

Electronic Spectra of Complexes

Splitting of d^n terms in various fields

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1 Electronic spectroscopy

This is also known as UV-vis spectroscopy and covers the region from 200 to 800 nm of the electromagnetic spectrum. The region from 200 to 400 nm is called the ultraviolet (UV) and that from 400 to 800 nm is known as the visible region. A substance appeared colored when the emitted light falls in this visible region. This spectroscopy is used to find out the geometry of complexes because the number of bands seen in the visible region due to d-d transitions depends on the geometry of the complex.

1.1 Colors of transition metal ions

The aqueous solutions of transition metal ions are differently colored. Some examples are given below:

| Complex | color |
|--|-------------|
| $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ | pink |
| $[\text{CoCl}_4]^{2-}$ | blue |
| $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ | green |
| $[\text{Ni}(\text{NH}_3)_6]^{2+}$ | blue |
| $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ | violet |
| $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ | bright blue |

The different colors are due to the transition of electrons from one d level to another d level. These are called d-d transitions and the energy falls in the visible region of the electromagnetic spectrum. The color of the solution seen is the complementary color of the light absorbed by the solution.

1.1.1 Why different colors are seen instead of only one color?

If the color of the aqueous solution is due to the transition of electrons from one d level to another d level, there should be only one color. But the fact that different colors are seen for different compounds shows that the d orbitals are at

different energy levels and hence there is not only one transition but many. In order to understand this, the splitting of d orbitals in different environments is to be understood. The splitting depends up on the geometry of the complex, the nature of the ligands present, and the oxidation state of the central metal atom.

1.2 Electronic spectrum of complex ions

Ex. 1: $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$; its electronic spectrum is given in Figure 1.2.1, which shows only one λ_{max} .

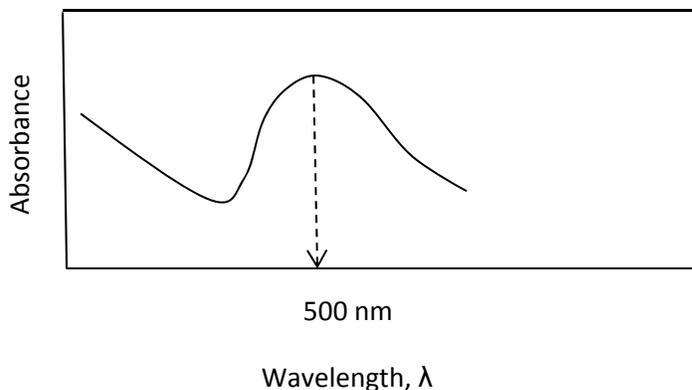


Fig 1.2.1 Electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

There is only one absorption near 500 nm, which indicates that there is only one transition taking place in this complex. It means that the d orbitals are split into only two levels.

Ex. 2: $[\text{Cr}(\text{en})_3]^{3+}$

Its electronic spectrum (Figure 1.2.2) shows two λ_{max} indicating two transitions. This shows that d-orbitals are split into more than one energy level.

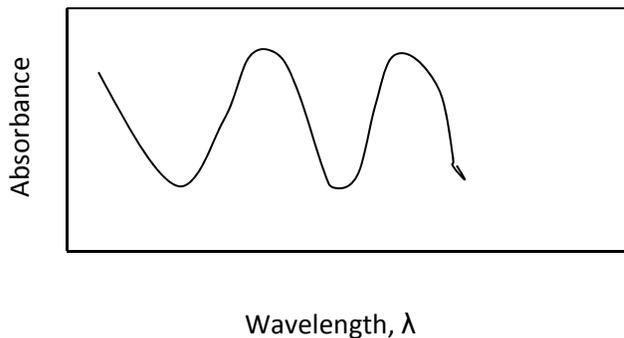


Fig 1.2.2 Electronic spectrum of $[\text{Cr}(\text{en})_3]^{3+}$

Ex. 3: $[\text{CrF}_6]^{3-}$

The electronic spectrum of this complex (Fig 1.2.3) shows three absorptions indicating three transitions. This shows the splitting of d orbitals in a different way.

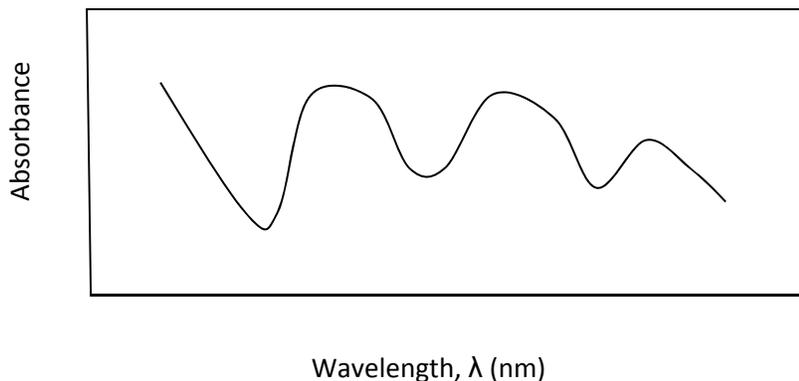


Fig 1.2.3 Electronic spectrum of $[\text{CrF}_6]^{3-}$

These examples show that the number of absorptions for the complexes varies even though all of them contain chromium and in the oxidation state +3. Moreover, all of them are octahedral complexes. Hence, the difference in the number of absorptions is due to the nature of the ligands. Similarly, it can be

shown that the number of absorptions will also vary depending up on the geometry of the complex as well as the oxidation state.

