

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 λ_{\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.

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

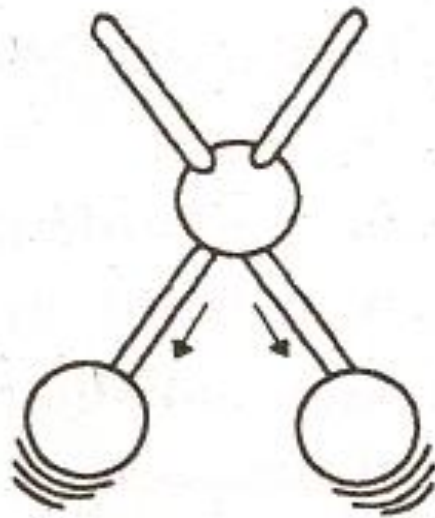
For a polyatomic molecule, several vibrational modes are possible therefore a complicated IR spectrum is obtained for it. Normal modes of vibrations are of two types:

(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**.

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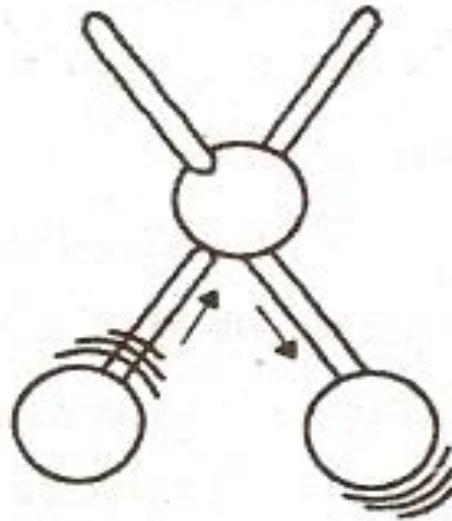
(a) Symmetric stretching: When the stretching and compressing occurs in a symmetric way, it is called symmetric stretching



Symmetric

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

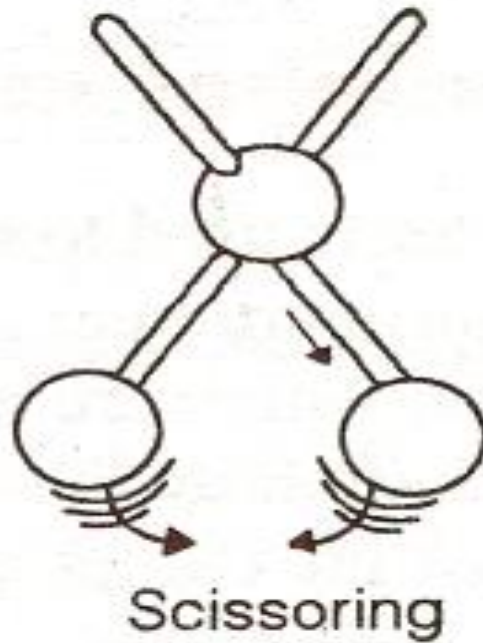


Asymmetric

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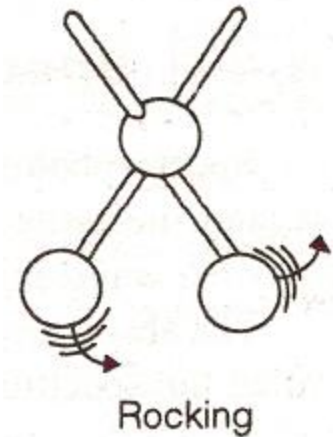
(ii) Bending or deformation vibrations : Such type of vibration may consist of a change in bond angle between bonds with a common atom. These are of four types:

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

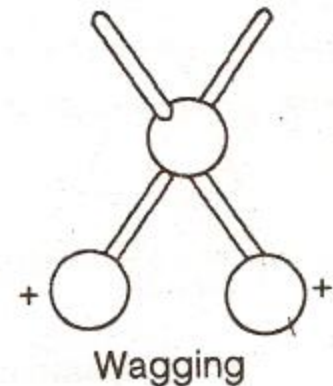


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(b) Rocking involves the movement of atoms in same direction.

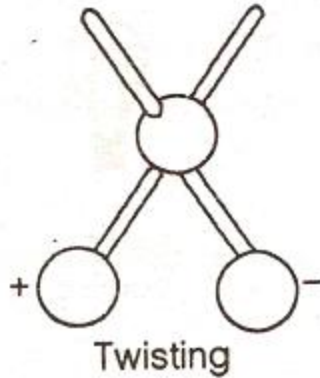


(c) Wagging in which the atoms move up and below the plane with respect to central atom.



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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.



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Characteristics IR Absorption Bands

Frequency Range 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 ₂	Nitro compounds

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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.

