

Spectroscopic Techniques

**UV Visible and Infrared (IR)
Spectroscopy**

- **Course Objective:**

To study spectroscopic techniques for chemical analysis

- **Course Outcome:**

Identify chemical compounds based on their structure.

Unit 5: Spectroscopic Techniques:

✓ Weightage : 18M

(only in End semester examination.)

✓ Teaching Hours: 08 hrs.

✓ **Questions asked in ESE paper:**

Q.5 a]7M, b] 6M, c] 5M

OR

Q.6 a]7M, b] 6M, c] 5M

A) UV-Visible Spectroscopy

Content:

- Introduction,
- Interaction of electromagnetic radiation with matter
- Statement of Beer's law and Lambert's law,
- Absorption of UV radiation by organic molecule leading to different electronic transitions,
- Terms involved in UV-visible spectroscopy-
chromophore, auxochrome, bathochromic shift,
hypsochromic shift, hyperchromic shift and
hypochromic shift,
- Instrumentation and basic principle of single beam spectrophotometer,
- Applications of UV-visible spectroscopy.

Spectroscopy



Introduction:

- **Spectroscopy** is branch of science deals with the study of interaction of electromagnetic radiation with matter
- Spectroscopic methods of analysis are based on the **measurement of electromagnetic radiation absorbed or emitted** by the sample
- **Physical and chemical properties** of the sample substance are directly related to the structure of the sample and sample substance absorb radiations based on its **bonding and structure**
- Structure elucidation can be done based on wavelength absorbed by sample substance

Spectroscopy

- Electromagnetic radiations consist of discrete packets of energy which are called photons of light.
- Energy of photon of EMR is given by $E = hc / \lambda$
- EMR travels at 3×10^8 m/sec. The speed of the wave is given by $\text{Velocity} = \text{Wavelength} \times \text{Frequency}$.
- These waves made of two components electrical and magnetic. They oscillates in space perpendicular to each other and perpendicular to the direction of propogation.
- Wavelength of radiation is inversely proportional to its energy.

Spectroscopy

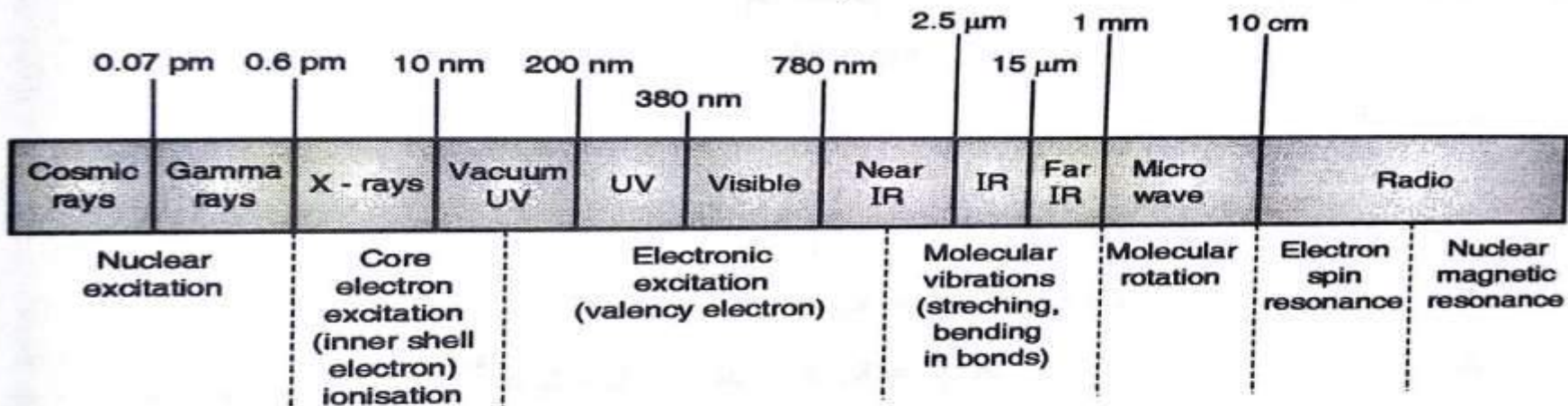
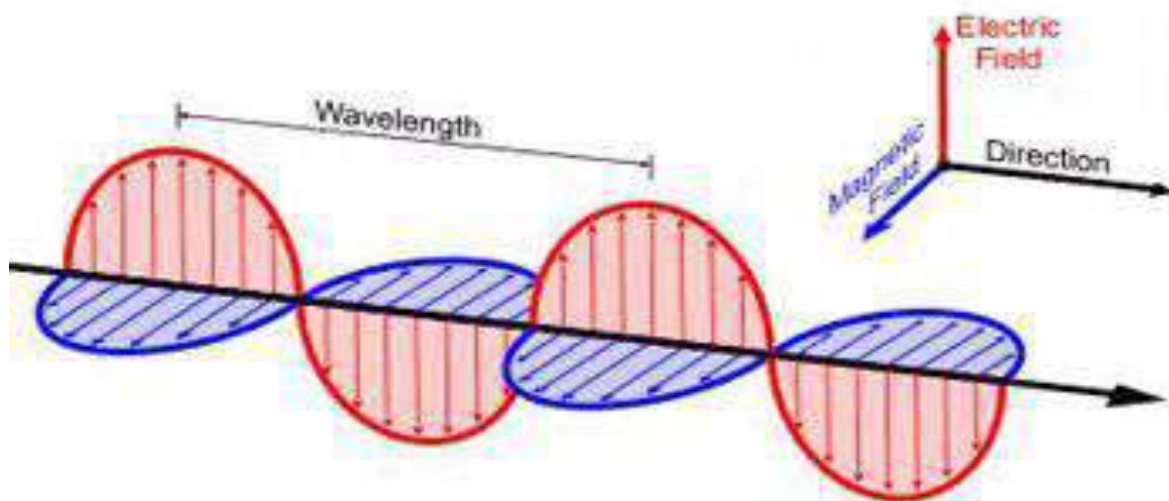


Fig. 2.14.1 : Electromagnetic spectrum (wavelength, regions and interaction with matter)



Interaction of electromagnetic radiation with matter



- Types of energies: Rotational, vibrational & electronic energy.
- Molecular energy levels: Rotational, vibrational & electronic energy levels.
- Interaction with EMR bring about changes in outermost electrons present in the molecule these changes depend on energy of EMR interacting.
- Energy associated with EMR can bring about either electronic or vibrational or rotational excitations.
- Absorption spectrum: Definition & graph with variables

Spectroscopy



Spectroscopic methods of analysis are based on the measurement of electromagnetic radiations absorbed or emitted by the sample solution.

Most common photometric methods are,

1. Colorimetric: (400 to 800 nm)
2. UV spectroscopy (180 to 400 nm)
3. Visible spectroscopy (400 to 800 nm)
4. UV visible spectroscopy (180 to 800nm)
5. IR (0.76 to 15 micrometer)

Spectroscopy



Interaction of electromagnetic radiation with matter

UV visible Radiation: bring **excitation of electrons** in the bond to higher energy anti bonding level

Absorption of IR: Cause **vibration in certain covalent bonds**

$$\Delta E_{\text{rotational}} < \Delta E_{\text{vibrational}} < \Delta E_{\text{electronic}}$$

Fundamental Laws of Spectroscopy

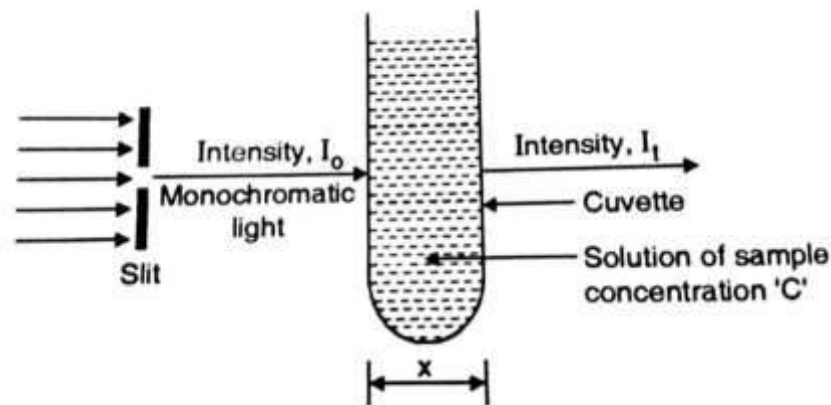


Fig. 2.15.1

Lambert's law : When a beam of light is allowed to pass through a transparent solution, the rate of decrease in intensity of light is directly proportional to thickness of solution.

Beer's law: When a beam of light is allowed to pass through a transparent solution, the rate of decrease in intensity of light is directly proportional to concentration of solution when thickness of solution is kept constant.

