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Engineering Chemistry

MODULE 2

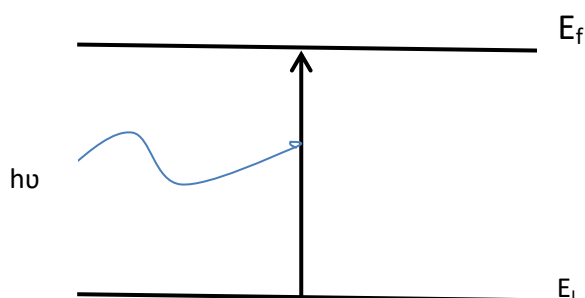
- **Spectroscopic Techniques And Applications**

- Spectroscopy deals with the interaction of atoms or molecules or matter with electromagnetic (EM) radiations.
 - All molecules possess different quantum mechanical energy states such as Electronic, vibrational, rotational and nuclear.
 - Transitions can occur between these states by absorption or emission of EM radiations. Only those transitions that comply with or follow quantum mechanical rules are allowed.
 - Spectroscopy provides information of the details regarding the structure and bonding.
 - The instrument used for spectroscopic study is called **Spectrometer**.
 - The plot obtained from a spectrometer is called **Spectra**.
 - A spectrum provides atomic and molecular information on the interaction of EM radiation with atoms and molecules.
 - Spectroscopic study (i) Gives accurate and reliable results (ii) Requires less time, (iii) sample unaltered.
- ❑ Electromagnetic radiation is a form of energy transmitted through space with velocity of light. ($c = 3 \times 10^8 \text{ ms}^{-1}$).
 - ❑ EM radiations are a bundle of radiations of different wavelengths ranging from Gamma, X-rays, Ultraviolet, visible, infrared and radio waves.

- ❑ On the basis of interaction of atoms/molecules with EM radiation, the spectra can be divided as, (i) Absorption spectrum,(ii) Emission spectrum.

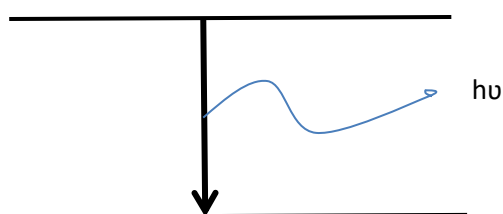
❑ **Absorption spectrum:**

Atom or molecule undergo transition from lower energy state (E_i) to a higher energy state(E_f),absorption of energy ($h\nu$) takes place E.g UV visible, IR, Microwave .and NMR



❑ **Emission spectrum:**

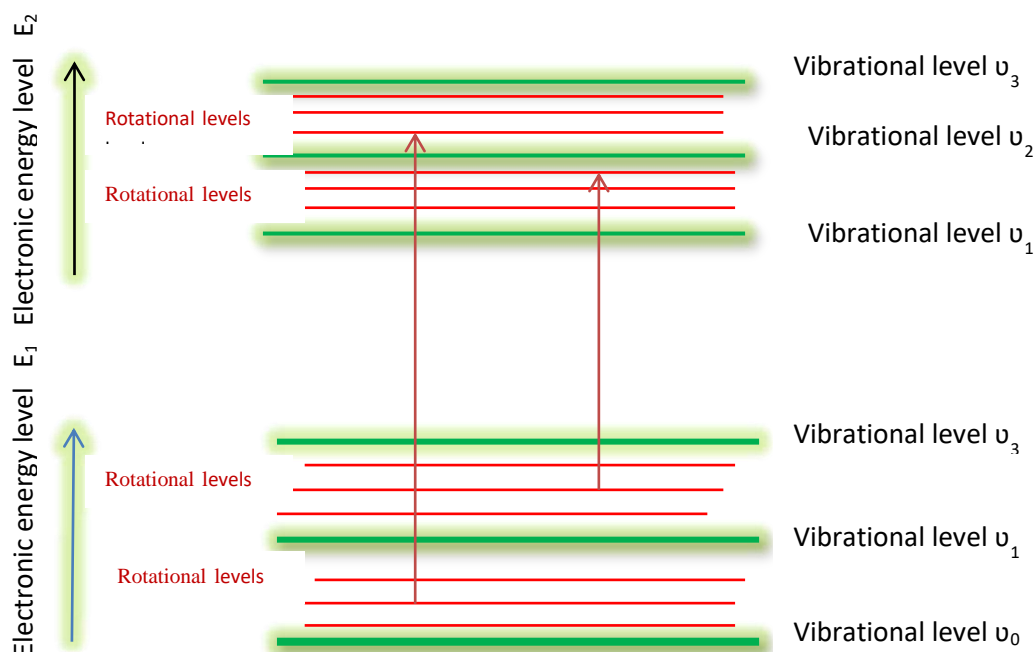
Atom or molecule undergo transition from higher energy state (E_f) to a lower energy state (E_i),emission of energy ($h\nu$) takes place. E.g Hydrogen spectrum, Atomic emission spectrum, Atomic fluorescence spectrum.



MOLECULAR ENERGY LEVELS

- **Electronic Energy (E_{el})**
 - Associated with electrons of molecules, Molecular Orbital may be bonding or antibonding, The energy gap between the electronic energy lies in the UV-Visible region.
- **Vibrational energy (E_{vib})**
 - Associated with vibration of atom/molecules about the center of mass. The energy gap between the vibrational energy level lies in the Infrared region.
- **Rotational energy (E_{rot})**
 - Associated with rotation of atoms/molecules in space about an axis. Possessed by molecules of gas or liquids. Energy gap lies in the microwave region.
- **Translational Energy (E_{trans})**
 - Associated with transition of atoms /molecules with change in center of mass.
- **$E_{total} = E_{el} + E_{vib} + E_{rot} + E_{Trans}$ and**
 - **$E_{el} > E_{vib} > E_{rot} > E_{Trans}$**
 - Electronic transitions are always accompanied by vibrational and rotational transitions.
 - Vibrational transitions are always accompanied by rotational transitions.

- Different molecular energy levels are shown below.



Electromagnetic Radiation

- **Properties**
- Consists of Electrical and Magnetic waves propagating on mutually perpendicular directions.
- EM radiation has both particle and wave character.
- The particle is called Photon
- The frequency (ν) and wave length (λ) are related to

$$\nu = c / \lambda \text{ \& } \nu = 1 / \lambda$$
- Energy of a photon of EM radiation $E = h \nu = h c / \lambda$ where h is called Planck's constant equal to $6.63 \times 10^{-34} \text{ Js}$

Beer-Lambert Law

- ❑ This law governs the absorption of electromagnetic radiation by matter
- When a beam of **monochromatic** electromagnetic radiation is passed through a solution of concentration (c), the rate of

decrease in intensity (-dl) of radiation with thickness of the solution (dx) is proportional to the intensity of incident radiation (I) at that point and also to the concentration (c) of the solution.

➤ Mathematically expressing the law, we have

$$-\frac{dl}{dx} \propto I c$$

ie- $\frac{dl}{dx} = k I c$, -----(1) where **k** is proportionality constant.

Above equation (1) is the differential form of the law. From this we can derive as follows.

- $dl / I = k c dx$
- On integration between the intensity of incident radiation (I_0) and intensity after passing through the solution, (I) we have

$$\int -dl/I = \int k c dx ;$$

$$\ln [I_0 / I] = k c x ;$$

$$2.303 \log [I_0 / I] = k c x$$

$\log [I_0 / I] = \epsilon c x$, ===== (2) where ϵ is $k / 2.303$ called molar extinction coefficient which depends on (i) nature of absorbing molecule, (ii) type of absorption.

Thus **$\log [I_0 / I] = \epsilon c x$, ===== (2) – integrated form of the law.**

We know, Absorbance (A) is logarithmic ratio of intensities of incident light (I_0) to the transmitted light (I)

$$A = \log [I_0 / I] ===== (3)$$

From (2) and (3) we can write,

$$A = \epsilon c x. ===== (4) \text{ (simplified form of the law)}$$

Above equation (2) can be expressed in exponential form as

$I = I_0 e^{-kcx}$ ===== (3) – exponential form of Beer-Lambert law

Transmittance is defined as ratio of intensities of transmitted to incident light ie

$$T = I / I_0$$

Therefore, $A = \epsilon c x = -\log T$

Molar Absorbtivity: (ϵ) :

$\epsilon = A/cx$; unit of molar absorptivity is moles/dm³.

Limitations of the law:

1. Law is invalid at high concentrations
2. Turbid solutions cannot be measured due to scattering of light.
3. Fails if the light is not monochromatic
4. Deviation is observed if there is fluorescence or phosphorescence is observed or different form of molecule.

Numericals:

1. The percentage transmittance of a 0.01M dye solution in ethanol is 20 in a 2 cm cel for a light of wave length 5000 Å⁰ . Find the absorbance (A) and molar absorption coefficient.

Let the incident intensity (I_0) be 100, then from the given data we can write, (I) shall be 20.

Therefore, $A = \log I_0 / I$,

$$A = \log 100/20, \quad A = 0.6989$$

From equation, $A = \epsilon c x$, where $x = 2 \text{ cm} = 0.2 \text{ dm}$,

Therefore, Molar extinction coefficient $\epsilon = A / cx = 0.6989 / 0.1 \times 0.2 = 349.4 \text{ mol}^{-1} \text{ dm}^2$

2. A Dye solution of concentration 0.04M shows absorbance of 0.045 at 530nm while a test solution of same dye shows absorbance of 0.022 under same conditions. Find the concentration of the test solution.

