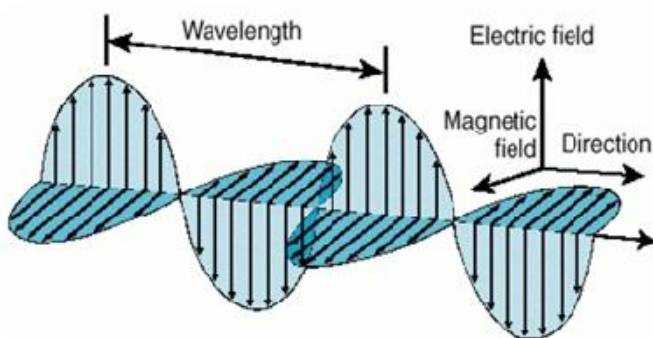


Unit-II Molecular structure and Spectroscopic techniques.

Spectroscopy: It is the study of interaction between light and matter.

Electromagnetic radiation:

- ☐ EMR is a form of energy which travels in space as waves or photons.
- ☐ Electromagnetic radiation has dual nature.
- ☐ Photon is a smallest energy particle of radiation.
- ☐ EMR consists of two components namely, magnetic field and Electric field which are perpendicular to each other.
- ☐ Hence the name Electromagnetic radiation.

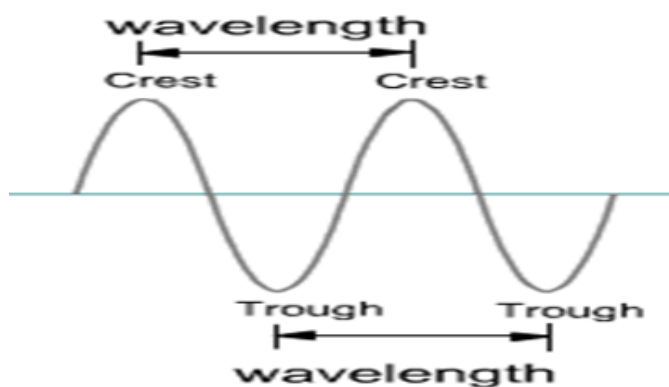


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The following are the important properties of Electromagnetic radiation,

Wavelength (λ):

- ☐ It is the distance the two adjacent crests or troughs in a particular wave.
- ☐ It is denoted by a letter λ (lambda).
- ☐ It can be expressed in Angstrom units or in millimicrons ($m\mu$)



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Amplitude:

- ☐ It is defined as the height of the crest or depth of the trough of the wave.
- ☐ Amplitude \propto strength of magnetic field /electric field.
- ☐ Amplitude of the wave \propto Energy of wave when wavelengths of the waves are same

Wavenumber ($\bar{\nu}$)

- ☐ It is the reciprocal of wavelength. Or it is defined as total number of waves which can pass through a space of one cm.
- ☐ It is denoted by $\bar{\nu}$
- ☐ It is expressed as per centimetre or per meter

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

Frequency(ν):

- ☐ The number of waves which can pass through a point in one second.
- ☐ It is denoted with ν (nu)
- ☐ It is expressed in cycles per second or in Hertz.

$$1\text{Hz} = 1 \text{ cycle/sec}$$

$$\text{Frequency} \propto \frac{1}{\text{Wavelength}}$$

$$\nu = \frac{c}{\lambda}$$

Where, c = velocity of EMR = $2.998 \times 10^{10} \text{ cm sec}^{-1}$

Energy(E):

- ☐ Energy of radiation is given by the following relation.

$$E = h\nu = h.c/\lambda = h.c \bar{\nu}$$

Where, h = Plank's Constant = $6.628 \times 10^{-27} \text{ ergs sec} = 6.628 \times 10^{-34} \text{ Joules sec}$

