

# Spectroscopy

**Definition :** Spectroscopy may be defined as the interaction between the matter and electromagnetic radiations. The arrangement of all types of electromagnetic radiations in order of their increasing wavelengths or decreasing frequencies is known as complete electromagnetic spectrum. The visible spectrum represents only a small portion of the electromagnetic spectrum.

- Advantages :**
1. Spectroscopic methods take much less time.
  2. For spectroscopic analysis, only a very small amount of the substance is sufficient.

# Spectroscopy

1. The substance remains generally unaffected or unchanged during spectroscopic examination and can be re-used for other tests, if required.
2. The spectroscopic methods are comparatively much reliable in establishing the structure and identity of a compound.

## **Classification of Electronic Spectra :**

Electronic spectra can be classified into following two types: (1) Emission spectra

(2) Absorption spectra

# Spectroscopy

## Types of Absorption Spectra :

**(i) Visible and ultra-violet radiations :** cover the wavelength range from 200-800 m $\mu$ . The absorption of radiation in this region causes the excitation of  $\pi$ -electron in a conjugated or an unconjugated system, the separation between the ground state and the excited energy level will be less and hence absorption occurs at a longer wavelength. Also carbonyl group of an aldehyde or a ketone absorbs at some characteristic wavelengths. Thus, an ultra-violet or visible spectrum is quite useful for the detection of conjugation, Carbonyl group etc.

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**(ii) The Infra-red radiations** which cover the wavelength range from 0.8 to 2.5  $\mu$  constitute near Infrared region and that from 15 to 25  $\mu$  is called far Infrared region. The most useful region for Infrared spectroscopy is 2.5 to 15  $\mu$ . The absorption of radiation by an organic compound in this region causes molecular vibrations. The changes in the vibrational levels are accompanied by the changes in the rotational levels. Thus, certain bands appear which characteristically absorb for the stretching vibrations and are very helpful in structure elucidation.

The absorptions at higher wavelength in the infrared region (Finger print region) are most characteristic of a compound and also help in distinguishing one compound from the other.

# Spectroscopy

**(iii) NMR Spectroscopy** provides a complete insight into the environment and the arrangement of atoms within a molecule. For this technique, radiations of longest wavelength range i.e., Radiowaves are useful. A sample under investigation is placed in a strong magnetic field and irradiated with Radiowaves.

# Spectroscopy

## ULTRA-VIOLET AND VISIBLE SPECTROSCOPY

### The Absorption Laws

- (i) Lambert's law
- (ii) Beer's law

**Lambert's law** : When a beam of monochromatic radiation passes through a homogeneous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation.

Mathematically, the law is expressed as.

$$- dl / dx = kl$$

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where  $I$  = intensity of radiation after passing through a thickness  $x$ , of the medium.

$dI$  = infinitesimally small decrease in the intensity of radiation on passing through infinitesimally small thickness,  $dx$  of the medium.

$-dI / dx$  = rate of decrease of intensity of radiation with thickness of the absorbing medium.

$k$  = Proportionality constant or absorption coefficient. Its value depends upon the nature of the absorbing medium.

Let  $I_0$  be the intensity of radiation before entering the absorbing medium ( $x = 0$ ).

Then  $I$ , the intensity of radiation after passing through any thickness, say  $x$  of the medium can be calculated as.

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$$\int_{I_0}^I \frac{dI}{I} = - \int_{x=0}^{x=x} k dx$$

or  $\ln \frac{I}{I_0} = -kx$  or  $\frac{I}{I_0} = e^{-kx}$

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

The intensity of the radiation absorbed,  $I_{abs}$  is given by.

$$I_{abs} = I_0 - I = I_0 (1 - e^{-kx})$$

The above Lambert's law equation can also be written by changing the natural logarithm to the base 10.

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

where  $a$  = extinction coefficient of the absorbing medium  
( $a = k / 2.303$ )



# Spectroscopy

## Beer's Law

This law states that; when a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution.

Mathematically, 
$$-\frac{dI}{dx} = K' Ic$$

where  $c$  = conc. of the solution in moles per litre.

$k'$  = molar absorption coefficient and its value depends upon the nature of the absorbing substance.

# Spectroscopy

Suppose  $I_0$  be the intensity of the radiation before entering the absorbing solution. (when  $n = a$ ), then the intensity of radiation,  $I$  after passing through the thickness  $x$ , of the medium can be calculated.

$$\int_{I_0}^I \frac{dI}{I} = - \int_{x=0}^{x=x} k' c dx$$

$$I = I_0 e^{-k' c x}$$

The above equation can also be written by changing the nature of logarithm to the base 10.

$$I = I_0 \cdot 10^{-a' c x} \quad \text{or} \quad \log \frac{I_0}{I} = \epsilon c l$$

# Spectroscopy

Here  $k' / 2.303 = a'$  where  $a'$  = molar extinction coefficient of the absorbing solution. Beer's law can also be stated as.

When a monochromatic light is passed through a solution of an absorbing substance, its absorption remains constant when the conc ( $c$ ) and the thickness of the absorption layer ( $x$ ) are changed in the inverse ratio.

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## Beer-Lambert's law

When a monochromatic light of intensity  $I$  is passed through a solution of concentration,  $c$  molar and thickness,  $dx$ , then intensity of transmitted light changes (due to absorption) by  $dI$ . Then, probability of absorption of radiation is given by

$$\frac{dI}{I} = -k c dx$$

where  $k$  is the proportionality constant. On integrating the above expression, between limits  $I = I_0$  at  $x = 0$  and  $I = I$  at  $x = l$ , we get

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

$$\ln \frac{I}{I_0} = -k c l$$

$$2.303 \log \frac{I}{I_0} = -k c l$$

$$\log \frac{I_0}{I} = \frac{k}{2.303} c \cdot l = \epsilon \cdot c \cdot l = A$$

Where  $\epsilon = k / 2.303$  is called the molar absorptivity coefficient and  $\log I_0 / I = A$  is called the absorbance.