1.2.1 Interpretation of electronic spectra

Electronic configuration is split into terms due to interelectronic repulsion, which is split into states by spin-orbit coupling, which is further split into microstates by magnetic field:

Electronic configuration $\xrightarrow[\text{repulsion}]{\text{electronic}}$ Terms $\xrightarrow[\text{coupling}]{\text{Spin-orbit}}$ States $\xrightarrow{\text{Mag. field}}$ Microstates

These are explained in Figure 1.2.1.1

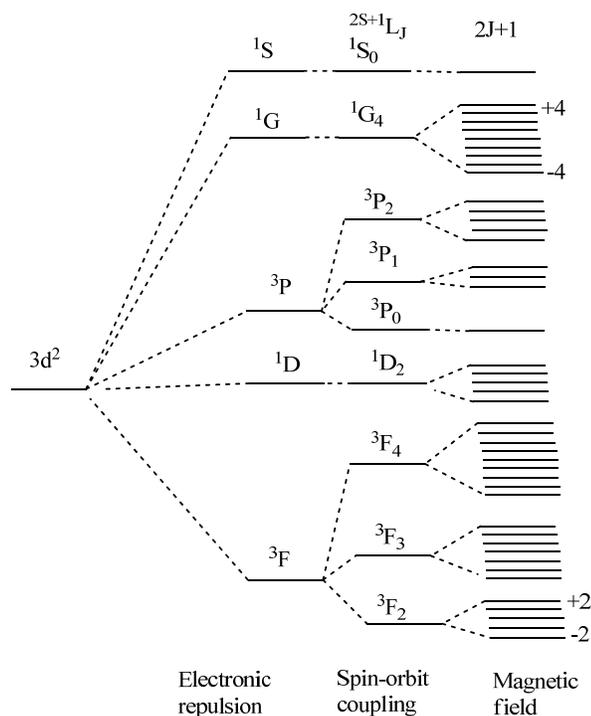


Fig 1.2.1.1 d^n splitting

1.2.2 Terms

These are nothing but the energy levels of atoms and ions. These arise due to interelectronic repulsion. These are called terms because they are nearly identical with the spectroscopic terms.

Term is denoted by the symbol, nL_J , where $n = (2S+1)$ and called the spin multiplicity. 'S' is the total spin of the electrons. 'L' is the total orbital angular momentum.

| L | Term |
|---|-------|
| 0 | S |
| 1 | P |
| 2 | D |
| 3 | F |
| 4 | G |
| 5 | H |
| 6 | I |
| 7 | K etc |

1.2.2.1 Values of total angular momentum quantum number, L

The allowed values of L are given below:

$L = (l_1 + l_2), (l_1 + l_2 - 1), (l_1 + l_2 - 2), \dots, 0, \dots, |l_1 - l_2|$, where l is the azimuthal quantum number.

1.2.2.2 Components of total angular momentum quantum number, L

The components of the total angular momentum quantum number, L, along a given axis are $M_L = L, L-1, L-2, \dots, 0, \dots, -L$

Thus the number of possible values of M_L is equal to $2L+1$

1.2.3 Total spin (S) and its components (M_S)

Total spin 'S' is equal to $n \times \frac{1}{2}$, where 'n' is the number of electrons and $\frac{1}{2}$ is the spin of one electron. For example, if there are four electrons, 'S' = $4 \times \frac{1}{2} = 2$.

Then the possible M_S values are: 2, 1, 0, -1, -2.

In general, $M_S = S, S-1, S-2, \dots, 0, \dots, -S$

1.2.3.1 Spin multiplicity

Spin multiplicity is given by the formula $(2S+1)$, where 'S' is the total spin. The value depends on the arrangement of electrons, that is, whether they are paired or not.

| No of Electrons | Arrangement | S | $2S+1$ | |
|-----------------|-------------|---------------|----------------------|---------|
| 1 | ↑ | $\frac{1}{2}$ | $2(\frac{1}{2})+1=2$ | doublet |
| 2 | ↑ ↑ | 1 | $2(1)+1=3$ | triplet |
| 2 | ↑ ↓ | 0 | $2(0)+1=1$ | singlet |

1.2.4 New quantum number, J

This quantum number arises when the orbital angular momentum (L) is coupled with the spin angular momentum (S). It is known as spin-orbit coupling. The possible values of this quantum number are given below:

$$J = L+S, L+S-1, L+S-2, \dots, 0, \dots, |L-S|$$

1.2.5 Assigning term symbols

Example 1: Helium atom

Atomic number is 2; electronic configuration is $1s^2$; $L = 0$ because of 's' orbital; $S = 0$ because both the electrons are paired.

