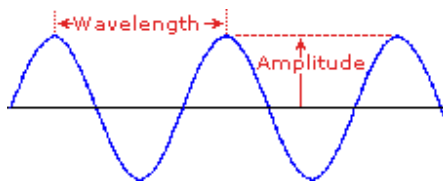

SPECTROSCOPY

Spectroscopy deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiation as determined by quantum mechanical selection rules. It is the study of electromagnetic radiation scattered, absorbed or emitted by molecules.

The structure of organic compounds can be determined by the study of their interaction with light (electromagnetic radiation). Spectroscopic techniques are non-destructive and generally require small amounts of sample. They help in fast analysis of sample.

Light is uniform or homogeneous in color, it is actually composed of a broad range of radiation having wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum. Different regions of the electromagnetic spectrum provide different kinds of information as a result of such interactions. Light may be considered to have both wave-like and particle-like characteristics. Like all wave characteristics, it is characterized by a wavelength or frequency.

Wavelength is defined, as the distance between adjacent peaks (or troughs), and may be designated in meters, centimeters or nanometers (10^{-9} meters).



- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

Frequency is the number of wave cycles that travel past a fixed point per unit of time, and is usually given in cycles per second, or hertz (Hz).

Frequency and wavelength are inversely related but has a direct relationship to energy.

$$\nu = c/\lambda \quad \nu = \text{frequency}, \lambda = \text{wavelength}, c = \text{velocity of light } (c = 3 \cdot 10^{10} \text{ cm/sec})$$

$$\Delta E = h\nu \quad E = \text{energy}, \nu = \text{frequency}, h = \text{Planck's constant } (h = 6.6 \cdot 10^{-27} \text{ erg sec})$$

Visible wavelengths cover a range from approximately 400 to 800 nm. The longest visible wavelength is red and the shortest is violet.

Origin of Spectra

Consider two energy levels of an atom or molecule. The one with lower energy level is called ground state energy level (E_g) and the one with higher energy level is called excited state energy level (E_e).

Absorption spectrum: results when an atom or molecule undergoes a transition from the lower energy level to the higher energy one with the absorption of a photon of energy $h\nu$. The energy $h\nu$ will be equal to the energy difference between the two energy levels.

$$h\nu = \Delta E = E_e - E_g = hc/\lambda$$

Emission spectrum: results when an atom or molecule undergoes a transition from the higher energy level to the ground state with the emission of a photon of energy $h\nu$.

Spectra can be classified into two categories:

1. **Atomic Spectra:** This arises from the transition of an electron between the atomic energy levels. Thus only electronic transitions are involved. It is used to obtain detailed information about electronic structure of atoms.
2. **Molecular Spectra:** This arises from the transition of an electron between the molecular energy levels. Here besides the electronic transitions, electrons can undergo rotation as well as vibration. So, molecular spectroscopy i.e the study of molecular spectra is more complicated than the atomic spectra but it also gives more information.

Application of Molecular Spectroscopy

- It is used in the structural investigations i.e we can determine electronic energy levels, bond lengths, bond angles and the strength of the bonds.
- It can be used to monitor changing concentration of reactants or products in kinetic studies.
- It gives us an understanding of color.

Molecular Spectroscopy

Total Energy of a molecule = E = Electronic energy + Vibration energy + Rotational energy + Translational energy

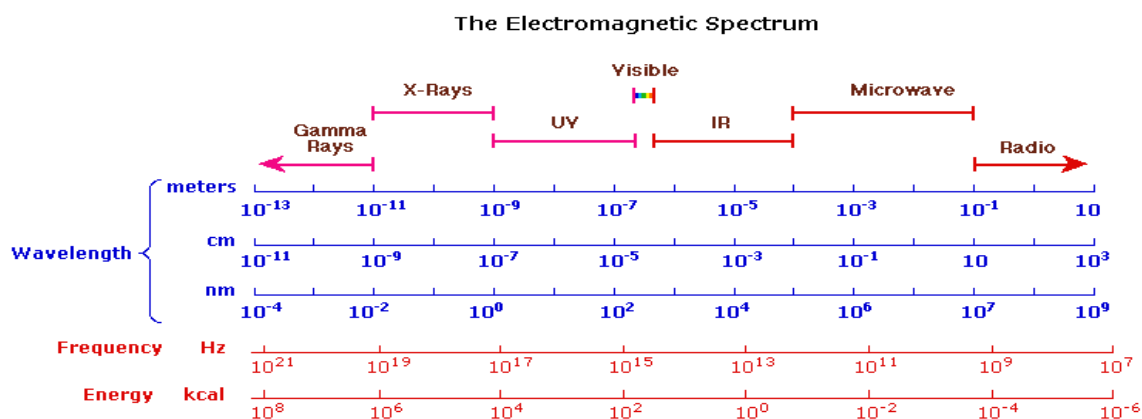
- **Electronic energy:** A molecule possesses electronic energy which is associated with the transition of an electron from the ground state energy level to the excited state by the absorption of photons of suitable frequency.
- **Vibration energy:** The nuclei of the molecule undergoes to and from motion but its centre of gravity does not change
- **Rotational energy:** The molecule undergoes rotation about the axis passing through the centre of gravity
- **Translational energy:** The molecule undergoes motion but its centre of gravity changes.

The Electromagnetic Spectrum

The visible spectrum constitutes but a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments. This electromagnetic spectrum ranges from very short wavelengths (including

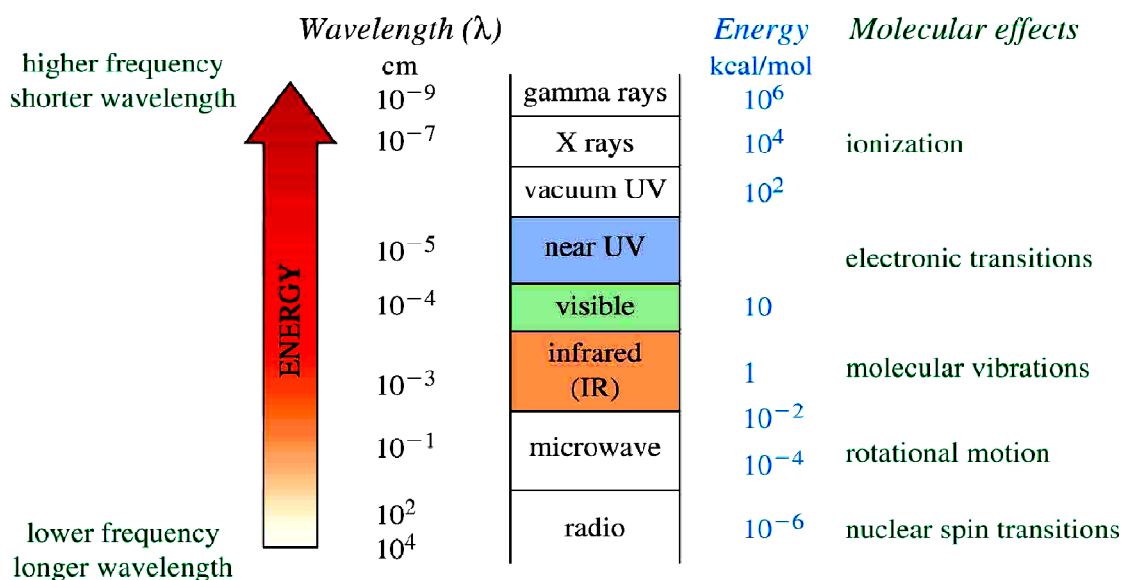
SPECTROSCOPY

gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency.



