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SFI GEC PALAKKAD

MODULE II

SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

The study of interaction of electromagnetic radiation with matter is called spectroscopy.

Absorption laws

The absorption of light by molecules is governed by certain laws. They are collectively known as absorption laws. They are

1. Beer's law
2. Lambert's law
3. Beer – Lambert's law

Beer's law

When a monochromatic light is incident on a homogeneous medium, then the intensity of transmitted light decreases with increase in concentration of absorbing solution.

$$\text{Log } \frac{I_0}{I_t} \propto c$$
$$\text{Log } \frac{I_0}{I_t} = kc$$

Lambert's law

When a monochromatic light is incident on a homogeneous medium, then the intensity of transmitted light decreases with increase in thickness of the medium.

$$\log \frac{I_0}{I_t} \propto t$$
$$\log \frac{I_0}{I_t} = kt$$

Beer – Lambert's law

When a monochromatic light is incident on a homogeneous medium, then the intensity of transmitted light decreases with increase in concentration of absorbing solution as well as thickness of the medium.

$$\log \frac{I_0}{I_t} \propto ct$$
$$\log \frac{I_0}{I_t} = \epsilon ct$$

Where I_0 is intensity of incident radiation, I_t that of transmitted radiation, ϵ is the molar extinction (absorption) coefficient, c is the concentration and t is the thickness of the medium.

Absorbance (A)

It is the logarithm of ratio of intensity of incident radiation to that of transmitted radiation.

$$A = \log \frac{I_0}{I_t}$$

Transmittance (T)

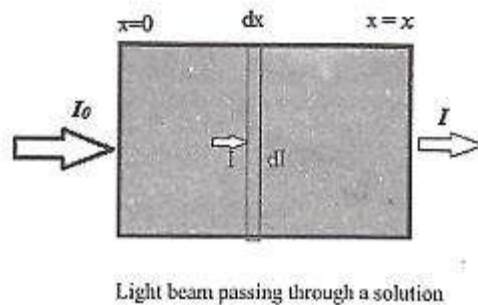
It is the ratio of intensity of transmitted radiation to that of incident radiation.

$$T = \frac{I_t}{I_0}$$
$$\log \frac{1}{T} = \epsilon ct$$
$$-\log T = \epsilon ct$$

Derivation of Beer – Lambert's law

When a mono-chromatic light is passed through the homogeneous medium of concentration (C), the rate of decrease in intensity of radiation (-dI) with thickness of the medium (dt) is proportional to the intensity of incident radiation (I) and also the concentration (C).

$$\frac{-dI}{dt} \propto IC$$
$$\frac{-dI}{I} = KCdt, \text{ where } K \text{ is the proportionality constant.}$$



Let I_0 be the intensity of incident radiation and I_t that of transmitted radiation passing through any finite thickness (t) of the medium, then

$$-\int_{I_0}^{I_t} \frac{dI}{I} = KC \int_0^t dt$$

$$-\ln \frac{I_t}{I_0} = KCt$$

$$\ln \frac{I_0}{I_t} = KCt$$

This is the integrated form of Beer-Lambert's law.

$$2.303 \log \frac{I_0}{I_t} = KCt \quad \log \frac{I_0}{I_t} = \frac{K}{2.303} Ct$$

$$A = \log \frac{I_0}{I_t} = \epsilon Ct$$

Where ϵ is the molar extinction (absorption) coefficient. It depends on the nature of medium and also the extent of absorption.

- The absorbance of a 0.01M dye solution in ethanol is 0.62 in a 2cm cell for light of wave length 5000 Å. If the path length of light through the sample is doubled and the concentration is made half, what will be the value of absorbance?

$$A = \epsilon ct$$

$$\frac{A_1}{A_2} = \frac{c_1 t_1}{c_2 t_2} = \frac{c_1 t_1}{\frac{c_1}{2} 2t_1} = 1, \text{ absorbance remains same}$$

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

$$A = \epsilon Ct, \text{ Here } \epsilon \text{ and } t \text{ are constants}$$

$$\frac{A_1}{A_2} = \frac{C_1}{C_2}$$

$$\frac{0.045}{0.022} = \frac{0.04}{C_2}$$

$$C_2 = 0.0195M$$

- The percentage transmittance of a 0.01m dye solution in ethanol is 20% in a 2cm cell for light of wave length 5000Å. Find the absorbance and molar absorption coefficient.

$$A = \log \frac{I_0}{I_t} = \epsilon Ct$$

$$A = \log \frac{100}{20} = 0.6989$$

$$\epsilon = \frac{A}{Ct} = \frac{0.6989}{0.01 \times 2} = 34.945 \text{ M}^{-1} \text{cm}^{-1}$$

- A 50ppm standard solution of Fe^{3+} after developing red colour with ammonium thio-cyanate shows a transmittance of 0.2 at 620nm. While an unknown solution of Fe^{3+} after developing colour with the same amount of ammonium thio-cyanate gives a transmittance of 0.4. Find the concentration of unknown Fe^{3+} solution.

$-\log T = \epsilon Ct$, where ϵ & t are constants.

$$\frac{\log T_1}{\log T_2} = \frac{C_1}{C_2}$$

$$\frac{\log 0.2}{\log 0.4} = \frac{50}{C_2}$$

$$C_2 = 28.4 \text{ ppm}$$

- A solution shows a transmittance of 20% when taken in a cell of 2.5 cm thickness. Calculate its concentration if molar absorption coefficient is $12000 \text{ dm}^2 \text{ mol}^{-1}$.

$$A = \log \frac{I_0}{I_t} = \epsilon ct = 0.6986$$

$$\log \frac{100}{20} = 12000 \times c \times 2.5$$

$$c = \frac{A}{\epsilon t} = \frac{0.6986}{12000 \times 0.25} = 2.3296 \times 10^{-4} \text{ mol dm}^{-3}$$

Fundamentals of spectroscopy

Interaction of electromagnetic radiations with matter produces spectrum. Spectrum can be explained in terms of energy levels present in the matter.

Interaction of electromagnetic radiations with atom produces atomic spectrum. Atomic spectrum can be explained in terms of energy levels present in the atom. When an electron jumps from one energy level to another energy level, energy can be emitted or absorbed. When the electron jumps from higher energy level E_2 to the lower energy level E_1 , the excess energy can be emitted in the form of radiation of definite frequency (ν).

$$\Delta E = E_2 - E_1$$

$$h\nu = E_2 - E_1$$

$$\nu = \frac{E_2 - E_1}{h}$$

where 'h' is the Plank's constant. The frequency of emitted radiation produces a bright line. Spectrum consists of bright lines produced by the emission of electromagnetic radiation by atoms is called atomic emission spectra or line spectra.

Types of spectrum

Based on the nature of interaction, the spectra can be broadly divided into absorption spectra and emission spectra.

Absorption Spectra

When an atom or molecule undergoes transition from lower energy level E_1 to the higher energy level E_2 , absorption of energy occurs in the form of radiation of definite frequency and the resultant spectrum is called absorption spectrum.

Emission Spectrum

When an atom or molecule undergoes transition from lower energy level E_1 to the higher energy level E_2 , absorption of energy occurs in the form of radiation of definite frequency and the resultant spectrum is called absorption spectrum.

Based on the nature of the interacting species, the spectra can be divided into two categories, atomic spectra and molecular spectra.

Atomic Spectra

Interaction of electromagnetic radiations with atoms produces transition of electrons between the atomic energy levels and the resultant spectrum is called atomic spectra.

Molecular Spectra

Interaction of electromagnetic radiations with molecules produces transition of electrons between the molecular energy levels and the resultant spectrum is called molecular spectra.

Electromagnetic radiations

Radiations having electric and magnetic field associated with them are called electromagnetic radiations. They are radio waves, micro waves, IR (far IR, middle IR, near IR), visible light, UV light (ordinary UV, vacuum UV), X- rays, γ – rays and cosmic rays. They are arranged in the increasing order of their frequency or the decreasing order of wave length. This is known as **electromagnetic spectrum**. They do not require any medium for their propagation. They possess wave like characteristics.

Characteristics of electromagnetic radiations

1. Wave length (λ)

It is the distance between two adjacent crests or two adjacent trough of a wave. Unit is nanometer and \AA .

$$1\text{nm} = 10^{-9}\text{ meter}$$

$$1\text{\AA} = 10^{-10}\text{ meter}$$

2. Frequency (ν)

Number of waves which pass through a given point in 1 second is called frequency. Its unit is Hertz or Cycles per Second (CPU).

$$1\text{ Hertz} = 1\text{ Cycles per Second (CPU)}$$

3. Velocity (v or c)

Distance travelled by a wave in 1 second is called velocity. Its unit is m/S. Velocity of all electromagnetic radiations in space is constant and is $3 \times 10^8 \text{ ms}^{-1}$

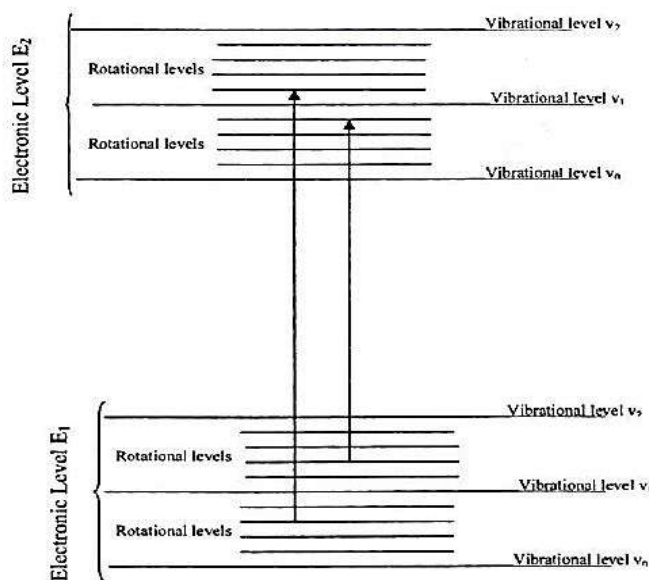
4. Wave number ($\bar{\nu}$)

It is the reciprocal of wave length. Its unit is cm^{-1} or m^{-1} .

$$\bar{\nu} = 1/\lambda$$

Molecular spectra

Interactions of electromagnetic radiation with molecules produce molecular spectra. In a molecule three types of energy levels are present. They are rotational, vibrational & electronic energy levels. The transition between these energy levels results in the emission or absorption of energy in the form of radiation of definite frequency. Generally large numbers of such transitions are possible.