ν = Frequency of radiation in cycles sec^{-1}

c = velocity of EMR

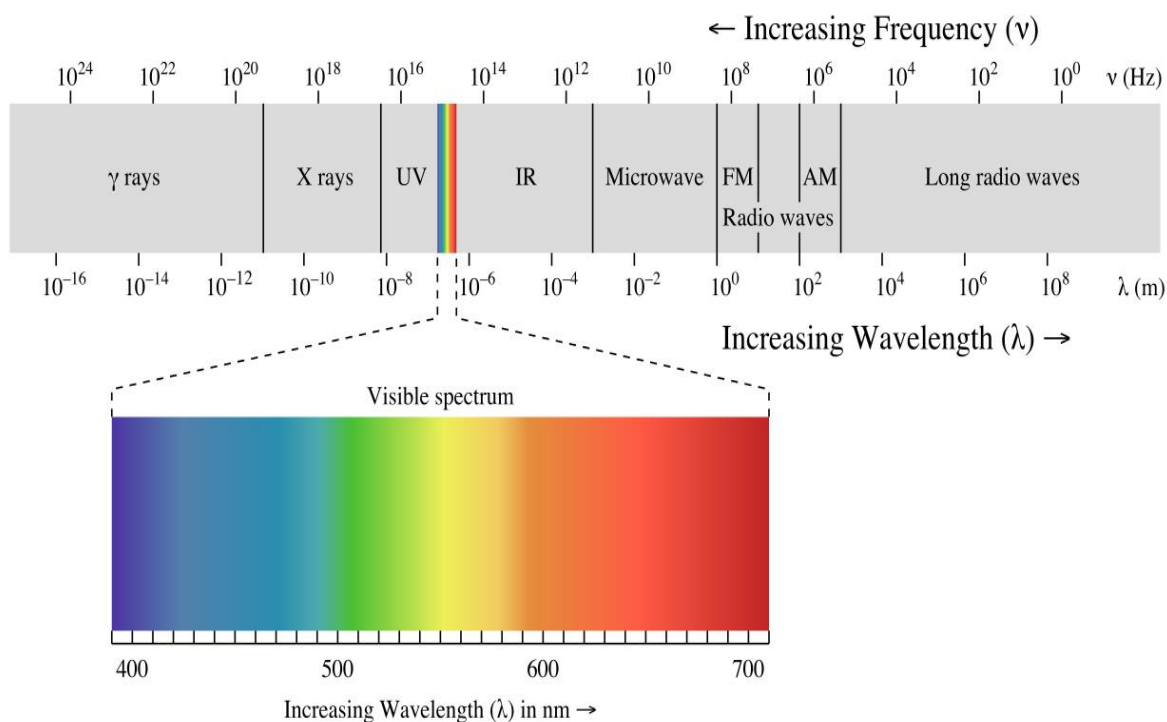
λ = wavelength of radiation.

- ☐ Avogadro number of photons is called Einstein.

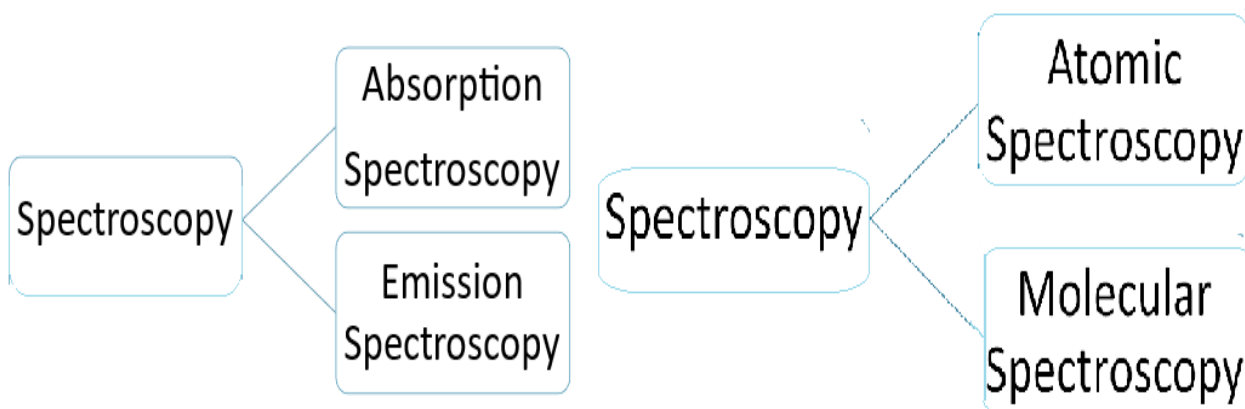
$$E = N_0 h \nu = N_0 h \cdot \frac{c}{\lambda} = N_0 h c \bar{\nu}$$

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Electromagnetic spectrum: Electromagnetic spectrum is the arrangement of electromagnetic radiations in the increasing order of wavelengths or decreasing frequencies.

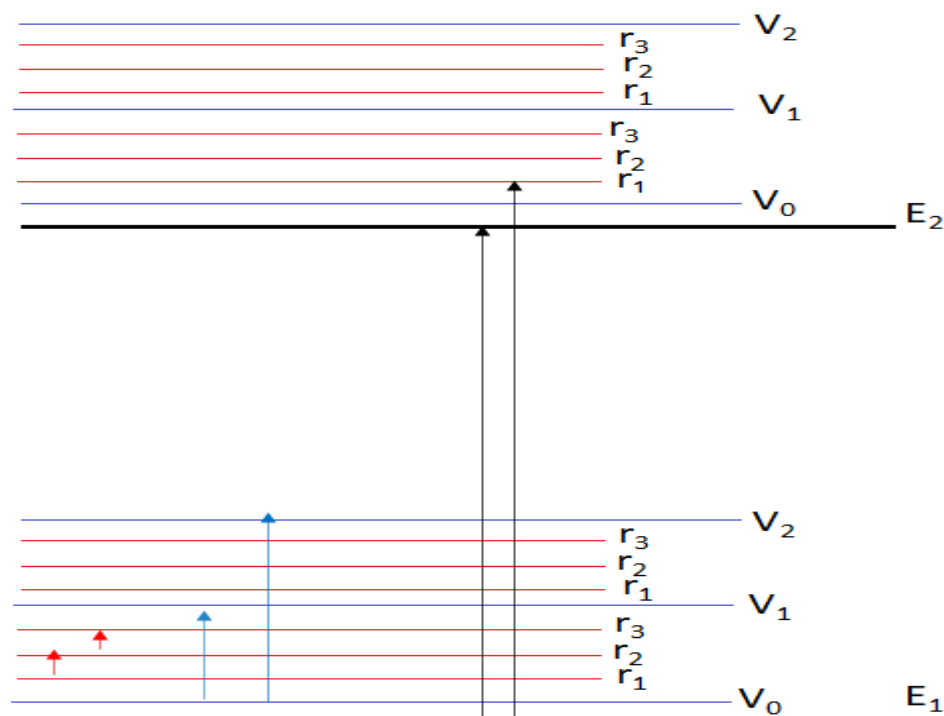


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Molecular Energy levels:



