

Unit-I

Ultra-violet and Visible Spectroscopy

This spectroscopy is also known as **Electronic Spectroscopy** because it involves the excitation of electrons from the ground state to the higher energy state. This branch of spectroscopy is generally useful to measure the number of conjugated double bonds, aromatic conjugation; to distinguish between conjugated and non-conjugated systems, α,β -unsaturated carbonyl compounds from β,γ -analogues; homoannular and heteroannular conjugated dienes etc. Visible and uv-spectroscopy deal in the range 200-800m μ wavelength of electromagnetic radiations where the promotion of electrons to the higher energy state takes place.

Since the energy associated with a molecule is quantised, the energy needed for excitation of electron is also fixed. Thus, electromagnetic radiations with only a particular wavelength will be able to cause electronic excitation. This can be said that radiation of different wavelengths when falls on a substance energy may not be absorbed by the substance and hence the emitted radiation will not suffer any loss of intensity. If a radiations of correct wavelength falls on a substance energy will be absorbed and hence emitted radiation will be either less intense or its intensity may be completely lost.

Substances absorbing radiations in the visible region will appear coloured to the naked human eye. On the hand, Substances absorbing radiations in the uv-region will not appear coloured to the naked human eye.

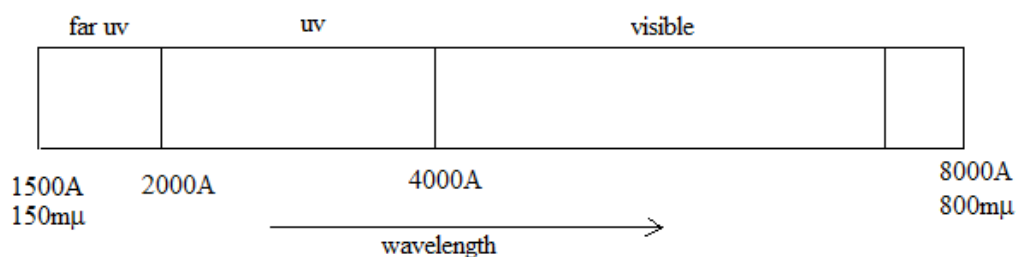


Fig. 1: The range of uv-visible spectra

$$1\mu = 10^{-4} \text{ cm}$$

$$1\text{m}\mu = 1\text{nm} = 10^{-7} \text{ cm} = 10\text{\AA}$$

The amount of light absorbed the substance can be recorded as a function of the wavelength of light in nm or m μ unit which is called absorption spectrum.

The far uv light is not much studied because this light is absorbed by oxygen and nitrogen. To study in this region requires vacuum instruments.

The Absorption Laws: The two laws which govern the absorption of light by the molecules. They are:

- i. **Lambert's law**
- ii. **Beer's law**

Lambert's law states that when a beam of monochromatic radiations is passed through a homogenous medium, the rate of change of intensity of radiations with thickness of absorbing medium is directly proportional to the intensity of the incident radiations.

Mathematically,

$$-dI/dx = kI$$

Where dI = infinitesimally small decrease in the intensity of the radiation

dx = the thickness of the absorbing medium

k = the proportionality constant or absorption coefficient

Beer's law states that when a beam of monochromatic radiations is passed through a solution of absorbing substance, the rate of change of intensity of radiations with thickness of absorbing solution is directly proportional to the intensity of the incident radiations as well concentration of the solution.

Mathematically,

$$-dI/dx = k'cI$$

Where dI = infinitesimally small decrease in the intensity of the radiation

dx = the thickness of the absorbing medium

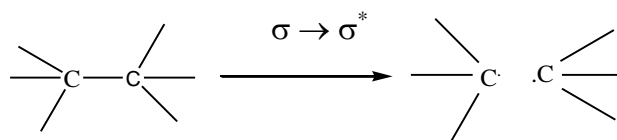
k' = the proportionality constant or absorption coefficient

