

Unit V

Spectroscopic Techniques

Introduction

Spectroscopy is the branch of science that deals with the study of interaction of electromagnetic radiations with matter.

Spectroscopy is one of the powerful tools available for the study of atomic & molecular structure. It is used in the analysis of wide range of substances.

The spectroscopic techniques uses either absorbed or emitted or scattered electromagnetic radiations by atoms or molecule present in the substances.

Spectroscopy deals with interaction of electromagnetic radiations with matter. Due to these interaction energy is absorbed or emitted by the matter. Therefore spectroscopy is of two types

1) Absorption spectroscopy —

In absorption spectroscopy a beam of polychromatic light falls on a sample. Part of light absorbed by the sample & remaining part is transmitted. The intensity of transmitted light is measured as a graph of intensity of absorbed radiations.

2) Emission spectroscopy —

In this technique, sample is subjected to intense source of energy & electrons in the sample are excited to higher energy state. When the electrons come back to ground state energy level they emit radiations. These radiations are analyzed.

- Sed by spectrophotometer to generate (graph) spectrum that gives information about atoms present in the sample.

- Electromagnetic radiations is a form of energy that is transmitted through space with high velocity.

- Electromagnetic radiations are in the form of transverse wave, is characterised by wavelength (λ), frequency (ν) & wave number ($\bar{\nu}$).

- wavelength (λ): — Wavelength of radiation is the distance betⁿ two successive crests or troughs. It is expressed in meters or cm

- Frequency (ν):

It is the number of waves pass through a fixed point in unit time. It is expressed in s^{-1} or Hertz (Hz)

- Wave number ($\bar{\nu}$)

It is the reciprocal of wavelength & expressed as cm^{-1}

The energy associated with electromagnetic radiations is given by,

$$E = h\nu = \frac{hc}{\lambda}$$

E = Energy of radiations in joules, ν = Frequency of radiation in Hz
h = Planks constant

c = Velocity of light

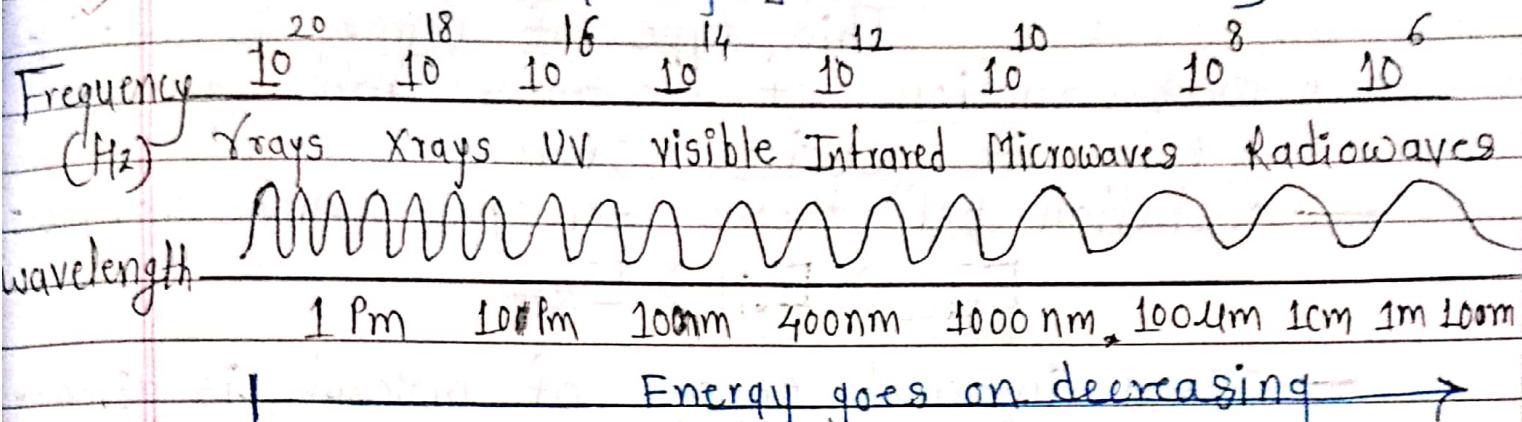
- Electromagnetic spectrum consists of arrangement of all types of electromagnetic radiations in the order of their increasing wavelength & decreasing frequency.
As the wavelength goes on increasing,

* Characteristics of electromagnetic radiations :-

- i) Electromagnetic radiations is a form of energy that is transmitted through space with high velocity.
- ii) Electromagnetic radiations consist of (discrete packets of energy) which are called photons.
- iii) Electromagnetic radiations propagates in space without any material medium in the form of transverse wave.
- iv) An electromagnetic radiation, being a transverse wave, is characterised by wavelength (λ), frequency (ν) & wave number (\bar{v}).

energy associated goes on decreasing.

frequency goes on increasing



~~★ Interaction of Electromagnetic radiation with matter :-~~

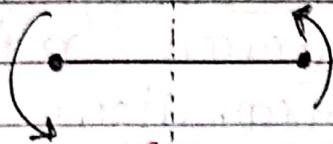
When an electromagnetic radiations falls on matter, it interacts with atoms/molecules present in the matter which exists in discrete energy levels.

i) Types of energies:-

Like atoms/molecules possess a set of discrete energy levels.

i) Rotational energy (E_{rot}):

This type of energy is associated with rotation of molecule about the axis passing through centre of gravity.



ii) Vibrational energy (E_{vib}):

This type of energy is associated with vibrations of molecule such as stretching or bending of bonds.



iii) Electronic energy (E_{elec}) :-

This type of energy is associated with (motion) of electrons from ground state to excited state.

— Relation betⁿ these energies can be shown as

$$E_{\text{elec}} > E_{\text{vib}} > E_{\text{rot}}$$

— Total internal energy of molecule is given by

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

2) Molecular energy Levels :-

Total energy states of molecule include electronic, vibrational & rotational levels.

i) Rotational energy Levels —

These are very closely spaced. Little energy is required for rotational energy transition which occurs in microwave region.

ii) Vibrational energy levels —

These are spaced further apart (i.e far apart). Vibrational energy transitions require more energy. These transitions occur in infrared region of spectrum. Vibrational transitions are observed with rotational transitions.

iii) Electronic (transition) energy levels —

If further higher energy is applied, electronic transition take place from ground state to excited state. Such transition occurs in U.V-visible region of spectrum. Electronic transitions are accom-

-caused by vibrational energy changes & each vibrational level change is accompanied by rotational level change. The resulting spectrum is more complicated because it consists of lines due to electronic, vibrational as well as rotational transitions.

