

Assignment

U-V Spectroscopy: It is technique used to measure the absorption of UV & visible light by a substance.

Principle: UV spectroscopy works on the principle that molecules absorb light at specific wavelength in the UV or visible range. The energy absorbed excites the e^- from lower to higher energy levels.

Regions of absorption: UV = 200-400nm Visible = 400-700nm

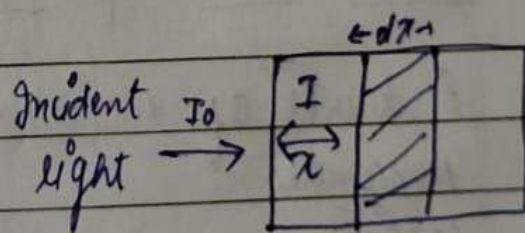
Absorption Law

Lambert Beer Law: When a monochromatic light is passed through a solⁿ, the decrease in intensity of light with thickness of solⁿ is not only to the intensity of light but also to the concentration of solⁿ.

$$-\frac{dI}{dx} = \epsilon I C$$

$$-\frac{dI}{dx} = \epsilon I C$$

$$\ln\left(\frac{I}{I_0}\right) = -\epsilon C x \quad , \quad \frac{I}{I_0} = e^{-\epsilon C x}$$



$$= \frac{C}{\rho^2 x}$$

$$V = \frac{y_1(f(x))}{W}$$

$$I_{\text{trans}} = I_0 (1 - e^{-\epsilon c x})$$

$$\log\left(\frac{I}{I_0}\right) = \frac{-\epsilon c x}{2.303}$$

$$\text{Take } \epsilon = \epsilon'$$

$$\log\left(\frac{I}{I_0}\right) = -\epsilon' c x$$

$$I = I_0 10^{-\epsilon' c x}$$

Transmittance: The ratio of intensity of transmitted light (I) from solⁿ to the intensity of incident light (I_0).

$$T = \frac{I}{I_0}$$

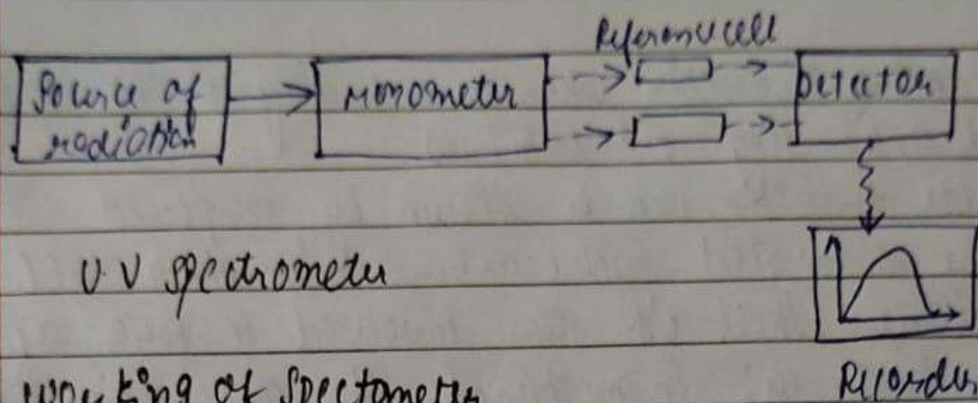
Absorbance: logarithm reciprocal of T .

$$A = -\log T \quad \text{or} \quad A = \log(1/T)$$

$$A = \epsilon' c x$$

Instrumentation for spectroscopy:

