STUDY MATERIAL

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Electronic transition in metal complexes

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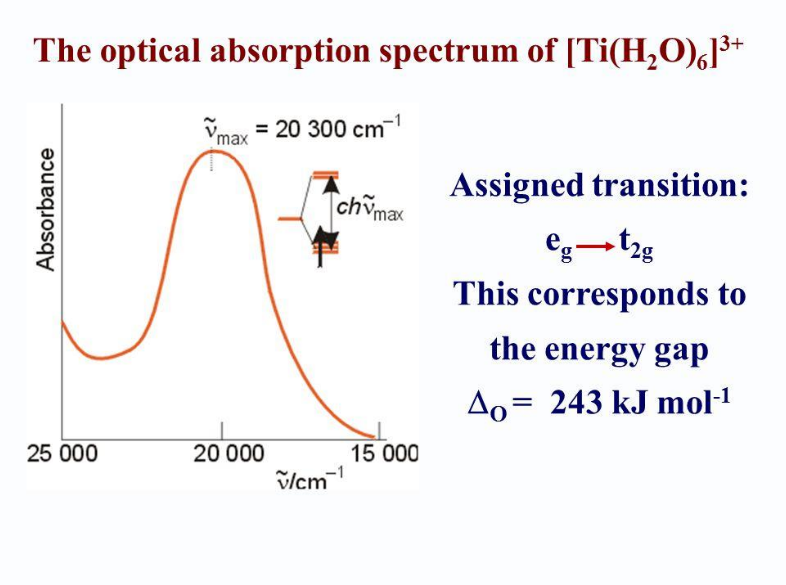
Electronic spectra of d^1 ion in octahedral complex: $[Ti(H_2O)_6]^{3+}$ complex.

In Ti^{3+} ion ($3d^1$), one d electron occupies in a t_{2g} orbital. If the ion absorbs a photon of appropriate energy , then the $t_{2g}{}^1$ electron can be promoted to higher energy eg orbital (eg^1). The energy required to promote this electron is just equal to the crystal field splitting(Δ_0 = 10 Dq) and expressed in $KJmol^{-1}$ or in cm^{-1}. (1 kJ/mol = 83.59 cm^{-1}). The absorption peak for $[Ti(H_2O)_6]^{3+}$ complex occurs at wavelength 493nm = 20300 cm^{-1} = $243KJmol^{-1}$. Therefore the peak is observed in the middle region of the visible region (visible range 200nm- 800nm). Hence, blue and green light are absorbed by the complex and the complementary red-violet color is transmitted. As a result , the $[Ti(H_2O)_6]^{3+}$ ion is red-violet in colour.


The optical absorption spectrum of $[Ti(H_2O)_6]^{3+}$

Assigned transition:

$e_g \rightarrow t_{2g}$

This corresponds to the energy gap

Δ_O = 243 kJ mol^{-1}

The magnitude of the crystal field splitting (Δ_0) depends on the nature of the ligands which is related to the position of the ligands in electrochemical series. Greater the strength of the ligand (CN^- > H_2O> F^- > Cl^-), greater will be the frequency of absorption at which the peak occurs. For example,

$[Ti(CN)_6]^{3-}$ peak occurs at 22300cm^{-1}, $[Ti(H_2O)_6]^{3+}$ peak occurs at 20300cm^{-1}

$[TiF_6]^{3-}$ peak occurs at 18900cm^{-1}, $[TiF_6]^{3-}$ peak occurs at 13000cm^{-1}

The effect of octahedral ligand field on d^1 metal ion is shown in the following way.

Ti^{3+} ion (3d^1)

m_l = +2 +1 0 -1 -1

↑				

L = $\sum m_l$ = 2= D term , S=$\sum s_i$ = ½

Spin multiplicity =2S+1= 2x1/2+1= 2, Orbital multiplicity= 2L+1=2x2+1=5

Term symbol= ^2D

Therfore the ground term for a free metal ion has ^2D term. In presence of ligand , the ^2D term will be spitted into two states which are described by the Mulliken symbol $^2T_{2g}$ and ^2E_g. The lower energy state $^2T_{2g}$ (triplet) corresponds to electron occupying in the t_{2g} orbital whereas the higher energy ^2E_g (doublet) corresponds to electron occupying in the e_g orbital.

