

$$\begin{aligned}
 NCV &= 4189.225 \cdot 97.12 - 8 \times 0.691 \times 587 \\
 &= 922.597 - \dots \\
 &= 8803.261 \text{ k cal/kg}
 \end{aligned}$$

out unit. μJ kg^{-1} K^{-1} W^{-1}

UNIT-II At room temperature \rightarrow 2 kcal

SPECTROSCOPY

It is the branch of science that deals with the study of interaction of electromagnetic radiation with an unknown sample.

Spectroscopy deals with the transition that a molecule (sample) undergoes between its energy level on absorption or suitable radiation.

It is the analysis of electromagnetic radiation absorbed or emitted by a sample.

Spectroscopic technique is useful because

- (i) It takes much less time.
- (ii) A small amount of sample is required for spectroscopic technique.
- (iii) Sample remain unaffected or unchanged after spectroscopic analysis.

LAWS OF LIGHT ABSORBANCE

The spectrum of organic compounds are usually recorded in solution form and therefore, it is convenient to involve the use of these two laws :-

(1) Lambert's Law :-

When a homogeneous solution of sample absorbs monochromatic radiation, then the rate of decrease in the intensity of radiation with respect to thickness of the medium is directly proportional to the intensity of incident radiation.

$$\frac{-dI}{dx} \propto I_0$$

$\frac{-dI}{dx} = kI$ absorption coefficient

By integrating,

$$\int_{I_0}^I \frac{-dI}{I} = k \int_0^x dx$$

$$I = I_0 e^{-kx}$$

$$I = I_0 \cdot 10^{-ax}$$

where $a = k$ extinction coefficient

(2) Beer's

When a monochromatic light passes through a medium, it follows Beer's law as well

$$\frac{-dI}{dx}$$

$$-d$$

$$I$$

$$I_0$$

$$0$$

$$0$$

$$0$$

$$0$$

(2) Brewer's Law

Given a homogeneous solution of example absorbed monochromatic radiation from the rays of source. If the intensity of radiation varies with thickness of the medium, or Intensity of incident radiation as well as concentration of the solution.

$$\frac{-dI}{dn} \propto I \cdot C \rightarrow \text{cone: } \text{fr. mol/L}$$

$$\frac{-dI}{dn} = K' I \cdot C \rightarrow \text{molar absorption coefficient}$$

By integrating,

$$\int_{I_0}^I \frac{-dI}{I} = K' c \int_{n=0}^{n=a} dn$$

$$\text{or } I = I_0 e^{-K' c n} \rightarrow \text{molar extinction coefficient}$$

$$\text{or } I = I_0 \cdot 10^{-\alpha' c n} \text{ where } \alpha' = \frac{K'}{2.303}$$

$$\text{or } \log \frac{I_0}{I} = \alpha' c n = \beta c n = A$$

molar extinction coefficient
or Absorptivity

$$\rightarrow \beta c n = A$$

$$\frac{1}{2} \times \frac{1}{2} = \alpha$$

Q. A solution of a compound having conc. 0.1 g/l gives 0.2 absorbance value when measured using 1 cm cell. Calculate absorptivity and molar absorptivity? Given: Molar mass of sample = 200 .

$$A = \epsilon c l$$

$$\epsilon = A / (c l) = 0.2 / (0.1 \times 1) = 2$$

$$\epsilon = A / (c l) = 0.2 / (0.1 \times 1) = 200$$

↓ ↓
molar (in mole) absorptivity

UV (ultraviolet) spectroscopy

Electronic spectroscopy = E.S.

UV Spectroscopy is also called Electronic Spectroscopy since it involves the transition of electrons (σ, π, π^*) from lower energy to higher energy level.

If a sample is exposed to radiation of UV range, then the electrons of that sample will absorb radiation of a particular frequency which is equal to their energy of transition.

The UV ^{range} radiation can be divided into two types

→ ① Near UV range

Radiation with wavelength between 2000 \AA to 1000 \AA falls in near UV range and the excitation of this range are responsible for transition by (σ, π, n).

