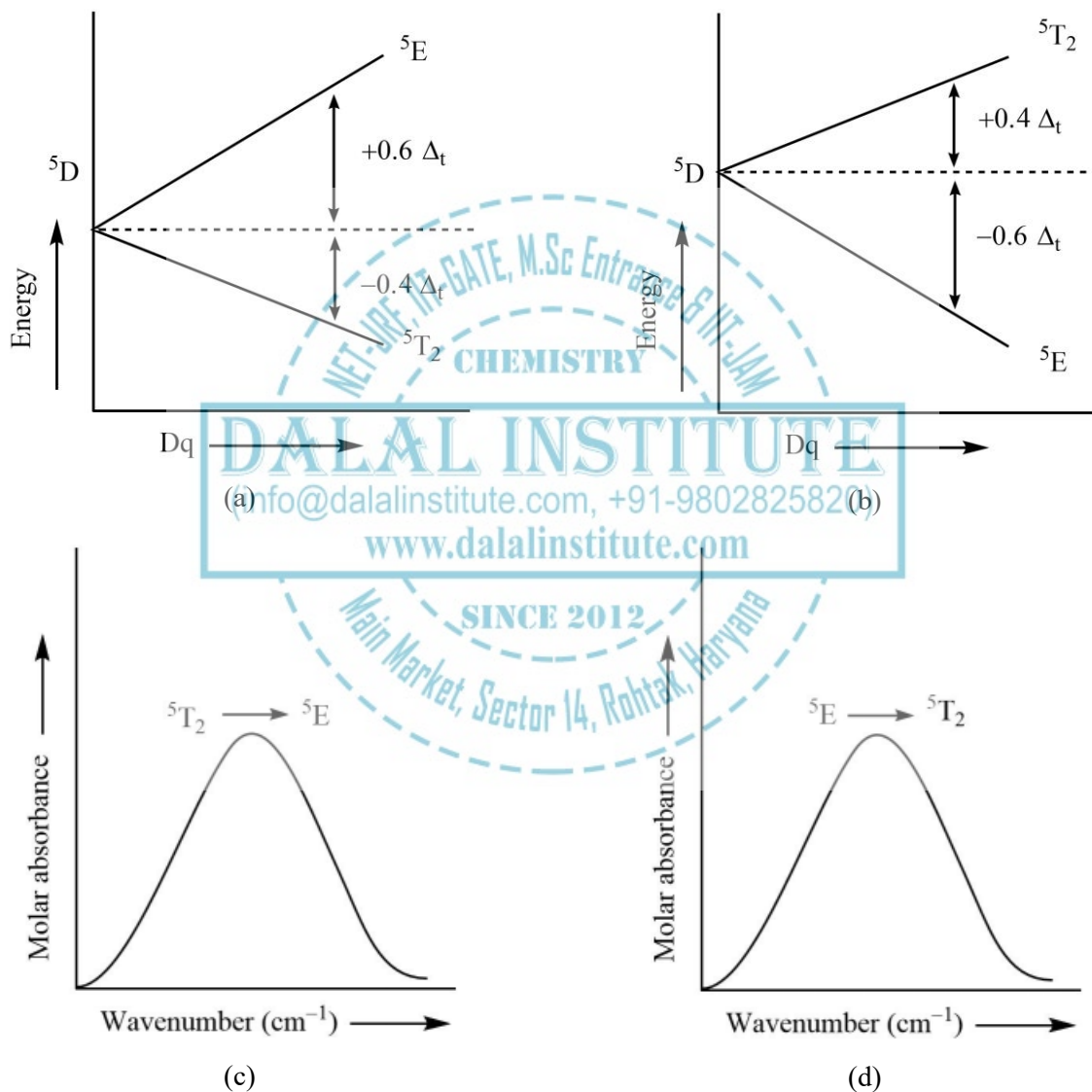


Figure 20. The splitting pattern of 5D state in tetrahedral complexes with (a) d^4 -configuration and (b) d^6 -configuration; and the corresponding electronic spectra of (c) ML_4 (d^4) and (d) ML_4 (d^6).

2. d^2 , d^8 , d^3 , d^7 systems:

For the “F” Orgel diagram, the left side contains d^2 and d^7 tetrahedral and d^3 and d^8 octahedral complexes. The right side contains d^3 and d^8 tetrahedral and d^2 and high spin d^7 octahedral complexes. The lowest energy absorption band on the left side of the spectrum is $A_{2g}(F) \rightarrow T_{2g}(F)$ while on the right side of the spectrum it is $T_{1g}(F) \rightarrow T_{2g}(F)$ transition. The difference in energy between these two states is solely attributable to electron-electron repulsions. The two free ion electronic states are separated by an energy difference $15B$, where B is the Racah parameter that acts as a measure of electron-electron repulsions. The value of B can be calculated experimentally in a very similar manner as the value of ligand-field splitting Δ is obtained.

For instance, in an octahedral d^2 complex, there are three ways of arranging the two d electrons. One is t_{2g}^2 , second is $t_{2g}^1 e_g^1$ and the last is e_g^2 . These are the three electronic states under consideration and are one should use the right-hand side of the diagram. Moreover, the energy gap between each state is equal to Δ since it requires the promotion of one electron from t_{2g} to e_g . It is clear from the Orgel diagram that there are four states: two T_{1g} states, one T_{2g} state, and one A_{2g} state. The spin multiplicities are omitted in the diagram that allows it to be generalized for d^8 complexes. The subscript g and u should be omitted if the same diagram is to be used to generalize the spectra of tetrahedral counterparts. It is also worthy to note that the ordering of the second and third transition on the right-hand side is reversed after the crossover point.

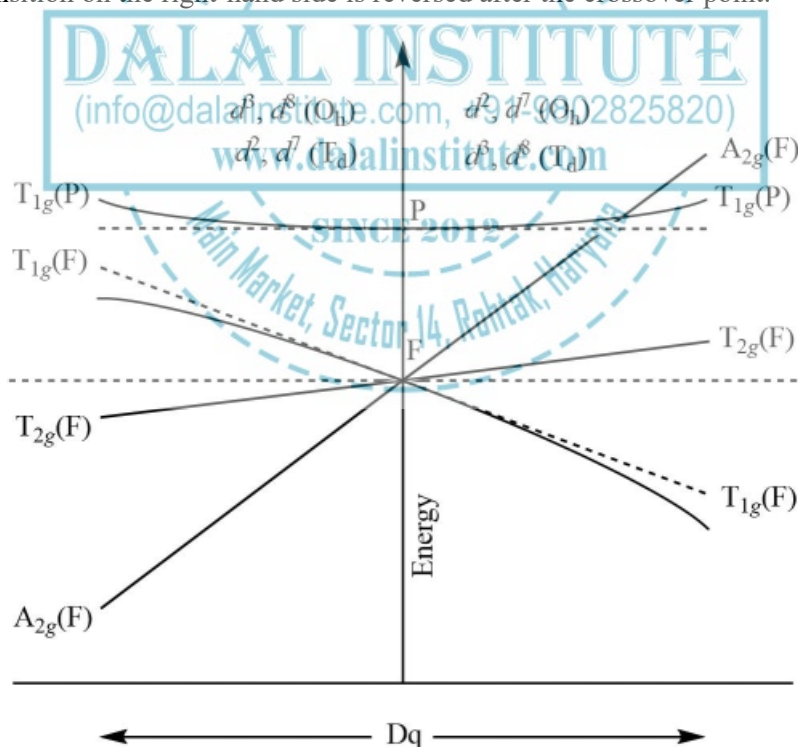


Figure 21. Orgel diagram for d^2 , d^8 , d^3 , d^7 complexes in octahedral (O_h) and tetrahedral (T_d) crystal fields.

i) Spectra of d^2 and d^8 octahedral complexes:

The ground state term symbol for d^2 and d^8 complexes is 3F ; but the splitting pattern of their 3F states is just the opposite of each other, which can be attributed to the electron-hole inverse relationship or simply the hole-formalism. In other words, a d^8 metal has two electron vacancies or “holes” in its d -subshell and thus can be considered as the inverse of the d^2 arrangement. Therefore, despite having identical ground state term symbol 3F (split into ${}^3A_{2g}$, ${}^3T_{2g}$ and ${}^3T_{1g}$ in the octahedral field), the energy order of Mulliken states in d^8 -configuration complexes will be just the inverse of what is in d^2 system.

