Spectroscopic terms determination of ground term Symbol for d^1 to d^9 :-

- Russell - Saunders or L-S Coupling scheme :-

- Electronic spectra obtained when one $e^{\ominus}$ being excited into higher energy level from lower energy level. While doing so other electrons that might interact with this $e^{\ominus}$ ~~is~~ is ignored.
- In d^1 case only Single $e^{\ominus}$ is there so no more Complications.
- If system contains more than one d $e^{\ominus}$ then the interactions or coupling bet^n quantum no. of individual $e^{\ominus}$ must be considered while explaining electronic spectrum.
- This interactions are spin-spin coupling, orbit-orbit coupling and spin-orbit coupling.
- For elements of low atomic no. and including those of first transition series order followed is

Spin-spin coupling > orbit-orbit coupling > spin-orbit coupling.

Elements with $Z = 30$, spin-orbit coupling is more prominent which is also termed as jj coupling.

- When several $e^{\ominus}$ occupy subshell, the energy state obtained depend upon result of orbital angular momentum quantum no. (l vector) & spin quantum number (s vector) of each $e^{\ominus}$.

Acc^n to L-S coupling scheme -

① All the 'l' ~~values~~ vectors of $e^{\ominus}$ of CMI couple together electrostatically to give resultant vector 'L' called as total orbital angular momentum quantum number.

'L' determines energy state of atom.

Different value of 'L' represented by particular term letter as shown below :

L	=	0	1	2	3	4 .....
Term letter	=	S	P	D	F	G .....

For empty, half filled and completly filled subshell, L = 0.

② All 's' vectors of $e^{\ominus}$ couple together to give resultant vectors 'S' called as total spin quantum number. 'S' determines spin multiplicity of atom.

③ Finally 'L' and 'S' vector couple together to give resultant vector 'J' called as total inner quantum number. Therefore $J = L+S$

④ The quantity $(2S+1)$ is k/as multiplicity of 'L' state. Depending upon value of $(2S+1)$ multiplicity can be singlet, doublet, triplet etc.

⑤ There are some permitted value of J. These values varies from $L+S$ to $L-S$.

⑥ Possible values of J are calculated by

$J = 2S+1$ when $L > S$
$J = 2L+1$ when $L < S$
If $L = 0$ then $J = S$

⑦ Term symbol can be represented as

$${}^{2S+1}\boxed{\text{Term Letter}}_{\text{value of } J}$$

⑧ The ground term symbol is selected by using following rules :

ⓐ Select the minimum J value (L−S) if the sub-shell is less than half filled i.e, select the term symbol with minimum J value as ground term symbol

ⓑ Select the maximum J value (L+S) if sub-shell is more than half filled; i.e, select the term symbol with maximum J value as ground term.

The term symbols and ground term symbol for various configuration are given below :

Configuration	Term Letter	Multiplicity (2S+1)	Term symbol	Ground term symbol
d^1	D	2	$^2D_{5/2}$, $^2D_{3/2}$	$^2D_{3/2}$
d^2	F	3	$^3F_4$, $^3F_3$, $^3F_2$	$^3F_2$
d^3	F	4	$^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$	$^4F_{3/2}$
d^4	D	5	$^5D_4$, $^5D_3$, $^5D_2$, $^5D_1$, $^5D_0$	$^5D_0$
d^5	S	6	$^6S_{5/2}$	$^6S_{5/2}$
d^6	D	5	$^5D_4$, $^5D_3$, $^5D_2$, $^5D_1$, $^5D_0$	$^5D_4$
d^7	F	4	$^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$	$^4F_{9/2}$
d^8	F	3	$^3F_4$, $^3F_3$, $^3F_2$	$^3F_4$
d^9	D	2	$^2D_{5/2}$, $^2D_{3/2}$	$^2D_{5/2}$
d^{10}	S	1	$^1S_0$	$^1S_0$

Spectra of Complexes :

- Spectra of Complexes are arises due to excitation of $e^{\ominus}$ from lower energy state to higher energy st.
- In order to know which transitions are taking place we must know the ground term undergoing splitting in octahedral field.
- S term does not undergoes splitting in octahedral field and it is termed as A_{1g}.
- P term also does not undergoes in splitting and term as T_{1g}.
- D term undergoes splitting into T_{2g} and E_g and termed as T_{2g} and E_g.
- Thus the term of metal ion undergoes transformation into mulliken state as shown below:

Spectroscopic term	Mulliken Symbol	
	octahedral field	Tetrahedral field
S	A_{1g}	A_1
P	T_{1g}	T_1
D	T_{2g} + E_g	T_2 + E
F	T_{1g} + T_{2g} + A_{2g}	T_1 + T_2 + A_2

Spectra of d^1 and d^9 octahedral complexes and orgel diagram for d^1 and d^9 states :

- When complex is formed, the d orbital of metal ion splits into two groups t_{2g} and e_g due to electrostatic field of ligand around [M].
- Example : $[Ti(H_2O)_6]^{3+}$ or $[TiCl_6]^{3-}$ in which Ti(III) is d^1 system. Due to presence of only one electron ~~e~~ one transition is possible i.e, t_{2g} to e_g.

