

---

# UNIT 7 ELECTRONIC SPECTRA-I

---

## Structure

- 7.1 Introduction
  - Objectives
- 7.2 Born-Oppenheimer Approximation
- 7.3 Electronic States of Diatomic Molecules
  - Molecular Orbital Treatment of Diatomic Molecules
  - Molecular Term Symbols
  - Deriving Term Symbols
  - Ground and Excited State Term Symbols of Diatomics
  - Selection Rules for Spectra of Diatomics
- 7.4 Franck-Condon Principle and Intensities of Electronic Spectra
- 7.5 Electronic Spectra of Polyatomic Molecules
- 7.6 Some Important Terms Used in Electronic Spectroscopy
  - Chromophore
  - Auxochrome
  - Hypsochromic Shift
  - Bathochromic Shift
  - Hyperchromic Shift
  - Hypochromic Shift
- 7.7 Absorptions due to Ethylenic and Carbonyl Chromophore
  - Ethylenic Chromophore
  - Acetylenic and Benzenoid Chromophore
  - Carbonyl Chromophore
- 7.8 Solvent Effects on Electronic Spectra
  - $\pi - \pi^*$  Transitions
  - $n - \pi^*$  Transitions
- 7.9 Summary
- 7.10 Terminal Questions
- 7.11 Answers

---

## 7.1 INTRODUCTION

---

In Units 4 and 5, we have discussed the IR spectra of diatomic and polyatomic molecules, respectively. We have learnt about the mass effects, electronic effects, solvent effects and hydrogen bonding effects on IR vibrational spectra. We have also learnt the usefulness of IR spectra for molecular structure determination. In Unit 6, we have studied the application of Raman spectroscopy in determination of molecular structure. A comparative study of Raman and IR spectra has also been included in Unit 6. This study helps us to identify different kinds of structures of molecules.

The study of IR, Raman and microwave spectra still does not give answer to the question 'why certain substances are coloured?' For example, the green colour of vegetation is due to a compound chlorophyll. Transition metal complexes, such as  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , are coloured. The answer to the origin of colours in substances and information about excited states of molecules can be obtained from a study of their

electronic spectra which occur in the visible (400 – 800 nm) and ultraviolet (200 – 400 nm) regions of electromagnetic spectrum. Unit 7 deals with a discussion of electronic spectra of diatomic and polyatomic molecules. This study will be followed by a discussion of electronic spectra of transition metal complexes in Unit 8.

In this unit, we will state the Born-Oppenheimer approximation. We will recapitulate the molecular orbital treatment for determining the electronic states of diatomic molecules. We will learn to write the term symbols for ground and excited states of diatomic molecules. The selection rules for transitions in diatomic molecules will then be outlined. The Franck-Condon principle will also be stated. This principle is used to understand the variation in intensities of electronic spectra. The different types of transitions possible in the electronic spectra of polyatomic molecules will then be discussed. The terms chromophore, auxochrome, hypsochromic and bathochromic effects, hyperchromic and hypochromic effects will be defined. The rules to predict the position absorption maxima in conjugated dienes, and enones will then be presented. The unit will conclude with a discussion of effect of solvent on  $n - \pi^*$  and  $\pi - \pi^*$  transitions in carbonyl and unsaturated compounds.

### Objectives

After studying this unit you should be able to:

- describe the molecular orbital approach for diatomic molecules,
- write the ground and excited state configurations for diatomics,
- derive term symbols for diatomic molecules,
- predict the allowed transitions between states in diatomics,
- apply Franck-Condon principle and explain the variation in intensities of spectra of  $\text{CN}^-$  radical, CO and  $\text{I}_2$  molecules,
- explain using diagrams the  $n - \pi^*$ ,  $n - \sigma^*$ ,  $\sigma - \sigma^*$ ,  $\pi - \pi^*$  transitions,
- define chromophore, auxochrome, hypsochromic and bathochromic effects, hyperchromic and hypochromic effects in electronic spectra,
- calculate dissociation energy of molecules in the ground state,
- apply Woodward rules to predict the absorption maximum for conjugated dienes and trienes,
- apply Fieser and Scott rules to predict the absorption maximum for  $\alpha, \beta$  unsaturated ketones, and
- explain the effect of solvent on  $n - \pi^*$  and  $\pi - \pi^*$  transitions in electronic spectra.

---

## 7.2 BORN-OPPENHEIMER APPROXIMATION

---

The structure of electronic spectra involves the change of at least three quantum numbers simultaneously, namely electronic, vibrational and rotational quantum numbers. This follows the Born-Oppenheimer approximation that rotational ( $E_R$ ), vibrational ( $E_v$ ) and electronic ( $E_e$ ) energy levels are independent of one another. The total energy  $E$  is written as

$$E = E_e + E_v + E_R$$

A change in the total energy as a result of electronic transition in a molecule is

$$\Delta E = \Delta E_e + \Delta E_v + \Delta E_R$$

In wave numbers the change is represented as

$$\Delta \nu = \Delta \nu_e + \Delta \nu_v + \Delta \nu_R$$

The approximate orders of magnitude of these changes are

$$\Delta \nu_e \approx \Delta \nu_v \times 10^3 \approx \Delta \nu_R \times 10^6 \text{ cm}^{-1}$$

Thus each electronic level comprises a number of vibrational levels and each vibrational level consists of several rotational levels, as is shown in Fig. 7.1.

From these values of relative order of energies, we find that the vibrational changes give a 'coarse structure' and the smaller rotational changes give a 'fine structure' to the electronic spectra. Since rotational energy changes are minimum, these energy changes are neglected and electronic band system is considered in terms of transitions between electronic levels each consisting of a series of vibronic levels of the same kind.

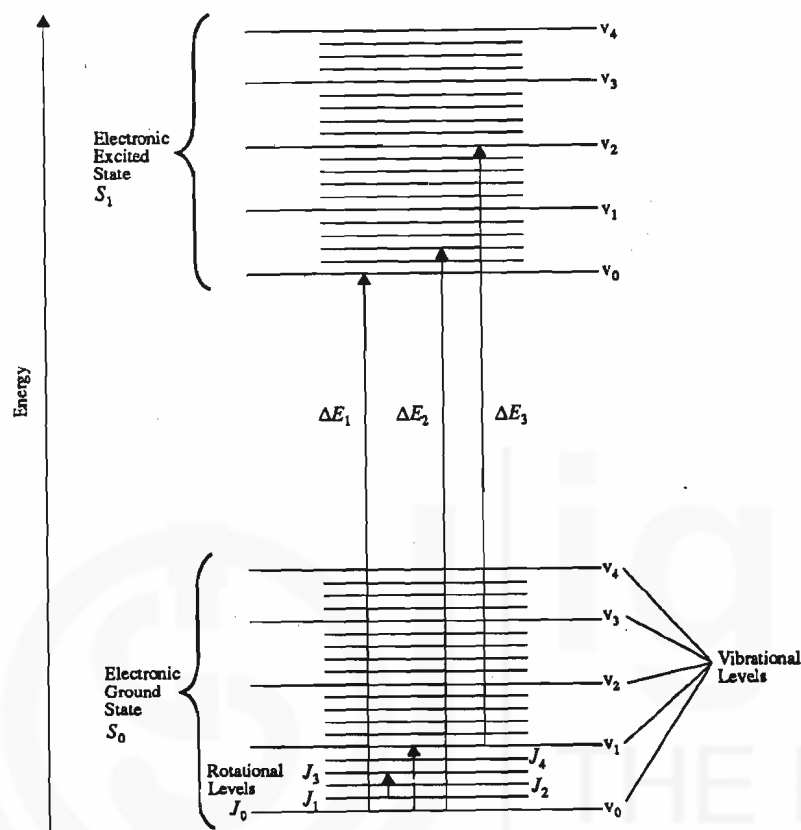


Fig. 7.1 : Rotational, vibrational and electronic energy levels in a molecule.

## 7.3 ELECTRONIC STATES OF DIATOMIC MOLECULES

In Unit 1 of this course, you studied that in an atom various electronic states can arise from a given electronic configuration due to coupling of orbital angular momentum and spin angular momentum of electron. You also studied that the atomic spectra arise due to transition between different electronic energy states. Similarly for molecules various electronic states can arise from a given electronic configuration of a molecule. The electronic configuration of a molecule can be derived on the basis of molecular orbital theory which you studied in Unit 5 of the CHE-01 course.

### 7.3.1 Molecular Orbital Treatment of Diatomic Molecules

According to the molecular orbital theory there exists a set of molecular orbitals which embrace all the nuclei forming the molecule. You have studied in the Atoms and Molecules (CHE - 01) course that the molecular orbitals can be created by linear combination of atomic orbitals (LCAO) of appropriate energy. Fig. 7.2 depicts the shape of  $\sigma$  and  $\pi$  molecular orbitals formed by the LCAO method. More complex orbitals,  $\delta$ ,  $\phi$  etc., can be formed by interaction between  $d$ ,  $f$  atomic orbitals. But this need not concern us; the simple molecules with which we shall deal with use  $\sigma$  and  $\pi$  orbitals only.