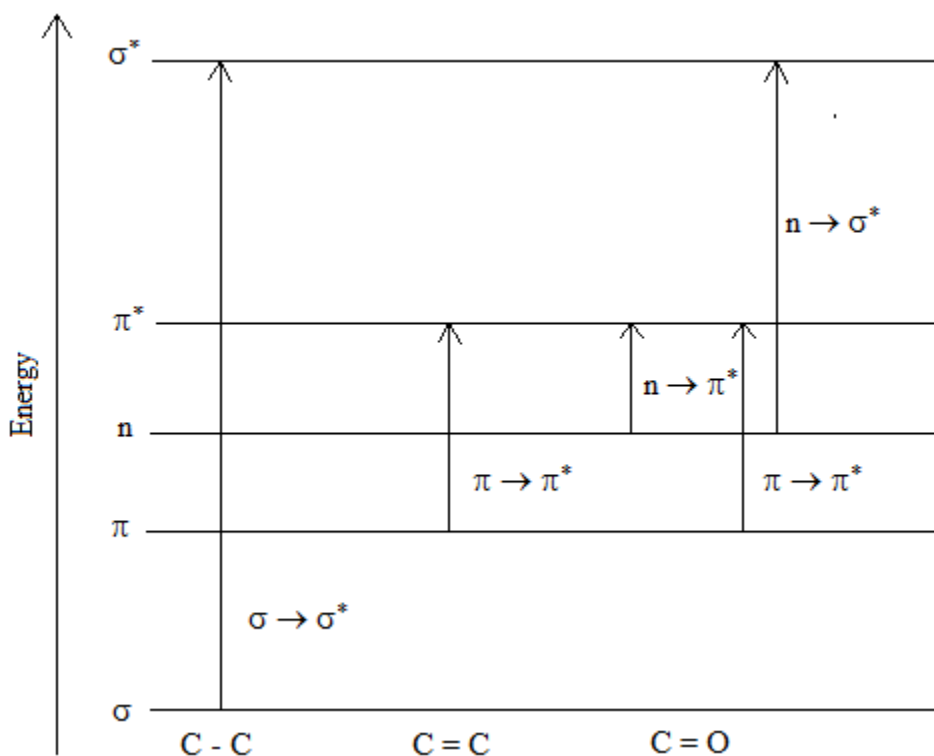
c = the concentration of the solution

Types of Electronic Transitions

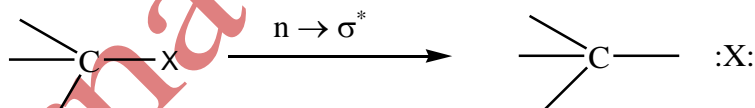
According to the MOT, when light of definite wavelength (uv-visible light) falls then the electrons in the molecule gets excited by promotion of electrons from a bonding MO to an anti-bonding MO. Thus, electronic excitation takes place by different ways as shown in figure 2.

(i) $\sigma \rightarrow \sigma^*$ Transition: When electron are promoted from σ MO to σ^* anti-bonding MO then it is called $\sigma \rightarrow \sigma^*$ transition. It is a high energy process since σ bonds are strong. This type of excitation generally takes place in saturated molecules. The wavelength of the radiations for such transition is in the range of far uv region.





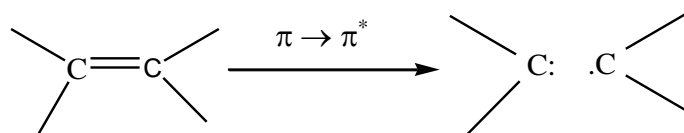
(ii) $n \rightarrow \sigma^*$ Transition: This type of transition generally occurs in saturated molecules having one hetero atom with unshared pair (n electrons). Saturated halides, alcohols, aldehydes, ketones, amines etc. undergoes this type of transition. Such transition require less energy than that required for $\sigma \rightarrow \sigma^*$ transition. Water absorbs at $167 \text{ m}\mu$, methyl alcohol at $174 \text{ m}\mu$ and methyl chloride at $169 \text{ m}\mu$.



In saturated halides the energy required for such transition decreases with the increase in the size of the halogen atom attached. For example, methyl chloride absorbs at $172\text{-}175 \text{ m}\mu$ whereas methyl iodide at $258 \text{ m}\mu$ and molar extinction coefficient is also higher compared to methyl chloride.

$n \rightarrow \sigma^*$ transitions are very sensitive to hydrogen bonding and well as solvent effects. Alcohols and well as amines forms hydrogen bonding with solvent molecules. Such association takes place due to the presence of non-bonded electrons on the hetero atom, thus requires higher energy. *Hydrogen bonding shifts the uv- absorptions towards shorter wavelength.*

(iii) $\pi \rightarrow \pi^*$ Transition: This type of transitions occurs in the unsaturated molecules. i.e. compounds containing double or triple bonds. This excitation requires less energy and hence transitions of this type occur at higher wavelength of uv- region. Alkenes, alkynes, carbonyl compounds, azo compounds etc. exhibit $\pi \rightarrow \pi^*$ transition.



Absorption usually occurs within the range of ordinary uv-spectrophotometer. In unconjugated alkenes, absorption bands appear around 170-190 m μ . In carbonyl compounds it appears around 180 m μ and is most intense.

