

Ultraviolet and Visible Spectroscopy

Table of Contents

1. Learning Outcomes
2. Introduction
3. Theory of UV and Visible spectroscopy
4. Selection rule
5. Absorption laws
6. Instrumentation and Sample preparation
7. UV spectrum
8. Terminologies
9. Woodward-Fieser rules
10. Solvent effect
11. Examples

Learning Outcomes

After studying this module, student shall be able to

- i) Understand what is electromagnetic radiation
- ii) Analyse the electromagnetic spectrum
- iii) Understand concept of UV-visible spectroscopy
- iv) Learn about the possible electronic transitions
- v) Learn about sample preparation, instrumentation and solvent effect

Introduction

Molecular spectroscopy is an important physical method for determining molecular structure of organic compounds. Ultraviolet and visible (UV-VIS) spectroscopy is the oldest form of spectroscopic technique used in determining of molecular structures. The absorption of UV-VIS radiation by a molecule depends on its electronic structure. The absorption of radiation leads to the electronic transitions among the different energy levels of the molecule that is why it is also called Electronic Spectroscopy. UV-VIS spectrum is directly obtained from instrument which is a plot of wavelength (λ) of absorption vs the molar absorptivity (ϵ) or absorbance (A) or transmittance (%T).

The wavelength region of UV-VIS spectroscopy is 200 nm to 800 nm out of which 200-380 nm is the near-ultraviolet region and 380-800 nm is the visible region. Molecules that absorb in the visible region are colourful to human eye. Thus, chlorophyll is green, carrots are yellow, benzene is colorless and nitrobenzene is light yellow. The phenomena of light absorption in the ultraviolet and visible regions are related to the electronic transitions between filled and empty molecular orbitals.

Electronic spectroscopy is qualitatively used to study – the extent of multiple bonds or aromatic conjugation within a molecule, the extent of conjugation of unshared pair of electrons of oxygen, nitrogen and sulphur with the multiple bonds. Electronic spectroscopy can also differentiate conjugated dienes from the non-conjugated dienes, conjugated dienes from conjugated trienes as well as α , β -unsaturated ketones from its α,γ -homologues. It is also used to study molecular strain and % enol content/equilibrium constant of keto-enol tautomerisation.

Energy of Photon in UV region

The energy of photon per mole in the middle range of ultraviolet region having wavelength $\lambda=290$ nm, can be calculated as

$E=N_Ahc/\lambda$ where N_A is Avogadro's number, h =Planck's constant and c =the velocity of light.

Thus the energy of photons in the UV radiation lays around 412 kJ/mole or around 100kcal/mole which may cause initiatiin of many chemical reactions, transitions of valence electrons in the molecules etc.

Theory of Ultraviolet and Visible spectroscopy

Electronic Transitions

When an organic sample is irradiated with ultraviolet radiation, absorption occurs due to the electronic transitions from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The resulting electronic state of molecule is called excited state. Thus, the UV-VIS spectroscopy is called electronic spectroscopy. These transitions are excitation of electrons from the occupied bonding molecular orbitals (σ, π) or non-bonding molecular orbital (n) to antibonding molecular orbitals (σ^*, π^*). The promotion of electrons from bonding MOs to antibonding MOs is designated $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ etc. Shown in Fig 1.

