# UNIT 8  ELECTRONIC SPECTRA – II

## Structure

## 8.1 INTRODUCTION

In Unit 7, we have developed the basic theory of electronic energy levels of many
simple molecules in their ground and excited state configurations. We also discussed
the basic selection rules which permit us to observe electronic spectra when these
molecules undergo energy transitions from the ground to the excited state. We have
also seen that a quantitative understanding of the colours of many chemical
substances, and even specific molecular groupings within substances, may be achieved
by studying their electronic absorption spectra.

Indeed, one of the most readily perceived properties of chemical substances is their
colour. For example, the wealth of colours displayed by a variety of 'everyday'
crystalline inorganic materials such as copper sulphate and potassium permanganate
has fascinated almost everyone of us right from our school years.

In this unit, we shall first take up the very interesting subject of the colour of transition
metal complexes and the interpretation of their electronic absorption spectra in terms
of what are called '*d–d*' and 'charge-transfer' electronic transitions. We shall then
consider the more general question of how an excited electronic state gets
'deactivated', i.e., returns to its ground state by losing its excess energy through various
mechanisms.

## Objectives

After studying this unit, you should be able to:

- describe the elements of crystal field theory and explain why, and how, the $d$-orbitals of transition metal ions show energy splittings,

- discuss the electronic spectra of transition metal complexes,

- explain charge-transfer spectra,

- use the Jablonski diagram to explain the various processes by which the excited electronic state gets deactivated, and

- to see how fluorescence and phosphorescence become two very important examples of emission spectroscopy in many natural chemical systems.

## 8.2 MODELS FOR METAL-LIGAND INTERACTIONS

You have learnt earlier (in Block 4) of the CHE-02 course that metal ions of the first transition series, from Ti to Cu in the Periodic table, are able to form a wide range of compounds. In these compounds the outermost 'valence' shell consisting of the five $3d$ orbitals is only partially occupied by electrons. In the 'free' or 'unbound' state of the transition metal (M), these five $d$-orbitals have the same energy (i.e., they are 'degenerate'); this five-fold degeneracy is, however, usually removed by the effects of ligands (L), which are molecules or ions linked to the metal, M. Very simply, transitions of electrons between the component $d$-orbitals of this partially filled shell cause the beautiful colours which are so characteristic of these compounds. We shall see that an understanding of not only the colours of transition metal complexes, but also the geometric arrangement of the ligands around M, can come from the electronic absorption spectra.

The most common ligands (L) are monoatomic or polyatomic negative ions ($Cl^-$, $CN^-$, etc.), and neutral polar molecules usually having one or more lone pairs of electrons ($H_2O$, $NH_3$, $CO$, etc.).

In a large number of transition metal complexes the ligands are found to be arranged around M in one of several definite symmetries: octahedral, tetrahedral, tetragonal, or square planar. Further, usually the negative ends of ionic ligands or the lone electron pairs of polar molecular ligands are attracted towards the positively charged metal ion. There are two models which are used to discuss the metal-ligand (L–M) interaction. In the first of these, known as the Crystal Field Theory, which was introduced by Bethe and Van Vleck, we simply consider the interaction as an electrostatic repulsion between the negative charge of the ligands and the electrons of the central metal; that is, the ligands are considered as 'point' electric charges. This model assumes that the bonds between metal and the surrounding ligands are completely ionic.

You may now wonder whether such a purely electrostatic, or 'ionic', model is always realistic. Indeed, it is not, because our every-day chemistry shows us that in some complexes the electrons which we have assumed to be entirely in the atomic $d$-orbitals of metal may actually 'spread out' and spend time in orbitals belonging to ligand, and vice-versa, thus giving considerable covalency to the $M-L$ bonds which are now made up of $M-L$ 'molecular orbitals'. Accordingly, in the second theory (called the Molecular Orbital Theory), the lone pair orbitals of ligand are combined with $s$, $p$ and $d$ orbitals of M to give 'bonding' and 'anti-bonding' orbitals. The electrons from the ligands then occupy the bonding orbitals, giving the complex its stability, and the remaining electrons partially fill the anti-bonding orbitals. You will notice, in any case, that both these theories explain the splitting of $d$-orbital degeneracy in different ways, but that they lead to the same general pattern of energy levels. A blend of these two theories is usually termed as Ligand Field Theory.

## 8.3 BASICS OF CRYSTAL FIELD THEORY

Let us first consider the crystal field approach to octahedral coordination, in which the M–L interaction is well approximated by placing six equal negative charges at the same distance away from the central M ion along the $\pm x$, $\pm y$ and $\pm z$ axes. Fig. 8.1 indicates that the lobes of the $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals all point between these charges, whereas the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals have lobes which point directly towards the charges. An electron in one of the first group of orbitals will therefore have a lower energy than an electron in one of the latter group of orbitals because of the smaller electrostatic repulsion.

Thus, in the presence of an octahedral crystal field, the five $3d$ orbitals (see Fig. 8.2) split into two groups separated by an energy difference $\Delta_o$; the upper group of two is doubly degenerate (and labelled $e_g$) and the lower group of three is triply degenerate (and labelled $t_{2g}$). The energy difference ($\Delta_o$) between the two separated sets of orbitals is of great interest, because it is this $\Delta_o$ which is identified with the $d$–$d$ electronic transition of the octahedral complex. In some textbooks, you may find this
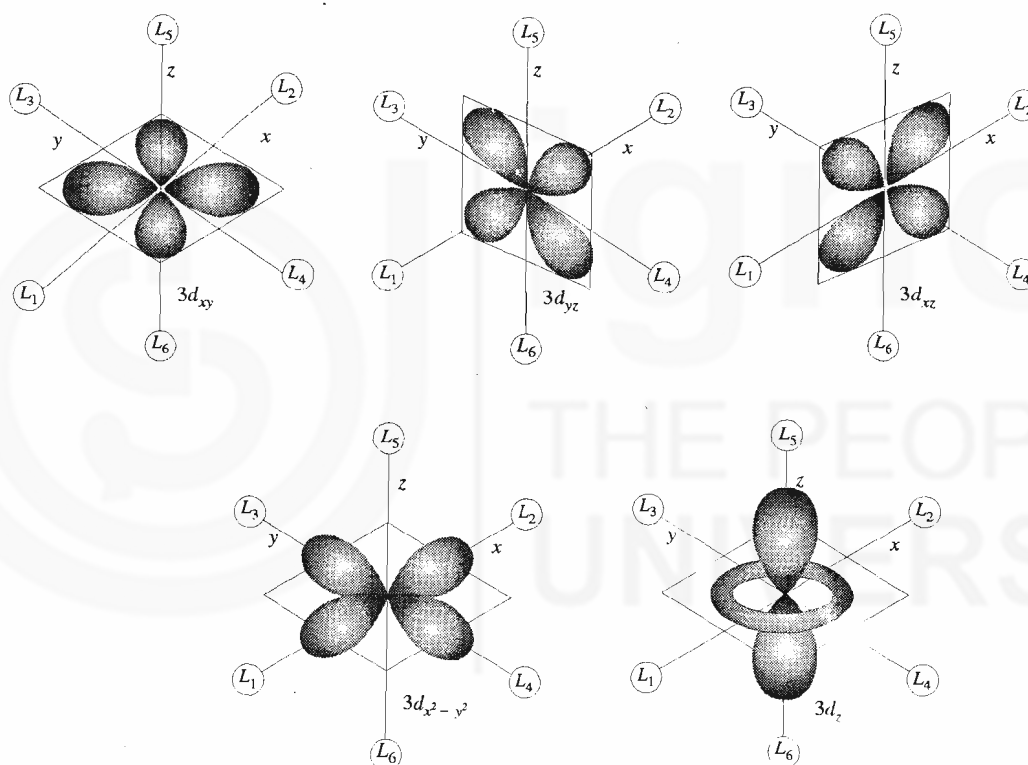