$J = L+S = 0$; $2S+1 = 2(0)+1 = 1$. Hence, the term symbol is 1S_0

Example 2: Boron atom

Atomic number is 5; electronic configuration is $1s^2 2s^2 2p^1$; closed shells do not contribute to term symbol. Hence, only $2p^1$ electrons are considered.

$L = 1$ because the electron is in the p orbital and the state is P

$S = \frac{1}{2}$ because only one unpaired electron is there.

$J = L+S = 1+\frac{1}{2} = \frac{3}{2}$

$2S+1 = 2(\frac{1}{2})+1 = 2$

Possible J values are $(L+S)$ to $(L-S)$

$$: 3/2, 3/2-1 = 1/2, 1/2 - 1 = -1/2, -1/2 - 1 = -3/2$$

That is, $3/2, 1/2, -1/2, -3/2$

Hence, the term symbols are: $^2S+1L_J$; $^2P_{\pm 1/2}, ^2P_{\pm 3/2}$,

Example 3: Carbon atom

At.No: 6; Electronic configuration: $1s^2 2s^2 2p^2$

$1s^2 2s^2$ do not contribute to the term symbol because they are closed shells

Only $2p^2$ electrons contribute.

Since the electrons are in the p orbital, $L = 1$.

$S = 1$ (electrons parallel), and 0 (electrons antiparallel)

$$2S+1 = 3, \text{ and } 1$$

$$L+S = 1+1 = 2$$

Possible L values are: 2, 1, 0

Possible J values are: 3, 2, 1, 0

Thus, the complication increases when the atomic number increases because there are several electronic configurations.

Therefore, a systematic procedure is required to identify the different terms and arrange them in the increasing order of energy.

1.2.6 Derivation of term symbols – a systematic approach

Example 1: p^2 configuration of carbon

Step 1: Total angular momentum quantum number M_L and total spin states M_S are determined.

Since the electrons are in the 'p' orbitals, L can have a maximum value of 2 and is explained as follows. There are three p orbitals, whose m_l values are +1, 0, -1. One probability is that both the electrons can be in the +1 orbital and hence maximum value of $L = 2(+1) = +2$.

Then the possible M_L values are 2, 1, 0, -1, -2 ($+L, L-1, \dots, 0, \dots, -L$)

Since two electrons are there, they can be paired or unpaired. Maximum S value is +1. Hence, possible M_S values are 1, 0, -1 ($S, S-1, \dots, 0, \dots, -S$)

Step 2: The electron configurations allowed by Pauli exclusion principle are determined (Pigeonhole diagram)

Since p orbital is considered here, three rows are drawn for the three p orbitals. The electrons are arranged in vertical columns (set of three p orbitals) corresponding to all the M_L and M_S values exhausting all the arrangements for the two electrons as follows

Possible arrangements of the two electrons: $\uparrow\uparrow$ $\uparrow\downarrow \downarrow\uparrow$ $\downarrow\downarrow$
 M_S +1 0 0 -1

| | | | | | | | | | | | | | | | |
|-------|------------|------------|------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|----------------------|----------------------|----------------------|
| M_S | +1 | +1 | +1 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | -1 | -1 | 0 | 0 | 0 |
| -1 | | \uparrow | \uparrow | | \downarrow | \downarrow | \downarrow | \uparrow | \uparrow | | \downarrow | \downarrow | | | $\uparrow\downarrow$ |
| 0 | \uparrow | | \uparrow | \downarrow | \downarrow | \downarrow | \uparrow | | \downarrow | \downarrow | | \downarrow | $\uparrow\downarrow$ | $\uparrow\downarrow$ | |
| +1 | \uparrow | \uparrow | | \downarrow | \uparrow | | \downarrow | \downarrow | | \downarrow | \downarrow | | $\uparrow\downarrow$ | | |
| M_L | +1 | 0 | -1 | +1 | 0 | -1 | +1 | 0 | -1 | +1 | 0 | -1 | +2 | 0 | -2 |

Each microstate consists of one combination of M_L and M_S . In other words, each column in this table has one value of M_L and M_S and this combination represents one microstate. For example, the microstate corresponding to the first vertical column in the table has $M_L = +1$ and $M_S = +1$.

Step 3: A chart of microstates is prepared (optional)

The microstates are entered into the following table under the appropriate M_L and M_S values from the previous table.

| | | | | |
|-------|----|----------|-------------------|----------|
| | | M_S | | |
| | | +1 | 0 | -1 |
| M_L | -2 | | \times | |
| | -1 | \times | \times | \times |
| | 0 | \times | \times \times | \times |
| | +1 | \times | \times | \times |
| | +2 | | \times | |

This serves as a cross check that we have entered 15 distinct microstates without any omission.

Step 4: How to check whether all the microstates have been identified without any omission using a formula?

Let the total number of microstates be denoted by N.

$$N = \frac{N_l!}{x!(N_l - x)!}, \text{ where } N_l = 2(2l+1), \text{ and it gives the number of } m_l, m_s$$

combinations for a single electron in the orbital set.