The relative energies of Molecular orbitals and expected electronic transitions

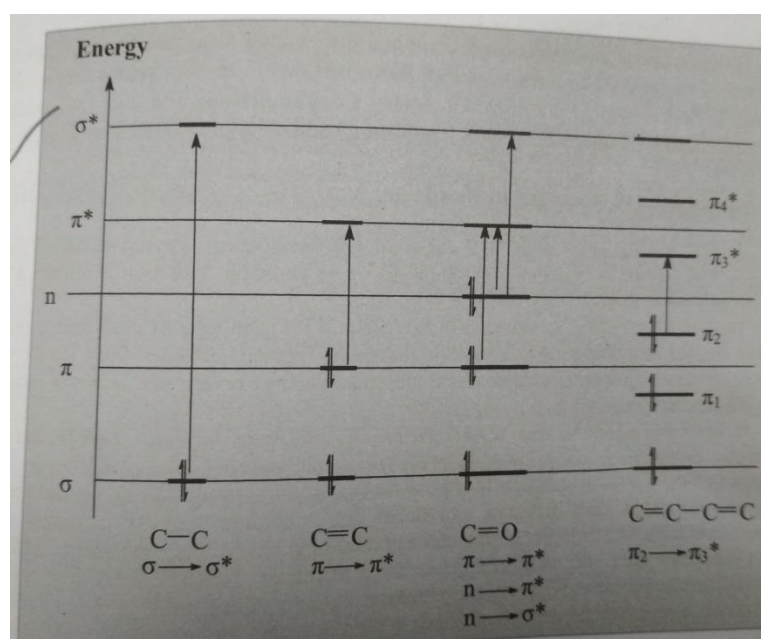


Fig 1

Effects of Energy Absorption

The relationship between energy absorbed (ΔE) and frequency (ν) or wavelength (λ) of radiation is given by the following expression.

$$\Delta E = h\nu = hc/\lambda$$

The energy absorbed in an electronic transition depends on the energy difference between the excited state and ground state. The consequences of absorption of radiation may be dissociation or ionisation of the molecule or may be reemitted as heat or light. The emission of absorbed energy as light ($h\nu$) is called fluorescence or phosphorescence.

If the wavelength of emitted light is longer than the wavelength of absorbed radiation then the phenomena is called fluorescence. However, phosphorescence occurs when the excited molecule emits radiation of longer wavelength than the wavelength absorbed even after removal of exciting radiation. In fluorescence, light emission occurs from singlet-excited state (S_1), while in phosphorescence light emission occurs from more stable triplet-excited state (T_1).

Spin selection rule

Spin Allowed Transitions: Singlet→Singlet or Triplet→Triplet

Spin Forbidden Transitions: Singlet→Triplet or Triplet→Singlet

Laws of Absorption: Beer-Lambert Laws

Beer-Lambert laws correlate the absorption of light by molecules with the other experimental parameters. Beer's law states that the rate of decrease in intensity of radiation absorbed is proportion to the intensity of radiation (I) and concentration (c) of the solute. i.e., $dI/dl = -k c I$

Again, the Lambert's law states that the rate of decrease of intensity with the thickness of absorbing medium is proportional to the intensity of radiation i.e. $dI/dl = k'I$

Combining Beer and Lambert laws and integrating between the two limits, it can be expressed as

$$\log_{10}(I_0/I) = \epsilon c l$$

or, $A = \epsilon c l$ where, I_0 = the intensity of incident radiation, i.e., the intensity of radiation passing through reference cell, I = the intensity of radiation transmitted through solution of the sample,

$\log_{10}(I_0/I) = A$, called absorbance or optical density (OD), c = concentration of solute (in mole/dm³), l = path length of the sample (in cm), ϵ = the molar absorptivity or molar extinction coefficient, conventionally, which has units 1000 cm²/mol but not expressed.

Limitations of Beer-Lambert Law:

1. Beer Lambert law is applicable for monochromatic radiation passing through the sample. Practically the radiation is polychromatic. If the absorptivity of the sample varies significantly throughout the used wavelength band, a deviation from Beer-Lambert law may be expected.
2. Chemical reactions leading to the change in concentration of sample can result deviation from Beer's law, e.g., association-dissociation reactions and acid-base reactions lead to the deviation from Beer's law.
3. Deviation from Beer's law may arise from the presence of a luminescing substance in solution and due to change of solvent.
4. Deviation from Beer's law may also arise from the change of temperature, since it causes change in equilibrium that alters the absorption at a specific wavelength.

Few other terms used in UV-VIS spectroscopy have been defined below:

λ_{\max} : It is the wavelength at which maximum absorbance take place for a particular transition.

ϵ_{\max} : The molar absorptivity ϵ is constant for a particular compound at a given wavelength

$E_{1\text{cm}}^{1\%}$: If the molecular weight (M) of the compound is unknown, the ϵ cannot be calculated. Then convenient expression is $E_{1\text{cm}}^{1\%}$. It is defined as absorbance of analyte at the concentration of 1% and 1 cm path length.