**Fig. 8.1 : The orientations of the five 3d orbitals when a transition metal ion is surrounded octahedrally by six ligands.**

energy separation written in terms of the notation '$Dq$' (or $10\,Dq$, for convenience). What does this mean? Well, it turns out that the $d$–$d$ energy difference depends on the product of the magnitude of the **charge** on the ligands, $q$, and the polarizability of the central metal ion, denoted by $D$. Since in practice we will be unable to separate $D$ and $q$, we treat the product $Dq$ as a single adjustable parameter. And all confusion will vanish if you remember that, in our notation, $\Delta_o = 10\,Dq$.

Energy relationships in terms of $\Delta_o$ are illustrated in Fig. 8.2, from which it can be seen that the energy of the $e_g$ orbitals increases by an amount $0.6\,\Delta_o$, and that of the $t_{2g}$ orbitals decreases by $0.4\Delta_o$. Thus, if the $3d$ electrons in an ion $M^{2+}$ of the first transition series are distributed among the available orbitals in such a way as to
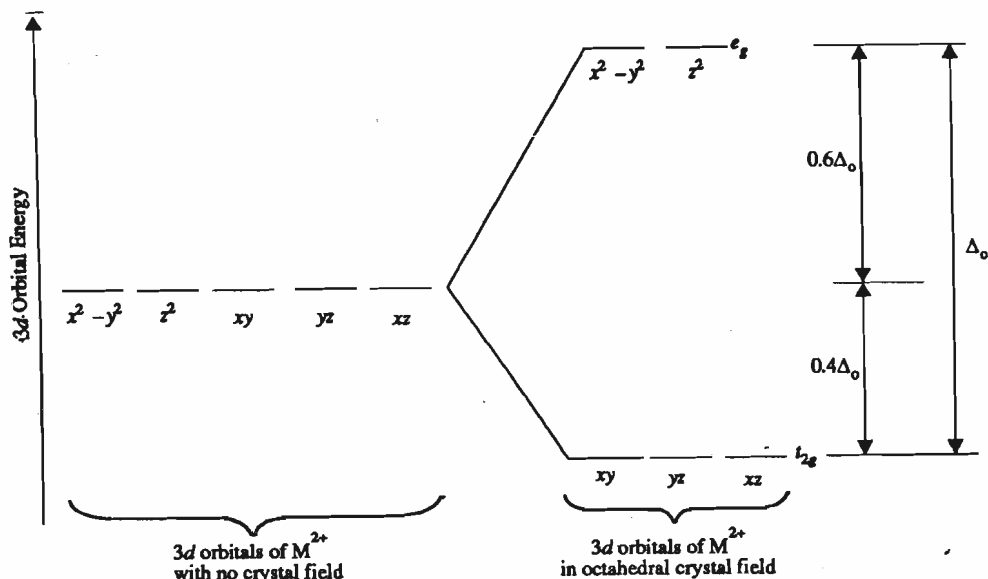
Fig. 8.2 : Effect of an octahedral crystal field on the energies of the five $3d$ orbitals

maintain the maximum number of electrons in the unpaired ('high spin') condition, a net lowering of the electronic energy will result in all cases except $Ca^{2+}$, $Mn^{2+}$ and $Zn^{2+}$ as shown in Table 8.1 below.

Table 8.1 : Crystal Field Stabilisation Energies of $Ca^{2+}$ to $Zn^{2+}$ Ions

|  | $Ca^{2+}$ | $Sc^{2+}$ | $Ti^{2+}$ | $V^{2+}$ | $Cr^{2+}$ | $Mn^{2+}$ | $Fe^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Zn^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Number of $3d$ electrons | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Distribution for high spin configuration: $e_g$ | – | – | – | – | 1 | 2 | 2 | 2 | 2 | 3 | 4 |
| $t_{2g}$ | 0 | 1 | 2 | 3 | 3 | 3 | 4 | 5 | 6 | 6 | 6 |
| Lowering of energy: $\Delta_o$ | 0 | 0.4 | 0.8 | 1.2 | 0.6 | 0 | 0.4 | 0.8 | 1.2 | 0.6 | 0 |

According to this simple electrostatic interpretation, all the $M^{2+}$ ions (with the exception of $Ca^{2+}$, $Mn^{2+}$ and $Zn^{2+}$) will, when subjected to an octahedral crystal field, be stabilized by various multiples of $\Delta_o$ and this actual energy of stabilisation is named 'crystal field stabilisation energy' (CFSE).

At this point you will be naturally curious to know how the $d$-orbital degeneracy will be split in the other most frequently met M–L coordination geometries, namely, the tetragonal, square planar, and tetrahedral geometries. Let us consider them now. Supposing that you pull the two ligands on the $\pm z$ axis of the octahedron away from the central metal, so that they are more remote from metal than the other four ligands in the $xy$ plane, then we achieve a tetragonal arrangement of ligands around metal. The resulting $d$-orbital splitting is shown in Fig. 8.3. The two sets of degenerate orbitals that characterise octahedral splitting are further split; the $d_{z^2}$ now sinks to a lower energy level than $d_{x^2-y^2}$, and the $d_{xz}$, $d_{yz}$ pair becomes lower than $d_{xy}$ because electrostatic repulsion along $\pm z$-axis is now reduced. If the two ligands on the $\pm z$ axis are then moved away to infinity (the extreme case!), then we have the square planar complex with the splitting shown in Fig. 8.3.