Example 1: p^2

Here, $x = 2$ (No of electrons), $l = 1$ (p orbital); hence, $N_l = 2[2(1)+1] = 6$

$$N = 6! / 2!(6-2)! = 6.5.4.3.2.1 / 2.1.4.3.2.1 = 15 \text{ microstates}$$

Example 2: d^1

Here, $x=1$, $l = 2$ (d orbital); hence, $N_l = 2[2(2)+1] = 10$

$$N = 10! / 1!(10-1)! = 10.9.8.7.6.5.4.3.2.1 / 1.9.8.7.6.5.4.3.2.1 = 10 \text{ microstates}$$

Example 3: d^2

Here, $x=2$, $l = 2$, hence, $N_l = 2(2l+1) = 2[2(2)+1] = 10$

$$N = N_l! / [x!(N_l-x)!]$$

$$= 10! / 2!(10-2)! = 10.9.8.7.6.5.4.3.2.1 / 2.1.8.7.6.5.4.3.2.1 = 45 \text{ microstates}$$

Step 5: Resolving the chart of microstates into appropriate atomic states

This is to find the group of microstates form an atomic state. In other words, an array of microstates consisting of $2S+1$ columns and $2L+1$ rows gives rise to an atomic state.

Example 1: 3P state

Here, $2S+1 = 3$ and $2L+1 = 2(1)+1 = 3$ (because $L=1$ for P state. Hence, 3×3 arrays of microstates will represent P state.

Example 2: 1D state

$$2S+1 = 1$$

$$2L+1 = 2(2)+1 = 5 \quad (L = 2 \text{ for } D)$$

Hence, a single column of 5 rows refers to 1D state.

Example 3: 1S state

After grouping the microstates of 3P and 1D , there is a unique microstate left in the chart having

$M_L = 0$ and $M_S = 0$. This refers to a 1S state.

States originating from a configuration

Thus the p^2 configuration gives rise to 1S , 1D and 3P configuration.

Step 6: J values

Singlet terms are not split. In other words, they have only one J value. However, other terms are split due to different J values.

Example: 3P

The possible J values are: $L+S, L+S-1, \dots, 0, \dots, L-S$

$L = 1$ because of the P state

$2S+1 = 3; 2S = 3-1 = 2$; hence, $S = 1$. That is electrons have parallel spins.

$$J+S = 1+1 = 2; J-S = 1-1 = 0$$

Possible J values are: 2, 1, 0.

Hence, the P state is split into three terms: $^3P_0, ^3P_1, ^3P_2$

Step 7: Arranging the terms in the increasing order of energy

Hund's rules

Rule 1: Maximum multiplicity will have minimum energy

According to this rule, ground state will have the maximum value of S. In other words, $2S+1$ value should be maximum.

When we have $^1S, ^1D$ and 3P states, 3P state should be the ground state;

${}^3P < {}^1D, {}^1S$ (However, this is not reliable always; there are deviations in many cases)

Reason

Stabilization by exchange energy is more in a system with maximum number of unpaired spins (parallel spins).

Rule 2: *If two states have the same multiplicity, then the one with higher L value will have lower energy.*

Example: 3P and 3F

$L = 1$ for P and 3 for F. Hence, ${}^3F < {}^3P$

1D and 1S

$L = 2$ for D and 0 for S. Hence, ${}^1D < {}^1S$

Rule 3: *If a subshell is less than half-full, lower J value will have lower energy.*

Example: p^2 ; the subshell consists only two electrons, which is less than three.

Hence, out of the three terms, 3P_0 , 3P_1 , and 3P_2 , 3P_0 will have the lower energy. Hence, the order will be ${}^3P_0 < {}^3P_1 < {}^3P_2$.

Thus, for the electronic configuration of C ($1s^2 2s^2 2p^2$), the states and terms are shown in Figure 1.2.6.1

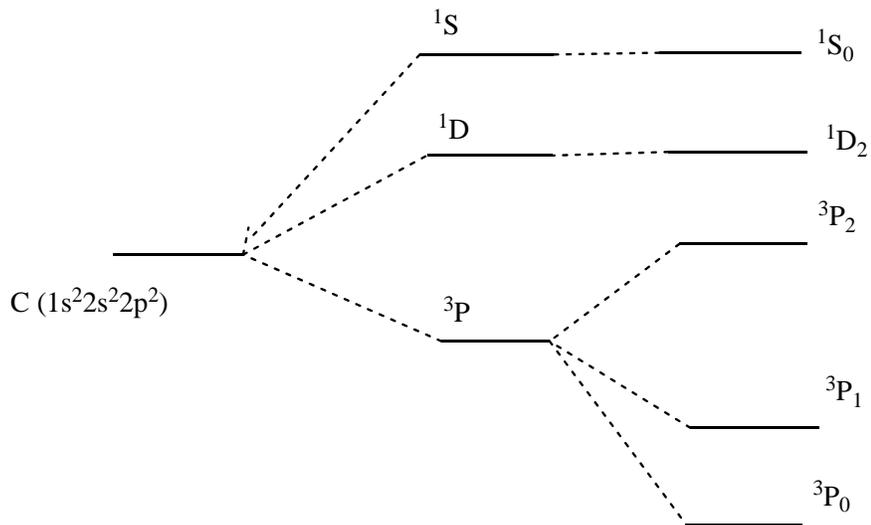


Fig 1.2.6.1 Terms and states of carbon

Example 2: d^2 configuration

Step 1: Maximum L value = +4 and is explained as follows. There are five d orbitals with +2,+1,0,-1,-2. One probability is that the two electrons can be in the +2 orbital and hence maximum value of L will be equal to +4.