$v = c/\lambda$ v =frequency, λ =wavelength, c =velocity of light ($c=3 \cdot 10^{10}$ cm/sec)
 $\Delta E = h\nu$ E =energy, ν =frequency, h =Planck's constant ($h=6.6 \cdot 10^{-27}$ erg sec)

Effect of electromagnetic radiation on molecules



SPECTROSCOPY

Summary of various types of molecular spectra

- **Mass Spectrometry:** Sample molecules are ionized by high energy electrons. The mass to charge ratio of these ions is measured very accurately by electrostatic acceleration and magnetic field perturbation, providing a **precise molecular weight**. Ion fragmentation patterns may be related to the structure of the molecular ion.
- **Ultraviolet-Visible Spectroscopy:** Absorption of this relatively high-energy light causes electronic excitation. The easily accessible part of this region (wavelengths of 200 to 800 nm) shows absorption only if **conjugated pi-electron systems** are present.
- **Infrared Spectroscopy:** Absorption of this lower energy radiation causes vibrational and rotational excitation of groups of atoms within the molecule. Because of their characteristic absorptions **identification of functional groups** is easily accomplished.
- **Nuclear Magnetic Resonance Spectroscopy:** Absorption in the low-energy radio-frequency part of the spectrum causes excitation of nuclear spin states. NMR spectrometers are tuned to certain nuclei (e.g. ^1H , ^{13}C , ^{19}F & ^{31}P). For a given type of nucleus, **high-resolution spectroscopy distinguishes and counts atoms in different locations in the molecule**.

Spectra	Transitions	Region of electromagnetic spectrum
Infrared	Between the vibrational energy levels	Infrared ($500\text{-}4000\text{cm}^{-1}$)
UV-Vis	Between the electronic energy levels	Visible ($12,500\text{-}25,000\text{cm}^{-1}$) UV ($25,000 - 70,000\text{cm}^{-1}$)
NMR	Between the magnetic energy levels of nuclei	Radiofrequency

SPECTROSCOPY

UV-Vis. Spectroscopy

- It involves transitions of electrons within a molecule from a lower to higher energy level or vice-versa by the absorption or emission of energy or radiations.
- The frequency of the radiations fall in the UV-Visible range of the electromagnetic spectrum. The Visible range is $12,500\text{--}25,000\text{cm}^{-1}$ (400-750nm) and the UV region is $25,000\text{--}72,000\text{cm}^{-1}$ (190-400 nm)
- They have limited use in sample identification but are highly useful in quantitative measurements.

For quantitative measurement,

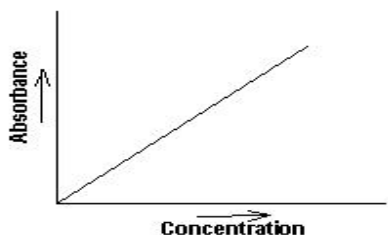
The concentration of an analyte in solution can be determined by measuring the absorbance at a specific wavelength and applying the Beer Lambert law.

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength.

Beer Lambert law: $A = \epsilon C l$

Where A= absorbance (no units, since $A = \log_{10} P_0 / P$); C= sample concentration in mole/L, l= length of light passing through the sample in cm; ϵ is the molar absorptivity with units of $\text{L mol}^{-1} \text{cm}^{-1}$

The law tells us that absorbance depends on the total quantity of the absorbing compound in the light path through the cuvette. If we plot absorbance against concentration, we get a straight line passing through the origin (0,0).



SPECTROSCOPY

Significance of the molar absorptivity, ϵ

As per Beer Lambert law: $A = \epsilon bc$

or $\epsilon = A / bc$

In words, this relationship can be stated as " ϵ is a measure of the amount of light absorbed per unit concentration".

Molar absorptivity is a constant for a particular substance, so if the concentration of the solution is halved so is the absorbance, which is exactly what you would expect. Thus, a compound with a high molar absorptivity is very effective at absorbing light (of the appropriate wavelength), and hence low concentrations of a compound with a high molar absorptivity can be easily detected.

Principle of UV-Vis Spectroscopy:

Electronic transitions

The absorption of UV or visible radiation corresponds to the excitation of outer most valence electrons. When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level. Thus each electronic level in a molecule is associated with a number of vibrational sub-level (with smaller energy separation) and each vibrational sub-level is again 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 (diag below). The spectrum of a molecule containing these chromophores is complex. This is because the superposition of rotational and vibrational transitions on the electronic transitions gives a combination of overlapping lines. This appears as a continuous absorption band.

SPECTROSCOPY



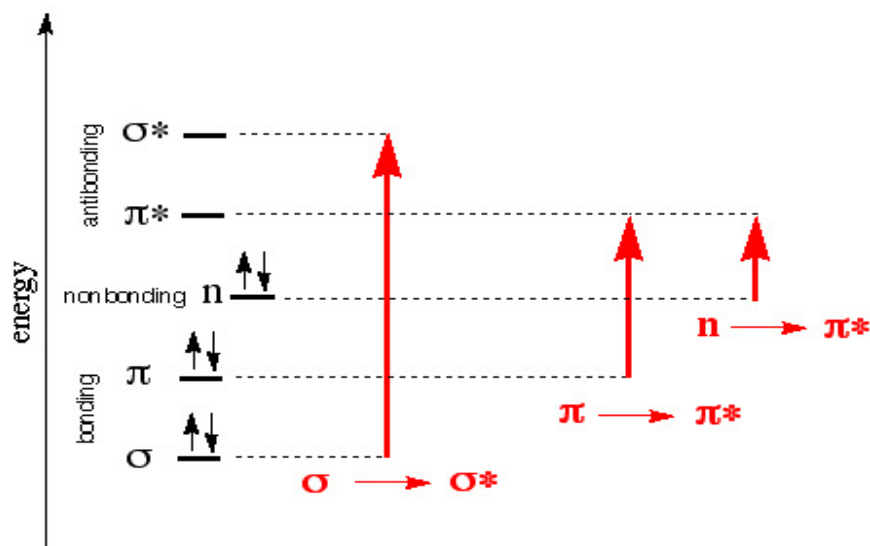
Absorbing species containing π , σ , and n electrons

Absorption of ultraviolet and visible radiation in organic molecules is restricted to certain functional groups (chromophores) that contain valence electrons of low excitation energy.