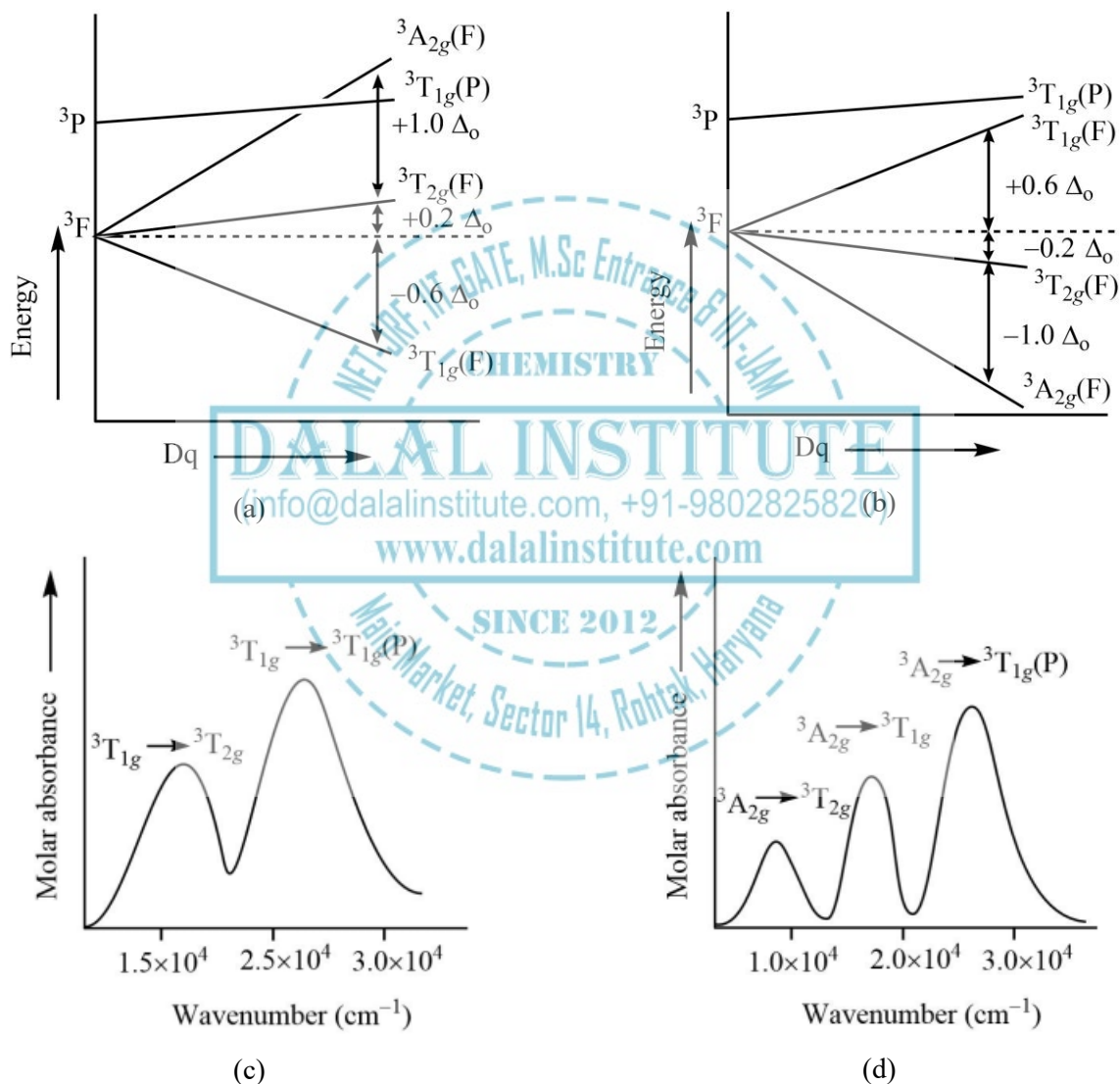


Figure 22. The splitting pattern of 3F state in octahedral complexes with (a) d^2 -configuration and (b) d^8 -configuration; and the corresponding electronic spectra of (c) $[V(H_2O)_6]^{3+}$ and (d) $[Ni(H_2O)_6]^{2+}$.

ii) Spectra of d^2 and d^8 tetrahedral complexes:

In addition to the electron-hole inverse relationship for d^2 and d^8 octahedral complexes, an inverse relationship for octahedral-tetrahedral crystal field symmetries also exists. This is simply because the crystal fields of these two symmetries produce the inverse splitting pattern of the d -subshell. Therefore, despite having identical ground state term symbol 3F (split into 3A_2 , 3T_2 and 3T_1 tetrahedral field), the energy order of Mulliken states in the tetrahedral field will be just the inverse of what is in octahedral systems. However, it is worthy to note that the subscript “g” or “u” cannot be used due to the lack of the center of symmetry.

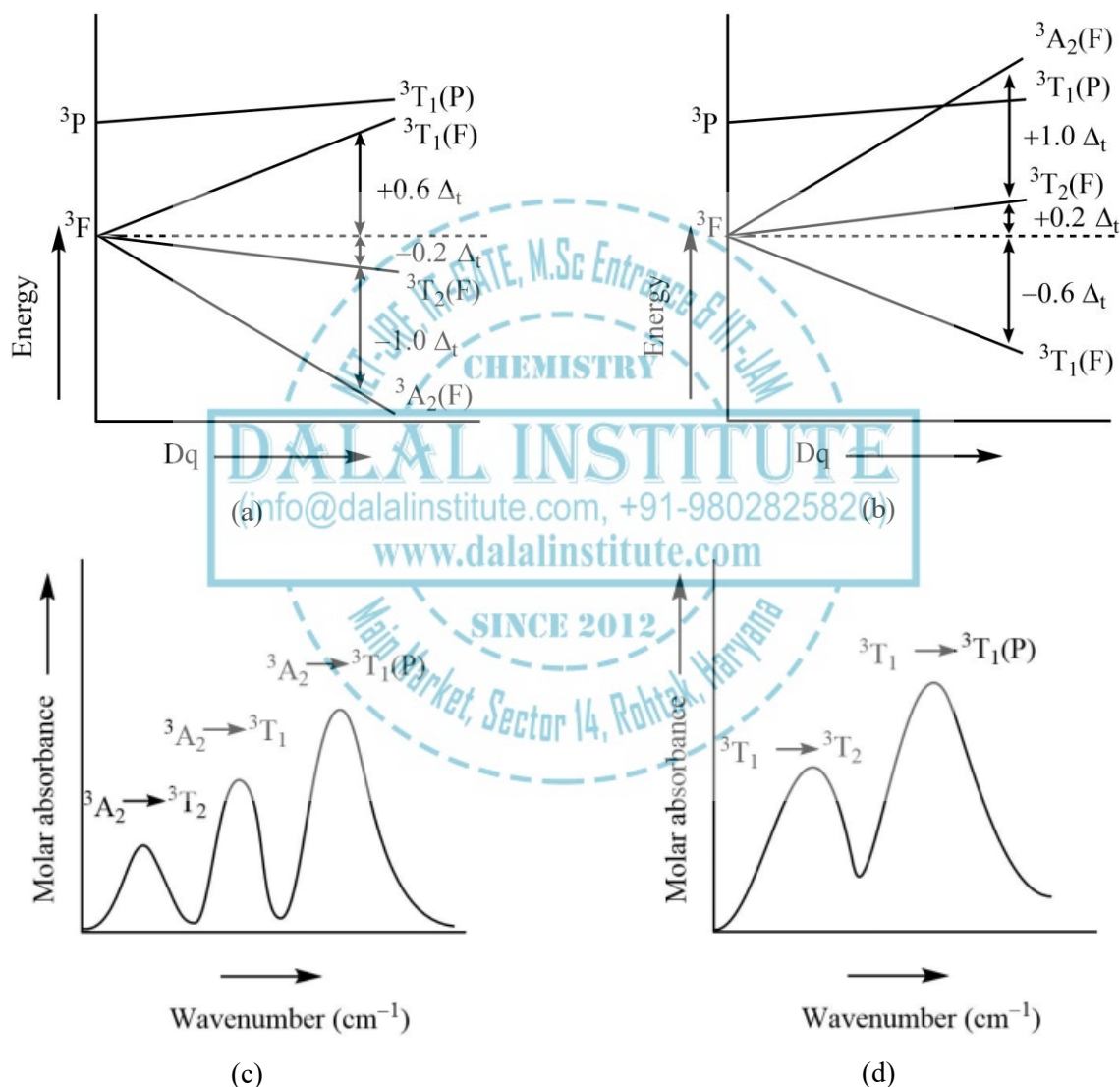


Figure 23. The splitting pattern of 3F state in tetrahedral complexes with (a) d^2 -configuration and (b) d^8 -configuration; and the corresponding electronic spectra of (c) $ML_4 (d^2)$ and (d) $ML_4 (d^8)$.

iii) Spectra of d^3 and d^7 octahedral complexes:

The ground state term symbol for d^3 and d^7 complexes is 4F ; but the splitting pattern of their 4F states is just the opposite of each other, which can be attributed to the electron-hole inverse relationship or simply the hole formalism. In other words, a d^7 metal has an electron vacancy or “hole” in its d -subshell and thus can be considered as the inverse of the d^3 arrangement. Therefore, despite having identical ground state term symbol 4F (split into ${}^4A_{2g}$, ${}^4T_{2g}$ and ${}^4T_{1g}$ in the octahedral field), the energy order of Mulliken states in d^7 configuration will be just the inverse of what is in d^3 system.