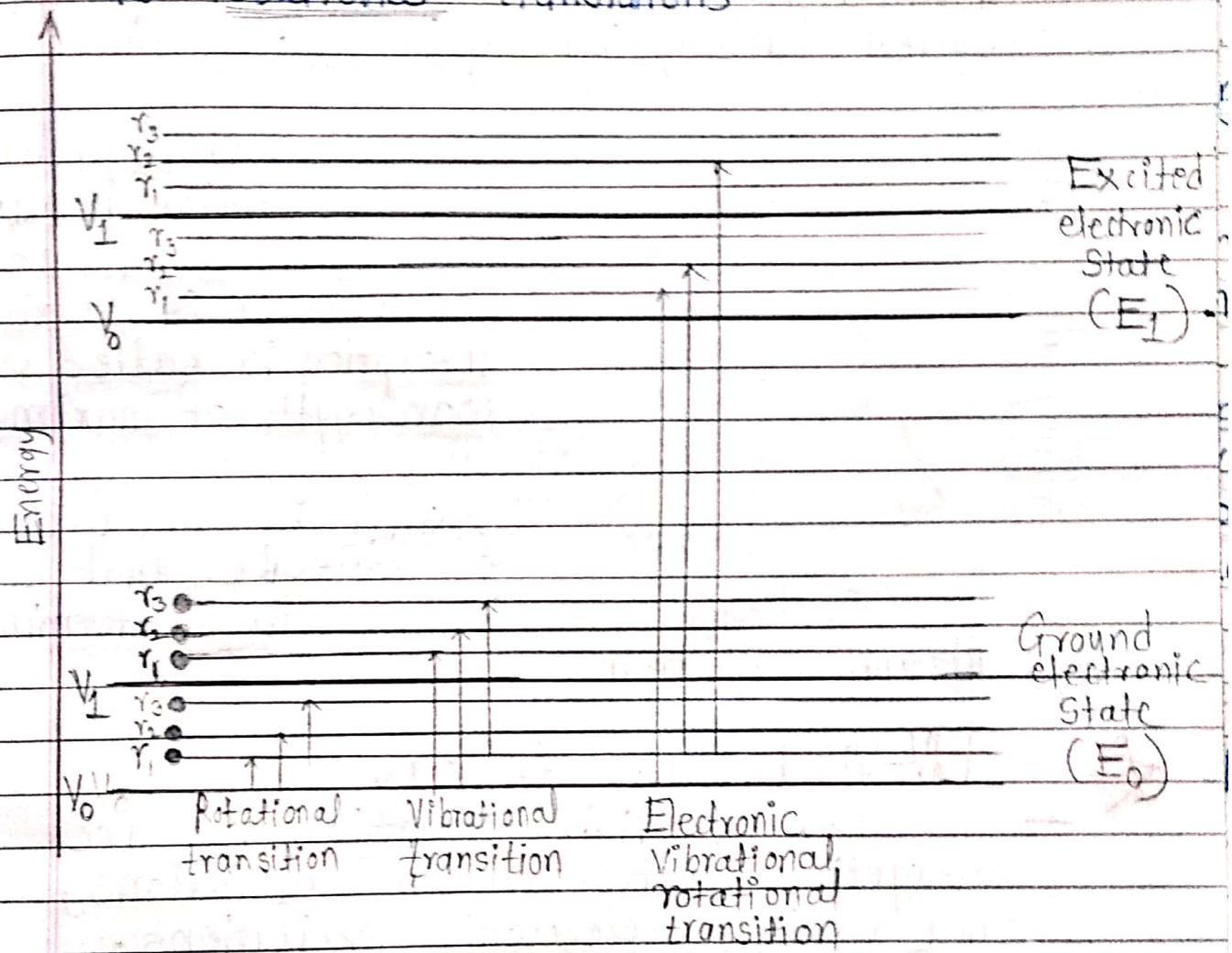


fig Energy level diagram
(r_1, r_2, r_3 are rotational levels & V_0, V_1 , etc are vibrational levels)

3) Absorption spectrum :-

Molecules absorb energy in the form of quanta to cause excitation from one energy level to another.

In absorption spectroscopy

the energy absorbed by sample at various wavelengths of incident radiations & measuring decrease in intensity of transmitted radiation.

A plot of energy absorbed as a function of wavelength or frequency is called absorption spectrum.

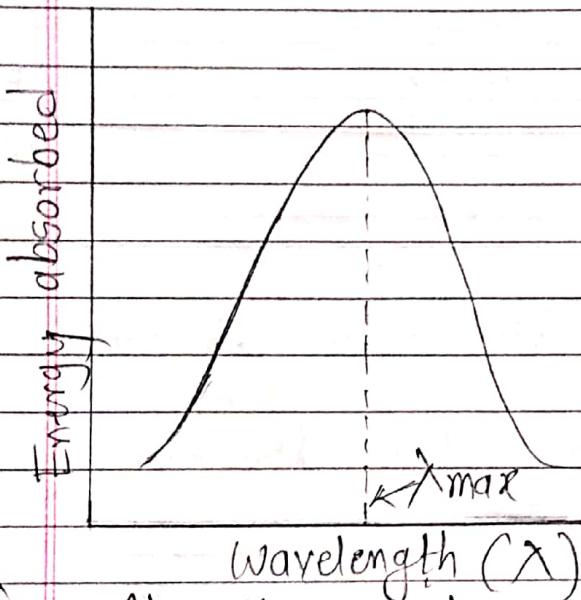


fig: Absorption spectrum

At particular wavelength the absorption is maximum. The wavelength at which there is maximum absorption is called as wavelength of maximum absorption (λ_{max}).

λ_{max} is characteristic of molecule that help in structure determination.