Fundamental Laws of Spectroscopy

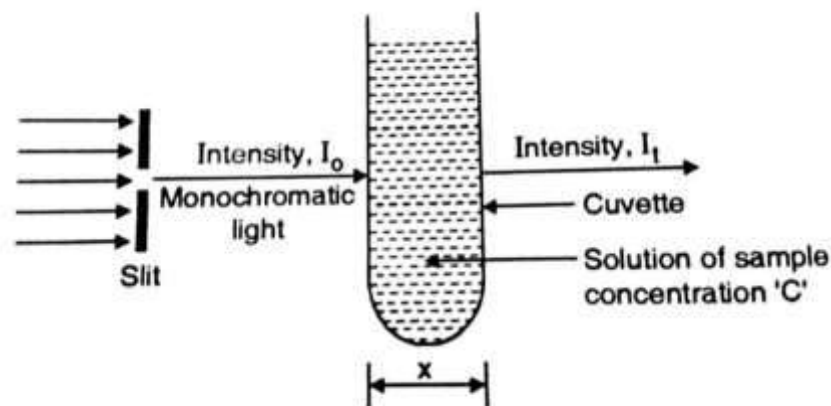
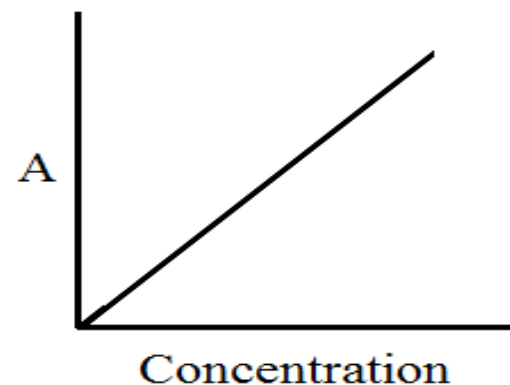


Fig. 2.15.1

$$-\frac{dI_0}{I_0} \propto dx \cdot dc \quad \text{Absorbance} = A = \log \frac{I_0}{I_t} = k \cdot x \cdot c \quad A = \epsilon \cdot x \cdot c$$

$$A = \log \frac{I_0}{I_t} \quad \text{Transmittance, } T = \frac{I_t}{I_0}$$

$$A = \log \frac{1}{T} = -\log T$$



Range of UV-Visible Spectroscopy



- Range of wavelengths belong to UV and Visible region.
UV region: 10nm to 400nm
Visible region: 400nm to 800nm
- Subdivision of Ultraviolet region based on wavelengths:
Far UV (below 200nm) & Near UV(from 200 – 400nm)
- UV-Visible wavelengths are used in Quantitative as well as Qualitative analysis in which absorption laws are used.
- In Quantitative analysis graph of absorbance against concentrations is usually plotted.

Absorption of UV radiation leading to Electronic transitions in organic molecules



- Absorption of UV-visible radiation by a molecule brings changes in the electronic energy of molecule because of transition of valence electrons from lower energy to higher energy
- Types of electrons present in organic molecule:
 1. **Sigma (σ) electrons:** Electrons forming single bonds like C-H bond present in saturated hydrocarbon
 2. **pi (π) electrons:** Electrons forming double bonds like C=C bond present in unsaturated hydrocarbon
 3. **Non bonded (n) electrons:** Non-bonded or lone pair of electrons and not involved in bonding between atoms in molecules. Lone pair of electrons present on Oxygen, Nitrogen etc.

Absorption of UV radiation leading to Electronic transitions in organic molecules



- When energy is absorbed in UV Visible region, electronic transitions occur:

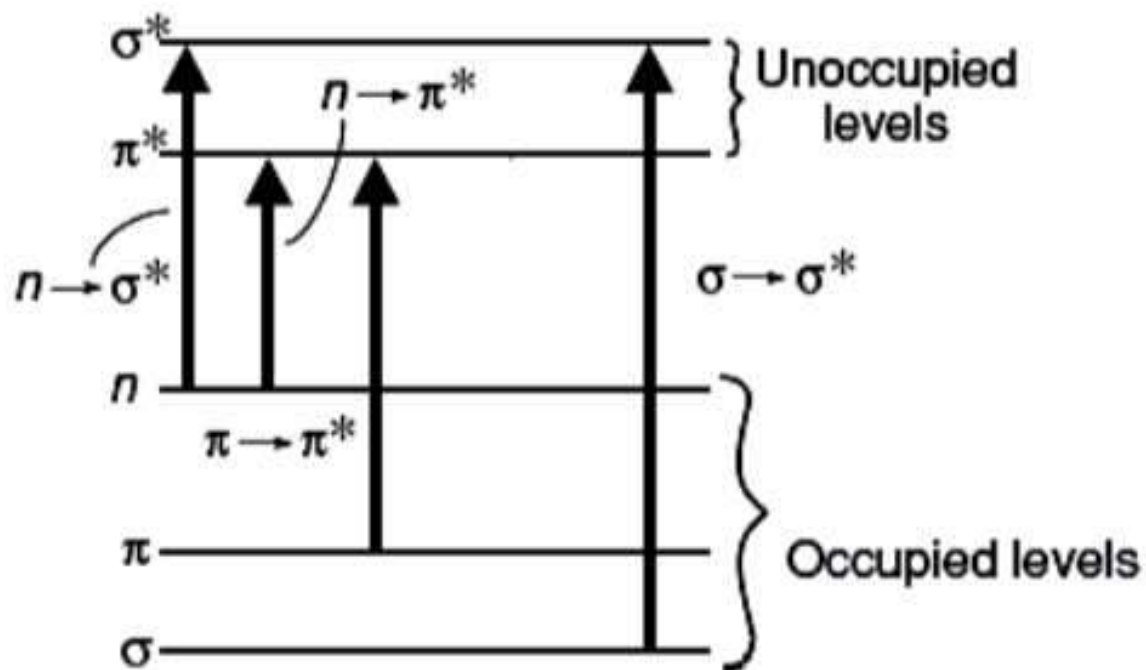
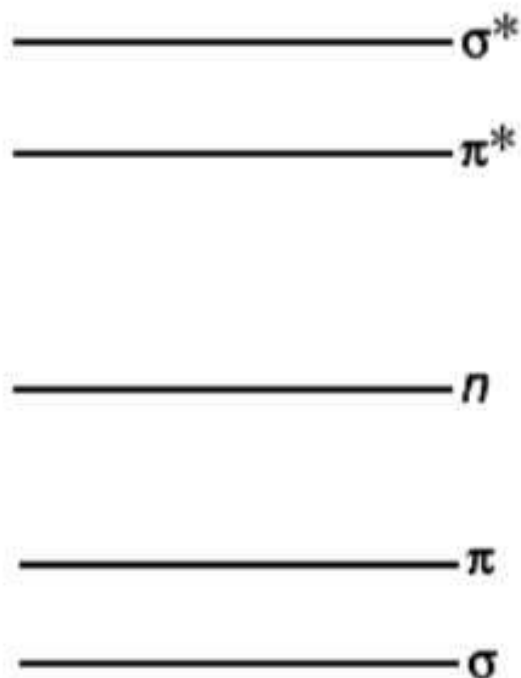
➤ Possible Electronic Transitions:

- 1) $\sigma \rightarrow \sigma^*$ transition
- 2) $\pi \rightarrow \pi^*$ transition
- 3) $n \rightarrow \sigma^*$ transition
- 4) $n \rightarrow \pi^*$ transition

➤ Forbidden Transitions:

- 1) $\sigma \rightarrow \pi^*$ transition
- 2) $\pi \rightarrow \sigma^*$ transition

Electronic Energy Levels and Transitions



Electronic transitions in organic molecules



➤ Possible Electronic Transitions:

1. $\sigma \rightarrow \sigma^*$ transition: (Less than 150 nm)

Such transitions from occur only in the compounds containing sigma electrons which are involved in single bonds and no lone pair of electrons on any atom in the molecule from sigma bonding orbital to the corresponding antibonding orbital.

Such transitions requires very large amount of energy, the absorption band occurs in the far ultraviolet region.

e.g. Saturated Hydrocarbons like Methane, Ethane etc.

Methane (CH_4) containing C-H bonds undergo this transition, shows absorbance maxima at 125 nm

Electronic transitions in organic molecules



➤ Possible Electronic Transitions:

2. $\pi \rightarrow \pi^*$ transition: (200 nm-700 nm)

Such transitions occur only in the compounds containing pi electrons which are involved in multiple bonds in the molecule. These electrons get excited from pi bonding orbital to the corresponding antibonding orbital π^* .

e.g. Unsaturated Hydrocarbons like alkenes, alkynes, nitriles, aromatic compounds etc. show these transitions.

Generally alkenes absorb in the region of 180-200 nm while compounds containing 2 or more conjugated bonds shows absorbance maxima above 200 nm

Electronic transitions in organic molecules



➤ Possible Electronic Transitions:

3. $n \rightarrow \sigma^*$ transition: (150 - 250 nm)

Such transitions occur in the saturated compounds containing atoms with lone pair of electrons (non-bonding electrons) like O, N, S and halogens. These electrons get excited from non-bonding orbital to the antibonding orbital σ^* .

e.g. Various functional groups show absorbance maxima at shorter wavelength in the range of 150 - 250 nm

Electronic transitions in organic molecules



➤ Possible Electronic Transitions:

4. $n \rightarrow \pi^*$ transition: (200 nm-700 nm)

Such transitions occur in the compounds containing double bonds involving hetero atoms with lone pair of electrons (non-bonding electrons) like O, N, S and halogens. These electrons get excited from non-bonding orbital to the antibonding orbital π^* . These transition requires minimum energy and show absorption at longer wavelength between 200 to 700 nm

Electronic Transitions in Organic Molecules

↑
Increasing energy
↓



In alkanes



In alkenes, carbonyl compounds, alkynes, azo compounds, and so on



In oxygen, nitrogen, sulfur, and halogen compounds



In carbonyl compounds

Content: UV-visible spectroscopy

Terms Involved in UV Visible Spectroscopy:

Definition and suitable examples to illustrate the following terms:

- Chromophore:
- Auxochrome:
- Bathochromic shift:
- Hypsochromic shift:
- Hyperchromic shift:
- Hypochromic shift:

Terms involved in UV-visible spectroscopy



CHROMOPHORE: Any isolated covalently bonded unsaturated group responsible for electronic absorption or shows characteristic absorption in the UV Visible region.

E.g.: -C=C- , -C=O , NO_2

Consequently chromophore is any substance (groups) which absorbs radiation at particular wave length which may or may not impart colour to the compound.

Chromophore types:

- The groups which contain π electrons and undergo π to π^* transitions and
- The groups which contain both π and n electrons and undergo n to π^* and π to π^* transitions.

Compounds which possess π to π^* and n to π^* transitions (150nm and 190nm) contains no chromophore within them.

Terms involved in UV-visible spectroscopy



AUXOCHROME: Any saturated group with non bonded electrons, which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum (longer wavelength)

Auxochrome is a colour enhancing group.