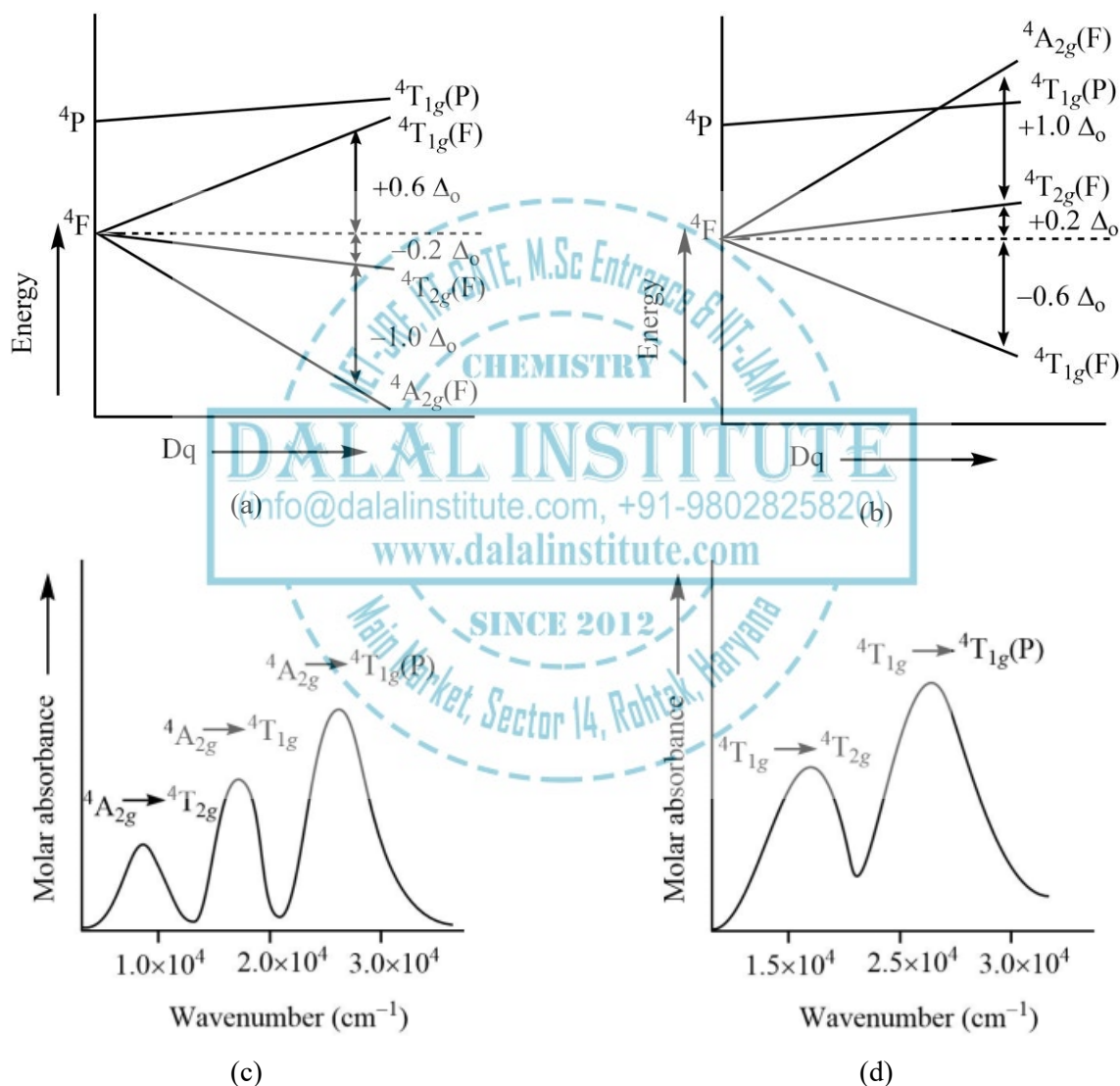


Figure 24. The splitting pattern of 4F state in octahedral complexes with (a) d^3 -configuration and (b) d^7 -configuration; and the corresponding electronic spectra of (c) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and (d) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

iv) Spectra of d^3 and d^7 tetrahedral complexes:

In addition to the electron-hole inverse relationship for d^3 and d^7 octahedral complexes, an inverse relationship for octahedral-tetrahedral crystal field symmetries also exists. This is simply because the crystal fields of these two symmetries produce the inverse splitting pattern of the d -subshell. Therefore, despite having identical ground state term symbol 4F (split into 4A_2 , 4T_2 and 4T_1 in the tetrahedral field), the energy order of Mulliken states in the tetrahedral field will be just the inverse of what is in octahedral systems. However, it is worthy to note that the subscript “g” or “u” cannot be used due to the lack of the center of symmetry.

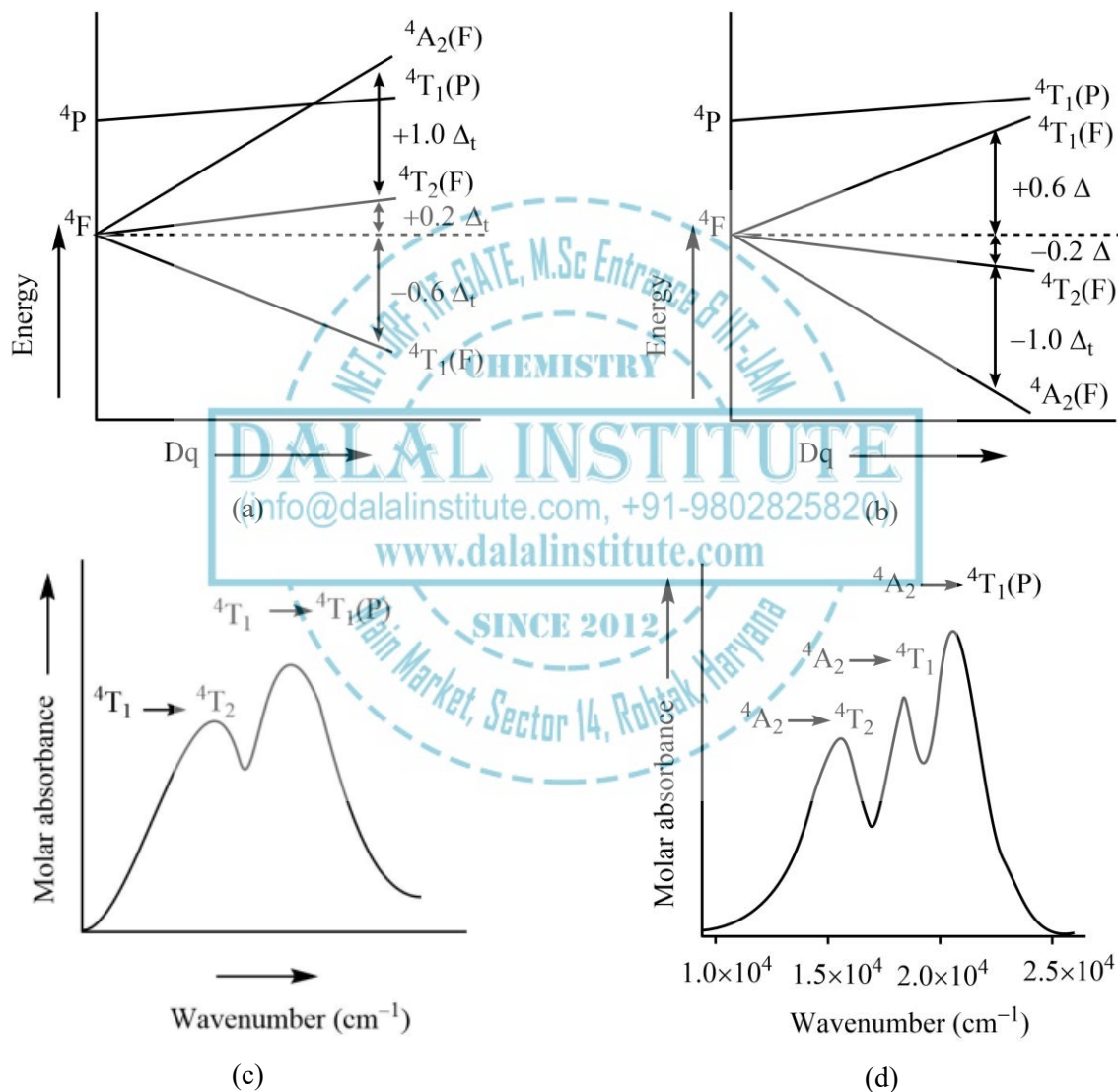


Figure 25. The splitting pattern of 4F state in tetrahedral complexes with (a) d^3 -configuration and (b) d^7 -configuration; and the corresponding electronic spectra of (c) ML_4 (d^3) and (d) $[CoCl_4]^{2-}$ (d^7).

3. d^5 systems:

Orgel diagrams we have studied so far include only spin allowed transitions. However, in the case of d^5 -configuration, this is not possible as there is only one electronic state with a multiplicity of six, ${}^6A_{1g}$. Therefore, all the transitions must occur with a change in the spin multiplicity and are spin forbidden for octahedral as well as tetrahedral complexes. The lowest energy absorption band of the spectrum is ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$ in octahedral; while in the tetrahedral complex, it is ${}^6A_1(S) \rightarrow {}^4T_1(G)$ transition. The difference in energy between these two states is also attributable to electron-electron repulsions and B, the Racah parameter that acts as a measure of electron-electron repulsions.

The electronic configuration for ground state term symbol is $t_{2g}^3 e_g^2$ with five unpaired electrons having parallel spins and any promotion or rearrangement of the electrons would lead to a lower multiplicity state. Moreover, if we combine this fact perfect octahedral complexes like $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, the absorption intensities become very weak due to the additional selection rule of Laporte forbiddance. This makes $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ pale pink in color but the tetrahedral complexes of Mn^{2+} are quite instance due to the absence of the centre of symmetry. The subscript g and u should be omitted if the same diagram is to be used to generalize the spectra of tetrahedral counterparts. It is also worthy to note that the electronic states with symmetry never cross each other but repel each other due to their quantum mechanical mixing.