Finally, in the most interesting case of the tetrahedral complexes, the $d$-orbital splitting is actually the reverse of the splitting in the octahedral case! You will visualise this
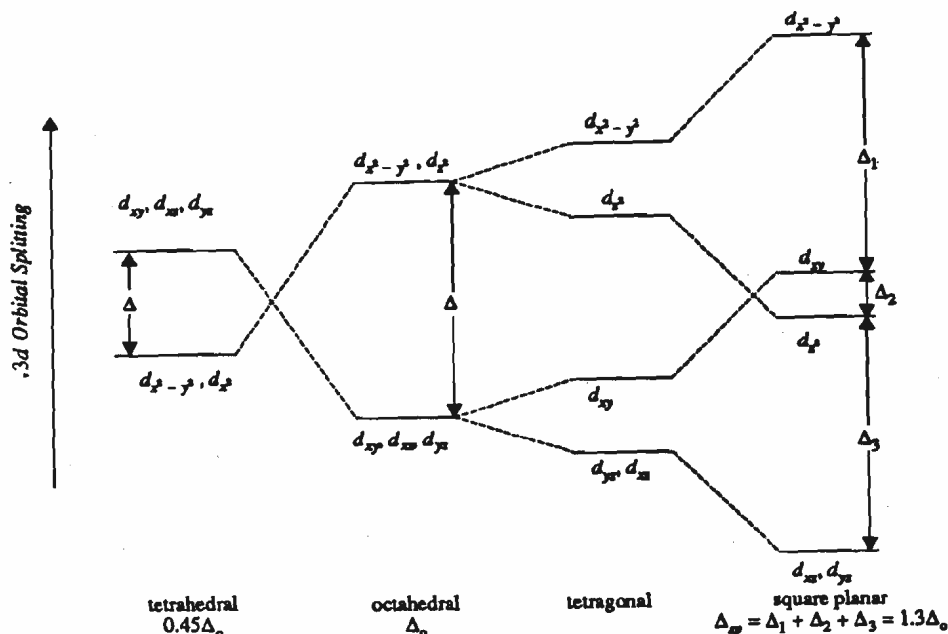
Fig. 8.3 : Crystal field splitting of $d$-orbitals of metal ion in complexes having different geometries.

more readily by inscribing the tetrahedron in a cube, Fig. 8.4 (a). The four ligands making up the tetrahedron appear as shaded circles at the alternate cube corners. The $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are now degenerate, and point towards the centres of cube faces, and the $d_{xy}$, $d_{yz}$, $d_{xz}$ orbitals are degenerate and point at the midpoints of the cube edges.
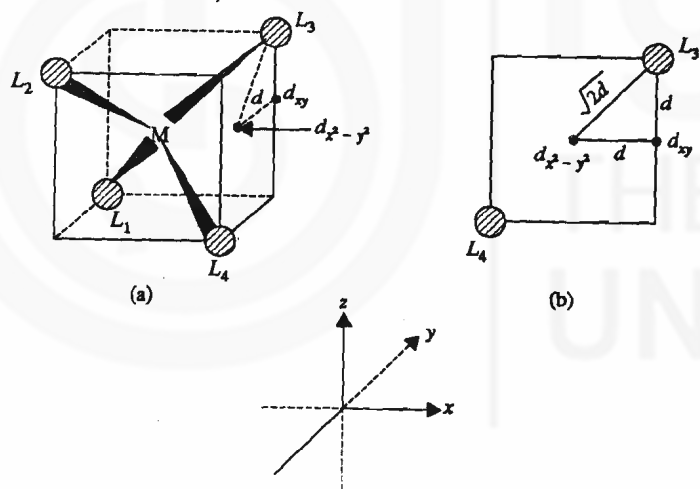


Fig. 8.4: The tetrahedral complex showing that the ligands repel the $d_{x^2-y^2}$ orbitals less than the $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals.

In Fig. 8.4 (b) we examine one face of the cube, on which ligands $L_3$ and $L_4$ are located. We see that $d_{x^2-y^2}$ falls at the centre of this face. $d_{xy}$ at the centre of the edge, and $L_3$ and $L_4$ at opposite corners. If $d$ is half the edge-length, then $L_3$ will be at distance $d$ from one lobe of $d_{xz}$ but at distance $(\sqrt{2})\,d$ from one lobe of $d_{x^2-y^2}$. Consequently, repulsion will be greater at those orbitals that are closer to the ligands, namely, the $(d_{xy}, d_{yz}, d_{xz})$ set, than at the other set $(d_{z^2}$ and $d_{x^2-y^2})$. Therefore, for the tetrahedral crystal field, the triply degenerate set (labelled $t_2$) is higher in energy than the doubly degenerate set (labelled $e$), just the reverse of the situation for the two sets in the octahedral crystal field case. By the way, you should not fail to note that, in a tetrahedron, there is no centre of symmetry about which the figure can be inverted; therefore, we omit the $g$-subscript from the $t_2$ and $e$ symmetry labels. Thus, for the same electron configuration $d^n$, the energy relationships between octahedral and tetrahedral fields are exactly reversed. This fact greatly facilitates the problems of interpreting electronic spectra.

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Analysis of a large number of experimental data for transition metal complexes of various geometries shows the $d-d$ splittings to be related as given below:

| Square planar | > | Octahedral | > | Tetrahedral |
|---|---|---|---|---|
| $(1.3\ \Delta_o)$ | | $(\Delta_o)$ | | $(0.45\ \Delta_o)$ |

We now take one very simple, but very typical and 'colourful', example: that of the $d-d$ electronic band in a complex with a single $d$ electron. An aqueous solution of $Ti_2(SO_4)_3$ is red-purple in colour, and has a single broad absorption maximum in the visible spectral region, around 20,400 $cm^{-1}$ (Fig. 8.5). However, this is a band of rather weak intensity, $(\varepsilon = 0.6\ m^2\ mol^{-1})$ and this is based on an important 'selection rule' which we shall discuss presently. Now our central metal ion is $Ti^{3+}$, but how is it coordinated, and to what ligands? Note that this is an aqueous solution, having plenty of water molecules to act as ligands! Actually, this electronic absorption band is ascribed to the octahedral complex $[Ti(H_2O)_6]^{3+}$, and may be understood as the excitation of the single $d$-electron from the $t_{2g}$ level to the $e_g$ level. This transition can be represented as follows :      $(t_{2g})^1\ (e_g)^0 \longrightarrow (t_{2g})^0\ (e_g)^1$

This is what we call a $d-d$ transition, or $d-d$ absorption band, for which $\Delta_o = 20,400$ $cm^{-1}$. The spectra of most complexes of the first transition series of elements can be explained with similar orders of magnitude for $\Delta$.
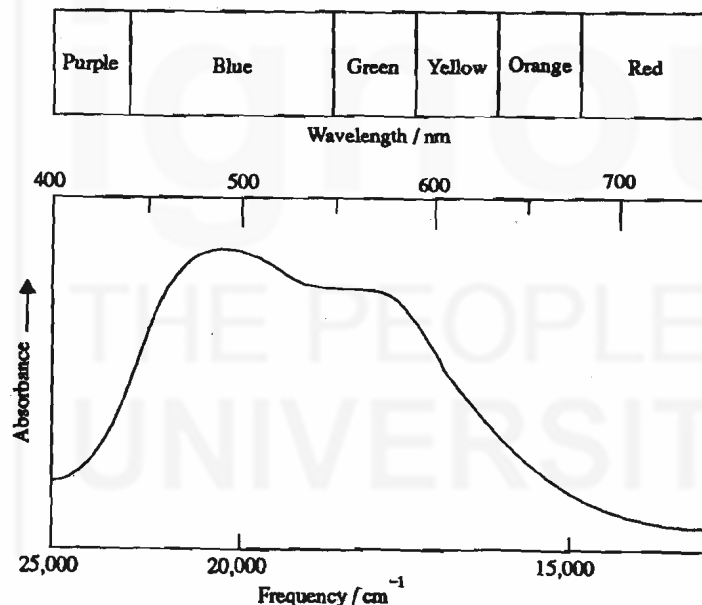
| Purple | Blue | Green | Yellow | Orange | Red |
|---|---|---|---|---|---|

Wavelength / nm



**Fig. 8.5 : Visible absorption spectrum of $[Ti(H_2O)_6]^{3+}$.**

The spectrum of $[Ti(H_2O)_6]^{3+}$ can be interpreted by means of the colour-scale given in Fig. 8.5. You can see that the complex absorbs strongly in the blue-green region of the visible region. Therefore, it appears purple-red in colour.