Within the same electronic energy level, there are large numbers of vibrational energy levels and within the same vibrational energy level, there are large number of rotational energy levels. The electronic, vibrational and rotational energy levels are represented by n, v, j .

Total energy of a molecule = $E_{\text{ele}} + E_{\text{vib}} + E_{\text{rot}}$

When a molecule emit or absorb radiation, it may results in the electronic vibrational and rotational energy changes. All these changes are quantized and give rise to three types of molecular spectra. They are rotational spectra, vibrational spectra and electronic spectra.

The energy involved in these transitions is in the following order.

$$E_{\text{ele}} - E_{\text{ele}}^1 > E_{\text{vib}} - E_{\text{vib}}^1 > E_{\text{rot}} - E_{\text{rot}}^1$$

Because of the change in energy level between the rotational, vibrational and electronic energy levels, molecular spectrum is obtained at three different regions of the electronic spectra.

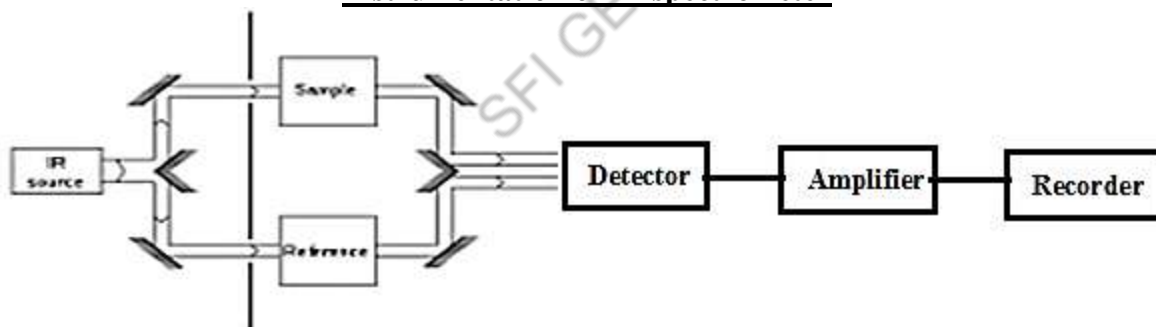
Vibrational Spectra (IR Spectra)

IR spectroscopy is concerned with the study of absorption of IR radiation (800nm-1mm), which causes vibrational transition in the molecule. When a gaseous molecule absorbs IR radiation, it produces transition between the vibrational energy levels. Resultant spectrum is called vibrational spectra.

The essential requirement for a molecule to produce IR spectrum is that **the dipole moment of the molecule must change during vibration**. Thus vibrational spectrum is given by hetero nuclear diatomic molecules. Polyatomic molecules with and without dipole moment also produces IR spectrum. Homo nuclear diatomic molecules such as O_2 , N_2 , H_2 etc. will not produce IR spectrum, since they have zero dipole moment. But molecules like HCl , HBr , NO_2 , H_2O , CO_2 , NH_3 , CH_3Cl and SO_2 can produce IR spectra and they are IR active molecules. In the case of polyatomic molecules without dipole moment, the exciting radiations can induce an oscillating dipole moment. Hence they are also IR active.

When a gaseous molecule having dipole moment vibrates, it generates an electric field which can interact with electrical component of IR radiation. During this interaction energy can be emitted or absorbed in the form of radiation of definite frequency. Thus the vibration of the molecule produces IR spectrum.

Instrumentation of IR spectrometer



Theory of IR spectra

In order to explain the theory of IR spectra, consider the vibration of hetero nuclear diatomic molecule. It is similar to the vibration of a simple harmonic oscillator.

Vibrational energy of simple harmonic oscillator = Vibrational energy of diatomic molecule

$$E_{\text{vib}} = (v + \frac{1}{2}) h\omega$$

Fundamental frequency of vibration, $\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, where 'k' is the force constant and it gives an idea about the strength of the bond.

$$\text{Reduced mass } (\mu) = \frac{m_1 m_2}{m_1 + m_2}$$

When the molecule is in the vibrational ground level ($v = 0$), $E_{\text{vib}} = \frac{1}{2} h\omega$. This is the lowest vibrational energy level and it is called **zero point energy**.

Let us consider the vibrational transition from lowest vibrational (v^1) to the next higher vibrational energy level (v).

$$\begin{aligned}\text{Energy change during vibrational transition } (\Delta E_{\text{vib}}) &= E_v - E_{v1} \\ &= (v + 1/2) h\omega - (v^1 + 1/2) h\omega \\ &= (v - v^1) h\omega = \Delta v h\omega\end{aligned}$$

The selection rule for vibrational spectrum is

$$\Delta v = \pm 1$$

$$\Delta E_{\text{vib}} = h\omega$$

Spectrum can be explained in terms of wave number.

$$\text{Thus the wave number of absorbed line } (\bar{\nu}) = \frac{\Delta E_{\text{vib}}}{ch} = \frac{h\omega}{ch} = \frac{\omega}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

According to **Hooke's law**,

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$K = 4\pi^2 c^2 \bar{\nu}^2 \mu$$

Thus the frequency or wave number of absorbed line depends on

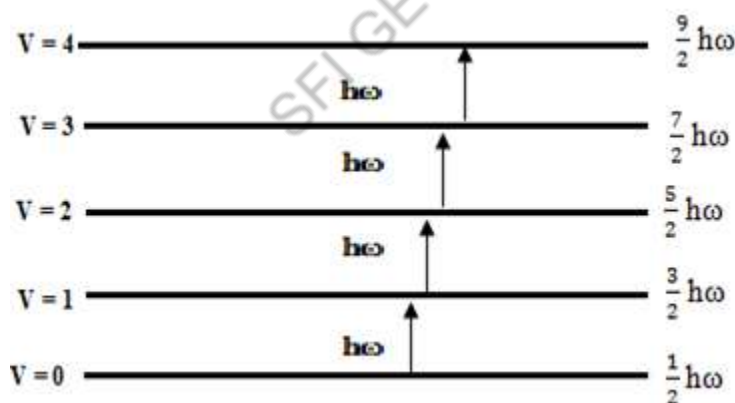
- Force constant(k)
- Reduced mass(μ)

Stretching frequency for $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, $\text{C}-\text{C}$ bond are in the following order etc.

$$\text{C}\equiv\text{C} > \text{C}=\text{C} > \text{C}-\text{C}$$

Since the force constant for each type of bond follows the order.

$$k_{\text{C}\equiv\text{C}} > k_{\text{C}=\text{C}} > k_{\text{C}-\text{C}}$$



Different vibrational transitions are possible between the vibrational energy levels, but all the vibrational energy levels are equally spaced with a spacing of ' $h\omega$ '. So all the lines in the spectrum would fall in the same region. **Hence vibrational spectrum is expected to consist of a single line.**

At ordinary conditions of temperature and pressure, most of the molecules are in the vibrational ground level ($V = 0$). So only one transition is possible according to the selection rule, i.e. $0 \rightarrow 1$ transition and the resultant lines are called **fundamental lines** and are **highly intense lines**. But in actual practice molecular vibrations are **not harmonic**. Such an oscillator is called **anharmonic oscillator**. For an anharmonic oscillator ΔV is rarely unity. Sometimes it is +2 and sometimes it is +3. If $\Delta V = +2$, then the most probable transition is **$0 \rightarrow 2$ transition** and the resultant lines are called **first overtones**. They have lesser intensity than the fundamental

lines. If $\Delta V = +3$, then the most probable transition is **0 → 3 transition** and the resultant lines are called **second overtones**. They have least intensity.

- Calculate the force constant of HCl molecule, if it gives IR absorption at 3050cm^{-1} . (Given that atomic masses of H = 1 amu and Cl = 35 amu)

$$\bar{\nu} = 3050\text{cm}^{-1} = 3050 \times 100 \text{ m}^{-1}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \times 1\text{u} = \frac{1 \times 35}{1 + 35} \times 1.67 \times 10^{-27} \text{ kg} = 1.63 \times 10^{-27} \text{ Kg.}$$

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu = 4\pi^2 \times (3 \times 10^8)^2 (3050 \times 100 \text{ m}^{-1})^2 \times 1.63 \times 10^{-27} \text{ kg} \\ = 532.8 \text{ Nm}^{-1}$$

- CO molecule absorbs at 2140cm^{-1} . Calculate the force constant of the molecule. Given atomic masses of C & O are 12u and 16u respectively. ($1\text{u} = 1.67 \times 10^{-27}\text{kg}$).