Classification of electronic transitions:

1. **$\sigma \rightarrow \sigma^*$ transition:** As (σ) electrons are held more firmly in the molecule, this transition takes place in the UV region.
2. **$\pi \rightarrow \pi^*$ transition:** This transition takes place in the near UV and the Vis region.
3. **$n \rightarrow n^*$ transition:** This transition takes place in the Vis region.

The relative energies of the molecular orbitals showing such transitions are shown:



SPECTROSCOPY

$\sigma \rightarrow \sigma^*$ Transitions

An electron in a bonding σ orbital is excited to the corresponding antibonding orbital.

The energy required is large. For example, methane (which has only C-H bonds, and can only undergo $\sigma \rightarrow \sigma^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to $\sigma \rightarrow \sigma^*$ transitions are not seen in typical UV-Vis. spectra (200 - 700 nm)

$n \rightarrow \sigma^*$ Transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow \sigma^*$ transitions. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Transitions

Most absorption spectroscopy of organic compounds is based on transitions of n or π electrons to the π^* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). These transitions need an unsaturated group in the molecule to provide the π electrons.

Molar absorptivity from $n \rightarrow \pi^*$ transitions is relatively low, and range from 10 to 100 $\text{L mol}^{-1} \text{cm}^{-1}$. $\pi \rightarrow \pi^*$ transitions normally give molar absorptivity between 1000 and 10,000 $\text{L mol}^{-1} \text{cm}^{-1}$.

The position of bands for different electronic transitions is summarized:

Organic compound	Electronic transitions	Position of bands
Alkanes	$\sigma \rightarrow \sigma^*$ transition	150 nm (requires high energy which does not lie in the UV region)
Alkenes	$\pi \rightarrow \pi^*$ transition	170-190nm
Aliphatic ketones	$n \rightarrow \pi^*$ transition	280 nm (forbidden and of low intensity)
	$n \rightarrow \sigma^*$ transition	185 nm (allowed and of high intensity)
	$\pi \rightarrow \pi^*$ transition	160 nm (allowed and of high intensity)
Conjugated dienes	$\pi \rightarrow \pi^*$ transition	217 nm (transition is of low energy and is due to conjugation)

Chromophores: A chromophore is the part of a molecule responsible for its color. The color arises when a molecule absorbs certain wavelengths of visible light and transmits or

SPECTROSCOPY

reflects others. The chromophore is a region in the molecule where the energy difference between two different molecular orbitals falls within the range of the visible spectrum. Visible light that hits the chromophore can thus be absorbed by exciting an electron from its ground state into an excited state.

Auxochrome: An auxochrome is a group of atoms attached to a chromophore which modifies the ability of that chromophore to absorb light. They themselves fail to produce the colour; but when present along with the chromophores in an organic compound intensifies the colour of the chromogen.

Examples include the hydroxyl group (-OH), the amino group (-NH₂), and an aldehyde group (-CHO).

Terminology for absorption shifts

The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from $n \rightarrow \pi^*$ transitions are shifted to shorter wavelengths (*blue shift*) with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the n orbital. Often (but *not* always), the reverse (i.e. *red shift*) is seen for $\pi \rightarrow \pi^*$ transitions. This is caused by attractive polarization forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state, and so the energy difference between the excited and unexcited states is slightly reduced - resulting in a small red shift. This effect also influences $n \rightarrow \pi^*$ transitions but is overshadowed by the blue shift resulting from solvation of lone pairs.

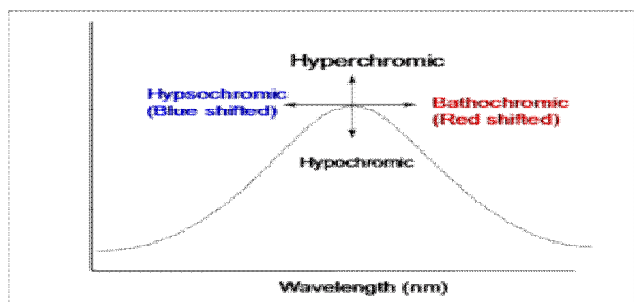
Bathochromic: a shift of a band to lower energy or longer wavelength (often called a red shift).

Hypsochromic: a shift of a band to higher energy or shorter wavelength (often called a blue shift).

Hyperchromic: an increase in the molar absorptivity.

Hypochromic: a decrease in the molar absorptivity.

SPECTROSCOPY



Importance of Conjugation in UV-Vis Spectroscopy

Conjugation of double bonds lowers the energy required for the electronic transition. As a result, molecules containing conjugated group such as $>C=C-C=C<$ and $>C=C-C=O$ exhibit $\pi \rightarrow \pi^*$ transitions and the absorption bands are within the ordinary ultraviolet range. For eg. butadiene ($CH_2=CH-CH=CH_2$) shows λ_{max} at 217 nm. But as the number of double bonds increases, the absorption moves to longer wavelengths. Thus the spectrum of 1, 3,5, 7 octatetraene ($CH_2=CH-CH=CH-CH=CH-CH=CH_2$) exhibits λ_{max} at 296 nm. If there are enough double bonds in conjugation, absorption will ultimately move into the visible region and the compound will appear colored. For example, β -carotene containing 11 double bonds in conjugation is a colored compound as its λ_{max} at 451 nm and falls in the visible region of the electromagnetic spectrum.

Applications of UV-Vis. Spectroscopy

1. For the identification of aromatic compounds and conjugated dienes or other olefins.
2. Detection of impurities
3. Quantitative determination of analyte
4. Determination of molecular weight
5. Study of kinetics of chemical reaction
6. Dissociation constant for weak acids and bases can be determined.