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$$A = \epsilon \cdot c \cdot l$$

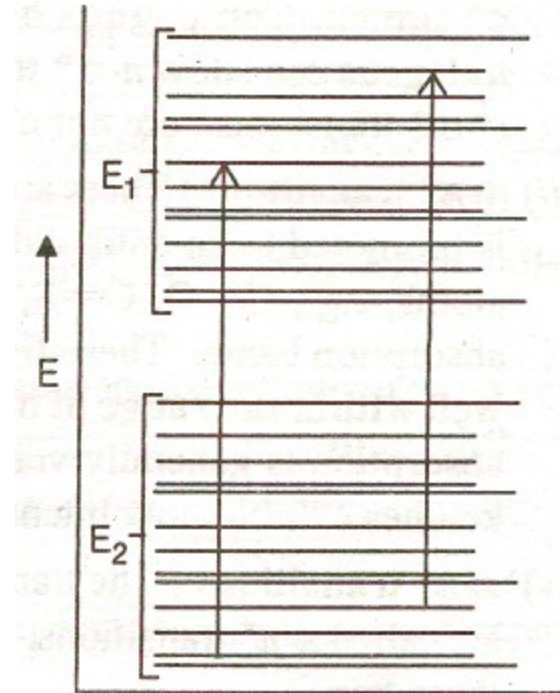
which is Beer-Lambert's law. Thus the absorbance  $A$  is directly proportional (i) to the molar concentration  $c$  as well as (ii) to the path length  $l$ .

# Spectroscopy

**Principle :** Absorption of ultraviolet and visible light brings changes in the electronic states of molecules associated with the excitation of an electron from a lower to a higher energy level. Each electronic level in a molecule is associated with a number of vibrational sub-levels (with smaller energy separation) and each vibrational sub-level in turn is associated with a number of rotational sub-levels (with still smaller energy separation). Thus, in its transition to a higher energy level, an electron can go from any of the sub-levels (corresponding to various vibrational and rotational states) in the ground state to any of the sub-levels in the excited state . Had the electronic excitation in the molecule occurred without any accompanying changes in vibrational and rotational sub-levels, the spectrum would have consisted of sharp lines with each line representing a change in electronic state.

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But due to the mixing of vibrational and rotational changes with electronic changes in the molecules, there will be a large number of possible transitions requiring only slightly different energies. This will require the absorption of a large number of wavelengths resulting in the formation of broad bands in the spectrum.

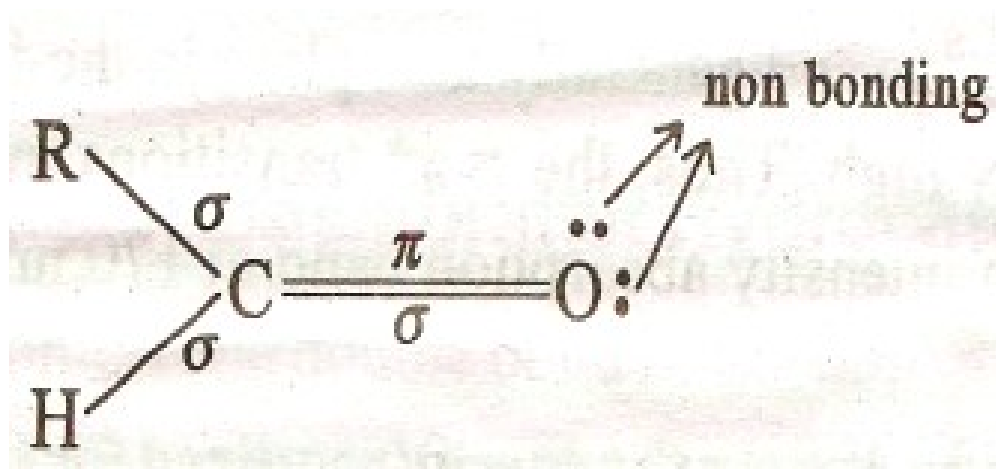




# Spectroscopy

**Electronic Excitations** : Electronic transition involves the promotion of an electron from one orbital to another orbital of higher energy. In a molecule, the electron promoted may be a  $\sigma$ -electron, a  $\pi$ -electron or an n-n electron.

**Example** : Aldehyde



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The higher energy orbitals where the electron can be promoted are those which are vacant in the ground state of the molecule and are commonly called **antibonding molecular orbitals**. The antibonding orbital associated with the  $\sigma$ -bond is called the  $\sigma^*$  orbital and that associated with  $\pi$ -bond is called the  $\pi^*$  orbital. Since the  $n$  electrons are not concerned in bond formation, here are no antibonding orbitals associated with them and hence during promotion they may promote either to  $\sigma^*$  or to  $\pi^*$ .

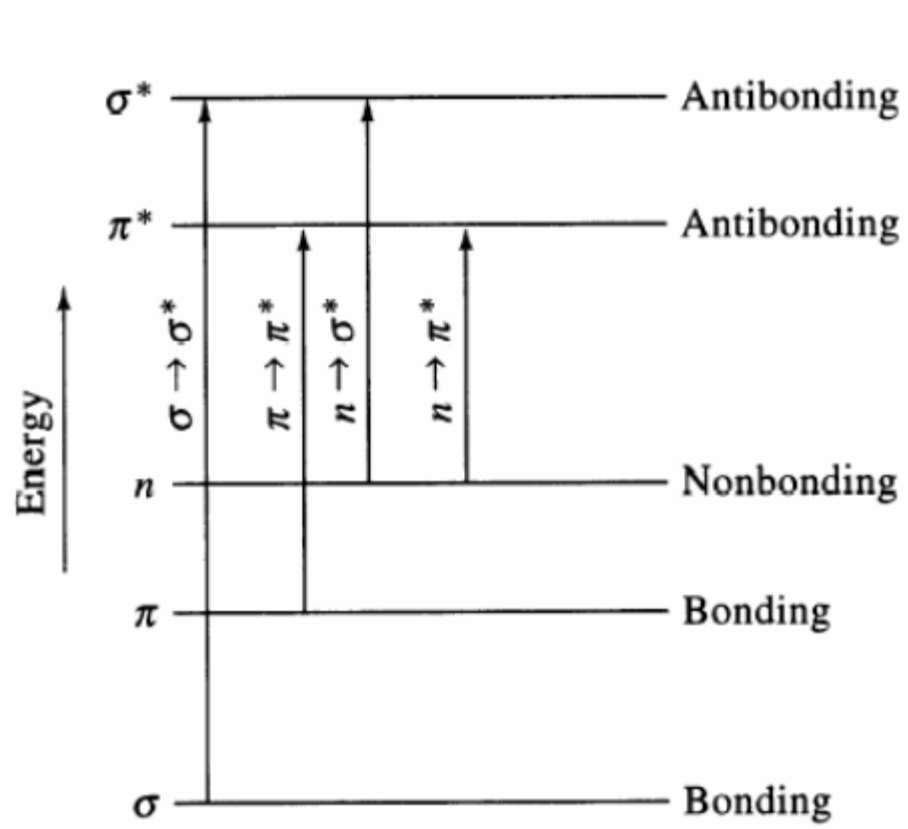
# Spectroscopy

Types of electronic transitions :

- (i)  **$\sigma$ -  $\sigma^*$  transitions** : The transition in which a  $\sigma$ -electron is excited to an antibonding  $\sigma^*$  orbital are called  $\sigma$  -  $\sigma^*$  transitions. The energy required for these transitions is very high and hence they occur at shorter wavelengths . Thus, the compounds in which all the valence shell electrons are involved in  $\sigma$  bond formation such as saturated hydrocarbons, do not show absorption in the ordinary ultraviolet region.
- (ii)  **$n$ -  $\sigma^*$  transition** : These are the excitations from a non-bonding atomic orbital to an antibonding  $\sigma^*$  orbital. Compounds having non-bonding electrons on oxygen, nitrogen, sulphur or halogens can show  $n$ -  $\sigma^*$  transitions. These transitions are of lower energy than  $\sigma$  -  $\sigma^*$  transitions.