The effect is due to its ability to extend the conjugation of a chromophore by sharing the non bonding electrons

Auxochrome when attached to a chromophore, alters both the wavelength and the intensity of the absorption

E.g. -NH_2 , -OH , -OR , -NHR , -SH etc.

Chromophore + Auxochrome = Newer Chromophore

Terms involved in UV-visible spectroscopy



BATHOCHROMIC SHIFT or RED SHIFT:

The shift of maximum absorption to a longer wavelength due to substitution or solvent effect.

Causes:

1. An auxochrome
2. Change of solvent

E.g.: Absorption Maximum of Benzene $\lambda_{\text{max}} = 255 \text{ nm}$ ($\epsilon_{\text{max}} = 203$)

While for Phenol $\lambda_{\text{max}} = 270 \text{ nm}$ and Aniline $\lambda_{\text{max}} = 280 \text{ nm}$ ($\epsilon_{\text{max}} = 1430$)

In alkaline medium, p-nitrophenol shows red shift with $\lambda_{\text{max}} = 265 \text{ nm}$ from $\lambda_{\text{max}} = 255 \text{ nm}$. Because negatively charged Oxygen delocalizes electron more effectively than the unshared n electron pair present on -OH groups.

Terms involved in UV-visible spectroscopy



HYPSOCHROMIC SHIFT or BLUE SHIFT: The shift of maximum absorption to a shorter wavelength.

Causes:

- 1) Change of solvent towards higher polarity or
- 2) Removal of conjugation

E.g.: Absorption Maximum of Aniline (conjugation of pair electrons of nitrogen with benzene ring) $\lambda_{\text{max}} = 280 \text{ nm}$ while Aniline shows $\lambda_{\text{max}} = 203 \text{ nm}$ as in acidic medium as it will form $-\text{NH}_3^+$, due to removal of lone pair of electrons or due to removal of π -conjugation.

Terms involved in UV-visible spectroscopy



HYPERCHROMIC EFFECT:

An increase in maximum absorption intensity

Cause: Introduction of auxochrome usually increases the intensity of absorption

E.g. : Pyridine $\lambda_{\text{max}} = 257 \text{ nm}$ and $\epsilon_{\text{max}} = 2750$ while pyridine with $-\text{CH}_3$ group shows increase in intensity of absorption that is 2-methyl pyridine $\lambda_{\text{max}} = 262 \text{ nm}$ and $\epsilon_{\text{max}} = 3560$

Terms involved in UV-visible spectroscopy



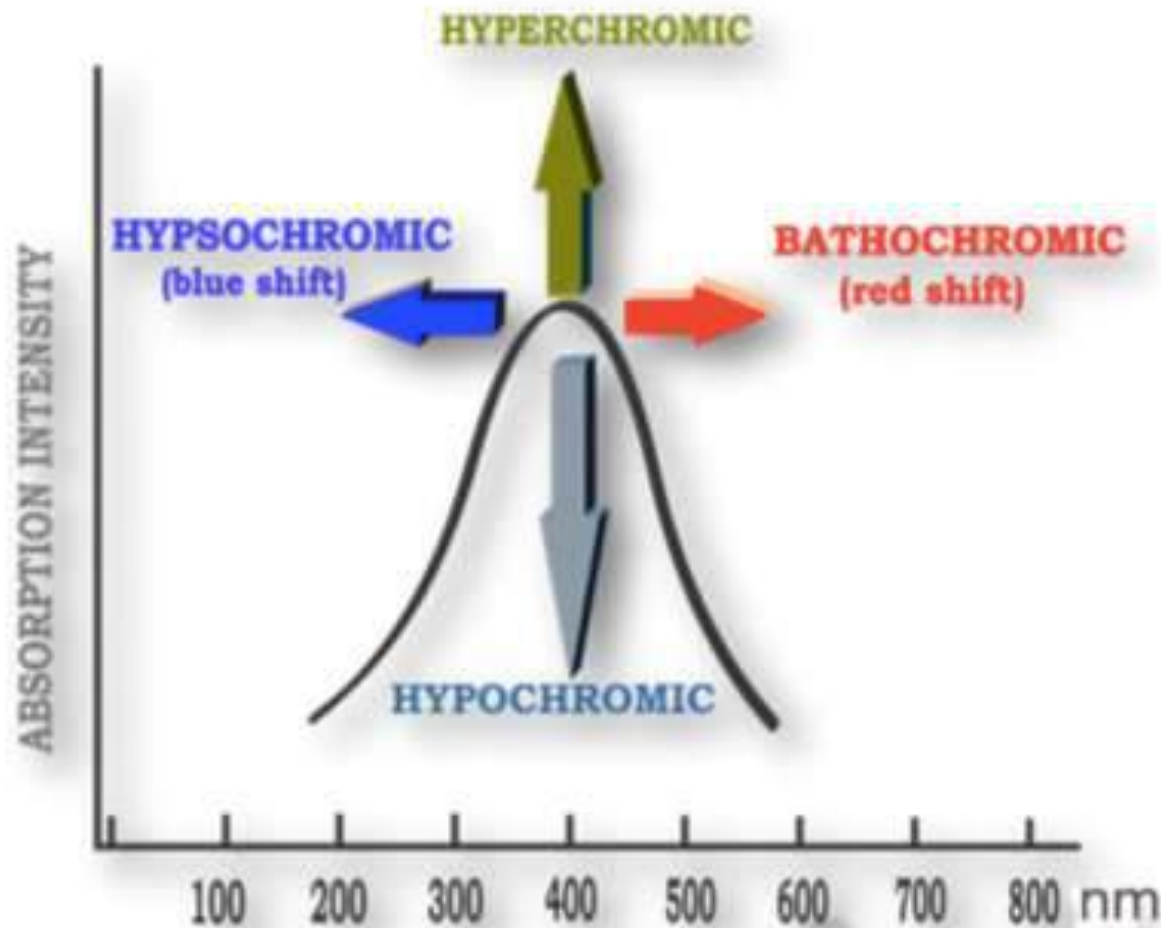
HYPOCHROMIC EFFECT:

A decrease in maximum absorption intensity.

Cause: Due to introduction of any group to the compounds which is going to alter the molecular pattern of the compound or distort the original geometry results in a hypochromic shifts

E.g.: Biphenyl (or naphthalene) has an absorption $\lambda_{\text{max}} = 250$ nm and $\epsilon_{\text{max}} = 19000$ whereas 2-methyl biphenyl has an absorption of $\lambda_{\text{max}} = 237$ nm and $\epsilon_{\text{max}} = 10250$

Effect of substituents on the position and intensity of an absorption band



UV-Visible Spectra



- **UV-Visible spectrophotometer** on analysis of an analyte solution gives data in the form of UV-Visible Spectra
- The **UV-Vis spectra** is a **graph**:
 - Absorbance** verses **wavelength** (λ) or
 - % Transmittance** verses **Wavelength** (λ)
- It gives information about λ_{max}

UV-Visible Spectroscopy



λ_{max} : It is defined as a **particular wavelength** at which **maximum absorbance** is observed

It is a **characteristic property** of an analyte and depends on structure of that analyte

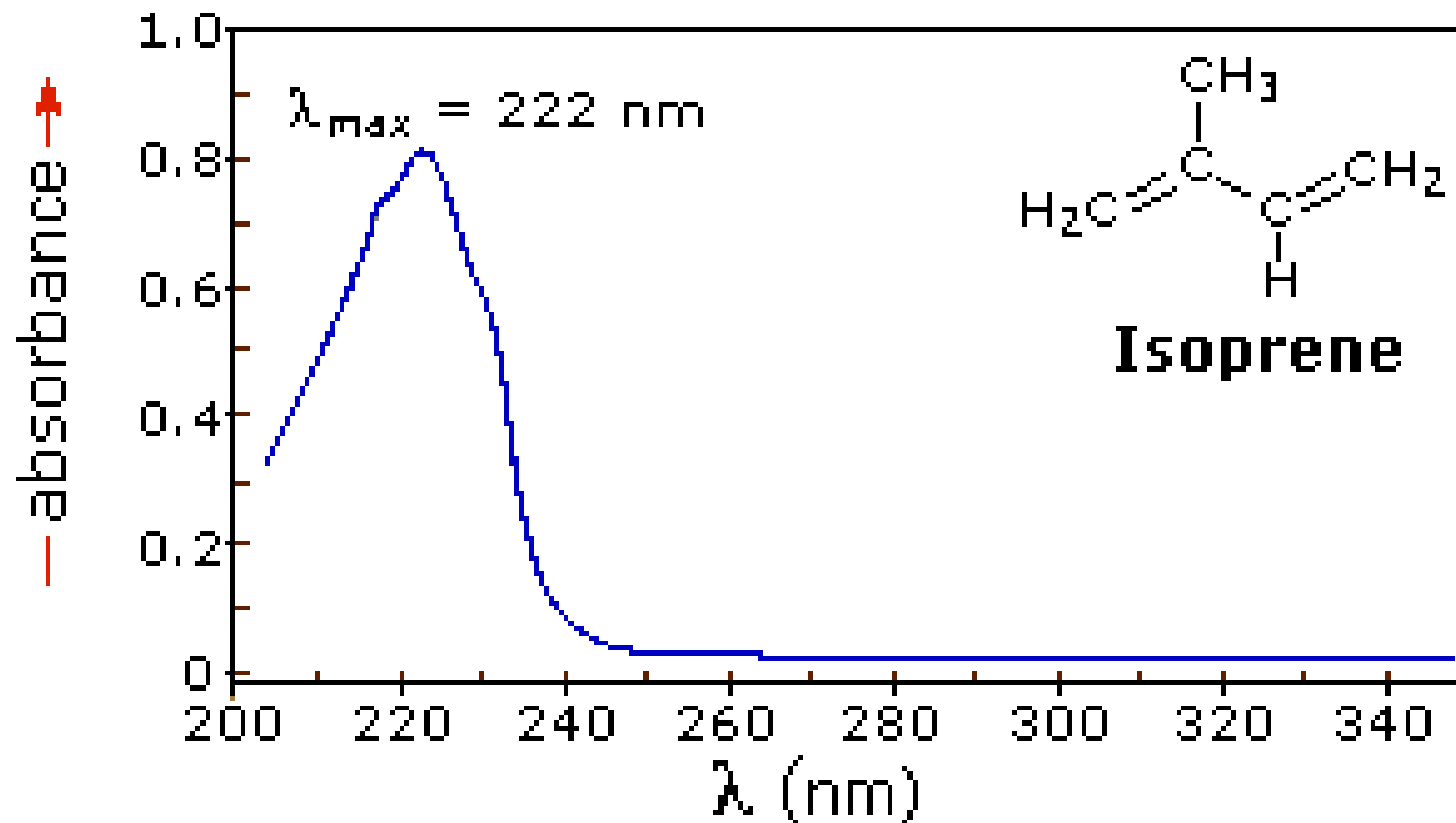
ϵ : It is called as **molar extinction coefficient** or **molar absorptivity**