M_L can have value from +4,+3,+2,+1,0,-1,-2,-3,-4

Since there are two electrons, possible M_S values are: +1, 0, -1

Step 2: Pigeon hole diagram is constructed in accordance with Pauli exclusion principle as explained in the case of p^2 configuration.

Step 3: Chart of microstates is constructed from the pigeon hole diagram as shown below:

| | | M_s | | |
|-------|----|---------------|--|---------------|
| | | +1 | 0 | -1 |
| M_L | +4 | | $(2^+, 2^-)$ | |
| | +3 | $(2^+, 1^+)$ | $(2^+, 1^-)(2^-, 1^+)$ | $(2^-, 1^-)$ |
| | +2 | $(2^+, 0^+)$ | $(2^+, 0^-)(2^-, 0^+)$ $(1^+, 1^-)$ | $(2^-, 0^-)$ |
| | +1 | $(2^+, -1^+)$ | $(2^+, -1^-)(2^-, -1^+)$ | $(2^-, -1^-)$ |
| | | $(1^+, 0^+)$ | $(1^+, 0^-)(1^-, 0^+)$ | $(1^-, 0^-)$ |
| | 0 | $(2^+, -2^+)$ | $(2^+, -2^-)(2^-, -2^+)$ | $(2^-, -2^-)$ |
| | | $(1^+, -1^+)$ | $(1^+, -1^-)(1^-, -1^+)$ $(0^+, 0^-)$ | $(1^-, 1^-)$ |

Step 4: Checking for the total number of microstates

Here, $x=2$, $l = 2$, hence, $N_l = 2(2l+1) = 2[2(2)+1] = 10$

$$N = N_l!/[x!(N_l-x)!]$$

$$= 10! / 2!(10-2)! = 10.9.8.7.6.5.4.3.2.1 / 2.1.8.7.6.5.4.3.2.1 = 45 \text{ microstates}$$

$M_L = 4$ occurs only once; thus it is a 1G state. ($L=4$ refers to G). This is given by $2S+1$ columns and $2L+1$ rows.

$$2S+1 = 1 \text{ column}$$

$$2L+1 = 2(4)+1 = 9 \text{ rows}$$

In other words, 1G is represented by 1 column of 9 rows.

$$(2S+1)(2L+1) = 1 \times 9 = 9 \text{ microstates}$$

$M_L = 3$ refers to F term; ($L = 3$ for F); occurs in three columns; hence 3F state.

$$2S+1 \text{ columns} = 3; 2L+1 = 2(3)+1 = 7 \text{ rows. } (2S+1)(2L+1) = 3 \times 7 = 21 \text{ microstates}$$

$M_L = 2$ refers to D term; ($L=2$ for D); occurs in one column; hence 1D state.

$$2S+1 = 1 \text{ (one column); } 2L+1 = 2(2)+1 = 5 \text{ rows; That is, } ^1D \text{ is represented by } (2S+1)(2L+1) = 1 \times 5 = 5 \text{ microstates.}$$

$M_L = 1$ refers to P state; occurs in three columns; hence it is a 3P state.

$$2S+1 = 3 \text{ (3 columns); } 2L+1 = 2(1)+1 = 3 \text{ rows; (L= 1 for P);}$$

This is represented by $3 \times 3 = 9$ microstates

$M_L = 0$ refers to S state; occurs only in one column; hence, it is a 1S state

$2S+1 = 1$; $2L+1 = 2(0)+1 = 1$; hence, 1S is represented by one column and one row.

This is represented by $1 \times 1 = 1$ microstate.

Thus, d^2 configuration gives rise to 1G , 3F , 1D , 3P and 1S states.

| State | No. of microstates |
|-------|--------------------|
| 1G | 9 |
| 3F | 21 |
| 1D | 5 |
| 3P | 9 |
| 1S | 1 |
| Total | 45 |

Step 6: J values (splitting due to spin-orbit coupling)

$$J = L+S, L+S-1, \dots, 0, \dots, L-S$$

1G state: $L = 4$; $S = 0$

$$L+S = 4+0 = 4; L-S = 4-0 = 4$$

It is, a singlet term and is not split. Hence, the term arising from 1G state = 1G_4

3F state: $L = 3$; $2S+1 = 3$, $2S = 3-1 = 2$, $S = 1$

$$L+S = 3+1 = 4; L-S = 3-1 = 2$$

Hence, $J = 4, 3, 2$

The terms arising from 3F state are: $^3F_4, ^3F_3, ^3F_2$

¹D state: L = 2; S = 0

$$L+S = 2+0 = 2; J = 2$$

The term arising from **¹D state** is **¹D₂**

³P state: L = 1; S = 1; L+S = 1+1 = 2; L-S = 1-1 = 0

$$J = 2, 1, 0$$

The terms arising from **³P state** are: **³P₂, ³P₁, ³P₀**

¹S state: L = 0; S = 0

$$L+S = 0$$

$$J = 0$$

The term arising from **¹S state** = **¹S₀**

Step 7: Arranging the terms in the increasing order of energy

³F < ³P < ¹G < ¹D < ¹S according to Hund's rules.