SPECTROSCOPY

Chromophore	Example	Excitation	λ_{max} , nm	ϵ	Solvent
C=C	Ethene	$\pi \rightarrow \pi^*$	171	15,000	hexane
C \equiv C	1-Hexyne	$\pi \rightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	$n \rightarrow \sigma^*$ $n \rightarrow \sigma^*$	205 255	200 360	hexane hexane

Infra-Red Spectroscopy

Theory or Principle of Infrared Absorption Spectroscopy

- a. IR photons have low energy (1-15kcal/mol); hence are not large enough to excite electrons (electronic transitions do not occur) but may induce vibrational excitation of covalently bonded atoms and groups in organic molecules.
- b. The covalent bonds in molecules are not rigid sticks or rods, but are more like stiff springs that can be stretched and bent. Thus, in addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms. Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations.
- c. There are three types of molecular transitions that occur during IR irradiation:
 - 1) Rotational transitions:
 - 2) Vibrational-rotational transitions
 - 3) Vibrational transitions
- d. **Conditions for IR absorbance to occur:**
 - The frequency of vibration must satisfy the equation: $E=h\nu$.
 - The intensity of absorption must be proportional to square of the rate of change of dipole.
 - The natural frequency of vibration of the molecule must be equal to the frequency of incident radiation.
 - Changes in the vibration must stimulate changes in the dipole moment of the molecule. Hence Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment.

Thus Infra red inactive molecules-

- a. do not show vibrational spectra.
- b. Do not have a permanent dipole moment
- c. Do not exhibit a change in dipole moment
- d. Eg - O₂, H₂, N₂ etc

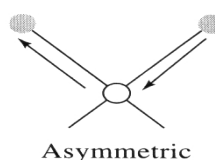
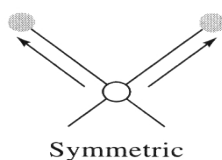
SPECTROSCOPY

Infra red active molecules –

- Show vibrational spectra
 - Have a permanent dipole moment
 - Exhibit a change in the dipole moment
 - CO₂ is a molecule which does not have a permanent dipole moment but still is IR active.
- e. The IR region is divided into three regions: the near, mid, and far IR. The mid IR region is of greatest practical use to the organic chemist. This is the region of wavelengths between 3×10^{-4} and 3×10^{-3} cm. In wave numbers, the mid IR range is $4000\text{--}400\text{ cm}^{-1}$. An increase in wave number corresponds to an increase in energy.

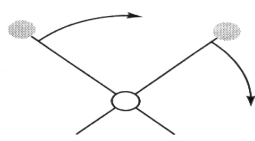
Region	Wavelength (λ) Range, μm	Wavenumber ($\bar{\nu}$) Range, cm^{-1}	Frequency (ν) Range, Hz
Near	0.78 to 2.5	12,800 to 4000	3.8×10^{14} to 1.2×10^{14}
Middle	2.5 to 50	4000 to 200	1.2×10^{14} to 6.0×10^{12}
Far	50 to 1000	200 to 10	6.0×10^{12} to 3.0×10^{11}
Most used	2.5 to 15	4000 to 670	1.2×10^{14} to 2.0×10^{13}

- f. The different Vibrational Modes occurring as a result of IR absorption:
- Stretching** -the rhythmic movement along a bond axis with a subsequent increase and decrease in bond length

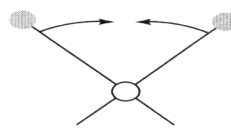


- Bending** - a change in bond angle or movement of a group of atoms with respect to the rest of the molecule.

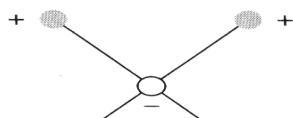
SPECTROSCOPY



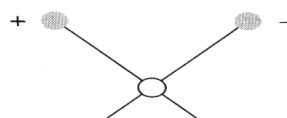
In-plane rocking



In-plane scissoring



Out-of-plane wagging



Out-of-plane twisting

- g. It is not necessary that all fundamental vibrations will exist in the IR spectrum. Some vibrations are inadequate and are called degenerate bonds. Since different bonds and functional groups absorb at different wavelengths, an IR spectrum is used in the identification of a compound or establishing the structure of an unknown substance.

Regions of IR spectra

1. **Functional group region:** is the high frequency region between $5000\text{-}1300\text{cm}^{-1}$. It is particularly useful in the identification of important functional groups present in the organic molecule.
2. **Finger print region:** is the middle frequency region between $1300\text{-}650\text{cm}^{-1}$. This region helps in the identification of unknown organic substance. No two compounds, however closely related can have identical or superimposable bands in this region.

Applications of IR Spectroscopy

1. **Determination of force constant from vibrational spectrum**
2. **Determination of purity of a sample**

IR spectroscopy is used widely for the detection of impurities for production of many chemicals on an industrial scale.

For e.g. a small quantity of ketone in a hydrocarbon is detected by the appearance of a band at 1720cm^{-1} which is a characteristic frequency of carbonyl group.

3. **Identification of an unknown compound**

This is done by fingerprint technique which involves matching the IR spectrum of the unknown compound with that of a known compound.

4. **Identification of functional groups in organic molecules.**

SPECTROSCOPY

The IR spectra permit the recognition of functional group present in organic compound. This is because it is possible to associate some absorption with stretching or bending vibrations characteristic of the particular functional group in any molecule. Such frequencies are called group frequencies and remain constant from molecule to molecule.

For e.g. functional group in alkenes is $\text{C}=\text{C}$ and its characteristic IR absorption frequency is in the range $1620\text{-}1670\text{ cm}^{-1}$

Functional group in alkynes is $\text{C}\equiv\text{C}$ and its characteristic IR absorption frequency is in the range $2100\text{-}2250\text{ cm}^{-1}$

Functional group in aldehyde is $\text{H}-\text{C}=\text{O}$ and its characteristic IR absorption frequency of $\text{C}=\text{O}$ is in the range $1720\text{-}1740\text{ cm}^{-1}$

Functional group in acid is $\text{HO}-\text{C}=\text{O}$ and its characteristic IR absorption frequency of $\text{C}=\text{O}$ is 1650 cm^{-1}

Functional group in alcohols is $-\text{HO}$ and its characteristic IR absorption frequency of $\text{O}-\text{H}$ in primary alcohols is 3630 cm^{-1}