→ ② Near or Far or Vacuum UV range

The radiation with wavelength below 2000 \AA falls in far UV range, Spectroscopic technique can not be used below this range because oxygen present in air begins to absorb & ionize. So, to study such high energy transition vacuum instruments are required.

UV transition or electronic Transition

By the absorption of UV radiation 4 types of electronic transition are possible,

① $\sigma \rightarrow \sigma^*$ transition

The transition of σ electrons from bonding orbital to anti-bonding by the absorption of UV radiation is known as $\sigma \rightarrow \sigma^*$ transition.

Three type of transition are possible in those molecules having only single bonds and no lone pair.

To study such high energy transition "special" vacuum instruments are required so, spectroscopy technique cannot be used to study such high energy transition.

(iii) $n \rightarrow \pi^*$ transition

The transition of non-bonded electrons if from $n \rightarrow \pi^*$ by the absorption of UV radiation is called $n \rightarrow \pi^*$ transition. These type of transition are formed in those compounds having only single bonds and an atom containing lone pair.

for ex:- Amines, alcohol and Saturated alkyl halides etc.

(iv) $\pi \rightarrow \pi^*$ transition

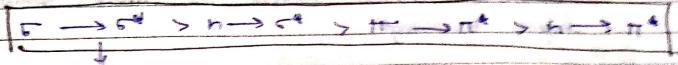
The transition of π -electrons from bonding to anti-bonding orbitals is called $\pi \rightarrow \pi^*$ transition. These transition are possible in those compounds only containing having double and triple bonds.

for ex:- Alkene and Alkyne

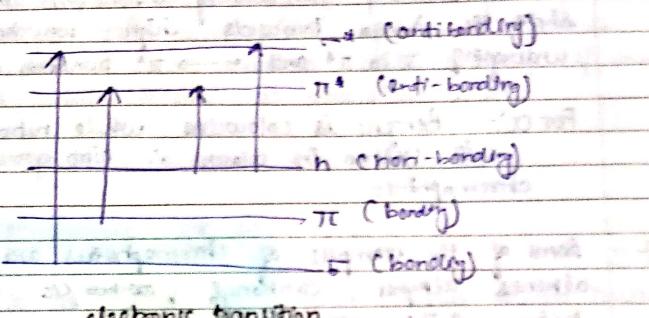
(v) $n \rightarrow \pi^*$ transition

Transition of lone pair of electrons from n to π anti-bonding orbital is called $n \rightarrow \pi^*$ transition. These type of transition are possible in those compounds having double or triple bond and an atom containing lone pair.

ex - Carbonyl compounds, O_2O groups etc



electronic transition in decreasing order of their energy.



Effect of polar solvents on electronic transition

In $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transition ground state is polar so high energy radiation is required for the transition of non-bonding electrons to π -anti-bonding and π -antibonding orbitals which shifts the λ_{max} towards lower wavelength.

For ex - carbonyl compound, alcohol, amines, $\text{C}=\text{O}$.

In $\pi \rightarrow \pi^*$ transition ground state is non-polar so low energy radiation is required from the

transition of π electrons to π^* anti-bonding orbitals which shift the λ_{max} towards higher wavelength.

c) Chromophore means colour causing. Chromophores are the covalently bonded groups containing π -electrons and non bonding electrons (n). They shift the λ_{max} towards higher wavelength by undergoing $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition.

For ex:- Benzene is colourless while nitro-benzene is yellow in colour. \therefore Nitro group is a chromophore.

d) Some of the examples of chromophores are :- alkenes, alkynes, carbonyls, carboxylic acids, nitro, $-C\equiv N$ groups.

① I

Auochromes \rightarrow (colour enhancing group)

An Auochromes is a colour enhancing group. It can be defined as any group which does not act as a chromophore but whose presence shifts the λ_{max} towards higher wavelength.

Auochromes have one or more lone pair of electrons and therefore they increase the conjugation of the sample by sharing their lone pair of electrons which shifts the λ_{max} towards higher wavelength.