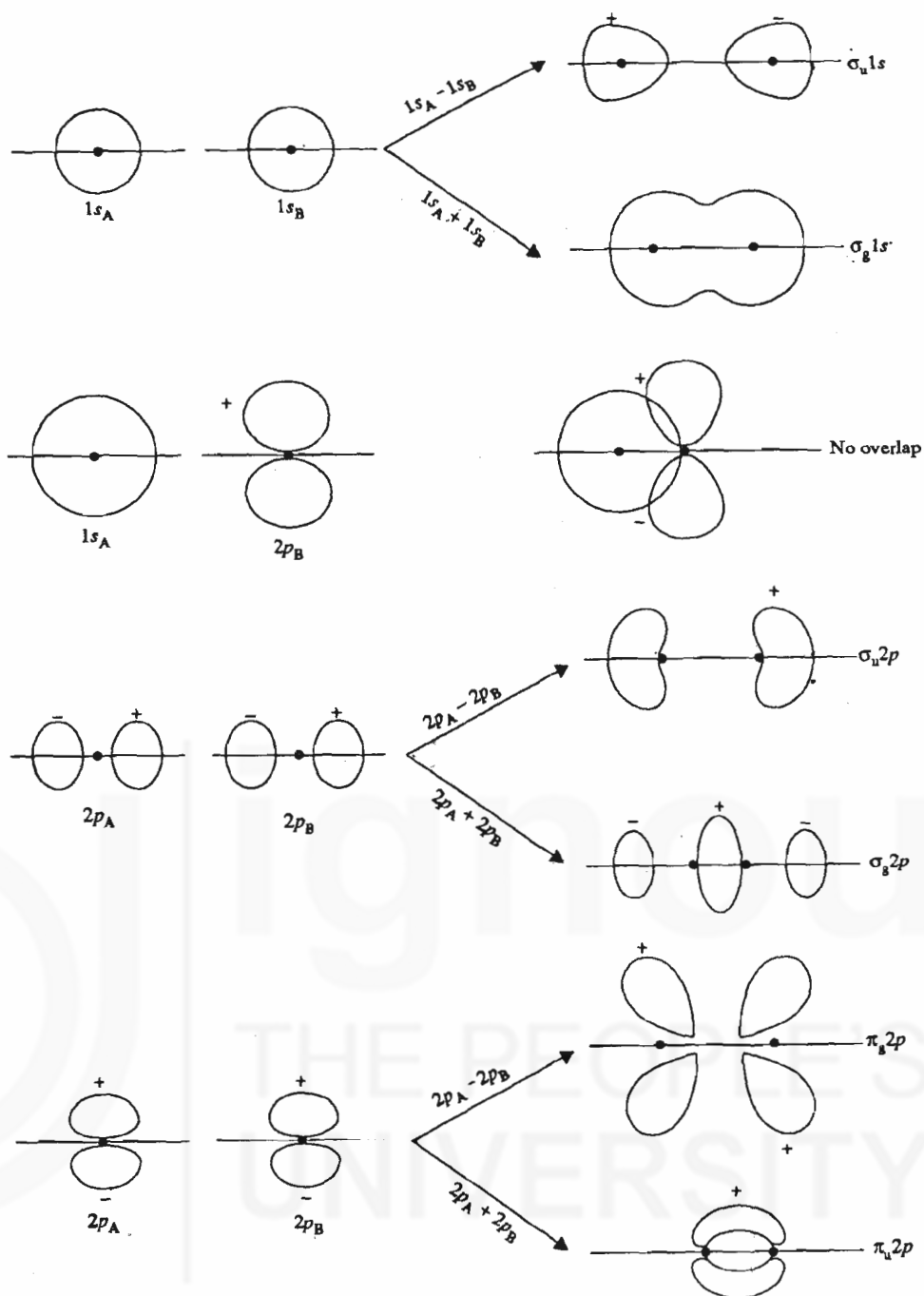


Fig.7.2 : Formation of  $\sigma$  and  $\sigma^*$ ,  $\pi$  and  $\pi^*$  molecular orbitals by LCAO.

Various molecular orbitals have different energies and are characterised by the four quantum numbers similar to the atomic orbitals. The principal quantum number,  $n$  and the azimuthal or subsidiary quantum number,  $l$  are retained from the atomic orbitals and have the same significance here also. But the magnetic quantum number,  $m_l$ , is replaced by a new quantum number  $\lambda$ , which represents (in the units of  $h/2\pi$ ), the component or the projection of electronic orbital angular momentum along the inter-nuclear axis.  $\lambda$  can take same values for molecules as  $m_l$  has for the atomic orbitals, i.e.  $\lambda = 0, \pm 1, \pm 2, \pm 3, \dots$ . When  $\lambda = 0$ , the molecular orbitals are symmetric for rotation about the inter-nuclear axis (i.e., the line joining the two nuclei) and hence are called  $\sigma$  orbitals. When  $\lambda = \pm 1$ , orbitals are known as  $\pi$  orbitals. The  $\pi$  orbitals are antisymmetric for rotation about the molecular axis, that is, if we rotate the molecular orbital by  $180^\circ$ , they change sign (see Fig. 7.2). Similarly,  $\lambda = \pm 2, \pm 3, \dots$  etc. represent  $\delta$ ,  $\phi$ , ... etc. molecular orbitals. The different types of molecular orbitals with their symbols and  $\lambda$  values are listed below:

MO symbols  $\sigma$   $\pi$   $\delta$   $\phi$  .....

Note that the designations  $\sigma, \pi, \delta, \phi$  are not strictly analogous to atomic designations  $s, p, d, f$  which depend on  $l$  and not on  $m_l$  values. Also note that except for  $\sigma$  orbital when  $\lambda = 0$ , for all other orbitals with  $\lambda \neq 0$ , there are two possible values of  $\lambda, +\lambda$  and  $-\lambda$ , i.e., each electronic state is doubly degenerate.

The spin quantum number  $s$  is similar to that for the atomic orbitals, and  $m_s$ , the component of spin angular momentum, can take the values  $\pm 1/2$ .

The order of energy of molecular orbitals has been determined from the spectroscopic data. The energy level diagrams for homonuclear diatomic molecules are shown in Fig. 7.3, where we also indicate to the right and left, the atomic orbitals which combine to form each molecular orbital. Fig. 7.3(a) shows the order of energies of the MOs of the larger molecules such as  $N_2, O_2$  and  $F_2$ , wherein the energies of  $\sigma 2p$  and  $\pi 2p$  orbitals are very close to one another. For lighter molecules such as  $Li_2, B_2$  and  $C_2$ , the order of energies of these orbitals is reversed, i.e.,  $\pi 2p$  becomes lower in energy than the  $\sigma 2p$  orbital, Fig. 7.3 (b).

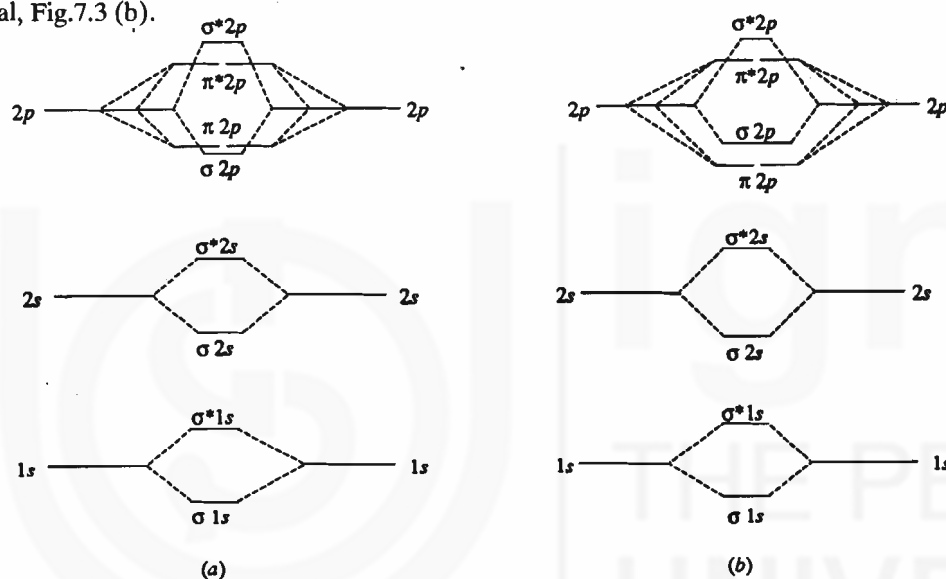


Fig. 7.3 : Energy level diagram for (a)  $N_2, O_2$  and  $F_2$  molecules (b)  $Li_2, B_2$  and  $C_2$  molecules.

Electronic configuration of a diatomic molecule can be derived by filling the electrons in molecular orbitals. Essentially the same rules apply to their filling as to their filling of atomic orbitals. That is

- i) the electrons occupy the available molecular orbitals one at a time, the lowest energy orbital being filled first (**aufbau principle**),
- ii) each molecular orbital can accommodate a maximum of two electrons, provided their spins are opposite (**Pauli's exclusion principle**),
- iii) no pairing of electrons in orbitals of equal energy will take place unless there is atleast one electron in each of them (**Hund's rule of maximum multiplicity**).

### 7.3.2 Molecular Term Symbols

As for atoms, the electronic state of the molecule depends on the net or total electronic arrangement. The electronic arrangement of the molecule as a whole can be best characterised by the component of total orbital angular momentum along the inter-nuclear axis and the total spin angular momentum. For a molecule, the total orbital component along the molecular axis is denoted by the quantum number  $\Lambda$ , which is the sum of the quantum numbers for each individual electron ( $\lambda_i$ ). Thus,

$$\Lambda = \sum \lambda_i \text{ where summation is over all electrons.}$$

The following symbols (capital Greek letters) are used to represent the various  $\Lambda$  values for a molecule:

Symbol	:	$\Sigma$	$\Pi$	$\Delta$	$\Phi$	.....
$\Lambda$ Value	:	0	$\pm 1$	$\pm 2$	$\pm 3$	.....

The total electron spin angular momentum of a molecule is represented by the total spin quantum number  $S$ . The multiplicity of a molecular state is, as for atoms,  $2S + 1$  and this is usually indicated as an upper prefix to the term symbol.

The values of  $\Lambda$  and  $S$  of a molecular state are represented in the form of a term symbol as :

$$^{2S+1}\Lambda$$

In addition, the term symbol has a subscript and a superscript on the right side. The subscript ( $g$  or  $u$ ) indicates whether on inversion through the centre of symmetry the orbital changes sign or not. This is referred to as parity. In a homonuclear diatomic molecule the overall parity is equal to the product of individual parities. If two occupied orbitals are gerade ( $g$ ), their product is also gerade ( $g$ ). If the two occupied orbitals are ungerade ( $u$ ), their product is also gerade ( $g$ ). However, the product of one gerade and one ungerade orbital will be ungerade, i.e.,

$$g \times g = g$$

$$u \times u = g$$

$$g \times u = u$$

The superscript (+ or -) on the right side of the molecular term symbol denotes the behaviour of the orbitals under reflection in a plane containing the nuclei. The  $\sigma$  molecular orbitals have a perfect cylindrical symmetry and are always symmetric (i.e., remain unchanged) with respect to this operation and are given a + sign. Therefore, any molecular wave function that is a product of  $\sigma$  type orbitals will be  $\Sigma^+$ . The  $\Sigma^-$  state arises when two electrons with parallel spin reside in  $\pi$  or  $\delta$  molecular orbitals. The  $\Pi$  and  $\Delta$  states are not classified + or -; these states always occur as degenerate pairs.

### 7.3.3 Deriving Term Symbols

In determining the term symbols of many-electron diatomics, the following rules should be kept in mind:

- All filled orbitals (e.g.,  $\sigma^2, \pi^4, \delta^4$ ) are  $^1\Sigma_g^+$ .

This is because there is no orbital angular momentum from a closed shell, net spin is zero and the overall parity is  $g$ . The last remark follows from the rule that in a many-electron molecule the overall parity is obtained from the product of the parities of each electron using

$$g \times g = g, u \times u = g, \text{ and } g \times u = u.$$

- The state of the "hole" is the state of the electron. As for atoms, the state can be determined from the holes that must be filled to complete a orbital. Thus  $\pi^1$  and  $\pi^3$  will have the same term symbol, so will have the  $\delta^1$  and  $\delta^3$  orbitals.