UV –Visible spectroscopy

(Electronic spectroscopy)

Principle:

- ❑ EM radiation in the range of 10-800nm region capable of interacting in the wavelength range 10-800nm, gives these type of electronic transitions.
- ❑ UV Visible spectroscopy involves the study of electronic transitions that occur from lower to higher electronic state.
- ❑ UV region 200-400 nm, (10-200 nm not measurable), Visible region: 400-800 nm.
- ❑ UV visible spectroscopy occurs between the energy levels corresponding to the molecular orbitals of the system.

Classification of Electronic Transition

Three distinctive types of electrons are involved in electronic transitions.

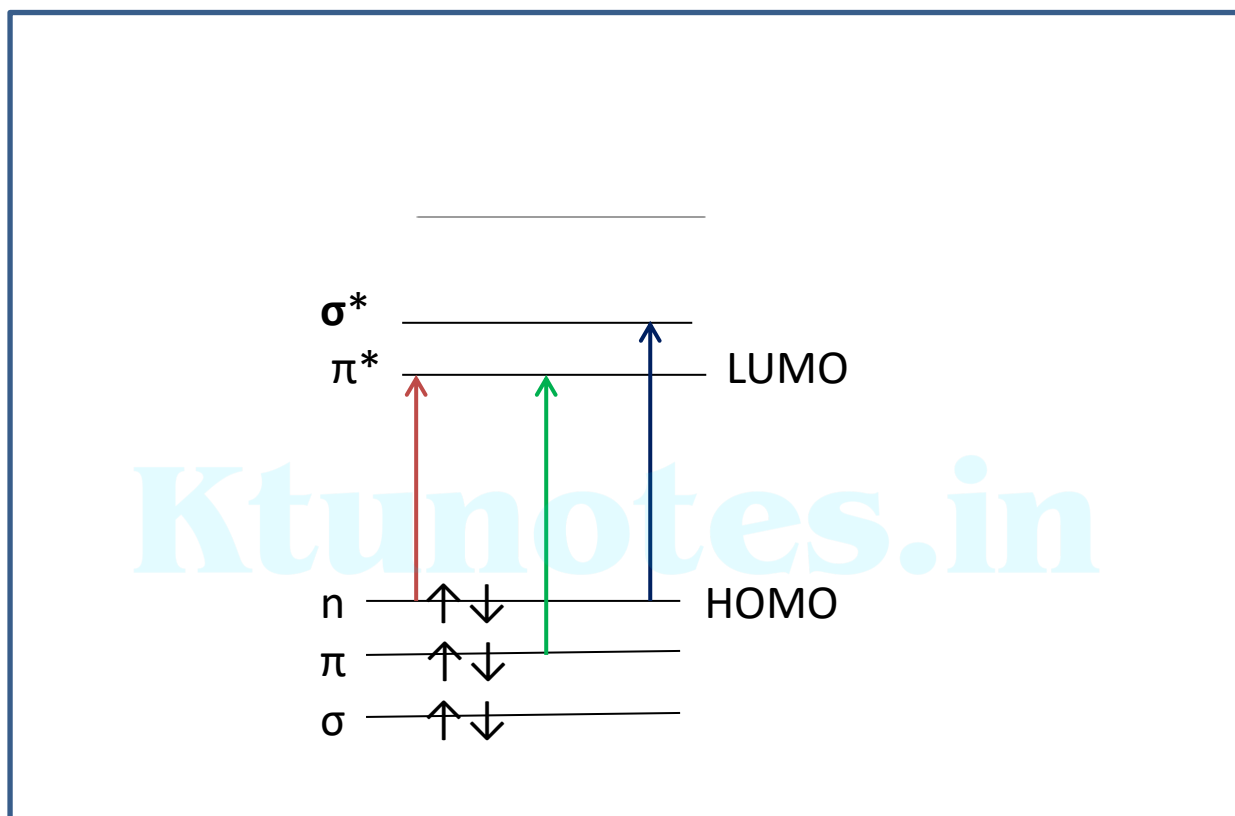
1. Sigma electrons(σ)
2. Pi electrons(π)
3. Nonbonding electrons(n).

Both bonding and anti-bonding electrons are associated with (σ), and (π) electrons.

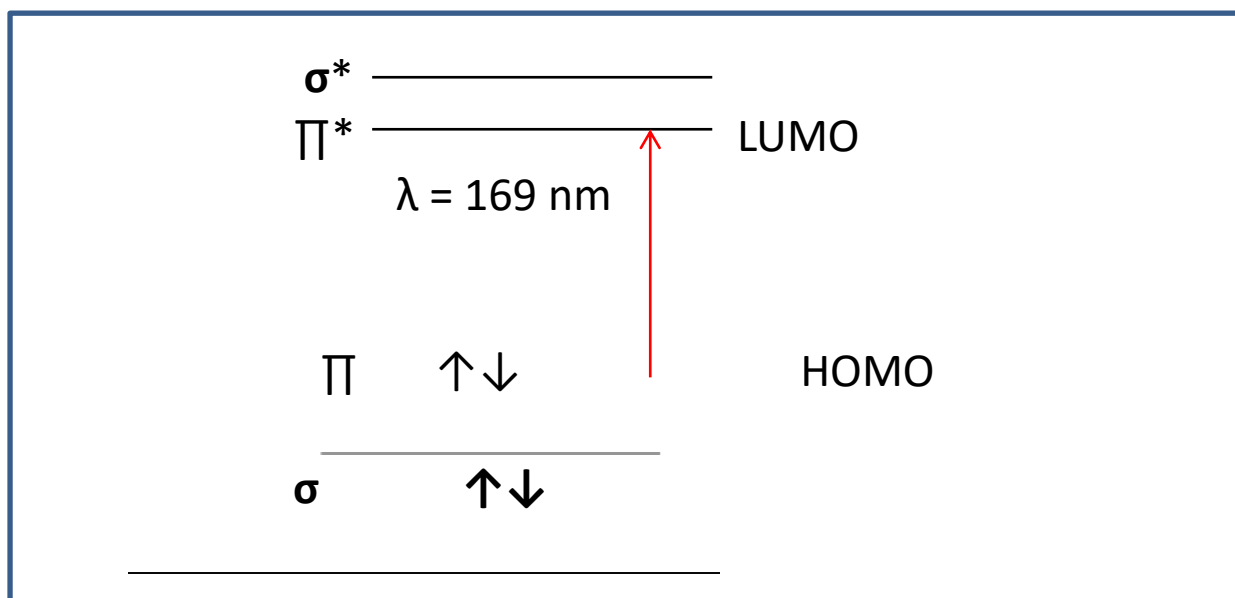
Electronic transitions are classified into four types

- $\sigma \rightarrow \sigma^*$; $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$
- $\sigma \rightarrow \sigma^*$: Exhibited by saturated hydrocarbons which are transparent to UV light only- C-C sigma bond, C-H sigma bond – λ at 150 nm-not detectable.
- $\pi \rightarrow \pi^*$: Exhibited by unsaturated hydrocarbons containing double or triple bond. -C=C can give absorption at 169nm-not detectable. E.g 1,3 Butadiene, 1,3,5 hexatriene, Benzene.

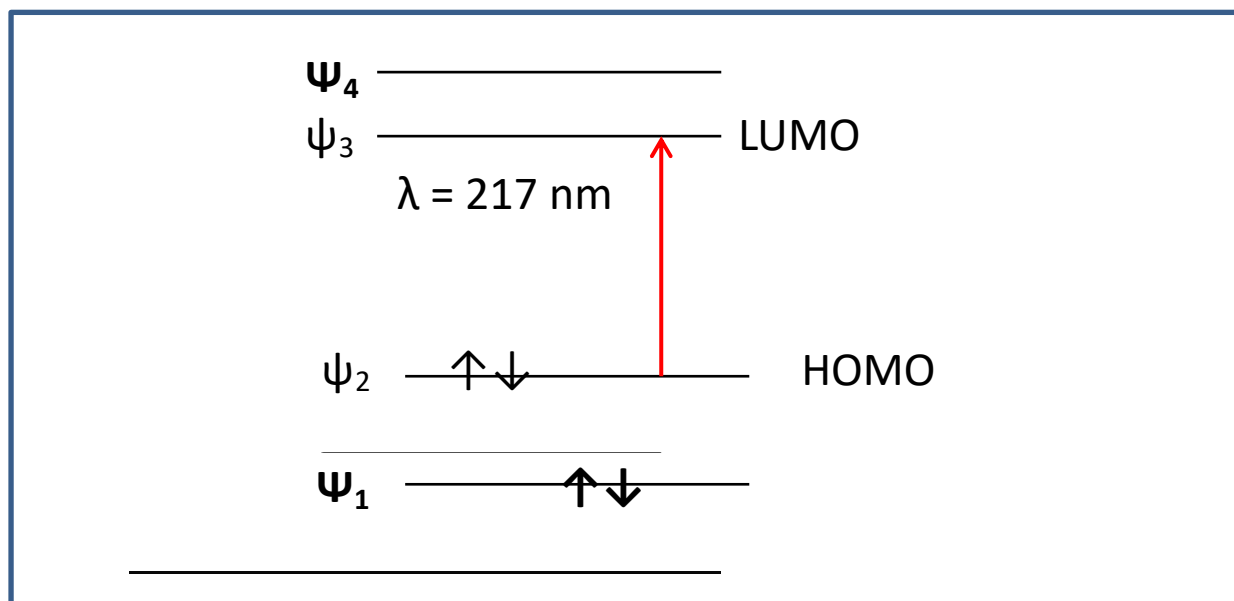
- $n \rightarrow \pi^*$: Exhibited by compounds containing a C=O group i.e. aldehydes and ketones which contain both π electrons and nonbonding electrons. These are low intensity transitions.
- $n \rightarrow \sigma^*$: Exhibited by compounds containing S, N, O etc which contain non-bonding e^- . weak transitions hence forbidden – λ below 200 nm.
- Electronic transitions in Formaldehyde molecule:



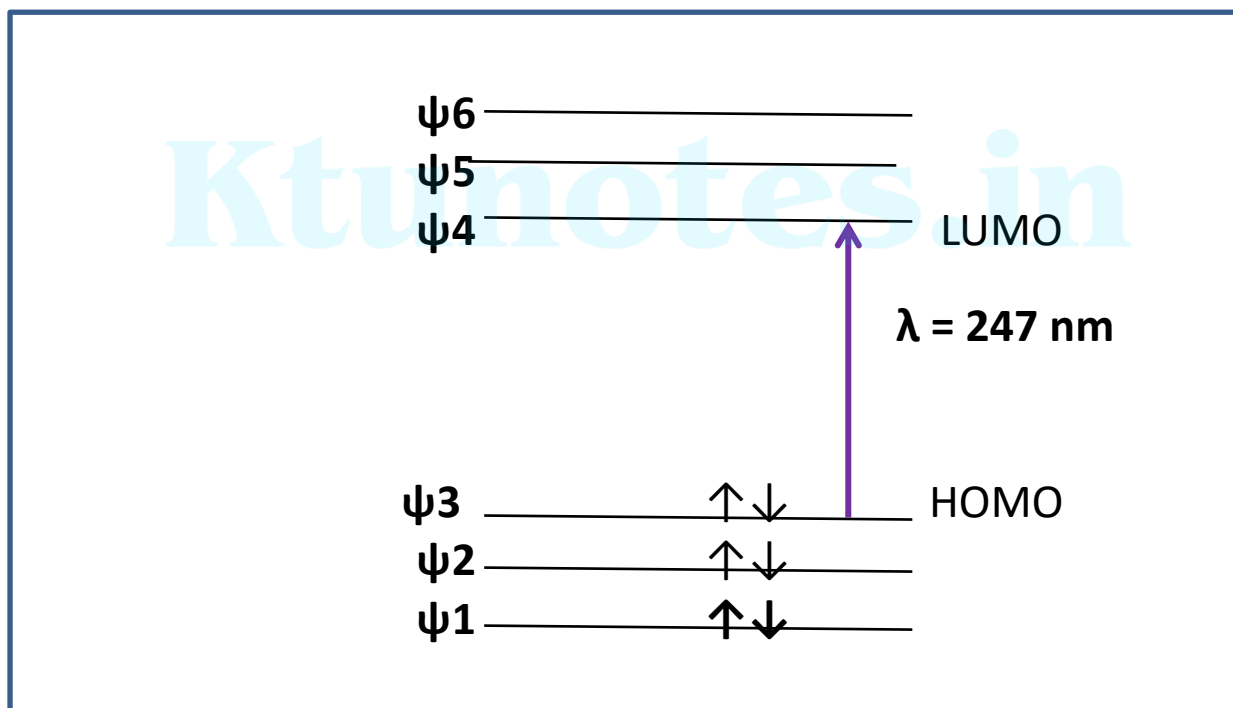
π - π^* transition in Ethene molecule



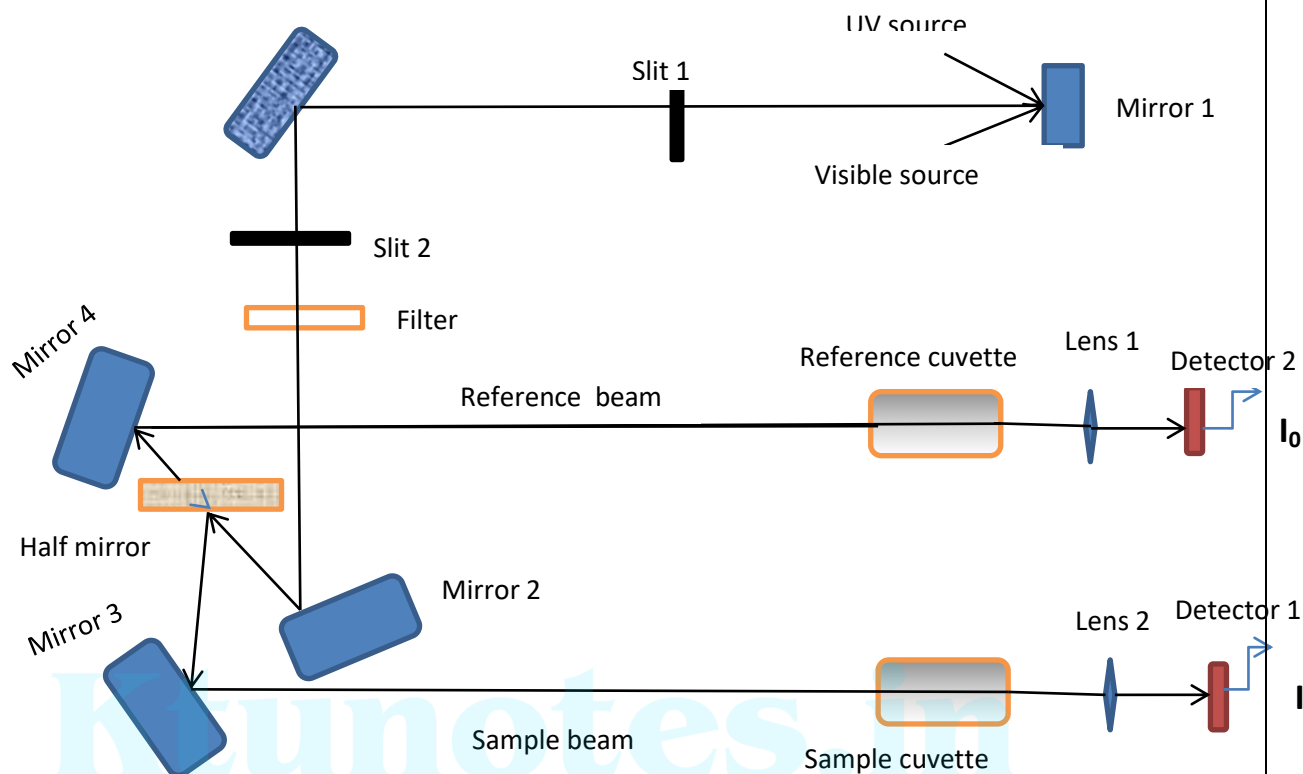
Pi-Pi* transition in 1,3 Butadiene molecule



Pi-Pi* transitions of Benzene

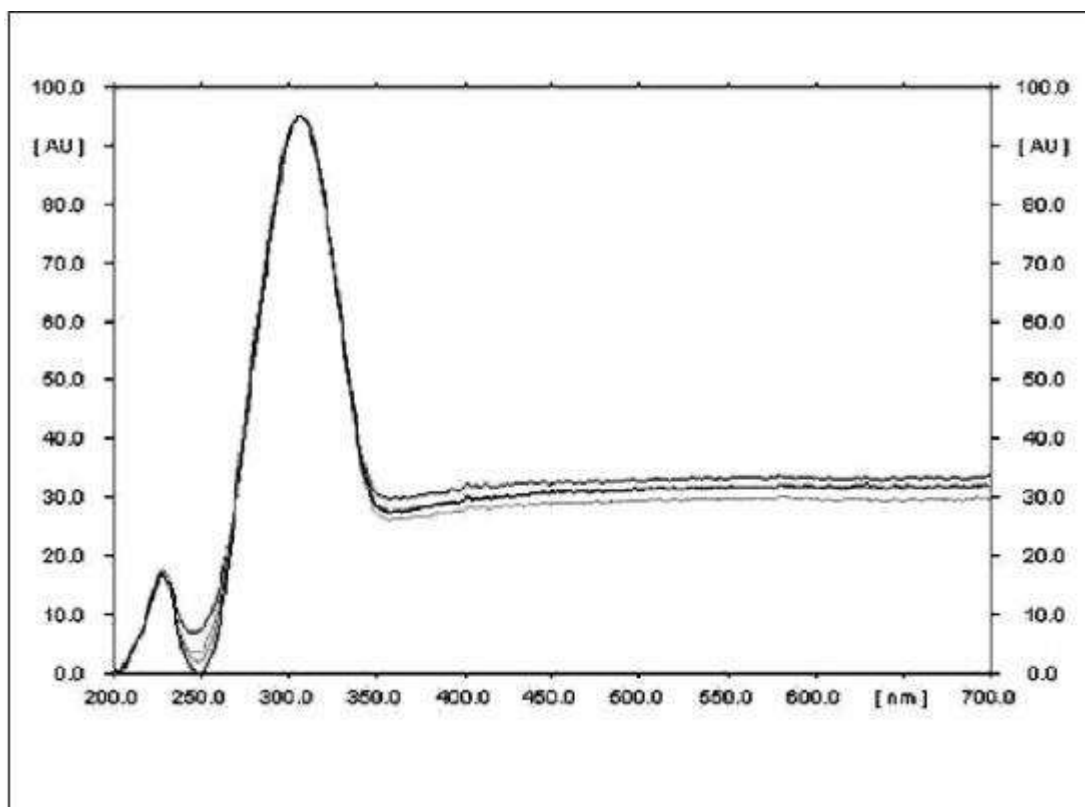


Instrumentation in UV Visible spectroscopy



UV-Visible spectrum:

It is a plot of Absorbance (A) against wave length (λ) of light. The wavelength maximum (λ_{\max}) is characteristic value. Different compounds have different (λ_{\max}) value, which is obtained by scanning a sample in the UV region. Discrete lines are not obtained in the spectrum since electronic transitions are accompanied by vibrational and rotational transitions. Hence it appears as a band spectrum. A typical UV visible spectrum is shown below.