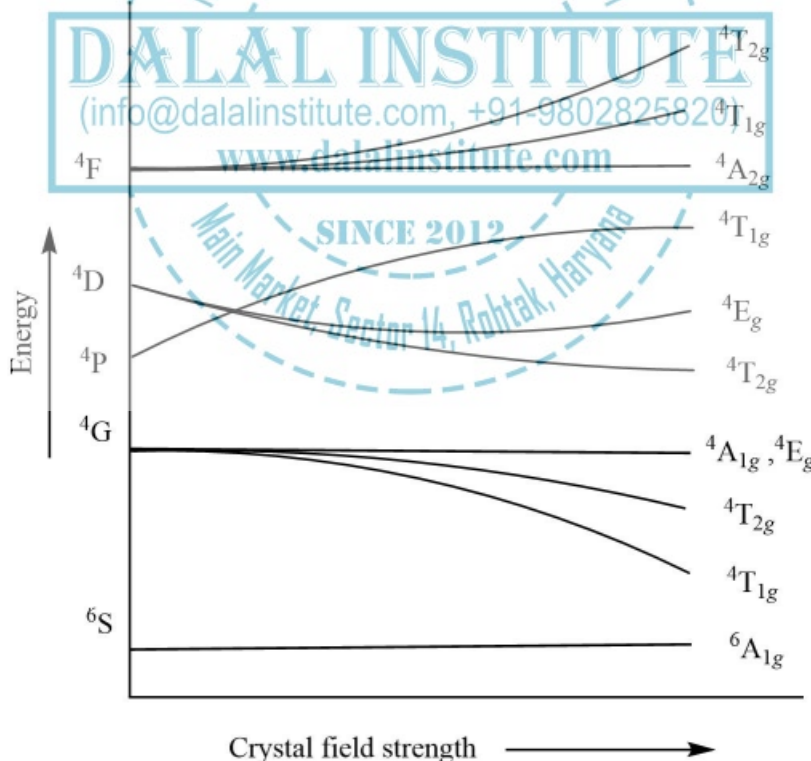


Figure 26. Orgel diagram for d^5 complexes in octahedral (O_h) and tetrahedral (T_d) crystal fields.

Unlike other electronic configurations, the ground state of d^5 system remains the same but the gerade subscript will be removed i.e. 6A . The same is true for other Mulliken states. In other words, the subscript “g” or “u” cannot be used due to the lack of the center of symmetry.

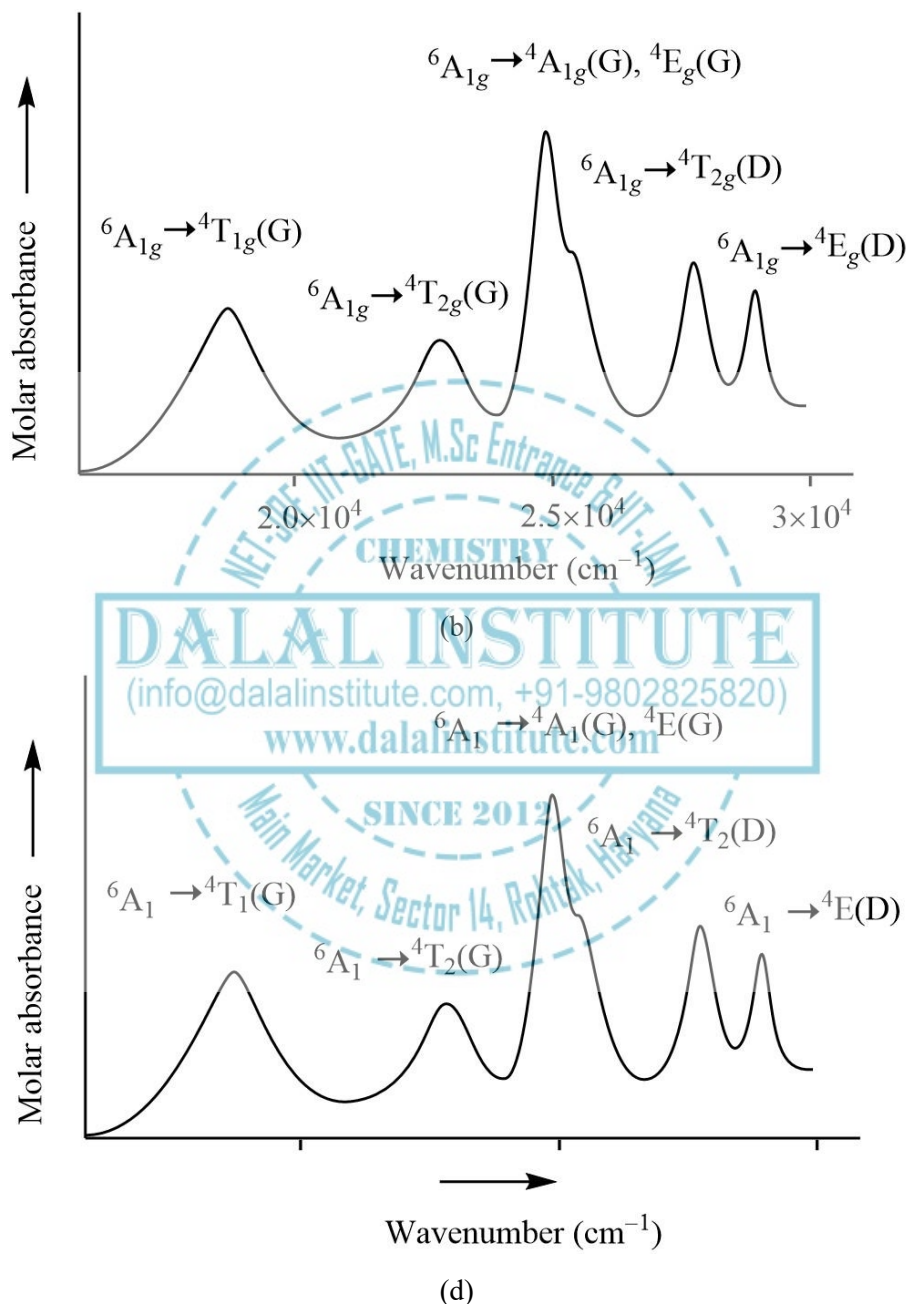


Figure 27. The electronic spectra of (a) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and (b) $[\text{ML}_4]^{d^5}$.

➤ *Tanabe-Sugano Diagrams*

In 1954, two Japanese scientists, Yukito Tanabe and Satoru Sugano published a paper entitled "On the absorption spectra of complex ions". Earlier than that, very little was available regarding the excited electronic states of transition metal complexes. Tanabe and Sugano used the Hans Bethe's CFT concept and Giulio Racah's linear combinations of Slater integrals (Racah parameters) to rationalize the absorption spectra of the octahedral metal complex in a quantitative frame than what had been accomplished earlier. After a number of spectroscopic experiments, they estimated the values B and C (two of Racah's parameters) for every d -electronic configuration based on the trends in the UV visible absorption spectrum of isoelectronic transition metals of $3d$ series. The energy plots of various electronic states of every electron configuration are now called as Tanabe-Sugano or simply the T-S diagrams. In other words, Tanabe-Sugano diagrams are nothing but some special kind of correlation diagrams that can be used in weak as well as strong field complexes. These diagrams are used in transition metal chemistry to forecast the UV-visible absorption spectrum of coordination compounds and the results from these diagrams can also be compared to experimentally obtained spectroscopic data. T-S diagrams can be used qualitatively to approximate the value of crystal field splitting energy (Δ). Unlike Orgel diagrams (applicable to high-spin complexes only), these diagrams can be used for spin-free as well as spin-paired complexes. T-S diagrams can also be exploited to find the size of the ligand field required to cause high-spin–low-spin transitions. In contrast to the Orgel diagrams, the ground state is set as a reference in a T-S diagram. The ground-state-energy is taken to be zero for all ligand field strengths, and the energy of all other states along-with their components are plotted with respect to the ground state term.

In Tanabe-Sugano diagrams, the x -axis is expressed in terms of the crystal field splitting parameter (Δ or Dq) divided by the Racah parameter (B). Along y -axis, the energy, E , divided by B is taken. Out of three Racah parameters (A, B, and C), which describe various aspects of inter-electronic repulsion, A is an average total inter-electron repulsion whereas B and C correspond with individual d -electronic repulsions. The value of A is constant for d -electronic configuration, and therefore, is unnecessary for obtaining relative energies, and so is absent from T-S diagram studies of metal complexes. The parameter C is required only in some special cases. The parameter B is the most significant of all Racah's parameters in transition metals complexes. Moreover, certain lines bend due to the mixing of states with same symmetry. Although transitions between the same spin-multiplicity are allowed, energy profiling of spin-forbidden states is also included in the T-S diagrams, which were absent in Orgel diagrams. All states are usually Labelled on the right side of the diagram; nonetheless, some labels may be allotted on other locations for more clarity in case of complicated T-S diagrams like d^6 . The free ion terms for a specific d^n configuration are shown in order of increasing energy on the y -axis of the T-S diagram. The relative of energies free ion terms are obtained using Hund's rules. The splitting of free ion terms has already been discussed in Table 7 and Table 8. Certain T-S diagrams like d^4 , d^5 , d^6 , and d^7 ; also have a starlight vertical line at a certain Dq/B value, which represents a discontinuity in the slopes of the excited-states' terms. This occurs when the pairing energy (P) becomes equal to the crystal field splitting energy. Metal complexes to the left of this vertical line are spin-free, while the complexes to the right are spin-paired. There is no low-spin or high-spin designation for d^2 , d^3 , or d^8 . The subscript "g" and "u" can be omitted as all designations are gerade.