Type of molecular spectra:

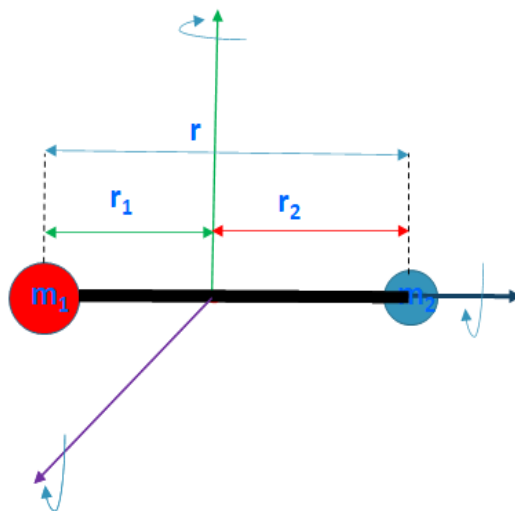
Spectra	Region of Electromagnetic spectrum	Type of transition	Criteria
Rotational or Microwave spectroscopy	Microwave region	Between rotational levels within the same vibrational level	Molecules should have a permanent dipole moment.
Vibrational or IR spectroscopy or Vibrational rotational spectroscopy	Infra -Red region	Between vibrational levels within the same electronic level	Molecules should have a permanent dipole moment or induced dipole moment
NMR spectroscopy	Radio wave region	Between magnetic energy levels	Spin quantum number (I) >1

Rotational Spectroscopy.

Principle of rotational spectroscopy:

The molecules which have a permanent dipole moment can generate electric field during its rotation which can interact with the microwave radiation which cause transition from one rotational energy level to another rotational energy level within the same vibrational energy level.

- ☐ Rotational spectra are obtained when microwave radiation (Far IR) is absorbed by molecules having permanent dipole moment.
- ☐ It is also called as microwave spectroscopy.
- ☐ Generally, Rotational spectroscopy studied in gaseous phase of the molecules since rotation of molecules is quenched in solids or liquids.



Rigid rotator/rotor model:

- ☐ Rotating diatomic molecule is regarded as rigid rotator.
- ☐ During rotation of molecule, bond length (internuclear distance) does not change.

Derivation of Moment of Inertia of rotating rigid diatomic molecule.

Consider a rigid diatomic molecule having two atoms of masses m_1 and m_2 .

$$r = r_1 + r_2 \text{ ----- (1)}$$

r = inter nuclear distance between the atoms in a molecule.

According to center of gravity,

$$m_1 r_1 = m_2 r_2 \text{ ----- (2)}$$

Moment of inertia of a diatomic molecule is given by

$$I = m_1 r_1^2 + m_2 r_2^2 \text{ ----- (3)}$$

$$\text{Using eq (2), } I = m_2 r_2 r_1 + m_1 r_1 r_2 \\ = r_1 r_2 (m_1 + m_2) \text{ -----}$$

$$\text{Using eq (1) } r_2 = r - r_1$$

$$\text{eq (2) becomes } m_1 r_1 = m_2 (r - r_1)$$

$$m_1 r_1 + m_2 r_1 = m_2 r$$

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$$r_1(m_1 + m_2) = m_2 r$$

$$r_1 = \frac{m_2 r}{(m_1 + m_2)}$$

$$\text{Similarly, } r_2 = \frac{m_1 r}{(m_1 + m_2)}$$

Substituting for r_1 and r_2 in eq (3)

$$I = m_1 \left(\frac{m_2 r}{m_1 + m_2} \right)^2 + m_2 \left(\frac{m_1 r}{m_1 + m_2} \right)^2$$

$$I = \frac{m_1 m_2 r^2}{(m_1 + m_2)^2} (m_1 + m_2) \text{ ----- (5)}$$

$$I = \frac{m_1 m_2 r^2}{(m_1 + m_2)}$$

$$I = \mu r^2$$

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

Expression for rotational energy:

Classically, the angular, momentum of rotating molecule is given by $L = I \omega$ ---- (1)

Where, ω = angular velocity.

However, Angular momentum quantized and given by

$$L = \sqrt{J(J+1)} \frac{h}{2\pi} \text{ ----- (2)}$$

Where, J = rotational quantum number

The energy of rotating molecule is given by $E_J = \frac{1}{2} I \omega^2$

$$E_J = \frac{1}{2} I \omega^2 = \frac{(I \omega)^2}{2I} = \frac{(L)^2}{2I}$$

Using equation (2), we have $E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joules ----- (3)}$

Where, $J = 0, 1, 2, 3, 4, \dots$

It is customary to express energy in cm^{-1} rather than in Joules.