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \times 1\text{U} = \frac{12 \times 16}{12 + 16} \times 1.67 \times 10^{-27} \text{ kg}$$

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

$$k = 1853 \text{ Nm}^{-1}$$

- The vibrational frequency of HCl molecule is 2886cm^{-1} . Calculate the force constant of the molecule. Reduced mass of HCl is $1.63 \times 10^{-27} \text{ Kg}$.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu = 4\pi^2 \times (3 \times 10^8)^2 (2886 \times 100)^2 \times 1.63 \times 10^{-27} \text{ Kg.}$$

$$k = 481.8 \text{ Nm}^{-1}$$

- The fundamental vibrational frequency of $^{12}\text{C}^{16}\text{O}$ is 2140 cm^{-1} . Without calculating force constant, find the fundamental frequency of $^{13}\text{C}^{17}\text{O}$ in cm^{-1} .

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

$$\mu^{^{12}\text{C}^{16}\text{O}} = \frac{12 \times 16}{12 + 16} \times 1.67 \times 10^{-27} = 1.145 \times 10^{-26} \text{ kg}$$

$$\mu^{^{13}\text{C}^{17}\text{O}} = \frac{13 \times 17}{13 + 17} \times 1.67 \times 10^{-27} = 1.23 \times 10^{-26} \text{ kg}$$

$$\frac{\bar{\nu}^{^{13}\text{C}^{17}\text{O}}}{\bar{\nu}^{^{12}\text{C}^{16}\text{O}}} = \sqrt{\frac{\mu^{^{12}\text{C}^{16}\text{O}}}{\mu^{^{13}\text{C}^{17}\text{O}}}}$$

$$\bar{\nu}^{^{13}\text{C}^{17}\text{O}} = \bar{\nu}^{^{12}\text{C}^{16}\text{O}} \times \sqrt{\frac{\mu^{^{12}\text{C}^{16}\text{O}}}{\mu^{^{13}\text{C}^{17}\text{O}}}}$$

$$\bar{\nu}^{^{13}\text{C}^{17}\text{O}} = 2140 \times \sqrt{\frac{1.145 \times 10^{-26}}{1.23 \times 10^{-26}}} = 2065 \text{ cm}^{-1}$$

- Calculate the force constant of HF molecule, if it shows IR absorption at 4138 cm^{-1} . Given that atomic masses of hydrogen and fluorine are 1u and 19u respectively. What would be the wave number if hydrogen atoms are replaced by deuterium atoms?

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

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \times 1\text{U} = \frac{1 \times 19}{1 + 19} \times 1.66 \times 10^{-27} \text{ kg} = 1.577 \times 10^{-27} \text{ kg}$$

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu = 4\pi^2 \times (3 \times 10^8)^2 (4138 \times 100)^2 \times 1.577 \times 10^{-27} \text{ Kg} = 958.3 \text{ Nm}^{-1}$$

When deuterium is substituted for hydrogen, k remains constant.

$$\bar{\nu}^2 \propto 1/\mu$$

$$\frac{\bar{\nu}_1^2}{\bar{\nu}_2^2} = \frac{\mu_2}{\mu_1}$$

$$\frac{4138^2}{\bar{\nu}_2^2} = \frac{\frac{2 \times 19}{2+19}}{\frac{1 \times 19}{1+19}}$$

$$\bar{\nu}_2 = 2998 \text{ cm}^{-1}$$

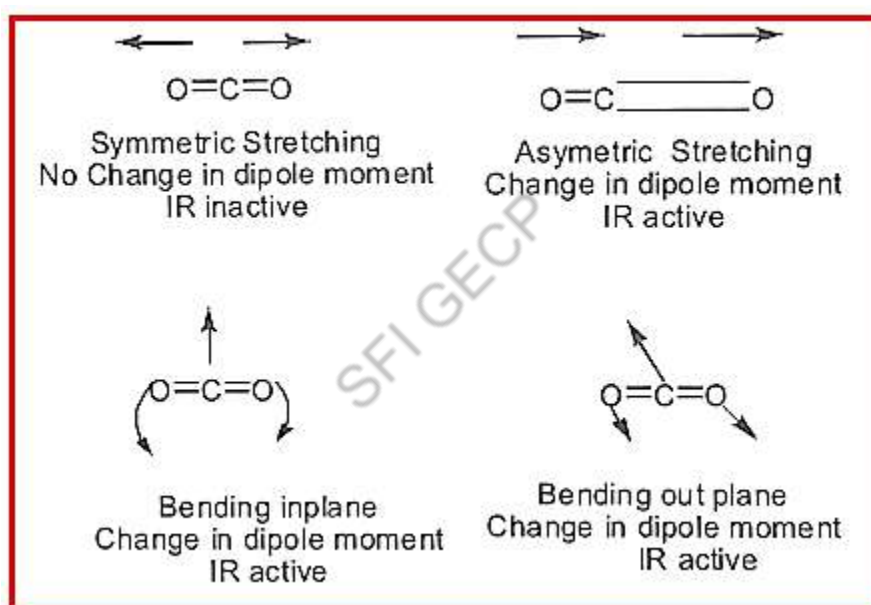
IR Spectrum of polyatomic molecules

In the case of polyatomic molecules, IR spectrum depends on the number of vibrational modes. But the number of vibrational modes depends upon the structure.

For linear molecules (CO_2), number of vibrational modes = $3n-5$ and for non-linear molecules (H_2O , SO_2), number of vibrational modes = $3n-6$.

CO_2 has four vibrational modes symmetric stretching, asymmetric stretching and two bending vibrations in two mutually perpendicular planes. Out of the four vibrational modes only three are IR active. The symmetric stretching does not involve the change of di-pole moment and is not IR active.

For CO_2 , which is a linear molecule, there are $3(3) - 5 = 4$ fundamental vibrations:

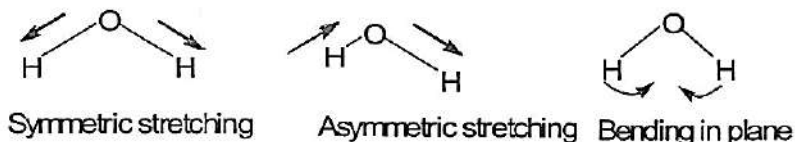


Asymmetric stretching and bending modes of vibration of $\text{O}=\text{C}=\text{O}$ molecule results in the variations of dipole moment. Hence these vibrational modes are IR active.

H_2O is a non-linear molecule.

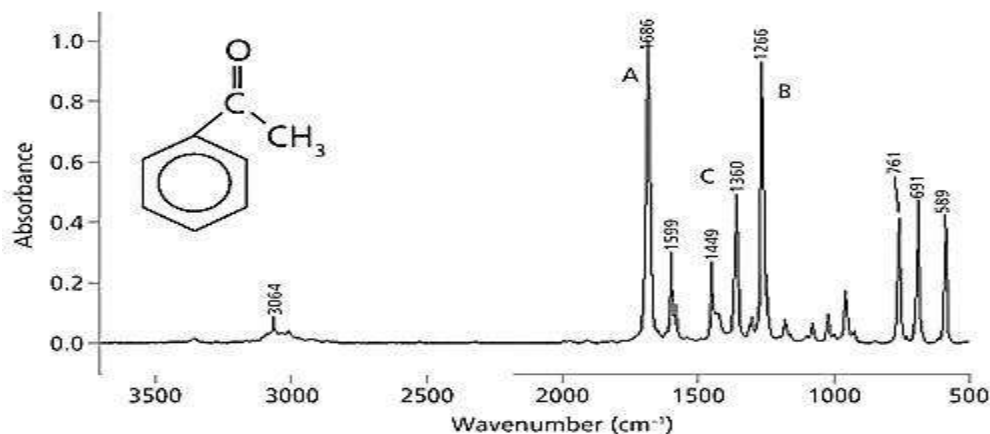
So number of vibrational modes = $3n - 6 = 3 \times 3 - 6 = 3$.

They are symmetric stretching, asymmetric stretching and bending in plane vibrational modes. In all these cases there is a change in dipole moment. So all are IR active.



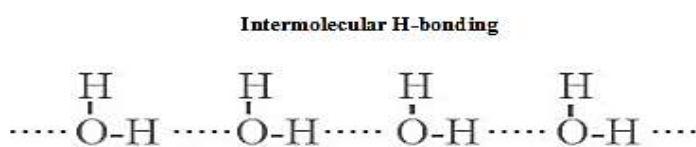
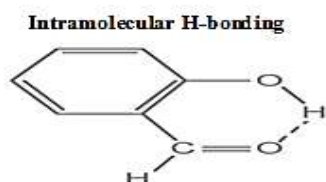
Features of IR spectrum

In order to explain the features of IR spectrum, let us consider the IR spectrum of acetophenone. Spectrum can be divided into two regions. First region lies in between $1600 - 4000 \text{ cm}^{-1}$. This region is called functional group region, since the vibrational modes of most of the functional groups occur in this region. A few broad bands in the functional group region show the presence of a functional group. Second region lies between $600 - 1600 \text{ cm}^{-1}$. A few broad bands in this region show the presence of an aliphatic group. Large numbers of sharp bands in this region show the presence of an aromatic group. Hence this region provides the confirmation of identity and this region is called finger print region.