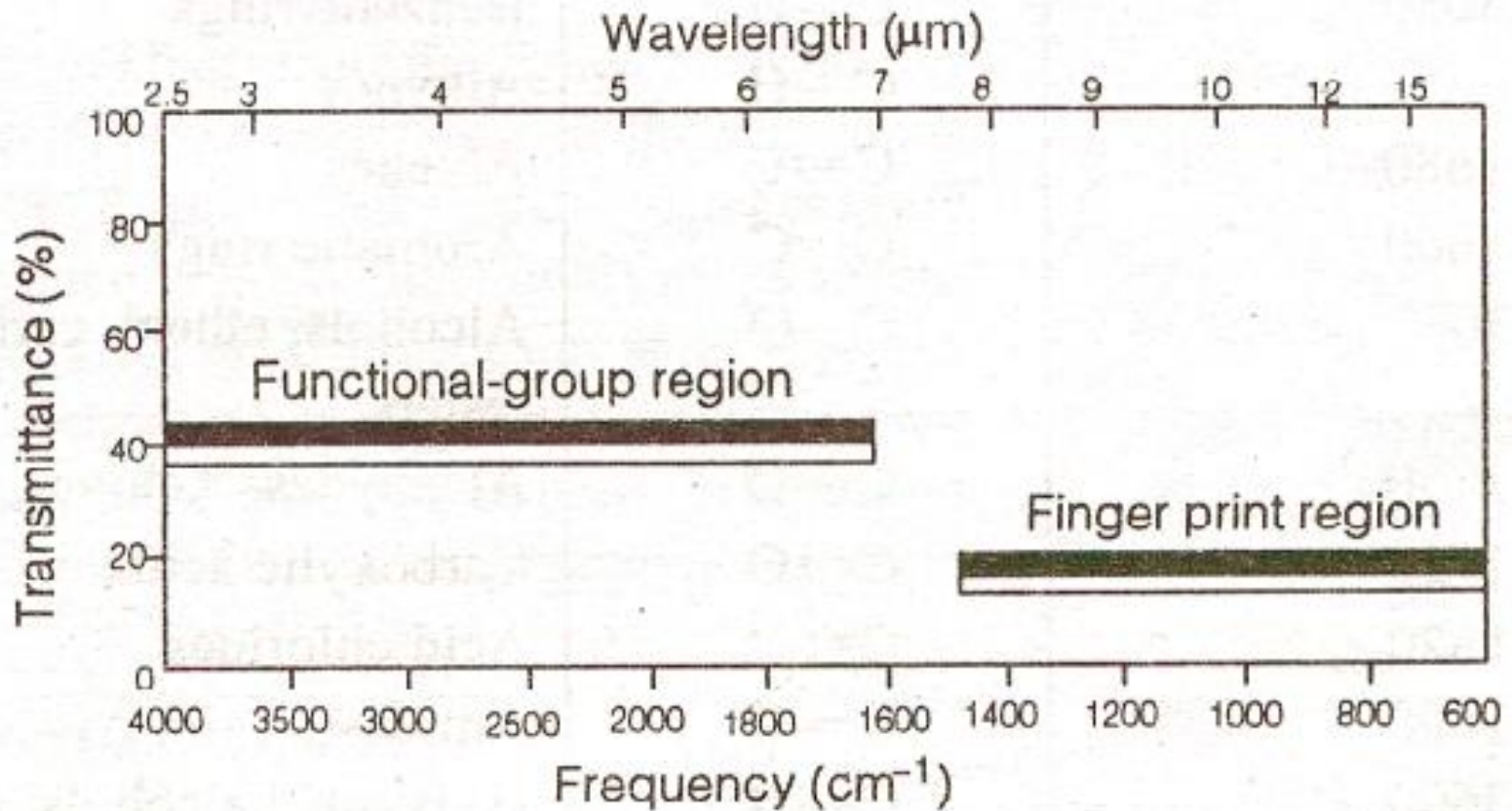
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Interpretation of IR Spectrum

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.

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Interpretation of IR Spectrum



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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 cm^{-1} to 1300 cm^{-1} .
- (ii) Finger print region:** The area from 1300 cm^{-1} to 687 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.

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IR Spectra of Hydrocarbons

In hydrocarbons, bands due to stretching may appear at about 1500 and 1600 cm^{-1} for aromatic bond at 1650 cm^{-1} or double bonds, and at 2100 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 cm^{-1} for sp -hybridized carbon (alkynes), at 3000 – 3100 cm^{-1} for sp^2 hybridized carbon (alkene and benzene rings) and at 2800 - 3000 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.