We shall examine just one more interesting result of a $d-d$ transition from experimental absorption spectra, and by using Table 8.1 we shall also illustrate a sample calculation of crystal field stabilisation energy (CFSE). Our example is solid $NiCl_2$ crystal, in which the $Ni^{2+}$ ion site is surrounded by six $Cl^-$ ligands in an octahedral arrangement. The crystal gives an electronic absorption spectrum peaking at 9270 $cm^{-1}$. Since the wavenumber corresponding to an energy of one electron volt is 8066 $cm^{-1}$, and also since 1 eV = 96.5 kJ $mol^{-1}$, the absorption maximum of 9270 $cm^{-1}$ indicates a crystal field splitting $(\Delta_o)$ of $(9270/8066) \times 96.5$ kJ $mol^{-1}$. The crystal field stabilisation energy for the $d^8$ $Ni^{2+}$ ion in an octahedral field is (see Table 8.1) 1.2 $\Delta_o$.

Hence,

$$CFSE = 1.2\,\Delta_o = 1.2 \times \frac{9270}{8066} \times 96.5 = 133 \text{ kJ mol}^{-1}$$

Thus the splitting of $3d$ orbitals leads to a crystal field stabilisation energy of 133 kJ $mol^{+1}$.

Before we proceed further, you may like to attempt the following SAQ to test your understanding of the concepts developed so far.

## SAQ 1

a) State whether the following statements are true or false. Write T or F in the boxes provided.

   i) five-fold degeneracy of $d$-orbitals is removed by effects of ligands attached to the metal.

   ii) an electron in $d_{xy}$, $d_{yz}$ or $d_{xz}$ orbitals is lower in energy than that in $d_{z^2}$ or $d_{x^2-y^2}$ orbitals in an octahedral complex.

   iii) an electron in $d_{z^2}$ or $d_{x^2-y^2}$ orbital is higher in energy than that in $d_{xy}$, $d_{yz}$ or $d_{xz}$ orbital in a tetrahedral complex.

   iv) energy of the $e_g$ orbital decreases by 0.4 $\Delta_o$ and that of the $t_{2g}$ orbitals increases by 0.6 $\Delta_o$ in an octahedral complex.

b) Fill in the blanks in the following statements using the words given below:
   centre of symmetry, polarizability, octahedral, point, reverse

   i) The $d$-orbital splitting for a tetrahedral complex is actually the _____ of the splitting in an octahedral case.

   ii) In a tetrahedron there is no _____ about which the figure can be inverted.

   iii) The electronic absorption spectrum of $Ti_2(SO_4)_3$ is ascribed to the _____ complex, $[Ti(H_2O)_6]^{3+}$

   iv) The $d$–$d$ energy difference depends on the product of charge and _____ of the central metal ion.

   v) In the crystal field theory, ligands are considered as _____ electric charges.

## 8.4 'FORBIDDEN' VS 'ALLOWED' $d$-$d$ ABSORPTIONS: THE ORIGIN OF 'WEAK' AND 'STRONG' $d$-$d$ BANDS

You will recall from Unit 7 that, by the operation of the Laporte selection rule, a $d$–$d$ electronic transition is highly forbidden in a free ion; in the case of transition metal complexes also, when the crystal field around the M has octahedral symmetry, the $d$–$d$ electronic transition is forbidden by the 'parity' selection rule 'even $\longleftrightarrow\!\!\!/\!\!\!\longrightarrow$ even', or 'gerade $\longleftrightarrow\!\!\!/\!\!\!\longrightarrow$ gerade', abbreviated as '$g \longleftrightarrow\!\!\!/\!\!\!\longrightarrow g$'. However, in the real world of chemistry, we sometimes find that rules, like the egg-shell, are "made only to be broken"! Therefore, instead of using the 'go', 'no-go' language of 'allowed' and 'forbidden', we, sometimes find it convenient to speak of 'strongly allowed' and 'weakly allowed' transitions. For example, the $g \longleftrightarrow\!\!\!/\!\!\!\longrightarrow g$ forbiddenness can be broken the moment the centre of symmetry of our M–L octahedron becomes destroyed by a vibrational displacement of 'odd', or '$u$' (ungerade) symmetry. The mechanism is that, in the **displaced arrangement** caused by this vibration, the $d$ orbitals of the central M ion can mix with $p$ (or $f$) orbitals, and also that the ligand orbitals may contribute

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unequally to the distorted $d$ orbitals. Thus, the totally not-allowed $d$-$d$ transition becomes allowed, though weekly. The rather small value of the absorbance about which we remarked earlier in the case of $[Ti(H_2O)_6]^{3+}$ is in accord with such a vibrationally induced, and therefore weakly allowed, electronic transition. Very suitably, the term 'vibronic transition' has been coined in the literature to describe this band.

If our argument above is correct regarding this so-called 'forbiddenness' of the $t_{2g} \rightarrow e_g$ transition, then in complexes without a centre of symmetry, such as the **tetrahedral** complexes, this mixing of the $d$-orbital with other orbitals can occur even for the equilibrium (i.e., non-vibrating) configuration, giving strongly 'symmetry-allowed' transitions with much larger absorbance values. This is indeed what happens for tetrahedral complexes such as the alkoxides of $Cr^{4+}$, $Cr(OR)_4$ (which have intense $d$-$d$ bands centred at 15,000 cm$^{-1}$), proving that our crystal field theory does go far in predicting the behaviour of electronic absorption in transition metal complexes.

## 8.5 CHARGE-TRANSFER (C.T.) SPECTRA : GENERAL CONSIDERATIONS

The various $d$-$d$ transitions so far discussed are, however, still comparatively weaker in relation to another possible kind of electronic transition called 'charge transfer transition'. Let us illustrate "charge transfer" by choosing a well-known, and again very colourful, example from organic chemistry. When chloroform solutions of chloranil (pale yellow) and aniline (colourless) are mixed, the resulting solution becomes deep purple, and its spectrum shows an absorption which is not possessed by any one of the components of the mixture when in the pure state. At the same time, there is no evidence of any appreciable reaction taking place. This is one example of a Charge-Transfer spectrum, where a photon (or light quantum) is absorbed by a weak complex between an electron 'donor' molecule (D) and an electron acceptor molecule (A) with the consequent shift of electronic charge from D to A. Charge transfer bands are usually broad, structureless bands since the binding energies of the complexes are sufficiently small so that many different configurations may exist in equilibrium with one another.