The following examples will illustrate the general procedure for determining the term symbols:

$(\sigma_g)^1$ :  $\Lambda = \Sigma \lambda_i = \lambda = 0$ , hence the state is  $\Sigma$ .  $S = 1/2$ ,  $2S + 1 = 2 \times 1/2 + 1 = 2$ . Hence a doublet state. Since, the electron is in a  $\sigma$  molecular orbital which is of  $g$  type, hence the subscript will be  $g$ . The orbital does not change sign under reflection in the

molecular plane, hence a + superscript. So the term symbol should be  ${}^2\Sigma_g^+$ . Similarly for  $(\sigma_u)^1$ , the term symbol should be  ${}^2\Sigma_u^+$

$(\sigma_u)^2$ :  $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$ , hence again a  $\Sigma$  state. As both the electrons are in the same molecular orbital, they have different  $m_s$  values. Thus,

$M_S = (m_s)_1 + (m_s)_2 = (\frac{1}{2}) + (-\frac{1}{2}) = 0$ . With  $M_S = 0, S = 0$ , and  $2S + 1 = 1$ . Hence, a singlet state. The product of two ungerade functions is gerade ( $u \times u = g$ ), parity is  $g$ . Since the electrons are in a  $\sigma$  orbital, the right superscript will be +. Therefore, the term symbol is  ${}^1\Sigma_g^+$ .

$(\pi_u)^1$ : The electron could be in either the  $\pi+$  ( $\lambda = +1$ ) orbital or the  $\pi-$  ( $\lambda = -1$ ) orbital. Therefore,  $\Lambda = \lambda = \pm 1$ , and the state is  $\Pi$ . Since, the molecular orbital has only one electron,  $S = \frac{1}{2}$ , hence multiplicity ( $2S + 1$ ) is 2. Parity is  $u$ . Therefore, the term symbol is  ${}^2\Pi_u$ .

$(\pi_u)^3$ : There are two possible configurations:

$$(\pi+)^2 (\pi-)^1, \Lambda = \lambda_1 + \lambda_2 + \lambda_3 = 1 + 1 - 1 = +1$$

$$(\pi+)^1 (\pi-)^2, \Lambda = \lambda_1 + \lambda_2 + \lambda_3 = 1 - 1 - 1 = -1$$

Therefore,  $\Lambda = \pm 1$  and the state is  $\Pi$ . Also, the state function is a product of three ungerade functions, hence ungerade ( $u \times u \times u = u$ ). Since, the electrons in filled molecular orbital  $(\pi+)^2$  or  $(\pi-)^2$  are paired, there is no net spin contribution from this orbital. There is only one electron present in  $(\pi+)^1$  or  $(\pi-)^1$  molecular orbital, hence  $S = \frac{1}{2}$ . Therefore, the multiplicity  $2S + 1 = 2 \times \frac{1}{2} + 1 = 2$ . Hence, the term symbol is  ${}^2\Pi_u$ . Note that this is identical to the term symbol for the  $(\pi_u)^1$  configuration.

### 7.3.4 Ground and Excited State Term Symbols of Diatomics

Now, we will derive the term symbols for the ground and excited states of three molecules, namely hydrogen,  $H_2$ , the lithium hydride, LiH and the oxygen molecule,  $O_2$ . Let us consider the  $H_2$  molecule first.

$H_2$ : The ground state electronic configuration of  $H_2$  is  $(\sigma_g 1s)^2$ . As both the electrons are in a  $\sigma$  orbital,  $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$ , hence the state will be  $\Sigma$ . Since electrons are paired, the net spin  $S$  is 0. Hence, multiplicity ( $2S + 1$ ) is 1. Both the electrons are in the same orbital which is of  $g$ -type. Hence, the overall parity is  $g \times g = g$  and the subscript is  $g$ . Both the electrons are in  $\sigma$  orbital which does not change sign under reflection in molecular plane. Hence, the superscript is a +. Thus we have the ground state of hydrogen represented by the spectroscopic term symbol,  ${}^1\Sigma_g^+$ .

Let us now consider the first excited state of the  $H_2$  molecule having configuration  $(\sigma_g 1s)^1 (\sigma_u 1s)^1$ . The value of  $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$ , hence again the state will be  $\Sigma$ . One electron is in an orbital of  $g$  parity, while the other is in that of  $u$  parity. The overall parity is  $g \times u = u$ , the subscript is  $u$ . The orbitals do not change sign under reflection in molecular plane, hence superscript is  $(+) \times (+) = +$ . Further, the electrons can have parallel or antiparallel spins, therefore, net spin  $S$  can be 1 or 0. The corresponding multiplicities ( $2S + 1$ ) can be 3 (triplet) or 1 (singlet). Therefore, the term symbol will be  ${}^1\Sigma_g^+$  or  ${}^3\Sigma_g^+$ . You can similarly obtain the term symbols for other excited states of the hydrogen molecule.

**LiH**: Now, we consider LiH, which is a heteronuclear diatomic molecule. The ground state electronic configuration of LiH is  $K (\sigma_g 2s)^2$ , where  $K$  is used to denote two

electrons in the  $1s$  orbital.  $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$ , hence it belongs to a  $\Sigma$  state. The net spin ( $S$ ) is zero, so multiplicity  $2S + 1$  is one. The orbitals remain unchanged under reflection in molecular plane, overall reflection symmetry will be  $(+) \times (+) = +$ . So we will have the  $+$  superscript in the term symbol. A heteronuclear diatomic molecule has no centre of symmetry and hence the term symbol will not have the subscript symbol  $g$  or  $u$ . Therefore, the ground state term symbol for  $\text{LiH}$  is  ${}^1\Sigma^+$ .

The excited state of  $\text{LiH}$  may have electronic configuration  $k(\sigma_g 2s)^1(\sigma_g 2p)^1$ . The value of  $\Lambda$  is again 0, hence a  $\Sigma$  state.  $S$  can be either 0 (opposite spins) or 1 (parallel spins), hence multiplicity  $(2S + 1)$  will be 1 or 3. Both  $\sigma_g 2s$  and  $\sigma_g 2p$  orbitals remain unchanged under reflection, hence overall reflection symmetry will be  $(+) \times (+) = +$ . Therefore, the term symbols for the above excited state of  $\text{LiH}$  will be  ${}^1\Sigma^+$  and  ${}^3\Sigma^+$ . There can be several other excited states also.

**O<sub>2</sub>:** Let us now consider the ground state term symbol for the oxygen molecule having the configuration  $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^2$ . As you know the completely filled molecular orbitals contribute nothing to the total orbital angular momentum and total spin angular momentum and the overall parity is  $g$ , we have to consider the contribution of  $(\pi_g^* 2p)^2$  orbitals only. The following configurations are possible:

$$\left. \begin{aligned} (\pi^+)^2(\pi^-)^0 : \Lambda = \lambda_1 + \lambda_2 = 1 + 1 = 2 \\ (\pi^+)^0(\pi^-)^2 : \Lambda = \lambda_1 + \lambda_2 = -1 - 1 = -2 \\ (\pi^+)^1(\pi^-)^1 : \Lambda = \lambda_1 + \lambda_2 = 1 - 1 = 0, \text{ a } \Sigma \text{ state.} \end{aligned} \right\} \text{a } \Delta \text{ state.}$$

The electrons in the  $\Delta$  state must be paired since they are in the same spatial orbital. Hence,  $S = 0$ ,  $2S + 1 = 1$ ; it is a singlet ( ${}^1\Delta$ ) state.

For the  $\Sigma$  state, the two electrons being in different molecular orbitals with value of  $\lambda = \pm 1$ , can have same  $m_s$  values (i.e. parallel spins) or different  $m_s$  values (i.e. antiparallel spins). The net spin  $S$  will be 1 or 0, respectively, giving rise to both triplet as well as singlet states,  ${}^3\Sigma$  and  ${}^1\Sigma$ . Since, the overall parity is  $g \times g = g$ , the terms are  ${}^3\Sigma_g$  and  ${}^1\Sigma_g$ . Thus for  $\text{O}_2$ , the ground state must be either  ${}^1\Delta$ ,  ${}^3\Sigma_g^-$  or  ${}^1\Sigma_g^-$ .

According to Hund's rule, the ground state has the highest spin multiplicity. The ground state is therefore,  ${}^3\Sigma_g^-$ . As stated earlier, when two electrons with parallel spin reside in  $\pi$  or  $\delta$  molecular orbitals, it gives rise to  $\Sigma^-$  states. Thus, the complete ground state term symbol for  $\text{O}_2$  is  ${}^3\Sigma_g^-$ ; the other  $\Sigma$  state is  ${}^1\Sigma_g^+$ .

You should note that the  $\pm$  symmetry is considered only for  $\Sigma$  states. This is because for the states with  $\Lambda \neq 0$ , reflection of the wave function in a plane through the nuclei changes the sign of  $\lambda$ . That is, one member of the degenerate pair of states is transformed into the other.

We have listed in Table 7.1, term symbols arising from various electronic configurations of diatomic molecules.

Table 7.1 : Electronic Terms of Diatomic molecules.

Configuration	Terms
$\sigma\sigma$	${}^1\Sigma^+, {}^3\Sigma^+$
$\sigma\pi; \sigma\pi^3$	${}^1\Pi, {}^3\Pi$
$\pi\pi; \pi\pi^3$	${}^1\Sigma^+, {}^3\Sigma^+, {}^1\Sigma^-, {}^3\Sigma^-, {}^1\Delta, {}^3\Delta$
$\pi\delta; \pi^3\delta; \pi\delta^3$	${}^1\Pi, {}^3\Pi, {}^1\Phi, {}^3\Phi$
$\sigma$	${}^2\Sigma^+$

Note that the term symbols for  $\pi^2$  configuration are  ${}^1\Delta$ ,  ${}^3\Sigma_g^-$  and  ${}^1\Sigma_g^+$ . The term for the ground state is  ${}^3\Sigma_g^-$ .



Configuration	Terms
$\sigma^2, \pi^4, \delta^4$	$1\Sigma^+$
$\pi, \pi^3$	$2\Pi$
$\pi^2$	$1\Sigma^+, 3\Sigma^-, 1\Delta$
$\delta, \delta^3$	$2\Delta$
$\delta^2$	$1\Sigma^+, 3\Sigma^-, 1\Gamma$

Before we describe selection rules for the electronic spectra of diatomic molecules, you may like to attempt the following SAQ.

### SAQ 1

State whether the following are true or false. Write either T or F at the end of each statement in the box provided. If false, write the correct statement in the margin.

- (a) If the molecular orbital for a homonuclear diatomic molecule has a subscript  $g$ , it indicates that the orbital is symmetric to reflection.
- (b) For oxygen molecule having  $\pi$ -electrons the state may be either  $\Sigma$  or  $\Delta$
- (c) For LiH molecule the spectroscopic term symbol will have a subscript  $g$  or  $u$  on the right side.
- (d) The spectroscopic term symbol for  $H_2$  in the ground state is  $2\Sigma_u^+$
- (e) The ground state of oxygen molecule is a triplet state.
- (f) When the axial component of total angular momentum has a value 3, the state is called a  $\Phi$  state.