Applications of UV-Visible spectroscopy:

1. For identification of unknown compounds: By comparing the spectrum its spectrum with the spectra of known compounds.
2. For detecting impurities in organic compounds.
3. For characterization of dyes and colorants.
4. For detection of conjugation in aromatic compounds
5. Determination of unknown concentrations in quantitative analysis.
6. Study of kinetics of chemical reations in which the a reaction shifts the absorption wave length.
7. Used in clinical laboratories for quantitative estimation of blood sugar and in other medical diagnostic purposes.
8. Determination of structure of compounds
9. Determination of molecular weight of compounds.
10. Determination of ozone and other pollutants in environment.

Engineering Chemistry

MODULE 2 : INFRA RED SPECTROSCOPY

(Vibrational Spectroscopy)

- Infra-red spectroscopy (IR) involves the transitions between vibrational energy levels of a molecule having change in dipole moment with vibrations of a bond.
- These transitions are brought about by absorbing IR radiations in the range of 400 to 4000 cm^{-1}
- Used to establish identity of a compound
- To predict functional group of a compound.
- Photons in IR regions are not energetic to cause electronic transitions but can cause rotational transitions.
- IR radiations are absorbed by molecules, thereby causing different type of vibrations like stretching, bending of bonds.
- An IR spectrum is a plot of %Transmittance (Y axis) against wave number (ν) in x axis.

Number of vibrational n modes in a Diatomic molecule:

- To describe position of an atom in a molecule, it requires three degrees of freedom, thus for a molecule with ' n ' atoms the number of freedom is equal to $3n$.

- Linear molecule:

For a linear molecule, there are three translational, two rotational degree of freedom. Thus **for a linear molecule of " n " atoms, the vibrational degree of freedom can be $(3n-5)$.**

A diatomic molecule like HCl, there are $(3 \times 2 - 5) = 1$, mode of vibrations are possible ie stretching vibration.

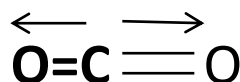
For e.g, HCl molecule can have $(3 \times 2 - 5) = 1$ can undergo only stretching vibration, which is IR active.

A triatomic linear molecule like CO₂, has $(3 \times 3 - 5) = 4$ vibrational modes, which includes symmetric stretching, Asymmetric stretching, Bending (in-plane) and Bending (out of plane) as depicted as follows.



Symmetric stretching

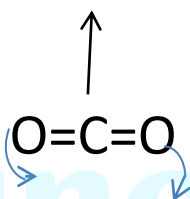
No change in dipole moment, **IR Inactive**



Asymmetric stretching,

Change in dipole moment,

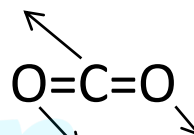
IR active (2349 cm⁻¹)



Bending in plane,

Change in dipole moment

IR active (667 cm⁻¹)



Bending out of plane,

Change in dipole moment

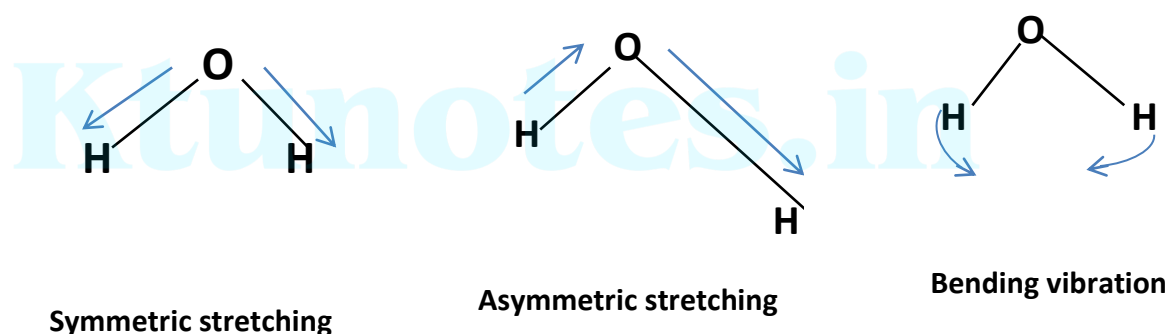
IR active, (667 cm⁻¹)

Of the four modes, only asymmetric stretching, in-plane bending and out of plane bending are IR active as they involve change in dipole moment during the vibration. Symmetric stretching does not produce any change in dipole moment, it is IR inactive. Also the two bending vibrations modes are equivalent, (degenerate), only two absorption signals are observed in the case of CO₂ at 2349 cm⁻¹, for asymmetric and 667 cm⁻¹ for bending vibration.

For HCN also $(3 \times 3 - 5) = 4$ modes, and all are IR active.

Non-Linear molecule: For a non-linear molecule, there are three translational, three rotational degree of freedom. Thus **for a non-linear molecule of “n” atoms, the vibrational degree of freedom can be $(3n-6)$.**

For example, molecules like (H_2O) , (SO_2) , (NO_2) are non-linear triatomic, there are 3 atoms and hence $(3 \times 3 - 6) = 3$ modes of vibrations are possible which includes, symmetric stretching, asymmetric stretching and a bending mode. All the three vibrations are IR active as there is change in dipole moment during the vibration. So IR spectrum of water exhibits three absorption bands.



Mechanism of interaction:

A vibrating molecule if it results in change in dipole moment, it generates electric and magnetic field and act as a source of EM radiation. Similarly when a photon of frequency interacts with the frequency of the vibrating molecule absorption of photon takes place.

Vibrational Energy of a Diatomic molecule:

A vibrating diatomic molecule is similar to a simple harmonic oscillator.

Consider two atoms of masses m_1 and m_2 , connected by means of a chemical bond of force constant k .

Acc to classical mechanics,

$$\text{Fundamental frequency of vibration } (\nu_0) = \frac{1}{2\pi} \times \sqrt{\frac{k}{\mu}} \quad \text{----- (1)}$$

Where μ is reduced mass given by $\frac{(m_1 \times m_2)}{m_1 + m_2}$

Consider the bond stretch by a distance of 'x' m from the mean position, the potential energy (V) is given by

$$V = - \frac{1}{2} kx^2 \quad \text{----- (2)}$$

Substituting this in the schrodinger equation and solving we get the eigen value

$$E = (v + 1/2)h\nu_0, \quad \text{----- (3)}$$

where 'v' is called the vibrational quantum number which has values 1,2,3...

In the ground state ($v=0$), $E = h\nu_0$, called Zero point energy, implying that even at absolute zero, there will be vibration,

Consider a molecule undergoing transition from lower vibrational state (V_1) to a higher vibrational state, (V_2),

$$\Delta E = h\nu$$

$$(V_2 + 1/2) h\nu_0 - (V_1 + 1/2) h\nu_0 = h\nu$$

$$(V_2 - V_1) h\nu_0 = h\nu \quad \text{----- (4)}$$

According to quantum mechanics, for the transition of vibrational levels, $\Delta v = \pm 1$

$$V_2 - V_1 = 1$$

Therefore eqn 4 becomes $h\nu_0 = h\nu$,

$$\nu_0 = \nu,$$

ie, the frequency of absorbed IR radiation (ν) is equal to the fundamental frequency of the molecule (ν_0).

Thus there should only a single line in IR spectrum of a diatomic molecule. But a band is observed. Due to unharmonicity of vibrations at higher quantum levels.

Expression for Force constant:

(1) Can be rearranged as

$$\nu_0 = 1/2\pi (k/\mu)^{1/2}$$

$$\text{or } (k/\mu)^{1/2} = 2\pi \nu_0$$

squaring both sides and rearranging for k ,

$k = 4\pi^2 \nu_0^2 \mu$ or $k = 4\pi^2 c^2 \nu_0^2 \mu$ is an expression for force constant.