5. To distinguish between inter and intra molecular hydrogen bonding

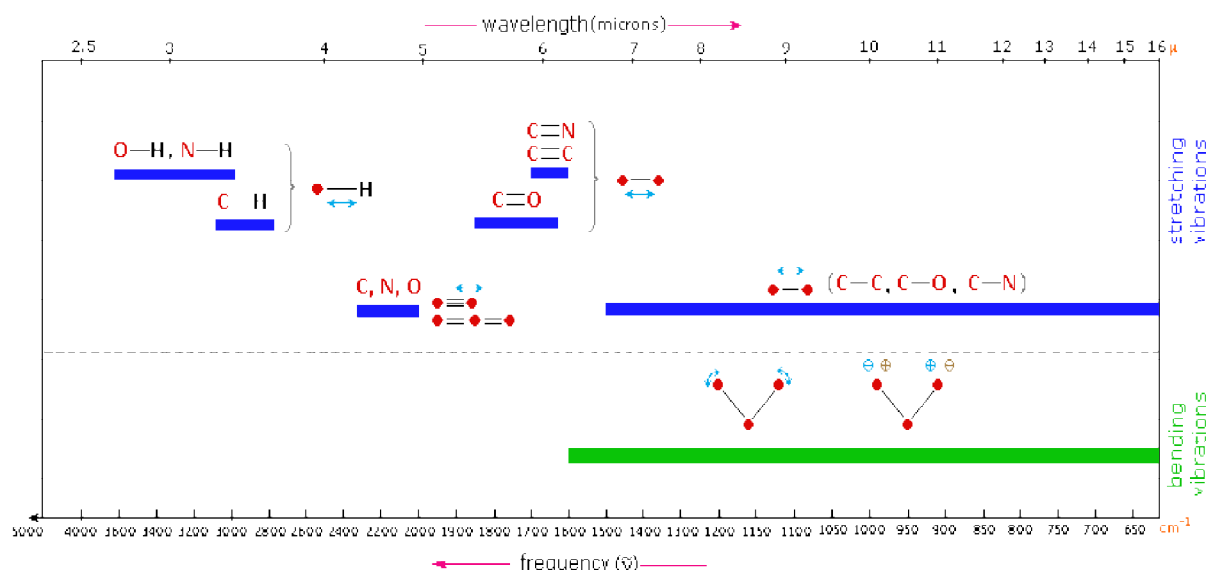
This is done by taking the IR spectrum of the compound at different concentrations. As the concentration is increased, the absorption band due to intermolecular hydrogen bonding increases while due to intramolecular hydrogen bonding remains unchanged.

6. To determine the structure of an organic compound

Structure determination is possible by IR spectroscopy because it gives valuable information regarding molecular symmetry, dipole moment, bond length, bond strength etc.

A typical IR spectrum showing frequencies of major functional groups in a organic molecule:

SPECTROSCOPY

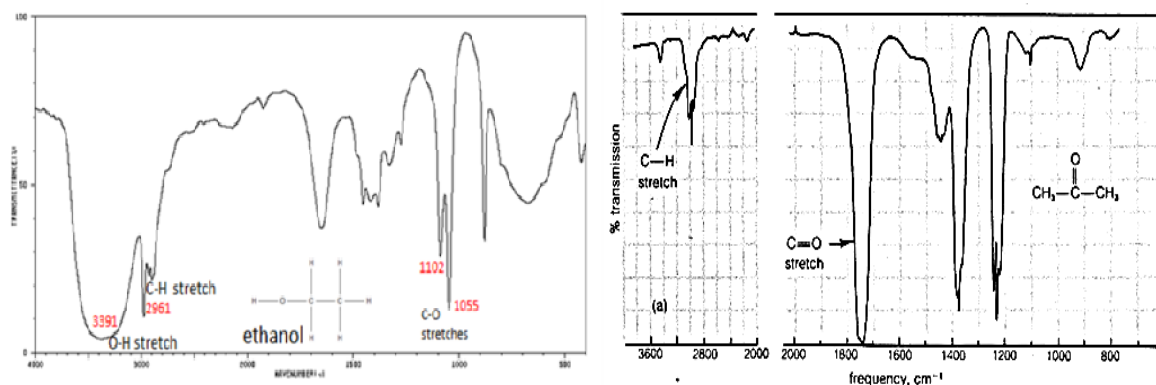


<i>Typical Infrared Absorption Frequencies</i>				
	Stretching Vibrations		Bending Vibrations	
Functional Class	Range (cm ⁻¹)	Assignment	Range (cm ⁻¹)	Assignment
Alkanes	2850-3000	CH ₃ , CH ₂ & CH 2 or 3 bands	1350-1470 1370-1390 720-725	CH ₂ & CH ₃ deformation CH ₃ deformation CH ₂ rocking
Alkenes	3020-3100 1630-1680 1900-2000	=C-H & =CH ₂ C=C(symmetry) C=C(asymmetric stretch)	880-995 780-850	=C-H & =CH ₂ (out-of-plane bending)
Alkynes	3300 2100-2250	C-H C≡C (symmetry)	600-700	C-H deformation
Arenes	3030 1600 & 1500	C-H C=C (in ring) (2 bands) (3 if conjugated)	690-900	C-H bending
Alcohols & Phenols	3580-3650 3200-3550 970-1250	O-H (free), O-H (H-bonded), C-O	1330-1430 650-770	O-H bending (in-plane) O-H bend (out-of-plane)
Amines	3400-3500 3300-3400 1000-1250	N-H (1°-amines), N-H(2°-amines) C-N	1550-1650 660-900	NH ₂ scissoring (1°-amines) NH ₂ & N-H wagging (shifts on H-bonding)
Aldehydes & Ketones	2690-2840 1720-1740	C-H (aldehyde C-H) C=O(saturated alde)	1350-1360 1400-1450	α-CH ₃ bending α-CH ₂ bending

SPECTROSCOPY

	1710-1720 1690 1675 1745	C=O(saturated ketone) arylketone cyclopentanone cyclobutanone	1100	C-C-C bending
Carboxylic Acids & Derivatives	2500-3300 (acids) 1705-1720 (acids) 1210-1320 (acids) 1785-1815 (acyl halides) 1750 & 1820 (anhydrides) 1040-1100 1735-1750 (esters) 1000-1300 1630-1695 (amides)	O-H (very broad) C=O (H-bonded) O-C C=O C=O (2-bands) O-C C=O O-C (2-bands) C=O (amide I band)	1395-1440 1590-1650 1500-1560	C-O-H bending N-H (1°-amide) II band N-H (2°-amide) II band
Nitriles	2240-2260	C≡N (sharp)		
Isocyanates, Isothiocyanates, Diimides, Azides & Ketenes	2100-2270	-N=C=O, -N=C=S -N=C=N-, -N ₃ , C=C=O		

IR Spectrum of ethyl alcohol and dimethyl ketone

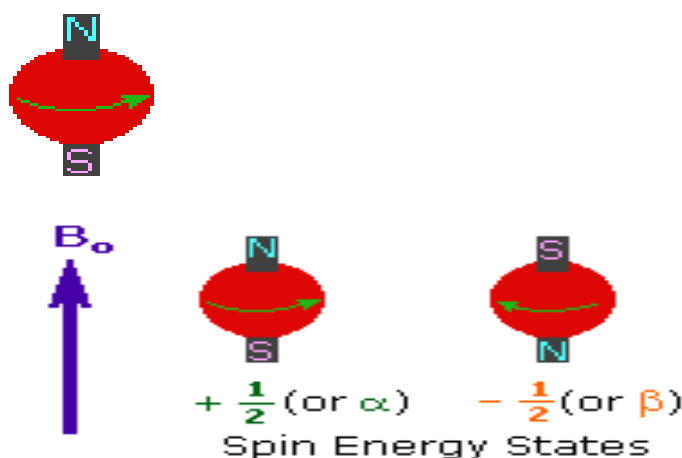


SPECTROSCOPY

NMR-Spectroscopy (Nuclear Magnetic Resonance Spectroscopy)

- The nuclei of many elemental isotopes have a characteristic spin (I).
- Some nuclei have integral spins (e.g. $I = 1, 2, 3 \dots$), some have fractional spins (e.g. $I = 1/2, 3/2, 5/2 \dots$), and a few have no spin, $I = 0$ (e.g. ^{12}C , ^{16}O , ^{32}S , ...).
- Isotopes of particular interest and use to organic chemists are ^1H , ^{13}C , ^{19}F and ^{31}P , all of which have $I = 1/2$.