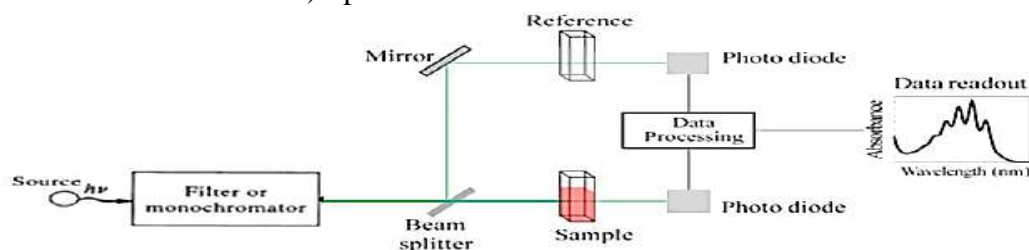
Applications of IR spectroscopy:

- The identity of unknown substance can be explained by considering the IR spectrum of unknown substance with that of a known substance.
- This will give valuable information about molecular symmetry and force constant.
- This can be used to detect the presence of impurities, since the impurities give rise to extra absorption bands.
- This can be used to distinguish intra molecular H-bonding & inter molecular H-bonding. This can be done by taking the IR spectrum at different dilutions. As the dilution increases intensity of absorption band diminishes when it is due to inter molecular H-bonding and as the dilution increases intensity of absorption band remains unchanged when it is due to intra molecular H- bonding.



Electronic (UV –Visible) Spectroscopy

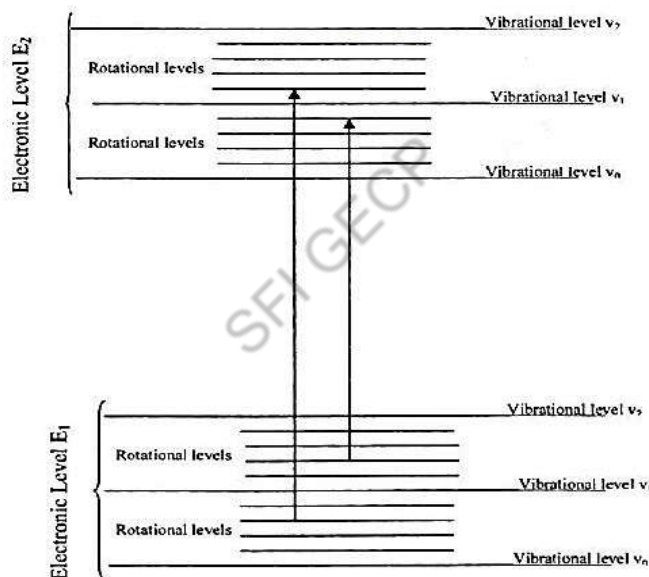
Instrumentation of UV –Visible) Spectrometer



Electronic spectrum of a molecule

Electronic spectrum of molecule arises due to the transition between electronic energy levels. Electronic transitions are highly energetic transitions. Hence it produces spectrum in the UV – Visible region.

In a molecule three types of energy levels are present. They are rotational, vibrational & electronic energy levels. Within the same electronic energy level, there are large numbers of vibrational energy levels and within the same vibrational energy level, there are large number of rotational energy levels. So electronic transitions are always followed by simultaneous vibrational and rotational transitions. Hence we get a broad spectrum consisting of lines for electronic, vibrational and rotational transitions.



Suppose $E^1_{(ele)}$, $E^1_{(vib)}$, $E^1_{(rot)}$ be the electronic, vibrational and rotational energy of the molecule before transition and $E_{(ele)}$, $E_{(vib)}$, $E_{(rot)}$ be the electronic, vibrational and rotational energy of the molecule after transition.

Total energy of the molecule before transition (E^1) = $E^1_{(ele)} + E^1_{(vib)} + E^1_{(rot)}$

Total energy of the molecule after transition (E) = $E_{(ele)} + E_{(vib)} + E_{(rot)}$

Change in energy during transition (ΔE) = ($E - E^1$)

$$= (E_{(ele)} + E_{(vib)} + E_{(rot)}) - (E^1_{(ele)} + E^1_{(vib)} + E^1_{(rot)})$$

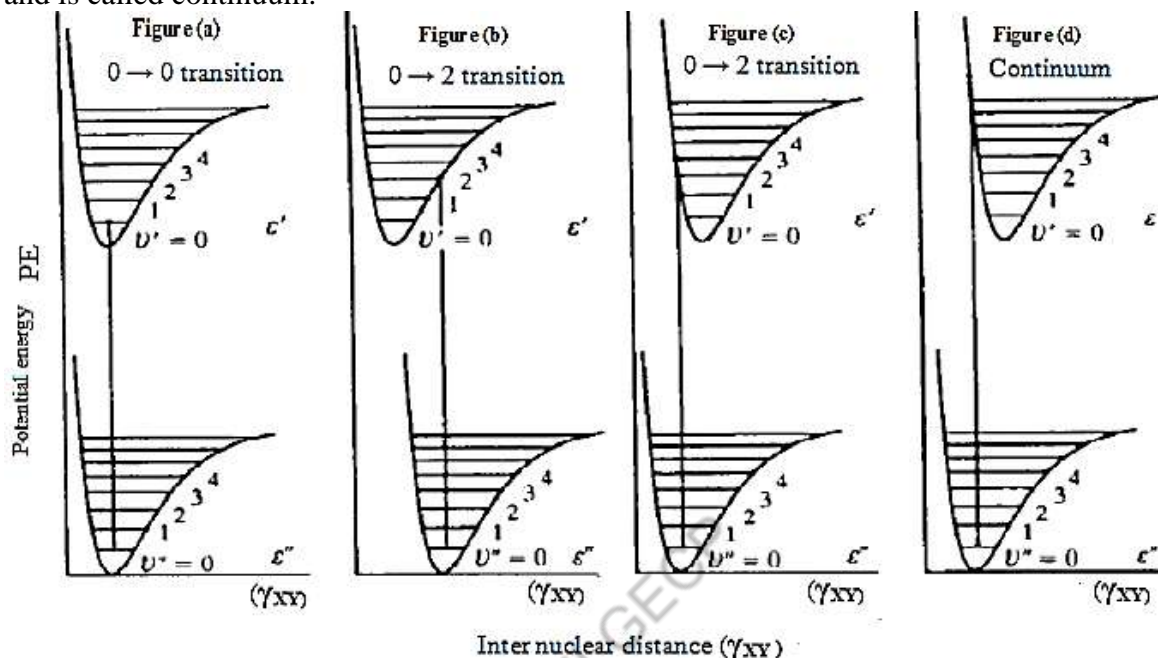
Principle of electronic spectroscopy

In order to explain the principle of electronic spectra, let us consider the Frank Condon principle. According to Frank Condon principle, during an electronic transition internuclear distance remains constant. Since the electrons move much more rapidly than the nucleus.

The figure shows the potential energy versus inter nuclear distance curve of ground state and first excited state of the diatomic molecule XY. Quantum mechanically molecule is at the

center of the ground vibrational level of ground electronic state. Electronic transitions are always represented by a vertical line.

In **figure (a)**, upper and lower inter nuclear distance is same. According to Frank Condon principle, most probable transition is $0 \rightarrow 0$ transitions. In **figure (b)**, upper state inter nuclear distance is slightly lesser than the lower state. According to Frank Condon principle, most probable transition is $0 \rightarrow 2$ transitions. In **figure (c)**, upper state inter nuclear distance is slightly greater than the lower state. According to Frank Condon principle, most probable transition is $0 \rightarrow 2$ transitions. In **figure (d)**, upper state inter nuclear distance is considerably greater than the lower state. Here there is no specific electronic transition; instead we get some dark faded lines and is called continuum.



Fundamentals of electronic spectroscopy Chromophore

Any isolated covalently bonded group that shows characteristic absorption in the UV Visible region irrespective of the fact that whether colour is produced or not.

Eg: $>C=C<$, $-C \equiv C-$, $-N \equiv N-$ etc.

Types of chromophores $\sigma - \sigma^*$, $\pi - \pi^*$, $n - \pi^*$ & $n - \sigma^*$

Chromophores are of two types

1. Chromophores containing π bond undergoes $\pi - \pi^*$ transition

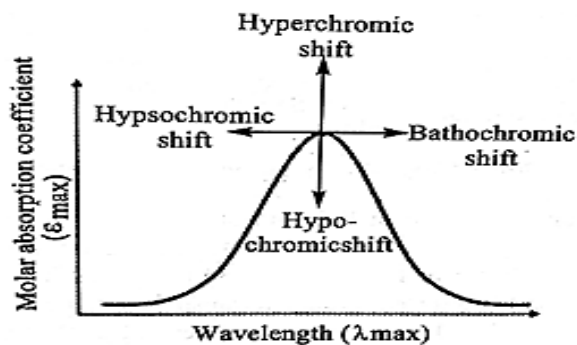
Eg. Ethylene, acetylene etc.

2. Chromophores containing both π and n electrons undergoes $\pi - \pi^*$, $n - \pi^*$ transitions.

Eg. CH_3-CH_2-CHO

Auxochromes

These are substituent on the Chromophore which leads to red shift. eg. NH_2^- , SH^- , OH^- etc.



Bathochromic shift (Red shift)

Shift of absorption band towards longer wavelength region (red region) is called Bathochromic shift. Reason for red shift is the presence of auxochrome and change in solvent.

Hypsochromic shift (Blue shift)

Shift of absorption band towards shorter wavelength region (blue region) is called Hypsochromic shift. Reason for blue shift is the presence of removal of conjugation and change in polarity of solvent.