Problem

CO molecule absorbs at 2140cm^{-1} . Calculate the force constant of the molecule, given atomic masses of C, and O are 12amu and 16 amu respectively

We know from (1) above.

$$\nu_0 = 1/2\pi (k/\mu)^{1/2}$$

and subsequently rearranging after squaring we get,

$$k = 4\pi^2 \nu_0^2 \mu$$

frequency of absorbed radiation (ν) is equal to fundamental frequency (ν_0)

$$k = 4\pi^2 \nu^2 \mu \text{ but } \nu = c \bar{\nu},$$

$$k = 4\pi^2 (c\bar{\nu})^2 \mu \text{ and } \mu = \frac{(m_1 \times m_2)}{m_1 + m_2}$$

$$m_1 + m_2$$

$$\mu = \frac{12 \times 1.66 \times 10^{-27} \times 16 \times 1.66 \times 10^{-27}}{(12+16) \times 1.66 \times 10^{-27}} \text{ Kg}$$

$$\text{since } 1\text{amu} = 1.66 \times 10^{-27} \text{ Kg}$$

Therefore

$$k = 4(3.14)^2 \times (3 \times 10^8 \text{ ms}^{-1})^2 \times (214000 \text{ m}^{-1})^2 \times 1.138 \times 10^{-27} \text{ kg}$$

$$k = 1849 \text{ Kgs}^{-2} = 1849 \text{ Nm}^{-1} \quad (1 \text{ N} = \text{kms}^{-2})$$

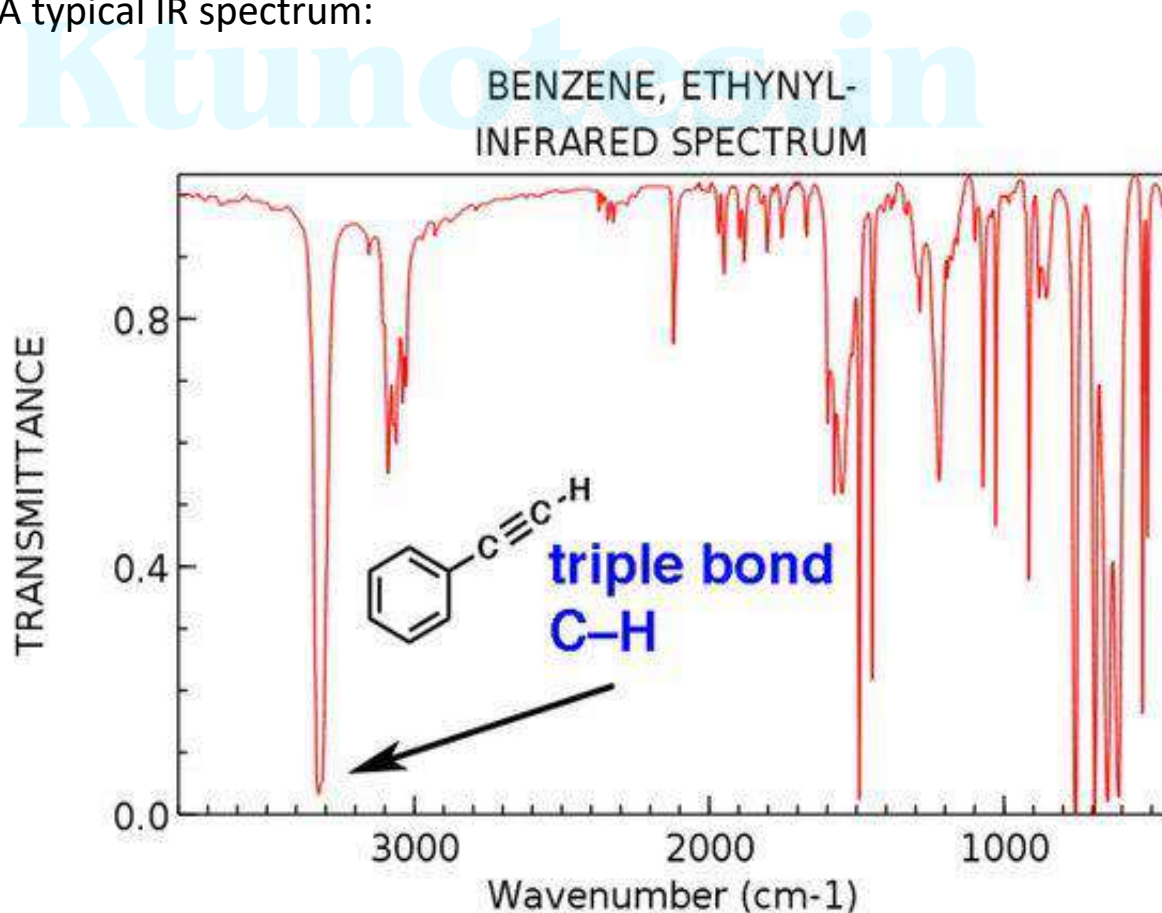
Practice problem:

If the fundamental frequency of HCl molecule is $8.667 \times 10^7 \text{ s}^{-1}$, calculate the force constant of HCl bond [H=1.008, Cl=35045] ro

IR spectra is recorded employing Fourier-Transform technology. Solid samples are mixed with potassium bromide and the mixture is pressed into a thin wafer, which is placed in the path of the IR beam.

Drop of liquid sample is placed between two sodium chloride discs through which IR beam is irradiated.

A typical IR spectrum:



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Applications of IR spectroscopy:

1. Determination of Force constant:
2. Identification of Functional groups in organic molecules

From the stretching vibrations of the bonds present in the functional group the presence of functional groups can be detected.(for e.g,the stretching frequency of C=O group in saturated ketones is $1700-1725\text{cm}^{-1}$ etc

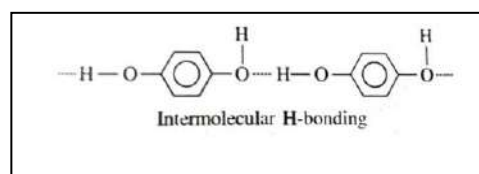
3. Identification of unknown compounds: By comparing the IR spectrum of unknown compound with that of a known compound, by finger print ($700-1500\text{cm}^{-1}$)region matching.
4. Determination of Purity
5. To detect and distinguish between intra, inter molecular Hydrogen bonding.

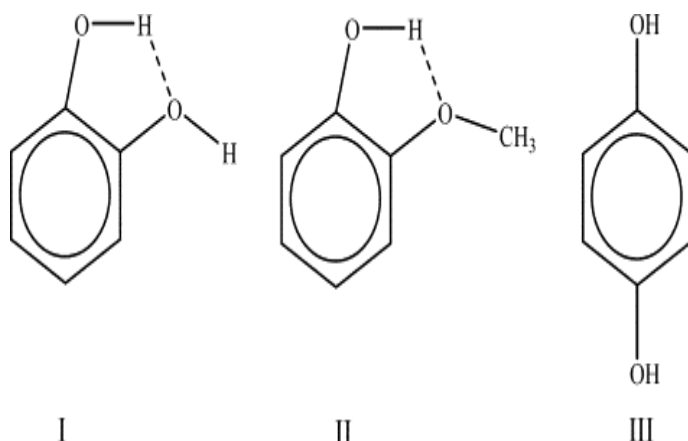
Detection: OH stretching frequency ($33000-3600\text{cm}^{-1}$) is lowered due to hydrogen bonding. From the decrease, the presence of hydrogen bonding can be detected.

Distinction: After detecting the presence of hydrogen bonding, noted the frequency of absorption. Dilute the sample. Then record the IR spectrum of the diluted sample and noted the absorption frequency of the diluted sample.

Intermolecular hydrogen bonding does not alter the absorption frequency on dilution while ther will be a shift in the absorption frequency.

e.g o-hydroxy phenol-No shift in absorption frequency is observed since there is intramolecular hydrogen bonding.,while for p-hydroxy phenol, absorption frequency shifts due to inter molecular hydrogen bonding.





6. To understand shape and symmetry of molecules.

7. Study of chemical reactions

8. Study of tautomeric equilibrium : amido-imido tautomerism can be studied by noting the absorption frequency of hydroxyl or carbonyl group in the compound.

9. Study of coordination compounds

10. To find Molecular symmetry and dipole moments.

ENGINEERING CHEMISTRY
MODULE-2 : Nuclear Magnetic spectroscopy (NMR)

H^1 NMR Spectroscopy.

NMR is the study of the properties of molecules containing magnetic nuclei by means of the application of a magnetic field and the observation of the frequency at which they come into resonance with applied radiofrequency electromagnetic field.

Principle: Radiofrequency waves of the electromagnetic spectrum induce transitions between magnetic energy levels of nuclei of a molecule, which are created by keeping the nuclei in a magnetic field. It depends on the absorption of energy when the nucleus of an atom is excited from its lowest energy nuclear spin state to the next higher one. The energy required for transition falls in radiofrequency region (60 to 500 MHz).

Theory: Nuclei of atoms and molecules spin, and develop magnetic field and act as a tiny magnet with a magnetic moment (μ).

Subatomic particles spin on their own axis. These spins in most of the atoms (^{12}C) are paired against each other, such that the nucleus has no overall spin. The rules for determining the net spin can be explained as follows.

It has been found that any nucleus consisting of either an odd number of protons or an odd number of neutrons or both has the property of nuclear spin and is NMR active.

If the mass number is even. (two cases arise)

, (a) Both n_p and n_n are even, (b) Both n_p and n_n are odd

(a) Both n_p and n_n are even

Protons and neutrons separately pair up inside nucleus, then the nucleus has no net spin. e.g ^4He , ^{12}C , ^{16}O . Hence, such nuclei are **NOT NMR active**.

(b) Both n_p and n_n are odd

Protons and neutrons separately pair up inside nucleus, leaving a half integral spin in each kind of particles giving a net integral spins for the nucleus. ($I = 1, 2, 3, \dots$) such nuclei are **NMR active**.
E.g ^2_1H , ($I = 1/2 + 1/2 = 1$) , $^{14}_7\text{N}$, ($I = 1$), $^{10}_5\text{B}$,

II If mass number is odd ;(two cases arise)

(a) If n_p is odd , and n_n is even- net spin of neutrons is zero, and protons pair leaves odd half integral spin.