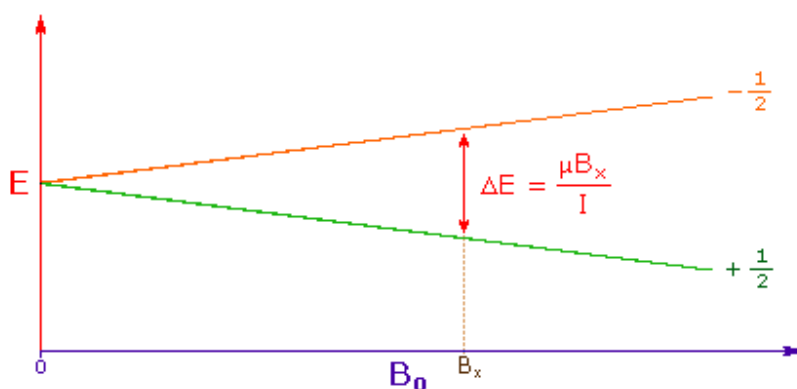
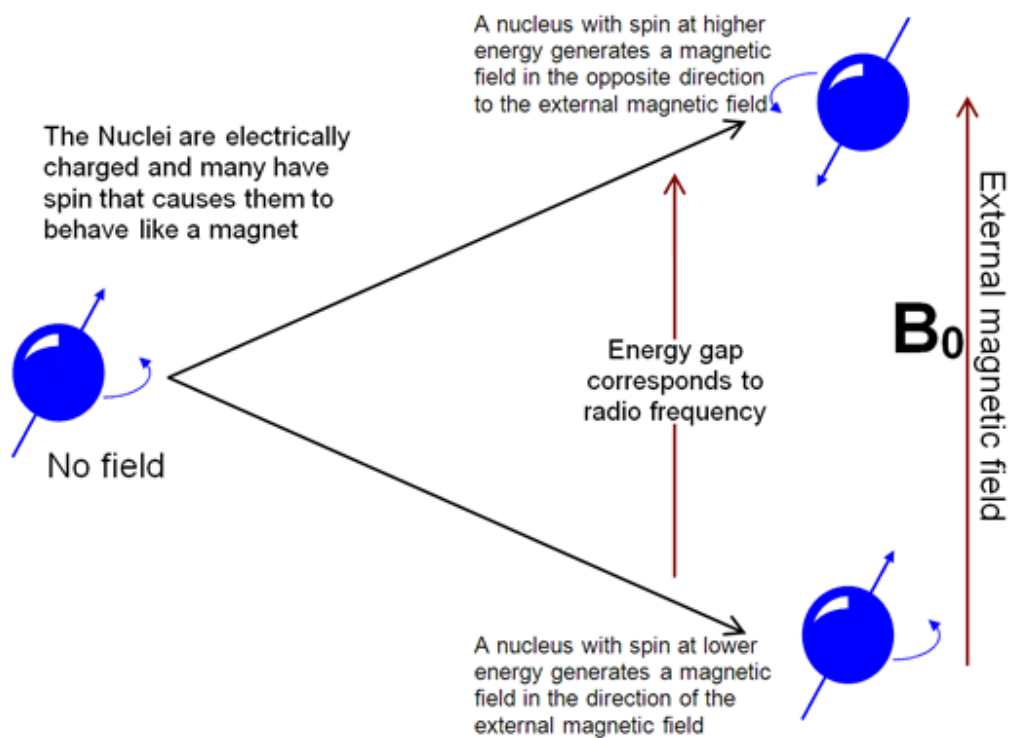
The theory behind NMR comes from the spin, I of a nucleus. Just as electrons have a $+1/2, -1/2$ spin, certain nuclei also experience charged spins that create a magnetic field (called the magnetic moment), which allows chemists to study them using NMR. Nuclei with even numbers of both neutrons and protons experience NO spin and nuclei with odd numbers of both neutrons and protons have integer spins. Nuclei that have the sum of protons and neutrons equal to an odd number (like ^1H and ^{13}C) have half-integer spins. When there is no external or applied magnetic field (B_0), the nuclear spins orient randomly; however, when there is an applied magnetic field, the nuclei orient themselves with or against the larger applied field. The α -spin state is parallel to the applied force and has lower energy than the β -spin state that is antiparallel to the applied force. The energy difference (ΔE) between the α - and β -spin states depends on the strength of the applied magnetic field. The greater the strength of the applied magnetic field, the greater is the ΔE between the α - and β -spin states. This (ΔE) is $\sim 0.02 \text{ cal mol}^{-1}$, which lies in the radio frequency region. The emitted energy in this region produces an NMR signal.



SPECTROSCOPY

Addition of energy results in a spin flip

The case of the spin- $\frac{1}{2}$ nucleus

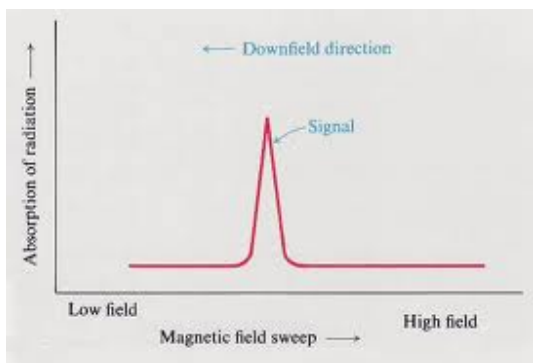


As the applied magnetic field increases, so does the energy difference between α - and β - spin states

SPECTROSCOPY

NMR Spectrum

The NMR spectrum is a plot of the intensity of NMR signal versus the magnetic field (frequency) in reference to a standard (TMS).