Divide eq (3) both the sides by hc , we get

$$\frac{E_J}{hc} = \bar{\nu}_J = \frac{h^2}{8\pi^2 I c} J(J+1) \text{ cm}^{-1} ; J = 0, 1, 2, 3, 4, \dots$$

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BE I semester 2021-2022
Engineering Chemistry
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$\bar{\nu}_J = BJ(J+1) \text{ cm}^{-1}$ Where, Rotational constant (B) = $\frac{h}{8\pi^2IC} \text{ cm}^{-1}$

For given J = 0, 1, 2, 3 values and Energy difference between two energy levels given below.

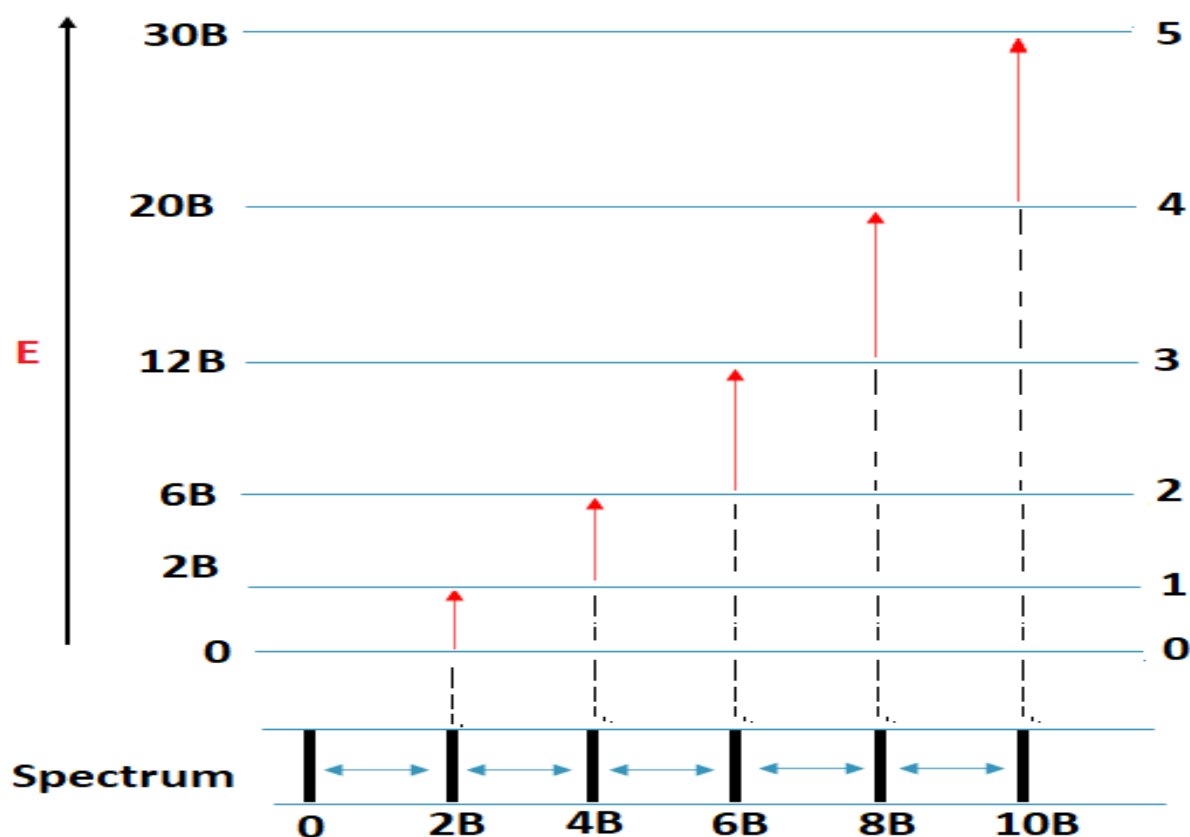
$$\bar{V}_0 = B \times 0(0+1) = 0 \text{ cm}^{-1}$$

$$\bar{V}_1 = B \times 1(1+1) = 2B \text{ cm}^{-1}$$

$$\bar{V}_2 = B \times 2(2+1) = 6B \text{ cm}^{-1}$$

$$\bar{V}_3 = B \times 3(3+1) = 12B \text{ cm}^{-1}$$

$$\begin{aligned} \Delta \bar{V} &= \bar{V}_{J+1} - \bar{V}_J \\ &= B(J+1)(J+1+1) - BJ(J+1) \\ &= B(J+1)(J+2) - BJ(J+1) \\ &= B(J+1)(J+2) - BJ(J+1) \\ &= B(J^2+2J+J-J^2-J) \\ &= 2B(J+1) \text{ cm}^{-1} \end{aligned}$$



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BE I semester 2021-2022
Engineering Chemistry
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The rotational spectrum of a rigid diatomic molecule consists of series of lines at $2B$, $4B$, $6B$, $8B$, $10B$, etc., It is clearly seen that spectral lines are equally spaced by an amount of $2B$.

