(HS octahedral) (octahedral) (Tetrahedral)

(Tetrahedral) (Tetrahedral) (Tetrahedral)

(HS octahedral) (HS octahedral)

Table : Terms arising for p and d configurations:

Electronic configuration	Ground state term	Other term
p^1, p^5	^2P	
p^2, p^4	^3P	$^1S, ^1D$
p^3	^4S	$^2P, ^2D$
p^6	^1S	
d^1, d^9	^2D	
d^2, d^8	^3F	$^3P, ^1G, ^1D, ^1S$
d^3, d^7	^4F	$^4P, ^2H, ^2G, ^2F, ^2D, ^2P$
d^4, d^6	^5D	$^3H, ^3G, ^3F, ^3D, ^3P, ^1I, ^1G, ^1F, ^1D, ^1S$
d^5	^6S	$^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G, ^2F, ^2D, ^2P, ^2S$

(3) Absorption of Light

In explaining the colors of coordination compounds, we are dealing with the phenomenon of complementary colors: if a compound absorbs light of one color, we see the complement of that color. For example, when white light (containing a broad spectrum of all visible wavelengths) passes through a substance that absorbs red light, the color observed is green. Green is the complement of red, so green predominates visually when red light is subtracted from white. Complementary colors can conveniently be remembered as the color pairs on opposite sides of the color wheel shown below.
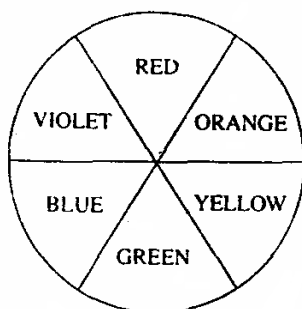
An example from coordination chemistry is the deep blue color of aqueous solutions of copper (II) compounds, containing the ion $[Cu(H_2O)_6]^{2+}$. The blue color is a consequence of the absorption of light between approximately 600 and 1000 nm (maximum near 800 nm;), in the yellow to infrared region of the spectrum. The color observed, blue, is the average complementary color of the light absorbed.

It is not always possible to make a simple prediction of color directly from the absorption spectrum in large part because many coordination compounds contain two or more absorption bands of different energies and intensities. The net color observed is the color predominating after the various absorption are removed from white light.
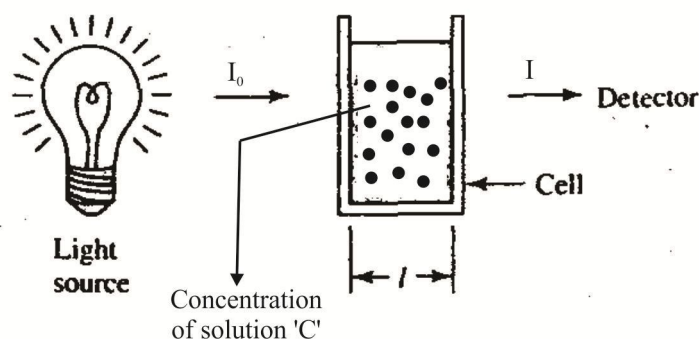
Beer-Lambert Absorption Law

If light of intensity I_0 at a given wavelength passes through a solution containing a species that absorbs light, the light emerges with intensity I, which may be measured by a suitable detector.
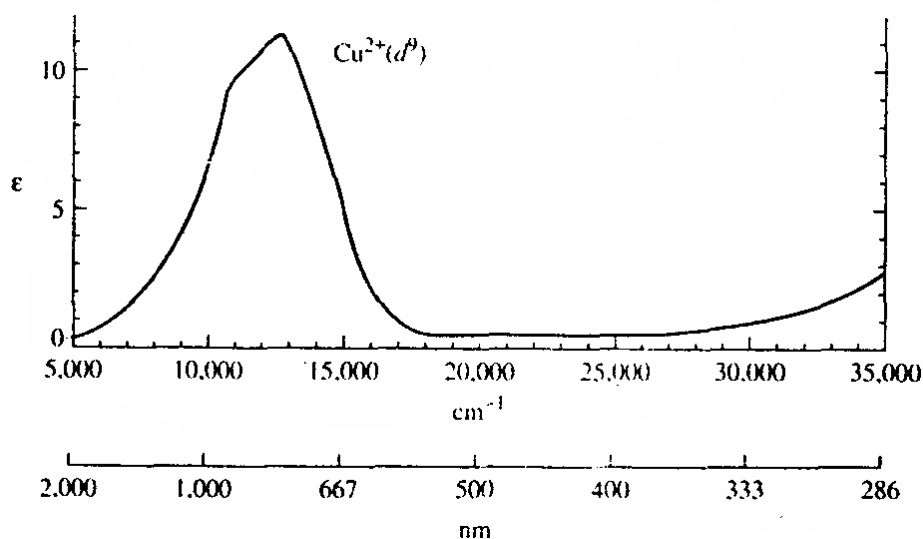
Visible Light and Complementary Colors