### 7.3.5 Selection Rules for Spectra of Diatomics

The following selection rules apply to electronic transitions in diatomic molecules:

- $\Lambda$ , the component of total angular momentum along the inter-nuclear axis can have the same value for ground and excited states ( $\Delta\Lambda = 0$ ) or  $\Delta\Lambda = \pm 1$ . Hence, transitions between  $\Sigma$  and  $\Sigma$  or between  $\Pi$  and  $\Sigma$  or between  $\Pi$  and  $\Delta$  states are permitted. Transitions between  $\Delta$  and  $\Sigma$  or between  $\Phi$  and  $\Pi$  states are not permitted.
- $\Delta S = 0$ , i.e., the electron does not change its spin during transition. Only transitions between two singlet or two doublet or two triplet states are allowed. This rule breaks down for molecules with heavy nuclei.
- $\Sigma^+$  states can undergo transitions only into other  $\Sigma^+$  states (or, of course, into  $\Pi$  states) whereas  $\Sigma^-$  can go only into  $\Sigma^-$  (or  $\Pi$ ) state. Symbolically,

$$\Sigma^+ \longleftrightarrow \Sigma^+, \Sigma^- \longleftrightarrow \Sigma^-, \Sigma^+ \not\longleftrightarrow \Sigma^-,$$

- In homodiatom molecules the parity for the excited state should be different from that of the ground state.  $g \longleftrightarrow u$  and  $u \longleftrightarrow g$  transitions are permitted;  $g \longleftrightarrow g$  or  $u \longleftrightarrow u$  transitions are forbidden, i.e.,

$$g \longleftrightarrow u, g \not\longleftrightarrow g, u \not\longleftrightarrow u$$

We list in Table 7.2 some of the allowed electronic transitions for diatomic molecules.

Table 7.2: Allowed Transitions for Diatomic Molecules.

Homonuclear	Heteronuclear
$\Sigma_g^+ \longleftrightarrow \Sigma_u^+$	$\Sigma^+ \longleftrightarrow \Sigma^+$
$\Sigma_g^- \longleftrightarrow \Sigma_u^-$	$\Sigma^- \longleftrightarrow \Sigma^-$
$\Pi_g \longleftrightarrow \Sigma_u^+$	$\Pi \longleftrightarrow \Sigma^+$
$\Pi_u \longleftrightarrow \Sigma_g^+$	$\Pi \longleftrightarrow \Sigma^-$
$\Pi_g \longleftrightarrow \Sigma_u^-$	$\Pi \longleftrightarrow \Pi$
$\Pi_u \longleftrightarrow \Sigma_g^-$	$\Pi \longleftrightarrow \Delta$
$\Pi_g \longleftrightarrow \Pi_u$	$\Delta \longleftrightarrow \Delta$
$\Pi_g \longleftrightarrow \Delta_u$	$\Delta \longleftrightarrow \Phi$
$\Pi_u \longleftrightarrow \Delta_g$	$\Phi \longleftrightarrow \Phi$
$\Delta_g \longleftrightarrow \Delta_u$	etc.
etc.	

Before we proceed further, you may like to try the following SAQ to test your understanding of the concepts discussed in this section.

### SAQ 2

Use the words given below to fill in the blanks in the following statements:

singlets, forbidden, multiplicity, same, parity

- The component of the angular momentum along the internuclear axis can have the \_\_\_\_\_ value for the ground and excited states of the molecule.
- Transitions between two \_\_\_\_\_ are permitted.
- In homodiatomics the \_\_\_\_\_ for the excited state must be different from that of the ground state.
- The transition  $\Sigma^+ \longleftrightarrow \Sigma^-$  is \_\_\_\_\_ in electronic spectra of diatomics.
- During an electronic transition, the ground and excited states must have the same spin \_\_\_\_\_.

We have learnt in Section 7.2 that the vibrational energy changes give rise to the coarse structure in electronic spectra. The appearance of the vibrational structure in an electronic band can be explained in terms of the Franck-Condon principle. The next section deals with this principle.

## 7.4 FRANCK-CONDON PRINCIPLE AND INTENSITIES OF ELECTRONIC SPECTRA

The Franck-Condon principle states that since the time required for a molecule to execute a vibration (about  $10^{-12}$  sec) is much longer than that required for transition of electrons (about  $10^{-15}$  sec.), during electronic transitions the nuclei do not appreciably alter their positions. This means that the internuclear distance remains unaltered during the transition. The meaning of Franck-Condon principle can be understood by considering the potential energy curves in Figure 7.4. Before the

absorption the molecule is in the ground vibrational state of the ground electronic state. The nuclei are located at the equilibrium separation  $R_e$ . When the transition occurs, the molecule is excited to the state represented by the upper curve. According to the Franck Condon principle the nuclear framework remains constant during the excitation, and so we may represent this transition by a vertical line (Fig. 7.4).

Thus we say that the electronic transition is vertical. A vertical transition indicates that an electronic transition occurs without change of nuclear geometry. The vertical transition cuts through several vibrational levels of the upper electronic state. The level marked \* is the one in which the nuclei are most probably at separation  $R_e$ . This happens to be the most probable level for the termination of the transition. However, we have many other vibrational levels nearby which have an appreciable probability of nuclei being at  $R_e$ . Hence, transitions occur to all vibrational levels in this region. But most intensely to the level marked by \*.

The intensities of bands in electronic spectra can be quantitatively predicted by calculating the Franck condon factor, (which is beyond the scope of this course).

It can be shown with the help of quantum mechanical calculations that the intensity of a band is related to the difference in the nuclear separations  $R_e$  and  $R'_e$  for the ground and excited electronic states, respectively. Three cases of electronic spectra arise depending on the relative values of  $R_e$  and  $R'_e$ . These are as follows:

Case 1 :  $R'_e = R_e$  (Fig. 7.5 a)

Case 2 :  $R'_e > R_e$  (Fig. 7.5 b)

Case 3 :  $R'_e \gg R_e$  (Fig. 7.5 c)

Case 1: Fig. 7.5 a shows the near ultraviolet spectrum of  $\text{CN}^-$  radical. The potential energy minima lie very nearly one above the other. The 0-0 band has maximum intensity. 1-0, 2-0, 3-0 bands decrease in intensity. The equilibrium bond lengths ( $R_e, R'_e$ ) and vibrational wavenumbers ( $w, w'$ ) for the 0-0 band for  $\text{CN}^-$  radical are given below:

$$R'_e = 0.11506 \text{ nm}, \quad w' = 2164.1 \text{ cm}^{-1}$$

$$R_e = 0.11718 \text{ nm}, \quad w = 2068.7 \text{ cm}^{-1}$$

Case 2 : Fig. 7.5 b shows the spectrum of CO. The minimum of the upper potential energy lies at a moderately greater  $R_e$  value (0.01-0.02 nm) than the lower potential energy. The 0-3 band has maximum intensity and other bands on both sides have decreased intensity. The equilibrium bond lengths and vibrational wave numbers are given below:

$$R'_e = 0.1235 \text{ nm}, \quad w' = 1515.6 \text{ cm}^{-1}$$

$$R_e = 0.1128 \text{ nm}, \quad w = 2170.2 \text{ cm}^{-1}$$

Case 3 : The minimum of the upper potential energy curve lies at a considerable distance away from that of the lower potential energy curve in the spectrum of  $\text{I}_2$  (Fig. 7.5 c). In this case, transition takes place to a very high vibrational level in the upper state, which corresponds to the continuum level. The continuum level has very high energy and the molecule undergoes dissociation. The 0-0 band is absent in this spectrum.

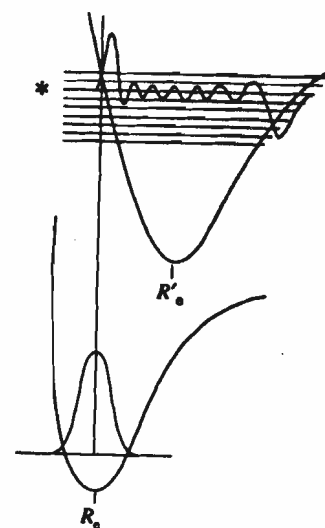


Fig. 7.4 : Representation of a vertical vibronic transition

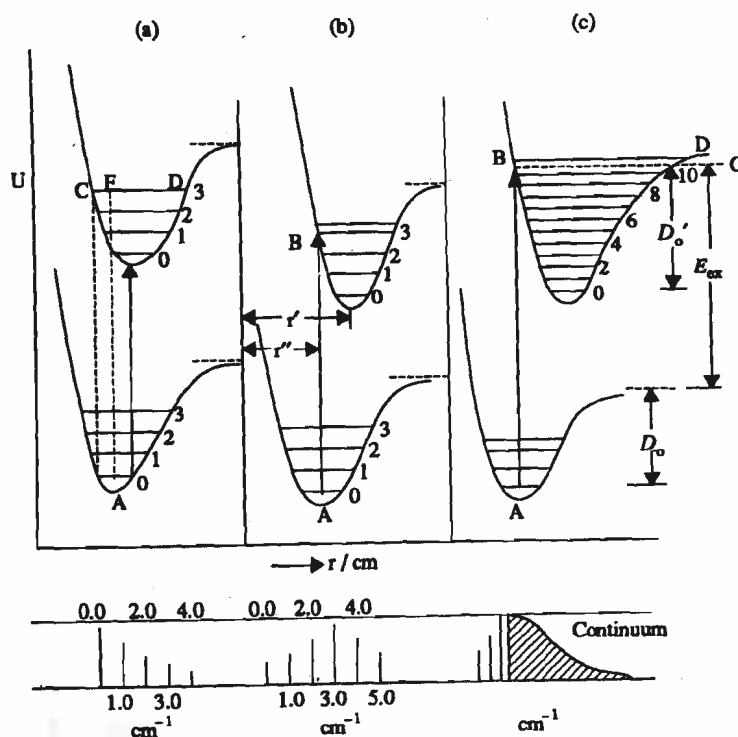


Fig. 7.5 : Application of Franck-Condon principle to the spectra of (a) CN radical (b) CO molecule (c) I<sub>2</sub> molecule.

Spectra corresponding to case 3 are useful in obtaining the dissociation energy of the molecule in the ground state. From the excited state, if a diatomic molecule dissociates into atoms, one of the atoms from fragmentation will be in the ground state and the other will be in the excited state. The energy of dissociation into atoms in the ground state ( $D_0$ ) can be obtained if we know the energy corresponding to continuum ( $hcw_m$ ) and the excitation energy ( $E_{ex}$ ). The formula for  $D_0$  is

$$D_0 = hcw_m - E_{ex}$$

This energy corresponds to that of one photon. To obtain the energy for one mole in kcal, we must multiply  $D_0$  by  $(N_0/4.2 \times 10^{10})$  where  $N_0$  is the Avogadro number. The following example illustrates the computation of dissociation energy for ground state for I<sub>2</sub> molecule.

### Example 7.1

The limit of continuum absorption for iodine gas occurs at 499.5 nm. The excitation energy for the iodine atom is 0.94 eV. Compute the ground state dissociation energy for I<sub>2</sub>.

