


A Text Book of Physical Chemistry

A Text Book of Physical Chemistry

B.Sc. Third Year Semester-V

A. K. Pathan



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A Text Book of Physical Chemistry

To My Mother Father and all Teachers

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Preface

I feel very happy to present this book to the teachers and students of B.Sc., Third Year Swami Ramanand Teerth Marathwada University, Nanded. This book has been written as per B.Sc., TY syllabus. I tried to make book simple to understand and use this book directly for preparation of various exams. This book is written keeping in mind that students will not require any notes after using this text.

I make no claim of originality. The concepts and points explained are those of well-known scholars in the field. I hope that teachers and students will like this book

I hope that this book will satisfy needs of B.Sc. students studying Physical Chemistry. Any suggestions for the further improvement of the book are most welcome.

A. K. Pathan
5 May ,2017

Unit 1: Spectroscopy-I

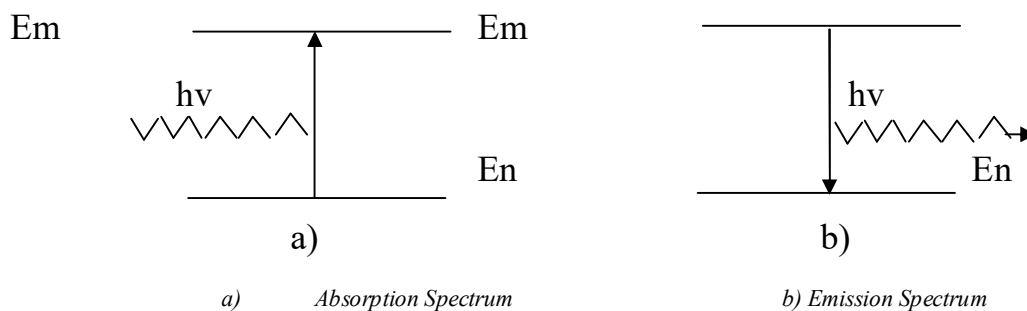
1.1 Introduction – What is spectroscopy?

Chemist, physicist, Biochemist and other scientist wants to know structure of molecules. We can't see molecules because these systems are of so infinitesimal dimensions. Our knowledge about structure of molecule is derived from the technique known as spectroscopy.

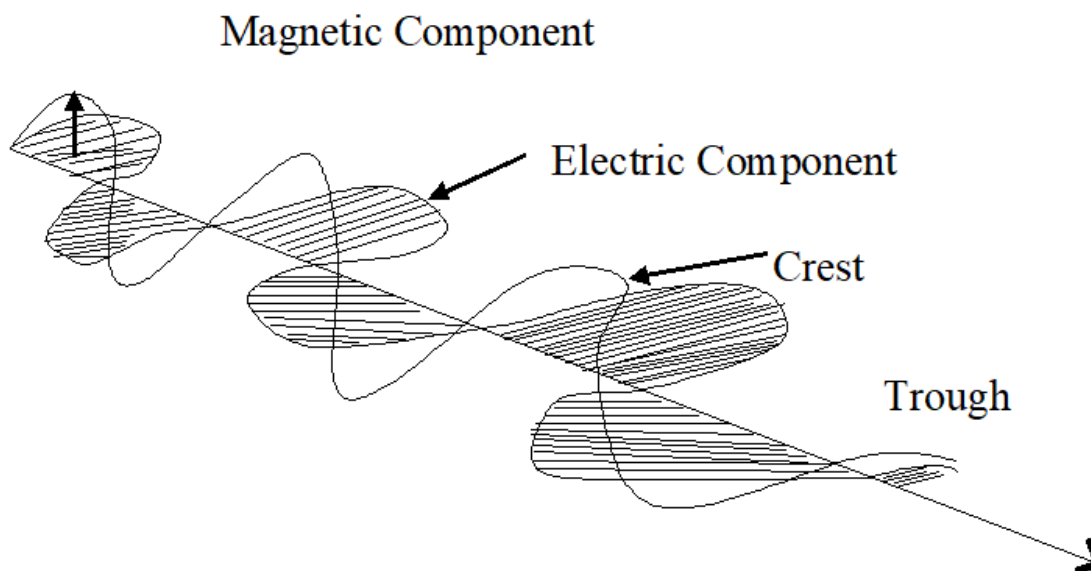
Spectroscopy deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiations determined by quantum mechanical selection rules. Quantum mechanics tells that the energy levels of all systems are quantized and are designated by quantum numbers. These quantum numbers are obtained by solution of Schrodinger (time independent) equation.