Wavelength Range (nm)	Wave numbers (cm^{-1})	Color	Complementary color
< 400	> 25,000	Ultraviolet	colourless
400–450	22,000–25,000	Violet	Yellow
450–490	20,000–22,000	Blue	Orange
490–550	18,000–20,000	Green	Red
550–580	17,000–18,000	Yellow	Violet
580–650	15,000–17,000	Orange	Blue
650–700	14,000–15,000	Red	Green
> 700	< 14,000	Infrared	colourless

The Beer-Lambert law may be used to describe the absorption of light (ignoring scattering and reflection of light from cell surfaces) at a given wavelength by an absorbing species in solution:

$$\log \frac{I_0}{I} = A = \varepsilon \, l \, c$$

where A = absorbance

ε = molar absorptivity (L mol^{-1} cm^{-1}) (also known as molar extinction coefficient)

l = path length through solution (cm)

c = concentration of absorbing species (mol L^{-1})

Absorbance is a dimensionless quantity. An absorbance of 1.0 corresponds to 90% absorption at a given wavelength, an absorbance of 2.0 corresponds to 99% absorption and so on.

Spectrophotometers commonly obtain spectrum as plots of absorbance versus wavelength. The molar absorptivity is a characteristic of the species that is absorbing the light and is highly dependent on wavelength. A plot of molar absorptivity versus wavelength gives a spectrum characteristic of the molecule or ion in question, figure. As we will see, this spectrum is a consequence of transitions between states of different energies and can provide valuable information about those states and in turn, about the structure and bonding of the molecule or ion.

Although the quantity most commonly used to describe absorbed light is the wavelength, energy and frequency are also used. In addition , the wave number the number of waves per centimeter, a quantity proportional to the energy, is frequently used. For reference, the relations between these quantities are given by the equations.

$$\Delta E = hv = \frac{hc}{\lambda} = hc\left(\frac{1}{\lambda}\right) = hc\bar{v} \quad \therefore \quad \Delta E \propto \frac{1}{\lambda} \propto \bar{v}$$

where ΔE = energy

h = Planck's constant = 6.626×10^{-34} J s

c = speed of light = 2.998×10^{8} ms^{-1}

v = frequency (s^{-1})

λ = wavelength (often reported in nm)

$\frac{1}{\lambda} = \bar{v}$ = wavenumber (cm^{-1})

(4)   Selection Rules:

(a)   Laporte 'Orbital' Selection Rule

Transitions which involve a change in the subsidiary quantum number $\Delta l = \pm 1$ are 'Laporte allowed' and therefore have a high absorbance. If $\Delta \, l = 0$ i.e., there is no change in subsidiary quantum number, then transitions are said to be forbidden. Laporte selection rule may also be given as follows:

Transitions between g (gerade) and u (ungerade) orbitals are permitted and the transition between g orbitals or u orbitals are not permitted.