Therefore, D (5)= T_2 (3)+ E(2)

We can arrange d^1 electron of t_{2g} in three ways at ground state and eg electron in two ways at excited state, hence the orbital degeneracy are 3 and 2 respectively. As the orbital degeneracy in ground state is three, so T is the ground state term. Greater the strength of ligand field, greater is the separation between two states ($^2T_{2g}$ and ^2E_g).

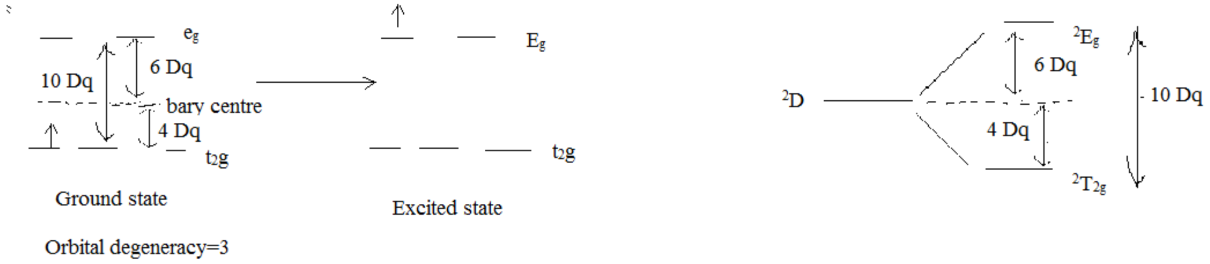
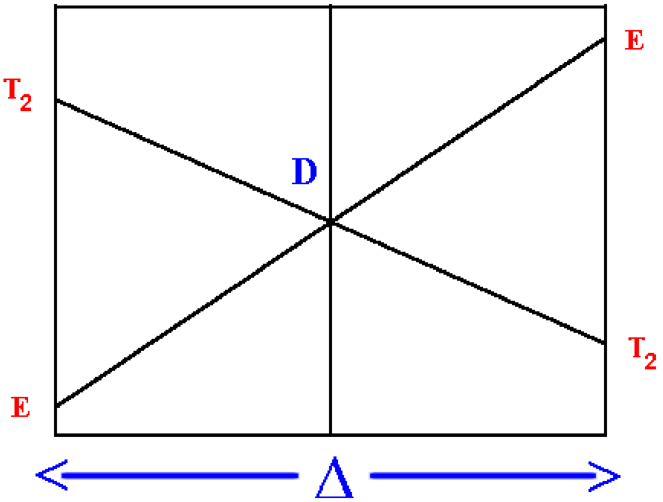


Fig: d-d transition and splitting of d^1 ion

Electronic spectra of d^9 ion in octahedral complex: $[Cu(H_2O)_6]^{2+}$ complex.

It is a d^9 system which is inverse of d^1 system. In d^1 configuration the single electron is occupied in the lower t_{2g} orbital whereas in d^9 configuration, there is a single hole in the upper e_g orbital. Therefore, in d^1 case, transition occurs from t_{2g} level to e_g level while in d^9 case there is a promotion of an electron as the transfer of a hole from to e_g level to t_{2g} level. Thus, the energy level diagram of d^9 is inverse of d^1 ion.

Orgel diagrams are useful for showing the energy levels of both high spin octahedral and tetrahedral transition metal ions. They only show the spin-allowed transitions. For complexes with D ground terms only one electronic transition is expected and the transition energy corresponds directly to D. Hence, the following high spin configurations are dealt with: d^1, d^4, d^6 and d^9



On the left hand side d^1, d^6 tetrahedral and d^4, d^9 octahedral complexes are covered and on the right hand side d^4, d^9 tetrahedral and d^1, d^6 octahedral. For simplicity, the g subscripts required for the octahedral complexes are not shown.

Electronic spectra of d^2 ion in octahedral complex: $[V(H_2O)_6]^{3+}$ complex.

In V^{3+} ion ($3d^2$), two d electrons occupy in a two t_{2g} orbital. When the electrons promoted from t_{2g} orbital to e_g orbital , two possible transitions are possible.

(i) one electron is promoted $(t_{2g})^2 \longrightarrow (t_{2g})^1\ (e_g)^1$

(ii) both electrons get promoted $(t_{2g})^2 \longrightarrow (t_{2g})^0\ (e_g)^2$

The effect of octahedral ligand field on d^2 metal ion is shown in the following way.