1. A source of radiation
2. monometer
3. detector
4. Sample holder
5. recorder chart paper.

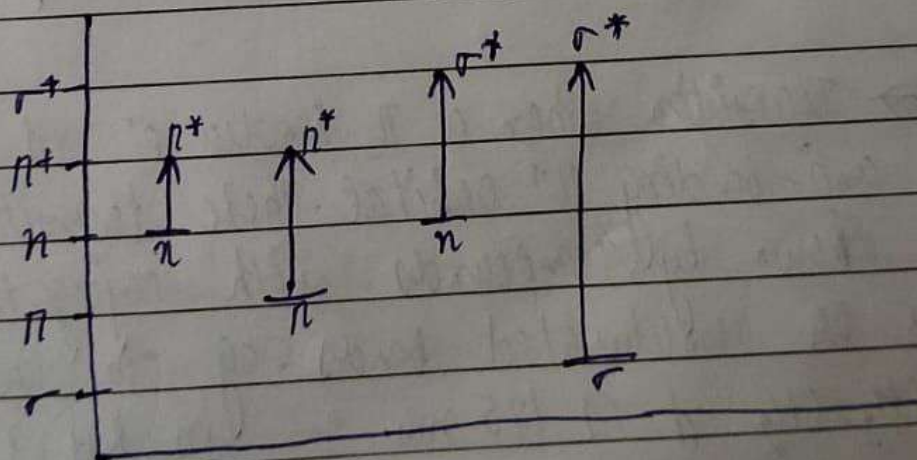


Working of Spectrometer

1. Light emission
2. Light passing through sample
3. Absorption of light
4. Detection of transmitted light
5. Generation of Absorption spectrum.

Electronic Transitions: The electronic transitions taking place in UV & visible region are as follows:

- (I) $\sigma \rightarrow \sigma^*$ (II) $n \rightarrow n^*$ (III) $n \rightarrow \sigma^*$ (IV) $n \rightarrow \pi$



$$= \left[\rho^2 x \right]$$

$$V = \frac{y_1(f(2))}{W}$$

$$y_2(f(2))$$

① $\sigma \rightarrow \sigma^*$ Transition when a σ bonding e^- is excited to antibonding σ^* orbitals. These transitions can be shown by compound like saturated hydrocarbons in which all valence shell e^- are involved in form of σ bond. eg: in methanol, the absorption of energy for $\sigma \rightarrow \sigma^*$ transition occurs at 195 nm.

② $n \rightarrow \sigma^*$ Transition when a non-bonded e^- is excited to anti-bonding σ^* orbital. Compounds having non-bonded e^- on heteroatom like sulphur, oxygen & nitrogen & halogens can show $n \rightarrow \sigma^*$ transition. eg in CH_3Cl λ is 174 nm & in CH_3I λ is 258 nm.

③ $n \rightarrow \pi^*$ Transition of non-bonded e^- to anti-bonding π^* orbital. Compounds having double bond with oxygen. eg $(N=O)$, $(C=O)$. In case of carbonyl group λ is 285 nm.

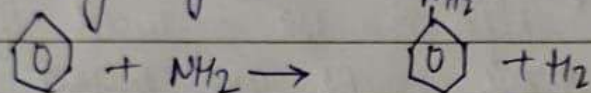
④ $\pi \rightarrow \pi^*$ Transition when a π bonded e^- is excited to an anti-bonding π^* orbital. These transitions can be shown by compounds with conjugated systems or unsaturated bonds. eg in case of $CH_2=CH_2$ λ is 175 nm & in But 1,3 diene

$$f = \frac{4\pi^2 \nu}{c} + \frac{12\pi^2 \nu}{c^2}$$

$$N = \begin{vmatrix} e^{3x} & x e^{3x} \\ 3e^{3x} & x 3e^{3x} + e^{3x} \end{vmatrix} = (e^{3x})^2 (3x+1) - (e^{3x})^2 (3x)$$

$\lambda = 219 \text{ nm}$

Auxochrome: It is a ~~gap~~ group which itself does not act as chromophore but when attached to a chromophore, it shifts the absorption max to longer wavelength along with increase in intensity. eg -OH & -NH_2



$\lambda = 255 \text{ nm}, \epsilon = 203$

$\lambda = 280 \text{ nm}, \epsilon = 1430$

Chromophore: These are functional groups which absorb EM radiations and may/may not impart colour to any compound. There are 2 types:-

- Chromophore like $\text{C}=\text{C}$ & $\text{C}\equiv\text{C}$ having π e^- which undergoes $\pi \rightarrow \pi^*$ transition.
- Chromophore like $\text{C}=\text{O}$, $\text{N}=\text{N}$ & NO_2 which contain both σ & π e^- which undergoes $\pi \rightarrow \pi^*$ transition.

