

Group-C, Unit-1 UV & Visible Spectroscopy

→ Principle: Ultraviolet (UV) & visible radiations cover the wavelength range from 200-800 nm.

When a molecule is exposed to visible or UV radiation, the molecule is excited from one electronic level (ground state) to another electronic level (excited state). The separation between two successive electronic levels is very large compared to vibrational separation. Vibrational energy levels are superimposed on electronic levels and during electronic transition, there is simultaneously vibrational and rotational transitions.

Thus, the electronic spectrum consists of a number of vibrational bands, each of which has rotational lines. Assuming that there is no interaction between the different forms of energy, the total energy of a molecule in the initial state is,

$$E' = E'_{ele} + E'_{vib} + E'_{rot} \dots (1)$$

and in final state is  $E = E_{ele} + E_{rot} + E_{vib} \dots (2)$

The change of energy ( $\Delta E$ ) due to electronic transition.

$$\Delta E = (E_{ele} - E'_{ele}) + (E_{vib} - E'_{vib}) + (E_{rot} - E'_{rot}) = \Delta E_{ele} + \Delta E_{vib} + \Delta E_{rot} \dots (3)$$

The frequency of the radiation is given as,  $\nu = \frac{\Delta E}{hc} = \frac{(\Delta E_{ele} + \Delta E_{vib} + \Delta E_{rot})}{hc} \dots (4)$

The values of  $\Delta E_{vib}$  &  $\Delta E_{rot}$  depend on vibrational and rotational quantum numbers involved. The number of possible lines for a given change in electronic level is large.

UV-Vis spectra is also called electronic absorption spectra or simply electronic spectra since it involves the promotion of electrons ( $\sigma, \pi, n$ ) from the ground state to the higher energy complex but are frequently studied in preference to other types.

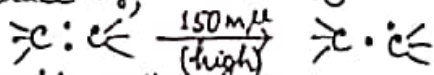
\* Advantages of Electronic or UV-Vis spectra:

- (i) Even homonuclear diatomic molecules give rise to vibrational bands in the electronic spectrum, since the dipole moment of the molecules changes during electronic excitation.
- (ii) Vibrational transitions with large  $\Delta v$  values occur in an electronic excitation.
- (iii) Dissociation energy of molecules can be evaluated from electronic spectra.

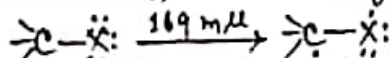
\* Types of Electronic transitions:

According to molecular orbital theory (MOT), when a molecule is excited by the absorption of energy (UV or visible light), its electrons are promoted from a bonding orbital to an antibonding orbital. There are four types of transitions as given below:

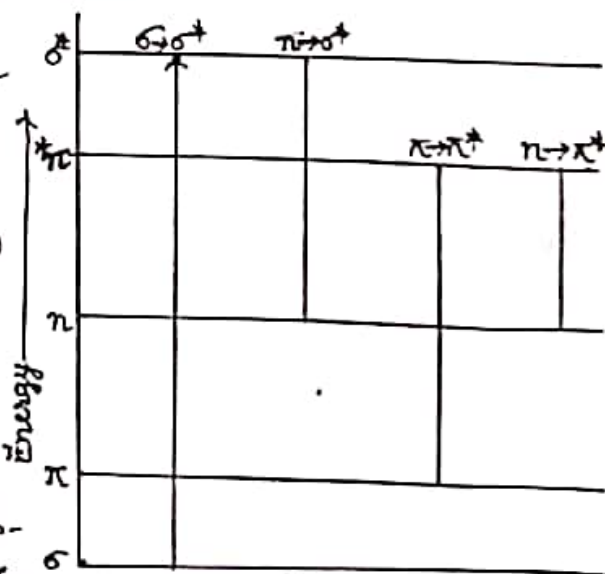
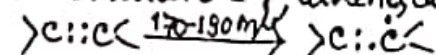
(i)  $\sigma \rightarrow \sigma^*$  transition: When  $\sigma$  (bonding) electron is promoted to  $\sigma^*$  (antibonding) orbital,  $\sigma \rightarrow \sigma^*$  transition takes place. e.g., saturated hydrocarbons.



(ii)  $n \rightarrow \sigma^*$  transition: When a non-bonding (unshared pair electron) ( $n$ ) gets promoted to an antibonding sigma orbital ( $\sigma^*$ ), then it represents  $n \rightarrow \sigma^*$  transition. e.g., saturated alkyl halide.



(iii)  $\pi \rightarrow \pi^*$  transition: When  $\pi$  (bonding) electron is promoted to antibonding  $\pi$  orbital ( $\pi^*$ ), then it represents  $\pi \rightarrow \pi^*$  transition. e.g., alkenes, carbonyls, cyanides etc.



Electronic excitation energies.