**Solution :**

$$w_m = 1/\lambda = 1/(499.5 \times 10^{-7}) = 10^7/499.5 \text{ cm}^{-1}$$

$$hcw_m = 6.6256 \times 10^{-27} \times 2.998 \times 10^{10} \times 10^7/499.5 = 3.976 \times 10^{-12} \text{ erg}$$

$$E_{ex} = 0.94 \text{ eV} = 0.94 \times 1.6 \times 10^{-12} \text{ erg} = 1.504 \times 10^{-12} \text{ erg}$$

$$D_0 = hcw_m - E_{ex} \text{ per photon}$$

$$= 3.976 \times 10^{-12} - 1.504 \times 10^{-12} \text{ erg per photon}$$

$$= (3.976 - 1.504) \times 10^{-12} \text{ erg per photon}$$

$$= 2.472 \times 10^{-12} \text{ erg per photon}$$

To obtain the energy in kcal per mole this value is multiplied by  $N_0/4.2 \times 10^{10}$

$$D_0 = 2.472 \times 10^{-12} \times 6.023 \times 10^{23} / 4.2 \times 10^{10} \text{ kcal per mole}$$

$$= 2.472 \times 6.023 \times 10 / 4.2 = 35.4496 \text{ kcal per mole}$$

We have learnt the Franck-Condon principle and its application to electronic band spectra of different diatomic molecules. You may now solve the following SAQ.

### SAQ 3

Fill in the blanks in the following statements using the words given below:

continuum, unaltered, dissociation.

- According to Franck-Condon principle the internuclear distance remains \_\_\_\_\_ during an electronic transition.
- When the nuclear separation  $R'_e$  for the excited electronic state is very much different from that for the ground electronic state, the molecule undergoes \_\_\_\_\_.
- The dissociation energy in the ground state for a molecule can be computed if we know the wave number for \_\_\_\_\_ level and the excitation energy of the molecule.

## 7.5 ELECTRONIC SPECTRA OF POLYATOMIC MOLECULES

Unlike diatomic molecules, the rotational fine structure is not observed in polyatomic molecules and the vibrational structure is present in the form of broad bands. The absence of rotational fine structure in polyatomics is due to the closely spaced rotational energy levels and high values of moments of inertia. Hence, spectra of polyatomics have poorer resolution as compared to spectra of diatomics. In spite of this limitation, spectra of polyatomics provide important information about electronic structure.

We make use of molecular orbital theory to understand theoretical aspects of spectra of polyatomics. In electronic transitions of polyatomics, we encounter three types of molecular orbitals:  $\sigma$  and  $\sigma^*$ ,  $\pi$  and  $\pi^*$ , and  $n$  (nonbonding) orbitals. Orbitals without \* are bonding orbitals and those with \* are antibonding orbitals. The energy levels of all these molecular orbitals, in increasing order of energy, are shown in Fig.7.6.

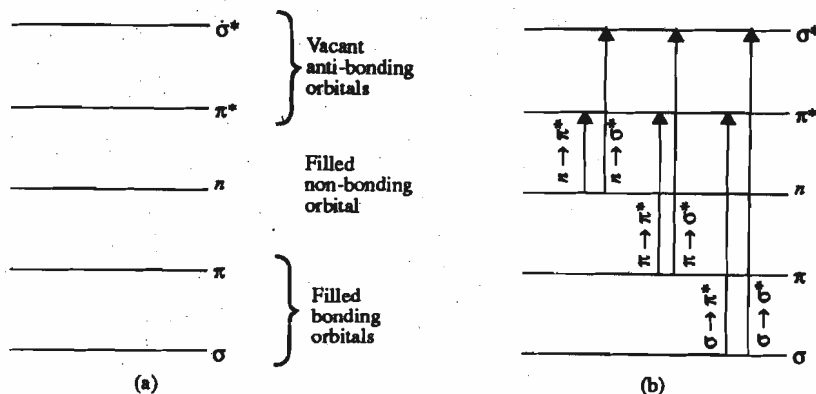
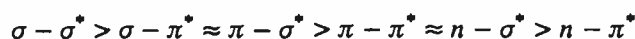


Fig. 7.6: Schematic diagram of (a) order of molecular orbital energies (b) possible electronic transitions.

When a molecule absorbs energy in the UV or visible region, an electron from a specific MO is excited to another of higher energy. The possible transitions of the electron between the MO's are:

$$\sigma - \sigma^*, n - \sigma^*, n - \pi^*, \pi - \pi^*, \pi - \sigma^* \text{ and } \sigma - \pi^*$$

The order of decreasing energy for these transitions is as follows:



Of all the possible transitions, the last three are responsible for absorptions in the region 200-800 nm, whereas others require much higher energy.

**$\sigma - \sigma^*$  transition :** Fig. 7.6 reveals that this transition requires very high energy. The absorption spectra obtained appear in the far ultraviolet region ( $< < 200$  nm). Molecules which give this type of spectrum are saturated hydrocarbons and other compounds in which all valence electrons are involved in single bond formation. Since a spectrometer generally cannot measure below 185 nm, the region involving  $\sigma - \sigma^*$  transitions is relatively of less importance for chemical analysis.

**$n - \sigma^*$  transition :** The spectra corresponding to  $n - \sigma^*$  transition appear in the near UV or visible region. Compounds containing non-bonding or lone-pair electrons show this transition. For example, methyl alcohol vapour shows an absorption maximum at 183 nm. Methyl chloride and methyl amine show absorption maxima at 173 nm and 213 nm, respectively.

**$n - \pi^*$  transition :** This type of transition is exhibited by unsaturated molecules containing non bonding electrons. Certain organic groups like  $>C=N-$ ,  $-N=O$ ,  $>C=O$  show this type of transition and we obtain absorption maxima for these systems at wavelengths greater than 280 nm. Groups such as  $>C=N-$ ,  $-N=O$ ,  $>C=O$ ,  $-COOH$  causing absorption at wavelengths greater than 175 nm are referred to as chromophores. More information on chromophores will be presented a little later.

**$\pi - \pi^*$  transition :** Band due to  $\pi - \pi^*$  transition appears in the spectra of compounds containing  $>C=C<$ ,  $-C\equiv C-$ ,  $>C=O$  and  $>C=N-$  functional groups. Ethylene and acetone exhibit  $\pi - \pi^*$  transition at 165 and 150 nm, respectively. The  $\pi - \pi^*$  transition is highly affected by conjugation.

You have studied in Unit 8 of the CHE-01 course, that the absorption bands in ultraviolet and visible spectra are characterised by two main parameters which are

i)  **$\lambda_{\max}$  Value:** The value of the wavelength at which absorption maximum occurs is called the  $\lambda_{\max}$  value. This corresponds to the wavelength of the radiation whose energy is equal to that required for an electronic transition. As different transitions require different energies, their  $\lambda_{\max}$  values are different.

ii)  **$\epsilon_{\max}$  Value :**  $\epsilon$  value, which is known as molar absorptivity or molar extinction coefficient, is a measure of extent of absorption or intensity of absorption. The  $\epsilon$  value is characteristic of a particular compound at a given wavelength. Usually for the wavelength of maximum absorption ( $\lambda_{\max}$ ), molar absorptivity is expressed as  $\epsilon_{\max}$

The intensity of absorption can be expressed as transmittance ( $T$ ), which is defined as the ratio of the intensity of the radiation transmitted from the sample ( $I$ ) to that of the radiation incident on the sample ( $I_0$ ), i.e.,

$$T = I/I_0$$

Intensity of absorption is more conveniently expressed in terms of absorbance ( $A$ ), which is the logarithm of reciprocal of transmittance ( $T$ ), i.e.,

$$A = \log_{10} (1/T) = \log_{10} (I_0/I)$$

Absorbance of a band is related to the sample thickness and the concentration of the absorbing species. The relationship is expressed in the form of Beer-Lambert law as shown below:

$$A = \epsilon cl = \log_{10} (I_0/I)$$

or 
$$\epsilon = \frac{A}{cl}$$

where  $\epsilon$  = molar absorptivity or molar absorption constant

$c$  = concentration of solute

$l$  = sample thickness or path length through the sample

Absorbance is a dimensionless quantity. Concentration ( $c$ ) is usually expressed in  $\text{mol dm}^{-3}$  and path length ( $l$ ) in cm, hence  $\epsilon$  has the units of  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ . If we use SI units of  $\text{mol m}^{-3}$  for concentration and m for path length, the units of  $\epsilon$  will be  $\text{m}^2 \text{mol}^{-1}$ . We can obtain the values of  $\epsilon$  in  $\text{m}^2 \text{mol}^{-1}$  units from those in  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  units in the following manner:  $\epsilon = \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1} = 10^{-3} \text{m}^3 \text{mol}^{-1} (10^{-2} \text{m})^{-1} = 10^{-1} \text{m}^2 \text{mol}^{-1}$

Values of  $\epsilon$  in SI units can, therefore, easily be obtained from published values in  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  by dividing the numerical quantity in latter units by 10.

Absorption bands with  $\epsilon_{\text{max}}$  value  $> 10^3 \text{ m}^2 \text{mol}^{-1}$  are considered to be high intensity or strong bands, whereas those with  $\epsilon_{\text{max}}$  values  $< 10^2 \text{ m}^2 \text{mol}^{-1}$  are known as low intensity or weak bands.

## 7.6 SOME IMPORTANT TERMS USED IN ELECTRONIC SPECTROSCOPY

### Chromophore:

In a number of molecules the absorption of a photon can be traced to the electrons of certain covalently unsaturated groups. Such groups, for example carbonyl in aldehydes or ketones which are responsible for electronic absorption, are referred to as chromophores. Other examples of chromophores are  $>C=C<$ ,  $-C \equiv C-$ ,  $-COOH$ ,  $-N=O$ ,  $-NO_2$ ,  $-N=N-$  and so on. Chromophore in Greek means colour bringer and the presence of a chromophore often accounts for colours of substances. The following table lists the absorption maxima for some typical chromophores.