V^{3+} ion ($3d^2$)

m_l = +2 +1 0 -1 -1

↑	↑			

$L = \sum m_l = +2 + 1 = 3$ = F term , $S = \sum s_i = ½ + ½ = 1$

Spin multiplicity =2S+1= 2x1+1= 3, Orbital multiplicity= 2L+1=2x3+1=7

Term symbol= ^3F

Therefore the ground term for a free metal ion has ^3F term and the other excited state terms are ^3F, ^3P, ^1G, ^1D, ^1S . Among these terms ^1G, ^1D, ^1S terms are spin forbidden and the remaining ^3F, ^3P are spin allowed. In presence of ligand , the ^3F term will be split into three states which are described by the Mulliken symbols $^3T_{1g}$ $^3T_{2g}$ and $^3A_{2g}$. We know, p orbitals are not splits, hence, ^3P state is not split, but transformed into $^3T_{1g}$ state. Therefore, F state splits in the following :

F state (7)= T_1 (3)+ T_2 (3)+ A_2(1)

We can arrange d^2 electron of t_{2g} in three ways at ground hence the orbital degeneracy is 3. So, T_1 is the ground state term.

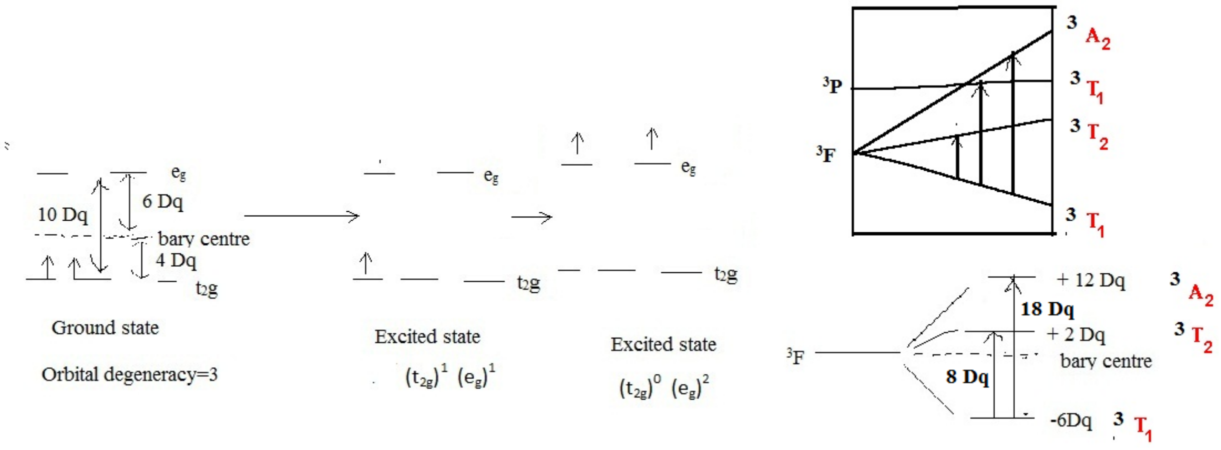


Fig: d-d transition and splitting of d^2 ion

From the figure it is clear that three transitions are possible from the ground state

(i) $^3T_{1g}$ (F) to $^3T_{2g}$ (F), (ii)) $^3T_{1g}$ (F) to $^3T_{1g}$ (P) and (iii) $^3T_{1g}$ (F) to $^3A_{2g}$(F) respectively. So, three peaks should be appearing for d^2 configuration. But $[V(H_2O)_6]^{3+}$ complex shows only two peaks. This is due to the weak field ligand of water . The transition from $^3T_{1g}$ (F) to $^3T_{1g}$ (P) and $^3T_{1g}$ (F) to $^3A_{2g}$(F) are not resolved due to close cross-over point between $^3T_{1g}$ (P) and $^3A_{2g}$(F). If the ligand is other than water then three peaks are observed.