$E_{1\text{cm}}^{1\%} = A/c l$ (when $c = 1 \text{ gm}/100 \text{ ml}$); Thus, $\epsilon = 10^{-1} E_{1\text{cm}}^{1\%} \times M$

Instrumentation and Sampling Techniques

Both single and double beam spectrophotometers are used to measure UV-VIS spectra of organic molecules.

a) *Source of radiation*: Tungsten filament lamp (350-2500 nm), hydrogen lamp or deuterium discharge lamp (180-350 nm)

b) *Monochromator*: It is a device which converts polychromatic radiation into monochromatic radiation obtained from the source of electromagnetic radiation (EMR).

c) *Chopper*: It sends EMR alternately through sample cell and reference cell

d) *Sample and reference cells*: The sample cell consists of sample solution. Generally cells of 1 cm path length are used. The reference cell is the cell of identical path length having the solvent, in which the sample is dissolved. The cell wall is prepared from quartz or fused silica.

e) *Detector*: Phototubes and photomultiplier tubes

f) *Readout Device*: Recorders, computer controlled recorders, xy-plotters and computer controlled printers. A plot of absorbance vs. wavelength is obtained.

Preparation of sample solution and choice of solvent

Since UV-Visible spectroscopic studies required very dilute solution (around 0.1%), the solution must be prepared in 100 ml volumetric flask taking 1 g sample in 100 ml solvent.

The list of solvents used in UV-Visible spectral regions is water, ethanol, n-hexane, cyclohexane, methanol, diethyl ether, acetonitrile, tetrahydrofuran, chloroform, carbontetrachloride, benzene and acetone.

Presentation of UV-Spectra

The UV-Visible spectra of organic compounds are plotted as absorbance or ϵ or $\log \epsilon$ or $E_{1cm}^{1\%}$ as a function of increasing λ . Typical UV-Visible spectra of an organic compound are shown below.

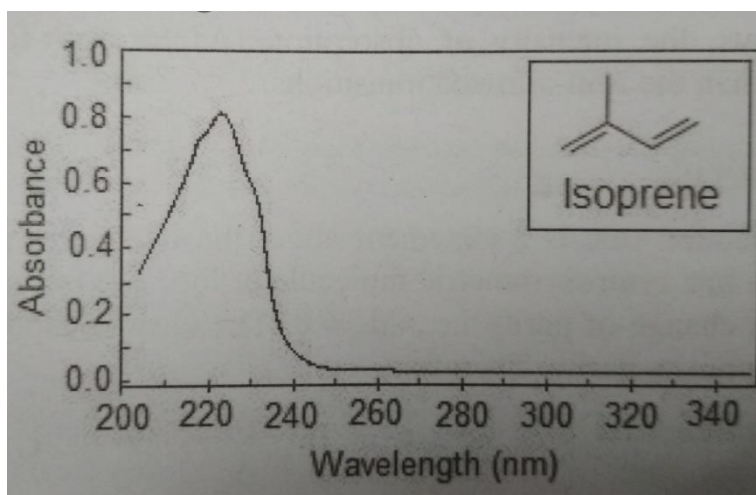


Fig 2

Designation of Absorption Bands

a) K-Band: $\pi \rightarrow \pi^*$ transition e.g. dienes, polyenes, aromatic hydrocarbons etc.

b) R-Band: $n \rightarrow \pi^*$ transition e.g. aliphatic aldehydes, ketones and nitro compounds

c) B-Band: benzenoid compounds and hetero-aromatic compounds

d) E-Band: benzene, naphthalene, pyrrole etc.

Terminologies

i) *Chromophores*: The groups which are responsible for colour of a compound. The important chromophores are azo, diazo, nitro etc. When these groups are attached to benzene ring the compounds absorb in the visible regions.

ii) *Auxochrome*: It is a functional group on an absorbing molecule that does not itself absorb UV-Visible radiation but change the absorptive maxima of the molecule. Generally the functional groups having unshared pair of electrons such as $-\text{NH}_2$, $-\text{NHR}$, $-\text{OH}$, $-\text{OR}$, $-\text{SH}$ and halogens act as auxochrome. The presence of auxochrome shifts the absorption maximum of a chromophore.

iii) *Bathochromic shift*: The presence of auxochrome in a molecule that contains chromophore shifts the absorptive maxima to longer wavelength. This shift of spectral band position in the absorption, reflectance, transmittance or emission spectrum of a molecule to longer wavelength is called bathochromic shift or red shift. Red shift can also occur due to change in environmental conditions: for e.g. a change in solvent polarity.