Table 7.3 : Absorption Data for Isolated Chromophores

Chromophoric Group	System	Example	Transition	$\lambda_{\text{max}}$	$\epsilon_{\text{max}}$	Solvent
				nm	$\text{m}^2 \text{mol}^{-1}$	
Ethylenic	$RCH=CHR$	Ethylene	$\pi \rightarrow \pi^*$	165	1500	Vapour
Acetylenic	$R-C \equiv C-R$	Acetylene	$\pi \rightarrow \pi^*$	173	6000	Vapour
Carbonyl	$RR_1C=O$	Acetone	$\pi \rightarrow \pi^*$	188	900	n-Hexane
			$n \rightarrow \pi^*$	279	1.5	
Carbonyl	$RHC=O$	Acetaldehyde	$n \rightarrow \pi^*$	290	1.6	Heptane
Carbonyl	$RCOOH$	Acetic acid	$n \rightarrow \pi^*$	204	6.0	Water
Amido	$RCONH_2$	Acetamide	$n \rightarrow \pi^*$	<208	-	-
Azomethine	$>C=N-$	Acetoxime	$\pi \rightarrow \pi^*$	190	5000	Water
Nitrile	$-C \equiv N$	Acetonitrile	$\pi \rightarrow \pi^*$	<160	-	-
Azo	$-N=N-$	Azomethane	$n \rightarrow \pi^*$	347	0.45	Dioxane

Chromophoric Group	System	Example	Transition	$\lambda_{\max}$	$\epsilon_{\max}$	Solvent
				nm	$\text{m}^2 \text{mol}^{-1}$	
Nitroso	-N=O	Nitroso-butane	$\pi \rightarrow \pi^*$	300	10	Ether
			$n \rightarrow \pi^*$	665	2.0	
Nitrate	-ONO <sub>2</sub>	Ethyl nitrate	$n \rightarrow \pi^*$	270	1.2	Dioxane
Nitro	-NO <sub>2</sub>	Nitromethane	$n \rightarrow \pi^*$	271	1.86	Alcohol
Nitrite	-ONO	Amyl nitrite	$\pi \rightarrow \pi^*$	218.5	112	Petroleum ether
			$n \rightarrow \pi^*$	346.5		

### Auxochrome

A saturated group with nonbonded electrons which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption is called an auxochrome, e.g., OH, NH<sub>2</sub> and Cl. The auxochrome, though by itself is unable to impart colour to a compound. The auxochromic effect depends on the ability of the chemical group to donate electrons into conjugated system. This has been most studied with aromatic systems and the spectral shifts of monosubstituted aromatic compounds have been correlated with electron donating power of auxochromes. The electron donating power of some common auxochromes decreases in the order  $\text{O}^- > \text{NHCH}_3 > \text{NH}_2 > \text{OH} > \text{Cl} > \text{CH}_3 > \text{NH}_3^+ = \text{H}$

In this list the effect of protonating the NH<sub>2</sub> group should be noted, the proton binds the nonbonding (lone pair) electrons on the nitrogen of the amino group and prevents them from interacting with the benzene  $\pi$ -electron system. Thus, the  $\lambda_{\max}$  value for aniline (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>) and the anilinium ion (C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>) are 230 nm and 203 nm, respectively as compared to 204 nm for benzene.

**Bathochromic or red shift :** A shift of the absorption maximum towards longer wavelength (lower frequency) produced by a change of medium or by the presence of an auxochrome, is called bathochromic shift or red shift.

**Hypsochromic shift or Blue shift :** A shift towards shorter wavelength (higher frequency) caused by a change of medium or by removal of conjugation is referred to as hypsochromic shift or blue shift. For example, the conjugation of the lone pair of electrons on the nitrogen atom of aniline with the  $\pi$ -bond system of the benzene ring is removed by protonation. Aniline absorbs at 230 nm, but in acid solution the main peak is shifted to 203 nm due to the presence of anilinium ions.

**Hypochromic effect :** An effect leading to decreased absorption intensity is called hypochromic effect.

**Hyperchromic effect :** An effect leading to increased absorption intensity is called hyperchromic effect.

## 7.7 ABSORPTION DUE TO ETHYLENIC AND CARBONYL CHROMOPHORE

In this section we shall discuss the electronic absorptions of only two of the more important chromophores in little more detail. These are the ethylenic and the



carbonyl chromophores. In addition, we shall have only a brief look at the absorptions of the acetylenic and the benzenoid chromophores.

### 7.7.1 Ethylenic Chromophore

As you know ethylene has five  $\sigma$  bonds (four C-H and one C-C) and one  $\pi$  bond. If we denote  $\sigma$  molecular orbitals as  $\sigma_1, \sigma_2$  etc., and consider only the twelve valence electrons, the ground state electronic configuration of ethylene is  $(\sigma_1)^2 (\sigma_2^*)^2 (\sigma_3)^2 (\sigma_4^*)^2 (\sigma_5)^2 (\pi)^2$ . If we consider only the highest  $\sigma$  orbital, the ordering of the molecular orbitals is as shown in Fig. 7.7.

In ethylene only four electronic transitions are possible which are  $\pi - \pi^*, \sigma - \sigma^*, \pi - \sigma^*$  and  $\sigma - \pi^*$ . Out of these the latter two are symmetry forbidden. Of the other two, as you can see from the Figure 7.7, the  $\pi - \pi^*$  transition would require less energy. In ethylene in the vapour phase the  $\pi - \pi^*$  transition appears at 165 nm ( $\epsilon_{\max} = 1000 \text{ m}^2 \text{ mol}^{-1}$ ). The transition is out of the normal range of most spectrometers.

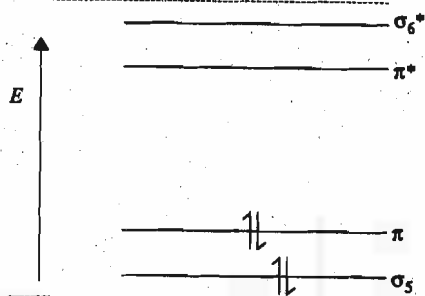
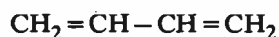


Fig.7.7: Orbital energy diagram for ethylene.

Alkyl substitution of the ethylenic compound moves the absorption to longer wavelengths (bathochromic shift). The effect is progressive as the number of alkyl groups increases. Attachment of a heteroatom (bearing nonbonded electrons) to the ethylenic linkage also gives rise to a red or bathochromic shift. Nitrogen and sulphur are the most effective heteroatoms shifting the absorption well into the near ultraviolet region. For example methyl vinyl sulphide ( $\text{CH}_3\text{SCH}=\text{CH}_2$ ) absorbs at 228 nm. The absorptions of cyclic monoolefins resemble those of the open chain olefins and the absorption has no relationship to ring size. When there are two or more isolated ethylenic bonds in a molecule, it absorbs at the same position as the single ethylenic chromophore. The intensity of absorption, however, is proportional to the number of isolated chromophoric groups in the molecule.

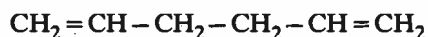
As the absorption due to isolated ethylenic chromophore takes place in far ultraviolet region, electronic spectroscopy has thus little use in detecting isolated double bond. Conjugation markedly affects the position of absorption due to the  $>\text{C}=\text{C}<$  chromophore giving rise to a bathochromic shift. Thus, the  $\lambda_{\max}$  value for  $\pi - \pi^*$  transition for the 1, 3-butadiene is 217 nm as compared to 185 nm for the 1, 5-hexadiene.



1, 3-butadiene

$\lambda_{\max}$  217 nm

$\epsilon_{\max}$  2100  $\text{m}^2 \text{ mol}^{-1}$



1, 5-hexadiene

$\lambda_{\max}$  185 nm

$\epsilon_{\max}$  2000  $\text{m}^2 \text{ mol}^{-1}$

This relatively large increase in the wavelength of absorption due to conjugation can be explained as follows. In ethylene the two  $2p$  atomic orbitals combine to form a set of  $\pi$  and  $\pi^*$  molecular orbitals. In conjugated dienes such as 1,3-butadiene, when  $\pi$  and  $\pi^*$  molecular orbitals of two ethylenic linkages are close enough, overlap can occur. As a result a combination of two  $\pi$  molecular orbitals gives two delocalised orbitals of lower and higher energy ( $\pi_1$  and  $\pi_2$ ). Similarly the two  $\pi^*$  orbitals give rise to two delocalised  $\pi^*$  orbitals of different energies ( $\pi_3^*$  and  $\pi_4^*$ ) (Fig.7.8). Thus, the lowest

energy  $\pi_2-\pi_3^*$  transition in 1, 3-butadiene occurs at a longer wavelength (217 nm) as compared to the lowest energy  $\pi-\pi^*$  transition of 1, 5-hexadiene (185 nm).

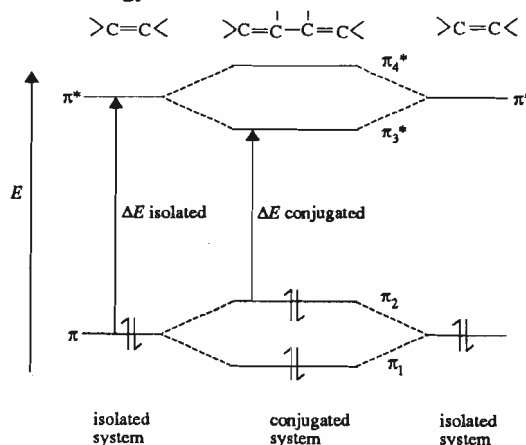


Fig.7.8 : Molecular orbital energy relationship between  $\pi$ -orbitals of isolated and conjugated dienes.

As the extent of conjugation increases, it lowers still further the energy of transition from the highest occupied  $\pi$  orbital to the lowest unoccupied  $\pi^*$  orbital, thereby the  $\lambda_{\max}$  value increases.

Table 7.4 gives the wavelengths of some conjugated polyenes that demonstrate this effect.

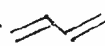
Table 7.4 :Absorption bands of conjugated polyenes  $H(CH=CH)_nH$

n	$\lambda_{\max}/nm$
2	217
3	268
4	304
5	334
6	364
7	390
8	410

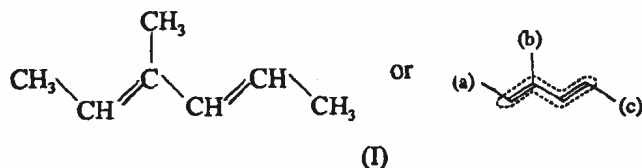
The effects of substituents and geometry on the absorption bands of conjugated dienes are fairly consistent. A set of empirical rules has been formulated by Woodward to predict the absorption of open chain (acyclic) and six-membered ring dienes. These rules have been modified by Feiser and Scott. The rules are summarised in Table 7.5.

Table 7.5 : Woodward Rules for predicting  $\pi-\pi^*$  Absorption in Dienes

Value assigned to parent open chain diene	217 nm
Value assigned to parent heteroannular diene	214 nm
Value assigned to parent homoannular diene	253 nm
Increments for	
a) each alkyl substituent or ring residue	5 nm
b) each exocyclic double bond	5 nm
c) each double bond extending conjugation	30 nm
d) auxochrome	
-O(acyl)	0 nm
-O(alkyl)	6 nm
-S(alkyl)	30 nm
-Cl, -Br	5 nm
-N(alkyl) <sub>2</sub>	60 nm
Calculated $\lambda_{\max} =$	Total

In order to be able to apply these rules you must be able to identify the types of structures referred to in Table 7.5. The basic chromophore unit is 1,3-butadiene which is considered the parent acyclic (or non-cyclic) diene:  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$  or 

If saturated alkyl groups are attached to the diene, then an additional contribution for each group is added, e.g.,  $\pi-\pi^*$  absorption in 1,2,4-trimethylbutadiene(I) is analysed in terms of the rules as follows:



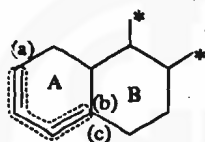
Base value for acyclic diene (I) = 217 nm

For three methyl groups, add  $3 \times 5 = +15$  nm

Predicted  $\lambda_{\text{max}}$  for  $\pi-\pi^*$  transition = 232 nm

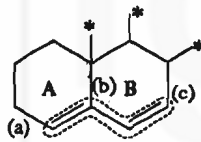
Observed  $\lambda_{\text{max}}$  for  $\pi-\pi^*$  transition = 231 nm

If the diene system is contained in a single ring, it is termed homoannular, e.g., compound (II). On the other hand if it is spread over two rings, it is said to be heteroannular, e.g., compound (III).