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- (iii) **n- $\pi^*$  transition** : These are the transitions in which an electron in a non-bonding atomic orbital is promoted to an antibonding  $\pi^*$  orbital. Compounds having multiple bonds between hetero atoms, e.g., C=O, C=S, N=O, show these transitions which appear as weak absorption bands. These transitions require only small amounts of energy and take place well within the range of ordinary ultraviolet region. The intensity of absorption is very low.
- (iv)  **$\pi^*$ - $\pi^*$  transition** : The transitions in which a  $\pi$ -electron is excited to an antibonding  $\pi^*$  orbital are called  $\pi$ - $\pi^*$  transitions. In case of simple molecules containing isolated unsaturated carbons, these transitions require relatively higher energy and generally take place in the far UV region.



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## Terms used in UV Spectroscopy :

1. **Chromophore:** A structural group such as a double bond that can absorb ultraviolet radiations is called a chromophore.
2. **Bathochromic shift:** When the absorption maximum of a compound shifts to a longer wavelength due to the presence of an auxochrome, the compound is said to have undergone a bathochromic shift or red shift .
3. **Auxochrome:** An auxillary group that causes bathochromic shift in a chromophore is called an auxochrome.

# Spectroscopy

- 4. Hypsochromic shift** : When the absorption maximum of a compound shifts to a shorter wavelength on certain treatment, the compound is said to have undergone a hypsochromic shift/ Blue shift .
- 5. Hyperchromic effect** : It is an effect due to which the intensity of absorption of maximum increases.
- 6. Hypochromic effect** : It is an effect due to which the intensity of absorption maximum decreases.

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**UV Spectra of Unsaturated Hydrocarbons :** Carbon-carbon double bond is the simplest chromophore.

Ethylene ( $\text{H}_2\text{C}=\text{CH}_2$ ), has  $\lambda_{\text{max}}$  at 165 nm ( $\epsilon = 100$ ). As the value 165 nm lies in the far UV region, such a  $\lambda_{\text{max}}$  can be determined only in a special vacuum spectrometer. When a C=C bond is substituted by auxochromic groups like alkyl, there is a bathochromic shift of  $\lambda_{\text{max}}$ . When there is an additional double bond in a non-conjugated position, the  $\lambda_{\text{max}}$  is almost the same but  $\epsilon$  is approximately doubled. When these bonds are conjugated as in 1,3,5-butadiene, there is significant bathochromic shift and the  $\lambda_{\text{max}}$  falls in the near UV or visible regions. 1,3-Butadiene, shows  $\lambda_{\text{max}}$  at 217nm. There is also a little increase in their  $\epsilon$  value.



# Spectroscopy

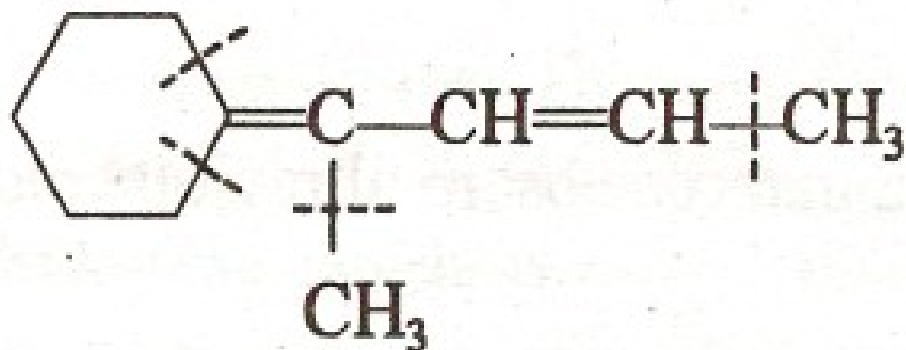
## Woodward Rules for Dienes :

The rules are as follows:

1. The basic  $\lambda_{\text{max}}$  of conjugated dienes is 217 nm.
2. Add 5 nm for each alkyl substituent on the doubly bonded carbon.
3. Add 5 nm for each exocyclic double bond. In case the same bond is exocyclic to two rings, 2 x 5 nm may be added.

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Example :



Butadiene (Basic Value) = 217 nm

2 Alkyl substituents (2 × 5) = 10 nm

2 Ring residues = 10 nm

1 Exocyclic double bond = 5 nm

Calculated Value = 242 nm

Observed Value = 242 nm

# Spectroscopy

## Applications of U.V. spectroscopy :

1. U.V. spectroscopy is used for characterizing aromatic compounds and conjugated olefins.
2. It is one of the best way for detecting impurities in organic compounds.
3. U.V. spectroscopy can be used to study the kinetics of chemical reactions.
4. Dissociation constants for weak acids and bases can be determined by U.V. spectroscopy.
5. Structure of chloral can be confirmed by U.V. spectroscopy.
6. **Detection of geometrical isomers:** UV spectroscopy can be used for detecting the geometrical isomers of a given compound. Trans isomers exhibit  $\lambda_{\max}$  at slightly longer wavelengths and have larger extinction coefficients than the cis-isomers.

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**Infrared Spectroscopy** : It is one of the most powerful analytical techniques which gives us the possibility of identification of a compound. Radiations in the infrared region are not energetic enough to cause electronic excitations in most organic molecules. Although infrared radiation is weak, it does supply sufficient energy for bonds in the molecule to vibrate by Stretching or Bending. The atoms of a molecule can be considered as attached by springs that are set in motion by the application of energy.

An infrared spectrum is a highly characteristic property of an organic compound and can be used both to establish the identity of two compounds and to reveal the structure of a new compound.