It is the extent of absorption for a solution of specific concentration

UV-Visible Spectroscopy

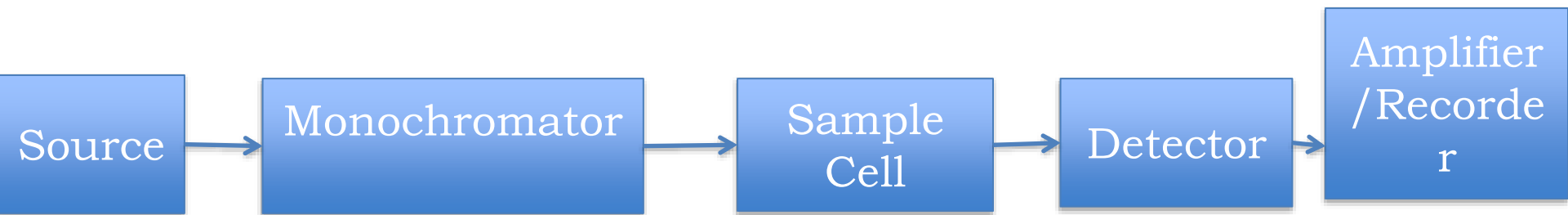


The UV-Vis spectra for isoprene is as follows:



Instrumentation: Single Beam UV Visible Spectrophotometer

Block Diagram of Single Beam UV Visible Spectrophotometer:



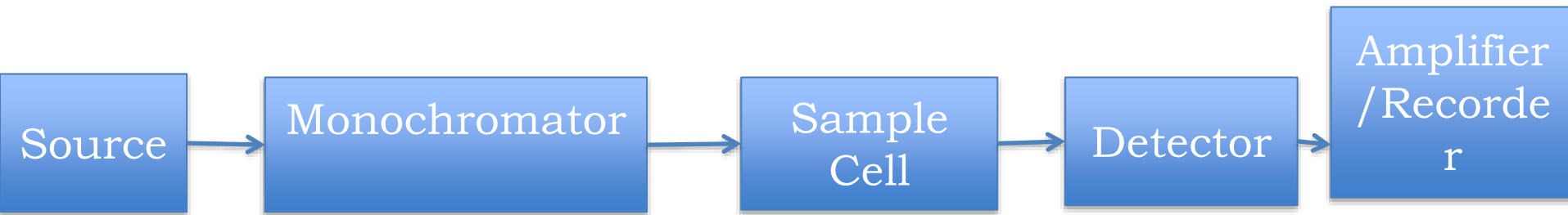
Components of Single Beam UV Visible Spectrophotometer:

1) Light Source: Provides wide range of UV Visible radiation and sufficient intensity over required wavelength.

Eg: Deuterium/Hydrogen Discharge Lamp (190-290 nm);

Tungsten filament (370-780 nm)

Instrumentation: Single Beam UV Visible Spectrophotometer

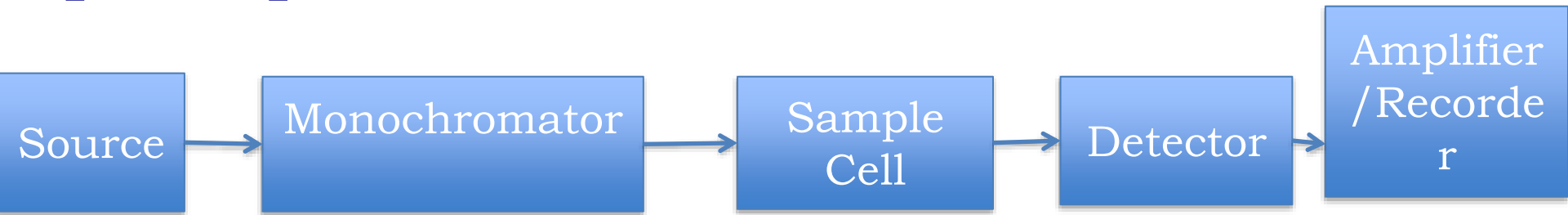


2) Sample Holder: All UV Visible spectra are recorded for the solution phase. Hence, Cells/Cuvettes made up of Glass or Quartz are used. But Quartz Cells only are transparent in full range of 200-780 nm.

3) Monochromator: Converts polychromatic radiation into monochromatic radiation using Prism/Filters/Gratings. Quartz prism is used for UV region

4) Detector: Transducer which converts transmitted radiation into electric signal/current. Commonly used are **Photomultiplier tube(PMT), Phototube** etc

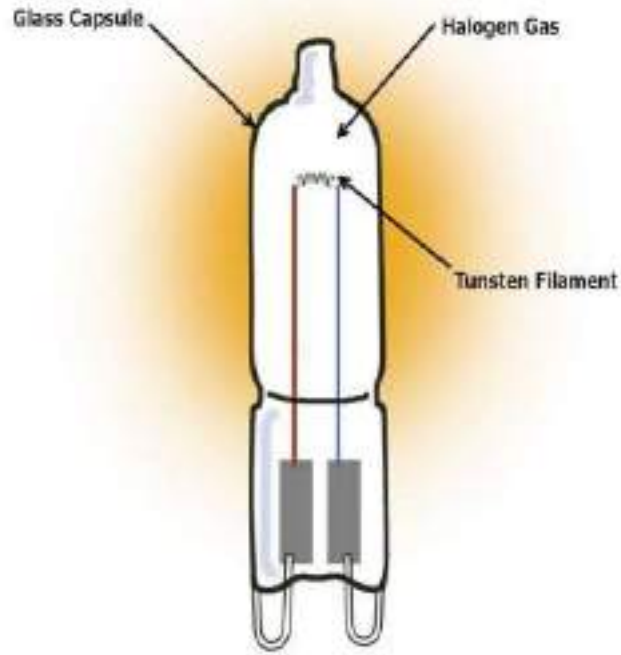
Instrumentation: Single Beam UV Visible Spectrophotometer



5) Amplifier: Amplify the signal received from detector

6) Recorder: Record output of the UV Visible spectrum data and Display it either in the graphical manner as absorption spectra or in the form of digital values of the Absorbance or transmittance verses wavelength

Instrumentation: Single Beam UV Visible Spectrophotometer



Source of radiation



Sample holder (Cuvette)

Applications of UV-Visible Spectroscopy

- **Structural Information:** λ_{max} is the characteristic property of a molecule due to presence of chromophore along with auxochrome. By knowing this value structural information can be extracted.
- **Qualitative analysis:** UV-Visible spectra of an unknown sample can be matched with spectra of known compound to analyse sample qualitatively.

Applications of UV-Visible Spectroscopy



- **Quantitative analysis:** By use of UV-Visible Spectroscopy, **unknown concentration** of analyte can be evaluated. Here same analyte solution is prepared with different concentration and its absorption is determined. A graph is plotted with absorption verses concentration, which gives a straight line.
- Now absorption of solution containing unknown concentration is evaluated and by use of graph its corresponding concentration can be determined.

Applications of UV-Visible Spectroscopy

➤ **Chemical Kinetics**: According to Beer's Law absorbance is proportional to concentration. Hence during the chemical reaction absorption intensity of reactant decreases, while that of Product increases which will help to study chemical kinetics.

➤ **Detection of Impurity**: Any change in the spectra of a specific compound will indicate the presence of impurity

B] Infra Red(IR) Spectroscopy



Content:

- Introduction,
- Principle of IR Spectroscopy,
- Types of vibrations: Stretching (symmetric & asymmetric) and bending (scissoring, rocking, wagging and twisting),
- Conditions of absorption of IR radiations,
- Vibrations of diatomic and polyatomic molecules,
- Instrumentation with block diagram,
- Parts of IR spectrum, fundamental group region, fingerprint region,
- Applications of IR spectroscopy

Infra Red(IR) Spectroscopy



- **IR spectroscopy** is an important analytical technique useful for chemical identification.
- IR spectra originate from the absorption of energy by a molecule in IR region and the transition occur between two vibration level.
- By measuring molecular vibrational frequencies, useful information regarding molecule can be obtained.
- UV visible spectra provides good deal of information about the structure of molecules that contain multiple bonds and conjugated bonds.

Infra Red(IR) Spectroscopy



- IR spectrum of an organic molecule provides good deal of information about **functional groups** present in the compound.
- IR spectroscopy is a type of absorption spectroscopy and mainly used to determine functional group (carboxylic, alcohol, ketone, aldehyde etc.).
- It is also called as vibrational and rotational spectroscopy.
- IR radiations of **higher wavelength** and **lower energy** are mainly responsible for vibration and rotation of the bonds.
- **The IR region** of the electromagnetic spectrum which extends from red end of visible spectrum to the microwave region may be divided into three regions.

Principle of IR Spectroscopy



- Atoms in molecules are not still, but they vibrate and rotate in variety of ways in certain quantized energy levels. These changes (vibrational, rotational) are caused by absorption of IR radiations.
- The absorption process involves excitation of the molecules to higher vibrational states and it is quantized. It require definite amount of energy.
- The vibrations increase in amplitude when EMR raises it to the next vibrational level.
- For a molecule to absorb IR the vibrations and rotations within a molecule must cause a net change in dipole moment of the molecule.