Effect of presence of auxochrome on chromophore:-

- 1) Bathochromic shift:- It involves shift of absorption max. towards longer wavelength. It can be due by:-

$$u = - \frac{y_2 f(x)}{W}$$

$$= \int \frac{y_1 f(x)}{W} dx, \quad v = \int \frac{y_1 f(x)}{W} dx$$

(i) By attachment of auxochrome to chromophore:- When an auxochrome such as $-OH$, $-OR$, $-NH_2$ is attached to a chromophore it leads to conjugation. As a result, absorption shifts to longer wavelength.

(b) By conjugation of 2 or more chromophoric groups:- Bathochromic shift is also produced if 2 or more chromophoric groups are present in conjugation in a molecule.

(c) By change of solvent:- It is also possible to achieve bathochromic shift by change of solvent. For eg:- use of solvent of lower polarity (such as hexane) produces a red shift in the $n \rightarrow \pi^*$ absorption of carbonyl compounds.

(ii) Hypsochromic Shift:- It involves the shift of absorption max towards shorter wavelength. It may be done by:-

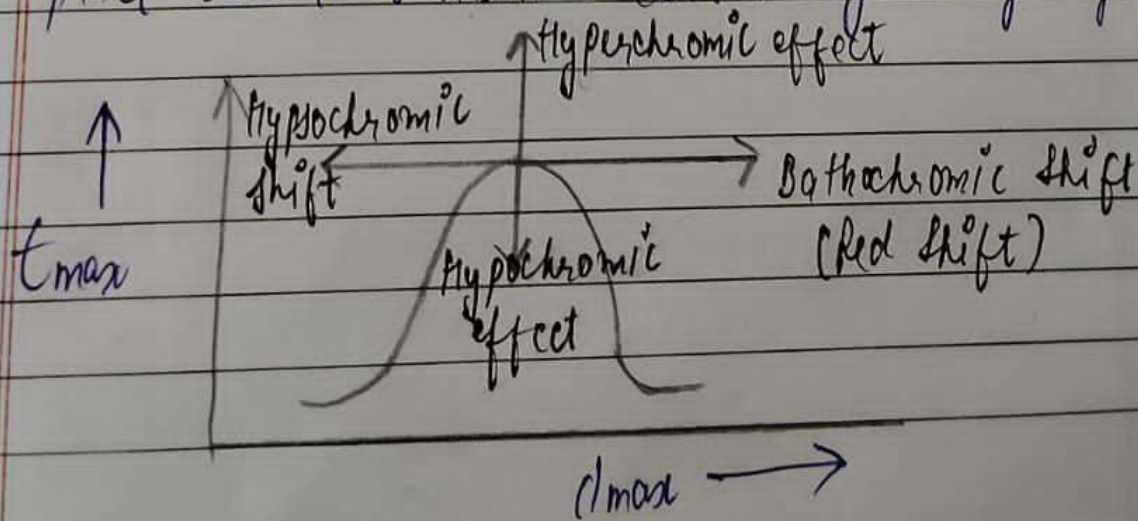
(a) By removal of conjugation:- For eg \rightarrow protonation of aniline causes a blue shift from 280 nm to 208 nm.

$$\frac{\begin{vmatrix} e^{3x} & xe^{3x} \\ 3e^{3x} & 3xe^{3x} + e^{3x} \end{vmatrix}}{\cdot (e^{3x})^2 (3x+1) - (e^{3x})^2 (3x)} = \frac{e^{6x} (3x+1 - 3x)}{e^{6x} (3x+1 - 3x)} = 1$$

(b) By change of solvent: for eg: use of solvent of higher polarity (such as H₂O) cause a blue shift in $n \rightarrow \pi^*$ absorption of acetone.

v) Hyperchromic shift: This effect involves an increase in intensity of absorption. It is usually brought about by intro of auxochrome. for eg: introduction of methyl group in position 2 of Pyridine increased ϵ_{max} from 9750 to 3560 for $\pi \rightarrow \pi^*$ transition. (λ_{max} shift from 250 nm to 237 nm).