UV-Visible Spectroscopy

- U.V & visible radiations are energetic electromagnetic radiations, that brings electronic excitations.
- The electromagnetic radiations with wavelength range 10-400 nm are called Ultraviolet radiations & 400-800 nm are called visible light radiations.
- The ultraviolet region is subdivided in to two regions as,
 - Near U.V region:— from 200-400 nm
 - Far or Vacuum U.V region:— Below 200 nm

* Principle of U.V-Visible spectroscopy :-

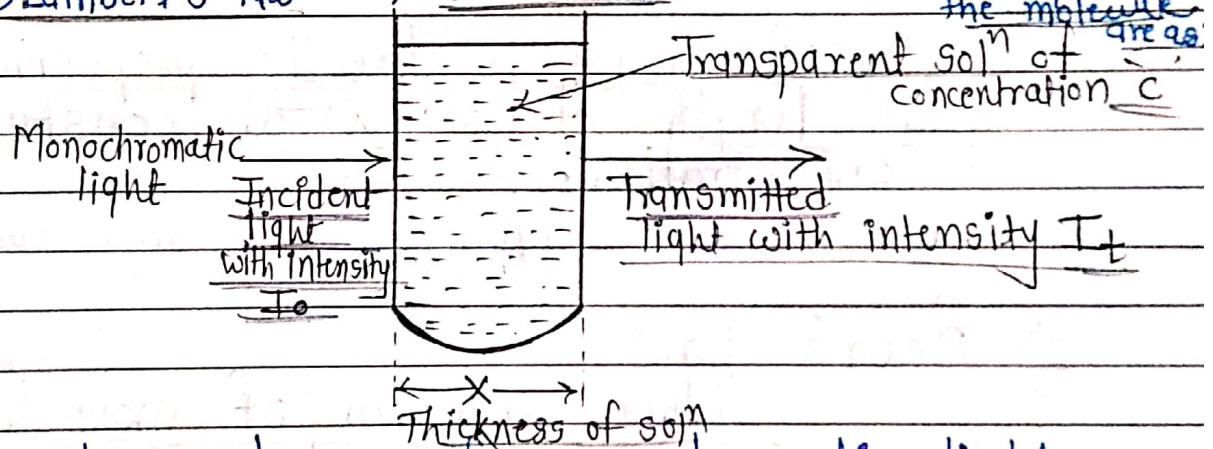
Absorption of U.V-visible radiations by sample brings about electronic excitation. Electronic excitations are accompanied by vibrational & rotational changes that results in relatively broad spectra.

Absorption spectra is a graph of absorption i.e. amount of light absorbed vs. wavelength of light & it is useful in determination of structure of molecule.

* Beers Law & Lambert's Law :-

The two laws which explain the absorption of light by the molecule.

1) Lambert's law \Rightarrow Beers law



Consider a beam of monochromatic light passing through transparent solution. Let I_0 be the intensity of incident radiation. When light is passed through a solⁿ, part of light is absorbed & remaining is transmitted. Let I_t be the intensity of transmitted light. Transmitted light has less intensity than incident light. Let 'x' be the diameter of sample holder (cuvette) which is the thickness (path length) of transparent solⁿ.

1) Lambert's Law:-

Statement -

When a beam of monochromatic light is passed through a transparent solution, decrease in intensity of incident radiation is directly proportional to path length at constant concentration.

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

where,

I_0 = Intensity of incident radiation

dx = Small thickness of solⁿ or path length

dI = small decrease in intensity of light = $I_0 - I_t$

or

Absorbance (A) is directly proportional to path length of solⁿ (X) at constant concentration.

$$A \propto X$$

2) Beer's Law:-

When a beam of monochromatic light is passed through a transparent solution, decrease in intensity of incident radiation is directly proportional to concentration at constant path length.

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

or

Absorbance (A) is directly proportional to concentration (C) of solution at constant path length.

$$A \propto C$$

3) Beer-Lambert's Law :-

It states that absorbance 'A' is directly proportional to path length (x) & concentration (c)

$$A \propto x \cdot c$$

$$A = k \cdot x \cdot c$$

Where k is proportionality constant called as absorptivity coefficient. If path length x is given in cm & concentration c is given in mol/lit, then proportionality constant is called as molar absorptivity coefficient or molar extinction coefficient indicated by ϵ .

Thus, Beer-Lambert's law can be represented as,

$$A = \epsilon \cdot x \cdot c$$

Amount of light transmitted is given by transmittance (T)

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

The relation betⁿ absorbance 'A' & transmittance (T) is given by

$$A = -\log T$$

Absorption of UV radiation by Organic molecule leading to different electronic transition

When energy is absorbed by a molecule in U.V-visible region, it brings changes in electronic energy of molecule because of transition of valence electrons from lower energy to higher energy.

3) types of electrons are involved in organic molecule:

i) σ electrons:

Electrons forming (single bonds) are called σ electrons. These are observed in (saturated hydrocarbons) such as $C-H$ bond.

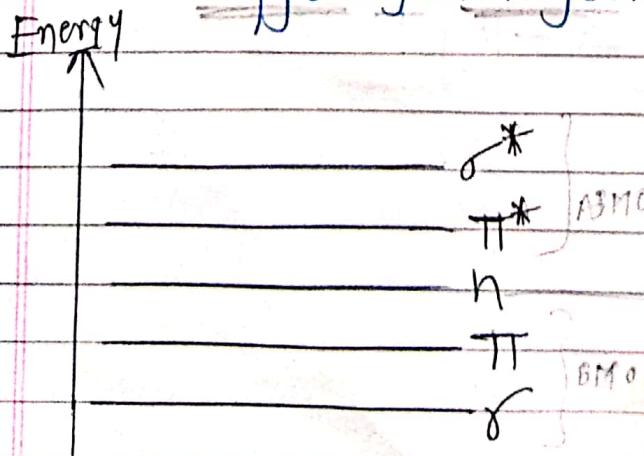
ii) π electrons:

Electrons forming (double bond) are called π electrons. These are observed in (unsaturated hydrocarbons) such as $C=C$ or $C\equiv C$ ($=C$ or $\equiv C$)