In the case of inorganic compounds, while colour is generally associated with the presence of a partially filled $d$-shell, many compounds with $d^0$ or $d^{10}$ configurations are also intensely coloured. Mercury(II) iodide (brick red, $d^{10}$), the familiar permanganate(VII) ion (intense purple, $d^0$) and bismuth(III) iodide (red-orange, $d^{10}s^2$) are some examples. In such cases the colour arises, at least in part, as a consequence of the absorption of light which occurs when an electron from a ligand orbital is transferred to a metal orbital and vice versa. Such charge transfer (or electron transfer) processes are termed 'L—to—M' and 'M—to—L (inverse)' charge transfer, respectively.

Charge transfer processes are commonly of higher quantum energy than $d$-$d$ transitions and generally lie in the ultraviolet or far ultraviolet spectral region. However, if the metal is easily oxidisable and the ligand readily reducible, or vice-versa, then charge transfer transitions may occur in the visible region. Often, these spectra are very intense and mask the $d$-$d$ transitions. Indeed, the $d$-$d$ spectra of transition metal iodide complexes are notoriously difficult to obtain for this reason, the iodide ion being so readily oxidisable. In the next section we shall explore the effects of 'Metal-Ligand' charge-transfer phenomena a little further, after first 'polishing up' the 'crystal field' model to represent 'ligand field' effects more faithfully.

## 8.6 EFFECTS OF THE LIGANDS AND 'POLISHING UP' THE CRYSTAL FIELD MODEL : THE LANGUAGE OF LIGAND FIELDS

Our earlier discussion of the simple crystal field theory may now be modified by including three important kinds of 'chemical bonding' involving M and L: (i) $L \rightarrow M$ sigma-bonding interactions, (ii) $L \rightarrow M$ pi-bonding interactions, and (iii) $M \rightarrow L$ "back bonding" ($\pi^*$) interactions. For example, in $ML_6$ octahedral complexes, a strong $L \rightarrow M$ sigma interaction raises the $e_g$ level, increasing the $\Delta_o$ value. On the other hand, the $L \rightarrow M$ pi-interaction raises the $t_{2g}$ and hence decreases $\Delta_o$. Finally, the $M \rightarrow L$ ($\pi^*$) interaction lowers $t_{2g}$ again, increasing $\Delta_o$. The information contained here represents the general situation for the $d$-orbital splitting for all common geometries which, as we have shown earlier, can be expressed as fractions of $\Delta_o$.

The manner in which various kinds of L and M interact will therefore affect $\Delta$, and hence the stabilisation energies which in the present model we call **Ligand Field Stabilisation Energies** (LFSE, as opposed to the earlier CFSE). For example, good $\pi$-electron 'acceptor' ligands such as $CN^-$ and CO favour strong $M \rightarrow L$ (back-bonding) interaction. As a result, these ligands cause **large** splittings, in the energy range of $30,000 \text{ cm}^{-1}$ or 3.72 eV. In contrast, ligands with a lone-pair of electrons, which we may call 'donors' (to the $\pi$-orbitals of metal), cause small splitting about $10,000 \text{ cm}^{-1}$ or 1.24 eV. The $Br^-$ and $I^-$ ions are good examples of these. In the intermediate range of splittings, we place ligands such as $NH_3$ and $H_2O$ which have no $\pi$-bonding capacity. At first glance, we may perhaps be surprised that the halogen anions, $I^-$ and $Br^-$, with their negative charge should cause smaller splittings than a neutral ligand like $NH_3$. At least our simple electrostatic or 'crystal field' model would tell us that this result is unexpected. But here is where we begin to appreciate that covalence effects are very important. The lone pair of $NH_3$ is in a well-directed $sp^3$ hybrid orbital and interacts well with the empty metal (hybrid) orbital. On the other hand, the filled $p$-orbitals on the halide ligand interact quite strongly with the empty $d$-orbitals of M; that is electric charge is transferred from ligand to metal. These $L \rightarrow M$ interactions therefore, give rise to charge transfer transitions. This transfer lowers the positive charge on the metal and reduces the $D$ term in '$10 Dq$'. For the same metal, the greater the reducing power of the ligand, (e.g., $I^- > Br^- > Cl^-$), the lower is the energy at which the charge-transfer band occurs. Similarly, for the same L, the greater the oxidising power of the metal ion, the lower the energy of the charge-transfer band. For transition metal ions carrying the same charge, the value of $\Delta$ would decrease as ordered in the series,

$$CO \approx CN^- > NO_2 > \text{'en'} > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-,$$
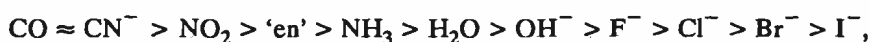
where the above ions and neutral molecules represent the ligands which may surround the transition metal ion. The above series is known as the **spectrochemical series**.

The electronic spectra of $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$, Fig. 8.6, demonstrate, in a simple way, the application of the spectrochemical series. An aqueous solution of $NiSO_4$ is pale green, but when ethylenediamine (en) is added, the colour turns deep blue. The $[Ni(H_2O)_6]^{2+}$ has a minimum in its absorption (or a maximum in its transmittance) where green absorbs, but in all other regions of the visible spectrum it has some absorption, and hence the green colour. On the other hand, $[Ni(en)_3]^{2+}$ absorbs green light strongly and transmits only blue-purple and a little red; hence its deep blue colour.
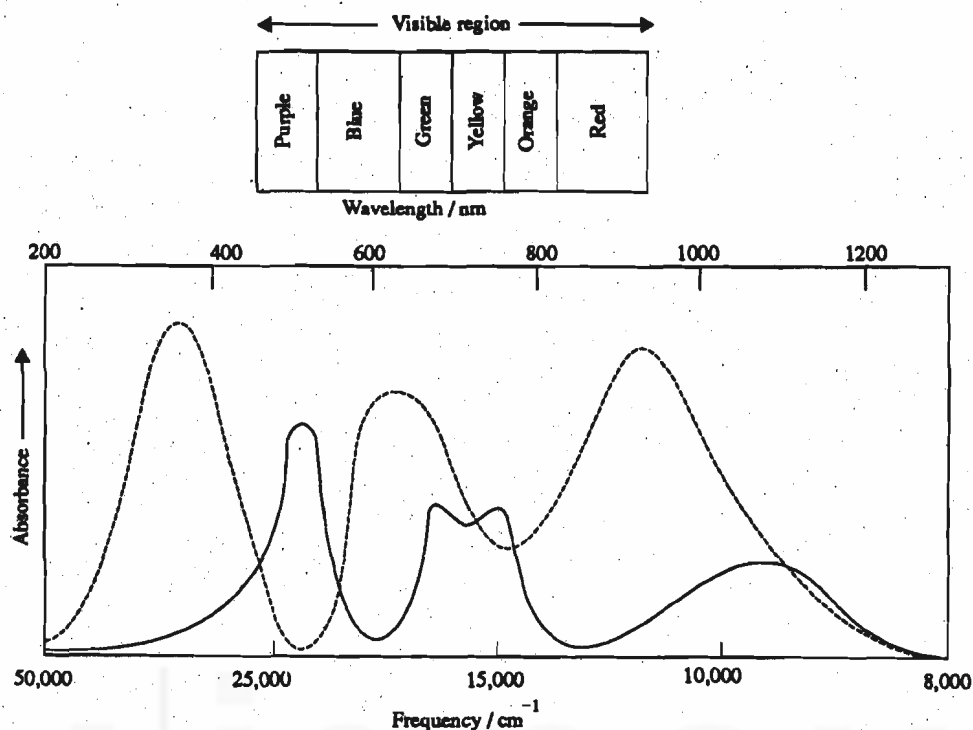
**Fig. 8.6 : Electronic absorption spectra of $[Ni(H_2O)_6]^{2+}$ (solid line) and $[Ni(en)_3]^{2+}$ (broken line).**