v) Hypochromic shift: It involves decreases in intensity of absorption. It is brought about by groups which distort the geometry of molecule. for eg: when a methyl group is introduced in position 2 of biphenyl, hypochromic effect take place due to distortion caused by methyl group.



$$u = - \int \frac{y_2 f(x)}{w} = \frac{[e^{2x}]}{2}, \quad v = \int \frac{y_1 f(x)}{w}$$

$$N = - \int \frac{e^{2x} \sin x}{x} dx$$

Application of UV Spectroscopy:

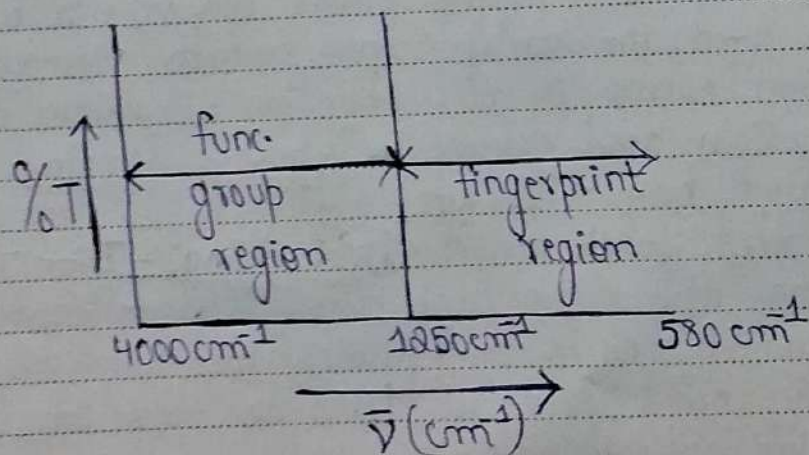
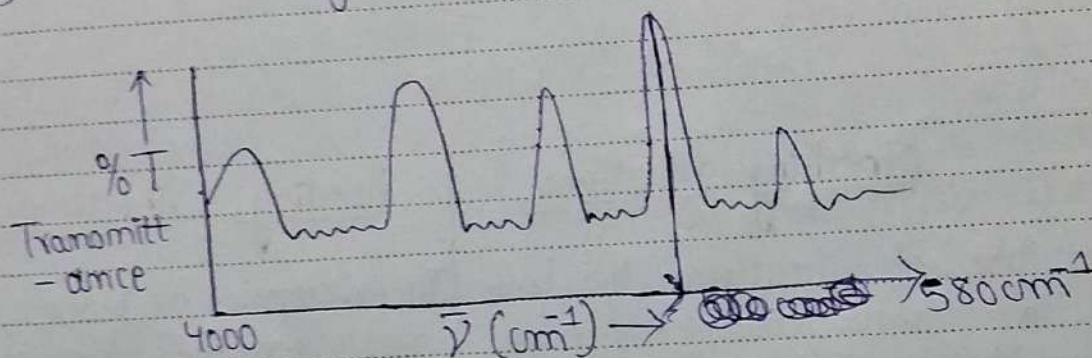
- 1) Detection of conjugation
- 2) Extent of conjugation
- 3) Determination of configuration of geometrical isomers
- 4) Detection of functional group
- 5) Determination of strength of H-bonded
- 6) Study of keto-enol tautomerism
- 7) Quantitative Analysis
- 8) Purification control

Part-2

Date.....

* IR Spectroscopy \rightarrow Infrared absorption spectroscopy concerns the absorption of radiation in the infrared range and is probably the single most widely used method for investigating the structures of organic substances. The instrument used for recording the infrared spectra is known as infrared spectrophotometer. Most of infrared spectrophotometers having a range of $2.5 \mu\text{m}$ (or 4000 cm^{-1}) to $17 \mu\text{m}$ (580 cm^{-1}). The IR region below $2.5 \mu\text{m}$ is generally known as near infrared and that above $17 \mu\text{m}$ is known as far-infrared region.

* Band intensity is expressed in terms of absorbance (A) or Transmittance (T); the two being related to each other as



* Absorption or Transmittance bands from 4000 to 1250 cm^{-1} are associated with changes in the vibrational state of the bond.