Some examples of auochromes are such as

Page No. _____
Date _____

-OH, -OR, -NH₂, -NHR, -NR₂

UV shift / absorption shift / Intensity shift

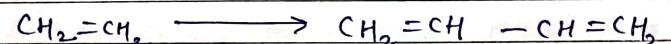
There are certain factors which are responsible for changing the energy of transition for a particular sample which cause shifting of λ_{max} towards higher or lower wavelength with shifting of λ_{max} is called UV shift or absorption shift.

It can be divided into four types.

① Bathochromic or red shift

It is an effect by which λ_{max} shifted towards higher wavelength. It is due to following factors are responsible for this shift.

→ Increase in conjugation



$$\lambda_{max} = 1750 \text{ Å}^\circ \quad \lambda_{max} = 2170 \text{ Å}^\circ$$

→ presence of auxochrome



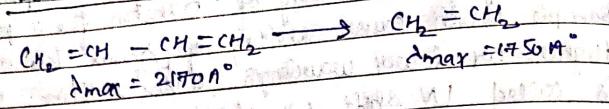
$$\lambda_{max} = 2550 \text{ Å}^\circ$$

$$\lambda_{max} = 2900 \text{ Å}^\circ$$

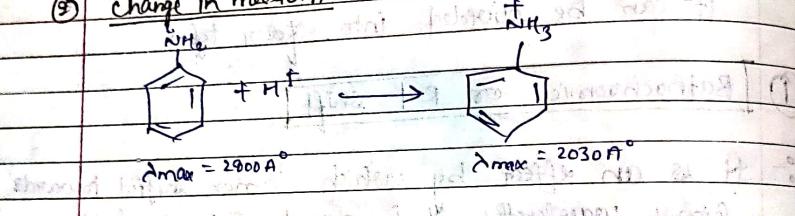
Hypsochromic or Blue shift

(2) It is an effect by which λ_{max} is shifted towards lower wavelength & it is due to following factors

(1) Decrease in conjugation



(2) change in medium

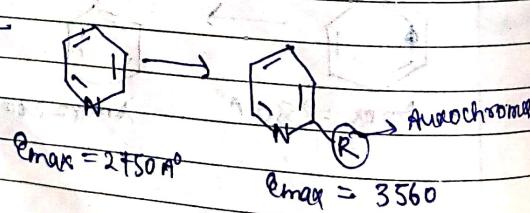


(3) Increase in polarity of solvent shifts the λ_{max} towards lower wavelength for $n \rightarrow \pi^*$ transition
eg:- Carbonyl compounds

Hyperchromic shift

It is an effect due to which intensity of absorption maximum (ϵ_{max}) increases.

for example:-



Hypochromic

If it is at maximum

It is

Ex:-

6

Apk

(1) Distinc
syst

eg:-

(2) Deter

dm

(3) Dba

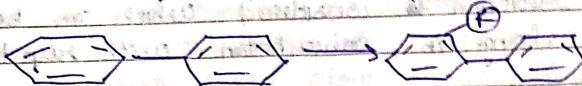
dp
gu
dq

④ Hypochromic drift

If it is an effect due to which intensity of absorption maximum (E_{max}) decreases

If it is due to following factors :-

e.g:-

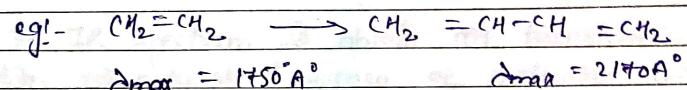


$$E_{max} = 19000$$

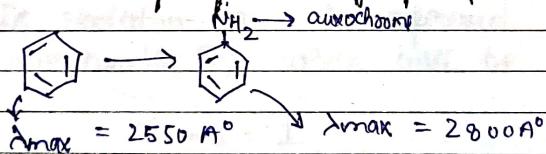
$$E_{max} = 10250$$

Applications of UV Spectroscopy

- ① Distinction between conjugated and non-conjugated system.



- ② Detection of a functional group present in a sample.



- ③ Distinction between inter and intra molecular H-Bonds.

Spectrum of sample is taken at different conc. is recorded. If all the effects are same, then there is intra molecular H-Bonding but if the effects

changes with change in conc. of solvent; then there is inter molecular H-Bonding.