## SAQ 2

Although the spectra of $[PtBr_4]^{2-}$ and $[PtCl_4]^{2-}$ are very similar, L→M band in the first complex is at 36,000 $cm^{-1}$, while in the chloride complex it is at 44,000 $cm^{-1}$. Suggest a reasonable explanation for this difference.

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## 8.7 DE-EXCITATION PROCESSES IN ELECTRONIC SPECTROSCOPY: THE JABLONSKI DIAGRAMS

In our discussion of electronic absorption spectra so far, we have devoted our attention to the absorption of light energy by a molecule in its ground state. The molecule thus becomes 'excited'. We would now be curious to know what happens to this excess energy in the excited molecule which has absorbed a quantum of light. Let us calculate the time required for a typical absorption process. A light photon travels at a velocity of $3 \times 10^8$ m $sec^{-1}$, or $3 \times 10^{18}$ Å $sec^{-1}$. Now, the diameter of a typical molecule with which the light photon interacts is ∼ 3 Å. Therefore, the photon will

remain 'at' the molecule for $3/(3 \times 10^{18}) = 10^{-18}$ sec. Accordingly, the absorption process has to occur in about $10^{-18}$ sec or less. In this very small time interval, the nuclei of molecules undergo virtually no motion, and this fact forms the basis of the Franck-Condon principle (Unit 7), according to which most molecules, upon electronic excitation, enter a vibrationally excited level of the excited state.

Virtually all organic molecules (which have filled molecular orbitals), except free radicals, have singlet ground state; these are usually denoted by $S_0$. We then refer to electronically excited singlets as $S_1$, $S_2$, etc., in the order of increasing energies (these together with $S_0$, are called the singlet manifold) and similarly to a possible manifold

of triplets as $T_1$, $T_2$, etc. Excitation normally leads to singlet excited states rather than to triplet states because the $S_o \to T_1$ transition involves a change in (electronic) spin multiplicity and is **highly forbidden** (Unit 7).

Excitation takes the ground-state molecule from the lowest vibrational level, in which it usually exists, to an excited singlet state. There are several possible excited singlet states $S_1, S_2$, etc. The various processes by which a molecule in the excited singlet states can become de-excited are illustrated collectively by the **Jablonski diagrams**, e.g. Fig. 8.7. In these diagrams, solid lines represent radiative processes, and wavy lines non-radiative processes. We shall now briefly discuss a number of the possible events which lead to de-excitation or dissipation of the excess energy. The events will be discussed in the order of the increasing time which they require, the first being the fastest.
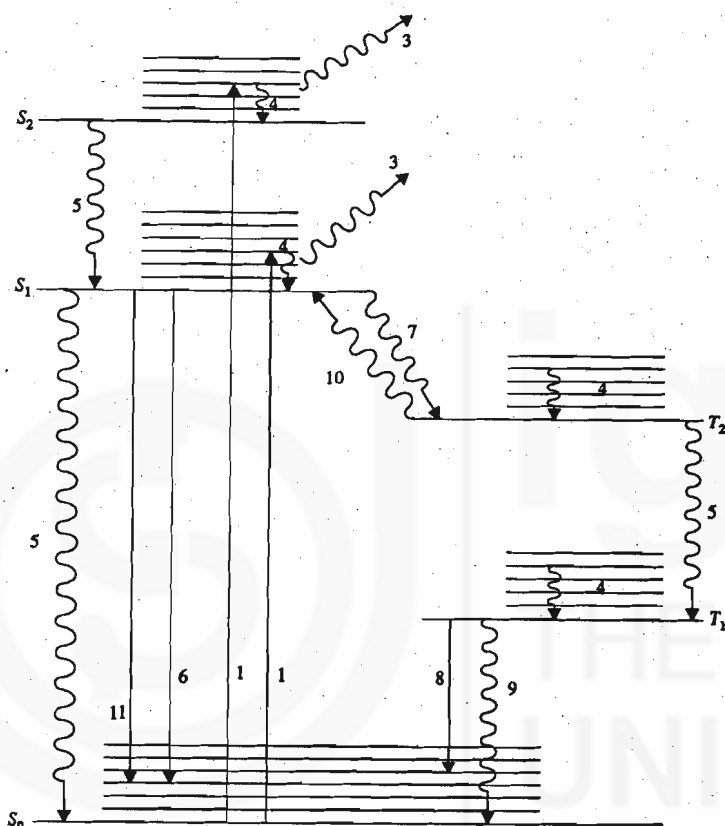


Fig. 8.7 : Jablonski diagram showing processes connecting various electronic states of molecules :
(1) absorption, (3) dissociation and predissociation (4) vibrational relaxation,
(5) internal and external conversion, (6) fluorescence, (7) intersystem crossing,
(8) phosphorescence, (9) quenching, (10) reverse intersystem crossing,
(11) delayed fluorescence.

## 8.7.1 Vibrational Redistribution

After excitation (process 1 in Fig. 8.7), probably the most rapid process to occur in the now electronically and vibrationally excited molecule is a redistribution of the excess vibrational energy among the different vibrational modes (process 2, not shown in Fig. 8.7). It is quite likely to be of major significance in the dissociation and pre-dissociation of large molecules.

## 8.7.2 Dissociation

Dissociation (Fig. 8.7, process 3) is almost certain to occur, if at all, within the period of time of a few vibrations. For example, if the vibration energy is between 300 and 3000 cm$^{-1}$ the vibrational frequency is between about $10^{13}$ and $10^{14}$ sec$^{-1}$. This, means

that the time required for one vibration is, classically, about $10^{-14}$ to $10^{-13}$ sec. Given sufficient energy, a diatomic molecule such as $H_2$ must dissociate in the time of a single vibration, provided some other process (such as a collision) does not intervene.