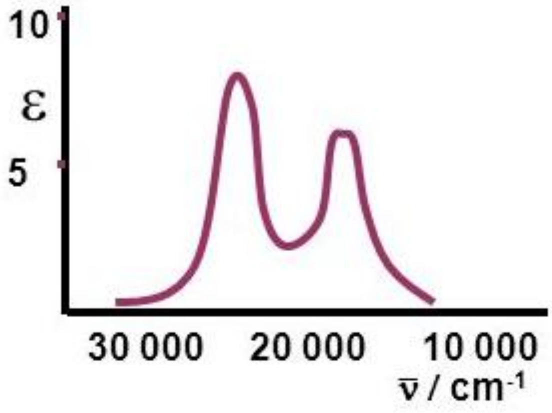
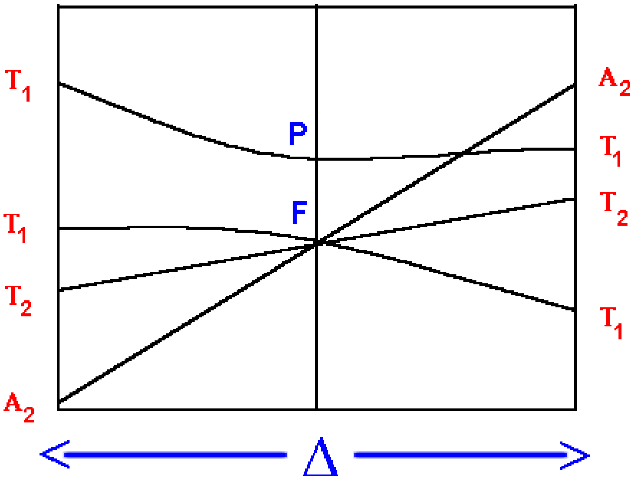


Figure: Uv-Vis spectra of $[V(H_2O)_6]^{3+}$ complex

For complexes with F ground terms, three electronic transitions are expected and D may not correspond directly to a transition energy. The following configurations are dealt with: d^2, d^3, high spin d^7 and d^8.



On the left hand side, d^2, d^7 tetrahedral and d^3, d^8 octahedral complexes are covered and on the right hand side d^3, d^8 tetrahedral and d^2 and high spin d^7 octahedral. Again for simplicity, the g subscripts required for the octahedral complexes are not shown..

An alternative method is to use **Tanabe Sugano diagrams,** which are able to predict the transition energies for both spin-allowed and spin-forbidden transitions, as well as for both strong field (low spin), and weak field (high spin) complexes. In this method the energy of the electronic states are given on the vertical axis and the ligand field strength increases on the horizontal axis from left to right. Linear lines are found when there are no other terms of the same type and curved lines are found when 2 or more terms are repeated. This is as a result of the "non-crossing rule". The baseline in the Tanabe-Sugano diagram represents the lowest energy or ground term state.

The electronic spectrum of the V^{3+} ion, shows three major peaks with frequencies of: n_1=17400 cm^{-1}, n_2=25400 cm^{-1} and n_3=34500 cm^{-1}.

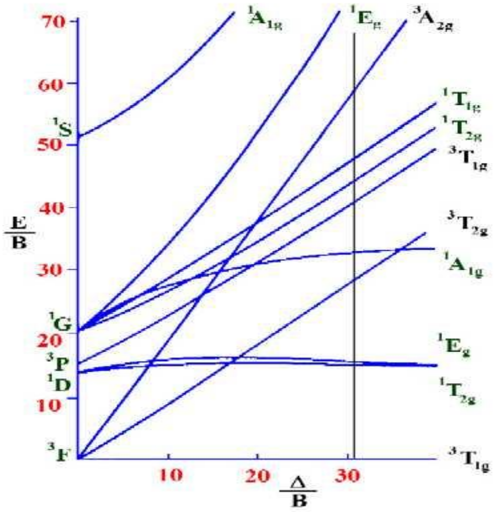


Figure : Tanabe-Sugano diagram for d^2 octahedral complexes

These have been assigned to the following spin-allowed transitions.

(i) $^3T_{1g} \rightarrow {}^3T_{2g}$ (ii)) $^3T_{1g} \rightarrow {}^3T_{1g}$ (P) and (iii) $^3T_{1g} \rightarrow {}^3A_{2g}$

The ratio between the first two transitions is calculated as n_2/n_1 which is equal to 25400 / 17400 = 1.448.

To calculate the Racah parameter, B, the position on the horizontal axis where the ratio between the lines representing $\nu_2$and ν is equal to 1.448, has to be determined. On the diagram below, this occurs at D/B=30.9. Having found this value, a vertical line is drawn at this position

On moving up the line from the ground term to where lines from the other terms cross it, we are able to identify both the spin-forbidden and spin-allowed transition and hence the total number of transitions that are possible in the electronic spectrum.