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IR Spectra of Alcohols and Ethers

For hydrogen-bonded alcohol, a strong, band appears in the 3200-3600 cm^{-1} region due to O-H stretching. (A monohydric alcohol gives a sharp, variable band at 3610-3640 cm^{-1}). Another strong, broad band, due- to C-O stretching, appears in the 1000-1200 cm^{-1} region, the exact frequency depending on the nature of the alcohol. (3° alcohol about 1150 cm^{-1} , 2° about 1100 cm^{-1} and for 1° about 1050 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 cm^{-1} ,

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IR Spectra of Aldehydes and Ketones

The strong band due to C=O stretching appears at about 1700 cm^{-1} , (R. CHO 1725 cm^{-1} , ArCHO 1700 cm^{-1} , R_2CO 1710 cm^{-1} and ArCOR 1690 cm^{-1}). The -CHO group of an aldehyde has a characteristic C-H stretching band near 2720 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 cm^{-1} region, the C=O band is at about 1700 cm^{-1} . Acids also show a C-O stretching band at about 1250 cm^{-1} and bands for O-H bending near 1400 cm^{-1} and 920 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.

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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 μm) tell about the nature of the functional group present in the molecule while those in the finger print region (7-11 μm) 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.

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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

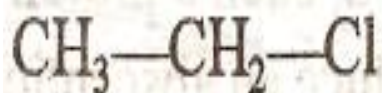
Number of Signals :

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

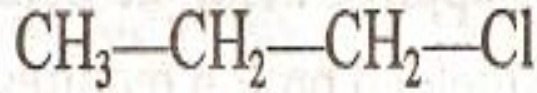
(2-NMR Signals)



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.

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

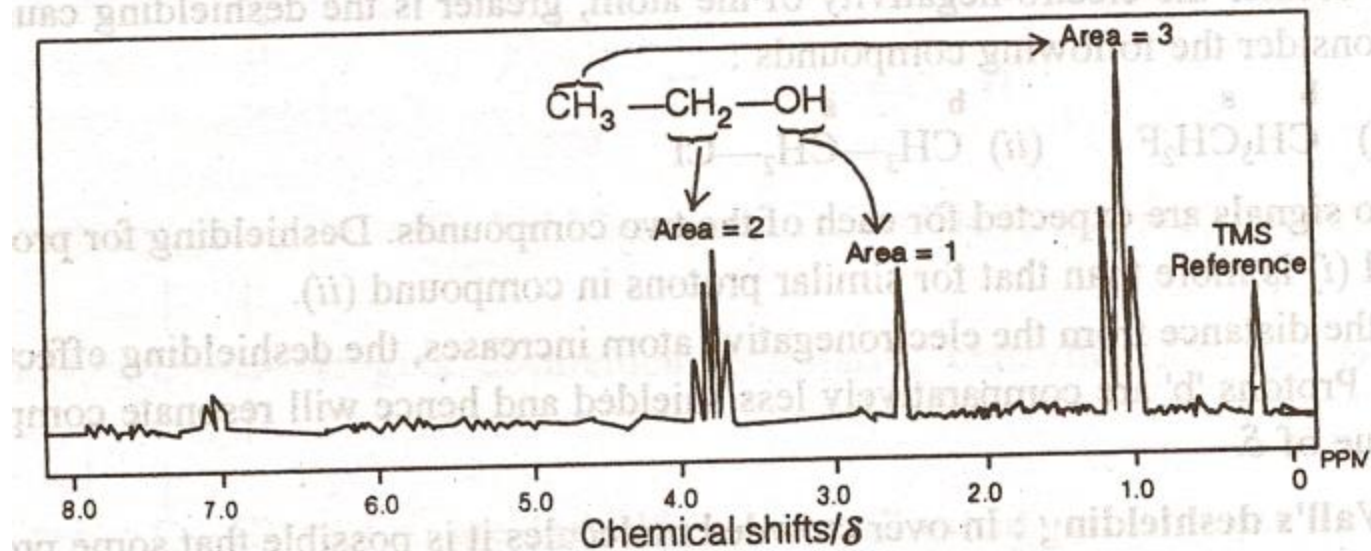
The proton-NMR spectrum of a molecule thus gives information about:

- (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.

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- (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.

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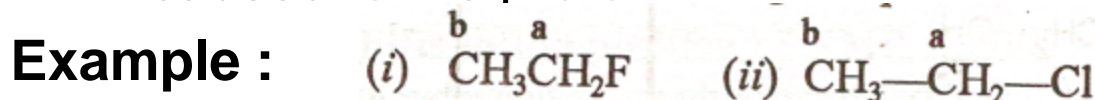
The spectrum shows 3-peaks, corresponding to the protons in -OH , -CH_2 , and -CH_3 respectively. The areas under the 3-peaks are in the ratio of 1:2:3 which correspond to the number of protons in OH, CH₂ and CH₃. At high resolution, the main peak for -CH_2 splits into three sub peaks, thereby indicating the presence of three protons on the adjacent carbon.

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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 .