$I = 1/2, 3/2, 5/2, \dots$, such nuclei are **NMR active**.

E.g ^1_1H ; ($I = 1/2$), $^{31}_{15}\text{P}$ ($I = 1/2$). $^{15}_7\text{N}$, $^{37}_{17}\text{Cl}$, $I = 3/2$, $^{11}_5\text{B}$ = $3/2$,

(b) If n_p is even, and n_n is odd.- Net spin due to protons is zero, neutrons pairing leaves odd half integral spins,- such nuclei are also **NMR active** E.g $^{13}_6\text{C}$ ($I = 1/2$).

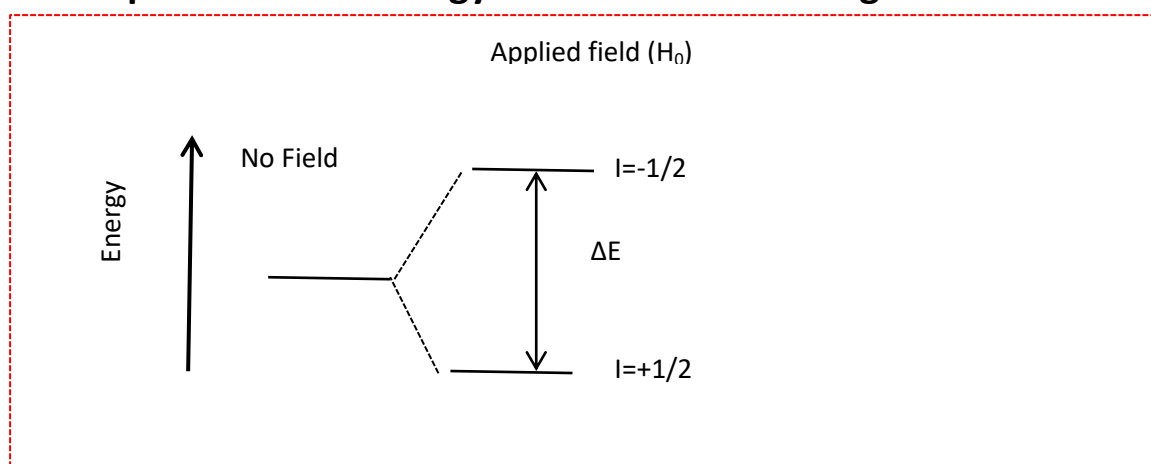
According to quantum mechanics a nucleus of spin 'I' will have $(2I + 1)$ orientations.

$I = 1/2$ will have 2 orientations. ^1H and ^{13}C are examples.

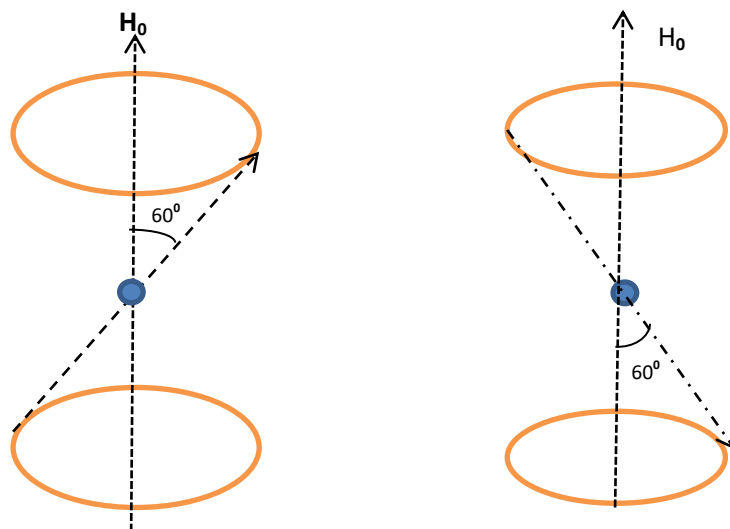
For $I = 1$, there are 3 orientations.

Energy levels of a nucleus with $I = 1/2$,

Nuclear spin and energy levels in Magnetic field:



Larmor Frequency :



Flipping of Spinning Nucleus

Imagine a hydrogen nucleus ($I=+1/2$) in a magnetic field. Here the nucleus is in lower energy level (magnetic moment vector align with the applied magnetic field). When the nucleus spins on its axis, in the presence of an external magnetic field (H_0), the axis of spin precess around the magnetic field (similar to the precessional motion of a spinning top in gravitational field). *The frequency of precession of the spinning nucleus in a magnetic field is called Larmor frequency. ($\nu = (\gamma / 2\pi) H_0$)*

When this frequency becomes identical to the radiofrequency, resonance occurs and flipping of spinning nucleus takes place with the absorption of radiation and spin orientation of nucleus becomes $-1/2$ from $+1/2$. and now the nucleus is at higher energy level, also its magnetic moment is aligned against the applied magnetic field.

Relation between radiofrequency and field strength:

The frequency of radiation needed is determined by the difference in energy between the energy levels. According to

quantum mechanics, the spinning nucleus can have only those spin angular momentum values permitted by the equation, $Spin\ angular\ momentum = I(I+1)^{1/2} h/2\pi$, where h is Planck's constant, I is the spin quantum number of the nuclei, which can have zero. Integral or half integral values.

But the magnetic moment of the nucleus (μ), can be equated to the spin angular momentum as $\mu = \gamma \times I(I+1)^{1/2} h/2\pi$.

On introducing the nucleus having a magnetic moment into external magnetic field H_0 , as shown in the above fig whose energy states can have energy given by the equations,

$$E_1 = -1/2(\gamma h/2\pi) H_0 \text{ (1).and}$$

$$E_2 = +1/2(\gamma h/2\pi) H_0 \text{ -----(2) ,there by}$$

When a nucleus absorbs energy equal to the difference between E_2 and E_1 ie $\Delta E = E_2 - E_1$

$$\therefore \nu = \Delta E / h ,$$

$$= \frac{+1/2(\gamma h/2\pi) H_0 - (-1/2(\gamma h/2\pi) H_0)}{h}$$

$\nu = (\gamma /2\pi) H_0$ is the relation between radio frequency and field strength.

From the above equation, it is clear that

- (1)The frequency of absorbed or emitted radiation by a nucleus in moving from one energy state to another is directly proportional to the applied magnetic field.
- (2)When the radiofrequency is kept constant and the strength of magnetic field is varied, at some field strength the energy required to flip the proton matches with the energy of radiation, when absorption occurs and we get absorption signal.
- (3)The resultant signal (spectrum) obtained is called NMR spectrum.

Note : A magnetic field of 4.7 T (about 100,000 > earth's magnetic field) separates the two spin states of ^1H nucleus by an energy difference of 200 MHz in the radiofrequency range of the electromagnetic spectrum.

Chemical shift (δ): Dependence of resonance frequency of a nucleus that results from its molecular environment is called its chemical shift.

ie the shift in the NMR signals due to shielding and deshielding by electrons is called chemical shift.

Chemical shifts are measured in relative to a reference.

The position of the NMR signals relative to the reference signal is also called as chemical shift.

$$\delta = \frac{(\nu_{\text{sample}} - \nu_{\text{ref}})}{\nu_{\text{ref}}} \times 10^6 \text{ ppm}; \quad \text{Or} \quad \delta = \frac{\Delta\nu \text{ in Hz}}{\nu_{\text{op}} \text{ (MHz)}}$$

Chemical shift is dimensionless. Expressed in ppm

Alternate system of defining position of NMR signals is by a scale called tau " τ " scale.

$$\tau = 10 - \delta$$

Different kind of protons in a molecule give different signals at different frequency.

Theoretical concept of chemical shift:

Shielding and De-shielding

When a nucleus is placed in a magnetic field (applied field), its electrons are caused to circulate and produce a secondary magnetic field. This induced secondary magnetic field may oppose or reinforce the applied magnetic field. Thus two possibilities arise.

They are as follows.

1. When induced secondary magnetic field *oppose applied field*
Here the net field felt by the nucleus (e.g ^1H) in a molecule will be less than the actual applied magnetic field and hence we can say that the hydrogen nucleus is shielded.

A more shielded hydrogen nucleus absorbs RF radiation at a lower frequency. E.g Field felt by the hydrogen nuclei of methane is less than that of free hydrogen nuclei.

When induced secondary magnetic field *reinforces applied field*, the net field felt by the nucleus (e.g ^1H) in a molecule will be greater than the actual applied magnetic field and hence we can say that the hydrogen nucleus is de-shielded.

A more de-shielded hydrogen nucleus absorbs RF radiation at a higher frequency.

Measurement of chemical shift in NMR spectroscopy involved the use of a reference standard- Tetramethylsilane (CH_3)₄Si. Called as TMS. TMS is the most commonly used reference compound because of the following reasons.