Terms arising from various electron configurations are given in the following table:

| Configuration | Terms |
|---|--|
| s ² , p ⁶ , d ¹⁰ | ¹ S |
| p, p ⁵ | ² P |
| p ² , p ⁴ | ³ P, ¹ D, ¹ S |
| p ³ | ⁴ S, ² D, ² P |
| d, d ⁹ | ² D |
| d ² , d ⁸ | ³ F, ³ P, ¹ G, ¹ D, ¹ S |
| d ³ , d ⁷ | ⁴ F, ⁴ P, ² H, ² G, ² F, ² D, ² D, ² P |
| d ⁴ , d ⁶ | ⁵ D, ³ H, ³ G, ³ F, ³ F, ³ D, ³ P, ³ P, ¹ I, ¹ G, ¹ G, ¹ F, ¹ D, ¹ D, ¹ S, ¹ S |
| d ⁵ | ⁶ S, ⁴ G, ⁴ F, ⁴ D, ⁴ P, ² I, ² H, ² G, ² G, ² F, ² F, ² D, ² D, ² D, ² P, ² S |

2 Splitting of d^n terms

Each of these free ion terms will be affected by the ligands in a complex and this will depend upon the geometry of the complex. As an example, d orbitals will be split into t_{2g} and e_g orbitals and in the same way, 2D terms will also be split into ${}^2T_{2g}$ and 2E_g terms in an octahedral complex. In the same way, other terms arising from the free ion terms will be transformed and split as follows in an octahedral field.

| Free ion | Splitting in an octahedral |
|----------|--|
| S | A_{1g} |
| P | T_{1g} |
| D | $E_g + T_{2g}$ |
| F | $A_{2g} + T_{1g} + T_{2g}$ |
| G | $A_{1g} + E_g + T_{1g} + T_{2g}$ |
| H | $E_g + T_{1g} + T_{2g} + T_{2g}$ |
| I | $A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$ |

2.1 Weak and strong field case

If the ligands cause large splitting between the terms, it is called strong field case. If they cause small splitting between the terms, it is called weak field case. In strong field case, electrons will try to pair whenever possible and in weak field case, the electrons will try to remain unpaired. The free ion terms, weak field and strong field environments for a d^2 configuration are shown in Figure 2.1.1.

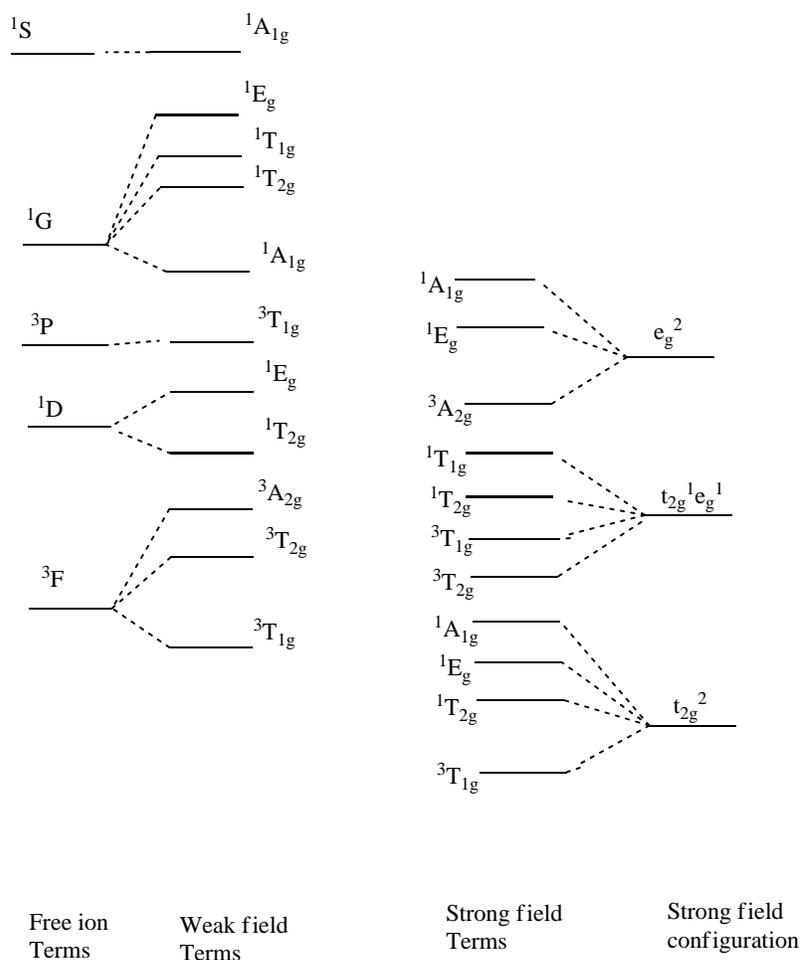


Fig 2.1.1 Strong and weak field configurations and terms of a d^2 system

2.1.1 Points to be noted

1. The wave functions for the **terms** have the **same symmetry** as those of the corresponding **orbitals**.

That is, the S,P,D,F.....terms have the same symmetry as those of s,p,d,f .. orbitals. This means that the terms are split exactly like the orbitals.