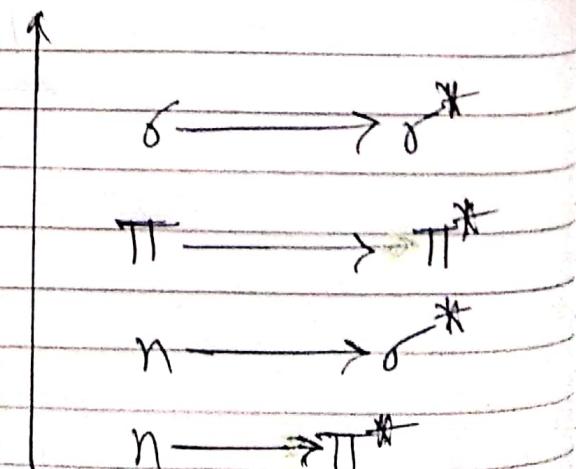
iii) n electrons:

These are (non bonded) or (lone pair of electrons). These are not involved in bonding betⁿ atoms in molecules eg lone pair of electrons present on oxygen, nitrogen, etc

Energy

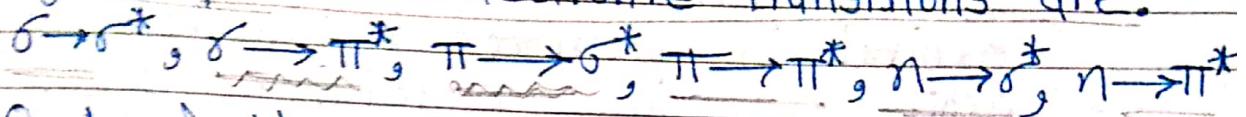


Electronic energy Levels



Possible electronic transitions.

When energy is absorbed in U.V-visible region possible electronic transitions are:



Out of these $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$ are considered as forbidden transitions.

The relative energies are in the following order:



i) $\sigma - \sigma^*$ Transition :-

σ electrons from bonding orbital is (excited) to the corresponding antibonding orbital. The energy required is large for this transition.

e.g. - Methane (CH_4) which has only C-H bonds & can only undergo $\sigma - \sigma^*$ transition (Range around 150 nm) e.g. all alkanes

ii) $\pi - \pi^*$ transition :-

π electrons in a (bonding) orbital is (excited) to corresponding (antibonding orbital) π^* . Compounds containing multiple bonds like alkenes, alkynes, nitriles, aromatic compounds undergoes $\pi - \pi^*$ transitions. (Range around $170-190 \text{ nm}$) e.g. All unsaturated compounds.

iii) $n - \sigma^*$ transition :-

Saturated compounds containing atoms with lone pair of electrons like O, N, S & halogens are capable of $n - \sigma^*$ transition. These transition usually require less energy than $\sigma - \sigma^*$ transitions. (Range around 185 nm)

iv) $n \rightarrow \pi^*$ transition :

An electron from non bonding orbital is promoted to antibonding π^* orbital. Compounds containing double bond involving heteroatoms $C=O$, $C\equiv N$, $C=S$ etc undergoes such transitions. It requires minimum energy & shows absorption at longer wavelength around 300 nm.

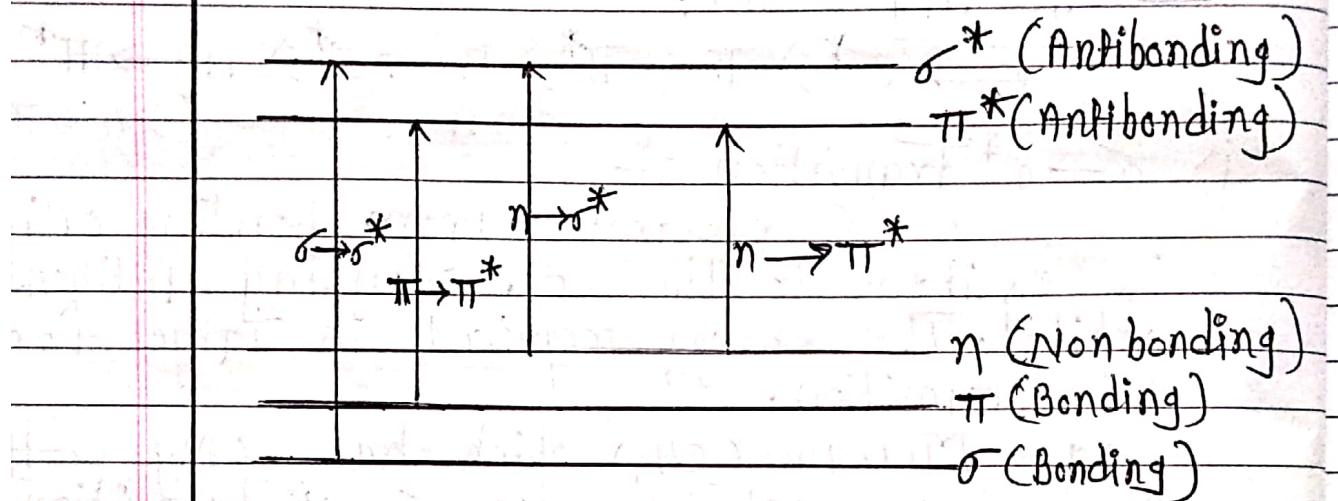


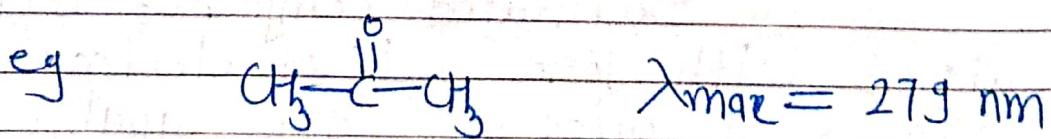
fig : Electronic transitions

★ Terms involved in UV-Visible Spectroscopy -

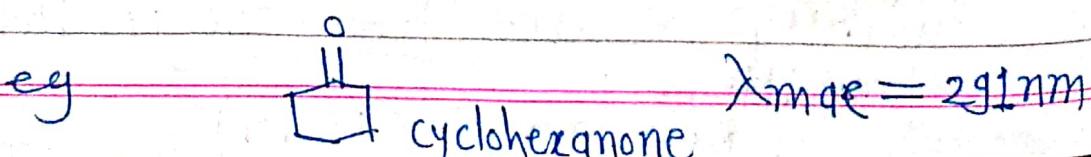
1) Chromophore :-

Chromophore is a functional group containing multiple bond capable of absorbing radiations above 200 nm due to $\pi \rightarrow \pi^*$ transitions & $n \rightarrow \pi^*$ transitions.

e.g. $N=O$, $C=O$, $C\equiv N$, $C=C$, $C=S$ etc



Acetone



2) Aurochrome

Aurochrome is a functional group with non-bonding electrons that does not absorb radiations in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

e.g.