1. d^1, d^9 systems:i) d^1 -configuration

Metal complexes with d^1 -configuration do not have any inter electronic repulsion and the single electron resides in the t_{2g} orbital ground state. When t_{2g} orbital set holds the single electron, six microstates will have ${}^2T_{2g}$ state energy of $-4 Dq$; and when the electron is promoted to the e_g orbital, the four microstates will have 2E_g state energy of $+6 Dq$. This is in accordance with the single absorption band in a UV-vis experiment; and thus, the transition from ${}^2T_{2g}$ to 2E_g does not require a Tanabe–Sugano diagram.

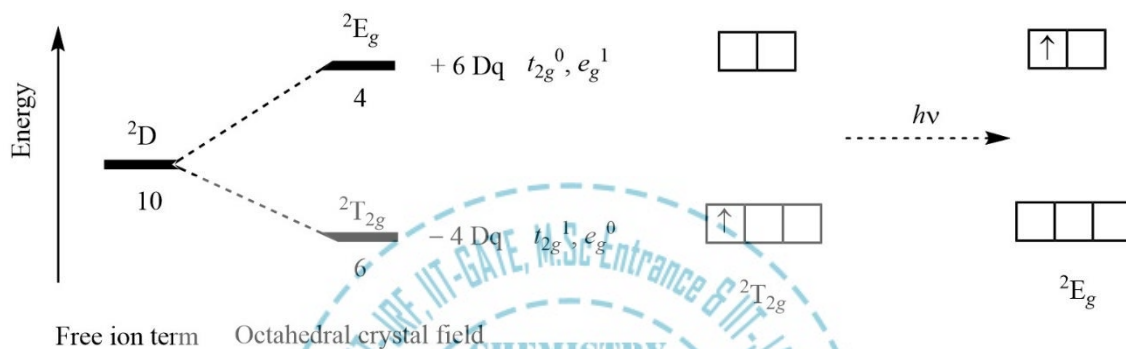


Figure 28. Splitting of free ion term for d^1 complexes in the octahedral crystal field.

ii) d^9 -configuration

In d^9 octahedral metal complexes, the ground state filling of electrons ($t_{2g}^6 e_g^3$) has only four microstates that have 2E_g energy state with $-6 Dq$. When the electron from t_{2g} is promoted to the e_g orbital set; the new configuration will have six microstates that have ${}^2T_{2g}$ energy state with $+4 Dq$. This could also be described as a positive "hole" that moves from the e_g to the t_{2g} orbital set. The sign of Dq is opposite that for d^1 , with a 2E_g ground state and a ${}^2T_{2g}$ excited state. Like the d^1 case, d^9 octahedral complexes do not require the Tanabe–Sugano diagram to predict their absorption spectra.

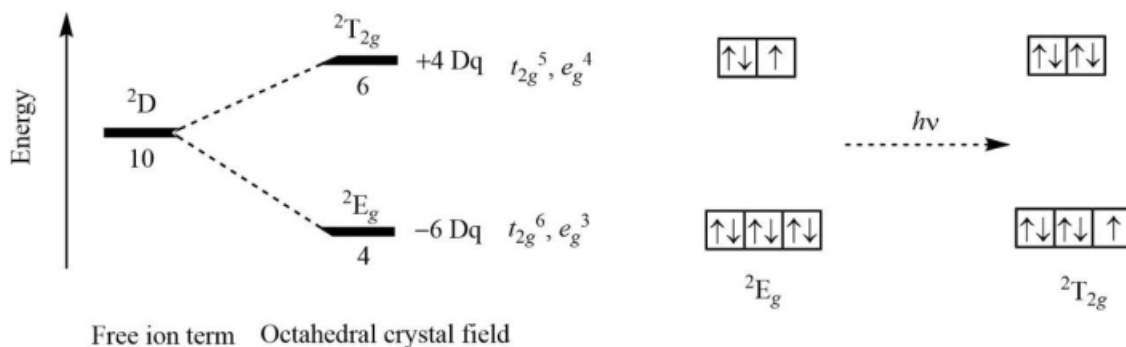


Figure 29. Splitting of free ion term for d^9 complexes in the octahedral crystal field.

2. d^2 systems:

Metal complexes with d^2 -configuration have 3F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes ${}^3T_{1g}$ and remains as such in the weak field as well as strong ligand field.

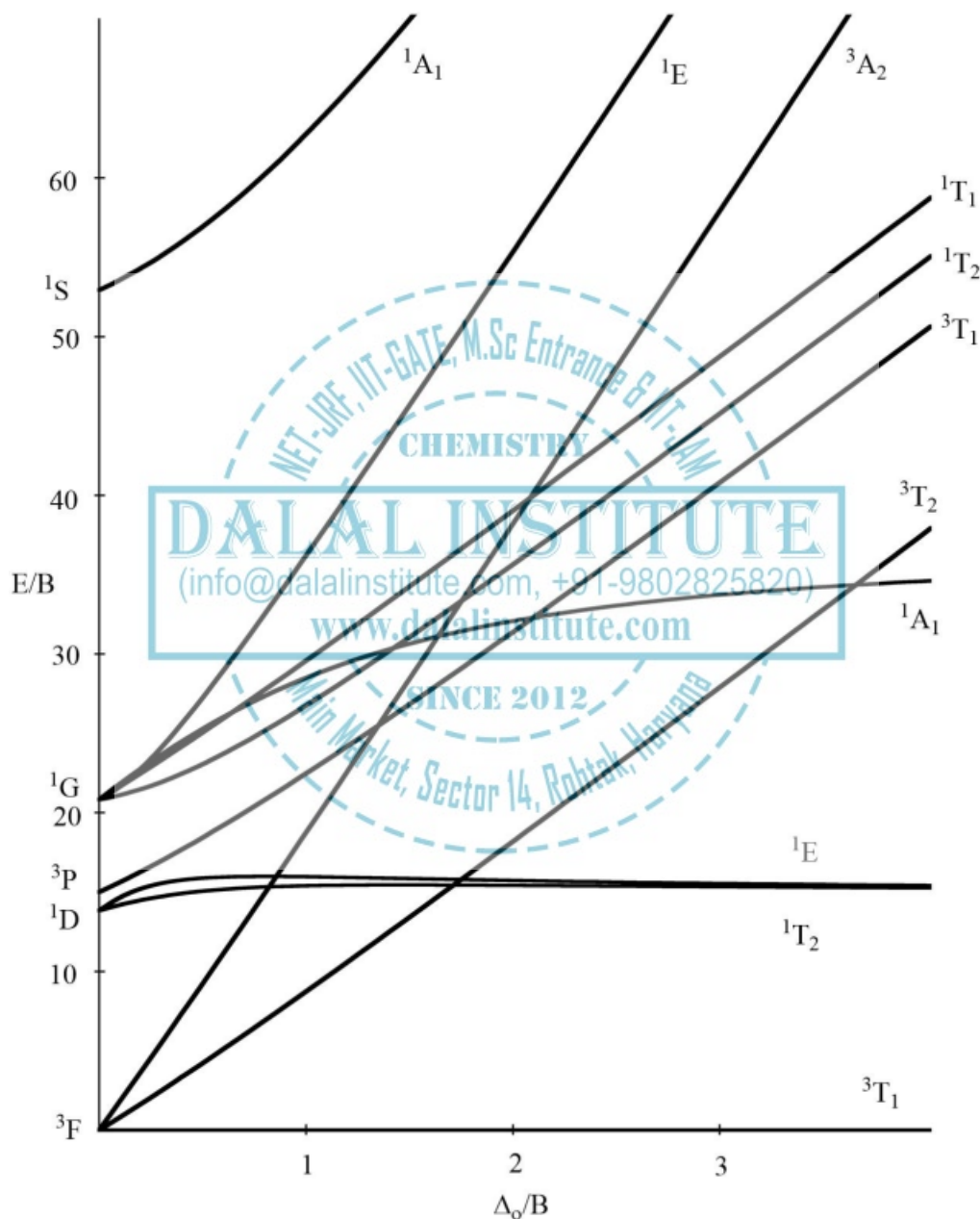


Figure 30. Splitting of free ion terms for d^2 complexes in the octahedral crystal field.

3. d^3 systems:

Metal complexes with d^3 -configuration have 4F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes $^4A_{2g}$ and remains as such in the weak field as well as strong ligand field.