(iv) $n \rightarrow \pi^*$ Transition: This type of transition requires least amount of energy out of all transitions discussed above and hence occur at higher wavelength. Saturated aldehydes have two types of transitions, i.e. low energy $n \rightarrow \pi^*$ and high energy $\pi \rightarrow \pi^*$ transitions which are occurring around 290 m μ and 180 m μ respectively. Out of these two $\pi \rightarrow \pi^*$ transition is intense because it occurs at lower wavelength. In carbonyl compounds, a high energy $n \rightarrow \sigma^*$ transition also occurs and is quite intense. Thus, in saturated carbonyl compounds two types of transitions takes place

(a) High energy transitions

(i) $n \rightarrow \sigma^*$ (intense)

(ii) $\pi \rightarrow \pi^*$ (intense)

(b) Low energy transition

$n \rightarrow \pi^*$ (weak)-R band

Transition Probability

The extinction coefficient can be described as

$$\epsilon_{\max} = 0.87 \times 10^{20} \cdot P \cdot a$$

Where P = the transition probability with values from 0 to 1.

A = target area of the absorbing system known as chromophore.

It is estimated that the values of ϵ_{\max} is about 10^5 when the chromophore has a length of the order 10 Å or 10^{-7} cm. The chromophore with low transition probability will have ϵ_{\max} value below 1000. Hence there is a direct relation between the area of the chromophore and the absorption intensity ϵ_{\max} . Depending upon the symmetry and the value of ϵ_{\max} , the transition can be classified as:

(a) Allowed transitions (b) Forbidden transitions

The transition with values of extinction coefficient, ϵ_{\max} more than 10^4 are usually called allowed transitions. They generally arise due to $\pi \rightarrow \pi^*$ transitions. In 1, 3- butadiene, the absorption at 217 m μ ϵ_{\max} 21000 is an example of allowed transition.

When the excitation of one electron from the lone pair present on the hetero atom to π^* orbital, results the forbidden transition. $n \rightarrow \pi^*$ transition near $300 \text{ m}\mu$ in case of carbonyl compounds with ϵ_{max} value between $10 - 100$, is the result of forbidden transition.

The Chromophore

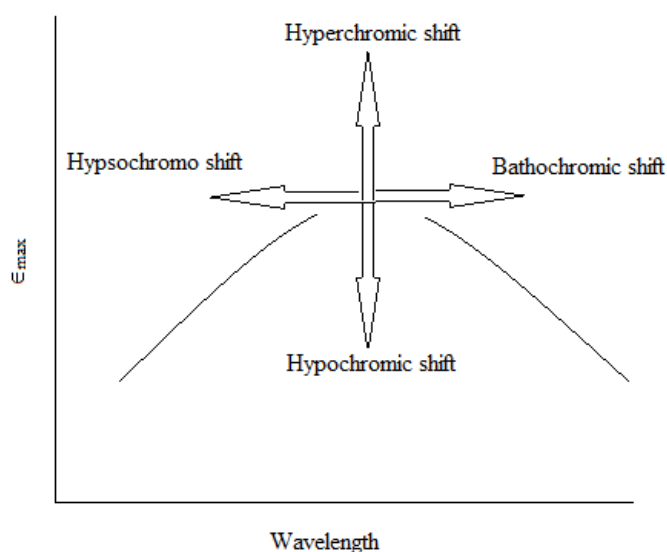
Compounds which absorb light of wavelength in the range $400 - 800 \text{ m}\mu$ are coloured to the human eye. A chromophore is any part of a substance which is responsible for imparting colour to the substance. Thus, nitro group is a chromophore which imparts yellow in colour. Aryl conjugated azo compound is another important example of chromophore which produce colour to azo dyes. Thus, the term chromophore can be defined as *any isolated covalently group that shows characteristic absorption in the uv- or the visible region*. Some other important chromophores are ethylenic, acetylenic, carbonyls, acids, esters, nitrile group etc.

The Auxochrome

An auxochrome can be defined as any group which does not itself act as a chromophore but whose presence in a compound brings about a shift of the absorption band towards the red of the spectrum (i.e. longer wavelength). Some common auxochromes are $-\text{OH}$, $-\text{OR}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{SH}$ etc. This effect is due to its ability to extend the conjugation of a chromophore by the sharing of non-bonded electrons. For example, benzene shows an absorption at $255 \text{ m}\mu$ ($\epsilon_{\text{max}} = 203$) whereas aniline absorbs at $280 \text{ m}\mu$. Thus amino group is an auxochrome.