Benzene



$$\lambda_{\text{max}} = 255 \text{ nm}$$

(chromophore)



Phenol

$$\lambda_{\text{max}} = 270 \text{ nm}$$

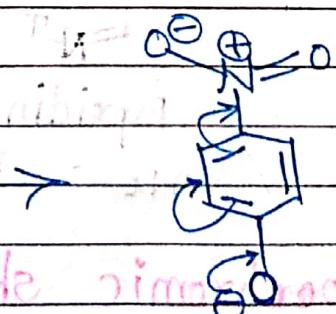
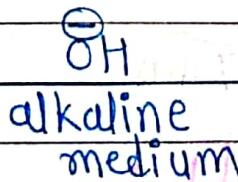
(Aurochrome)

3) Bathochromic shift (Red shift) :-

When absorption maxima (λ_{max}) of a compound shifts to longer wavelength it is known as bathochromic shift or red shift.

This effect is due to the presence of an aurochrome or by the change of solvent.

e.g. → An aurochrome group like $-\text{OH}$, $-\text{OCH}_3$ causes absorption of compound at longer wavelength.



$$\lambda_{\text{max}} = 255 \text{ nm}$$

$$\lambda_{\text{max}} = 265 \text{ nm}$$

p-nitrophenol

p-nitrophenoxide ion

In alkaline medium p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes electron more effectively than lone pair of

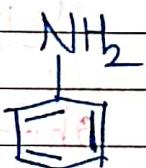
4) Hypsochromic shift (Blue shift) :-

When absorption maxima (λ_{max}) of a compound shifts to shorter wavelength it is known as hypsochromic shift or blue shift.)

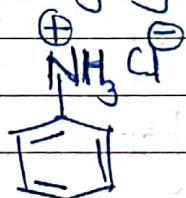
This shift caused due to -

- a) Removal of conjugation or / &
- b) Changing the polarity of the solvent.

eg → Aniline shows blue shift in acidic medium because it loses conjugation.



Acidic (HCl)
medium



$$\lambda_{max} = 280 \text{ nm}$$

Aniline

$$\lambda_{max} = 265 \text{ nm}$$

5) Hyperchromic shift :-

An increase in intensity of absorption maxima is called hyperchromic shift.

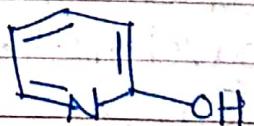
Introduction of quencher usually increases the intensity of absorption.

eg -



Pyridine

$$\lambda_{max} = 257 \text{ nm}$$

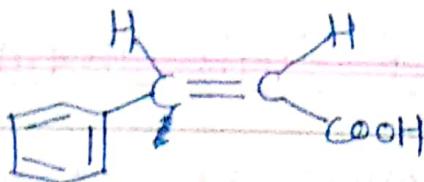


2 hydroxy pyridine

$$\lambda_{max} = 270 \text{ nm}$$

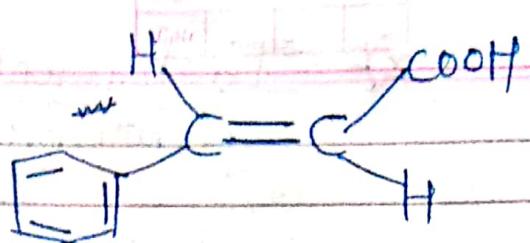
6) Hypochromic shift :-

Decrease in intensity of absorption maxima is called hypochromic shift. When the geometry of molecule is disturbed due to a group attached to chromophore the intensity of absorption or λ_{max} decreases.



cis cinnamic acid

$$\lambda_{\text{max}} = 268 \text{ nm}$$



Trans cinnamic acid

$$\lambda_{\text{max}} = 272 \text{ nm}$$

Trans isomers are coplanar so absorb at higher wavelength

* Single Beam UV-Visible Spectrophotometer:-

Defn - The instrument that is used to measure the amount of electromagnetic radiation absorbed by the substance is called spectrophotometer or spectrometer.

* Instrumentation of Single beam UV-visible Spectrophotometer -

Basic Principle of Single Beam Spectrophotometer -

- Spectrophotometer measures the amount of electromagnetic radiations emitted or absorbed by the sample.
- The monochromatic light is made incident on sample soln present in cuvette. Part of incident light is reflected, a part is absorbed by sample & remaining is transmitted.
- If I_0 denotes incident light, I_r = reflected light, I_a = absorbed light & I_t = transmitted light then,

$$I_0 = I_a + I_t + I_r$$

- I_r is very small hence can be neglected
- The intensity of radiation transmitted through sample is measured & thus the radiation absorbed by the sample can be detected, analyzed & recorded.

Instrumentation of Single beam UV-Visible Spectrophotometer:

Various components of U.V-visible spectrophotometer & their functions are as follows —

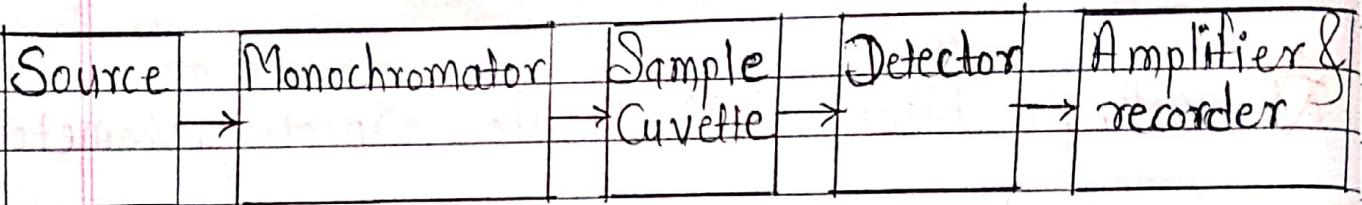


fig: Block diagram of single beam UV-visible spectrophotometer.