g $\longleftrightarrow$ u   g $\longleftrightarrow$ g | u $\longleftrightarrow$ u |
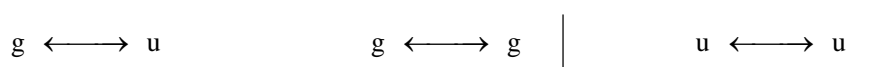
Thus for Ca, $s^2 \rightarrow s^1 p^1, l$ changes by $+ 1$ and the molar absorption coefficient ε is 5000–10,000 litres per mol per centimetre. In contrast d-d transition are 'Laporte forbidden', since the change in l = 0, but spectra of much lower absorbance are absorbed ($\varepsilon = 5 - 10 \, l \, \text{mol}^{-1} \, \text{cm}^{-1}$) because of slight relaxation in the Laporte rule. When the transition metal ion forms a complex it is surrounded by ligands, and some mixing of d and p orbitals may occur, in which case transitions are no longer pure d-d in nature. Mixing of this kind occurs in complexes which do not possess a centre of symmetry, for example tetrahedral complexes, or asymmetrically substituted octahedral complexes. Thus $[\text{MnBr}_4]^{2-}$ which is tetrahedral and $[\text{Co(NH}_3)_5\text{Cl}]^{2+}$ which is octahedral but non-centrosymmetric are both coloured. Mixing of p and d orbitals doe not occur in octahedral complexes which have a centre of symmetry such as $[\text{Co(NH}_3)_6]^{3+}$ or $[\text{Cu(H}_2\text{O)}_6]^{2+}$. However, in these cases the metal-ligands bonds vibrate so that the ligands spend an appreciable amount of time out of their centro-symmetric equilibrium position. Thus a very small amount of mixing occurs and low-intensity spectra are observed. Thus Laporte allowed transitions are very intense, whilst Laporte forbidden transitions vary from weak intensity if the complex in non-centrosymmeetric to very weak if it is centrosymmetric. Since p-d mixing is much more pronounced in tetrahedral complexes (non-centro symmetric) than octahedral complexes (centro symmetric). Thus tetrahedral complexes give more intense colour than octahedral complexes.

(b)   Spin Selection Rule
During transitions between energy levels, an electron does not change its spin, that is $\Delta S = 0$ i.e., any transition for which $\Delta S = 0$ (no change in spin state) is allowed. if $\Delta S \neq 0$ (change in spin state) transition is forbidden. In other words, for allowed transitions spin multiplicity does not change. e.g.,

$^3T_{2g} \longrightarrow {}^3T_{2g}$

$^3T_{1g} \longrightarrow {}^3A_{2g}$

$^3T_{1g} \longrightarrow {}^3T_{1g(P)}$
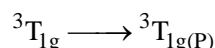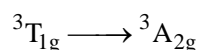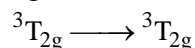
Here, there are fewer exceptions than for the Laporte selection rule. Thus in the case of Mn^{2+} in a weak octahedral field such as $[\text{Mn(H}_2\text{O)}_6]^{2+}$ the d-d transitions are spin forbidden because each of the d orbitals is singly occupied. Many Mn^{2+} compounds are off white or pale flesh coloured, but the intensity is only about one hundredth of that for a spin allowed transition. Since the spin forbidden transitions are very weak, analysis of the spectra of transition metal complexes can be greatly simplified by ignoring all spin forbidden transitions and considering only those excited states which have the same multiplicity as the ground state. Thus for a d^2 configuration the only terms which need to be considered are the ground state ^3F and the excited state ^3P.

Ti^{3+} in weak octahedral field (spin allowed), if electron in t_{2g} level is excited to e_g level then spin state will not change. Thus this transition is spin allowed.
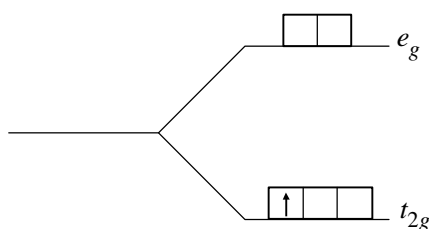
Mn^{2+} in weak octahedral field (spin forbidden transition), if one of the electrons in t_{2g} level is excited to e_g state then spin state is changed (from clockwise to anticlockwise) thus this electronic transition is spin forbidden.
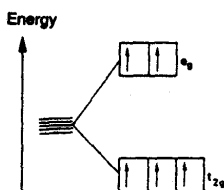

Molar absorption coefficient for different types of transition are given in the following table:

Laporte (orbital)	Spin	Type of Spectra	ε (L mol^{-1} cm^{-1})	Example
Allowed	Allowed	Charge transfer	10000	$[TiCl_6]^{2-}$
Partly alllowed, some p-d mixing	Allowed	d-d	500	$[CoBr_4]^{2-} \cdot [CoCl_4]^{2-}$
Forbidden	Allowed	d-d	8–10	$[Ti(H_2O)_6]^{3+} \cdot [V(H_2O)_6]^{3+}$
Partly allowed, some p-d mixing	Forbidden	d-d	4	$[MnBr_4]^{2-}$
Forbidden	Forbidden	d-d	0.02	$[Mn(H_2O)_6]^{2+}$

(5) Splitting of Electronic Energy Levels and Spectroscopic States

s orbital is spherically symmetrical and is unaffected by an octahedral (or any other) field, p orbitals are directional, and p orbitals are affected by an octahedral field. However, since a set of three p orbitals are all affected equally, their energy levels remain equal, and no splitting occurs. A set of d orbtials is split by an octahedral field into two level t_{2g} and e_g The difference in energy between these may be written as Δ_0 or $10D_q$. The t_{2g} level is triply degenerate and is $4D_q$ below the barycentre and the e_g level is doubly degenerate and is $6D_q$ above the barycentre. For a d^1 configuration, the ground state is a 2_D state, and the t_{2g} and e_g electronic energy levels correspond with the T_{2g} and E_g spectroscopic states. A set of f orbitals is split by an octahedral field into three levels. For an f^{1} arrangement the ground state is a ^3F state and is split into a triply degenerate T_{1g} state which is $6D_q$ below the barycentre, a triply degenerate T_{2g} level which is $2D_q$ above the barycentre and a single A_{2g} state which is $12D_q$ above the barycentre.
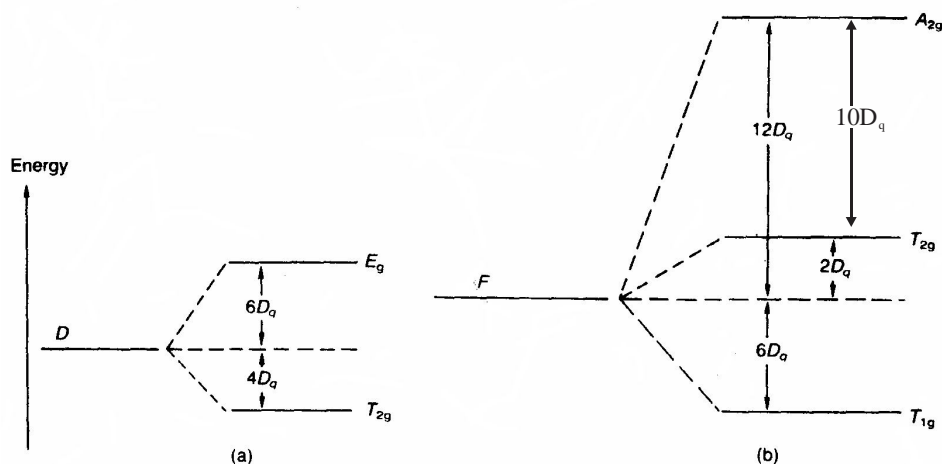
In the one electron cases s^1, p^1, d^1 and f^1 there is a direct correspondence between the splitting of electronic energy levels which occurs in a crystal field and the splitting of spectroscopic states. Thus in an octahedral field the S and P states are not split. D states are split into two states and F states are split into three states.