Let us consider how a spectrum arises. Consider two molecular energy levels E_n and E_m as shown in fig. If a photon of frequency ν falls on a molecule in ground state and its energy $h\nu$ is exactly to the energy difference ΔE ($E_m - E_n$) between the two molecular energy levels, then the molecule undergoes a transition from the lower energy level to the higher energy level with absorption of $h\nu$. The spectrum obtained is called as absorption spectrum.

If the molecule falls from the excited state to the ground state with the emission of a photon of energy $h\nu$, the spectrum obtained is called as emission spectrum.



Electromagnetic Radiation and Characteristics: -



Electromagnetic Radiation

An electromagnetic wave is characterized by following parameters.

- i) Wave length (λ) The distance between two adjacent crest or troughs in particular wave is called as wavelength.

It can be expressed in meters (m) centimetres (cm), mm, μm , nm, \AA . $1\text{nm} = 10^{-9}\text{m}$ & $1\text{\AA} = 10^{-10}\text{m}$

- ii) Frequency (ν) – It is defined as the number of waves which can pass through a point in one second

It is expressed as ν (nu) in cycles per second (Kcps or KHz) where $1\text{Hz} = 1\text{ cycle sec}$

The other units of frequency are kilocycles per second (Kcps or KHz) or megacycles per second (Mcps or MHz) $1\text{MHz} = 10^3\text{Hz} = 10^6\text{Hz}$ frequency is also expressed as Fresnel. $1\text{ Fresnel} = 10^{12}\text{Hz}$

iii) Wave number ($\bar{\nu}$) – it is the reciprocal of wavelength.

It is defined the number of waves per centimetre in vacuum. It is expressed as $\bar{\nu}$. It is generally used in infrared spectroscopy. The product of frequency and wavelength is equal to the velocity of wave in the medium.

$$c = \lambda\nu, c = \frac{v}{\bar{\nu}} \text{ etc. also } E = h\nu$$

$$\text{But } \nu = \frac{c}{\lambda} \therefore E = \frac{hc}{\lambda} = hc\bar{\nu}$$

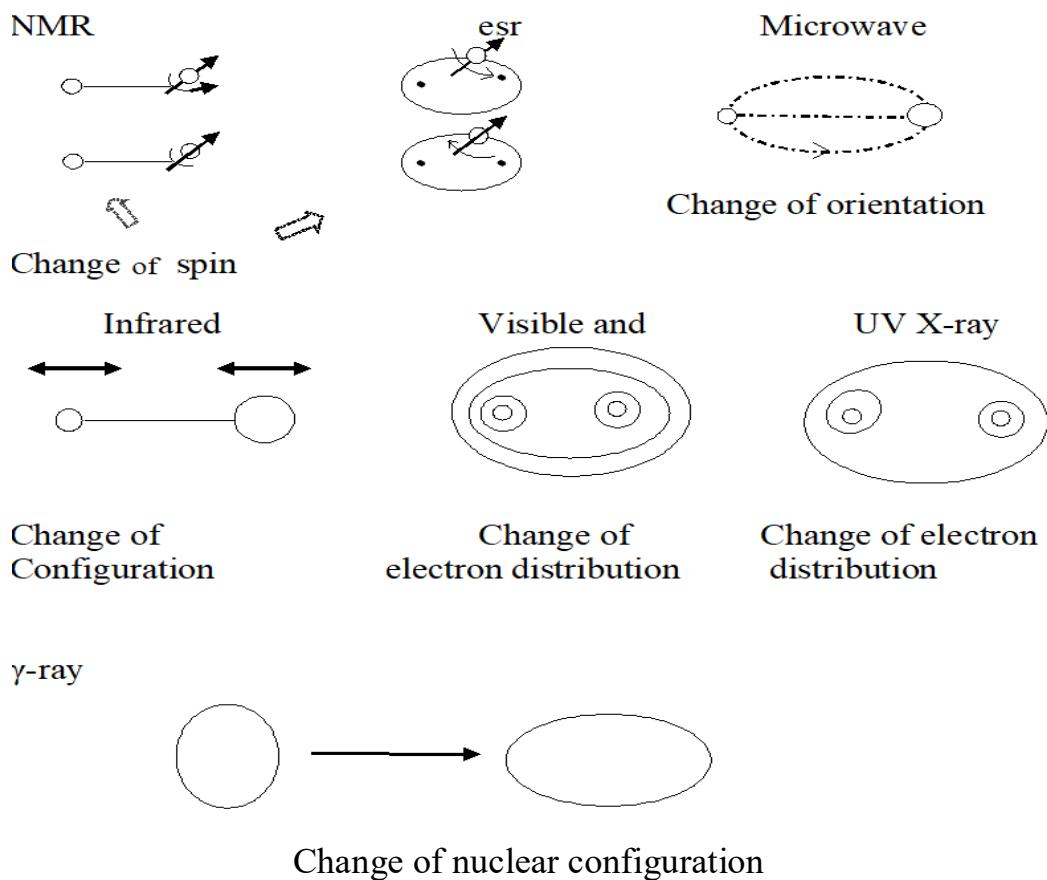
$$1 \text{ Joule} = 10^{-7} \text{ erg} = 0.239005736 \text{ cal}$$