Example: D term is split in an octahedral field into T_{2g} and E_g terms; d orbitals are split into t_{2g} and e_g orbitals in an octahedral field.

2. Overall degeneracy is conserved

That is, the degeneracies of the terms are the same as those of the orbitals as shown in the following table:

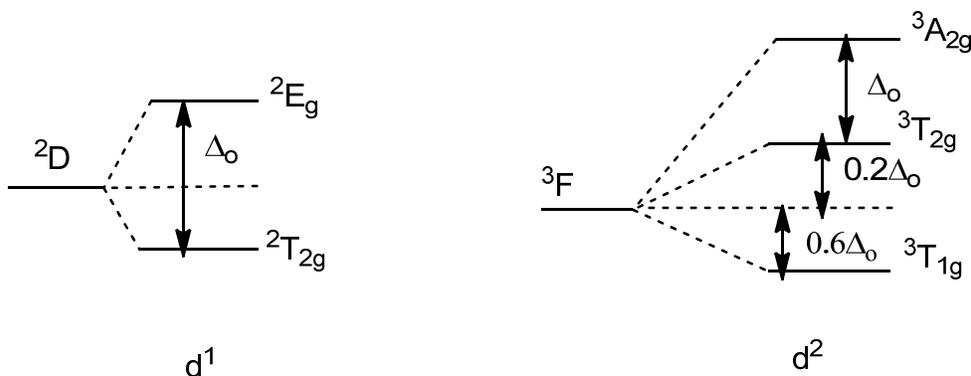
| Orbital | Degeneracy | Term | Degeneracy | In octahedral field | Degeneracy | Total |
|---------|------------|------|------------|---------------------|------------|-------|
| s | 1 | S | 1 | A_{1g} | 1 | 1 |
| p | 3 | P | 3 | T_{1g} | 3 | 3 |
| d | 5 | D | 5 | E_g | 2 | 5 |
| | | | | T_{2g} | 3 | |
| f | 7 | F | 7 | A_{1g} | 1 | 7 |
| | | | | T_{1g} | 3 | |
| | | | | T_{2g} | 3 | |

Spin multiplicity of the term and its components are same. The reason is that the spin state of an electron is not disturbed by the symmetry of external field, i.e., octahedral, tetrahedral etc.

| Term | components |
|-------|--------------------------------|
| 1S | $^1A_{1g}$ |
| 1D | $^1T_{2g}, ^1E_g$ |
| 3P | $^3T_{1g}$ |
| 3F | $^3T_{1g}, ^3T_{2g}, ^3A_{2g}$ |

2.1.2 d^n and d^{10-n} systems

The ground state terms obtained from d^1 and d^2 configurations are split by octahedral field and the resulting energy diagrams are shown below:



2.1.2.1 Hole formalism

A d^9 system can be considered as the inverted d^1 system as far as energy levels can be considered because d^9 system has an electron vacancy, which is called a 'hole'. Similarly, d^8 system is considered as inverted d^2 system as far as the energy levels are considered. This is called hole formalism. In short, an inverted energy level relationship exists between d^n and d^{10-n} systems.

Hence, with the help of only these two diagrams, all the d^n energy level diagrams can be explained in terms of d^1 and d^2 systems as given below:

$$d^9 = d^{10-1} = \text{inverted } d^1 \text{ system}$$

$$d^8 = d^{10-2} = \text{inverted } d^2 \text{ system}$$

$$d^7 = d^{5+2} = \text{same as } d^2 \text{ system}$$

$$d^6 = d^{5+1} = \text{same as } d^1 \text{ system}$$

$$d^4 = d^{5-1} = \text{inverted } d^1 \text{ system}$$

$$d^3 = d^{5-2} = \text{inverted } d^2 \text{ system}$$

3 Selection rules & Correlation diagrams for d^{10}

3.1 Selection rules for electronic transitions

These rules help us in finding out the possible transitions between the different energy levels. Transitions taking place obeying the selection rules are called **allowed transitions** and those taking place without obeying the selection rules are called **forbidden transitions**.

Rule 1 – Laporte Selection Rule

Transitions will be allowed only when there is a change in parity. That is, gerade \rightarrow ungerade ($g \rightarrow u$) and vice versa ($u \rightarrow g$) transitions are allowed but not $g \rightarrow g$ and $u \rightarrow u$.

Thus, in centrosymmetric molecules, that is, molecules with center of symmetry, the d orbitals have gerade symmetry (i.e., g symmetry) and hence, d-d transitions are forbidden (i.e., not allowed). In other words, if an octahedral complex has a center of symmetry, the d-d transitions in that complex are forbidden.

However, in complexes, d-d transitions are taking place in electronic spectra and they not only give important clues about the structure of the complex but also proof for the theories of bonding in complexes.

3.1.1 d-p Mixing and the breakdown of Laporte selection rule

In tetrahedral complexes, there is no center of symmetry and hence, this selection rule is not applicable. Moreover, the MOs formed have the character of both d and p orbitals from which they are formed. This is called d-p mixing because the p orbitals have 'u' character and the 'd' orbitals have 'g' character. The e-orbitals in the tetrahedral complex are purely metal d-orbitals and the t_2 orbitals are formed from the d- and p-orbitals.