1. TMS is *chemically inert*
2. *Do not interfere* with other compounds under study
3. IT is *highly volatile* (b.pt 27°C) hence *samples can be recovered* after analysis.
4. TMS gives a single sharp absorption peak due to twelve equivalent protons, at a lower frequency than samples, due to lower electronegativity of Si than C.
5. *Soluble in most organic solvents.*

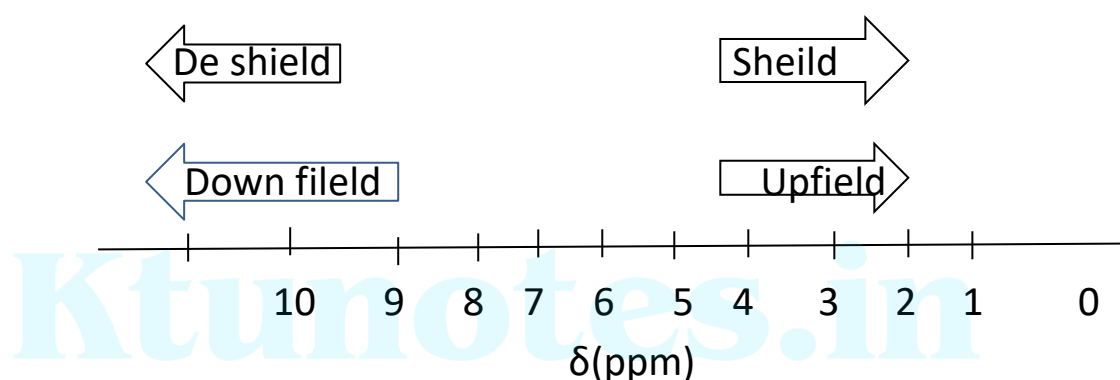
Factors affecting chemical shift:

1. Shielding and de-shielding: Compared with an isolated proton, a shielded (diminishing of applied magnetic field

by the electrons of the atom) proton requires higher applied field strength and therefore **a more shielded proton absorbs at lower frequency of RF radiation.**

While a de-shielded (increasing of applied magnetic field by the p electrons of the atom) proton requires a lower applied field strength. Therefore **a more deshielded proton absorbs at higher frequency of RF radiation.**

Thus shielding and de-shielding of protons by electrons causes chemical shift.



2. All aromatic protons and olefinic protons differ widely because of the deshielding due to the circulation of π electrons. **Deshielding effect increases the chemical shift.** (δ lies between 6.5 to 8.5).
3. Electronegativity of the attached atoms: Presence of electronegative atom attached to aliphatic compounds influences chemical shift. When an electronegative atom is present in the $-\text{CH}$ system, and there is less shielding (more deshielded) and chemical shift increases.
For e.g., in the compound CH_3X ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$), the shielding of the methyl protons decreases as the electronegativity of X becomes more and more.

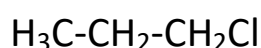
Thus chemical shift depends on the degree to which an electronegative atom draws electrons towards it from the methyl group.

Compound	Chemical shift(δ) ppm for X		
CH ₃ X	F	Cl	I
	4.3	3.1	2.2

Deshielding effect of electronegative substituents is cumulative

	Compound		
Chemical shift(δ) ppm	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃
	3.1	5.3	7.3

Shielding effect decreases when an electronegative atom substituted in the hydrocarbon chain, the electron density around the protons decreases as the proton gets closer towards the electronegative atom. i.e. δ value increases
e.g: 1-chloropropane



δ (ppm) : 1.0 1.4 3.4

4. Hydrogen Bonding: Protons that are involved in hydrogen bonding typically change the chemical shift. More the hydrogen bonding, more protons are deshielded, and the chemical shift is higher.

Chemical shift of some of protons

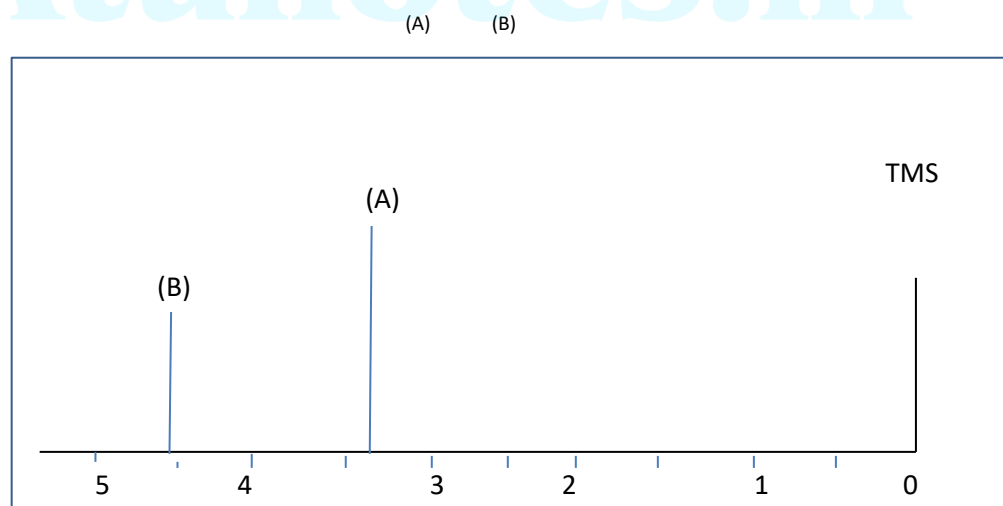
Proton type	Chemical shift(δ) ppm	Proton type	Chemical shift
H-R (aliphatic)	0.9-1.8	H-C-Br	2.7-4.1
H-C \equiv C-(alkynal)	2.5	H-C-Cl	3.1-4.1
H-C=C-(alkenyl)	4.5-6.5	H-C-O-R	3.3-3.7
H-Ar(aromatic)	6.5-8.5	OH-R	0.5-5
H-CO-R	9.10	H-O-CO-R	10-13

Interpretation of chemical shift

1. Number of NMR signals indicate the no of types of protons present
2. The position of the signal indicates about the protonic environment.
3. The intensity of the signal (peak area) indicates how many protons of the same kind are present. Also the relative peak ratios of different kinds of protons in the molecule can be understood.

For e.g. there are two kinds of protons in $\text{CH}_3\text{-OCH}_2\text{-CN}$, NMR spectrum will have two signals, apart from that of reference (TMS), and the two signals will be at different position due to their different environment. Their relative intensities are also different since they have three protons of one kind and two protons of another kind.

A typical NMR spectrum of $\text{CH}_3\text{-OCH}_2\text{-CN}$ is given below.



Spin-spin Splitting (coupling): Fine splitting of the NMR signals due to the interaction between protons on adjacent atoms is referred to as Spin-spin Splitting or Spin-spin coupling.

Each nucleus in a molecule spins and possess its own magnetic moment. The electronic environment of each proton distinguishes it from all others in the molecule and the magnetic field associated with a given proton be affected by the magnetic field of an adjacent proton.

At low resolution, the NMR spectrum is broad and at higher resolution, splitting of NMR signal is caused by Spin-spin interaction.

Rules for spin-spin splitting

1. Chemically equivalent protons do not show spin-spin splitting.
2. Only nonequivalent protons couple and split
3. Protons on adjacent carbons normally will couple.
4. Splitting of signal is based on (n+1) rule .ie The multiplicity (No of peaks into which a particular proton is split) of a proton is calculated. .If “n: number of protons are present in an adjacent nucleus, the signal will split into n(n+1) peaks.
Zero hydrogen as neighbor it will split into (0+1) ie singlet
One hydrogen as neighbor it will split into (1+1) ie doublet
Two hydrogen as neighbor it will split into (2+1) ie Triplet
Three hydrogen as neighbor it will split into (3+1) ie Quartet
and so on.
- 5 If a set A of n_A equivalent protons and another set X of n_x set of equivalent protons both spin couple with a particular set M with are present, n_m equivalent protons; then the signal for M is split into $(n_A+1) (n_x+1)$ component lines.

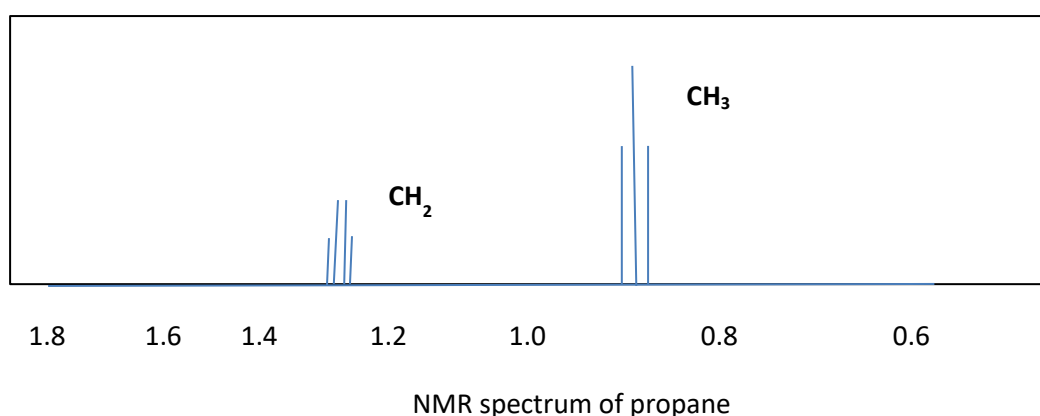
Let us take the following compounds as example and discuss the spin –spin coupling in these molecules.

1. The NMR spectrum of **CH₃-OCH₂-CN** gives two signals, both are singlet.
2. In the case of **CH₃CHCl₂**, a doublet at $\delta=2.1$ ppm for methyl proton and a quartet at $\delta=5.9$ ppm for CH proton. The CH₃ proton split into a doublet under the influence of one CH proton while the CH proton splits into a quartet under the influence of three CH₃ protons. The intensity ration of the quartet of CH proton is 1:3:3:1, while that of the doublet is 1: 1.