- Free metal ion with d' configuration spectral term is ^2D. This ^2D term split into two states ^2E_g and $^2T_{2g}$ described as mulliken symbol.

- The lower t_{2g} state have one d $e^{\ominus}$ present in one of the ~~d~~ t_{2g} orbital and E_g state corresponds to electron occupying one of the e_g orbital

t_{2g} and e_g states are seperated by 10 Dq or Δ_o

The Δ_o for $[Ti(H_2O)_6]^{3+}$ complex ion is 20300 cm^{-1}

- In case of d^9 configuration as in Cu^{2+}, d^9 case is also same like d^1 configuration only difference is that in d^1 case only one $e^{\ominus}$ is there present in t_{2g} level while in d^9 one hole is there in e_g level. So in d^1 transition of $e^{\ominus}$ from t_{2g} to e_g takes place but in d^9 transition of hole from e_g to t_{2g} level. Hence d^9 is the inverse of d^1 arrangement

- Splitting of terms in octahedral complex is reverse to that of tetrahedral. so, transition of d^1 octahedral complex is reverse to that of d^1 tetrahedral and d^9 octahedral is reverse to that of d^9 tetrahedral.

octahedral d^n and tetrahedral d^{10-n} gives rise to simillar type of splitting while octahedral d^n and octahedral d^{10-n} shows ~~reverse~~ inverse type of splitting.

- Oregel diagram helps to understand electronic spectra of complexes and applied to high spin complexes. Oregel diagram is a plot of spectroscopic states of metal ion on y-axis as a function of ligand field (x-axis).

Energy level diagram of d^1 and d^9 configuration can be obtained into single diagram called as oregel diagram.

The oregel diagram for d^1 and d^9 is shown in following fig:

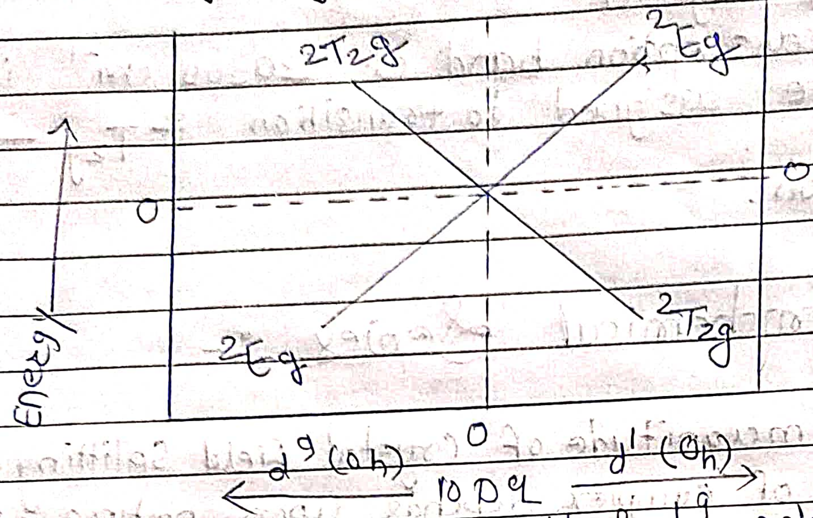
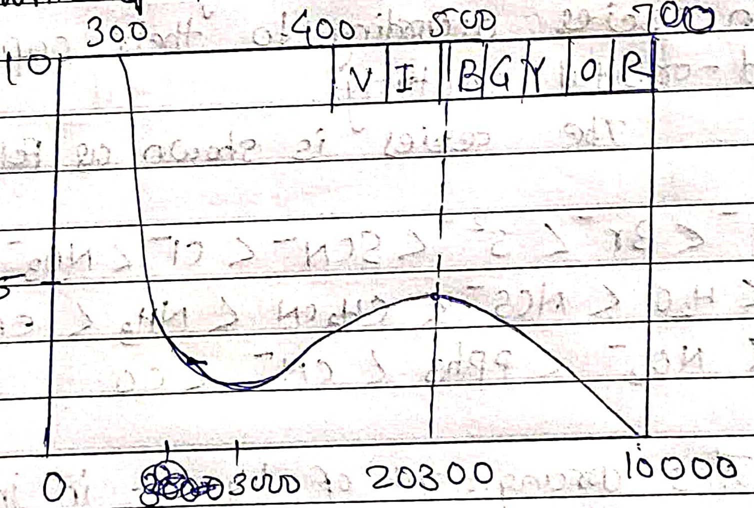


Fig : orgel diagram of d^1 & d^9 octahedral complexes

Electronic Spectrum of $[Ti(H_2O)_6]^{3+}$ complex ion

The electronic spectrum of $[Ti(H_2O)_6]^{3+}$ is shown below:



- The spectra shows one absorption band of crystal field or d-d origin at 20300 cm^{-1}. Aqueous sol^n of $[Ti(H_2O)_6]^{3+}$ is pueple in colour. Ti^{3+} ion have single $e^{\ominus}$ in d-orbital hence it have only one energy term i.e, ^2D.