Selection Rules for rotational spectroscopy:

- ☐ Molecules must have a permanent dipole moment.
- ☐ $\Delta J = \pm 1$

Where, J -Rotational Quantum number (0,1,2, 3, 4...)

Applications of rotational spectroscopy:

- ☐ Rotational Spectroscopy helps to calculate moment of inertia and bond lengths.

Numerical Problems:

Problem 1: The pure rotational spectrum of gaseous HCl consists of series of equally spaced lines separated by 20.80 cm^{-1} . Calculate the inter nuclear distance of the molecule. The atomic masses are: $^1\text{H} = 1.673 \times 10^{-27} \text{ kg}$; $^{35}\text{Cl} = 58.06 \times 10^{-27} \text{ kg}$.

Given, $2B = 20.80 \text{ cm}^{-1}$ $B = 10.4 \text{ cm}^{-1}$

$$I = \frac{h}{8\pi^2 Bc} \text{ cm}^{-1} = \frac{6.626 \times 10^{-34} \text{ J s}}{8(3.14)^2 (10.4 \text{ cm}^{-1})(3 \times 10^{10} \text{ cms}^{-1})}$$
$$= 0.2689 \times 10^{-46} \text{ kg m}^2 \quad (J = \text{kg m}^2 \text{ s}^{-2})$$

Reduced mass is given by ,

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)} = \frac{(1.673 \times 10^{-27} \text{ kg})(58.06 \times 10^{-27} \text{ kg})}{(1.673 \times 10^{-27} \text{ kg} + 58.06 \times 10^{-27} \text{ kg})} = \frac{(1.673 \times 10^{-27} \text{ kg})(58.06 \times 10^{-27} \text{ kg})}{59.73}$$

$$\mu = 1.626 \times 10^{-27} \text{ kg}$$

We know, $I = \mu r^2$

Therefore ,

$$r = \left[\frac{I}{\mu} \right]^{\frac{1}{2}} = \left[\frac{0.2689 \times 10^{-46} \text{ kg m}^2}{1.626 \times 10^{-27} \text{ kg}} \right]^{\frac{1}{2}} = 1.29 \times 10^{-10} \text{ m} = 129 \text{ pm}$$

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BE I semester 2021-2022
Engineering Chemistry
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Problem 2: The pure rotational spectrum of gaseous CN consists of series of equally spaced lines separated by 3.7978 cm^{-1} . Calculate the inter nuclear distance of the molecule. The atomic masses are: $^{12}\text{C} = 12.011 \times 10^{-27} \text{ g mol}^{-1}$; $^{14}\text{N} = 14.007 \text{ g mol}^{-1}$

Ans: 117 pm

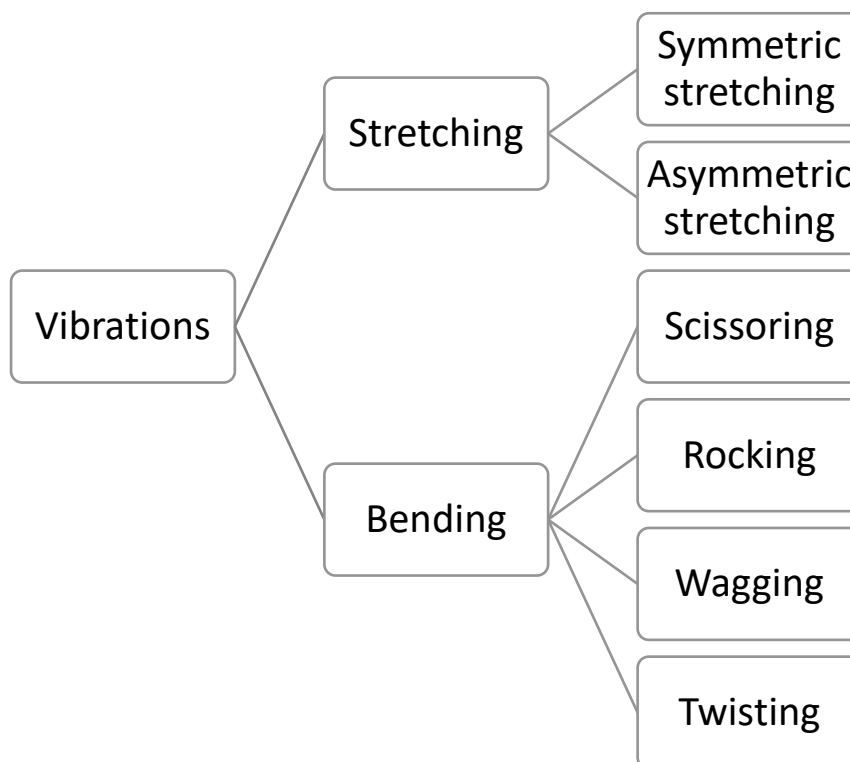
Infra-red spectroscopy:

Principle of vibrational spectroscopy:

The molecules which have a permanent dipole moment or induced dipole moment when interact with the Infrared radiation which cause transition from one vibrational energy level to another vibrational energy level within the same electronic energy level which results IR spectra.