Next, find the values on the vertical axis that correspond to the spin-allowed transitions so as to determine the values of n_1/B, n_2/B and n_3/B. From the diagram above these are 28.78, 41.67 and 59.68 respectively.

Knowing the values of n_1, n_2 and n_3, we can now calculate the value of B. Since $n_1/B=28.78$ and n_1 is equal to 17,400 cm^{-1}, then

B= $n_1/28.78$ =17400/28.78=604.5 cm^{-1}

then it is possible to calculate the value of D. Since D/B=30.9, then: D=B x30.9 and hence: D = 604.5 x 30.9 = 18680 cm^{-1}

Electronic spectra of d^8 ion in octahedral complex: $[Ni(H_2O)_6]^{2+}$ complex.

It is a d^8 system which is inverse of d^2 system. In d^2 configuration both the electrons are occupied in the lower t_{2g} orbital whereas in d^8 configuration, there are two holes in the upper e_g orbital. Therefore, in d^2 case, transition occurs from t_{2g} level to e_g level while in d^8 case there is a promotion of an electron which is equivalent to transferring a hole from to e_g level to t_{2g} level. Thus, the energy level diagram of d^8 is inverse of d^2 ion.

Electronic spectra of d^3 ion in octahedral complex: $[Cr(H_2O)_6]^{3+}$ complex.

In Cr^{3+} ion ($3d^3$), three d electrons occupy in a two t_{2g} orbital. When the electrons promoted from t_{2g} orbital to e_g orbital , two possible transitions are possible.

(i) one electron is promoted $(t_{2g})^3 \rightarrow (t_{2g})^2 (e_g)^1$

(ii) Two electrons get promoted $(t_{2g})^3 \rightarrow (t_{2g})^1 (e_g)^2$

The effect of octahedral ligand field on d^2 metal ion is shown in the following way.

Cr^{3+} ion ($3d^3$)

m_l = +2 +1 0 -1 -1

↑	↑	↑		

L = $\sum m_l$ = +2 +1 + 0= 3 = F term , $S=\sum s_i$ = ½ +½ + ½ = 3/2

Spin multiplicity =2S+1= 2x3/2+1= 4, Orbital multiplicity= 2L+1=2x3+1=7

Term symbol= ^4F

Similarly , F state splits in the following :

F state (7)= T_1 (3)+ T_2 (3)+ A(1)

We can arrange d^3 electron of t_{2g} in one way only at ground state hence the orbital degeneracy is 1. So, A_2 is the ground state term. Similar to d^2 ion, three peaks should be present but $[Cr(H_2O)_6]^{3+}$ complex shows only two peaks.

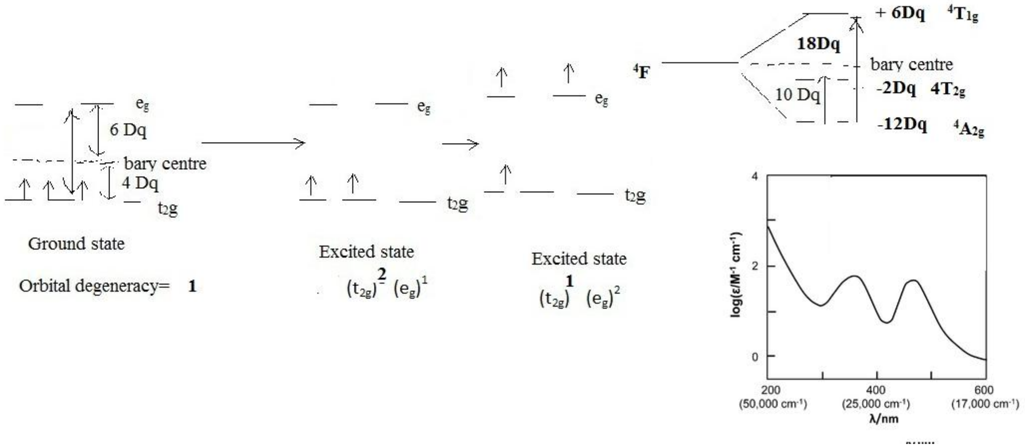


Fig: d-d transition and splitting of d^3 ion

Question: Calculate the value of B and D for the Cr^{3+} ion in $[Cr(H_2O)_6)]^{3+}$ if

n_1=17000 cm^{-1}, n_2=24000 cm^{-1} and n_3=37000 cm^{-1}.