# Spectroscopy

**Vibrations** : A diatomic molecule has only one vibrational mode and hence it yields a rather simple system.

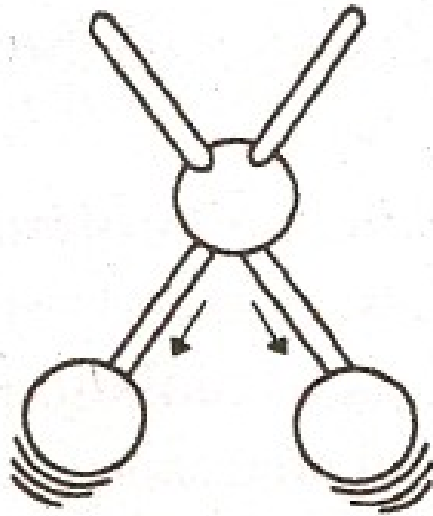
For a polyatomic molecule, several vibrational modes are possible therefore a complicated IR spectrum is obtained for it. Normal modes of vibrations are of two types:

**(i) Stretching vibrations**

In this type of vibrations, the distance between two atoms increases or decreases but the atoms remain in same bond axis. Stretching vibrations are of two types; viz., **Symmetric** and **asymmetric**.

# Spectroscopy

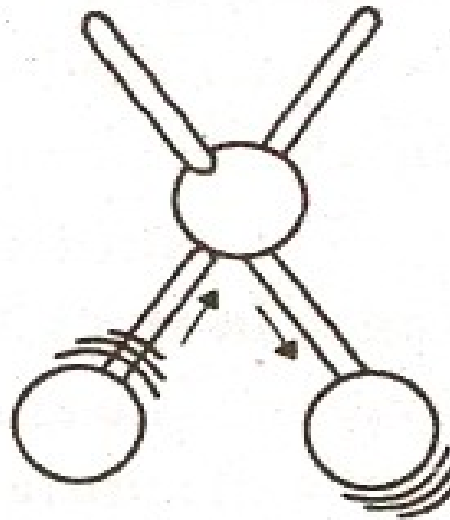
(a) **Symmetric stretching:** When the stretching and compressing occurs in a symmetric way, it is called symmetric stretching



Symmetric

# Spectroscopy

**(b) Asymmetric stretching :** When one bond is compressing and the other is stretching than it is known as asymmetric stretching.

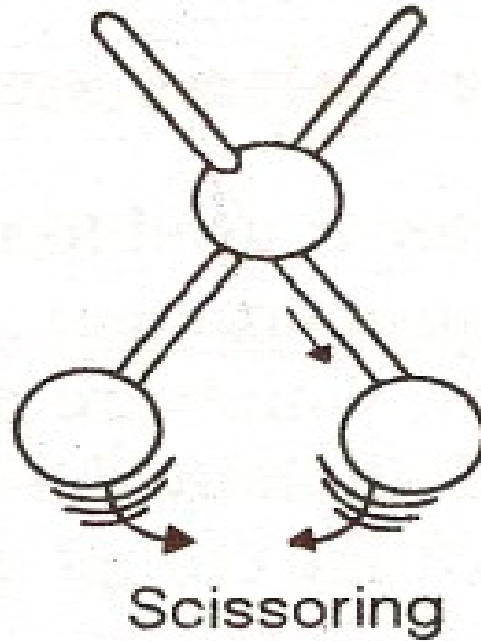


Asymmetric

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(ii) **Bending or deformation vibrations** : Such type of vibration may consist of a change in bond angle between bonds with a common atom. These are of four types:

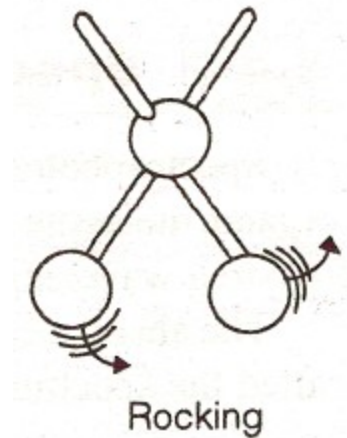
(a) **Scissoring** in which two atoms approach each other.



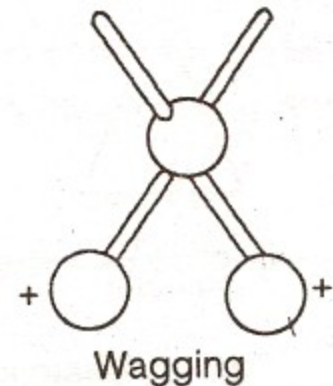


# Spectroscopy

**(b) Rocking** involves the movement of atoms in same direction.

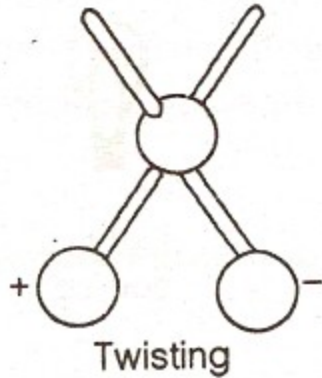


**(c) Wagging** in which the atoms move up and below the plane with respect to central atom.



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(d) **Twisting** involves the movement of one atom up and the other atom down the plane with respect to central atom.



# Spectroscopy

## Characteristics IR Absorption Bands

Frequency Range $\text{cm}^{-1}$	Bond	Compound
2850 – 2960	C—H	Alkanes
1350 – 1470	C—H	Alkenes
3020 – 3080	C—H	Benzene rings
3300	C—H	Alkynes
1620 – 1680	C=C	Alkenes
1500 – 1600	C=C	Aromatic rings
1080–1300	C—O	Alcohols, ethers, carboxylic acids, esters
1690 – 1750	C=O	Aldehydes, Ketones, Esters
1700 – 1725	C=O	Carboxylic acids
1770 – 1820	C=O	Acid chlorides
1630 – 1690	C=O	Amides
3200 – 3600	O—H	H -bonded alcohols, phenols
3610 – 3640	O—H	Monohydric alcohols, phenols
2100 – 2200	C≡C	Alkynes
2210 – 2260	C≡N	Nitriles
3300 – 3500	N—H	Amines
1180 – 1360	C—N	Amines
1340 – 1500	—NO <sub>2</sub>	Nitro compounds

# Spectroscopy

## Conditions for the Infra-red Absorption

- (a) The frequency of the vibration must satisfy the equation  
$$E = h\nu.$$
- (b) The intensity of absorption must be proportional to square of the rate of change of dipole.
- (c) The natural frequency of vibration of the molecule must be equal to the frequency of incident radiation.
- (d) Changes in vibration must stimulate changes in the dipole moment of the molecule.