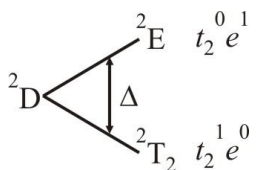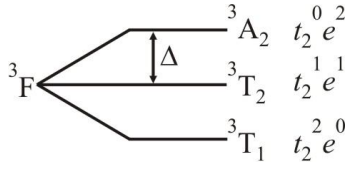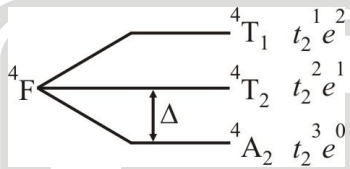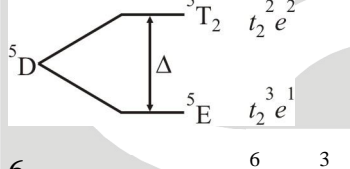**Table :** Transforming spectroscopic terms into Mulliken symbols
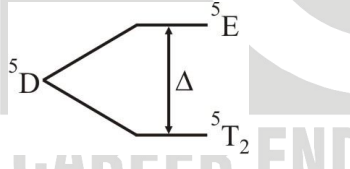
Spectroscopic term	Mulliken Symbols	
	Octahedral field	**Tetrahedral field**
S	A_{1g}	A_1
P	T_{1g}	T_1
D	$E_g + T_{2g}$	$E + T_2$
F	$A_{2g} + T_{1g} + T_{2g}$	$A_2 + T_1 + T_2$
G	$A_{1g} + E_g + T_{1g} + T_{2g}$	$A_1 + E + T_1 + T_2$

(6)   Table

Ground and excited terms having the same spin multiplicities for weak field octahedral (oct) and tetrahedral (tet) complexes

Configuration	Ground term	Excited terms with the same spin multiplicity as the ground term
d^1 oct, d^9 tet	$^2T_{2(g)}$	$^2E_{2(g)}$
d^2 oct, d^8 tet	$^3T_{1(g)}F$	$^3T_{2(g)}, {}^3A_{2(g)}, {}^3T_{1(g)},(P)$
d^3 oct, d^7 tet	$^4A_{2(g)}$	$^4T_{2(g)}, {}^4T_{1(g)}(F), {}^4T_{1(g)}(P)$
d^4 oct, d^6 tet	$^5E_{2(g)}$	$^2T_{2(g)}$
d^5 oct, d^5 tet	$^6A_{1(g)}$	None
d^6 oct, d^4 tet	$^5T_{2(g)}$	$^5E_{2(g)}$
d^7 oct, d^3 tet	$^4T_{1(g)}(F)$	$^4T_{2(g)}, {}^4A_{2(g)}, {}^4T_{1(g)}(P)$
d^8 oct, d^2 tet	$^3A_{2(g)}$	$^3T_{2(g)}, {}^3A_{1(g)}(F), {}^3T_{1(g)}(P)$
d^9 oct, d^1 tet	$^2E_{2(g)}$	$^2T_{2(g)}$

**Configuration**   **Correlation of Spectroscopic Ground Term**

1. d^1

$$^2D \begin{cases} ^2E \quad t_2^0 e^1 \\ \quad \Delta \\ ^2T_2 \quad t_2^1 e^0 \end{cases}$$

2. d^2 ^3P ------------------ $^3T_1 \quad t_2^1 e^1$

$$^3F \begin{cases} ^3A_2 \quad t_2^0 e^2 \\ \quad \updownarrow \Delta \\ ^3T_2 \quad t_2^1 e^1 \\ ^3T_1 \quad t_2^2 e^0 \end{cases}$$

3. d^3 ^4P ------------------ $^4T_1 \quad t_2^1 e^1$

$$^4F \begin{cases} ^4T_1 \quad t_2^1 e^2 \\ ^4T_2 \quad t_2^2 e^1 \\ \quad \updownarrow \Delta \\ ^4A_2 \quad t_2^3 e^0 \end{cases}$$

$$^5D \begin{cases} ^5T_2 \quad t_2^2 e^2 \\ \quad \updownarrow \Delta \\ ^5E \quad t_2^3 e^1 \end{cases}$$

4. d^4

5. d^5 ^6S ------------------ $^6A_1 \quad t_2^3 e^2$

$$^5D \begin{cases} ^5E \\ \quad \updownarrow \Delta \\ ^5T_2 \end{cases}$$

6. d^6

7. d^7 $^4P \quad ^4T_1$

(1)   Spectra of d^1:

In a free gaseous metal ion the d orbitals are degenerate, and hence there will be no spectra from d-d transitions. When a complex is formed, the electrostatic field from the legands splits the d orbitals into two groups t_{2g} and e_g. The simplest example of a d^1 complex is Ti(III) in octahedral complexes such as $[TiCl_6]^{3-}$ or $[Ti(H_2O)_6]^{3+}$. The splitting of the d orbitals is shown in the following figure (a). In the ground state the single electron occupies the lower t_{2g} level, and only one transition is possible to the e_g level.