Solution:

These values have been assigned to the following spin-allowed transitions.

(i) $^4A_{2g} \rightarrow {}^4T_{2g}$ (ii)) $^4A_{2g} \rightarrow {}^4T_{1g}$ and (iii) $^4A_{2g} \rightarrow {}^4T_{1g}$ (P)

From the information given, the ratio n_2 / n_1 = 24000 / 17000 = 1.412. Using a Tanabe-Sugano diagram for a d^3 system this ratio is found at D/B=24.00

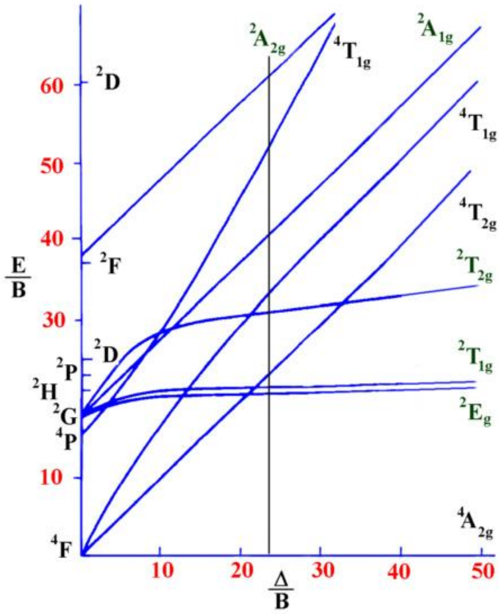


Figure : Tanabe-Sugano diagram for d^3 octahedral complexes

Recall that n_1=17000 cm^{-1}. Therefore for the first spin-allowed transition,

17000 /B =24.00 from which B can be obtained, B=17000 / 24.00 or B=708.3 cm^{-1}.

This information is then used to calculate D. Since D / B=24.00 then D = B x 24.00 = 708.3 x 24.00 = 17000 cm^{-1}.

Electronic spectra of d^7 ion in octahedral complex: $[Co(H_2O)_6]^{2+}$ complex.

It is a d^7 system which is inverse of d^3 system. In d^3 configuration both the electrons are occupied in the lower t_{2g} orbital whereas in d^7 configuration, there are three holes in the upper e_g orbital. Therefore, in d^3 case, transition occurs from t_{2g} level to e_g level while in d^7 case there is a promotion of an electron which is equivalent to transferring a hole from to e_g level to t_{2g} level. Thus, the energy level diagram of d^7 is inverse of d^3 ion.

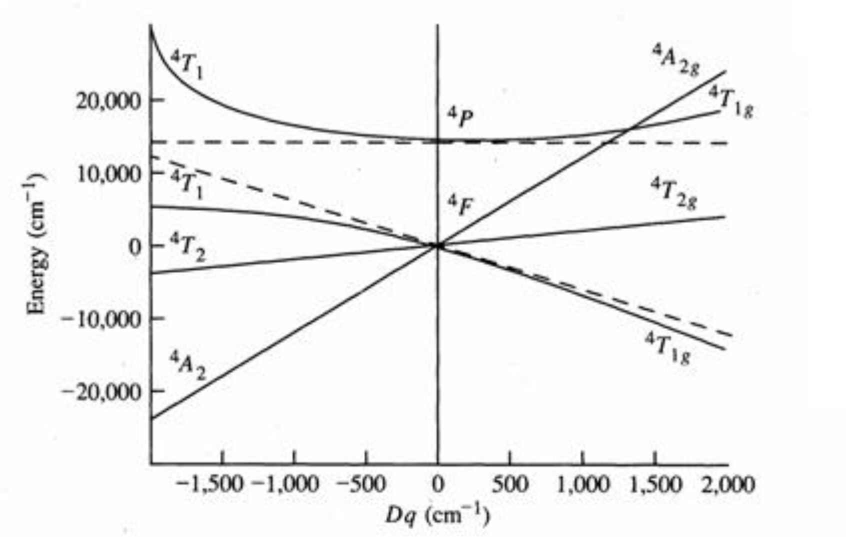
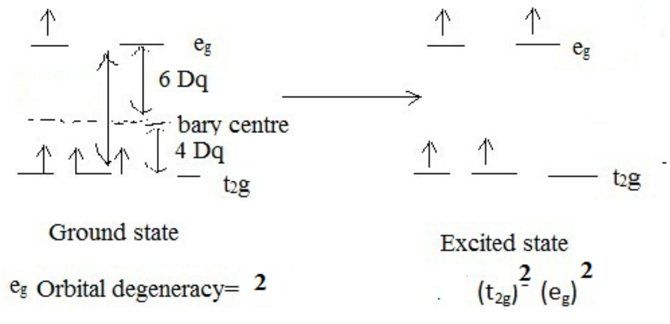
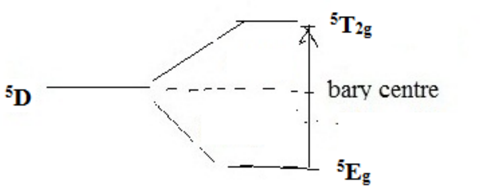