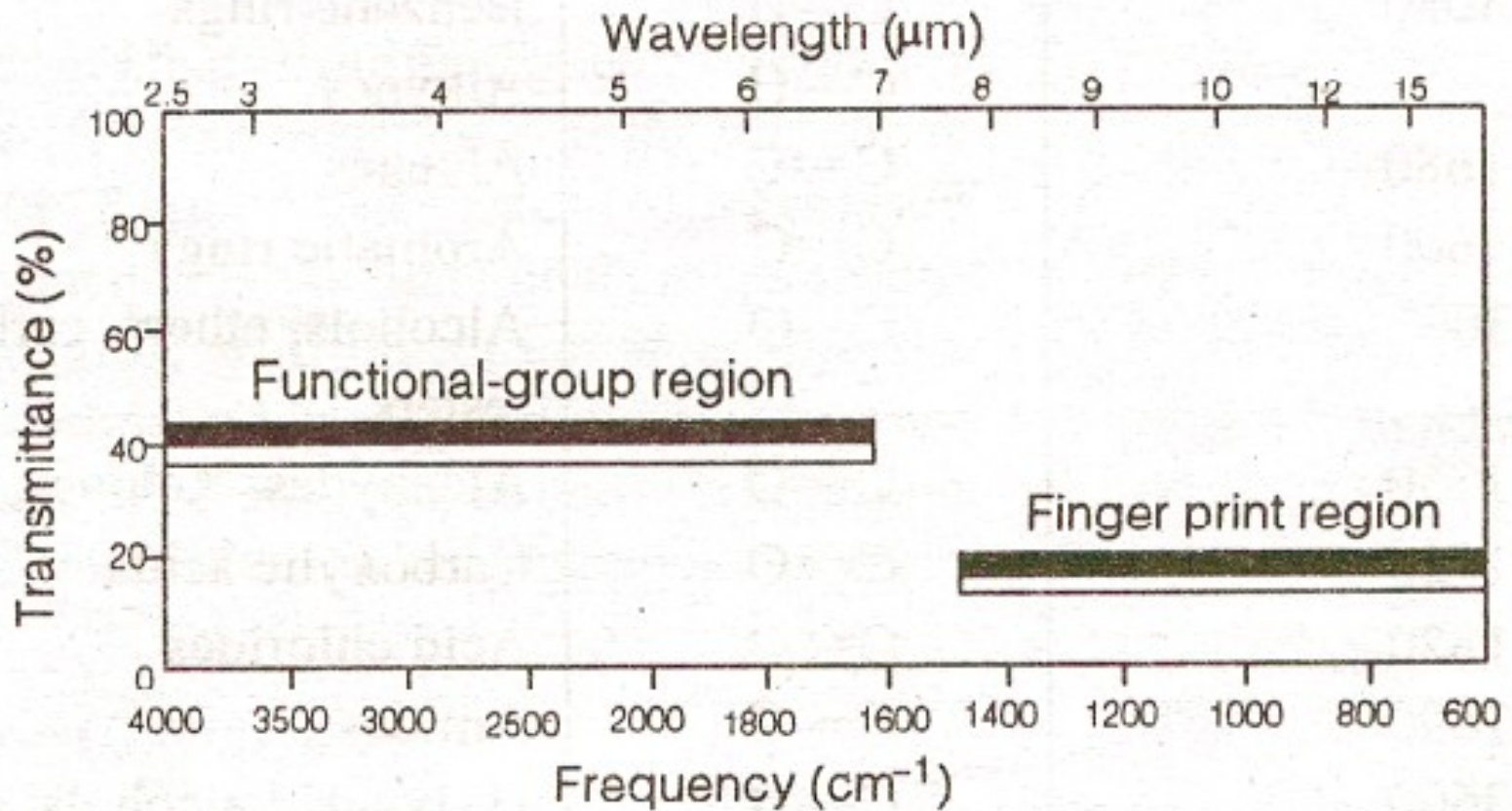
# Spectroscopy

## Interpretation of IR Spectrum

Some bands of weak intensity may occur at shorter wavelengths and these are called combination bands or overtone bands. The absorption bands of a particular group may be shifted by certain structural features- conjugation, angle strain or vander Waals strain, hydrogen bonding. Overtone bands should not be confused with the intense fundamental bands originating from normal vibrational modes. An IR spectrum is generally studied in two parts.

# Spectroscopy

## Interpretation of IR Spectrum



# Spectroscopy

## Interpretation of IR Spectrum

- (i) **Functional group region:** The bands in this region are particularly useful in identification of the type of functional groups present in the organic molecule. This region lies in between  $5000\text{ cm}^{-1}$  to  $1300\text{ cm}^{-1}$ .
- (ii) **Finger print region:** The area from  $1300\text{ cm}^{-1}$  to  $687\text{ cm}^{-1}$  is called the finger print region. The IR spectrum of an unknown substance is compared with spectra of possible substances. It is associated with complex vibrational and rotational energy changes and is characteristic of the molecule as a whole. No two compounds, however, closely related can have identical or superimposable bands in this region.

# Spectroscopy

## IR Spectra of Hydrocarbons

In hydrocarbons, bands due to stretching may appear at about 1500 and 1600  $\text{cm}^{-1}$  for aromatic bond at 1650  $\text{cm}^{-1}$  or double bonds, and at 2100  $\text{cm}^{-1}$  for triple bonds. These bands are generally unreliable. Absorption due to carbon-hydrogen stretching, occurs at highest frequency side of the spectrum, is characteristic of the hybridization of the carbon, at 3300  $\text{cm}^{-1}$  for  $sp$ -hybridized carbon (alkynes), at 3000 – 3100  $\text{cm}^{-1}$  for  $sp^2$  hybridized carbon (alkene and benzene rings) and at 2800 - 3000  $\text{cm}^{-1}$  for  $Sp^3$  hybridized carbon (alkanes).

Absorption due to different kinds of carbon-hydrogen bending, occurs at the lowest frequency side of the spectrum, is also be characteristic of structure.



# Spectroscopy

## IR Spectra of Alcohols and Ethers

For hydrogen-bonded alcohol, a strong, band appears in the 3200-3600  $\text{cm}^{-1}$  region due to O-H stretching. (A monohydric alcohol gives a sharp, variable band at 3610-3640  $\text{cm}^{-1}$ ). Another strong, broad band, due- to C-O stretching, appears in the 1000-1200  $\text{cm}^{-1}$  region, the exact frequency depending on the nature of the alcohol. (3<sup>o</sup> alcohol about 1150  $\text{cm}^{-1}$ , 2<sup>o</sup> about 1100  $\text{cm}^{-1}$  and for 1<sup>o</sup> about 1050  $\text{cm}^{-1}$ ). Phenols also give both these bands, but the C-O stretching appears at higher frequencies.