Consequently the absorption spectrum of $[Ti(H_2O)_6]^{3+}$ which is shown in figure (b) shows only one band with a peak at 20300 cm^{-1}. The magnitude of the splitting Δ_0 depends on the nature of the ligands, and affects the energy of the transition, and hence the frequency of maximum absorption in the spectrum. Thus the peak occurs at 13000 cm^{-1} in $[TiCl_6]^{3-}$, 18900 cm^{-1} in $[TiF_6]^{3-}$, 20300 cm^{-1} in $[Ti(H_2O)_6]^{3+}$ and 22300 cm^{-1} in $[Ti(CN)_6]^{3-}$. The amount of splitting caused by various ligands is related to their position in the spectrochemical series. The symbol ^2D at the left is the ground state term for a free ion with a d^1 configuration. Under the influence of a ligand field this splits into two states which are described by the

Mulliken symbols ^2E_g and $2T_{2g}$. The lower $2T_{2g}$ state corresponds to the single d electron occupying one of the t_{2g} orbitals, and the ^2E_g state corresponds to the electron occupying one of the e_g orbitals. The two states are separated more widely as the strength of the ligand field increases.
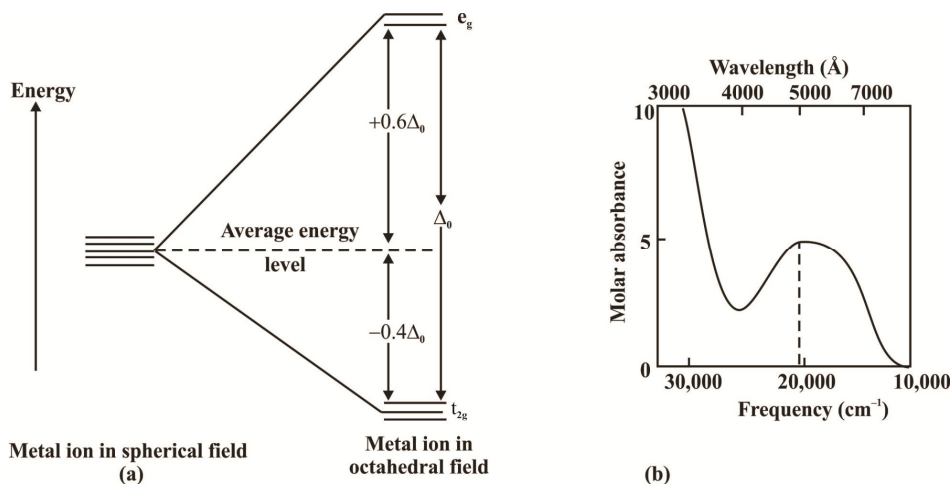
(a) Diagram of energy levels in octahedral field. (b) Ultraviolet and visible absorption spectrum of $[Ti(H_2O)_6]^{3+}$
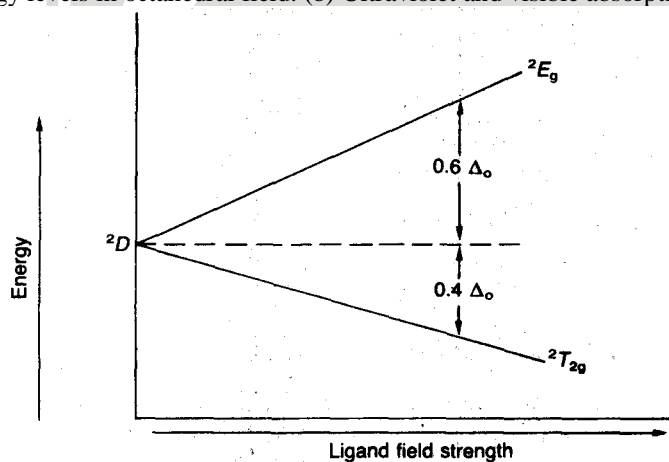
Splitting of energy levels for d^1 configuration in octahedral field.