Principle of IR Spectroscopy



- If the frequency of the radiation matches the vibrational frequency of the molecule then the radiation will be absorbed causing a change in the amplitude of the molecular vibrations.
- The type of IR wavelength absorbed by the molecule depends on the types of atoms and chemical bonds in the molecule.
- The IR spectrometer measures the absorption at each frequency in turn and so produce the IR spectrum.

Infrared spectroscopy is the study by measurements of the wavelength and intensity of the absorption of infrared radiation by a sample.

- **IR Radiation (0.8 μ to 15 μ)** which has longer wavelength, low energy and capable of affecting both the vibrational and rotational energy levels in the molecules
- **The unit commonly used is wavenumbers (cm^{-1})**
Wavenumber is proportional with energy (E) and frequency (ν), but reciprocal with wavelength.

Range of IR: 0.8 μ to 15 μ or 4000-400 cm^{-1}

- IR Spectrum shows Transmittance and Wavenumbers
- IR Spectrum of an organic compound reveals good information about functional groups

Division of IR Region



The Whole IR region is subdivided into 3 parts:

1) Near Infrared Radiation : 0.8 to 2.5μ (12500 - 4000 cm^{-1})
Energy range: (1.55 - 0.5eV)

2) Middle Infrared Radiation: 2.5 to 15μ (4000 - 667cm^{-1})

a) Functional Group: 2.5 to 7.7μ (4000 - 1300cm^{-1})

b) Finger Print: 7.7 to 11μ (1300 - 909cm^{-1})

c) Aromatic Region: 11 to 15μ (909 - 667cm^{-1})

3) Far Infrared Radiation: 15μ to 200μ (667 - 50cm^{-1})

Energy range for Middle & Far IR: (0.5 - 0.0012eV)

Conditions for absorption of IR radiation



1. Correct frequency of radiation:

Energy of IR radiation is insufficient to cause electronic excitation but can cause vibrational or rotational excitations in molecule.

- If the **frequency** of the **radiation matches** the **vibrational frequency** of the **molecule** then radiation will be absorbed, causing **a change in the amplitude of molecular vibration**.
- For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule.
- When the **frequency of ER** is **equal** to that of **alternating electrical field produced by change in the dipole moment** vibrational motions are excited in the molecule, and the **radiation is absorbed**.

Conditions for absorption of IR radiation



2. Electric dipole:

- ✓ Molecule must give rise to change in dipole moment due to absorption of IR radiation.

Thus, Vibrational Modes are IR active only if a change in dipole moment occurs during the vibration

What kind of sample be able to absorb IR light?

- Only vibration which alters molecule dipole moment (the magnitude of positive and negative charge between two bonded atoms) and having the IR absorption frequency in the IR region
- Gas molecules such as O_2 , H_2 and Cl_2 don't have a dipole moment, means no IR absorption occurs
- SO_2 and CO_2 have a dipole moment so it will give IR absorption or show IR spectrum
- Every functional group has their own IR absorption
- The more complex molecule structure, the more complex IR absorption
- It is used to identify any functional group presents in a molecule structure

Conditions for absorption of IR light



Selection Rule: Requirement that absorption of a Vibrational quantum be accompanied by a change in dipole moment is known as Selection Rule

IR active transition: The vibrational transitions which results in a change in dipole moment of a molecule are absorbed in IR are known as IR active transitions

Eg: CO_2 , SO_2 , CHCl_3

IR inactive transition: The vibrational transitions which do not results in a change in displacement of a molecule are not absorbed in IR are known as IR inactive transitions

Eg: H_2 , N_2 , Cl_2 , CCl_4

Types of Vibrations

- Covalent bonds are not rigid but almost elastic
- A molecule can be said to resemble a system of balls of different masses, corresponding to atoms of a molecule
- The bonds between two atoms are analogous to spring of a molecule
- A molecule is constantly vibrating; its bond stretch, contract or bend with respect to each other
- There are two modes of vibrations

Types of Vibrations

Modes of vibrations: Two modes of vibrations

1) Stretching Vibrations:

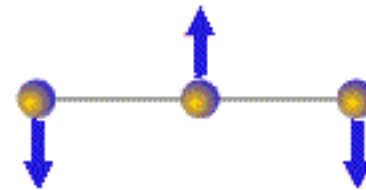
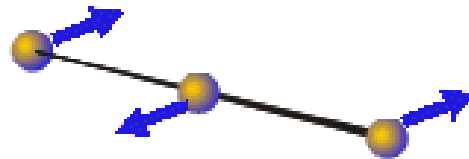
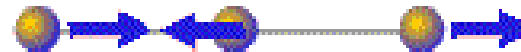
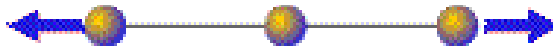
- i) **Symmetric** Stretching Vibrations
- ii) **Asymmetric** Stretching Vibrations

2) Bending Vibrations:

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

Types of Vibrations

Stretching and Bending Vibrations:

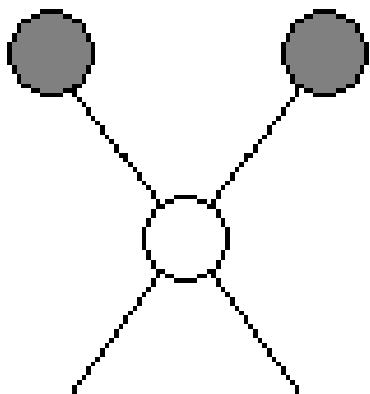


Stretching Vibrations

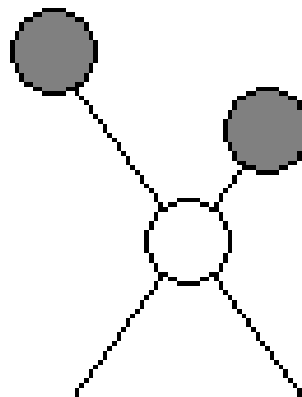
- Characterized by change in inter-nuclear distance, thus the distance between two atoms increases or decreases, but atoms remain in the same bond axis.

These modes are further divided into:

a) Symmetrical Stretching and b) Asymmetrical Stretching



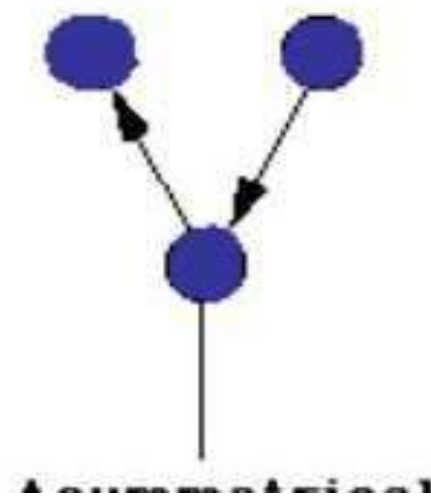
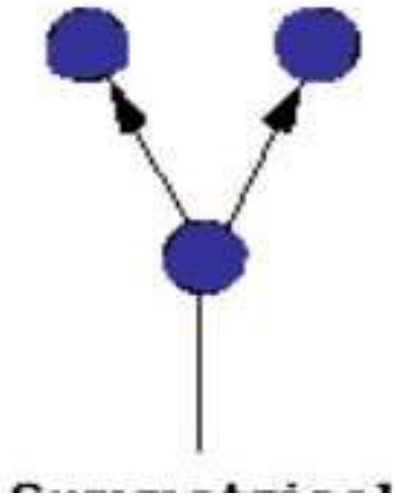
Symmetric



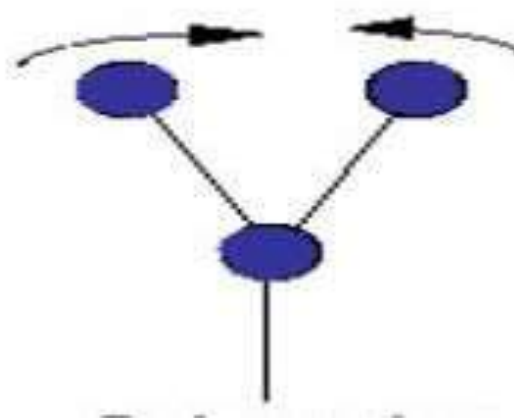
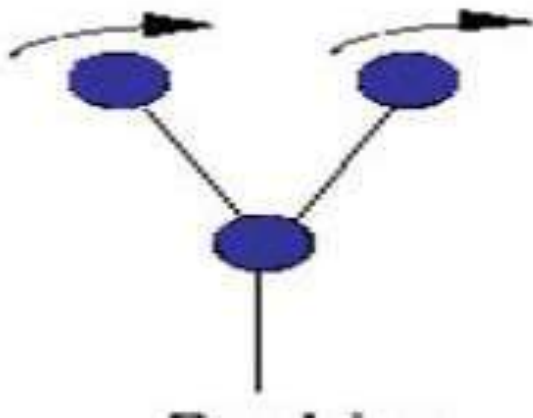
Asymmetric

a. Symmetrical stretching: The atoms of a molecule either move away or towards the central atom, but in the same direction.