iv) *Hypsochromic shift*: It is defined as a change of spectral band position in the absorption, reflectance, transmittance or emission spectrum of a molecule to a shorter wavelength. As the blue colour in the visible spectrum has a shorter wavelength than most other colours, this effect is called blue shift.

v) *Hyperchromic effect*: When absorption intensity (ϵ_{max}) of a compound is increased, it is known as hyperchromic effect. If auxochrome is introduced to a compound, the intensity of absorption increases.

vi) *Hypochromic effect*: When absorption intensity (ϵ_{max}) of a compound is decreased, it is known as hypochromic effect. The decrease in absorbance may occur due to the addition of a substituent to a molecule called auxochrome.

Calculation of λ_{max} : Woodward-Fieser Rules

The base values and additions for substituents λ_{max} for $\pi \rightarrow \pi^*$ in ethanol

Types of dienes and trienes	Base values (nm)
Acyclic and heteroannular dienes	215
Homoannular dienes	253
Acyclic trienes	245
Substituents	Increment (nm)
Alkyl group or ring residue	5
Alkoxy group	6
Thioether	30
-Cl or -Br	5
Acyloxy	0
Additional conjugation	30
Exocyclic double bond	5
If one double bond is exocyclic to two rings	10

$$\lambda_{\text{max}} (\text{Calculated}) = \text{Base value} + \text{Substituents contribution}$$

Saturated carbonyl groups show two principal absorption bands for the following transitions

1. $\pi \rightarrow \pi^*$ 190 nm (allowed, strong)

2. $n \rightarrow \pi^*$ 270-300 nm (R-band, forbidden, weak)

In α, β -unsaturated carbonyl compounds, the possible electronic transitions are $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$

Woodward Rule – Calculation of λ_{\max} for $\pi \rightarrow \pi^*$ (in ethanol) of α, β -unsaturated carbonyl compounds

Types of α, β -unsaturated carbonyl compounds	Base values			
Acyclic or Six-membered cyclic ketones	215			
Five-membered cyclic ketones	202			
Aldehydes	207			
Acids or esters	197			
Substituents	Increment (nm)			
Additional conjugation	30			
If the $\gamma\delta$ -double is homoannular to the $\alpha\beta$ -double bond	39			
For each exo-cyclic double bond	05			
Other Substituents	Increment for Positions of Substituents (nm)			
	α	β	γ	δ
Alkyl group	10	12	17	17
Alkoxy group	35	30	17	31
Hydroxy group	35	30	30	50
-SR	-	80	-	-
-Cl	15	12	12	12
-Br	25	30	25	25

Solvent effect

UV spectra of organic compounds are recorded in ethanol. However change of solvent may change λ_{\max} value. The position (λ_{\max}) and the intensity of absorption (ϵ_{\max}) remain same on changing the solvents in the cases of unsaturated hydrocarbons such as dienes, trienes or polyenes etc. However compounds having unshared pair of electrons, the positions as well as the intensity of absorption are changed when the spectra of same compound are recorded in different solvents. In polar or polar protic solvents, the lone pair of electrons (n) is more stabilized compared to π^* antibonding MO or π bonding MO.

In polar solvent, the ΔE for $n \rightarrow \pi^*$ transition increases compare to ΔE for the $n \rightarrow \pi^*$ transition in non-polar solvent. Therefore, $n \rightarrow \pi^*$ transition shows a blue shift in polar solvents. However, the ΔE for the $\pi \rightarrow \pi^*$ transition decreases compare to the ΔE for the $\pi \rightarrow \pi^*$ transition. Thus the $\pi \rightarrow \pi^*$ transition shows a red shift in polar solvents. The solvent correction terms are shown in the Table which may be added/subtracted to find out the λ_{\max} for $\pi \rightarrow \pi^*$ transition in a solvent other than ethanol.