Interpreting ^1H NMR Spectra

Four types of Information from NMR:

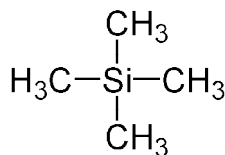
1. **Number of signals:** Protons within a compound experience different magnetic environments, which give a separate signal in the NMR spectrum

Equivalent: Protons that reside in the same magnetic environment are termed chemically equivalent protons. As a general rule of thumb, H's in CH_3 and CH_2 groups are usually equivalent. Symmetrical compounds, such as benzene, are also equivalent; however, since many compounds are not symmetrical, it is important to know how to identify nonequivalent protons. Protons that are different in any way (even in their stereochemistry) are not equivalent and will absorb at different frequencies (give a separate signal on the NMR spectra).

2. **Position of signals (chemical shift):** The position of 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 a halogen or to other atoms or groups etc. The position of the signal arising from the shielding or deshielding by electrons around the proton is referred to as chemical shift (measured in ppm).

SPECTROSCOPY

Measuring and expressing chemical shift: In order to standardize the NMR spectra, chemical shifts are measured with reference to some fixed standard set at 0.00ppm. The reference compound Tetramethylsilane (TMS) $[(CH_3)_4Si]$, is the standard for 1H NMR



TMS is used as the standard in NMR because of the following reasons:

- TMS has 12 equivalent protons so it gives an intense peak even at low concentrations. Few compounds have a lower frequency reading than TMS.
- TMS has low boiling point so it can be easily removed from the recoverable sample.
- It is chemically inert, hence does not react with the sample.
- It is soluble in organic solvents.

In practice the chemical shift is usually indicated by a symbol δ which is defined in terms of TMS.

$$\delta = \frac{(\nu_S - \nu_R) \times 10^6}{\nu_R} \quad \text{quoted as ppm}$$

The signal shift is very small, parts per million, but the great precision with which frequencies can be measured permits the determination of chemical shift to three or more significant figures.

Q. what is the shift of the resonance from TMS of a group of nuclei with $\delta = 3.50$ and an operating frequency of 350MHz?

Ans. 1.23kHz

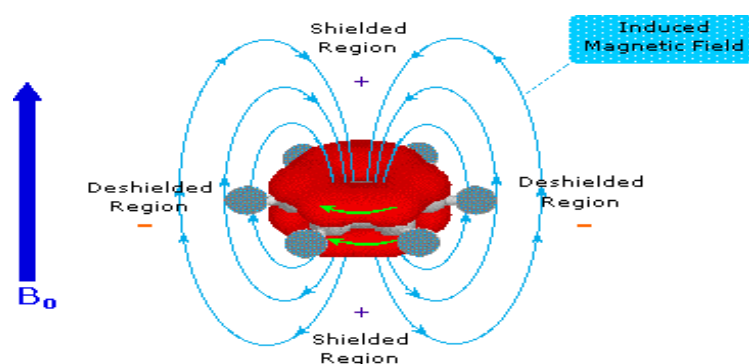
What influences a chemical shift?

Shielding effects: Under an applied magnetic field, circulating electrons in the electron cloud produce a small opposing magnetic field, ultimately decreasing the effective magnetic field felt by the proton, shifting the signal to the right (or upfield). This effect, in which the electron cloud “shields” the proton from the applied magnetic field is called local diamagnetic shielding. The diamagnetic shielding effect is directly proportional to

SPECTROSCOPY

the electron density around the protons; hence more is the tendency for the signal to shift towards the TMS signal (lower chemical shifts)

Electronegativity and deshielding: Protons that are attached to more electronegative atoms (-I effect) experience higher chemical shifts. Electronegative atoms also remove electrons around the protons thereby decreasing their density. This results in less shielding; hence electronegative atoms are said to deshield the proton and cause it to have a higher chemical shift, moving the signal to the left (or downfield). The magnitude of the deshielding effect, however, rapidly decreases as the distance between the proton and electronegative atom increases.



Proton Chemical Shifts of Methyl Derivatives

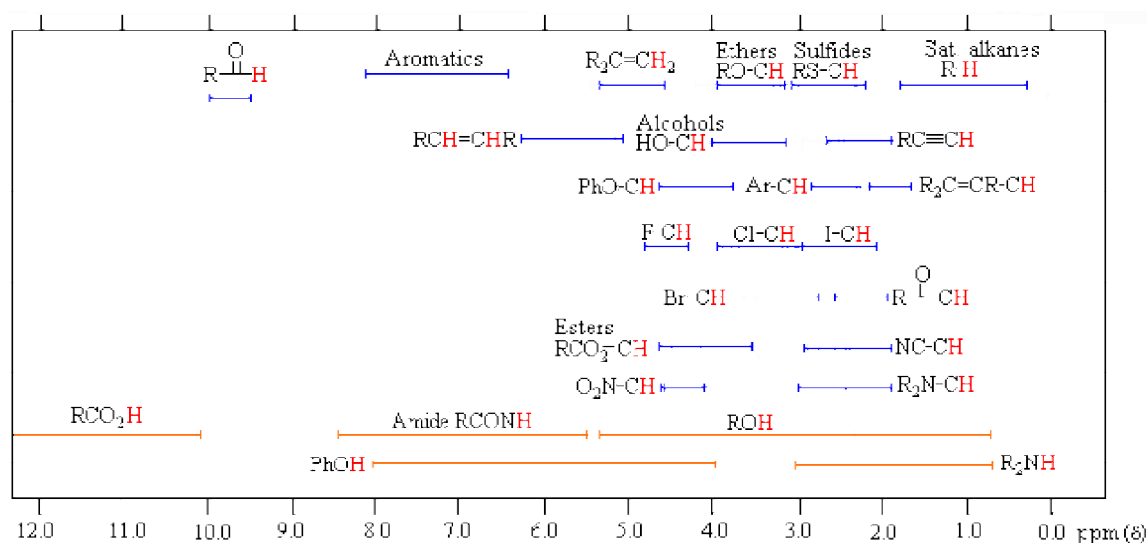
Compound	(CH ₃) ₄ C	(CH ₃) ₃ N	(CH ₃) ₂ O	H ₃ F
δ	0.9	2.1	3.2	1

Compound	(CH ₃) ₄ Si	(CH ₃) ₃ P	(CH ₃) ₂ S	H ₃ Cl
δ	0.0	0.9	2.1	0

Proton Chemical Shifts (ppm)

Cpd. / Sub.	=Cl	=Br	=I	=OR	=SR
CH ₃ X	.0	.7	.1	.1	.1
CH ₂ X ₂	.3	.0	.9	.4	.7
CHX ₃	.3	.8	.9	.0	

SPECTROSCOPY



Factors influencing the Chemical Shift:

- Inductive effect:** A proton is said to be deshielded if it is attached to an electronegative atom or group. Greater the Electronegativity of the atom, greater is the deshielding caused to a proton. Also, as the distance from the electronegative atom increases, the deshielding effect due to it decreases.
- Van der Waals deshielding:** In overcrowded molecules, it is possible that some proton may be occupying sterically hindered position. Clearly, electron cloud of the bulky group will tend to repel the electron cloud surrounding the proton. Thus, such a proton will be deshielded and will resonate at higher value of δ than expected in the absence of this effect.
- Magnetic Anisotropy:** The deshielding effect on protons attached to $\text{C}=\text{C}$ is higher than that can be accounted for by the inductive effect only. Aldehydes and aromatic protons are much more deshielded. Alkyne protons appear at relatively lower δ values. The value of δ in each case can be justified by explaining the manner in which the Π electrons circulate under the influence of the applied magnetic field. In the case of an alkene, the plane of the double bond is at right angles to the applied field. Induced circulation of Π electrons generates induced magnetic field which is diamagnetic around the carbon atom and paramagnetic in the region of the alkene.