Absorption and Intensity Shifts

- (a) **Bathochromic effect:** When the absorption maximum is shifted towards longer wavelength due to the presence of a chromophore or by the change of solvent then the effect is called bathochromic shift. Such shift towards longer wavelength is called **red shift**. The $\pi \rightarrow \pi^*$ transition in carbonyl compounds experiences bathochromic shift when polarity of the solvent is decreased.



- (b) **Hypsochromic shift:** When the absorption wavelength is shifted toward the shorter wavelength then the effect is called hypsochromic shift. This is commonly known as **blue shift**. This effect is due to the removal of conjugation or change in polarity of the solvent. The absorption maximum of aniline is 280 m μ whereas in acidic medium it is shifted to 203 m μ . It is because in acidic medium the lone pair of electron on nitrogen atom forms bond with acidic hydrogen and hence electron pair is no longer present and conjugation is removed.
- (c) **Hyperchromic shift:** When the intensity of the absorption maximum is increased the effect is called Hyperchromic shift. i.e. ϵ_{\max} increases. The incorporation of an auxochrome in an organic molecule usually increases the intensity of absorption and hence exhibits hyperchromic shift.
- (d) **Hyperchromic shift:** It is the shift where intensity of absorption maximum decrease. When the geometry of a molecule is distorted due to the introduction of group this type of shift may take place. For example, biphenyl absorbs at 250 m μ , whereas 2-methyl biphenyl absorbs at 237 m μ .

Solvent Effects

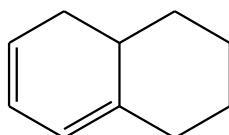
In uv-spectrophotometer, when a sample is analysed a solution of the sample is generally used. So, choice of solvents is very important for analysis of sample. A ideal sample is one which does not absorb radiations in region where investigation takes place. On the other the solution should be dilute and transparent. 95% pure ethanol is treated as best sample for such analysis as it is cheap and transparent. It absorbs light below 210 m μ . Commercial ethanol cannot be used as it contains benzene as impurity which absorbs light in the uv- region. Some other solvents which absorb light below 210 m μ are cyclohexane, n- hexane, methyl alcohol etc.

Woodward-Fieser Rules for calculating absorption maximum in Dienes

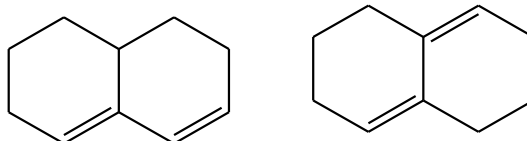
- i. **Alicyclic dienes or dienes** contained in an **open chain system:** the basic unit is butadiene system.



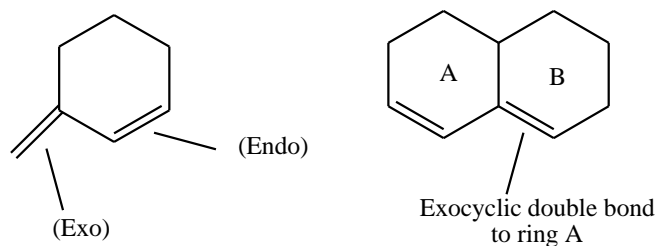
- ii. **Homoannular conjugated double bonds** are the conjugated double bonds present in the same ring.



- iii. **Heteroannular conjugated double bonds** are the conjugated bonds which are not present in the same ring.



- iv. **Exocyclic and endocyclic conjugated double bonds** are shown as



Woodward formulated certain empirical rules which was modified by Fieser for calculating λ_{\max} in case of dienes.

According to these rules, each type of diene has a fix basic value and the value of absorption maximum, λ_{\max} depends upon

- (i) The number of alkyl substituents or ring residues on the double bond
- (ii) The number of double bonds which extend conjugation
- (iii) The presence of polar group such as -Cl, -Br, -OR, -SR etc.