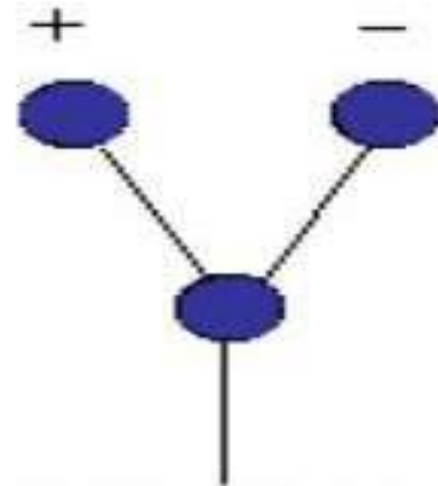
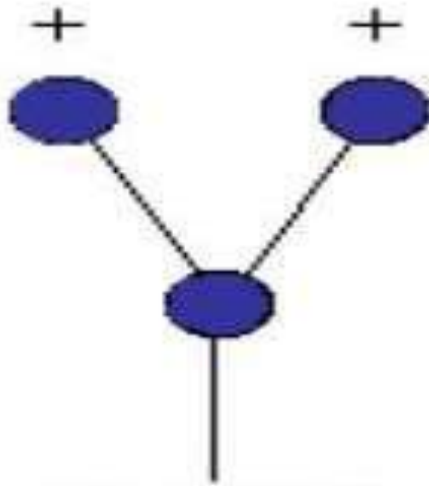
b. Asymmetric Stretching: One atom approach towards the central atom while other departs from it.



- a) **Rocking:** In-plane bending of atoms occurs wherein they swing back and forth with respect to the central atom.
- a) **Scissoring:** In-plane bending of atoms occur wherein they move back and forth. i.e., they approach to each other.



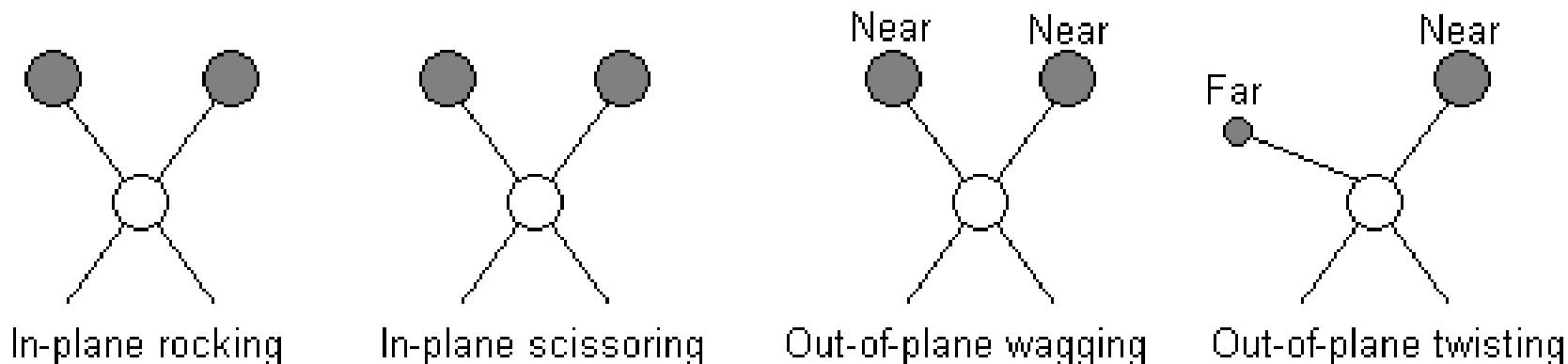
- a) **Wagging:-** Two atoms oscillate up and below the plane with respect to the central atom.
- b) **Twisting:-** One of atom moved up the plane while other down the plane with respect to central atom.



Bending Vibrations

- Characterized by change of angle between two covalent bonds, due to change in the position of the atoms relative to the original bond axis. These modes are further divided into four types:
a) Scissoring, b) Rocking c) Wagging and d) Twisting

Bending vibrations



Fundamental Modes of Vibrations



- Stretching and bending occur at a certain quantized frequencies.
- A particular vibration will absorb radiations only if it causes change in Dipole Moment of the molecule.
- Vibrational frequency increases with the increase in the bond strength
- **No. of fundamental modes of vibrations** for a molecule can be calculated from the no of atoms in a molecule and its geometry.
- Molecule containing N atoms have $3N$ degrees of freedom
- 1) For **linear** molecule: **$3N-5$** possible modes of vibration
- 2) For **non-linear** molecule: **$3N-6$** possible modes of vibration

Fundamental Modes of Vibrations



Examples:

Molecule	Atoms (N)	Geometry of Molecule	Fundamental modes of vibrations
NO	2	Linear	1
CO₂	3	Linear	4
H₂O	3	Non-linear	3
NH₃	4	Non-linear	6
CH₄	5	Non-linear	9

Regions in IR spectrum



- **Middle IR Region**
- **4000- 667 cm^{-1} (2.5 to 15 μ)**
- Divided into **three** sub regions as

I. Functional group region: **4000- 1300 cm^{-1} (2.5 to 7.7 μ)**

II. Finger print region: **1300- 909 cm^{-1} (7.7 to 11 μ)**

III. Aromatic region: **909- 667 cm^{-1} (11 to 15 μ)**

Functional group region



- The region extends from: 2.5-7.7 μ (4000-1300 cm^{-1})
- It contains absorption bands due to stretching vibrations of functional groups such as O-H, N-H, C-H, multiple bonds, carbonyl group may be aldehyde or ketone etc.
- Useful for Organic Chemists

Intensity Trends

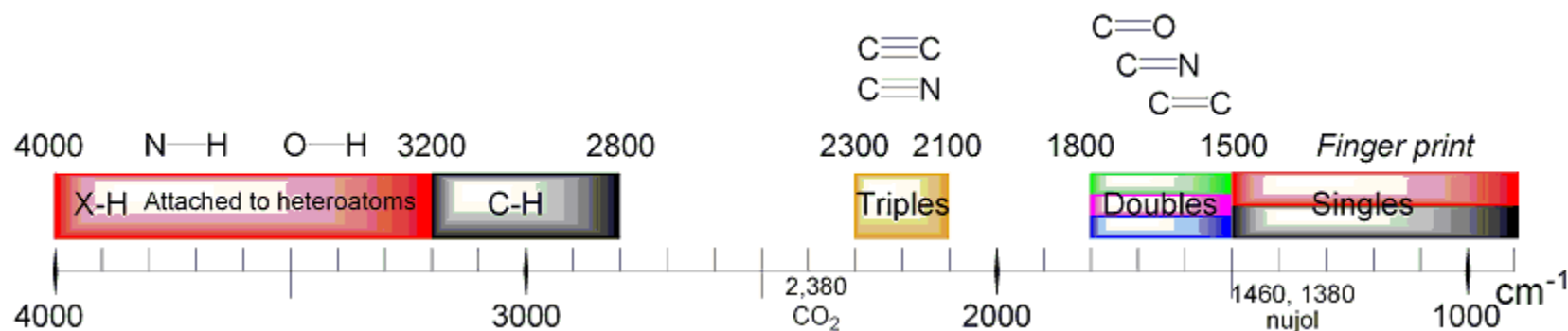
- Follows change in dipole caused by vibrating atoms
 - Polar bonds (strong bond dipoles) absorb strongly
 - O-H
 - C=O, C=N
 - C-O
 - Nonpolar bonds absorb weakly
 - C=C, C≡C
- Follows overlapping bands
 - CH bands tend to overlap
 - Molecules contain many CH
 - CH absorptions tend to be strong

Energy Trends

- Energy follows vibration frequency of atoms
- light atoms vibrate more rapidly: C-H, N-H, S-H, O-H vibrations ($2500\text{--}3700\text{ cm}^{-1}$)
- Multiple bonds vibrate less rapidly:
 - Triple bonds ($2500\text{--}2000\text{ cm}^{-1}$) :
 - $\text{C}\equiv\text{C}$ ($2100\text{--}2200\text{ cm}^{-1}$)
 - $\text{C}\equiv\text{N}$ ($2240\text{--}2280\text{ cm}^{-1}$)
 - Double bonds ($2000\text{--}1500\text{ cm}^{-1}$):
 - $\text{C}=\text{O}$ ($1680\text{--}1750\text{ cm}^{-1}$)
 - $\text{C}=\text{C}$ ($1620\text{--}1680\text{ cm}^{-1}$)
 - Single bond : C-O ($1025\text{--}1200\text{ cm}^{-1}$)
- $1500\text{--}400\text{ cm}^{-1}$, an absorption that involves the deformation of other bondings.

IR Spectrum Distribution

1. 4000-2500 cm^{-1} , absorption of atom which is bond to H atom, ex: C-H, O-H and N-H
2. 2500-2000 cm^{-1} , triple bond, ex: $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$
3. 2000-1500 cm^{-1} , double bond, ex: $\text{C}=\text{O}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$
4. 1500-400 cm^{-1} , an absorption that involves the deformation of other bondings.



2000-1500 cm^{-1} , double bond, ex: $\text{C}=\text{O}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$

$\text{C}=\text{O}$ (1680-1750)

Fingerprint region

- The region extends from: $11\text{-}15\ \mu$ ($1300\text{-}909\ \text{cm}^{-1}$)
- It is the most complex part of IR spectrum.
- The absorption bands in this region are due to stretching as well as bending vibrations.
- This region is not useful for interpretation but can be used for identification of compounds.
- If FP region of 2 samples are identical then these samples are also identical.

Aromatic Region

- 11-15 μ (909-667 cm^{-1})
- This region is useful for determination of aromatic character.
- The absorption bands in this region are due to bending vibrations.
- The absorption bands in this region provides information about aromatic substitution pattern such as ortho, meta and para substitution.