Hyper chromic shift

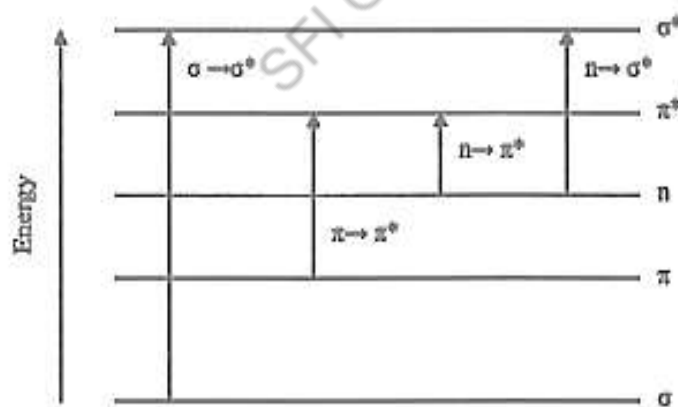
Shift in which there is an increase in intensity of absorption band is called hyper chromic shift.

Hypo chromic shift

Shift in which there is an decrease in intensity of absorption band is called hypo chromic shift.

Electronic spectrum of polyatomic molecules

In the case of polyatomic molecules, electronic transitions give rise to absorption spectra in the UV-Visible region. From the investigations of UV-Visible spectra we get information about various energy levels in the molecule depending on the energy of the molecular orbitals. The electronic transitions are $\sigma - \sigma^*$, $\pi - \pi^*$, $n - \pi^*$ & $n - \sigma^*$ respectively.



Electronic transitions in molecules

1) $\sigma - \sigma^*$ transitions

The energy required for this transition is very high. Since the σ electrons are held more strongly in the molecule and are highly energetic. Hence the absorption band occurs in far UV region. All saturated hydrocarbons will undergo this transition. These types of transitions occur only below 150nm. **The ordinary UV spectrometers can take spectra only from 200 – 780nm. Hence saturated hydrocarbons cannot be detected using UV-Visible spectra.**

2) $\pi - \pi^*$ transition

Unsaturated hydrocarbons containing π bonds can produce this type of transition. But $C=C$ of $CH_2=CH_2$ molecule gives absorption maxima at 169nm. So it cannot be detected using ordinary UV spectrometer. But in compounds containing conjugated double bonds, due to the presence of conjugated double bonds absorption occurs in visible region. In such molecules $\pi - \pi^*$ transition produces absorption bands in the UV-Visible region.

(eg. Butadiene, absorption occurs at 217nm). Due to this transition high intensity absorption bands are produced in the near UV region. Benzene also produces these transitions, due to the presence of three conjugated double bonds. In the case of lycopene red coloured of tomato, there are eleven double bonds in conjugation, its λ_{max} is 505 nm. For every double bond in conjugation, there is an increment of 30 nm.

3) $n - \pi^*$ transition

Unsaturated compounds containing atoms such as O, N, S, X etc, containing lone pair of electrons produces absorption band due to $n - \pi^*$ transition and the absorption bands are observed in the visible region. (eg., aldehydes and ketones containing $C=O$ and $C \equiv C$ bonds)

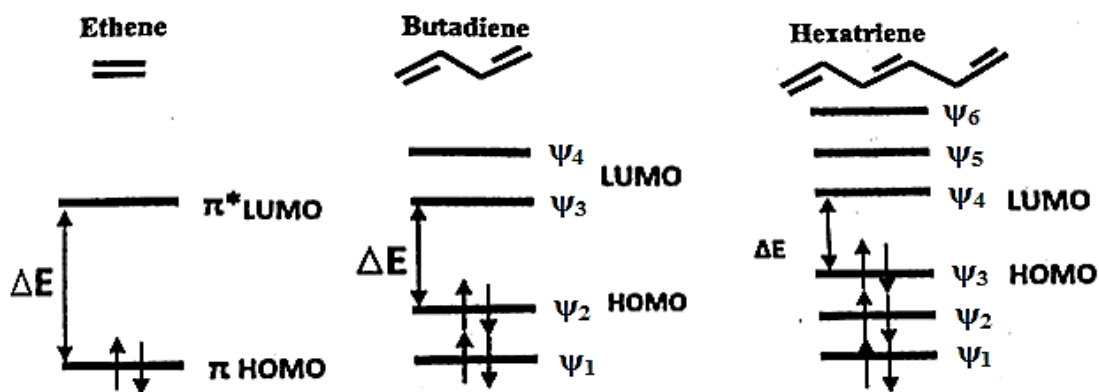
4) $n - \sigma^*$ transition

Saturated compounds containing atoms such as O, N, S, X etc, containing lone pair of electrons produces absorption band due to $n - \sigma^*$ transition and the absorption bands are observed in the near UV region. Generally absorption takes place below 200nm. (eg., CH_3OH , CH_3NH_2 & $(CH_3)_2NH$ etc.)

UV- VIS energy level diagram of conjugated systems

The energy levels of π molecular orbitals of conjugated systems can be obtained from Huckel's molecular orbital theory. In such molecules, the ground state electrons occupy the low energy Huckel molecular orbital in spin paired state. Out of the occupied orbitals, the one with higher energy is termed as HOMO (highest occupied molecular orbital). Similarly, out of the unoccupied orbitals, the one with lower energy is termed as LUMO (lowest unoccupied molecular orbital). If the molecule absorbs electromagnetic radiation in the UV – VIS region, electrons get promoted from HOMO to LUMO and the wavelength of absorption depends upon HOMO-LUMO energy gap.

UV- VIS energy level diagram of ethylene, butadiene and hexatriene

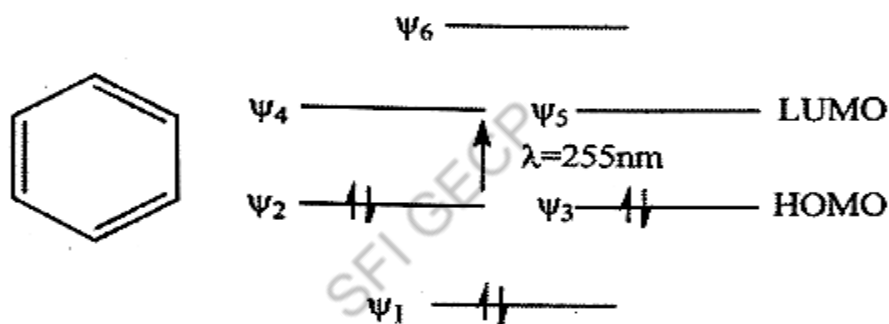


Note that the energy gap ΔE (HOMO-LUMO gap) decreases (becomes smaller) as the number of conjugated pi orbitals increases

Ethylene contains a simple isolated C=C bond, but the other two have conjugated double bonds. In the case of ethylene, there is one π bonding molecular orbital and one π^* antibonding molecular orbital. So $\pi \rightarrow \pi^*$ transition occurs and ethylene gives an absorption maxima at 169 nm. In 1, 3-butadiene, there are two double bonds in conjugation. So it has four π molecular orbitals ($\psi_1, \psi_2, \psi_3, \psi_4$) formed by the linear combination of four atomic orbitals (p orbitals). Here ψ_1 & ψ_2 are the bonding π molecular orbitals and ψ_3 & ψ_4 are the antibonding π^* molecular orbitals. In the ground state the four π electrons occupy bonding molecular orbitals. Here the transition takes place from HOMO (ψ_2) to LUMO (ψ_3) and absorption occurs at 217nm. In 1, 3, 5-hexatriene, there are three double bonds in conjugation. So it has six π molecular orbitals ($\psi_1, \psi_2, \psi_3, \psi_4, \psi_5, \psi_6$) formed by the linear combination of six atomic orbitals (p orbitals). In the ground state the six π electrons occupy bonding molecular orbitals. Here the transition takes place from HOMO (ψ_3) to LUMO (ψ_4) and absorption occurs at 247nm.

UV- VIS energy level diagram of benzene

In benzene, there are three double bonds in conjugation. So it has six π molecular orbitals ($\psi_1, \psi_2, \psi_3, \psi_4, \psi_5, \psi_6$) formed by the linear combination of six atomic orbitals (p orbitals). In the ground state the six π electrons occupy bonding molecular orbitals. Here the transition takes place from HOMO to LUMO and absorption occurs at 255nm. Here ψ_2, ψ_3 are degenerate orbitals and ψ_4, ψ_5 are also degenerate orbitals



Applications of UV – Visible spectroscopy

- In medical lab test for determining cholesterol and blood sugar.
 - For the characterization of dyes and colourants
 - For the detection of aromatic compounds
 - Detection of impurities. (Benzene is present as an impurity in cyclohexane can be detected)
- Write three points of comparison between UV & IR spectrum.