To study the kinetics of reaction

Kinetics in a chemical reaction is considered which can be defined as change in concentration with respect to time.

As absorption or concentration, so with the help of UV spectrum path of reaction can easily be followed

Infrared (IR) Spectroscopy

'or'

Vibrational Spectroscopy

In IR spectroscopy, IR radiations are used. IR radiations are more energy radiation, therefore they do not cause transition of electrons. However, IR radiations are capable for the atoms or group of atoms to vibrate faster about the covalent bond connecting them. Since absorption of IR radiation results in the transition of atoms from lower to higher in the change in vibrational and rotational energy therefore some fine lines are also observed in IR spectrum.

Therefore IR spectrum is also known as vibrational - rotational spectrum.

In IR spectrum is obtained when transition takes place when the natural frequency of molecular vibration matches with the frequency of Incident IR radiation.

IR radiation can be expressed in terms of wave number (ν) which will be

$$\nu \text{ (cm}^{-1}\text{)} = \frac{1}{\lambda \text{ (cm)}}$$

The Radiation of IR range can be divided into three near IR range:- Radiation with wave number ($12500 - 4000 \text{ cm}^{-1}$) belongs to the near IR range.

① Models or normal IR range

The oscillation with wave number $4000 - 167 \text{ cm}^{-1}$ belongs to middle IR range. The oscillation of this range are responsible for stretching and vibrations transition of CH_3 molecules.

② For IR range: ~~for IR range~~ ~~for IR range~~

The oscillation with wave number $167 - 50 \text{ cm}^{-1}$ belongs to far IR range.

In IR spectroscopy change in vibrational energy by the absorption of IR radiation depends on

- ① masses of atoms involved - homotropies
- ② arrangement of atoms
- ③ strength of bonds involved in molecule

Two kinds of molecular vibration which are possible in a diatomic are

- ① Stretching vibration: H_2 and nitrobenzene etc.
- ② Bending vibration: nitro NO_2 etc.

① In this type of vibration, the distance between the atoms increase or decrease but they remain in the same bond axis. i.e. bond length changes but the bond angle remains constant.

There are two

- ① Symmetric
- ② Asymmetric

- ① In this type particularly atoms



- ② In this type atom is in the



Bending

In this atoms change shape

Bending

In this direction

I can't
find this
information

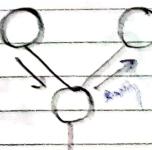
There are two types of stretching vibration

- ① Symmetric stretching
- ② Asymmetric stretching

- ① In this type, movement of atoms w.r.t a particular atom is in the same direction



- ② In this vibration, movement of atoms w.r.t a particular atom is in the opposite direction.



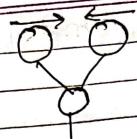
Bending vibration

In this type of vibration, the distance between the atoms remains constant but the position of atoms change w.r.t. original bond angle i.e. bond angle changes but the bond length remains constant

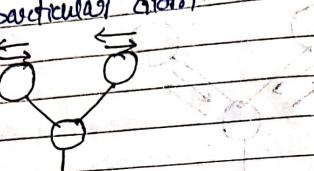
Bending vibration are of 2 types

- ① Scissoring

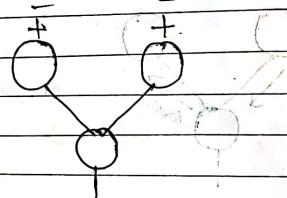
- In this type, movement atoms swing in opposite direction w.r.t. a particular atom



(2) Rocking:- In this type atoms swing in same direction w.r.t a particular atom

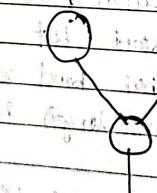


(3) wagging :- In this type both the atoms move above or below the plane w.r.t a particular atom



(4) Twisting

In this type one atom move above the plane while other move down the plane w.r.t a particular atom



Number of

Free

In polyatomic
molecules or SI

three fundamental
degree of
equal to
degree of

Degrees of freedom

(3n)

no. of atoms
in d.mot

In Non

3n =

V =

In di

3n

V =

Number of Fundamental vibration

or

Fundamental Bands

In polyatomic molecules large number of fundamental bands or sharp peaks are observed.