Figure: Orgel diagram of Co^{2+} ion in tetrahedral (left) and octahedral field (right)

Electronic spectra of d^4 ion in octahedral complex(same for d^6 ion)





Electronic spectra of d^5 ion in octahedral complex: $[Mn(H_2O)_6]^{2+}$ / $[MnF_6]^{4-}$

In $[Mn(H_2O)_6]^{2+}$ complex, Mn^{2+} is d^5 system. The weak field ligand water or fluoride forms high spin complex with Mn^{2+}. Any transition should remain unaltered of spin (i.e . $\Delta S = 0$, spin allowed transition), but any transition within d level involves a reversal of spin , hence d-d transitions are spin forbidden. . Again, any d- d transitions are ($\Delta l = \pm 1$ are allowed transition and $\Delta l = 0$ are forbidden transition) are Laporte forbidden. Hence, Mn^{2+} is doubly forbidden. Absorptions that are doubly forbidden transitions are extremely weak. As a result , the absorption band will be extremely weak and hence most of the Mn(II) salt becomes very pale pink colour.

$t_{2g}^{3}eg^{2}$ (S=5/2) → $t_{2g}^{2}eg^{3}$(S=3/2) ; $\Delta S \neq 0$, i.e . spin forbidden transition.

$t_{2g}^{3}eg^{2}$ (l=2) → $t_{2g}^{2}eg^{3}$(l=2) ; $\Delta l = 0$, i.e . . Laporte forbidden transition.

The effect of octahedral ligand field on d^5 metal ion is shown in the following way.

Mn^{2+} ion ($3d^5$)

m_l = +2 +1 0 -1 -1

↑	↑	↑	↑	↑

L = $\sum m_l$ = +2 +1 + 0+ (-1+)+(-2)= 0 = S term , $S=\sum s_i$ = 5x ½ = 5/2

Spin multiplicity =2S+1= 2x5/2+1= 6, Orbital multiplicity= 2L+1=2x0+1=1

Term symbol= ^6S

Therefore, the ground state term is ^6S which has only one state, hence no splitting occurs , it only changes its term to $^6A_{1g}$ and there are 11 excited state term. Among the excited state term only four quartets ^4G, ^4F, ^4D, ^4P involve the reversal of only one spin. In octahedral field , these four states split into 10 states . So, maximum 10 weak absorption bands may be observed.