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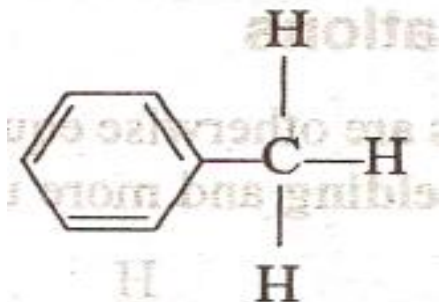
- (ii) van der Waals deshielding :** In over crowded molecules it is possible that some proton may be occupying sterically hindered position. Clearly, electron cloud of the bulky group (hindered group) will tend to repel the electron cloud surrounding the proton. Thus, such a proton will be deshielded and will resonate higher value of δ 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.

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Rules Governing the Splitting of Proton Signals

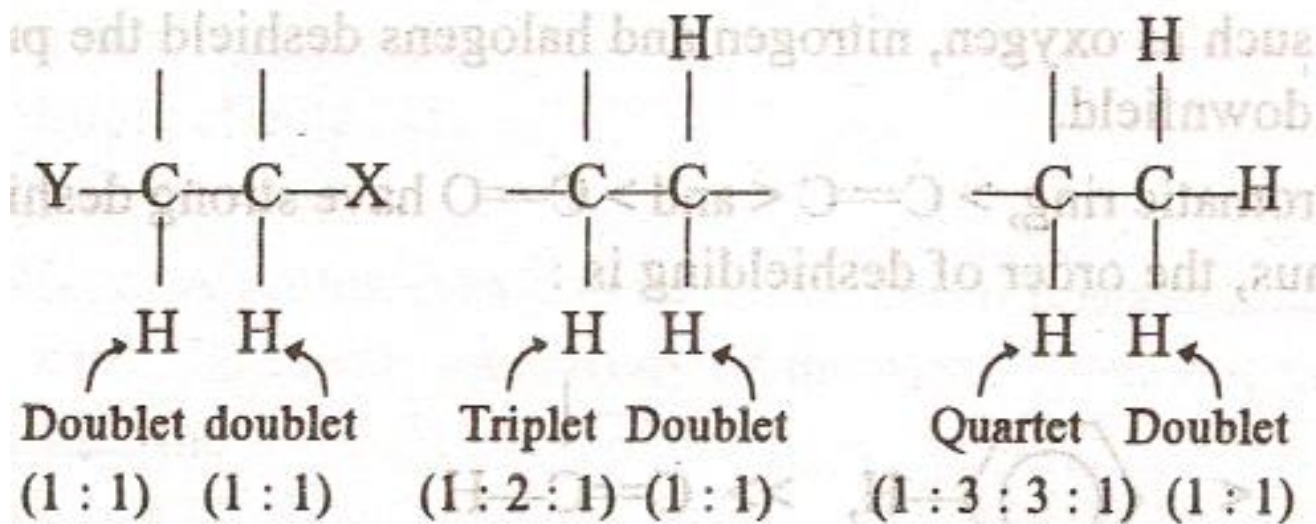
- (i) Splitting of a proton signal is caused only by neighbouring or vicinal protons (i.e., protons on adjacent carbon atoms) provided these are non-equivalent to the absorbing proton. Thus, there would be no splitting in the spectrum of ethylene chloride $\text{ClCH}_2\text{CH}_2\text{Cl}$ (since adjacent 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.

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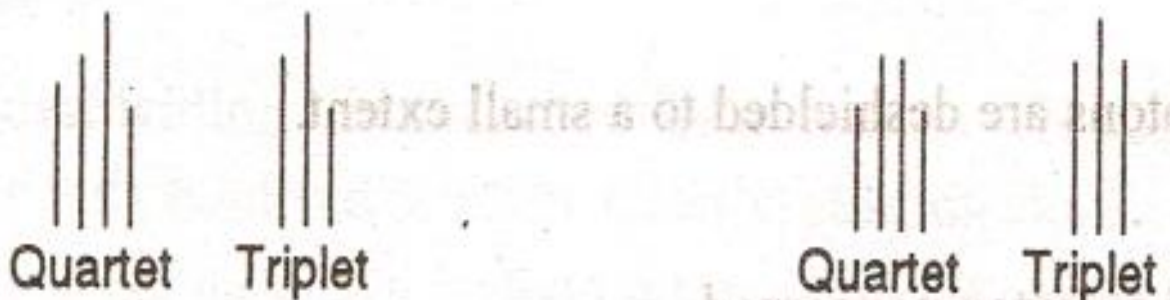
(iv) The number of peaks (N) obtained after the splitting is one more than the number of vicinal protons (n), i. e., $N = n + 1$. Thus, an NMR signal due to a proton is split into a doublet by one vicinal proton, into a triplet by two vicinal protons, into a quartet by three vicinal protons, into a quintet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

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- (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 :

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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.

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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 δ 9.5, is indicative of -CHO group in the sample.

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- 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, Phenacetin 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.