Some standard values of λ_{\max} for conjugated dienes and trienes are summarised below

Parent value for butadiene system or acyclic conjugated diene	217 m μ
Acyclic triene	245 m μ
Homoannular conjugated diene	253 m μ
Heteroannular conjugated diene	215 m μ
Increment for each substituent	
Alkyl substituent or ring residue	5 m μ
Exocyclic double bond	5 m μ
Double bond extending conjugation	30 m μ
Auxochrome	
-OR	+6 m μ
-SR	+30 m μ
-Cl, -Br	+5 m μ
-NR ₂	+60 m μ

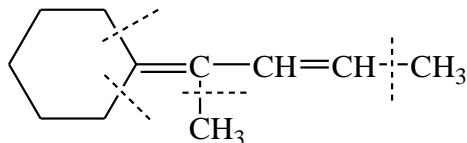
Ex. 1: Calculate the absorption maximum in the uv-spectrum of 2,4-hexadiene

The basic unit 2,4-hexadiene is butadiene where two alkyl substituents on it

Basic value = 217 m μ

2- alkyl substituents (2x5)	=10 m μ
Calculated value	=227 m μ

Ex. 2: Calculate the absorption maximum in the uv spectrum of



It is a butadiene system with two alkyl substituents and two ring residues on the double bonds. Moreover, there is an exocyclic double bond

Basic value	= 217 m μ
2-alkyl substituents (2x5)	= 10 m μ
2-ring residues (2x5)	= 10 m μ
1-exocycle double bond	= 5 m μ
Calculated value	= 242 m μ

Ex. 3: Calculate the absorption maximum in the uv spectrum of



It is a heteroannular diene with four ring residue

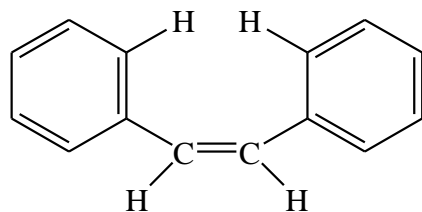
Basic value	= 214 m μ
4-ring residue (4x5)	= 20 m μ
Calculated value	= 234 m μ

Applications of UV Absorption Spectroscopy

Some important applications of uv- spectroscopy are:

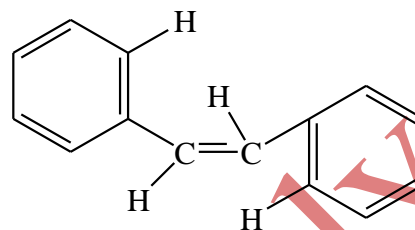
1. Detection of functional groups: This technique is useful of detection of functional groups i.e. chromophore and auxochrome.
2. Distinction between conjugated and non-conjugated systems: It distinguishes between conjugated and non-conjugated compounds.
3. Identification of unknown compound: An unknown compound can be identified by comparing with the spectra of known compounds.
4. Examination of polyannular compound: Whether the compound is homoannular or polyannular can be confirmed by this spectroscopy.

- Elucidation of structure of vitamins: It is useful to determine the structures of vitamins K₁ and K₂ also those of A₁ and A₂
- Detections of impurities: This spectroscopy is useful for detection of impurities present in organic compounds.
- Determination of configuration of geometrical isomers: Cis and Trans isomers can be distinguished by uv-spectroscopy.



Cis-stilbene

$$\lambda_{\max} = 283 \text{ m}\mu$$

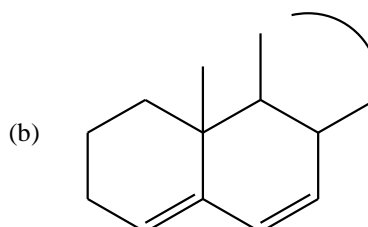
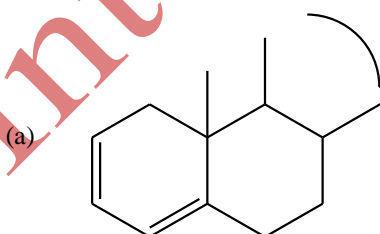


Trans-stilbene

$$\lambda_{\max} = 295.5 \text{ m}\mu$$

Conceptual Questions

- What is electronic spectroscopy? Which part of the electromagnetic radiation is responsible for electronic spectrum?
- What are absorption laws? Derive mathematical expression of absorption laws.
- What are different electronic excitations in uv-light? Explain with examples.
- Explain the effect of polar solvents on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions
- Define the following terms
 - Bathochromic shift
 - Solvent effect
 - Charge transfer spectra
 - Hyperchromic shift
 - Hypochromic shift
- Write some important applications of uv-spectroscopy
- Define the term chromophore? How will you detect the presence of carbonyl group in aldehydes and ketones?
- Calculate the λ_{\max} for the following compounds



References

- Elementary Organic Chemistry Principles and Chemical Applications, 2nd Edn, Y.R. Sharma, S. Chand & Company Ltd, New Delhi.

2. Spectroscopy (Atomic and Molecular), 3rd Edn, G. Chatwal, S. Anand, Himalaya Pub. House, Bombay.
3. Ultraviolet and Visible Spectroscopy: Chemical Applications, C.N.R. Rao, Plenum Press, 1975

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