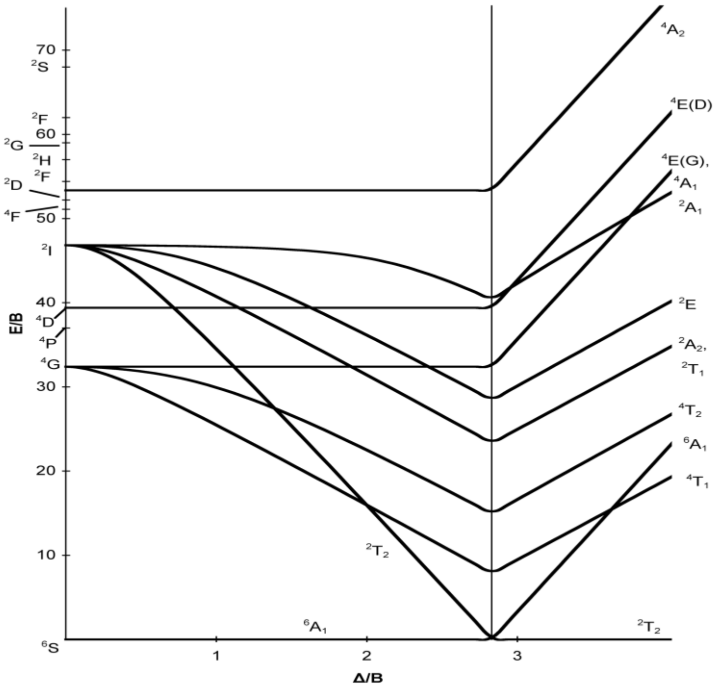


Figure: Orgel energy level diagram for Mn^{2+} (d^5) octahedral complex.

The absorption bands are assigned as follows:

(i)$^6A_{1g}$ (S) →$^4T_{1g}$(G) (18900 cm^{-1}), (ii)$^6A_{1g}$ (S) →$^4T_{2g}$(G) (23100 cm^{-1}), (iii)$^6A_{1g}$ (S) →^4E_g(G) and $^6A_{1g}$ (S) →$^4A_{1g}$(G), (24970 cm^{-1} and 25300 cm^{-1}), (iv)$^6A_{1g}$ (S) →$^4T_{2g}$(D) (28000cm^{-1}), (i)$^6A_{1g}$ (S) →^4E_g(D) (29700cm^{-1}).

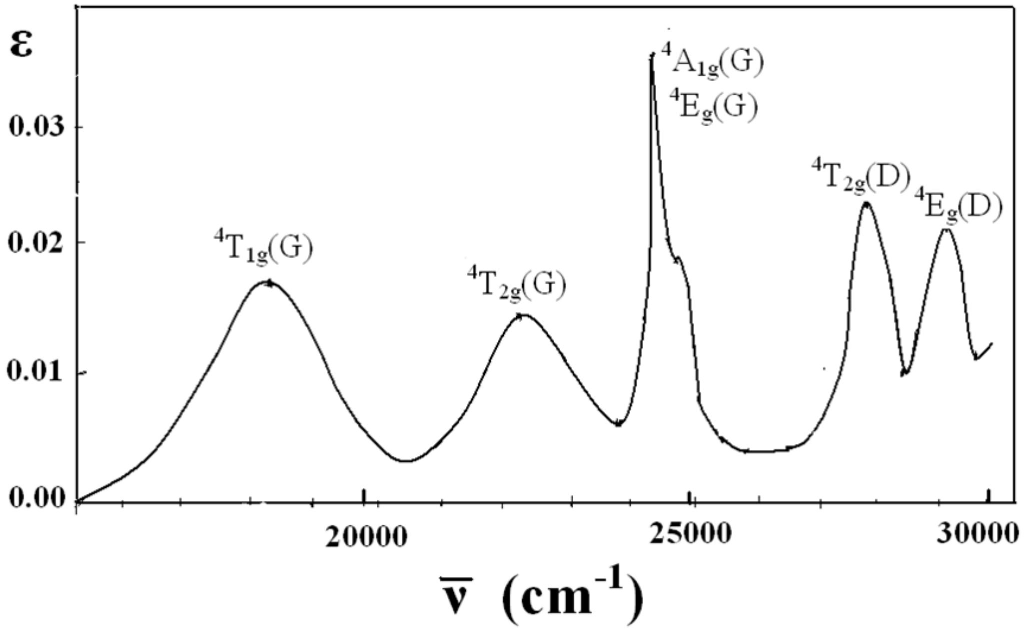


Figure: The spectrum of $[Mn(H_2O)_6]^{2+}$ complex

Table: Different d^n ion , ground term and octahedral splitting

d^n	Free ion ground state Term Symbol	Splitting of states in Oh ligand field
d^1 d^9	^2D	$^2D \rightarrow {}^2T_{2g} + {}^2E_g$
d^2 d^8	^3F	$^3F \rightarrow {}^3T_{1g} + {}^3T_{2g} + {}^3A_{2g}$
d^3 d^7	^4F	$^4F \rightarrow {}^4T_{1g} + {}^4T_{2g} + {}^4A_{2g}$
d^4 d^6	^5D	$^5D \rightarrow {}^5T_{2g} + {}^5E_g$
d^5	^6S	$^6S \rightarrow {}^6A_{1g}$