(II)

Homoannular diene



(III)

Heteroannular diene

For Compound (II) we have a base value of

$$= 253 \text{ nm}$$

For three ring residues (a), (b) & (c): add  $3 \times 5$  nm

$$= +15 \text{ nm}$$

The lower double bond in A is attached to but is outside ring B, i.e., it is exocyclic to ring B, add 5 nm

$$| = +5 \text{ nm}$$

Predicted  $\lambda_{\text{max}}$  value

$$= 273 \text{ nm}$$

Observed  $\lambda_{\text{max}}$  value

$$= 275 \text{ nm}$$

Note that the groups marked with a \* do not contribute as they are not directly attached to the diene system.

For compound (III) we have a base value of

$$= 214 \text{ nm}$$

For three ring residues (a), (b), (c): add  $3 \times 5$  nm

$$= +15 \text{ nm}$$

The double bond in ring A is in exocyclic position to ring B: add 5 nm

$$= +5 \text{ nm}$$

Predicted  $\lambda_{\text{max}}$  value

$$= 234 \text{ nm}$$

Observed  $\lambda_{\text{max}}$  value

$$= 235 \text{ nm}$$

Thus in all the three cases, the predicted  $\lambda_{\text{max}}$  values are in very good agreement with the observed values.

### 7.7.2 Acetylenic and Benzenoid Chromophore

The electronic spectra of the acetylenic and the benzenoid chromophore are more complex than those of the ethylenic chromophore. These cannot be explained by following the model presented for the ethylenic chromophore. They exhibit three absorption bands each as shown below.

Acetylene: 152 nm (strong), 182 nm (moderate), 220 nm (weak)

Benzene: 184 nm (strong), 204 nm (strong), 254 nm (weak).

In each case, you can see, the lowest energy absorption band is weak, which is characteristic of a forbidden transition, e.g.,  $n-\pi^*$ . But there are no non-bonding electrons in these molecules. Thus all the three transitions arise from  $\pi-\pi^*$  transitions. Acetylene and benzene are highly symmetrical molecules having degenerate molecular orbitals. Transitions between degenerate orbitals in these cases give rise to the complexity in their electronic spectra.

### 7.7.3 Carbonyl Chromophore

You know that the carbonyl group contains, in addition to a pair of  $\sigma$  electrons, a pair of  $\pi$  electrons and two pairs of nonbonding electrons. Saturated aldehydes and ketones exhibit three absorption bands due to  $\pi-\pi^*$ ,  $n-\sigma^*$  and  $n-\pi^*$  transitions

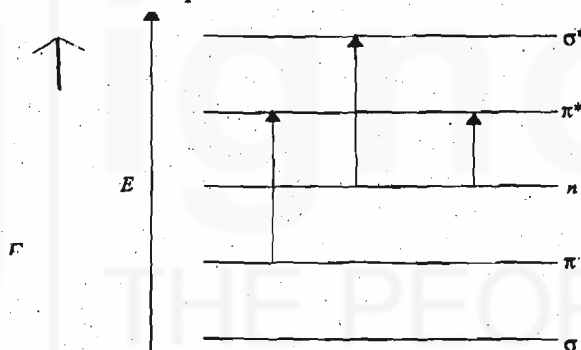


Fig.7.9: Electronic transitions of a carbonyl group in aldehydes and ketones.

(Fig.7.9). Two bands appear in the far ultraviolet region near 150 nm and 190 nm region and are due to the  $\pi-\pi^*$  and  $n-\sigma^*$  transitions, respectively. The third band is due to the forbidden  $n-\pi^*$  transition which appears as a weak band ( $\epsilon_{\max} < 3.0 \text{ m}^2 \text{ mol}^{-1}$ ) in the near ultraviolet region in the 270-300 nm region. In formaldehyde the  $n-\pi^*$  absorption band is found at 310 nm. In contrast to the situation in alkenes, alkyl substitution moves this absorption to higher energy. Thus in acetaldehyde and acetone this band appears at 290 nm and 279 nm, respectively. Auxochromes such as Cl, OH and  $\text{NH}_2$  cause a larger shift in the carbonyl  $n-\pi^*$  absorption to shorter wavelengths. The shift in absorption results from a combination of resonance and inductive effects. The resonance effect ( $\pi$ -electron release) of the lone pair of the substituent raises the energy of the  $\pi^*$  orbital, but leaves the nonbonding electrons of the carbonyl group unchanged in energy (Fig. 7.10 (a)). The negative inductive effect ( $\sigma$ -electron withdrawal) lowers the energy of the nonbonding orbital by making the carbon atom of the group more positive (Fig. 7.10 (b)). The overall shift arises from the sum of these two effects.

When a carbonyl group of a ketone is conjugated with a carbon-carbon double bond ( $>\text{C}=\text{C}<$ ), the compound is known as an enone or  $\alpha,\beta$ -unsaturated ketone, e.g., methyl vinyl ketone ( $\text{CH}_3\text{COCH}=\text{CH}_2$ ). Conjugation has an effect on the energy of  $\pi-\pi^*$  transition similar to that in alkenes. As the energy of the  $\pi^*$  orbital is lowered

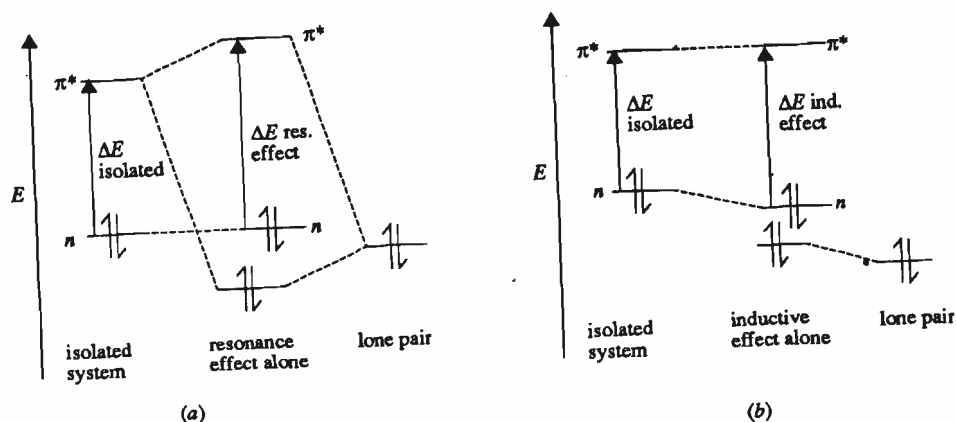


Fig. 7.10: Schematic diagram of a) the resonance effect alone and b) the inductive effect alone of a substituent on the  $n - \pi^*$  transition of a carbonyl group.

by conjugation (Fig.7.11), the  $\pi - \pi^*$  and  $n - \pi^*$  absorptions move to longer wavelengths. Thus for propenal ( $\text{CH}_2 = \text{CH} - \text{CHO}$ ), the  $\pi - \pi^*$  and  $n - \pi^*$  absorptions occur at 202 nm and 336 nm, respectively.

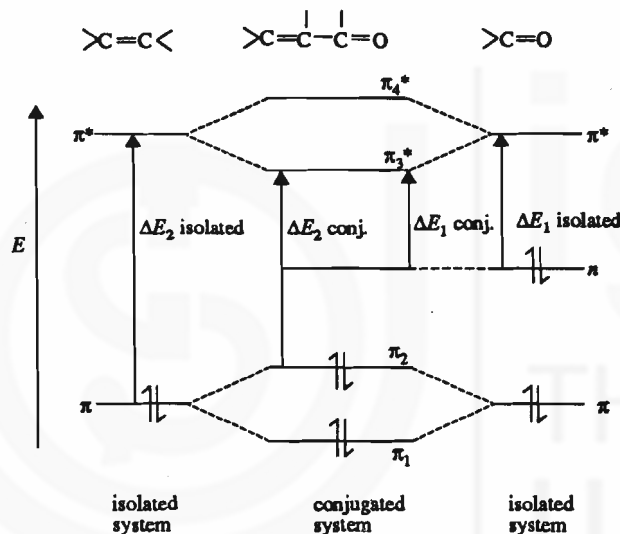
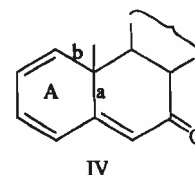


Fig. 7.11 : Orbital energy relationships between isolated and conjugated  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  groups.

As with the conjugated dienes, there are empirical rules to predict the position of the  $\pi - \pi^*$  band in enones. These rules were put forth by Woodward and modified by Feiser and Scott. These rules are summarised in Table 7.6.

We will now apply the rules for  $\alpha, \beta$  unsaturated ketones to predict the absorption maximum in compound IV.

Value for parent $\alpha, \beta$ -unsaturated ketone	= 215 nm
for $\beta$ -substituent (marked a); add 12 nm	= + 12 nm
for $w$ -substituent (marked b); add 18 nm	= + 18 nm
for two double bonds extending conjugation; add $2 \times 30$ nm	= + 60 nm
for homoannular diene component; add 39 nm	= + 39 nm
for exocyclic double bond ; add 5nm	= + 5 nm
calculated $\lambda_{\text{max}}$ value	= 349 nm



Three  $\lambda_{\text{max}}$  values have been observed for this compound and these are 230 nm, 278 nm and 348 nm. The longest wavelength peak is in excellent agreement with the calculated value.

Table 7.6: Feiser and Scott rules for predicting  $\pi-\pi^*$  absorption in  $\alpha, \beta$  - unsaturated ketones (enones) and aldehydes

Value for parent acyclic ketone		215 nm	
Value for parent six-membered ring ketone		215 nm	
Value for parent five membered ring ketone		202 nm	
Value for parent unsaturated aldehyde		207 nm	
Increments for			
a) each double bond extending the conjugation		30 nm	
b) each alkyl group or ring residue	$\alpha$	10 nm	
	$\beta$	12 nm	
	$\gamma$ and higher	18 nm	
c) auxochromes	(i) -OH	$\alpha$	35 nm
		$\beta$	30 nm
		$\delta$	50 nm
	(ii) -OAc	$\alpha, \beta, \delta$	6 nm
	(iii) -OMe	$\alpha$	35 nm
		$\beta$	30 nm
		$\gamma$	17 nm
		$\delta$	31 nm
	(iv) -Salk		85 nm
	(v) -Cl	$\alpha$	15 nm
$\beta$		12 nm	
(vi) -Br	$\alpha$	25 nm	
	$\beta$	30 nm	
(vii) NR <sub>2</sub>	$\beta$	95 nm	
d) exocyclic double bond		5 nm	
e) homodiene component		39 nm	
Calculated $\lambda_{\max}$ value		= Total	

The next section describes the effect of solvent on electronic spectra.