Rule 2: Spin selection rule

According to this selection rule, $\Delta S = 0$ for an allowed transition. In other words, there should not be any change in the spin of the states and their multiplicities should be the same during the transition of electrons. That is, singlet-singlet and triplet-triplet transitions are allowed, while singlet-triplet and vice-versa transitions are not allowed.

3.1.1.1 Break down of Laporte selection rule: (Selection rule 1)

1. This rule is broken down because of the vibrations of the ligand atoms in the complex. These vibrations combine with the electronic levels both in the ground and excited states. This is called vibronic coupling. This vibronic coupling breaks down the selection rule because there are no pure 'g' or 'u' states now. Ground and excited states will be a mixture of 'g' and 'u' symmetries.

2. Another possibility is that reduction in symmetry of the complex may break the selection rule. For example, distortion of the octahedral complex along the z-axis (compression or elongation) may affect the symmetry and hence 'g' becomes insignificant or removed. Hence, this selection rule may not apply and the transitions are allowed.

3.1.1.2 Break down of Spin selection rule (Selection rule 2)

Spin-orbit coupling breaks down this selection rule. That is, the spin angular momentum and orbital angular momentum couple so that at any given instant, they exist together and not separately and hence, this selection rule is broken.

3.1.1.3 How to distinguish between 'allowed' and 'forbidden' transitions?

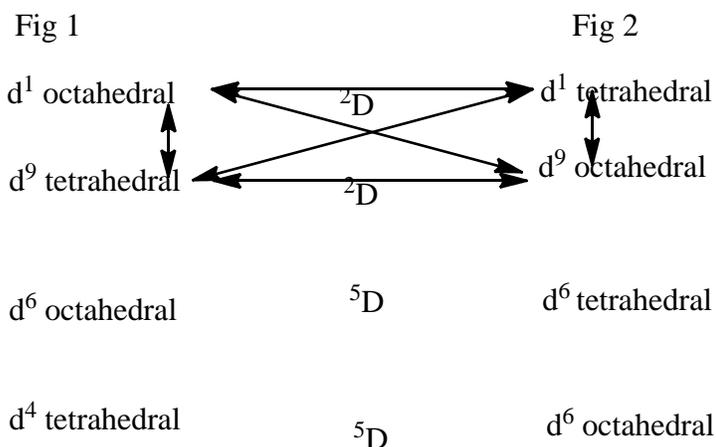
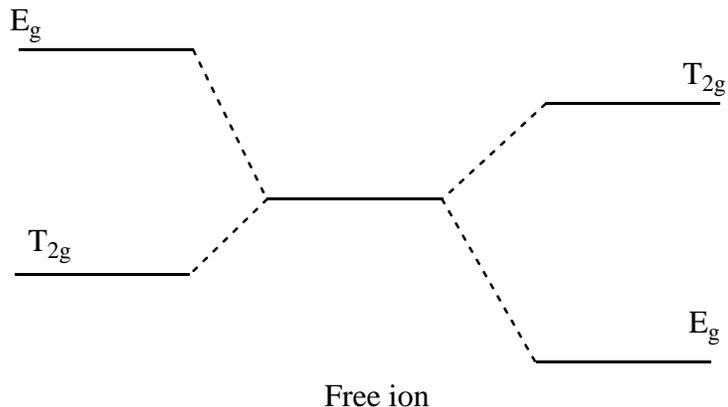
The allowed and forbidden transitions can be distinguished with the help of the intensities of the bands. Allowed transitions will be more intense, i.e., strong, than the forbidden transitions.

3.1.1.4 Intensity stealing

Sometimes, the forbidden transitions will be more intense than expected because (i) a forbidden transitions may lie close in energy to an allowed transition and/or (ii) the forbidden transition may lie close to a charge transfer (CT) transition, which will be more intense. In these cases, the forbidden transition steals some intensity from the allowed / CT transitions because the energy levels lie closer.

3.2 Correlation diagrams

An inverse relation exists between d^n and d^{10-n} systems (hole formalism) and also between octahedral and tetrahedral symmetries. Considering these, the energy level diagrams for the d^n system, strong field configuration is given below. These four diagrams can explain all the seven systems, viz., d^2 to d^8 .



3.2.1 Interpretation of Figures 1 and 2

The energy levels of d^9 octahedral and d^1 tetrahedral (Fig 2) will be the inverted levels of d^1 octahedral (Fig 1). The energy levels of d^1 octahedral and d^9 tetrahedral will be the same. Similarly, the energy levels of d^1 tetrahedral and d^9 octahedral will be the same. In the same way correlation for other levels can be explained.

The energy levels are labeled based on the transformations of the wave functions due to the symmetry operations of the O_h or T_d . Actually, the labels are given for the octahedral field. The labels for the tetrahedral field can be obtained from that of the octahedral simply by dropping the 'g' subscript.

The free ion terms such as D or F are given in the middle. The multiplicities will vary according to the d^n system.

4 References

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