UV-VIS spectroscopy	IR-spectroscopy
Electronic spectrum is due to the electronic transitions in atoms and molecules.	Vibrational spectrum is due to the vibrational motions of atoms and molecules.
It arises by the interaction of EMR with matter	It arises by the interaction of EMR with matter.
EMR in the UV-Vis region is responsible for electronic spectrum	EMR in the IR region is responsible for electronic spectrum

All molecules gives this spectrum	Molecules with a permanent and fluctuating dipole moment give this spectrum.
Examples are organic, inorganic and coordination compounds.	Examples HCl, HBr, HF, H ₂ O, CO ₂ , NH ₃ , CO, CH ₃ Cl

NMR (Nuclear Magnetic Resonance) Spectra

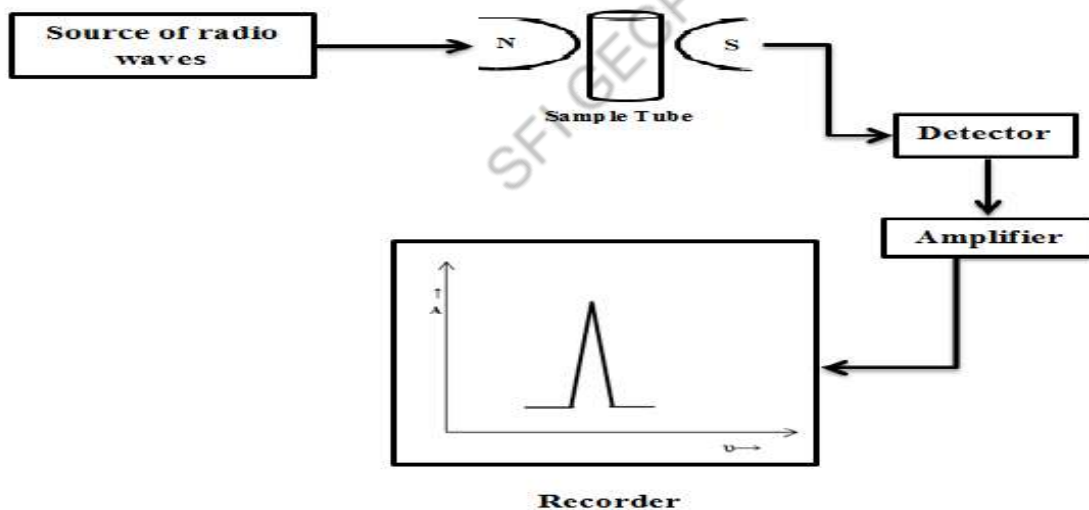
NMR spectrum is obtained by the interaction of radio waves on the nuclei of molecules. In the absence of magnetic field, spin states of nuclei are degenerate, ie, they possess same energy. Hence no transition is possible. When the nucleus is placed in a magnetic field, the spin states lost its degeneracy and are splitted into magnetic energy levels. Then the interaction of radio waves can produce transition between the magnetic energy levels.

Nucleus with net spin ($I = 0$) will not produce NMR spectra and are NMR inactive.

Rules for determining net spin (I)

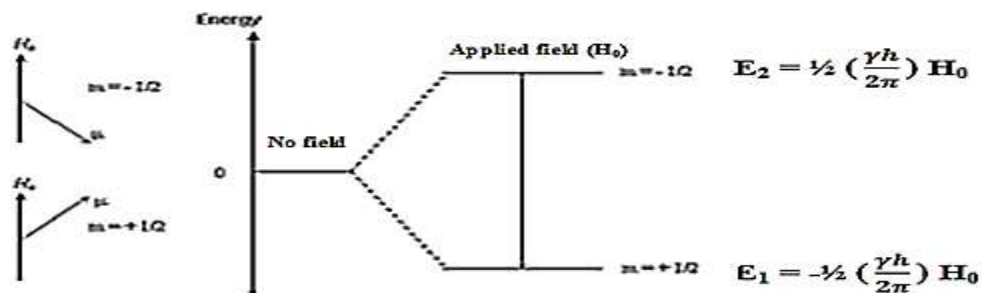
- If the number of protons & number of neutrons, both are even, then $I = \text{Zero}$. (${}^{12}_6\text{C}$, ${}^{16}_8\text{O}$)
- If the number of protons & number of neutrons, both are odd, then I is an integer such as 1, 2, 3 etc. (${}^{14}_7\text{N}$, ${}^2_1\text{H}$)
- If the sum of the number of protons and number of neutrons is an odd number, then I has half integral values such as $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, etc. (${}^1_1\text{H}$, ${}^{13}_6\text{C}$, ${}^{19}_9\text{F}$, ${}^{31}_{15}\text{P}$ etc, $I = \frac{1}{2}$)

Instrumentation of NMR spectrometer



According to quantum mechanics, a nucleus with net spin (I) has $(2I+1)$ orientations are possible. In the absence of magnetic field, these orientations are of equal energy. But if a magnetic field is applied, these orientations are splitted into energy levels. Each energy level is characterized by its own specific magnetic quantum number (m)

Nucleus with net spin only produce NMR spectrum, eg; H^1 (two orientations are possible. But in the absence of magnetic field, these two orientations have equal energy. In the presence of magnetic field, energy levels split into two. Each one is having its own specific magnetic quantum number.



The energies E_1 & E_2 corresponds to the two states $m = +1/2$ and $m = -1/2$

$E_1 = -1/2 \left(\frac{\gamma h}{2\pi} \right) H_0$ and $E_2 = 1/2 \left(\frac{\gamma h}{2\pi} \right) H_0$, where H_0 is the applied field strength, γ is the gyro magnetic constant.

When the nucleus absorbs energy it get promoted from lower energy level E_1 to the next higher energy level E_2 , then the change in energy (ΔE)

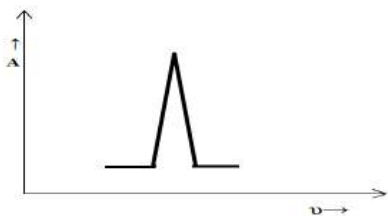
$$\Delta E = E_2 - E_1 = 1/2 \left(\frac{\gamma h}{2\pi} \right) H_0 - \left\{ -1/2 \left(\frac{\gamma h}{2\pi} \right) H_0 \right\} = \left(\frac{\gamma h}{2\pi} \right) H_0 = h\nu$$

$$\nu = \left(\frac{\gamma}{2\pi} \right) H_0 \quad \text{or} \quad \nu \propto H_0$$

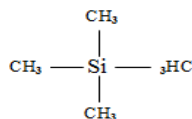
$$\nu \propto H_0$$

Thus frequency emitted or absorbed by the nucleus in moving from one energy level to another is directly proportional to the applied field strength.

When the nucleus having net spin is placed in a magnetic field (H_0), then the nucleus absorbs energy get excited. Thereafter it loses energy and returns to the ground state. Again it absorbs energy get excited and then returns to the ground state. This process continuous. This state of the nucleus is called resonance. This motion of the nucleus is just like a spinning top. This motion of the nucleus is called precessional motion and the frequency required for the nucleus to perform precessional motion is called precessional frequency (resonance frequency) (larmor frequency) . As the field strength increases, precessional frequency increases and this causes transition between the magnetic energy levels and the energy absorbed in this process produces a signal at the detector which is amplified and recorded as a band in the NMR spectrum. NMR spectrum is obtained by plotting absorbance against frequency.



It is not possible to find out the absolute value of resonance frequency. To solve this problem, resonance frequency of nucleus in a sample is measured relative to that of a reference compound. Usually used reference compound is TMS (Tetra methyl silane).



TMS is the most ideal reference compound in NMR because of its characteristics.

- All the 12 protons in the TMS are equivalent. Hence it produces a single absorption line.
- It is chemically inert.

iii) It is soluble in most of the organic solvents.

iv) It is highly volatile and can be easily removed from the system

In the NMR spectra, we get a reference peak corresponding to TMS. The position of peaks in the NMR spectra is measured relative to that of reference compound and is expressed in terms of chemical shift (δ)

Shift in position of NMR signals due to shielding and de-shielding of protons by the circulation of electrons is called **chemical shift**.

Chemical shift can be calculated by the expression,

$$\text{Chemical shift, } \delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\nu_0} \times 10^6 \text{ ppm}$$

ν_0 – operating frequency

ν_{sample} – frequency of sample

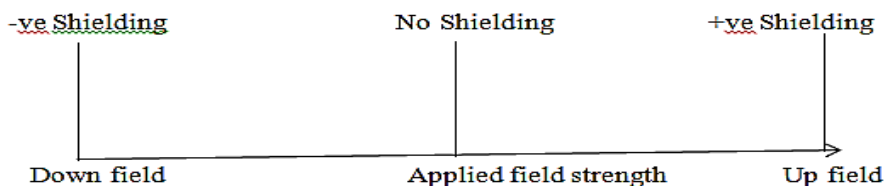
ν_{TMS} – frequency of reference (TMS)

Generally chemical shift value is in between 0 and 10 ppm. There are two scales are used for the measurement of chemical shift. They are δ - scale & τ - scale. These two scales are related to each other by the expression,

$$\tau = 10 - \delta$$

In τ – scale, signal for TMS is obtained at 10ppm. But in δ – scale, TMS signal is obtained at 0 ppm.

When a molecule is placed in a magnetic field, the electrons are forced to circulate about its own protons or nearby protons and this circulation produce an induced magnetic field. The rotation of electrons about its own protons produces an induced magnetic field, which opposes the applied field. Thus the field felt by the proton is diminished and the proton is said to be shielded. Shielding shift the absorption upfield. If the protons are rotated about nearby protons, then the induced magnetic field either opposes or reinforces the applied field. If the induced magnetic field opposes the applied field, proton is said to be shielded. If the induced magnetic field reinforces the applied field, then the proton feels higher field strength and the proton is said to be de-shielded. De-shielding shifts the absorption downfield. Chemical shift for different kinds of protons are measured relative to that of the reference peak (TMS signal). The NMR signals for different types of protons in a molecule appear at different field strengths with respect to TMS signal. This difference in absorption position of protons with respect to TMS signal is called chemical shift.