Ethers show C-O stretching, but the O-H band is absent (characteristic of alcohols)

alkyl ethers 1060 - 1150  $\text{cm}^{-1}$ ,

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## IR Spectra of Aldehydes and Ketones

The strong band due to C=O stretching appears at about 1700  $\text{cm}^{-1}$ , (R. CHO 1725  $\text{cm}^{-1}$ , ArCHO 1700  $\text{cm}^{-1}$ ,  $\text{R}_2\text{CO}$  1710  $\text{cm}^{-1}$  and ArCOR 1690  $\text{cm}^{-1}$ ). The -CHO group of an aldehyde has a characteristic C-H stretching band near 2720  $\text{cm}^{-1}$ ; this in conjunction with the carbonyl band, as a good evidence for an aldehyde.

## IR Spectra of Carboxylic Acids and Derivatives

For hydrogen-bonded (dimeric) acids, O-H stretching gives a strong, broad band in the 2500-3000  $\text{cm}^{-1}$  region, the C=O band is at about 1700  $\text{cm}^{-1}$ . Acids also show a C-O stretching band at about 1250  $\text{cm}^{-1}$  and bands for O-H bending near 1400  $\text{cm}^{-1}$  and 920  $\text{cm}^{-1}$  (broad). Enols, also give both O-H and C=O absorption. These can be differentiated by the particular frequency of the C=O band.

# Spectroscopy

## Applications of IR Spectroscopy

- 1. Detection of functional groups:** Since a particular functional group absorbs IR radiation of nearly same wavelength in all molecules, the presence of characteristic absorption band in that range confirms the presence of that functional group in a molecule.
- 2. Determination of molecular structure:** The absorption bands in the functional group region (2.5-7 $\mu\text{m}$ ) tell about the nature of the functional group present in the molecule while those in the finger print region (7-11 $\mu\text{m}$ ) give substantial information about the structure of the molecule, particularly about the patterns of substitution.

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- 3. Identity of the compounds:** Due to the appearance of a large number of absorption bands in the IR spectra of organic compounds, the probability that any two compounds will produce identical spectra is practically zero. Thus, if two samples afford identical spectra under similar conditions of measurement, they must be samples of the same substance.
- 4. Testing the purity of a sample:** It is possible to test the purity of a given sample by comparing its IR spectrum with that of the pure sample. The spectrum of a pure sample, in general, is sharp and well defined while that of crude or impure sample is blurred, has broad and poorly resolved absorption bands and also contains many extra bands characteristic of the impurities.

# Spectroscopy

5. It has been useful to study inter-molecular and intra-molecular hydrogen bonding.
6. It is useful in the determination of the shape or symmetry of a molecule.
7. It can be used in studying tautomeric equilibria, such as keto-enol.
8. It has been used to determine molecular weight of polymers by measuring end group concentration.

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## **Nuclear Magnetic resonance (NMR) Spectroscopy :**

NMR spectroscopy involves absorption of electromagnetic radiation in the radio frequency region. NMR is the most powerful tool for the structural elucidation and identification of organic substances.

The technique concerns with the nuclei of atoms involved.

Like electrons, the nuclei of certain atoms are in a spinning state. The spinning of these charged particles generates a magnetic moment along the axis of the spin and nuclei act as tiny bar magnets. It is the presence of these magnetic nuclei in most of the molecules which forms the basis of NMR spectroscopy. **The spectroscopy dealing with the NMR spectra of only hydrogen nuclei or protons is often referred to as proton magnetic resonance (PMR) spectroscopy.**

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**Study of NMR spectra deals with the study of following points:**

- (i) *The number of signals*** : This tells about the number of different kinds of protons in the molecule.
- (ii) *The position of signals***: This tells about the electronic environment of each kind of proton.
- (iii) *The intensities of signals***: This tells about the number of each type of proton.
- (iv) *The splitting of a signal into several peaks***: This tells about the environment of a proton with respect to its neighbouring protons.

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## Instrumentation

Two types of NMR spectrometers are in use :

- (i) Wide line NMR spectrometers:** These are useful for quantitative elemental analysis and for studying physical environment of a nucleus.
- (ii) High resolution NMR spectrometers :** This type of instrument can resolve the fine structure that is associated with the absorption peak for a particular nucleus, the chemical environment of which reveals the nature of this fine structure.



# Spectroscopy

**Number of Signals :**

**Equivalent and Non-Equivalent Protons :** The protons with the same environment (*i.e.*, *equivalent protons*) absorb at the same applied field strength and produce only one signal while protons with different environment (*i.e.*, *non-equivalent protons*) absorb at different applied strengths and produce different signals. Thus, the **number of signals** in the NMR spectrum tells us how many kinds of protons are present in a given molecule.

The equivalence of protons can be judged by following the method of isomer number. We imagine each hydrogen or proton in the molecule to be substituted by some other atom (say Z). If the substitution of two protons by Z is expected to furnish either the same product or two enantiomeric products (*i. e.*, mirror images), the two protons are chemically and magnetically equivalent, otherwise not.

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## Examples :



*a*      *b*

Ethyl chloride

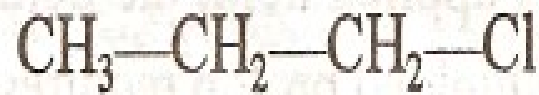
(2-NMR Signals)



*a*      *b*      *a*

Isopropyl chloride

(2-NMR Signals)



*a*      *b*      *c*

*n*-Propyl chloride

(3-NMR Signals)

Equivalent protons are represented by the same letter, and non-equivalent protons by different letters. In the above example *n*-propyl chloride gives 3-NMR signals and has 3-non-equivalent set of protons, whereas its isomer isopropyl chloride gives 2-NMR signals and has two sets of equivalent protons and one non-equivalent proton.

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## **Position of Signals :**

The position of the signals reveals the electronic environment of various protons and thus indicates their nature, i e., whether they are aliphatic or aromatic; primary, secondary, tertiary, acetylenic, vinylic or benzylic; adjacent to halogen or to other atoms or groups, etc.

**Shielding :** When a molecule is placed in a magnetic field, its electrons are made to circulate and thus generate a secondary magnetic field called induced magnetic field which may either reinforce or oppose the applied magnetic field. In case the induced field opposes the applied field, the field felt by the proton is diminished; such a proton is said to be shielded. A shielded proton requires a stronger magnetic field to produce an absorption signal and thus is said to absorb upfield.