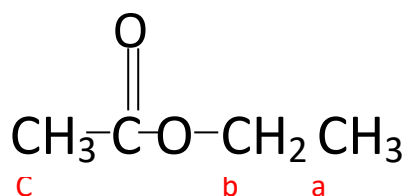
3. n-propane: CH₃CH₂CH₃

Two different kinds of protons. The two terminal methyl protons are of same kind, will generate one signal (a), and the CH₂ protons will generate another signal(b).

'a' will split into a triplet under the influence of the two CH₂ protons with an intensity ratio of 1:2:1, and 'b' signal will split into a septet (as per n+1 rule 4 above) (6+1=7) under the influence of six equivalent protons, with an intensity ratio of 1:6:15:20:15:6:1.



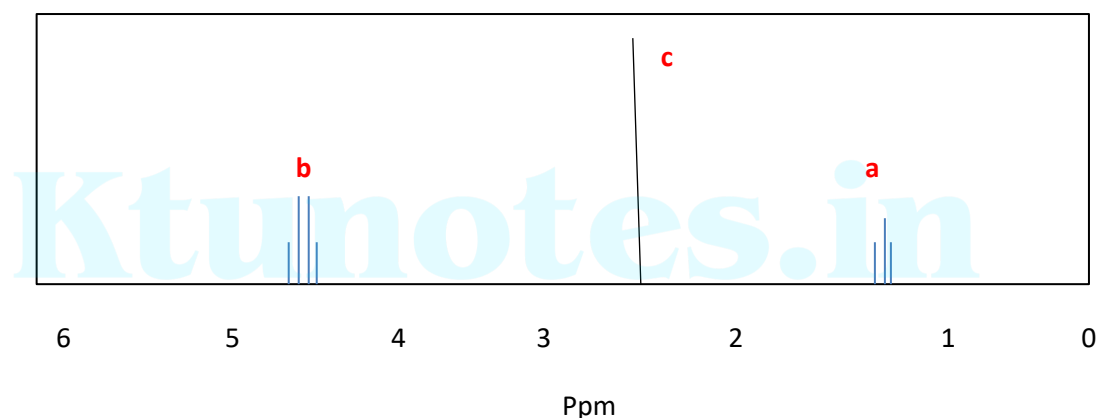
Predict the ¹H NMR signals ,their relative positions and multicplities for ethylacetate.



Three types of protons-(a,b,c)-

The δ for methyl proton 'a' is closer to TMS,(low δ value), because the H atoms are far away from the electronegative oxygen atom.

"c" type methyl proton appears next and the 'b' type methylene proton appear last with high δ value



^1H NMR spectrum of ethyl acetate.

Explain the ^1H NMR spectrum of ethanol.

A: The NMR Structure of **pure ethanol** is $\text{CH}_3\text{CH}_2\text{OH}$ shows

- (i) A triplet for methyl protons (due to their coupling with methylene proton) at around $\delta=1.15$ ppm.
- (ii) An octet for methylene proton (due to their coupling with methyl proton and hydroxyl proton) at $\delta= 3.6$ ppm,the multiplicity observed being in accordance with (n_A+1) (n_x+1) formula.

B: The NMR spectrum of acidified ethanol or 20% solution of ethanol shows,

A triplet for methyl protons as expected (due to their coupling with methylene proton) at around $\delta=1.15$ ppm, but the CH_2 signal is a quartet and the OH signal is a singlet only. NO spin-spin coupling takes place between OH proton and CH_2 protons.

This is due to chemical exchange i.e. there is rapid exchange of protons between the ethanol molecules.



Coupling constant (J): The magnitude of separation between (i.e. distance or spacing) the peaks in a multiplet arising from spin-spin coupling constant or coupling constant. It is denoted by the letter 'J', expressed in Hz . J value is independent of the applied field strength or operating frequency of the instrument.

It is a measure of how strongly a nucleus is affected by the spin states of its neighbor.

For example, in the NMR spectrum of ethanol, the coupling constant between the methyl triplet is equal. In the case of methylene signal, the spacing between the signals is not constant due to the difference in coupling constants of $-\text{OH}$ and CH_3 protons.

Applications of NMR spectroscopy:

1. In magnetic resonance imaging for medical diagnosis
2. For identification of atomic configuration in molecules.
3. Used in quantitative analysis of materials for isotope content determination
4. A rapid non-destructive method for analyzing protein content of oils and fats.

5. For determination of water in Liquid N_2O_4 and in heavy water.
6. Used in the structural diagnosis and study of Keto-enol tautomerism.
7. In the study of hydrogen bonding
8. In the study of reaction kinetics
9. In sample Purity determination.
10. For data acquisition in petroleum industry for exploration and recovery of petroleum and Natural gas.

Magnetic Resonance Imaging (MRI)

- Used in Radiology to visualize internal structure of the body in detail.
- Make use of the property of nuclear magnetic resonance to image the nuclei of atoms inside the body.
- Make use of the water present in the body tissues.

Working When the person is inside a powerful magnetic field of the scanner, average magnetic moment of protons becomes aligned with the direction of the field.

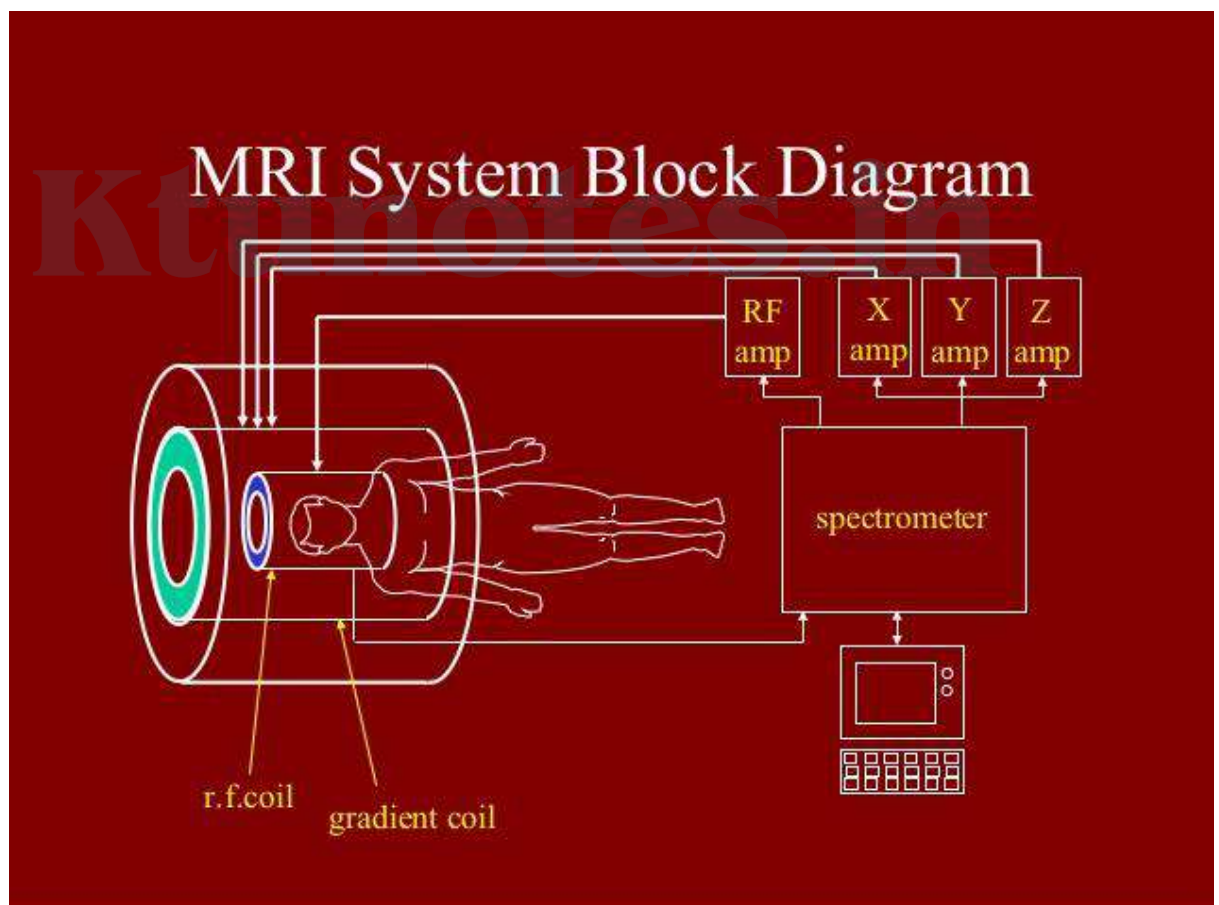
A radiofrequency current is briefly turned on, producing resonance frequency and the radio waves are absorbed and flip the spins of the protons. After the electromagnetic field is cut off, the spins of the protons reach thermodynamic equilibrium called **relaxation**. Due to this a radio signal is generated from the body, which is measured with a receiver coils and recorder.

Once the RF signal is removed, the nuclei realign themselves and return to equilibrium by emitting their own RF signal. This signal is called free-induction decay. Relaxation time for molecules to regain their natural

alignment vary depending on the type of tissues being scanned. This allows thw scan to detect different type of tissues.

Applications Of MRI

- 1 Diffusion MRI is useful for diagnosis of neurological disorder and also to understand central nervous system.
- 2 Used to measure the different metabolites.
- 3 To generate picture of arteries (Magnetic resonance angiography)
- 4 Functional MRI is used to measure signal changes in brain.



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<https://youtu.be/nFkBhUYynUw?t=2>

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