Date.....

It gives the information about the functional group.

* Transmittance bands from 1250 to 580cm^{-1} are sharp bands which are not easy to read

* Basic theory of Infrared spectroscopy: Molecular vibrations

Atoms in a molecule are not held rigidly in fixed positions. They are rotating and vibrating in a number of ways. So the two major types of vibrations are

- (i) Stretching vibrations
- (ii) Bending vibrations

Stretching vibrations

In these type of vibrations the position of the atoms change. Thereby producing change in the bond length instead of bond angle. In a simple diatomic molecule A-B, the only vibration which can occur is a rhythmic compression and extension along the A-B bond. This type of periodic back and forth movement of the atoms along the covalent bond axis which can be compared to that of a coiled spring is known as stretching vibration or bond stretching.

Bending Vibrations

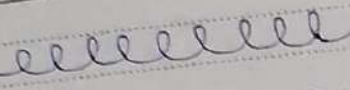
In diatomic or higher molecules there can be another type of vibrations involving change of bond angles. Such vibrational movements are referred to as bending vibrations or deformations.

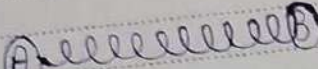
* Types of Bending vibrations \Rightarrow

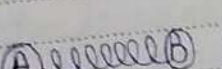
(i) Scissoring \Rightarrow This is an in-plane bending vibration, in which the two atoms move towards each other (Fig. 2.3a)



Swastik

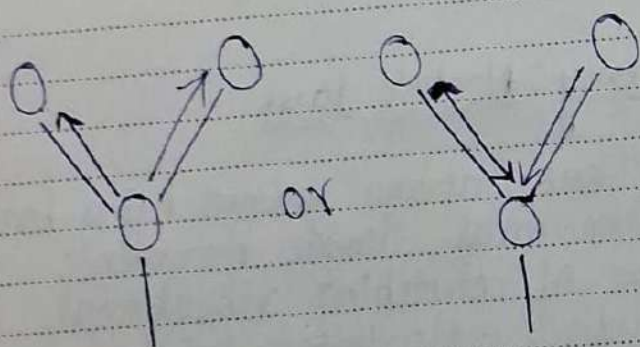
(A)  (B) Extended

(A)  (B) Average

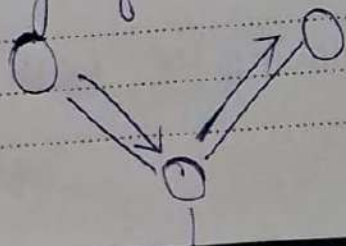
(A)  (B) Compressed

In triatomic or higher molecules, the stretching vibrations can be of two types:-

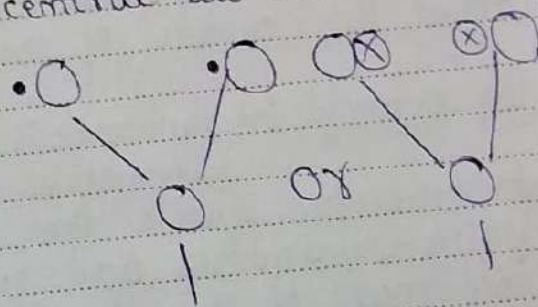
(i) Symmetric stretching:- It is the stretching vibration in which the movement of atoms with respect to the central atom in the molecule is in the same direction.



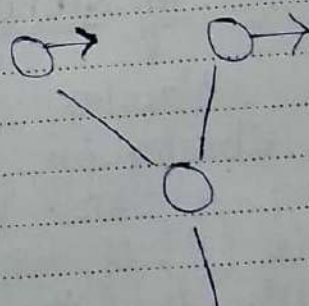
(ii) Asymmetric stretching:- It is the stretching vibration in which one atom moves towards the central atom while the other moves away from it.



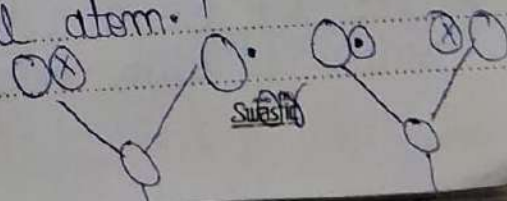
(ii) Wagging:- This is an out of plane bending vibration in which the two atoms move simultaneously either above or below the plane with respect to the central atom.