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**Deshielding :** If the induced field reinforces the applied field, the field felt by the proton is increased; such a proton is said to be deshielded. A deshielded proton requires a lower applied field to produce an absorption signal and thus is said to absorb down field.

**Chemical shift :** The shifts in the position of NMR signals arising from the shielding or deshielding, by electrons are referred to as chemical shifts.

## **Measuring and Expressing the Chemical Shift :**

Chemical shifts are measured with reference to Tetramethyl silane (TMS),  $(\text{CH}_3)_4\text{Si}$ , which is the standard used in proton magnetic resonance spectroscopy. A small quantity of TMS is added to the sample while running its NMR spectrum.

The choice of TMS, as the standard is one to following advantages: (i) TMS is chemically inert.

(ii) It is miscible with almost all organic substances.

(iii) It is highly volatile and is readily removed from the system.

# Spectroscopy

The most commonly used scale is the  $\delta$  (delta) scale. The position of the tetramethyl Silane (reference) signal is taken as 0.0 ppm. Most chemical shifts have  $\delta$  values between 0 and 10. A small  $\delta$  value represents a small down field shift; and a large  $\delta$  value represents a large down field shift. Some times tau ( $\tau$ ) scale is used where the  $(\text{CH}_3)_4\text{Si}$  signal is taken as 10.0 ppm.  $\tau = 10 - \delta$ .

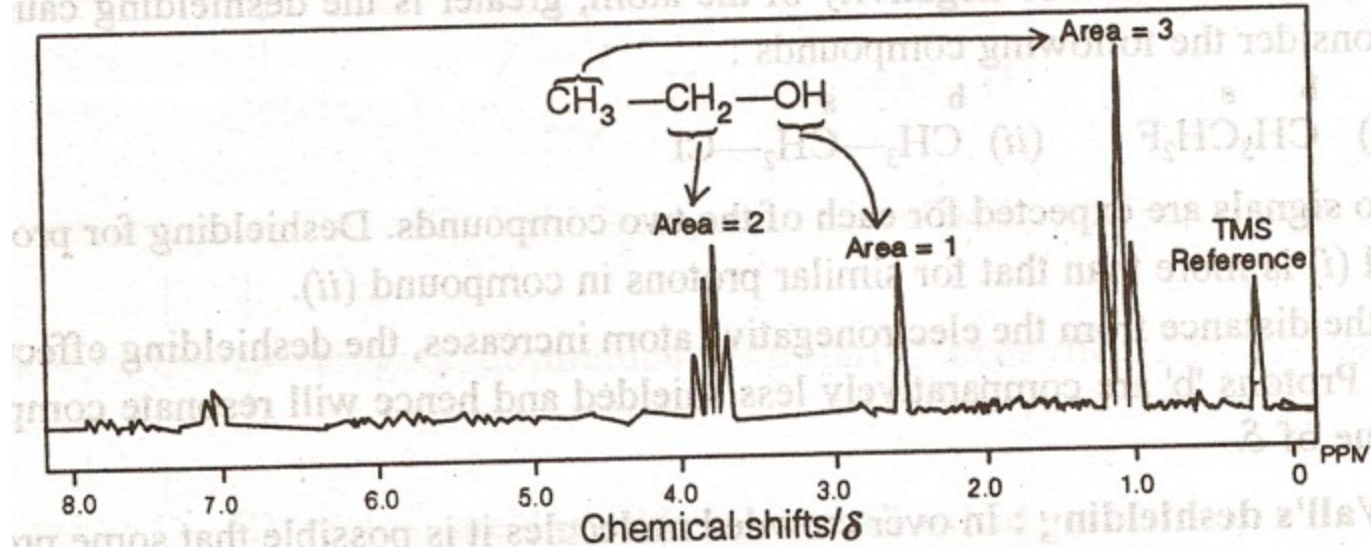
**The proton-NMR spectrum of a molecule thus gives information about:**

- (i) The number of signals or peaks which enables us to know about the kinds of protons present in a molecule.
- (ii) The intensities of the peaks which tell us about the number of protons of each kind that are present.

# Spectroscopy

- (iii) The positions of the peaks which tell us about the electronic environment of each kind of proton.
- (iv) The spin-spin splitting or multiplicity reveals the possible arrangements of groups in the molecule. At high resolution, the main peak for each group may split into two or more peaks, which indicates the number of protons present in the adjacent carbon.

# Spectroscopy



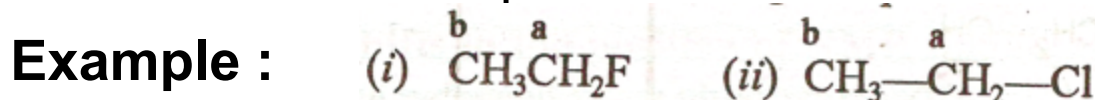
The spectrum shows 3-peaks, corresponding to the protons in  $-\text{OH}$ ,  $-\text{CH}_2$ , and  $-\text{CH}_3$  respectively. The areas under the 3-peaks are in the ratio of 1:2:3 which correspond to the number of protons in  $\text{OH}$ ,  $\text{CH}_2$  and  $\text{CH}_3$ . At high resolution, the main peak for  $-\text{CH}_2$  splits into three sub-peaks, thereby indicating the presence of three protons on the adjacent carbon.

# Spectroscopy

## Factors Influencing Chemical Shift

- (i) Inductive effect
- (ii) van der Waals's deshielding
- (iii) Hydrogen bonding

**(i) Inductive effect:** A proton is said to be deshielded if it is attached to an electro-negative atom or group. Greater the electro-negativity of the atom, greater is the deshielding caused to the proton.



Two signals are expected for each of the two compounds. Deshielding for protons 'a' in compound (i) is more than that for similar protons in compound (ii). As the distance from the electronegative atom increases, the deshielding effect due to it decreases. Protons 'b' are comparatively less shielded .



# Spectroscopy

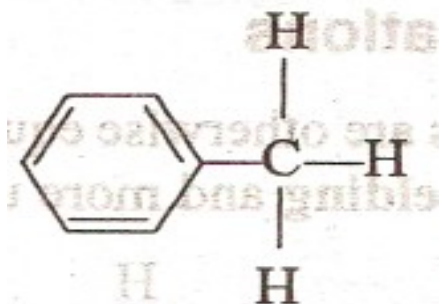
- (ii) van der Waals deshielding :** In over crowded molecules it is possible that some proton may be occupying sterically hindered position. Clearly, electron cloud of the bulky group (hindered group) will tend to repel the electron cloud surrounding the proton. Thus, such a proton will be deshielded and will resonate higher value of  $\delta$  than expected in the absence of this effect.
- (iv) Hydrogen bonding :** If a hydrogen atom exhibits the property of hydrogen bonding in a compound, it will get deshielded due to the strongly electronegative atoms attached to it. As a result, absorption is shifted down-field.