### 8.7.3    Predissociation

In polyatomic molecules, there are usually additional states between the attractive and repulsive states shown in Fig. 8.8. An excited state which is not a repulsive state is shown in curve $C$ in this figure. Excitation to a low vibrational level of curve $C$ (arrow a) behaves like a normal electronic transition. But excitation to a high vibrational level of curve $C$ (arrow b) places the molecule energetically above the intersection of curves $B$ and $C$. Its vibrational motion on curve $C$, from points $x$ to $y$ and back, passes this intersection point, and there is a fair probability that a molecule will "lose its way" and continue on curve $B$, which again results in dissociation. This process, called **predissociation**, is very common in heavy diatomic and polyatomic molecules.
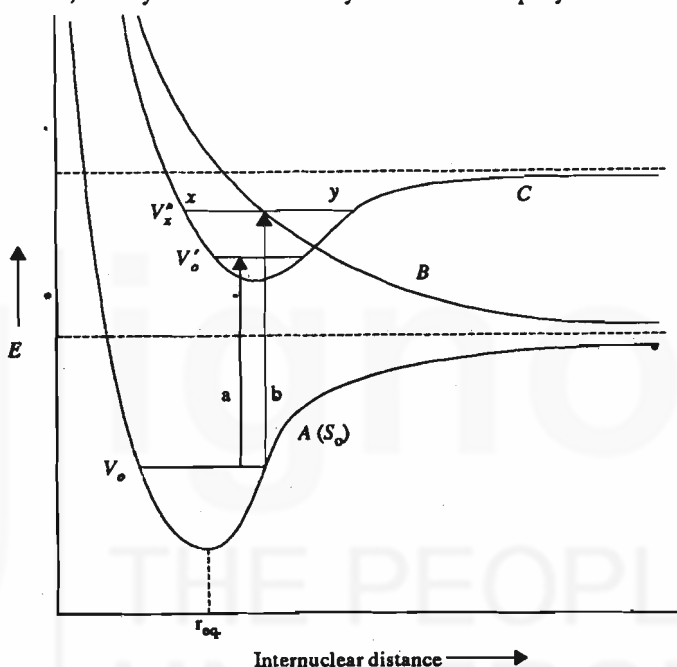


**Fig. 8.8 : Potential energy curves for ground and excited electronic states of molecules showing predissociation.**

When the molecules are in the higher vibrational excited state, it is also possible that they can undergo rearrangements involving bond formation, bond breaking, or both. However, we must remember that the lifetime in excited singlet states higher than $S_1$ is very-very short, and even in the lowest vibrational level of $S_1$ the lifetime is relatively short. Other interesting processes are possible if the molecule can somehow cross over to the $T_1$ state (in the triplet manifold) where, as we shall see, it has much greater lifetime.

### 8.7.4    Vibrational Relaxation

In our time scale, the next process (process 4, Fig. 8.7) is vibrational relaxation or the dropping to the lowest vibrational level that does not involve a change in **electronic energy**. The mechanism of this process undoubtedly requires either collision (in the gas phase) or a collision-like interaction with the environment (in the liquid phase). Gas phase collisions require, depending on gas pressure, about $10^{-13}$ to $10^{-12}$ sec or longer, while the liquid-phase collision-like process occurs in about the same time as a vibration ($10^{-14}$ to $10^{-13}$ sec)

### 8.7.5    Internal and External Conversion

These processes (shown as number 5 in Fig. 8.7) are slower than those previously discussed and result in the relaxation of the molecule into a lower energy state within a given (i.e., singlet or triplet) manifold.

As originally defined from observations of the luminescence of gases, **internal conversion** is referred to the de-activation (quenching) of excited molecules by collision with other molecules of the same species, while **external conversion is** referred to the de-activation by collision with dissimilar molecules. In solution, this distinction becomes meaningless, of course, and we speak only of internal conversion, referring thereby to a deactivation process in which the electronic excitation energy is dissipated as thermal energy by collision with any other (usually solvent) molecule. We note from Fig. 8.7 that this **non-radiative** conversion occurs between different electronic states.

### 8.7.6  Fluorescence

All the processes discussed upto this point are relatively very fast, and only in rare cases are they separately observable by spectroscopy. Consequently, our knowledge about these processes is often only by inference.

The emission of radiation (process 6, Fig. 8.7), which results in a transition of the molecule from an excited state to the ground state, **without a change in multiplicity**, is called **fluorescence** and occurs typically in $10^{-8}$ sec. Therefore, fluorescence practically always occurs from the lowest excited state of the singlet manifold, since this is the only state in the manifold with a lifetime longer than the time required for the various collision dependent relaxation and conversion processes.

Since fluorescence usually occurs from the lowest vibrational state of $S_1$, and emission like absorption, is always **vertical**, the molecule descends to an excited vibrational level of the ground state, Fig. 8.7. This is just the reverse of the usual case in absorption, in which promotion occurs from the $v = 0$ level in $S_0$ and the molecule ends up in higher vibrational levels, $v > 0$, in $S_1$. Accordingly, we expect a "mirror-image" relationship between absorption and fluorescence spectra, with the fluorescence spectrum appearing at longer wavelength (or lower frequency) than the absorption spectrum.

### 8.7.7  Inter-System Crossing and Phosphorescence

Phosphorescence is another process of de-activation of the excited state. It involves emission of radiation as a result of transition of electron between the states of different spin multiplicities (Fig. 8.7, process 7). This occurs through spin-orbit coupling, in which states with different spin angular momenta and orbital angular momenta mix slightly because they have the same total angular momentum.
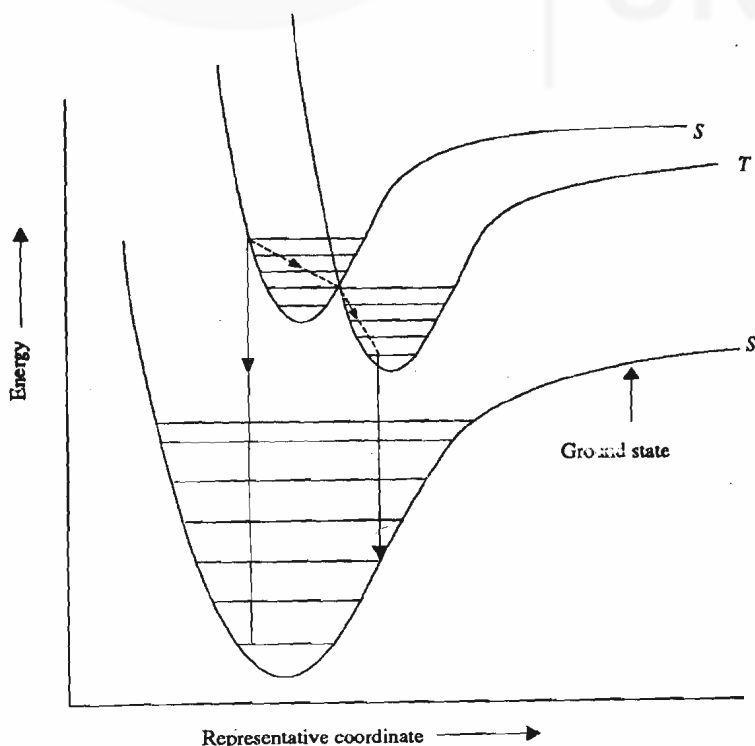


Fig. 8.9 : Potential energy curves of singlet and triplet states involved in phosphorescence.