(iv)  $n \rightarrow \pi^*$  transition: When an non-bonding (n) electron is promoted to antibonding  $\pi$  orbital ( $\pi^*$ ), it represents  $n \rightarrow \pi^*$  transition. e.g., saturated aldehyde.  $R_2C=O \xrightarrow{290m\mu} R_2C=O^*$

The energy required for various transitions in the order:  $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > n \rightarrow \pi^* > n \rightarrow n^*$ .  
 \* Transition probability: It is not always necessary that the excitation of an electron takes place from a bonding orbital or lone pair to an antibonding or non-bonding orbital, when a compound is exposed to UV or visible radiation. It can be shown that, extinction coefficient ( $\epsilon_{max}$ ) =  $0.87 \times 10^6 \rho a$  [where  $\rho$  = transition probability with values from 0 to 1,  $a$  = large area of the absorbing system, usually called a chromophore (covalently bonded group that shows a characteristic absorption in the UV-vis region).

If  $\epsilon_{max} = 10^5$ , when the chromophore has a length of the order  $10 \text{ \AA} \approx 10^{-7} \text{ cm}$ .

$\epsilon_{max} < 10^3$ , when the chromophore with low transition probability.]

Depending upon the symmetry & the value of  $\epsilon_{max}$ , the transitions are two types:

(a) allowed transitions (b) forbidden transitions.

(a) Allowed transitions: The transition with values of  $\epsilon_{max}$  (extinction coefficient) more than  $10^4$  or  $10$  are usually called allowed transitions. They generally arise due to  $\pi \rightarrow \pi^*$  transition. e.g., in buta-1,3-diene, the absorption at  $217 \text{ m}\mu$  (i.e.,  $\epsilon_{max} = 21700$ ).

(b) Forbidden transitions: The transitions with values of  $\epsilon_{max}$  below  $10^4$  (generally  $10-100$ ) are called forbidden transitions. They generally arise due to excitation of one electron from the lone pair present on the heteroatom to an antibonding  $\pi$  orbital ( $\pi^*$ ), i.e.,  $n \rightarrow \pi^*$  transition. e.g., in carbonyl compounds,  $n \rightarrow \pi^*$  transition occurs near

$300 \text{ m}\mu$ .  
 → Applications of UV-vis/Electronic spectra/spectroscopy:

UV-vis or electronic spectra is very useful in detection of functional groups (Chromophore), the extent of conjugation (i.e., no. of conjugated double bonds), aromatic conjugation within various molecules distinguish between conjugated and non-conjugated systems;  $\alpha, \beta$ -unsaturated carbonyl compounds from  $\beta, \delta$ -analogues; homoannular and heteroannular conjugated dienes etc. Some important applications of UV-vis spectroscopy are:

1. Detection of functional groups (Chromophore): If UV-vis spectrum is transparent above  $200 \text{ m}\mu$ , it shows the absence of (i) conjugation ( $-C=C-$ ) (ii) a carbonyl group ( $-C=O$  or  $-C=O$ ) (iii) benzene or aromatic compounds, and (iv) bromo or iodo atoms. An isolated double bond or some other atoms/groups may be present. No definite conclusions can be drawn if the molecule absorbs below  $200 \text{ m}\mu$ , and molecule is very complicated.

2. Extent of conjugation: The extent (i.e., no. of double bonds) of conjugation in polyenes,  $R-(CH=CH)_n$  can be estimated by UV-vis spectra. Addition in unsaturation with the increase of  $n$  value, shifts the absorption to longer wavelength. It is found that the absorption occurs in the visible region, i.e., at about  $420 \text{ m}\mu$ , if  $n=8$  in the polyenes, such an alkene appears coloured.

3. Distinction between conjugated & non-conjugated compounds: The following isomers can

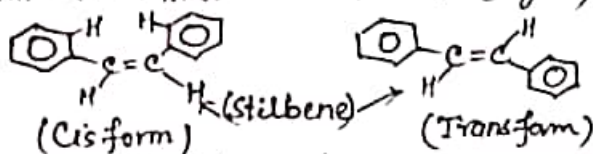
be readily distinguished by UV-vis spectra:  $CH_2=C(CH_3)-CH=CH_2$  (I) (Conjugated) and  $CH_2=C(CH_3)-C(CH_3)=CH_2$  (II) (Non-conjugated).  
 The forbidden  $n \rightarrow \pi^*$  band for the  $C=O$  group in the compound (I) will appear at longer wavelength compared to that for compound (II). The allyl substitution in an alkene causes

(3)

a bathochromic shift. The technique is not much useful for the identification of individual alkenes.

4. Identification of an unknown compound: An unknown compound can be identified by comparing its spectrum with the known spectra. If the two spectra coincide, the two compounds must be identical, and if not coincide then different.

5. Determination of geometrical isomers: The cis forms suffer distortion and absorption occurs at lower wave length than that of trans form. e.g; In spectra of cis and trans stilbenes, trans form show  $\lambda_{max}$  value 295.5 m $\mu$  (higher).



6. Identification of polynuclear hydrocarbons: Benzene & polynuclear hydrocarbons have characteristic spectra in the UV-VIS region. Thus, the identification of the polynuclear hydrocarbons can be made by comparison with the spectra of known polynuclear compounds. The presence of substituents on the ring generally, shifts the absorption maximum to longer wavelength.