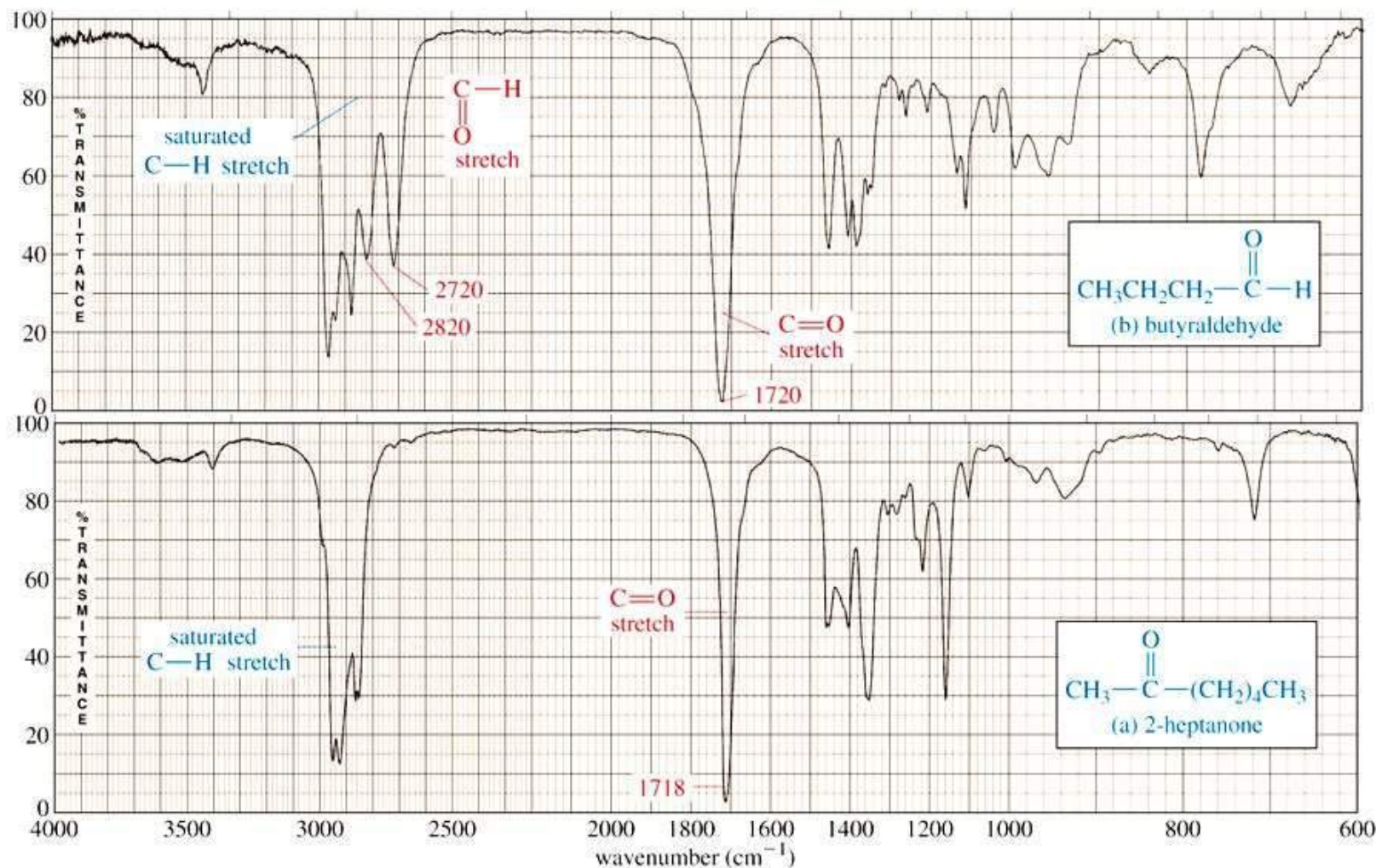
Bond	Type of Compound	Range of Abso.
C-H	Alkane	2800-3000
=C-H	Alkene	3000-3100
=-C-H	Alkyne	3200-3300
Ar-H	Aromatic Rings	3000-3100
-O-H	Alcohols(Phenols)	3200-3600 (Broad)
-C-H (C=O)	Aldehyde	2720 (1700)
	Ketone	1700
C==O (OH)	Carboxylic Acid	1730 (3300-2700 Broad)

Parts of IR Spectrum



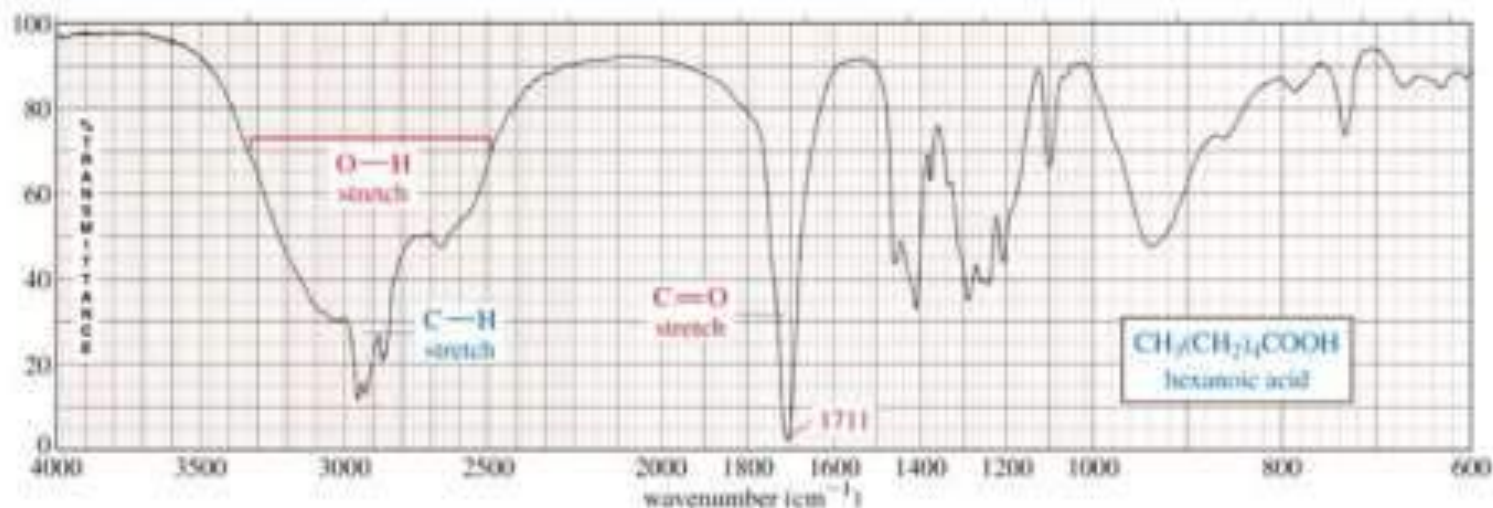
- The IR spectrum is basically **a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption).**
- Frequencies appear on the x -axis in units of inverse centimeters i.e. cm^{-1} (wave numbers), and intensities are plotted on the y -axis in percentage units.
- IR is most useful in providing information about the presence or absence of specific **functional groups.**
- IR can provide a **molecular fingerprint** that can be used while comparing samples.
- IR can provide information about **aromatic substitution** pattern.

IR SPECTRUM OF ALDEHYDES AND KETONES



IR SPECTRUM OF A CARBOXYLIC ACID

A carboxylic acid functional group combines the features of alcohols and ketones because it has both the **O-H bond** and the **C=O bond**. Therefore carboxylic acids show a very strong and broad band covering a wide range between **2800** and **3500 cm^{-1}** for the O-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** corresponding to the C=O stretch.

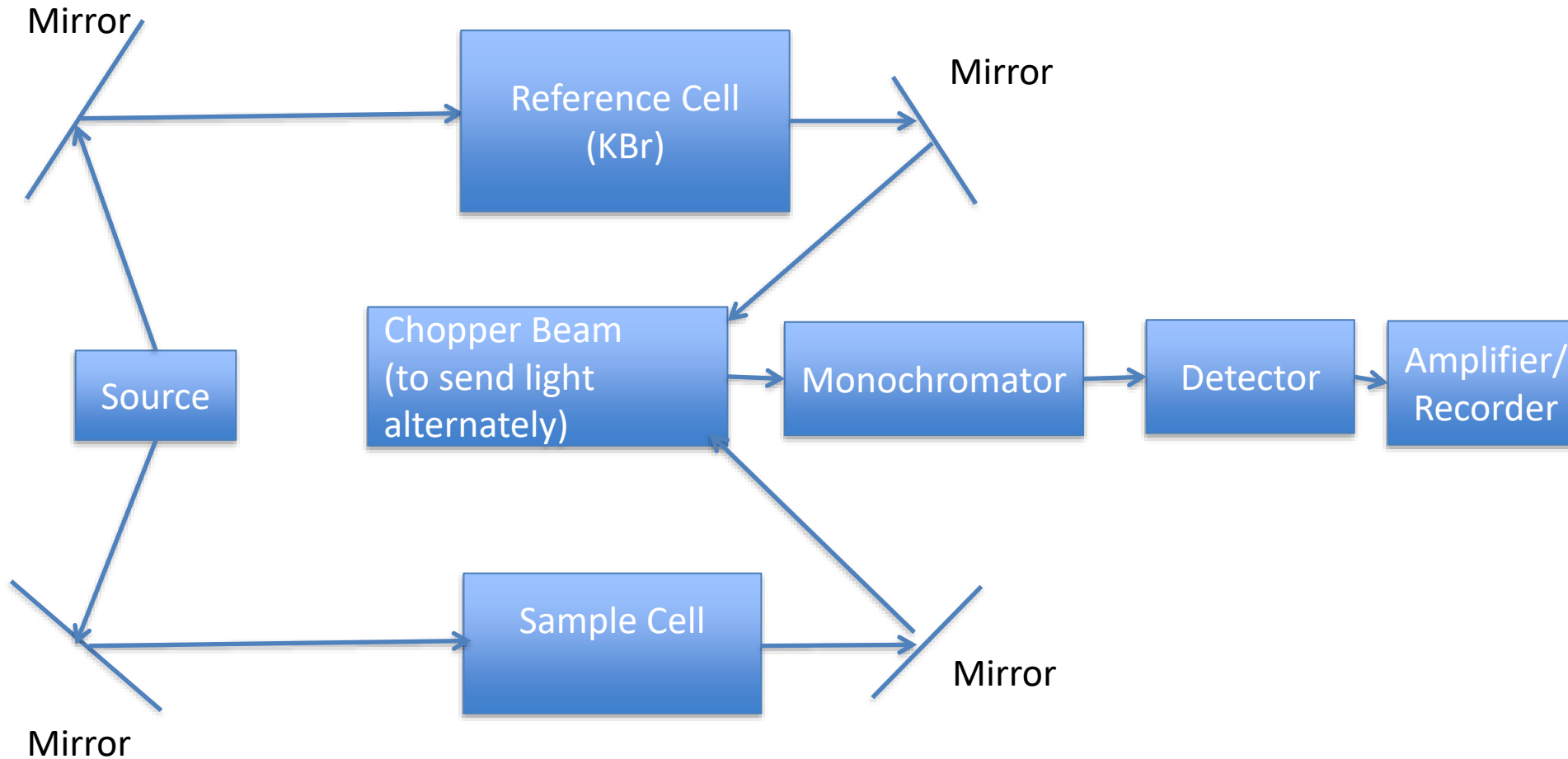


Instrumentation of IR spectroscopy



- Schematic / block diagram with function & material of each component
 - Source
 - Monochromator
 - Sample cell
 - Detector
 - Amplifier & recorder

