

## Free ion term and their splitting octahedral symmetry

Determination of ground state terms - Hund's rule:

The application of Hund's rules allows us to identify the ground state of an atom/ion from the terms arising from an electronic configuration.

e.g. Electronic arrangement of microstates for  $p^2$  configuration

$M_L =$	0	1	2	3
	S	P	D	F

$2S+1$  T

(no. of distinguishable configuration of electrons in an orbital is called microstates)

$m_L$	+1			1	1											
	1		1	1	1	1	↓	↓	↓	↓	↓	↓	↑	↓	↑	↓
	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↑	↓	↑	↓
Terms	$^1D$	$^1D$	$^1S$	$^3P$	$^3S$	$^3P$	$^3P$	$^3P$	$^3P$	$^3P$	$^3P$	$^3P$	$^3P$	$^3P$	$^3P$	$^3P$

$$M_L \rightarrow +2$$

$$m_S \rightarrow 0$$

## Electronic Spectra of transition metal complexes:

\* Electronic spectra arises due to promotion of electrons from one energy level to another.

\* Electronic transitions are of high energy (and in addition much lower energy vibrational and rotational transitions occur which results in considering broadening of the electronic absorption bands in d-d spectra

\* Band width in electronic spectra are usually of the order of  $1000 - 30,000 \text{ cm}^{-1}$ .

\* principle: If  $I_0 =$  Intensity of the original beam of light.

$I =$  Intensity after passing through the single solution.

$$\text{Then } \log \frac{I_0}{I} = A \quad \begin{array}{l} A = \text{absorbance} \\ = \text{optical density} \end{array}$$

$$\text{also, } A = \epsilon c l$$

$c =$  concentration of sample in  $\text{mole/l}$

$l =$  path length of cell (1 cm)

$\epsilon =$  Molar absorption coefficient



The electronic transitions are governed by two selection rules:

- 1. Laporte 'orbital' selection rule.
- 2. Spin selection rule.

### Laporte 'orbital' selection rule (explanation)

Electronic transitions which involve a change in orbital angular momentum quantum no  $\Delta l = \pm 1$  are Laporte allowed.

eg for  $ca, s^2 \rightarrow s^2 p^1$ ,  $l$  changes by  $+1$  and is Laporte allowed. transition for which  $\epsilon = 5000 - 10,000 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

In contrast,  $d-d$  transitions are Laporte forbidden because change in  $l=0$  during transition, but spectra of much lower absorbance with  $\epsilon = 10^1 - 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$  are observed. This is due to the slight relaxation in the Laporte rule.

### Relaxation of Laporte rule: [100 Day and Selbin]

In a coordination complex, metal ion is surrounded by ligands.

So, a mixing of  $d$ -orbital of metal and  $p$ -orbital of ligands may occur and the electronic transitions are no longer pure  $d-d$  in nature.

$d-p$  mixing of orbitals occurs in complexes which do not possess a centre of symmetry e.g.

tetrahedral complexes e.g.  $[MnBr_4]^{2-}$  or asymmetrically substituted octahedral complexes e.g.  $[Co(NH_3)_5Cl]^{2+}$  are coloured because of the Laporte allowed transition.

Mixing of  $p$  and  $d$  orbitals does not occur in octahedral complexes which have a centre of symmetry. eg  $[Cr(H_2O)_6]^{3+}$

However in these cases, the  $M-L$  bonds vibrate, so that the ligands spend an appreciable amount of time out of their centrosymmetric equilibrium position which allows a very small amount of  $d-p$  mixing and results in low intensity spectra.



Therefore, Laporte allowed transitions are very intense, while Laporte forbidden transitions vary from ~~weak~~ <sup>weak</sup> intensity. If the complex is non centrosymmetric to ~~very weak~~ <sup>very weak</sup> if it is centrosymmetric.

Spin selection rule: According to this rule, during electronic transitions bet<sup>n</sup> energy levels, an electron does not change its spin i.e.,  $\Delta S = 0$ , i.e. electronic transitions are possible only bet<sup>n</sup> the states with same spin multiplicity.

Exceptions: For  $Mn^{2+}$  is a weak octahedral field eg  $[Mn(H_2O)_6]^{2+}$ , d-d transitions are spin forbidden because each of the d-orbital is singly occupied (half filled). Therefore, many  $Mn^{2+}$  compounds are all white/pale flesh coloured (spin forbidden, but Laporte rule is relaxed) and the intensity of spectral line is  $\frac{1}{100}$  of that for a spin allowed transitions.

1 - analysis of spectra of transition metal complexes

For analysis of spectra, the spin forbidden transitions are ignored and only considered transitions are to those excited states which have the same spin multiplicity with the ground states. eg for  $d^2$  configuration, the only terms that are considered for electronic transition are  $3F$  and  $3P$ . (Other terms are ignored due to their different spin multiplicity with ground term)

Examples	Laporte (orbital)	Spin	Types of spectra	$\epsilon$	more intense more is the colour
$[TiCl_6]^{2-}$	$e^- \rightarrow T_1^{gt}$ $L \rightarrow M$ allowed	allowed	charge transfer	10,000	
$[Co(BH_4)_2], [CoCl_4]^{2-}$	partly allowed (d-p mixing)	allowed	d-d	~500	
$[Ti(H_2O)_6]^{3+}$	Forbidden	allowed	d-d	8-10	
$[V(H_2O)_6]^{2+}$	partly allowed	Forbidden	d-d	4	
$[Mn(BH_4)_2]^{2-}$	some d-p mixing	Forbidden	d-d	0.02	
$[Mn(H_2O)_6]^{2+}$	Forbidden	Forbidden	d-d		