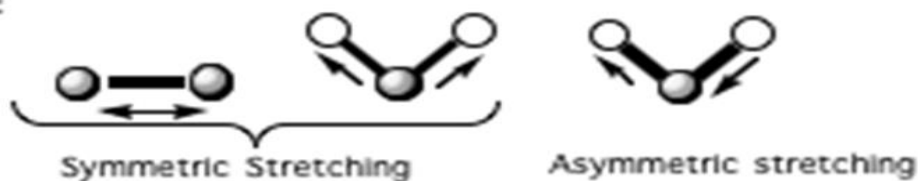
- ☐ Vibrational spectra of molecules are obtained when IR radiation is absorbed by molecules having permanent dipole moment or induced dipole moment.
- ☐ It is also called as vibrational -rotational spectroscopy.

Types of vibrations:



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Stretching:



Bending or Deformation:



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Simple Harmonic Oscillator model:

- ❑ A diatomic molecule (A-B) is regarded as a simple harmonic oscillator.
- ❑ According to Hook's law, $F = -kx$

$$F = -k(r - r_{eq})$$

Where, k- Force constant
x- displacement

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- ❑ P.E = $\frac{1}{2} kx^2 = \frac{1}{2} k (r - r_{eq})^2$
- ❑ Vibrational frequency(V) = $\frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$

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

Where, k- force constant
 μ -reduced mass



- ❑ Energy of Simple Harmonic Oscillator is given by,

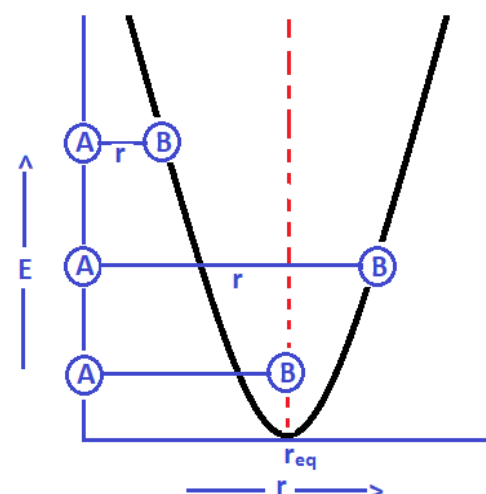
$$E = (V + \frac{1}{2}) h\nu$$

$$E_{vib}/hc = (V + \frac{1}{2}) h\nu/hc$$

$$E_{vib}/hc = (V + \frac{1}{2}) \nu/c$$

$$E_{vib}/hc = \bar{\nu}_v = (V + \frac{1}{2}) \bar{\nu}_e$$

$$\bar{\nu}_v = (V + \frac{1}{2}) \bar{\nu}_e$$



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Engineering Chemistry
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Where $\bar{\nu}_e$ = fundamental vibrational frequency .

when $v = 0$,

$\bar{\nu}_v = 1/2 \bar{\nu}_e$ = zero-point energy.

Note: In case of simple harmonic oscillator, energy difference between two (lower and higher) energy levels is equal to $\bar{\nu}_e$.

The molecule does not always vibrate as simple harmonic oscillator; there is present what is called anharmonicity. Morse suggested an empirical equation for the potential energy of anharmonic diatomic oscillator, given by

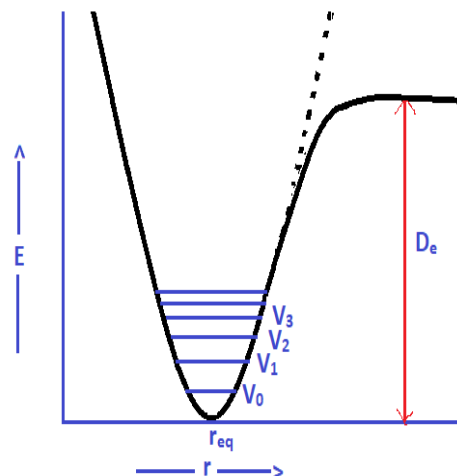
$$V(r) = D_e [1 - e^{-a(r-r_{eq})^2}]$$

Energy of anharmonic oscillator is given by,

$$\bar{\nu}_v = \left(v + \frac{1}{2}\right) \bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e x_e$$

Where , $\bar{\nu}_e x_e$ = **anharmonicity constant** .

When anharmonicity of molecule is taken into consideration vibrational energy levels of Anharmonic diatomic oscillator steadily decreases as vibrational quantum number (v) increases .



Number of Fundamental Vibrations:

- Vibrational degrees of freedom for **a linear** molecule having N atoms = $3N-5$

Where, Total number of degrees of freedom = $3N$

Translation degrees of freedom = 3

Rotational degrees of freedom = 2

- Vibrational degrees of freedom for **a non- linear** molecule having N atoms = $3N-6$

Where, Total number of degrees of freedom = $3N$

Translation degrees of freedom = 3

Rotational degrees of freedom = 3

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Selection rules for Vibrational spectroscopy:

- ☐ Molecules should have a permanent dipole moment or induced dipole moment
- ☐ $\Delta v = \pm 1$ (In case of SHO)
- ☐ $\Delta v = \pm 1, \pm 2, \pm 3 \dots$ (When anharmonicity is taken into consideration)

Where, V-Vibrational Quantum number ($V = 0, 1, 2, 3, 4 \dots$)

Fundamental band: Peak resulted from $v=0$ to $v=1$ transition.