- When Ti^{3+} ion come in contact with six water molecule octahedrally, then one $e^{\ominus}$ get enters into t_{2g} set of orbitals. Thus ground state configuration of $[Ti(H_2O)_6]^{3+}$ is $(t_{2g})^1 (e_g)^0$.

- on absorption of radiation of 20300 cm^{-1} frequency the single $e^{\ominus}$ in t_{2g} set gets excited to higher energy e_g set.
- The absorption band at 20800 cm^{-1} is therefore assigned to transition $^2T_{2g} \rightarrow {}^2E_g$ transition.

Spectrochemical Series :-

- The magnitude of crystal field splitting of d-orbitals of complex depends upon nature of ligands in complex.
- This spectrochemical series is experimental study of of spectra of large no. of complexes having various metal ion and various ligands. This ligands arranged in series according to their capacity to cause d-orbital splitting.

The series is shown as follows :

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < C_2O_4^-$
$< H_2O < NCS^- < CH_3CN < NH_3 <$ en $<$ bipy $<$ phen
$< NO_2^- < PPh_3 < CN^- < CO$

- This arrangment of ligands in increasing order of their d-orbital splitting strength is called Spectrochemical series.
- This series use to predict d orbital splitting and hence frequency of visible absorption band ~~of~~ for two different complexes having same metal ion but different ligands.
- ~~for~~ Example :

Consider two octahedral complexes of Co^{3+} $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ where Co^{3+} is d^6 configuration.

- Since F^- is weaker ligand than NH_3 so value of splitting energy (Δ_o) is smaller for $[CoF_6]^{3-}$ than $[Co(NH_3)_6]^{3+}$.
- $[CoF_6]^{3+}$ have six d electrons of Co^{3+} occupy both t_{2g} and e_g orbitals and have four unpaired ligand so complex is paramagnetic and high spin.
- In $[Co(NH_3)_6]^{3+}$, NH_3 is strong ligand so difference betⁿ t_{2g} and e_g level increases due to greater splitting. Hence six $e^\ominus$ remain paired in t_{2g} set only. Due to this the complex is diamagnetic and ~~high~~ low spin.

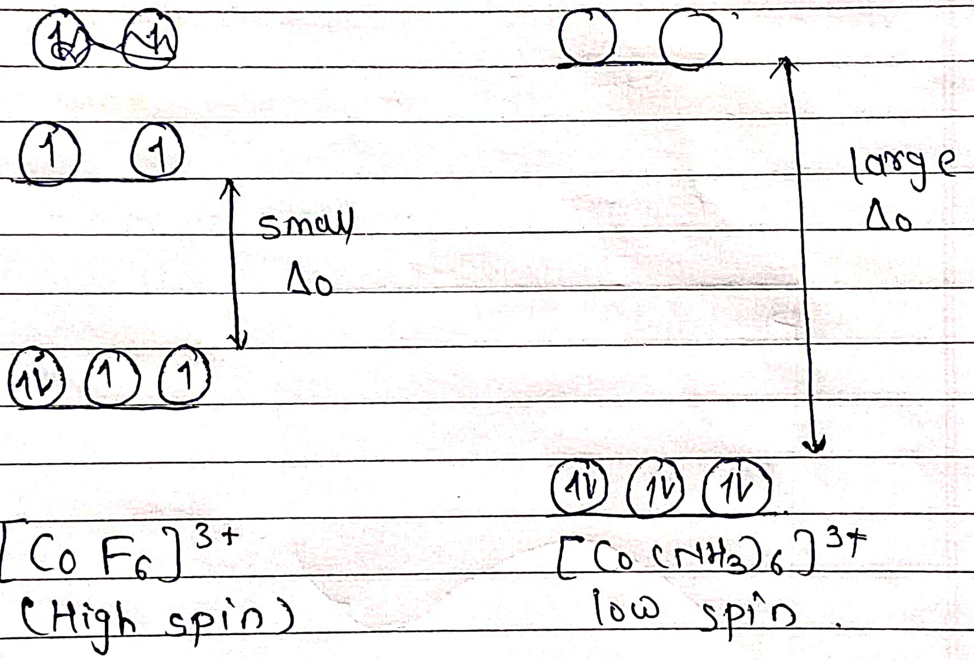


Fig: Magnitude of splitting ~~of~~ in high spin & low spin complexes of Co^{3+} ion.

While applying this rule following points should be remember.

- The series is based on data for metal ion in common oxidation st. because nature of metal ligand interaction of high or low oxidation state of metal may be in certain cases different than for metal ion in normal state.

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* Even for the metal ion in their normal oxidation state inversion of order of adjacent or nearly adjacent members of series is some time time found.