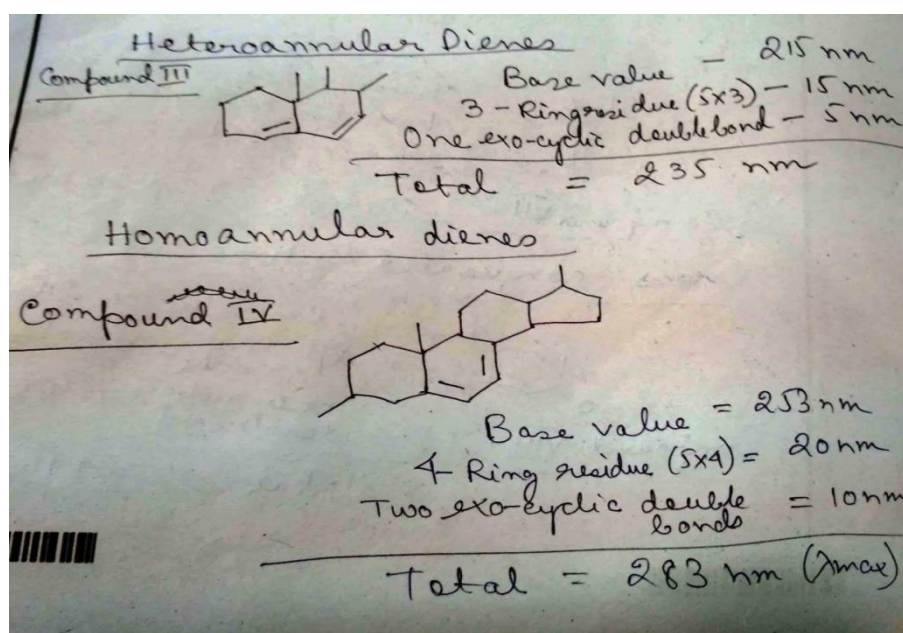
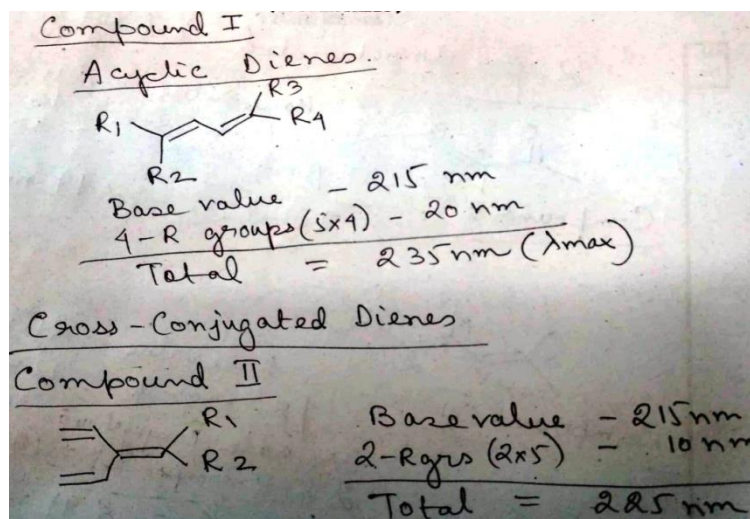
Solvent shift of λ_{\max} for $\pi \rightarrow \pi^*$ transition of α, β -unsaturated carbonyl compounds