(iii) Rocking:- This is an in-plane bending vibration in which the two atoms move in the same direction.



(iv) Twisting:- This is an out of the plane bending vibration in which one atom moves above the plane while the other moves down the plane with respect to the central atom.



* Selection Rules \Rightarrow

for the Infrared spectrum, the selection rule states that only those vibrations are effective in causing absorption which are not centre-symmetric (i.e. the vibrations are not symmetrical about the centre of the molecule)

for example \Rightarrow symmetric stretching vibrations of CO_2 are centre-symmetric and are not effective in infrared spectroscopy while the asymmetric stretching vibrations are not centre-symmetric and give rise to absorption in infrared region. Since most of the functional groups in organic chemistry such as $\text{C}=\text{O}$, $\text{O}-\text{H}$ and $\text{N}-\text{H}$, HCl , HBr , which are not centre-symmetric, they respond very well to infrared spectroscopy.

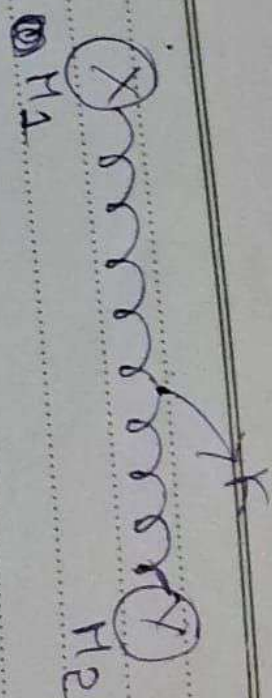
* Calculation of vibrational frequency: Hooke's law

Diatomic molecules consisting of two atoms joined by a bond which vibrates by a one-dimensional Simple Harmonic Oscillating motion. So, the value of stretching vibrational frequency (ν) of the bond can be calculated fairly accurately by the application of Hooke's law which may be represented as: \Rightarrow

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

\rightarrow force constant
 \rightarrow reduced mass

* Let XY be a diatomic molecule having X with mass M_1 and Y with mass M_2



Now, the reduced mass of the molecule is given by μ

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

* k is the force constant of the bond which relates to the strength of the bond.

We know that $\lambda = \frac{c}{\nu}$

$$\nu = \frac{c}{\lambda}$$

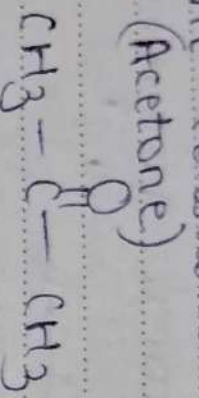
$$\text{or } \bar{\nu} \cdot \lambda = c$$

So,
$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

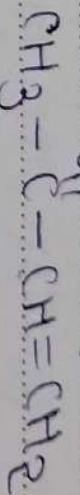
and hence $\nu_{\text{C=O}}$ is around 1700 cm^{-1}

methyl vinyl ketone

* Example



$\nu = 1715 \text{ cm}^{-1}$



$\nu = 1690 \text{ cm}^{-1}$

* Applications of Infrared Spectroscopy

① Identification of substance: \rightarrow Infrared Spectroscopy is very

Date.....

often used to establish whether given sample of an organic substance is identical with another or not. - Due to the large number

* But infrared spectroscopy fails to distinguish between enantiomers.

(ii) Determination of functional group and molecular structure:->

from the position of absorption bands in the spectrum, it is often possible to establish the nature of the groups present in the molecule.

(iii) Studying the progress of reactions:-> Progress of a chemical reaction can be readily

followed by examining spectra of small portions of reaction mixture withdrawn from time to time. The rate of disappearance of a characteristic absorption band of a reactant group or the rate of increasing absorption bands due to the formation of some products help in studying the progress of the reaction.

(iv) Detection of impurities:-> In contrast with the spectrum of the pure compound, the spectrum of an impure compound is blurred and not so sharp and contains many extra bands. Thus the impurity can be detected