1) light source or Source of radiation —

Function: It generates a beam of polychromatic radiation which covers the desired range of wavelengths. It has high intensity. e.g. (Tungsten filament lamp) is most commonly used for visible radiations. (wavelength 400-800 nm)

e.g. (Deuterium lamps) are used for UV radiations (wavelength range 200 to 400nm)

2) Monochromator :-

Function — Radiation source provides polychromatic light which is passed through monochromator through entrance slit. Monochromator disperses radiations according to wavelength. Radiations of only particular wavelength leaves the monochromator through exit slit.

3) Slits :-

Entrance slit & exit slit are placed on opposite sides of prism. The slits are used for selecting desired light by monochromator.

4) Sample holder / Cuvette:-

Sample holders or cuvettes are used to hold the sample. They are made up of transparent material which does not absorb radiation in UV or visible range.

5) Detectors:-

Functions - Transmitted light from sample cuvette falls on the detector where it is converted in to electric current. It converts light energy directly in to electrical energy.

6) Amplifiers & recorder:-

Signal received from detector is amplified & read on recorder. Recorder can record output in the graphical manner as absorption spectra.

★ Applications of UV-Visible Spectroscopy:-

i) Qualitative analysis:-

Detection of functional groups:- This technique is used to determine presence or absence of chromophore. If spectrum is (transparent) above 200nm, it indicates absence of conjugation, carbonyl gr, aromatic compounds.

ii) Extent of Conjugation:-

Extent of conjugation can be detected by - UV-visible Spectroscopy.

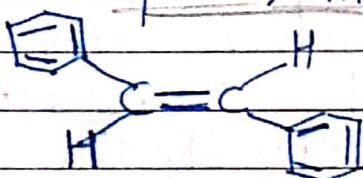
This technique is used for distinguishing conjugated & non-conjugated compounds.

Unknown compound is identified by comparing spectrum of given compound with

that of spectrum of known compound.

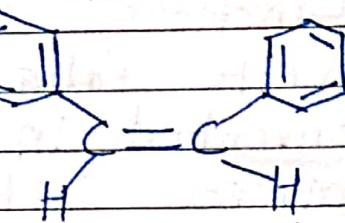
2) Detection of cis & trans isomers :

This technique is useful to distinguish geometrical isomers (cis & trans). Disturbance in planarity in one of the isomers is responsible for difference in λ_{max} value. Trans isomer being more coplanar absorbs at higher λ_{max} .



Trans-stilbene

$$\lambda_{max} = 295 \text{ nm}$$



Cis-stilbene

$$\lambda_{max} = 280 \text{ nm}$$

3) Determination of molecular weight :-

(Molecular weight) of the compound can be determined by recording absorbance. Using Beer-Lambert's law molecular weight of compound can be determined by determining concentration.

4) Detection of Impurities -

V.V-visible spectroscopy is one of the best method for determination of impurities in organic compounds. Additional peaks can be observed due to impurities in the sample & it can be compared with that of standard material & the impurities can be detected.

5) Quantitative analysis :-

V.V visible absorption spectroscopy can be used for quantitative determination of compound.

→ Study of kinetics of chemical reactions —
kinetic study of chemical reactions
is done by measuring changes in concentration
of reactant or product & can be used to
study the progress of reaction.

Part B : Infra Red (IR) Spectroscopy —

Introduction —

(U.V visible spectrum) provides information about the structure of molecules that contains double or triple bonds or conjugated double bonds. IR spectrum provides information about functional groups of molecule. IR spectrum is recorded with the help of (IR spectrophotometer.)

Principle of IR Spectroscopy —

- i) A molecule is (not rigid). The atoms in the molecule (vibrate) in different ways. (Each vibrations requires different energy i.e molecule has number of vibrational energy levels.)
- ii) If molecule (absorbs IR radiation), it gets (excited) to higher vibrational energy level (such as $V_0 \rightarrow V_1$). The type of IR wavelength absorbed by the molecule depends on the type of atoms & chemical bonds in the molecule.
- iii) In IR spectrum, position of peak is specified in (terms of frequency (ν) or wavelength (λ) or wave number ($\bar{\nu}$) of IR radiation absorbed.

A. Types of Vibrations :-

Molecules consist of atoms that are bonded by covalent bond. Several covalent bonds in the molecule behave as molecular springs & are constantly vibrating with certain frequency. All vibrations fall in to two basic categories—

- i) Stretching vibrations
- ii) Bending vibrations

i) Stretching Vibrations :

These are characterized by change in inter-nuclear distance. The distance between two atoms increase or decrease but atoms remain in the same plane.

These are of two types :

i) Symmetric stretching vibrations :

These involve the movement of the atom with respect to particular atom in a molecule in the same direction.

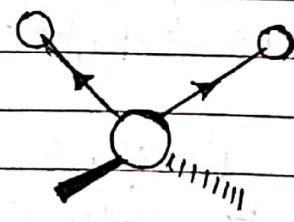


fig-

Symmetric stretching

ii) Asymmetric stretching vibrations :

These involve the movement of the atom with respect to a particular atom in a molecule in the same plane but not in the same direction.

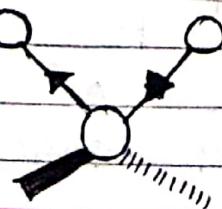


fig-

Asymmetric stretching

2) Bending Vibrations:

These are characterized by a change in the angle b/w two covalent bonds, due to change in the position of the atoms relative to the original bond axis.