SPECTROSCOPY

protons. Thus the proton will feel greater field strength and hence resonance occurs at lower applied field.

- d) **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 downfield.

3. **Relative Intensity of Signals (Integration):** The area under the signals (integration) corresponds to the number of protons responsible for that signal. Therefore, the relative intensities of the signal are proportional to the relative number of proton equivalents. It is important to remember that integration only provides ratios of protons, not the absolute number. For convenience in calculating the relative signal strengths, the smallest integration is set to 1 and the other values are converted accordingly

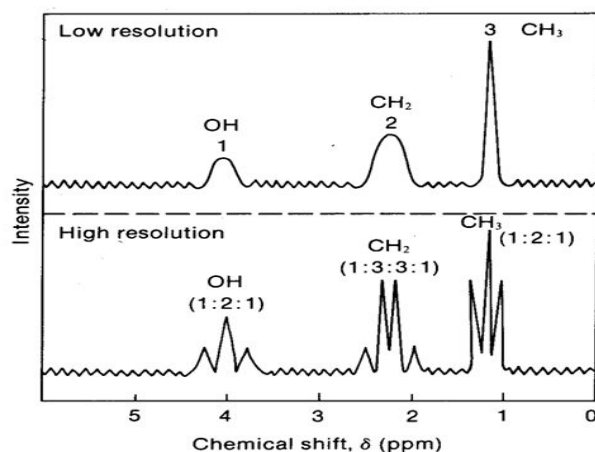
4. **Splitting of proton signals (spin-spin coupling) and coupling constant:** NMR signals are not usually single triangles, but a complex pattern of split triangles labeled as doublets (2 peaks of intensity 1:1), triplets (3 peaks with intensity ratio of 1:2:1), quartets (4 peaks of intensity ratio of 1: 3:3:1), etc. Splitting of a proton signal is caused by neighboring or vicinal protons i.e proton on adjacent carbon atoms, provided these are non-equivalent to the absorbing proton. Thus there will be no splitting of ethylene chloride $\text{ClCH}_2\text{CH}_2\text{Cl}$ (since adjacent carbon has equivalent protons). The interaction between nearby protons produce different spin flips energies (ΔE) as they can orient themselves in a pattern of parallel or anti parallel to the applied magnetic force. This phenomenon, where the spin of the nucleus of one proton is close enough to affect the spin of another, is called spin-spin coupling. Splitting is always reciprocated between the protons—if H_a splits H_b , then H_b must split H_a —and provides information on the neighbors of a proton within the molecule.

The distance between the split peaks are called coupling constants, denoted by J . This constant is a measure of the splitting effect. The J values are independent of the applied magnetic field but depend on the molecular structure.

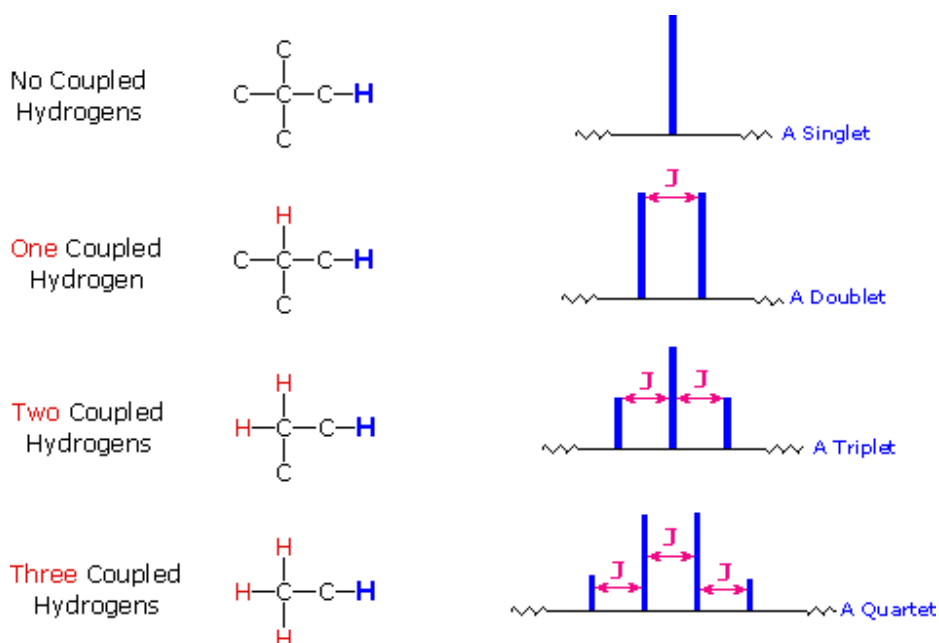
1. Case of germinal protons: These are protons present on the same carbon atom. $J=0-20$ cps (cycles per sec)
2. Case of vicinal protons: These are protons on the adjacent carbon atoms. $J=2-18$ cps

SPECTROSCOPY

3. Case of vinylic protons: In a substituted ethylene or in the case of a pair of geometrical isomer, cis protons have $J=2-15$ cps, whereas trans protons have $J=10-21$ cps.



NMR absorption spectra of ethyl alcohol. The numbers designate the relative areas of the groups in the low resolution spectrum and of the peaks within a functional group in the high resolution spectrum



SPECTROSCOPY

NMR Applications

Today, NMR has become a sophisticated and powerful analytical technology that has found a variety of applications in many disciplines of scientific research, medicine, and various industries. Modern NMR spectroscopy has been emphasizing the application in biomolecular systems and plays an important role in structural biology. With developments in both methodology and instrumentation in the past two decades, NMR has become one of the most powerful and versatile spectroscopic techniques for the analysis of biomacromolecules, allowing characterization of biomacromolecules and their complexes. Together with X-ray crystallography, NMR spectroscopy is one of the two leading technologies for the structure determination of biomacromolecules at atomic resolution. In addition, NMR provides unique and important molecular motional and interaction profiles containing pivotal information on protein function. The information is also critical in drug development.