First overtone: Peak resulted from $v=1$ to $v=2$ transition.

Second overtone: Peak resulted from $v=2$ to $v=3$ transition

Applications of Vibrational Spectroscopy:

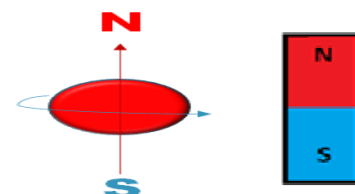
1. It can give information about bond strength and reduced mass of a molecule. i.e force constant can be calculated.
2. Identification of unknown compound.
3. Detection of functional groups.
4. Purity of compound can be known.
5. The progress of a chemical reaction can be easily monitored by examining the IR spectrum of test solution at different intervals.
6. Determination of Shape or symmetry of a molecule.
7. Presence of hydrogen bonding can be predicted.

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Nuclear Magnetic Resonance Spectroscopy

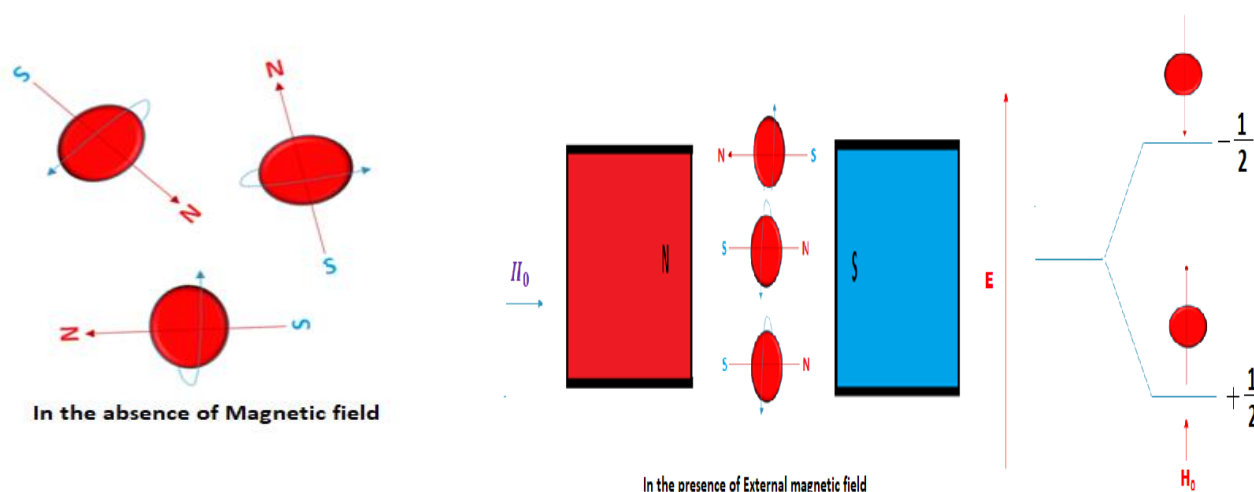
Introduction to NMR:

The nucleus (hydrogen atom: proton) behaves as a spinning bar magnet because it possesses both electric and magnetic spin. Nucleus of hydrogen atom (proton) generates magnetic field just like any other spinning charged body.

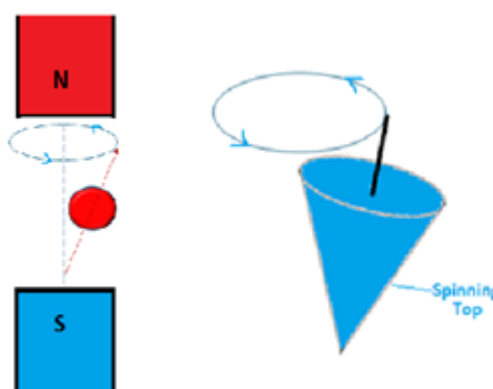


A spinning nucleus (proton) can orient any of the direction in the absence of magnetic field but when it is kept in external magnetic field it can take up one of the two possible orientations.

- (i) Alignment with the field (α Spin has low energy)
- (ii) Alignment against the field (β spin has high energy)



A nucleus with $I > 0$ kept in an external magnetic field not only take up one of the two possible orientations (i) alignment with the field (ii) alignment against the field but also precesses in precessional path same as a gyroscope/spinning top precesses under the influence of gravity.



From Larmer equation we have, $\omega = \gamma H_0$ ----- (i)

We also have $\omega = 2\pi\nu$ ----(ii)

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From equation (i) & (ii) $\gamma H_0 = 2\pi\nu$

Therefore, $\nu = \frac{\gamma H_0}{2\pi}$

Where, ν = precessional frequency of proton(nuclei)

ω = angular precessional velocity

H_0 = Applied magnetic field in gauss

γ = Gyromagnetic ratio = $\frac{2\pi\mu}{hI}$

μ = Magnetic moment of spinning bar magnet.

I = Spin quantum number of the spinning magnet.