## 7.8 SOLVENT EFFECTS ON ELECTRONIC SPECTRA

As with vibrational spectra, the phase of the sample or the solvent used while measuring the spectrum can make a marked difference on electronic spectra. Broadly, there are two extremes; the vapour phase and non-polar solvents on the one hand, and polar and hydroxylic solvents on the other. Let us consider the effect of solvent on  $\pi-\pi^*$  and  $n-\pi^*$  transitions one by one.

### $\pi - \pi^*$ transitions

When a polar solvent is used, the dipole-dipole interaction with the solvent molecules lowers the energy of the excited state more than that of the ground state (Fig. 7.12). This is due to the fact that excited states are more polar than ground states. The energy difference between the excited and ground states is reduced. This leads to a small red shift of the absorption maximum in polar solvents. Thus the  $\pi-\pi^*$  transition shows a red shift of the order of 10–20 nm when the solvent is changed from hexane to ethanol.

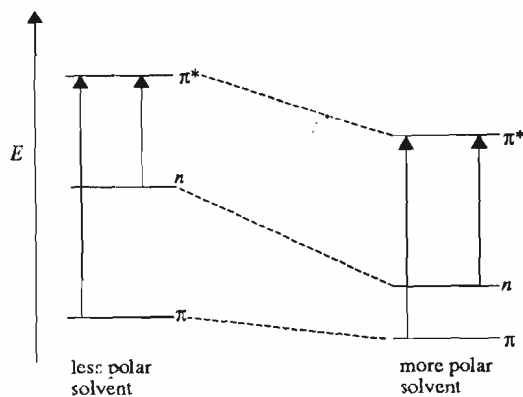


Fig. 7.12 : Solvent effects on  $n-\pi^*$  and  $\pi-\pi^*$  transitions.

### $n-\pi^*$ transitions

Solvent effect for  $n-\pi^*$  transitions is opposite to that found for  $\pi-\pi^*$  transitions. Polar solvents cause a shift to lower wavelengths (blue shift) relative to non-polar solvents or the vapour phase. The effect is particularly pronounced in hydroxylic solvents. The lone-pair electrons in the non-bonding orbital hydrogen bond or otherwise interact strongly with the polar solvent, leading to a lowering in energy of the non-bonding orbital whereas  $\pi^*$  orbital is affected much less (Fig.7.12). The result is an increase in the transition energy on going from a less polar to a more polar solvent. For example, in hexane solution, acetone shows absorption maximum at 279 nm whereas in aqueous solution, the absorption maximum is at 264.5 nm.

You may now try to answer the following SAQ.

#### SAQ 5

Fill in the blanks in the following statements using the words given below:

Polar, red, increased, decreased

- The  $\pi-\pi^*$  transition shows a \_\_\_\_\_ shift in more polar solvents.
- The  $n-\pi^*$  transition shows a blue shift in more \_\_\_\_\_ solvents.
- hyperchromic effect means that the intensity of an absorption is \_\_\_\_\_
- hypsochromic effect means that the intensity of an absorption is \_\_\_\_\_

## 7.9 SUMMARY

In this unit, you have learnt the molecular orbital treatment of diatomic molecules. You have also studied about the ground and excited state configurations and term symbols of diatomics. Selection rules for transition between different energy states have also been described.

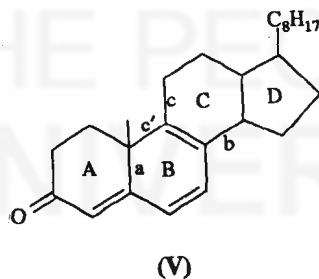
We have discussed the Franck-Condon principle and its application to explain variation in intensities of spectra of different kinds of molecules. You have learnt some important definitions of terms used in electronic spectroscopy. We have also discussed the rules to predict absorption maxima in conjugated dienes, trienes and  $\alpha,\beta$ -unsaturated aldehydes and ketones. We now summarise that we have learnt in this unit.

- When we write the molecular term symbols for homodiatomics, we must find out the effects of symmetry operations such as reflection and inversion on these molecules.

- Spin multiplicity of the excited and ground states must be the same for a transition in a diatomic molecule.
- The parity must change during a spectroscopic transition in a diatomic molecule with centre of symmetry.
- The  $\pi-\pi^*$  transition is strong in carbonyl compounds since it is electronically allowed whereas the  $n-\pi^*$  transition is weak since it is magnetically allowed.
- The rules of Woodward modified by Feiser and Scott help us in predicting the absorption maxima for conjugated dienes, trienes and  $\alpha, \beta$ -unsaturated aldehydes and ketones.
- The  $\pi-\pi^*$  transition shows a red shift in more polar solvents. The  $n-\pi^*$  transition shows a blue shift for a solvent which is more polar.

## 7.10 TERMINAL QUESTIONS

- 1) Obtain the molecular term symbols for the following three excited states of hydrogen molecule:  
 $(\sigma_g 1s)^1 (\sigma_g 2s)^1$ ;  $(\sigma_g 1s)^1 (\sigma_g 2p)^1$ ;  $(\sigma_g 1s)^1 (\pi_u 2p)^1$
- 2) In the ultraviolet absorption spectrum of oxygen, continuum absorption begins at  $56876 \text{ cm}^{-1}$ . The excitation energy of oxygen atom is  $15868 \text{ cm}^{-1}$ . Find the dissociation energy of the  $\text{O}_2$  molecule in the ground state in kcal/mole.
- 3) The dissociation energy for chlorine molecule in the ground state is 239.42 kilojoule per mole. If the excitation energy for chlorine is  $881 \text{ cm}^{-1}$ , compute the continuum vibrational wave number for chlorine molecule.
- 4) Calculate the  $\lambda_{\text{max}}$  for the unsaturated ketone (V) using Fieser and Scott rules.



## 7.11 ANSWERS

### Self Assessment Questions

- 1) a) F. The correct statement is "if the molecular orbital for a homonuclear diatomic molecule has a subscript  $g$ , it indicates that the orbital does not change sign on inversion through centre of symmetry.
- b) T.
- c) F. The correct statement is "for LiH molecule, the spectroscopic term symbol will not have a subscript  $g$  or  $u$  on the right side because it is a heteronuclear molecule which has no centre of symmetry.
- d) F. The correct statement is "the spectroscopic term symbol for  $\text{H}_2$  in the ground state is  $^1\Sigma_g^+$ .
- e) T
- f) T



- 2) a) same b) singlets c) parity d) forbidden  
 e) multiplicity
- 3) a) unaltered b) dissociation c) continuum
- 4) a) red b) polar c) increased d) decreased e) increased

### Terminal Questions

1. a) Since, both the electrons are  $\sigma$  electrons,  $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$ . It gives rise to a  $\Sigma$  state. The net spin  $S$  can have two values 0 and 1. The corresponding multiplicities ( $2S + 1$ ) will be 1 (singlet) and 3 (triplet). Since, both constituent orbitals are of  $g$  parity, the overall parity will be  $g \times g = g$ . Under reflection, the orbitals remain unchanged, hence reflection symmetry will be  $(+) \times (+) = +$ . The term symbols will be  $^1\Sigma_g^+$  and  $^3\Sigma_g^+$ .
- b) Since, both the electrons are  $\sigma$ ,  $\Lambda = \lambda_1 + \lambda_2 = 0 + 0 = 0$ , we have a  $\Sigma$  state. The net spin  $S$  can be 0 or 1, the multiplicity will be 1 or 3. The overall parity will be  $g \times g = g$ . Under reflection, both the orbitals remain unchanged, hence the reflection symmetry will be  $(+) \times (+) = +$ . The term symbols will be  $^1\Sigma_g^+$  and  $^3\Sigma_g^+$ .
- c) Since one electron is in a  $\pi$  orbital, the value of  $\Lambda = \lambda_1 + \lambda_2 = 0 \pm 1 = \pm 1$ . The state will be  $\Pi$ . Again, since one electron is in a  $\sigma_g$  orbital and the other in a  $\pi_u$  orbital, the overall parity is  $g \times u = u$ . The net spin  $S$  can be 0 or 1, the multiplicity will be 1 or 3. The term symbol will be  $^1\Pi_u$  or  $^3\Pi_u$ .

2.  $D_0 = hc (\nu_m - \nu_e)$  erg per photon

$$= 6.6256 \times 10^{-27} \times 2.998 \times 10^{10} \times (56876 - 15868)$$

$$= 8.14564 \times 10^{-12} \text{ erg per photon}$$

$$= 8.14564 \times 10^{-12} \times 6.023 \times 10^{23} / 4.2 \times 10^{10} \text{ kcal mole}$$

$$= 11.681 \times 10 = 116.81 \text{ kcal/mole}$$

The dissociation energy is 116.81 kcal/mol

3.  $D_0 = hc\nu_m - E_{ex}$

$$D_0/\text{per photon} = (D_0/6.023 \times 10^{23}) \times 10^{10} \text{ erg}$$

$$= 239.42 \times 10^{10} / 6.023 \times 10^{23}$$

$$= 39.75 \times 10^{-13} \text{ erg}$$

$$E_{ex} = hc\nu_m$$

$$= 6.6256 \times 10^{-27} \times 2.998 \times 10^{10} \times 881 \text{ erg}$$

$$= 1.7499 \times 10^{-13} \text{ erg}$$

$$\nu_m = (D_0 + E_{ex})/hc$$

$$= (39.75 \times 10^{-13} + 1.7499 \times 10^{-13}) / (6.6256 \times 10^{-27} \times 2.998 \times 10^{10})$$

$$= (39.75 + 1.7499) \times 10^{-13} / (6.6256 \times 2.998 \times 10^{-17})$$

$$= (41.4999 \times 10^4) / (6.6256 \times 2.998)$$

$$= 20892.4 \text{ cm}^{-1}$$

4.	value for parent six membered ring ketone	= 215 nm
	for two double bonds extending conjugation, add $(2 \times 30)$ nm	= + 60 nm
	for ring residue B (marked a), add $1 \times 12$ nm	= + 12 nm
	for ring residue (marked b), add $1 \times 18$ nm	= + 18 nm
	for ring residues (marked c and c'), add $2 \times 18$ nm	= + 36 nm
	for one exocyclic double bond in ring marked A, add $1 \times 5$ nm	= + 5 nm
	for homodiene component, add $1 \times 39$ nm	= + 39 nm
	Calculated $\lambda_{\text{max}}$	<u>= 385 nm</u>