Orgel Diagrams: If the assumption is made that the Racah parameter B has the same value in complex that it has in the free ion, then the energy of the each level may be plotted out for various value of Δ_0 as the variable. This was first done by orgel in 1955 and weak field method type of energy level diagrams constructed in this way are usually referred to as orgel diagram.

Orgel diagrams are used for interpretation of electron spin absorption bands of crystal field of d-d origin in electronic spectra of tetrahedral and octahedral transition metal complexes. The energy level order of states arising from splitting of a state for a particular ion in an octahedral field is opposite of that for ion in a tetrahedral field.

Orgel diagrams are particularly useful in interpretation of spin allowed electronic transitions of tetrahedral and high spin octahedral complexes but not for low spin octahedral complexes. The spin allowed electronic transitions occur between the two energy states that have same spin multiplicity. In all d^1, d^2, d^3, d^8, d^9 metal ions octahedral complexes, Orgel diagrams can be used as they give identical energy states .

**Some feature of this diagram may be stated as follows:**

(a) For the d^1 configuration note that the energy levels diverge linearly, as they must do since the energy gap is a function of only the one parameter Δ_0.

(b) In the other diagram only some of the levels diverge linearly,

(c) Those levels which do not diverge linearly are the ones involved in configuration interaction.

Spectrum of $[Ti(H_2O)_6]^{3+}$: The absorption band in spectra of $[Ti(H_2O)_6]^{3+}$ is broad because of **Jahn-Teller Distortion** which splits ^2E_g state into $^2A_{1g}$ and $^2B_{1g}$. This splits ground state $^2T_{2g}$ into ^2E_g and $^2B_{2g}$ also in some extent.
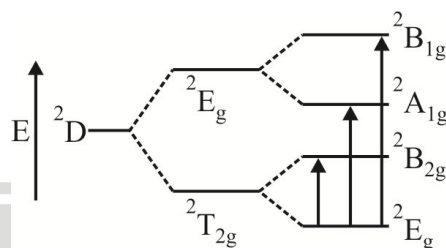

In complex ion $[Ti(H_2O)_6]^{3+}$ absorption maximum observed at 20300 cm^{-1} and also the absorption maximum has a shoulder at 17400 cm^{-1} because of John-Teller Distortion. The shoulder is responsible for broad band.

It has also been suggested that the electronic excited state of $[Ti(H_2O)_6]^{3+}$ has the configuration $t^0{}_{2g}$ $e^1{}_g$ and so in the excited state of complex e_g orbitals are electronically degenerate. Therefore the single electronic transition is really the superposition of two transitions, one from an octahedral ground state ion to an octahedral excited state ion and a lower energy transition from an octahedral ground state ion to a lower energy tetragonally distorted excited state ion. Since these transitions have slightly different energies, therefore the bands overlap one another and can not be resolved. Thus unresolved superimposed band results in an asymmetric broad band.
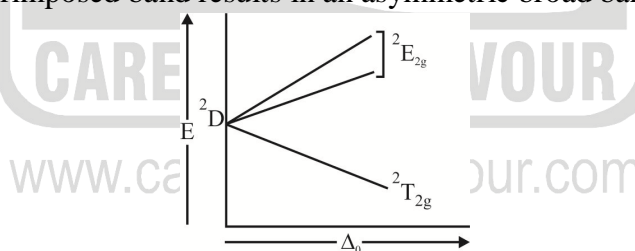
Spectra of d^9 octahedral Complex: In octahedral d^9 complexes the term ^2D splitted into ^2E_g and $^2T_{2g}$. In d^9 octahedral a hole may be considered in e_g orbital. When transition takes place hole moves from e_g to t_{2g}. This is similar to electron transition i.e. $^2T_{2g} \leftarrow {}^2E_g$. However hole and electron as moves in opposite direction hence the diagram of d^9 will be inverse of d^1.
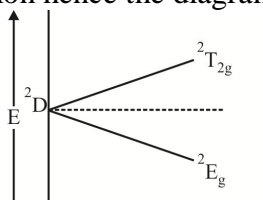
Note: Hence it can be concluded that the orgel diagrams of d^n and d^{10-n} are inversely related.