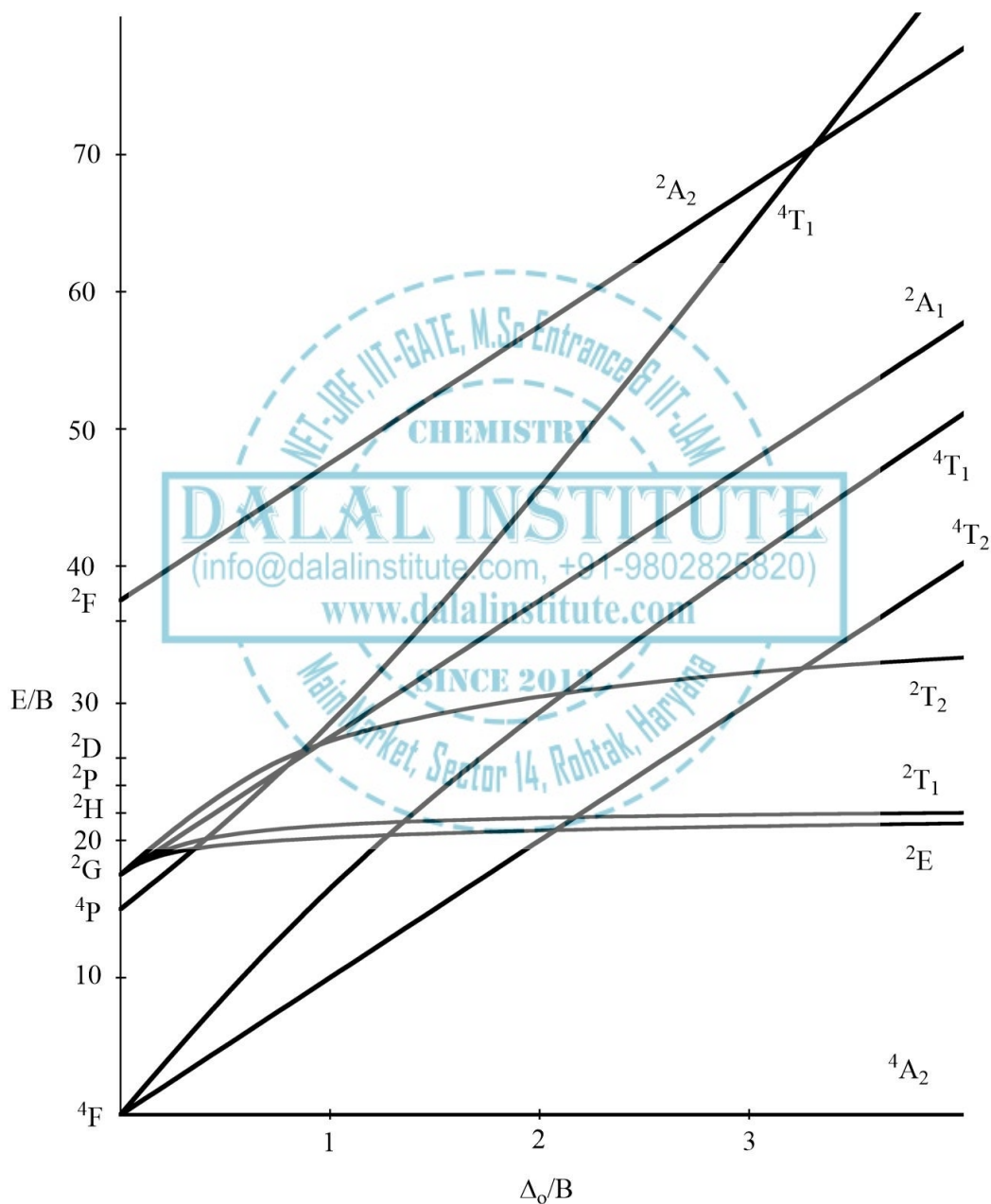


Figure 31. Splitting of free ion terms for d^3 complexes in the octahedral crystal field.

4. d^4 systems:

Metal complexes with d^4 -configuration have 5D ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes 5E_g in the weak field and $^3T_{1g}$ in a strong ligand field.

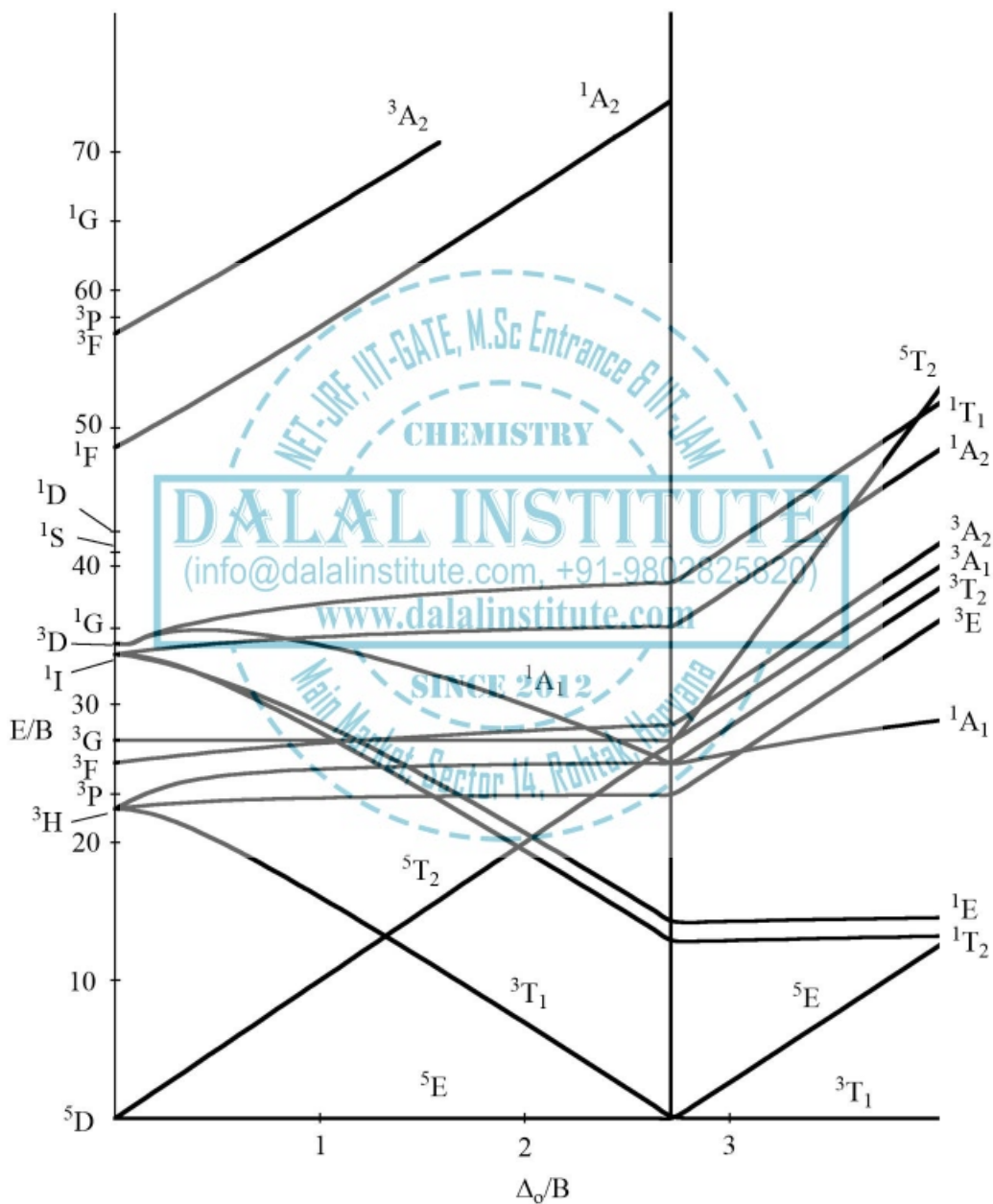


Figure 32. Splitting of free ion terms for d^4 complexes in the octahedral crystal field.

5. d^5 systems:

Metal complexes with d^5 -configuration have 6S ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes ${}^6A_{1g}$ in weak field and ${}^2T_{2g}$ in strong ligand field.