The no. of these fundamental bands are depend on the degree of freedom in a molecule which will be equal to translational, vibrational and rotational degrees of freedom.

$$\text{Degree of freedom} = T + V + \text{Rotational degree of freedom}$$

$$(3n)$$

no. of atoms in a molecule

In Non-linear molecule:

$$3n = 3 + V + 3 \times 6, \text{ Ex: } \text{O}_2 \Rightarrow 3 + 3 = 3n - 5$$

$$V = 3n - 6$$

In Linear molecule:

$$3n = 3 + V + 2, \text{ Ex: } \text{CH}_4 \Rightarrow 3n - 6$$

$$V = 3n - 5 \Rightarrow 3 \times 5 - 6$$

9

Vibrational frequency

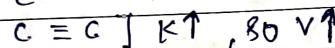
The frequency of IR radiation required for the transition of a diatomic molecules with atomic masses m_1 and m_2 , joined by a chemical bond is given by Hooke's law

According to Hooke's law

$$V = \frac{1}{2\pi c} \sqrt{\frac{k}{m}} \quad \text{Force const. it depends on the strength of bond}$$

Reduced mass $(m_1 m_2) / (m_1 + m_2)$

e.g. (1) C-C



e.g. (2) C-H



Conditions for IR absorption:

(1) IR absorption takes place when the natural frequency of molecule matching with the frequency of incident IR radiation ν

(2) If change in vibrational energy resulted in changes in the dipole moment of the

molecules, IR a

Finger poi

IR spectrum

- (i) Functional group
- (ii) Fingerprint region

- (iii) The region we is called few useful for group in a

for ex:-

(1) peak at 167cm^{-1}

(2) peak at 1

(3) peak at 3

(4) peak at 3

(5) peak at 1

(2) Molecules

Fingerprint region spectrum can be assigned to finger number

molecules, IR absorption takes place?

Finger print region

IR spectrum can be divided into two regions

(i) Functional group region

(2) Fingerprint region

(i) The region which extends from 4000 to 1500 cm^{-1} is called functional group region. This region is useful for the detection of presence of functional group in an unknown sample.

for ex:-

Functional group region	
(1) peak at $1670 - 1620\text{ cm}^{-1}$	presence of $\text{C}=\text{C}$
(2) peak at 1650 cm^{-1}	Carbonyl group
(3) peak at 3570 cm^{-1}	alcohol
(4) peak at $3550 - 3250\text{ cm}^{-1}$	Amide group
(5) peak at 1725 cm^{-1}	Ketone

(2) Molecules having same functional group gives same spectrum in functional fingerprint region but they can be distinguish in fingerprint region as this region is rich in sharp peaks but very rich in number of fine lines due to bending vibrations

For example:-

→ range

peak at 1350 cm^{-1}

peak at 1200 cm^{-1}

peak at $1380 - 1050\text{ cm}^{-1}$

Peak at $1350 - 1260\text{ cm}^{-1}$

possible group

- No group

Phenol

Ester

primary alcohol

The sample - P1

at $3600 - 3$

Free proton

bond to fit

bond will a

Determination

If impurity is
in splitting

Applications of IR Spectroscopy

(1) Distinction between Intra and Inter molecular Hydrogen bonding.

(2) To Study the Kinetics of the reaction

IR spectrum is useful in the study of reaction kinetics for example, during oxidation of alcohol to ketone the peak at 3870 cm^{-1} disappeared and got obtained at 1725 cm^{-1} when etho → ketone is formed.

(3) To detect presence of water in a sample

If a sample is crystallised by water, it may be possible that some water remains in

Page No.		
Date		

the sample. If that case the peak will appear in the range of $3600 - 3200 \text{ cm}^{-1}$. But if the water molecule is present as ligand and form a coordinate bond to the metal ion of the sample then the band will appear in the range of $800 - 650 \text{ cm}^{-1}$.

Determination of purity of a sample

If impurity is present in the sample, it will result in splitting of peaks or blurring of spectrum.