Phenomenon of phosphorescence can be understood in the following manner. Fig. 8.9 represents the arrangement of potential energy curves of singlet $S$ and triplet $T$ states that can lead to phosphorescence. Absorption of radiation can lead to the excitation of electron from the ground singlet state to the excited singlet state. Collision deactivation can then drop the energy past the point where the potential energy curve of the singlet state crosses that of the triplet state. Although internal conversion between states of different multiplicities is not easy, this process, known as inter-system crossing (process 7, Fig. 8.7), can occur leading to the triplet state molecules.

Once a different multiplicity manifold is attained by intersystem crossing (e.g., singlet → triplet), the same relaxation processes are important as were relevant in the original manifold. Following the same reasoning, the molecule will relax to the lowest vibrational level of the lowest electronic state of the new manifold. Once this point is reached, however, the final decay to the ground state is much slower and gives rise to a great variety of phenomena.

Intersystem crossing from the lowest excited singlet to the lowest triplet is one of the most important photochemical processes because of the long lifetime of the lowest triplet. The loss of energy from the lowest triplet to the ground state may occur by a radiative process called phosphorescence (process 8, Fig. 8.7) or by a relaxation process consisting of a reverse intersystem crossing (process 10, Fig. 8.7) involving internal or external conversion. The lowest triplet is difficult to pupulate by direct singlet → triplet absorption and equally difficult to de-populate by emission of radiation. If the non-radiative paths for de-activation are eliminated (for example, by using a very low temperature), the natural radiative lifetime of the triplet can be estimated. Phosphorescence spectra are usually determined in solutions that are frozen at 70-80 K. The phosphorescence spectra occur at longer wavelength (lower frequency) than the fluorescence spectra. Why? (Study the Jablonski diagram carefully).

### 8.7.8 Fluorescence and Phosphorescence Quenching

The most readily observed, and therefore the most readily studied, are the two radiative processes, **fluorescence and phosphorescence**. When they are not observed or, particularly, when they disappear under certain circumstances, they are said to be quenched (process 9, Fig 8.7). What this means is that, in the competition between processes, the radiative one has lost out because some alternative process was more rapid in the systems. Thus, fluorescence competes with internal and external conversion, with intersystem crossing, and possibly with some photochemical processes. Only when fluorescence is more rapid than, or at least as fast as, any of the others, can it be observed. Similarly, phosphorescence competes with relaxation by reverse intersystem crossing to the ground state, delayed fluorescence (process 11, Fig. 8.7), photochemical reactions, and other 'exotic' processes such as triplet-triplet annihilation and excimer fluorescence.

### SAQ 3

State whether the following statements are true or false. Write T or F in the boxes provided.

a)  In intersystem crossing there is a change in spin multiplicity of states

b)  Fluorescence occurs in $10^{-8}$ seconds

c)  The phenomenon of predissociation is very common in heavy diatomic and polyatomic molecules

d)   Most of the organic molecules except free radicals are in triplet
     state

## 8.8   SUMMARY

In this unit you had studied that in the presence of ligands, the five fold degeneracy of
$d$ orbitals of a metal ion is removed. By absorption of energy in the visible region of
spectra, the electrons can undergo $d$–$d$ transitions. The origin of colours of transition
metal complexes can be explained in the light of $d$–$d$ and charge transfer electronic
transitions and the crystal field theory. You have also studied various processes by
which de-activation of an electronic state takes placed.

## 8.9   TERMINAL QUESTIONS

1.   The $e_g$ orbitals are higher in energy than the $t_{2g}$ orbitals in octahedral
     environment but the order is reversed in tetrahedral arrangement. Explain.

2.   Give the absorption spectrum of $Ti_2(SO_4)_3$ and explain the type of electronic
     transition taking place.

3.   HgS, $KMnO_4$ and $K_2CrO_4$ – all are intensely coloured, though there is no
     possibility of $d$–$d$ transitions in them. Explain.

## 8.10   ANSWERS

### Self Assessment Questions

1.  a)  i) T   ii) T   iii) T   iv) F

    b)  i) reverse   ii) centre of symmetry

        iii) octahedral   iv) polarizability   v) point

2.   In charge-transfer spectra, the greater the reducing power of the ligand, the
     lower is the energy at which the charge transfer band occurs. As $Br^-$ ion has a
     greater reducing power than the $Cl^-$ ion, the charge-transfer bands occur at
     36,000 cm$^{-1}$ and 44,000 cm$^{-1}$ in the spectra of $[PtBr_4]^{2-}$ and $[PtCl_4]^{2-}$,
     respectively.

3. a)  T   b) T   c) T   d) F

### Terminal Questions

1.   See Section 8.3

2.   See Section 8.3

3.   The intense colours of HgS, $KMnO_4$ and $K_2CrO_4$ are due to charge-transfer
     transitions as there is no possibility of $d$–$d$ transition in any of them. The red
     colour of HgS is due to the transition $S^{2-}(n) \rightarrow Hg(6s)$ i.e., due to the transfer of
     lone pair electrons of sulphide ion to the empty $6s$ orbital of the mercury (II)
     ion. The intense colours of $KMnO_4$ and $K_2CrO_4$ are due to the transfer of lone
     pair electrons on $O^{2-}$ ion to the empty $t_{2g}$ orbitals on $Mn^{7+}$ and $Cr^{6+}$ ions. You
     should note that $Mn^{7+}$ and $Cr^{6+}$ are examples of $d^0$ ions, whereas $Hg^{2+}$ has a
     $d^{10}$ configuration.

# UNIT 9 OPTICAL SPECTROSCOPY: INSTRUMENTATION AND SAMPLING

## Structure

## 9.1 INTRODUCTION

In the earlier units on different kinds of spectra namely – rotational, vibrational, electronic and Raman – we have looked into the origin of a particular spectra and the information it can give us about the molecular structure. However, we had not discussed how these spectra are experimentally obtained. Since there is a lot of similarity in the experimental techniques in obtaining different kinds of spectra, we shall learn them in this unit. At the same time each one of them differs in detail from the other and hence they have been treated separately in different sections. You would notice that nmr, esr and mass spectra have not been included here since their experimental techniques are quite different from the ones discussed in this unit. Hence the experimental techniques associated with nmr, esr and mass spectra are included in their respective units. The spectrum of a sample is recorded with the help of an instrument called spectrometer or spectrophotometer. A spectrometer generally records some function of radiant power (e.g. percent absorption or transmission) transmitted through the sample at different wave lengths in the given region. A spectrophotometer gives us the ratio of the radiant power of two electromagnetic beams. Since the absorption spectrum is much more intense than the emission spectrum, we generally record the absorption spectrum of a sample. In this unit, we shall deal with absorption spectrometers used in different regions of spectrum.