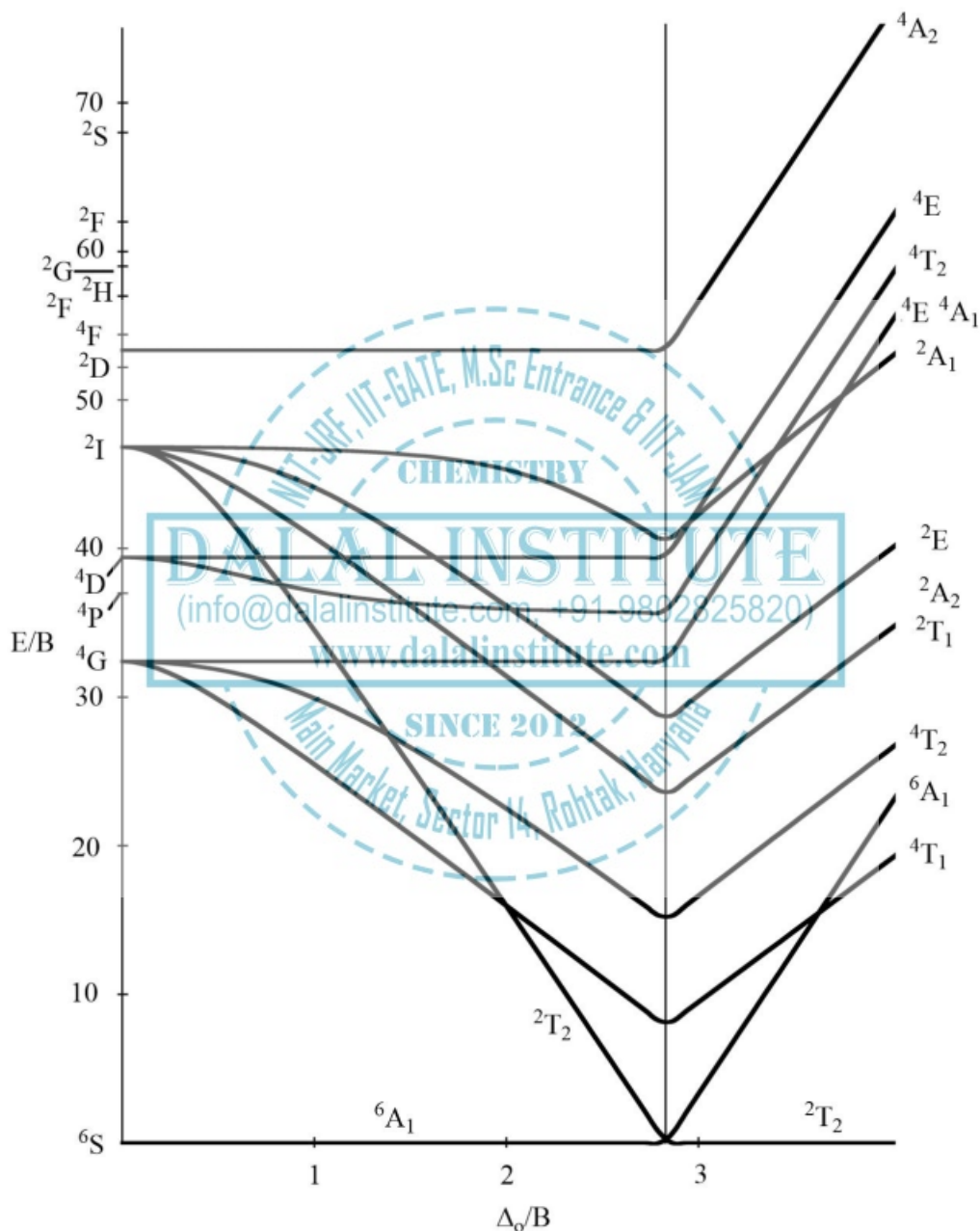


Figure 33. Splitting of free ion terms for d^5 complexes in the octahedral crystal field.

6. d^6 systems:

Metal complexes with d^6 -configuration have 5D ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes $^1T_{2g}$ in weak and $^1A_{1g}$ in strong ligand fields.

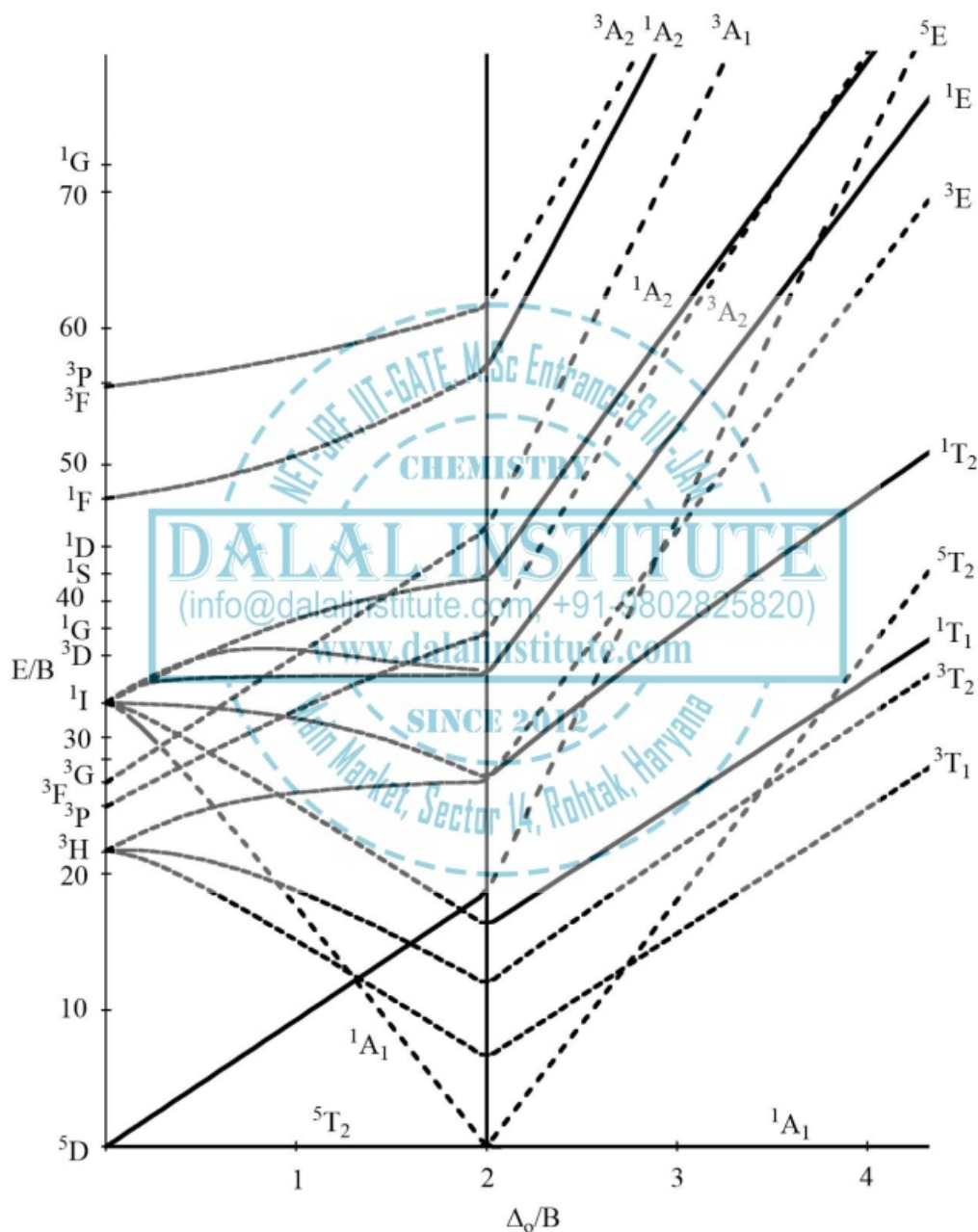


Figure 34. Splitting of free ion terms for d^6 complexes in the octahedral crystal field.

7. d^7 systems:

Metal complexes with d^7 -configuration have 4F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes $^4T_{1g}$ in weak 2E_g in strong ligand fields.

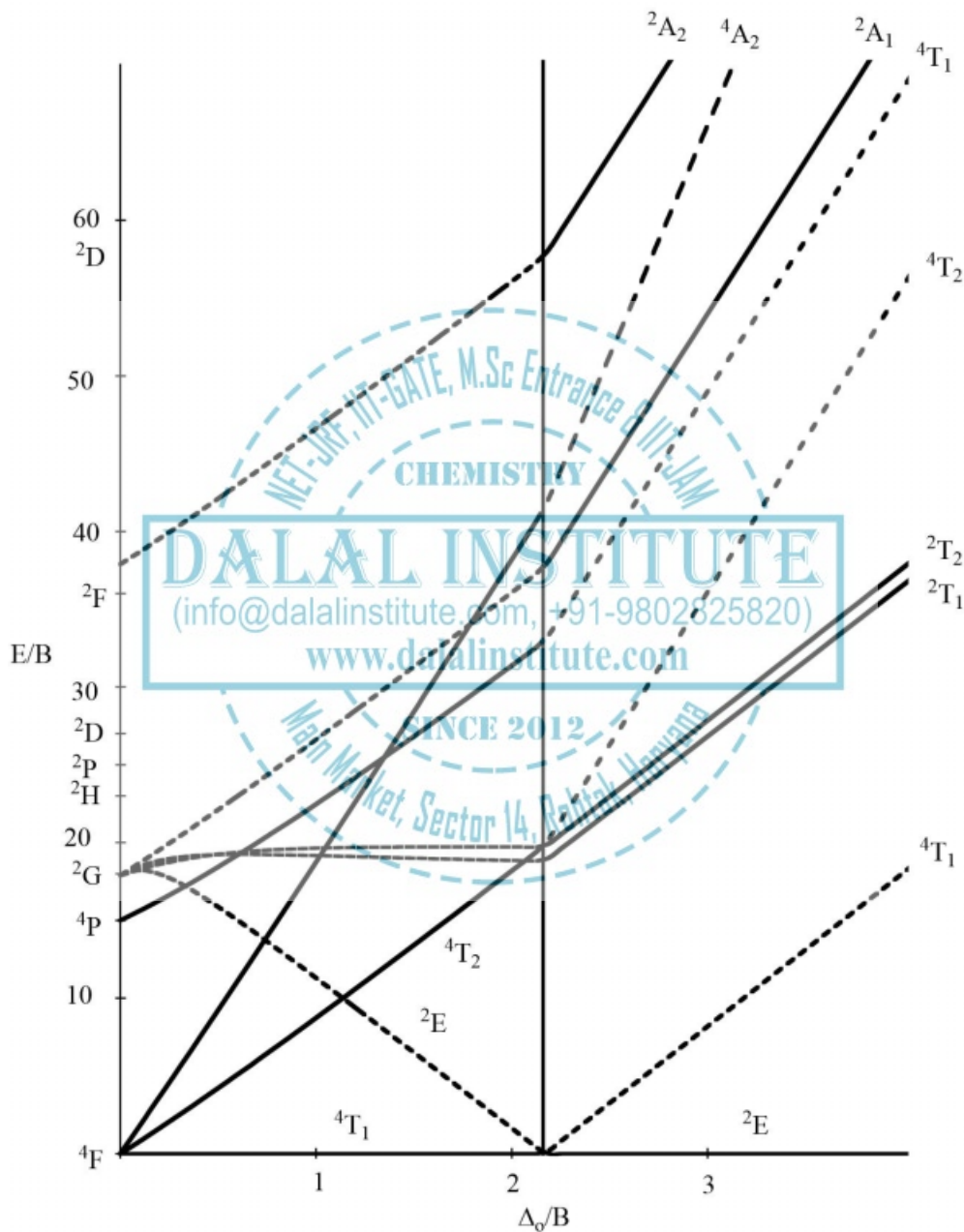


Figure 35. Splitting of free ion terms for d^7 complexes in the octahedral crystal field.