- Calculate the frequency of operation of NMR instrument, if particular proton of δ value 4.2 shows a difference in frequency 1260 Hz from the TMS.

$$\text{Chemical shift, } \delta = \frac{\nu_{\text{Sample}} - \nu_{\text{TMS}}}{\nu_{\text{Instrument}}} \times 10^6$$

$$4.2 = \frac{1260}{\nu_0} \times 10^6$$

$$\nu_0 = \frac{1260}{4.2} \times 10^6$$

$$= 300 \times 10^6 \text{ Hz} = 300 \text{ MHz}$$

- CHCl_3 protons show a shift in frequency of 728 Hz from TMS signal in a 100 MHz NMR instrument. How much would be the shift in frequency for the same proton from TMS in a 300 MHz NMR instrument?

$$\text{Chemical shift, } \delta = \frac{\nu_{\text{Sample}} - \nu_{\text{TMS}}}{\nu_{\text{Instrument}}} \times 10^6 = \frac{\Delta \nu}{\nu_{\text{Instrument}}}$$

Chemical shift, δ is constant

$$\Delta \nu \propto \nu$$

$$\frac{\Delta \nu_1}{\Delta \nu_2} = \frac{\nu_1}{\nu_2}$$

$$\frac{728}{\Delta \nu_2} = \frac{100}{300}$$

$$\Delta \nu_2 = \frac{728 \times 300}{100} = 2184 \text{ Hz}$$

- If gyromagnetic ratio of ^{13}C is $\frac{1}{4}$ of that of ^1H . What is the frequency must be irradiated to take ^{13}C NMR spectrum if same instrument take ^1H NMR spectrum at 300 MHz.

$$\nu = \left(\frac{\gamma}{2\pi}\right) H_0, \text{ Here field strength } H_0 \text{ is constant.}$$

$$\frac{\nu_1}{\nu_2} = \frac{\gamma_1}{\gamma_2}$$

$$\frac{300}{\nu_2} = \frac{1}{1/4}$$

$$\nu_2 = \frac{300}{4} = 75 \text{ MHz}$$

Factors affecting chemical shift

i) Electronegativity

If the electronegativity of substituents attached to the protons increases, then electron density around the protons decreases and the protons feel higher field strength & the protons are said to be de-shielded. In the case of methyl halides, protons of CH_3F are least shielded (most de-shielded) and those of CH_3I (2.2 ppm) are most shielded (least de-shielded).

Compounds	CH_3F	$\text{CH}_3\text{-O-CH}_3$	$(\text{CH}_3)_3\text{N}$	$\text{CH}_3\text{-CH}_3$
δ of CH_3 protons	4.3 ppm	3.2 ppm	2.2 ppm	0.9 ppm

ii) Cumulative effects of electronegative substituents

If the number of electronegative substituents attached to the protons increases, then the protons feel higher field strength and the proton is said to be de-shielded. For example, consider the chemical shifts for various chlorinated methane derivatives,

Compounds	CHCl_3	CH_2Cl_2	CH_3Cl
δ of CH_3 protons	7.3 ppm	5.3 ppm	3.1 ppm

iii) Distance from the electronegative atom

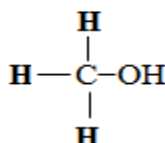
If the distance from the electronegative atom substituted in the hydrocarbon chain increases, electron density around protons increases and shielding increases so chemical shift value decreases.

Compound	$\text{H}_3\text{C} - \text{CH}_2 - \text{CH}_2\text{Cl}$		
Chemical shift (δ)(ppm)	1	1.4	3.4

iii) De-shielding

In de-shielding, induced magnetic field reinforces the applied magnetic field. Therefore de-shielding increases the chemical shift (δ) values. In the case of aromatic protons and olefinic protons δ value is high due to the de-shielding effect.

Low resolution NMR Spectrum of $\text{CH}_3\text{-OH}$



In methanol ($\text{CH}_3\text{-OH}$) there are three identical CH bonds and one OH bond are present. The chemical environment of CH bonds and one OH bond are different. Since oxygen is more electronegative than carbon. So electron density around -OH proton is lesser than that around CH_3 - protons. As a result, CH_3 - protons are more shielded than -OH proton. That means shielding constant (σ) is greater for CH_3 - protons.

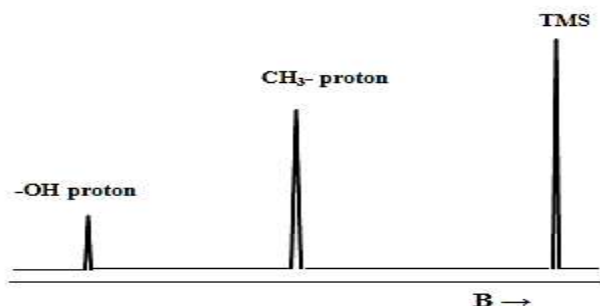
$$\sigma_{\text{CH}_3} > \sigma_{\text{OH}}$$

Shielded proton feels lower field strength. So observed magnetic field (B) is greater for -OH proton.

$$B_{\text{OH}} > B_{\text{CH}_3}$$

That means actual field felt by the CH_3 - protons is lesser than that felt by -OH proton. Hence on increasing the external magnetic field, -OH proton will come into resonance earlier than CH_3 - protons. As a result NMR signal for -OH proton will be observed at a lower field strength and that of CH_3 - protons will be observed at higher field strength.

The area under each peak is directly proportional to the number of protons. Thus the area under the signal of CH_3 - protons will be three times larger than that under -OH proton.



High Resolution NMR Spectrum

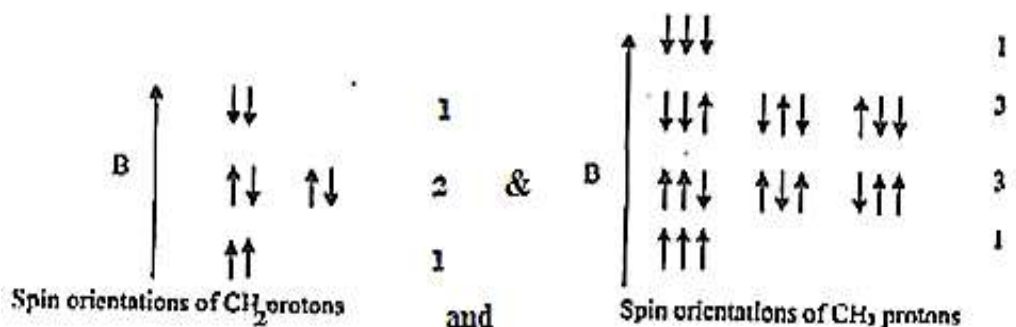
If we take the high resolution NMR Spectrum of molecule, we can see a multiplet instead of a single peak. It is due to a phenomenon called spin-spin splitting.

Spin -spin splitting (spin-spin coupling)

The interaction between spins of neighbouring nuclei in a molecule can cause splitting of lines in the NMR spectrum. This is called spin -spin splitting (spin-spin coupling)

In order to explain spin -spin splitting (spin-spin coupling), let us consider the high resolution spectrum of $\text{CH}_3\text{-CH}_2\text{-Br}$. This compound contains two types of protons, so two signals are expected in the low resolution NMR spectrum. But in high resolution NMR spectrum,

we do not get singlet for each type of proton, instead a group of peaks (multiplet) are observed. For CH_3 - protons, singlet will split into a triplet with intensity ratio 1:2:1 and for CH_2 < protons, singlet will split into a quartet with intensity ratio 1:3:3:1. This can be explained by considering the spin orientation of each type of protons.

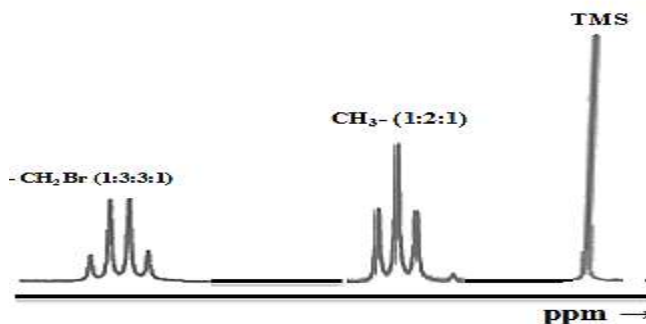


The spin of CH_2 < protons can couple with adjacent CH_3 - protons in three different ways relative to the external field. Hence the field felt by the CH_3 - protons can be modified in three different ways. That means NMR signal due to CH_3 - protons will split into three (triplet).

Similarly the spin of CH_3 - protons can couple with adjacent CH_2 < protons in four different ways. Hence the field felt by the CH_2 < protons can be modified in four different ways. That means NMR signal due to CH_2 < protons will split into four (quartet).

Area under the broad NMR and the multiplet remains the same. Spin – spin coupling is independent of the applied field strength. The spacing between peaks of multiplet is the measure of spin – spin coupling and is called spin – spin coupling constant (J).

We can easily determine the relative intensity of multiplet using Pascal's triangle method.



Applications of NMR spectroscopy

- i) Structural elucidation of many organic and inorganic compounds.
- ii) NMR spectroscopy is used to study keto-enol tautomerism.
- iii) It is used in the study of isotopes.
- iv) MRI technique is based on the principle of NMR.

Magnetic Resonance Imaging (MRI)

MRI is the medical technique used in radiology to get the detailed pictures of internal body parts. MRI uses a very strong magnetic field, radio frequency wave and a computer to produce the detailed pictures of body parts such as soft tissues, bones etc. These images can be examined in the computer monitor, transmitted electronically, printed or copied to a CD.