Instrumentation of IR Spectroscopy



Instrumentation of IR Spectroscopy



Source: Provides IR radiation

- Common IR radiation source are inert solids that are heated electrically to a range of 1000°C to 1800°C to promote thermal emission of radiation in IR region of EM spectrum

Most common sources are:

- 1) **Nernst filament/Glover** :composed of rare earth oxides such as Zirconium, Yttrium and Erbium or mixture of Ln_xO_y
 - 2) **Globar** : Rod (5mm D & 50mm L) of Silicon Carbide
 - 3) **Incandescent Wire**: Nichrome coil
- All produce continuous radiations, but with different radiation energy profiles. Beam is divided into 2 equivalent beams, one passing through sample and the other as reference beam

Instrumentation of IR Spectroscopy



- **Reference Cell and Sample Cell:** Keep the sample (Solid/Liquid/ Gas/Solution) to be analyzed and the material of cells are transparent to IR region.

Cells are commonly made up of **Alkali metal halides** such as: NaCl, KBr and KCL

Solid Sampling: Solid is dissolved in non aqueous solvent. A drop of solution placed on the disc of alkali halide. Solvent is dried to give thin film on surface.

Amorphous solid are deposited on KBr or NaCl plates/cell by evaporation of solution of solid

Sample mixed with mineral oil (Nujol) to make fine paste and thin film of paste applied on the KBr pellet

Sample is finely ground with KBr and pressed to pellet

Liquid Sampling: Liquids sandwiched using cells made up of KBr or NaCl

Gas Sampling: Gases are filled in KBr/NaCl cells

Instrumentation of IR Spectroscopy



- **Chopper Beam:**

Splitter, Used to send the transmitted radiation alternatively to the monochromator

- **Monochromator:** Converts polychromatic radiation into monochromatic radiation Consists of Prism/ Filters/Diffraction Gratings made up of **Alkali halides** (NaCl, KBr, LiF)

Detectors: Transducer converting radiation into electric signal or current. Various types:

Thermal Detectors:

Thermocouple : Consists of Antimony and Bismuth wires welded to form 2 junctions wherein one becomes hotter (due to IR) and other one is colder. PD gets developed between two junctions as a result of Temperature difference. Current is directly \propto IR falling on detector

Instrumentation of IR Spectroscopy



Bolometer: Thin metal (Pt/Ni) conductor based on thermal radiation; used to measure increase in the resistance (in turn current flow changes) with the increase in temperature (per $^{\circ}\text{C}$)

Thermister: Fused Metal oxide mixture, Increasing Temperature, Decreasing resistance by $5\%/^{\circ}\text{C}$

Golay Detector: Contains Xenon and Used as a Gas sensing thermometer

Photoconducting Detectors

Semiconductor Detectors

Amplifier: Used to amplify the signal

Recorder: IR Spectra gets Displayed

Applications of IR Spectroscopy



- Determination of structure & functional group.
- Study of kinetics of chemical reaction.
- Distinction between intra & inter molecular hydrogen bonding.
- Detection of impurities.
- Study of isomerism.
- Detection of size of ring ketones.

Applications of IR spectroscopy



1. Identification of functional group and structure elucidation

The IR spectrum is divided in two parts:

1) **Group frequency region ($4000\text{-}1400\text{ cm}^{-1}$)**

2) **Fingerprint region ($1400\text{-}400\text{ cm}^{-1}$)**

In Group frequency region, each peak corresponds to specific functional group .

For example: If IR Spectrum shows a broad peak in the region $3500\text{-}3200$, it indicates presence of O-H group of alcohol or phenol.

Applications of IR spectroscopy



1. Identification of functional group and structure elucidation

- Hence based on the peaks observed in functional group region functional group present in sample can be determined.
- These functional group helps to determine the possible structure of sample.
- Also peaks in the finger print region helps to decide characteristic peaks of a particular bond between two atoms, based on vibration frequency of that bond.
- Such peaks will also help to determine structure of sample

Applications of IR spectroscopy



2. Identification of substances

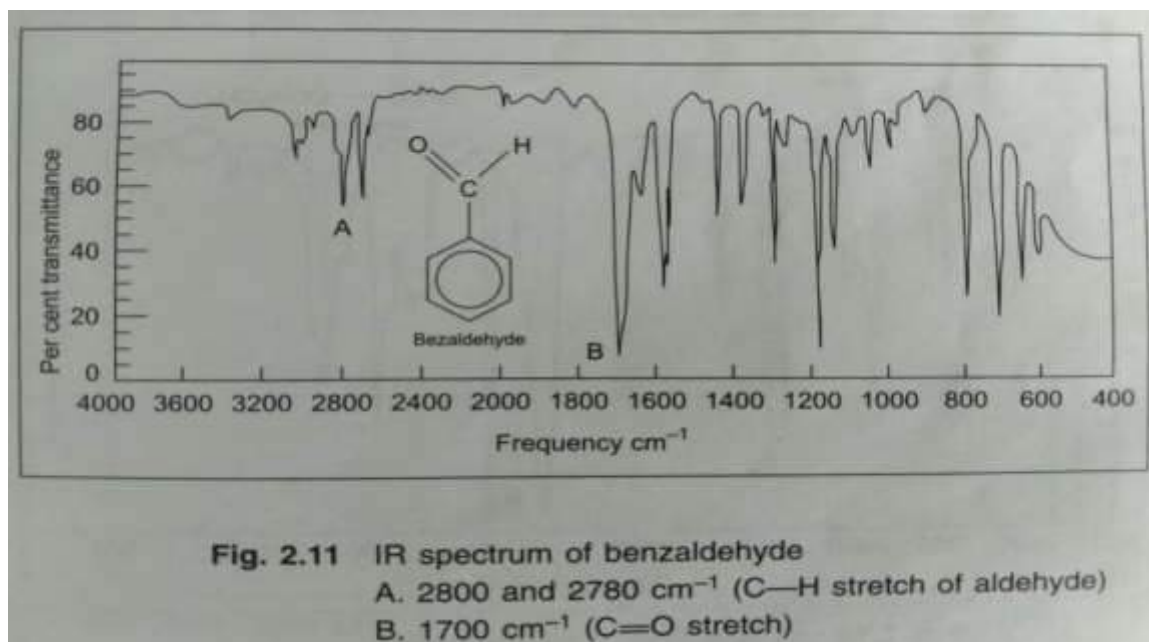
- Depending upon the number of atoms present in a molecule and whether the structural arrangement is linear or non-linear. Large number of absorption bands are observed in the IR spectra of organic molecule.
- Hence the two molecules having same IR spectra is not possible.
- Hence based on the IR spectral data the two samples are identical or not can be decided.
- So if two compounds have identical IR spectra then both of them must be samples of the same substances.

Applications of IR spectroscopy



2. Identification of substances

IR spectra of two enantiomeric compounds are identical. So IR spectroscopy fails to distinguish between enantiomers. For example, an IR spectrum of benzaldehyde is observed as follows.



No other compound then benzaldehyde produces same IR spectra as shown above.

3. Detection of impurities

- IR spectrum of an organic molecule does not matches with any other molecule.
- Now if a test sample to be determined is compared with the standard spectra of same compound, then both should have same spectral pattern.
- If any additional peaks are observed in the IR spectrum, then it suggest these additional peaks are due to impurities present in the compound.

4. Quantitative analysis

- In case of Quantitative analysis baseline technique is used to determine quantity of a substance or a mixture.
- Here absorbance ($\log I_0/I_t$) of chosen characteristic peaks of substance under analysis is compared with the same characteristic peaks of same pure sample of known concentration.
- This comparison will be helpful to find quantity of analyte substance.
- The method can be used to determine quantity of a substance either in pure form or in the form of mixture of two or more compounds.

Applications of IR spectroscopy



5. Progress of Reaction

In case of chemical reaction of organic molecule, generally one functional group gets converted to another. That means one functional group will disappear and another gets formed.

If a small portion of reaction mass is analyzed by IR spectrophotometer then progress of reaction can be determined.

Just for example if $\text{C}=\text{O}$ is converted to $-\text{OH}$ then sharp peak of $\text{C}=\text{O}$ will disappear and broad band of $-\text{OH}$ will appear.

References

- 1) Instrumental Methods of Chemical Analysis by Chatwal
- 2) Elementary Organic Spectroscopy by Sharma Y. R.

Principles

- When the certain molecules are exposed to IR light, it will absorb the energy to make the atoms of molecules vibrating
- The vibration frequency depend on the amount of atoms and the length and the strength of atomic bonding
- Molecule vibration is stimulated by absorption radiation in the same frequency with the frequency of its origin vibrations

Principles IR Spectroscopy



- Atoms in a molecule are not still. They vibrate & rotate in variety of ways (in certain quantized energy levels) due to absorption of IR radiation
- ER of IR region is absorbed to various extents by all substances
- The absorption involves excitation of molecules to higher **Vibrational States** and therefore, is **Quantized**

The vibrations increase in amplitude when ER raises it to the next vibrational level.