8. d^8 systems:

Metal complexes with d^8 -configuration have 3F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes ${}^3A_{2g}$ and remains as such in weak as well as strong ligand fields.

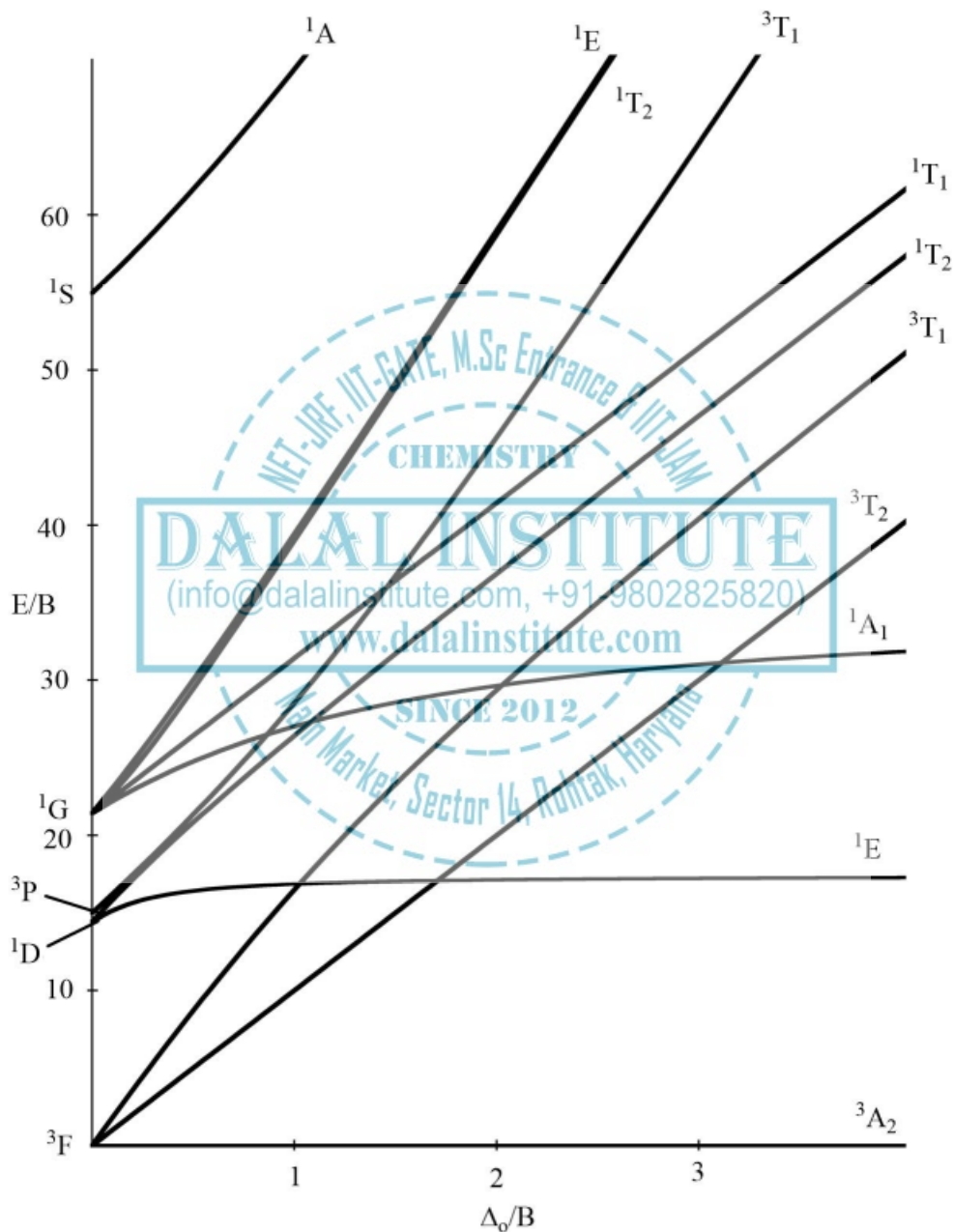


Figure 36. Splitting of free ion terms for d^8 complexes in the octahedral crystal field.

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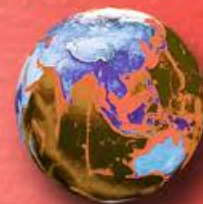
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Table of Contents

CHAPTER 1	11
Stereochemistry and Bonding in Main Group Compounds:.....	11
❖ VSEPR Theory	11
❖ $d\pi-p\pi$ Bonds	23
❖ Bent Rule and Energetic of Hybridization.....	28
❖ Problems	42
❖ Bibliography	43
CHAPTER 2	44
Metal-Ligand Equilibria in Solution:.....	44
❖ Stepwise and Overall Formation Constants and Their Interactions	44
❖ Trends in Stepwise Constants.....	46
❖ Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand.....	49
❖ Chelate Effect and Its Thermodynamic Origin.....	56
❖ Determination of Binary Formation Constants by pH-metry and Spectrophotometry.....	63
❖ Problems	68
❖ Bibliography	69
CHAPTER 3	70
Reaction Mechanism of Transition Metal Complexes – I:.....	70
❖ Inert and Labile Complexes.....	70
❖ Mechanisms for Ligand Replacement Reactions	77
❖ Formation of Complexes from Aquo Ions.....	82
❖ Ligand Displacement Reactions in Octahedral Complexes- Acid Hydrolysis, Base Hydrolysis....	86
❖ Racemization of Tris Chelate Complexes	89
❖ Electrophilic Attack on Ligands	92
❖ Problems	94
❖ Bibliography	95

CHAPTER 4	96
Reaction Mechanism of Transition Metal Complexes – II:	96
❖ Mechanism of Ligand Displacement Reactions in Square Planar Complexes.....	96
❖ The Trans Effect.....	98
❖ Theories of Trans Effect.....	103
❖ Mechanism of Electron Transfer Reactions – Types; Outer Sphere Electron Transfer Mechanism and Inner Sphere Electron Transfer Mechanism.....	106
❖ Electron Exchange.....	117
❖ Problems.....	121
❖ Bibliography.....	122
CHAPTER 5	123
Isopoly and Heteropoly Acids and Salts:	123
❖ Isopoly and Heteropoly Acids and Salts of Mo and W: Structures of Isopoly and Heteropoly Anions	123
❖ Problems.....	152
❖ Bibliography.....	153
CHAPTER 6	154
Crystal Structures:	154
❖ Structures of Some Binary and Ternary Compounds Such as Fluorite, Antifluorite, Rutile, Antirutile, Cristobalite, Layer Lattices - CdI_2 , BiI_3 ; ReO_3 , Mn_2O_3 , Corundum, Pervoskite, Ilmenite and Calcite.....	154
❖ Problems.....	178
❖ Bibliography.....	179
CHAPTER 7	180
Metal-Ligand Bonding:	180
❖ Limitation of Crystal Field Theory.....	180
❖ Molecular Orbital Theory – Octahedral, Tetrahedral or Square Planar Complexes.....	184
❖ π -Bonding and Molecular Orbital Theory	198
❖ Problems.....	212
❖ Bibliography.....	213

CHAPTER 8	214
Electronic Spectra of Transition Metal Complexes:	214
❖ Spectroscopic Ground States	214
❖ Correlation and Spin-Orbit Coupling in Free Ions for 1st Series of Transition Metals.....	243
❖ Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes ($d^1 - d^9$ States).....	248
❖ Calculation of Dq , B and β Parameters	280
❖ Effect of Distortion on the d -Orbital Energy Levels	300
❖ Structural Evidence from Electronic Spectrum	307
❖ Jahn-Teller Effect	312
❖ Spectrochemical and Nephelauxetic Series	324
❖ Charge Transfer Spectra	328
❖ Electronic Spectra of Molecular Addition Compounds.....	336
❖ Problems	340
❖ Bibliography	341
CHAPTER 9	342
Magnetic Properties of Transition Metal Complexes:	342
❖ Elementary Theory of Magneto-Chemistry	342
❖ Guoy's Method for Determination of Magnetic Susceptibility	351
❖ Calculation of Magnetic Moments	354
❖ Magnetic Properties of Free Ions.....	359
❖ Orbital Contribution: Effect of Ligand-Field	362
❖ Application of Magneto-Chemistry in Structure Determination	370
❖ Magnetic Exchange Coupling and Spin State Cross Over	375
❖ Problems	384
❖ Bibliography	385
CHAPTER 10	386
Metal Clusters:	386
❖ Structure and Bonding in Higher Boranes.....	386
❖ Wade's Rules.....	401

❖ Carboranes.....	407
❖ Metal Carbonyl Clusters- Low Nuclearity Carbonyl Clusters.....	412
❖ Total Electron Count (TEC).....	417
❖ Problems.....	424
❖ Bibliography.....	425
CHAPTER 11.....	426
Metal-II Complexes:	426
❖ Metal Carbonyls: Structure and Bonding.....	426
❖ Vibrational Spectra of Metal Carbonyls for Bonding and Structure Elucidation.....	439
❖ Important Reactions of Metal Carbonyls.....	446
❖ Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes.....	450
❖ Tertiary Phosphine as Ligand.....	463
❖ Problems.....	469
❖ Bibliography.....	470
INDEX.....	471



Mandeep Dalal

(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)

Founder & Director, Dalal Institute

Contact No: +91-9802825820

Homepage: www.mandeepdalal.com

E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

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