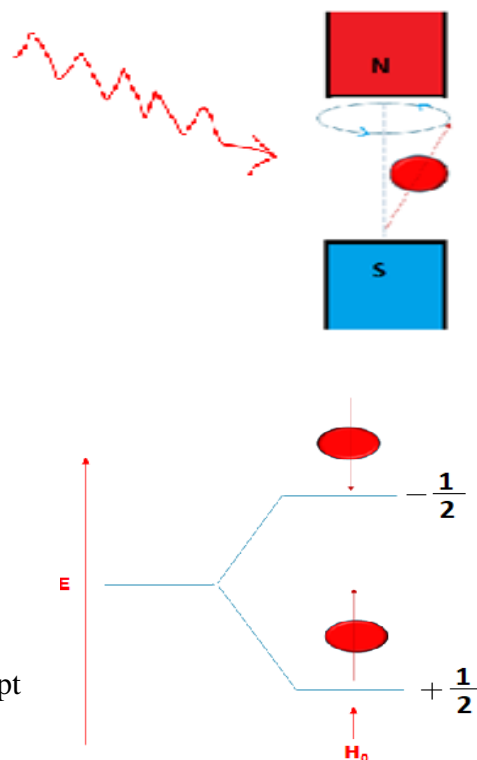
h = Planck's constant

Precessional frequency (ν): It is defined as number revolutions made by magnetic moment vector per second.

Principle of NMR spectroscopy:

The principle involved NMR spectroscopy is that, when the frequency of oscillating magnetified of radio waves matches (equal) with the precessional frequency of precessing nuclei (protons) kept in external magnetic field both are said to be in resonance, and it is called as Nuclear Magnetic Resonance which results absorption of radio wave energy and flipping of the proton from lower energy state (alpha spin state) to high energy state that gives signal(s) in NMR spectrum.

i.e., When, $\nu = \nu_0$, oscillating magnetic field of radio waves in resonance with precessing proton kept in external magnetic field and it is called nuclear magnetic resonance.



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Where, Precessional frequency of (nuclei)

$$\text{proton } (\nu) = \frac{\gamma H_0}{2\pi}$$

Let the frequency of radio waves be ν_0 .

Criteria for NMR Activity:

Mass Number(A)	Atomic Number(Z)	Spin Quantum Number (I)	NMR	Examples
Odd	Odd or even	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$	Active	$^1_1\text{H}, ^{15}_7\text{N}, ^{19}_9\text{F}, ^{13}_6\text{C}$
Even	Even	0	Inactive	$^{12}_6\text{C}, ^{16}_8\text{O}$
Even	Odd	1,2,3	Active	$^2_1\text{H}, ^{14}_7\text{N}$

Nucleus with $I > 0$ has magnetic moment, and NMR active.

Magnetic nuclei: Nuclei with $I > 0$

Non-magnetic nuclei: Nuclei with $I < 0$

It may be noted that magnetically equivalent protons are chemically equivalent protons.

Magnetically equivalent protons have same I value.

Magnetically not equivalent protons have different I value.

Number of signals: Numbers signals in the nmr spectrum is equal to the number of different sets of equivalent protons in a molecule. Each signal corresponds to a set of equivalent protons.

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Chemical Shift (δ):

It is the position of a signal (absorption peak) in nmr spectrum relative to that of a reference compound which is usually TMS (Tetramethyl silane).

Or

The difference in the absorption position of the proton with respect to TMS signal is called chemical shift.

$$\delta = \frac{v_{\text{samples}} - v_{\text{reference}}}{\text{Operating frequency in megacycles (per sec)}}$$

Where, $\Delta v = v_{\text{samples}} - v_{\text{reference}} = \text{Frequency shift.}$

The value of δ (delta) is expressed in ppm. Chemical shift values of most organic compounds are between 0 to 10.

δ (delta) value for TMS reference has been fixed as 0 and in τ (Tau) TMS value has been fixed as 10.

The two scales are interrelated as shown, **$\tau = 10 - \delta$**

Tetramethyl Silane (TMS) is internal reference standard for NMR spectra.

The following are the reasons to choose TMs as standard reference.

1. It is chemically inert and miscible with many solvents.
2. It has 12 magnetically equivalent protons.
3. It is highly volatile and can be easily removed to get back the sample.

Magnetic Resonance Imaging (MRI):

MRI is one of important applications of NMR spectroscopy which helps to diagnose /monitor the treatment progress of tumours, liver, heart problems, inflammatory Bowel Disease (IBD).

MRI makes use of NMR principle. When a human body is kept external magnetic field of MRI instrument the protons (^1H) of body tissues get aligned the direction of magnetic field which produces different energy levels and then radio waves with certain frequency are passed through human body kept in external magnetic field of MRI instrument which results absorption of radio wave energy by the protons (nuclei) in lower energy state and go to high energy level (excited state), then the radio waves are cut off that results the emission of radiation

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BE I semester 2021-2022
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absorbed by (Nuclei) protons which have gone to high energy state. This is known as **relaxation**.

The signal produced during relaxation is known as **free radiation decay (FID)**. the FID signal is measured by a conductive film placed around the object (human body) being imaged. The measured response signal is processed to get 3D MR Images.