

## Selection Rules for d-d Transitions

Number of bands and their intensity obtained in a spectrum is decided by quantized selection rule. It is derived from wave function and these are given below -

### 1) Spin Selection Rule -

Spin multiplicity of electron gets changed if the number of unpaired electron changes on exciting electron from ground to excited state.

According to selection rule only those transition are said to be allowed in which no change in spin multiplicity occurs i.e. no difference is found in spin angular momentum quantum number (S) in ground state and excited state. It means after electron transition  $\Delta S = 0$ .

For example, if two electron are present in an s-suborbital and one of this electron gets excited to p-suborbital, there will be two possibilities of spin of excited electron out of which one will be allowed transition.

	S	P	
Ground state	$\uparrow\downarrow$	$\uparrow\uparrow\uparrow$	$S = +\frac{1}{2} - \frac{1}{2} = 0$
(i) Excited state	$\uparrow$	$\uparrow\uparrow\uparrow$	$S = +\frac{1}{2} + \frac{1}{2} = 1$ Forbidden transition
(ii) Excited state	$\uparrow$	$\downarrow\uparrow\uparrow$	$S = +\frac{1}{2} - \frac{1}{2} = 0$ Allowed transition

Spin multiplicity  $(2S+1)$

when  $S=0$  then  $\rightarrow 2S+1 = 1$  Singlet state

and  $S=1$  then  $\rightarrow 2S+1 = 3$  Triplet state

Singlet state is allowed transition and Triplet state is forbidden transition

In the same way forbidden and allowed transition are  ${}^3T_{1g} \rightarrow {}^1T_{2g}$  and  ${}^3T_{1g} \rightarrow {}^3T_{2g}$  respectively

### 2) Laporte's Selection Rule -

When an electron transits in the same suborbital this transition is called Laporte's forbidden

Transition. Laporte allowed transition is excitation of an electron from one suborbital to another. In this way transitions which involve change of azimuthal quantum number are allowed transitions. For example -  $d-d$  transition is Laporte forbidden transition and  $p-p$  also. For Laporte allowed transition,  $\Delta l$  (Change in azimuthal quantum no.) should be  $+1$  or  $-1$ . All transition between gerade and ungerade are allowed transitions, and from  $s$  suborbital to  $p$  suborbital is Laporte allowed transition.

### Breakdown of Selection Rule —

Breakdown is found in both selection rule.

#### 1) Breakdown of Laporte selection Rule —

In some complexes mixing of two orbitals take place. Due to this mixing each of two orbitals acquires characteristics of second orbitals to some extent. This causes relaxation in Laporte selection rule giving a very weak band in the spectrum due to transformation of forbidden transition into allowed transition. Absorption of such bands is very low,  $d$  and  $p$  orbitals get mixed during formation of complex from metal ion and ligand. This process occurs in complexes which do not possess a centre of symmetry e.g. tetrahedral or asymmetrically complexes, substituted octahedral. However in these cases the metal ligand bonds vibrate so that the ligands spend an appreciable amount of time out of their centrosymmetric equilibrium position. Thus a very small amount of mixing occurs and low intensity spectra are observed.

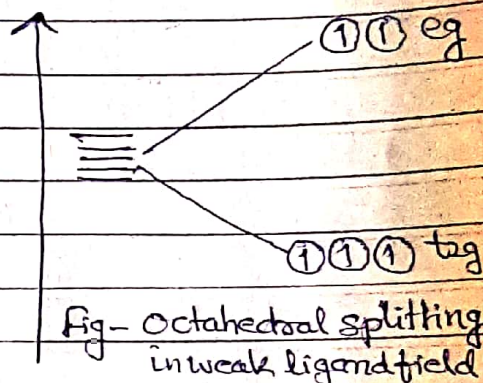
Thus Laporte forbidden transitions vary from weak intensity if the complex is non-centrosymmetric to very very weak if it is centrosymmetric.

2) Breakdown of Spin Selection rule -

Complexes in which spin multiplicity change is definite by electronic transition, sometimes produce very weak band. At this time, they do not follow the spin selection rule. According to it the change in spin multiplicity is a forbidden transition.

Breakdown of spin selection rule is due to spin orbital coupling (L-S). For example,  $^1S_0$  is the ground state and  $^3P$  is the excited state of a metal ion.

Transition from  $^1S_0$  to  $^3P$  will be spin forbidden. But  $^3P$  state has three values of J due to L-S coupling. The values of J are 0, 1, and 2. In this way  $^3P$  excited state gets further split into three energy levels  $^3P_0$ ,  $^3P_1$  and  $^3P_2$ . Now the



resultant angular momentum of  $^1S_0$  and  $^3P_0$  states are equal. Hence these two states will combine to give two new states, one is less energy  $^1S_0$  and other more energy  $^3P_0$ . Hence  $^1S \rightarrow ^3P$  transition will be partially allowed.

In this way for  $d^2$  electronic configuration in ground state only  $^3F$  and in excited state only  $^3P$  states should be selected for study

In following table values of molecular extinction coefficient for some transition are given.

Orbital (Laporte)	Spin	Types of Transition	$\epsilon$	Example
Allowed	Allowed	Charge transfer	10000	$[TiCl_6]^{2-}$
Partly allowed (p-d) mixing	Allowed	d-d	500	$[CoBr_4]^{2-}$ , $[CoCl_4]^{2-}$
Forbidden	Allowed	d-d	8-16	$[Ti(H_2O)_6]^{3+}$ , $[V(H_2O)_6]^{3+}$
Partly allowed (p-d) mixing	Forbidden	d-d	4	$[MnBr_4]^{2-}$
Forbidden	Forbidden	d-d	0.02	$[Mn(H_2O)_6]^{2+}$