Principle:

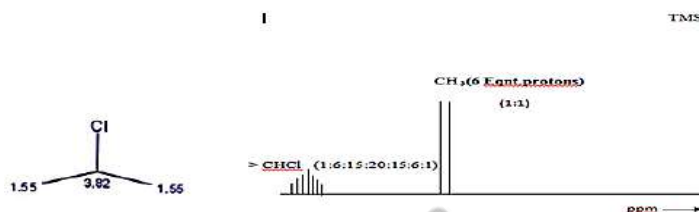
It is the medical version of NMR. This method uses magnetic properties of hydrogen present in the body cells and its interaction with external magnetic field to produce highly detailed pictures of internal body parts. In order to perform MRI scanning, a very strong magnetic field of 0.5 – 1.5T is required

Applications

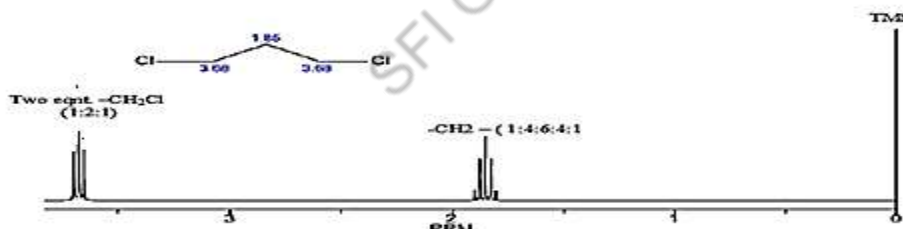
- Physicians use MRI for the treatment of diseases like tumors of abdomen, liver cirrhosis, heart problems etc.
- Measuring physiological functions like neuromuscular skeletal functions.
- Magnetic resonance angiography is used for getting pictures of arteries.

NMR Spectra of compounds

1. Predict NMR spectrum of $\text{CH}_3\text{-CHCl-CH}_3$ (2-chloro propane)

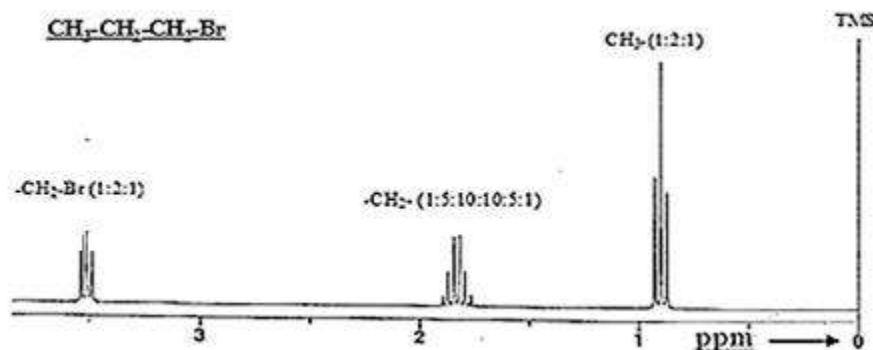


2. Write splitting pattern in the NMR spectrum of $\text{CH}_2\text{Cl-CH}_2\text{-CH}_2\text{Cl}$ (1, 3- dichloro propane)



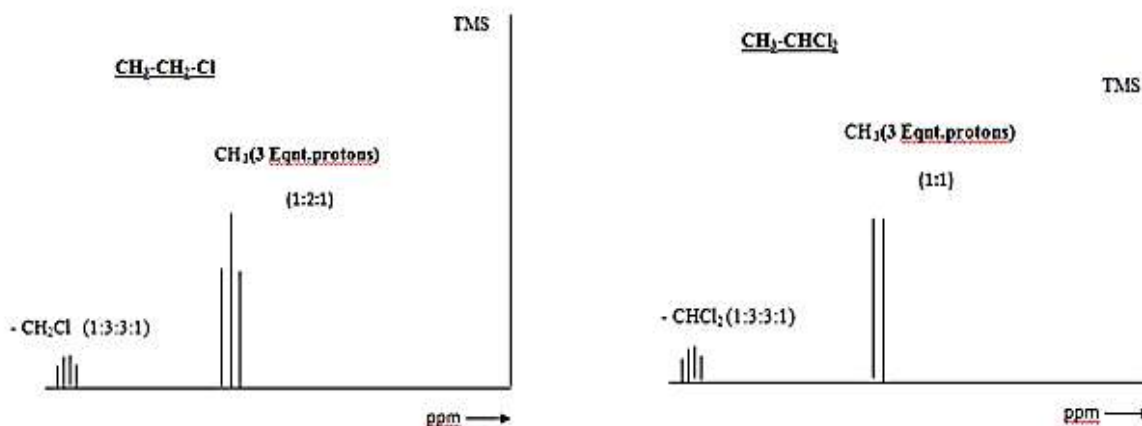
3. Give number of signals, peak ratio and multiplicity of different sets of protons in the nmr spectrum of 1-bromopropane.

In 1-bromopropane, three types of protons are present. So three signals are expected. The Br attached CH_2 - has lesser electron density, so signal is obtained far away from TMS. (i.e, at higher δ value)

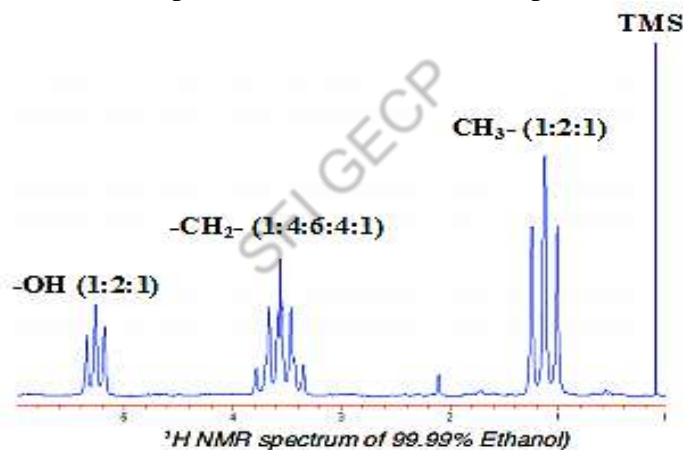


4. How can you distinguish NMR spectrum of $\text{CH}_3\text{CH}_2\text{Cl}$ and CH_3CHCl_2 applying the concept of spin – spin splitting

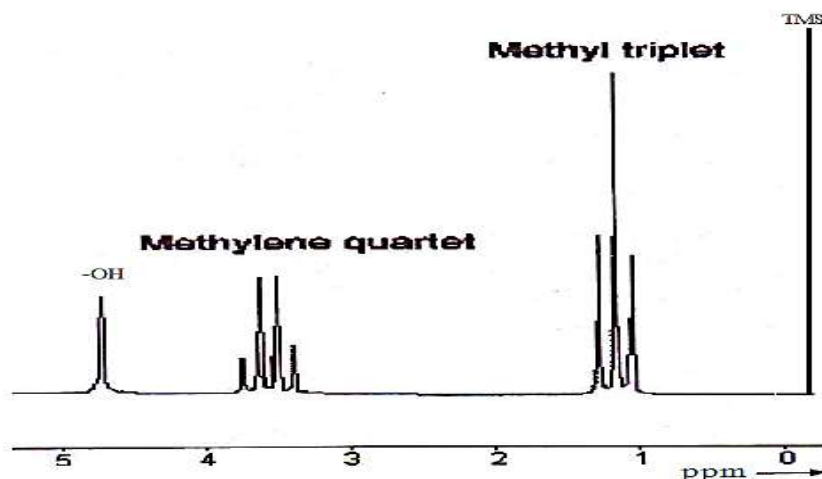
NMR spectrum of both the compounds has two peaks. In $\text{CH}_3\text{-CH}_2\text{Cl}$, the $\text{-CH}_2\text{Cl}$ is attached to the more electronegative Cl atom and is less shielded, so its signal is obtained away from TMS signal. But $\text{CH}_3\text{-}$ is more shielded, so its signal is obtained near to TMS. But in high resolution spectra each singlet is splitted into a multiplet due to spin - spin splitting. In $\text{CH}_3\text{-CH}_2\text{Cl}$, the $\text{CH}_3\text{-}$ signal is splitted into triplet with intensity ratio 1:2:1, whereas in $\text{CH}_3\text{-CHCl}_2$, the $\text{CH}_3\text{-}$ signal is splitted into doublet with intensity ratio 1:1. But in both cases $\text{-CH}_2\text{Cl}$ & -CHCl_2 , we get a quartet with intensity ratio (1:3:3:1).



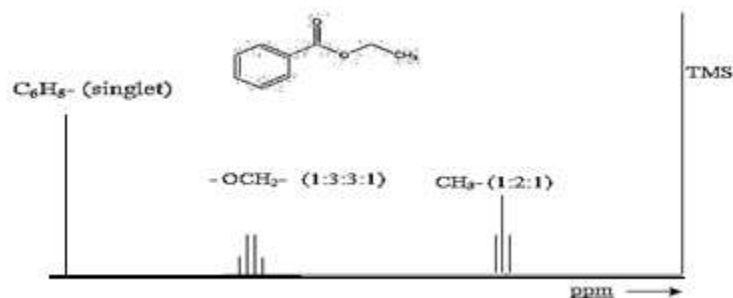
5. Draw the high resolution nmr spectrum of ethanol (99.99% pure)



6. Draw the high resolution NMR spectrum for ethanol containing impurities such as water, acetic acid etc.



7. Predict the number of signals, their relative positions and their multiplicities for ethyl benzoate.



Prepared by *Raji Sankar, Assistant Professor*
Dept. of mathematics & Basic sciences,
Sree Buddha College of Engineering, Pattoor

SFI GECP