These vibrations are four types :

- i) Scissoring
- ii) Rocking
- iii) Wagging
- iv) Twisting

The first two vibrations scissoring & rocking, occurs in the plane while other two vibrations i.e. Wagging & twisting, occurs out of plane.

i) Scissoring vibrations:-

These involve movement of two atoms in opposite directions i.e. towards each other or away from each other in the same plane.

ii) Rocking vibrations:-

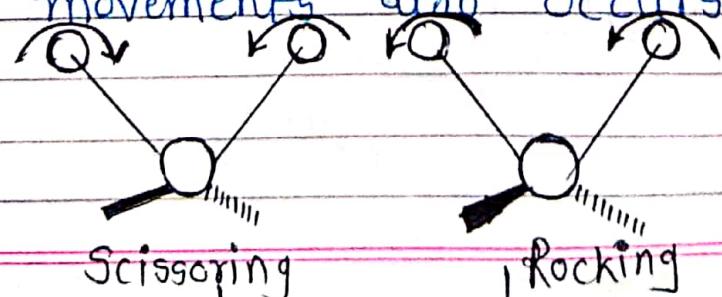
These involve movement of atoms in the same direction in the same plane.

iii) Wagging vibrations:-

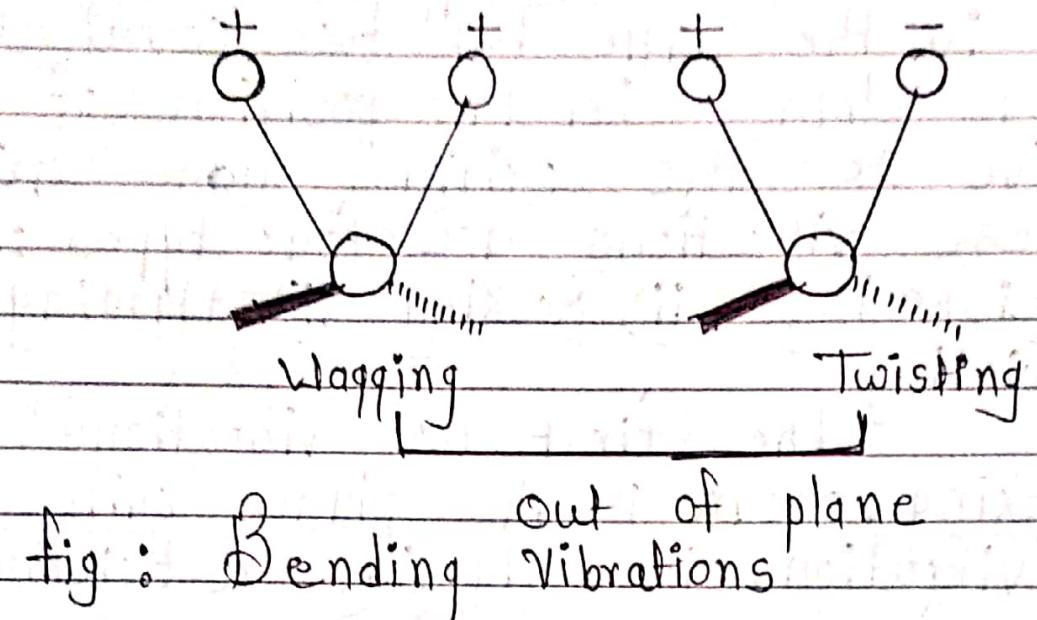
These involve movement of atoms up the plane or below the plane with respect to central atom. These movements occur out of plane.

iv) Twisting vibrations:-

These involve movement of one atom up & the other atom down the plane with respect to central atom. These movements also occurs out of plane.



In the
plane



Vibrations of Diatomic & polyatomic molecules:

In (polyatomic) molecule, each atom is having (three) degrees of freedom in three directions. Thus a molecule of N atoms has $3N$ degrees of freedom which is equal to sum of translational, vibrational & rotational degree of freedom.

For (non-linear) molecule, out of the $3N$ degrees of freedom, three describe rotation & three describe translation & remaining $(3N-6)$ degrees are vibration degrees of freedom.

In a (linear) molecule, only two degrees of freedom are required to describe translation. Thus the remaining $(3N-5)$ degrees are vibration degrees of freedom.

eg →

Molecule	No. of atoms 'N'	Geometry of molecule	Fundamental modes of vibrations
H ₂ O	3	Non-linear	3
NH ₃	4	Non-linear	6
CH ₄	5	Non-linear	9
C ₂ H ₆	8	Non-linear	18
C ₆ H ₆	12	Non-linear	30
NO	2	Linear	1
CO ₂	3	Linear	4

* (Conditions) of absorptions of I.R radiations or Requirements of I.R absorption :-

For a molecule to absorb I.R radiations it has to fulfil following requirements -

1) Correct frequency of radiation -

[A molecule absorbs radiations only when the natural frequency of vibration of some part of]

When (frequency of vibration) of a bond & (frequency of I.R radiation) used for excitation, match perfectly then only I.R energy is absorbed.

e.g. Natural frequency of vibration of HCl molecule is about 8.7×10^{13} sec⁻¹. When I.R radiation is passed through a sample of HCl & transmitted radiation is analysed by I.R spectrophotometer, it is observed that the part of radiation which has frequency 8.7×10^{13} sec⁻¹ is missing from transmitted radiation. Thus the part of radiation which has frequency 8.7×10^{13} sec⁻¹ has been absorbed by HCl molecule.

& remaining frequencies of radiation are transmitted.

2) Electric dipole :-

A molecule can only absorb IR radiation when its absorption causes a change in electric dipole or dipole moment.

— Only those vibrations which result in change in dipole moment, absorb IR radiation. Such vibrations are said to be IR active.

— A molecule is said to have electric dipole when there is slight +ve or -ve electric charge on its atoms. e.g. $HCl \rightarrow H^+Cl^-$

— (Symmetrical) diatomic molecules like H_2 , Cl_2 , O_2 , N_2 do not possess electric dipole & are IR inactive.

★ Instrumentation of IR Spectrophotometer-

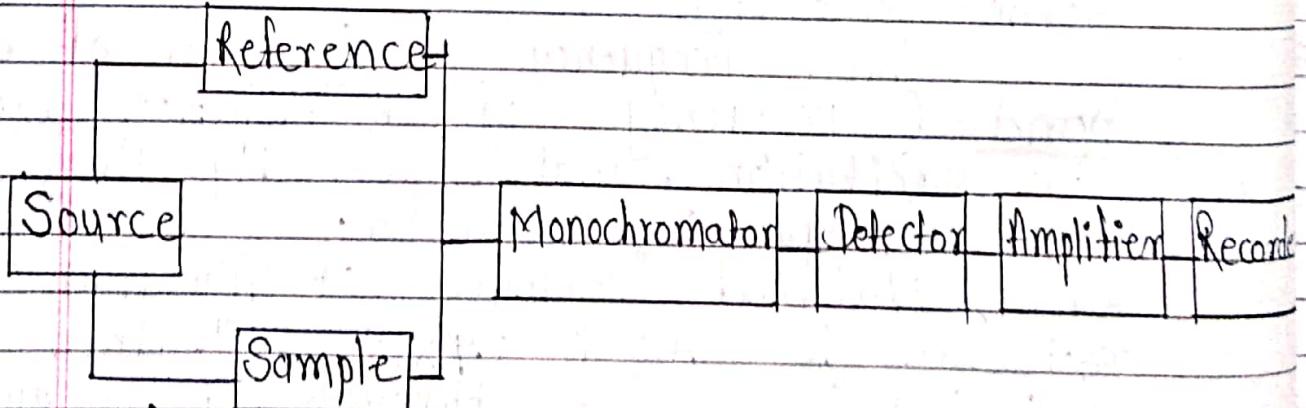


fig diagram of (double) beam IR spectrophotometer

The important components of IR spectrophotometer are as follows :