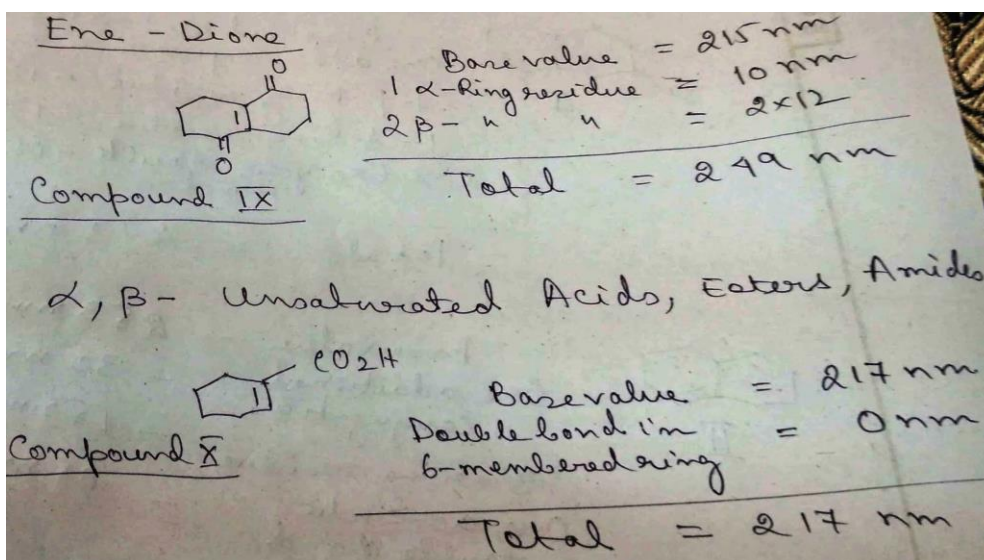
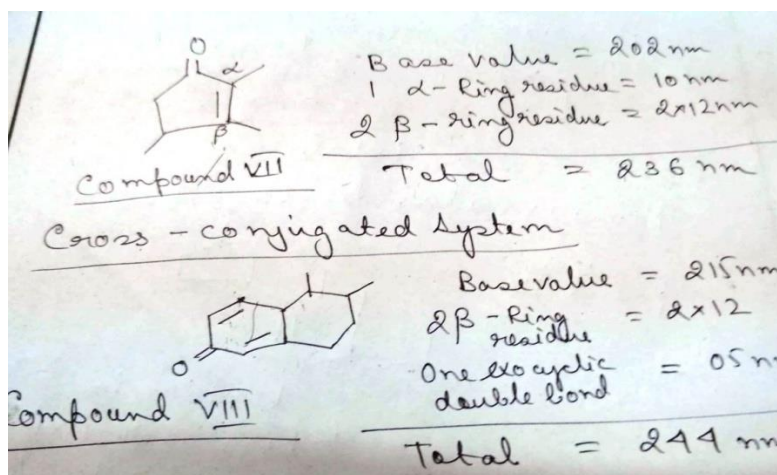
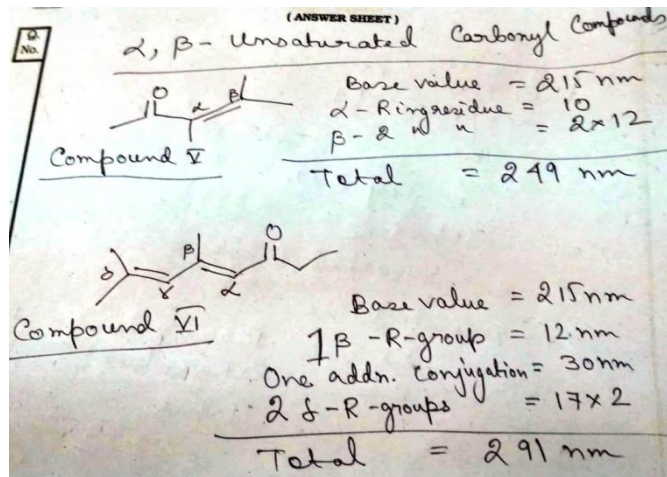
Solvent	Shift(nm)
Water	+8
Methanol	0
Ethanol	0
Chloroform	-1
Dioxan	-5
Diethylether	-7
Hexane	-11
Cyclohexane	-11

Woodward Rule – Calculation of λ_{\max} for $\pi \rightarrow \pi^*$ transition (in ethanol) of α, β -unsaturated acids and esters

Type of Substituents on α, β -unsaturated acids/esters	Base values (nm)
β -monosubstituted cyclic/acyclic compounds	208
$\alpha\beta$ - or $\beta\beta$ -disubstituted cyclic/acyclic compounds	217
$\alpha\beta\beta$ -trisubstituted cyclic/acyclic compounds	225
Increment for substituents/additional conjugation	
A double bond extending the conjugation	30
Exocyclic double bond	05
When the double bond is endocyclic in a five or seven-membered ring	05

Examples:





More problems

Q. λ_{max} value for p-aminophenol in water is longer than in acid solution. Justify

→ In p-aminophenol, the lone pair of amino-group is undergoing resonance more with benzene ring than the -OH group since oxygen is more electronegative (more -I effect) than nitrogen. In acid solution the lone pair of nitrogen is being protonated; it cannot undergo resonance with benzene ring as a result λ_{max} is lowered in acid solution.