# Spectroscopy

## Rules Governing the Splitting of Proton Signals

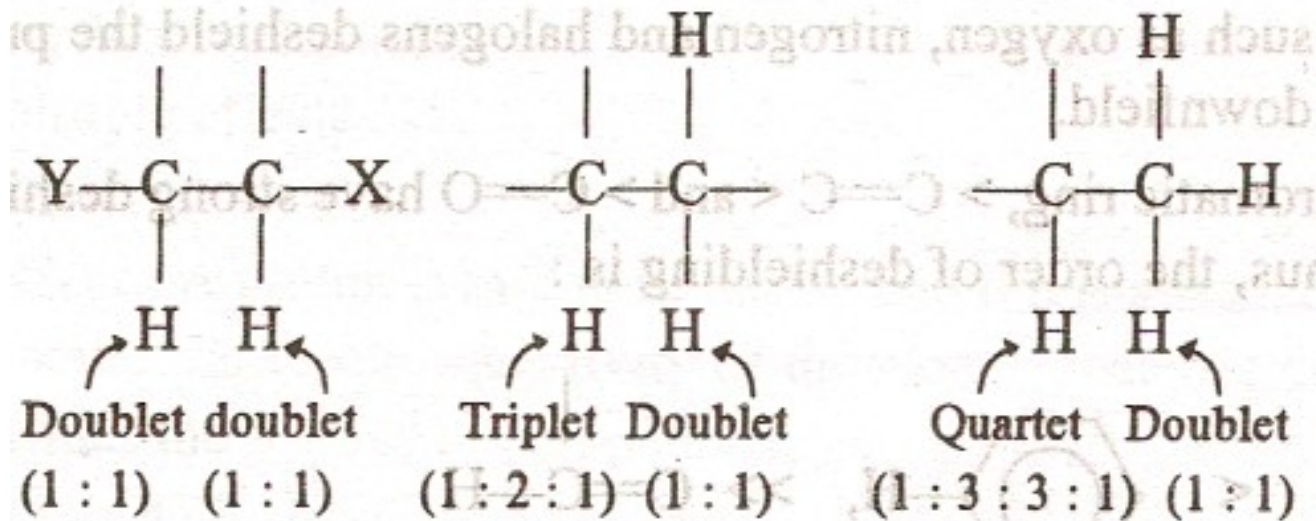
- (i) Splitting of a proton signal is caused only by neighbouring or vicinal protons (i.e., protons on adjacent carbon atoms) provided these are non-equivalent to the absorbing proton. Thus, there would be no splitting in the spectrum of ethylene chloride  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (since adjacent carbon has equivalent protons.)
- (ii) Splitting of one proton by another on the same carbon is rare because such protons are generally equivalent to each other.
- (iii) The mutual splitting of protons separated by more than two carbon atoms is very uncommon. Thus, there is no splitting of signals in toluene since the non-equivalent protons are separated by more than two carbon atoms.

# Spectroscopy



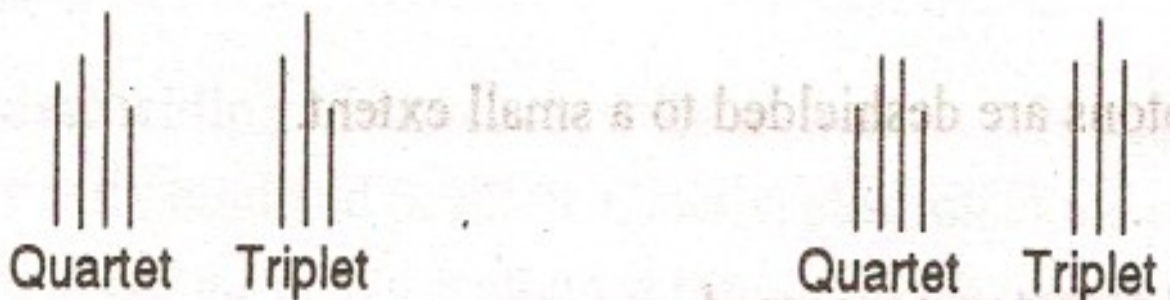
- (iv) The number of peaks ( $N$ ) obtained after the splitting is one more than the number of vicinal protons ( $n$ ), i. e.,  $N = n + 1$ . Thus, an NMR signal due to a proton is split into a doublet by one vicinal proton, into a triplet by two vicinal protons, into a quartet by three vicinal protons, into a quintet of four vicinal protons.

# Spectroscopy



- (v) All the peaks of a given multiplet are not symmetrical. The inner peaks, i. e., the peaks near the other coupled multiplets, are relatively larger than the other peaks. Thus, in case of ethyl bromide, the triplet and quartet obtained are as :

# Spectroscopy



**Coupling Constant :** The distance between the peaks in a multiplet is referred to as coupling constant. It is represented by the symbol 'J' and is expressed in the unit of Hertz.

This constant is a measure of the magnitude of the splitting effect. Unlike the chemical shifts, the 'J' values are independent of the applied magnetic field but depend on the molecular structure.

# Spectroscopy

## Application of NMR Spectroscopy :

- 1. Identification of substances:** Like infrared spectrum, the NMR spectrum of a substance often serves as the 'fingerprint' of the substance. If the NMR spectrum of a given sample is exactly the same as that of a Known substance, its structural identity is established.
- 2. Qualitative analysis :** The NMR spectrum helps to establish the presence or absence of functional groups or other characteristic structural features of a given substance from their characteristic chemical shifts, Appearance of a signal at  $\delta$  9.5, is indicative of -CHO group in the sample.

# Spectroscopy

- 3. Rate of reactions:** The NMR spectroscopy forms a means of studying certain reactions which are too fast for measurement by ordinary techniques. One such relation is the fast exchange of protons between two molecules having protons attached to electronegative atoms with lone pair of electrons.
4. Determination of molecular structure.
5. It is used to assay pharmaceutical formulations such as aspirin, Phenacitin and Caffeine.
6. It is used for the determination of fluorine content in plastics.

# Spectroscopy

## Advantages of NMR Spectroscopy

1. It is a totally non-destructive technique.
2. Compared to IR spectroscopy, it is much easier to study solid samples by this technique as a wide variety of solvents is available.
3. The NMR spectrometers used now-a-days are so improved that the spectra can be recorded as fast or even faster than IR spectra.
4. It is possible to have computer calculation of NMR spectra.