1) Source :-

a) Nernst filament — Consist of (mixer of rare earth oxides) such as Zirconium

oxide, & Yttrium oxide & erbium oxide.

- ii) Globar - It is a rod of silicon carbide.
- iii) Incandescent wire - It is a spiral wire of nichrome.

2) Monochromator -

Prisms or gratings are used as monochromators. They are used to select desired radiation frequency. Prisms are normally made of metal halides like NaCl , KBr .

3) Sample cells

Infrared spectra can be obtained for solid, liquid or gases. Material containing sample must be transparent to the IR radiation, so the material made up of certain salts like NaCl , KBr , LiF etc are used.

4) Detectors :-

In IR Spectroscopy, thermal detectors are used

e.g.) ~~Golay detector~~ → It is sensitive gas thermometer containing Xenon.

i) Bolometer →

Pt or Ni is used to (prepare bolometer). It is the type of resistance thermometer used to (detect & measure weak thermal radiation).

5) Amplifier & Recorder :- (i.e power of signals)

Amplifier amplifies the signals from detector & sends to recorder. Recorder gives IR spectra of compound as a graph of percentage transmission of IR radiation vs wavelength or frequency or wave number.

★ Parts of IR Spectrum

- The (IR region) is further divided in to three regions —
 - Near infrared region
 - Middle infrared region
 - Far infrared region.
- Middle infrared region is further subdivided in to functional group region, fingerprint region, aromatic region.

1) Functional group region —

The region extending from $4000-1500\text{ cm}^{-1}$ (2.5 to 6.5 μ) is called functional group region. This part of IR spectrum contains absorption bands due to stretching vibration of functional groups such as O-H , N-H , C-H etc. The common functional groups show absorption bands in this region.

2) Finger print region —

The region $1500-900\text{ cm}^{-1}$ (6.5-11 μ) is called finger print region. This is most complex part of IR spectrum & contain number of absorption bands appear due to stretching & bending vibrations.

This region is not useful in interpretation but can be used for identification of compounds eq — Finger print region of unknown compound can be compared with other to identify the compound.

3) Aromatic region —

This region is useful for detection of (aromatic character) of the compound. It provides information

about (aromatic substitution pattern) such as ortho, meta, para substitution. The bands that occur in this region are due to bending vibrations in the molecule.

★ Applications of IR Spectroscopy—

1) Determination of structure & functional groups

a) Identification of functional group—

In IR spectroscopy, all functional groups absorb characteristic radiations within definite range.

e.g.— Strong absorption band betⁿ 1600–1900 cm⁻¹ indicates the presence of carbonyl gr. Further study of spectra decides whether it is aldehyde, ketone, ester, amide etc.

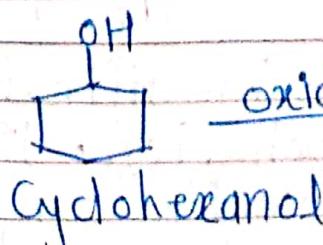
b) Identification of structure—

(Identification of structure) can be done by comparison with fingerprint region. Some molecules containing same functional group may show similar absorption above 1500 cm⁻¹ but their spectra differ in fingerprint region.

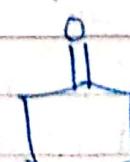
2) Study of kinetics of a Chemical reaction—

A comparison betⁿ IR spectra of reactants & products can help to determine the course of reaction.

e.g.



oxidation



cyclohexanone

I.R spectrum of cyclohexanol shows strong I.R absorption band at about 3550 cm^{-1} of alcoholic gr. For product cyclohexanone this band disappears & a new band appears at 1710 cm^{-1} for keto group.

3) Hydrogen bonding—

I.R. Spectroscopy gives information regarding to hydrogen bonding:

4) Distinguish betⁿ intermolecular & intramolecular hydrogen bonding—

I.R spectroscopy is used to distinguish betⁿ inter & intra molecular hydrogen bonding. This is done by taking series of I.R spectra of compound at different dilutions.

5) Detection of impurities—

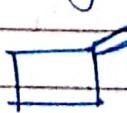
I.R Spectra of impure sample sample will shows extra absorption bands. By comparing with I.R spectra of pure compound, presence of impurity can be detected.

6) Determination of size of ring ketones:—

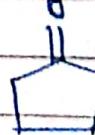
(Ring strains) in cyclic ketones shifts the carbonyl group stretching frequency to higher wavelength.



1818 cm^{-1}



1715 cm^{-1}



1740 cm^{-1}



1710 cm^{-1}

7) It is used for identification of atmospheric pollution. Measurement of ethanol in breath can be detected by I.R Spectroscopy

IR region

Near T.R.
regionMiddle T.R.
regionFar T.R.
region $\bar{\nu} \rightarrow 12800 - 4000 \text{ cm}^{-1}$
 $\lambda \rightarrow (0.8 \text{ to } 2.5 \mu)$ $4000 - 667 \text{ cm}^{-1}$
 $(2.5 \text{ to } 15 \mu)$ $667 - 50 \text{ cm}^{-1}$
 $(15 \text{ to } 200 \mu)$ Functional group
regionFingerprint
regionAromatic
region $4000 - 1500 \text{ cm}^{-1}$
 $(2.5 \text{ to } 6.5 \mu)$ $1500 - 909 \text{ cm}^{-1}$
 $(6.5 \text{ to } 11 \mu)$ $909 - 667 \text{ cm}^{-1}$
 $(11 \text{ to } 15 \mu)$