1.2 Regions of spectrum: -

With increasing of electromagnetic radiations are divided into following regions.

1. Radio frequency region – $3 \times 10^6 - 5 \times 10^{10}$ Hz, λ , 10cm – 1cm, energy 0.001-10 J/ mol used in NMR, esr, spectroscopy
2. Microwave region – $3 \times 10^{10} - 3 \times 10^{14}$ Hz, λ 1 μ m – 100 μ m wavelength, energy 10 J – 100J/mol, rotational spectroscopy.
3. Infrared region – $3 \times 10^{12} - 3 \times 10^{14}$ Hz, λ 100 μ m, energy, 10^4 Joules /mol vibration spectroscopy.
4. Visible and UV, energy 100 KJ/mol, Electronic spectroscopy.
5. X- ray region – $3 \times 10^{16} - 3 \times 10^{18}$ Hz, λ 10nm – 100 pm, energy 1000 KJ/mol Inner electron transitions.
6. γ - ray region – 1 pm, energy – $3 \times 10^{18} - 3 \times 10^{20}$ Hz, λ 100pm – 1 pm, energy $10^9 - 10^{10}$ Joules /mol Involved rearrangement of nuclear particles.

Regions of electromagnetic radiations



1.3 The natural line width: -The natural line width (life time broadening) of a spectral line is determined by the Heisenberg's uncertainty principle

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

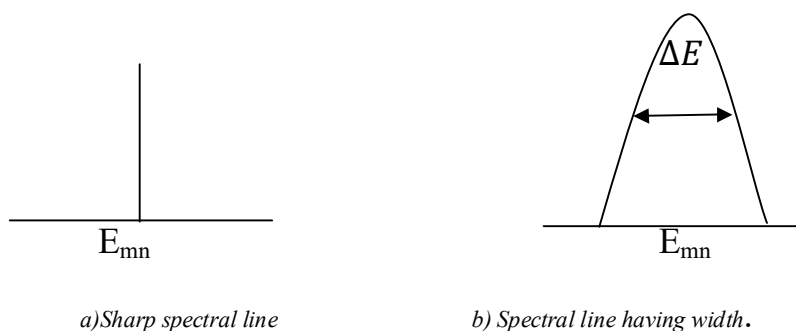
Where, ΔE =uncertainty in the energy Δt = uncertainty in the life time of energy level. for a photon, $E = h\nu$ so, $\Delta E = h\Delta\nu$ hence natural line width $\Delta\nu$ given by.

$$\Delta\nu \geq (4\pi\Delta t)^{-1}$$

$$\Delta\nu \geq \frac{1}{4\pi\Delta t}$$

Heisenberg's uncertainty principal says that if a system exists in an energy state for a limited time δt seconds then the energy of that state will be uncertain (fuzzy) to an extent δE .

1.4 Width and intensity of spectral lines: -



In the analysis of spectrum, we focus on how sharp and how intense (strong) is spectral line i.e. the width and intensity of spectral line, fig (a) shows a spectral line having a width ΔE at half height.

Two factors contribute to the broadening of spectral line (i) The collision broadening and (ii) Doppler broadening. (i) The collision Broadening-

The collision broadening is largely responsible for the width of spectral lines in the ultraviolet (UV) and visible regions. These transitions mostly take place between. Electrons in the outer shells in a molecule. When a molecule collides with one another, they deform clouds of outer electrons and slightly perturb the energy levels of electrons, Hence, spectral transitions between these perturbed energy levels are broadened.

ii) Doppler Broadening: -

It is due to Doppler Effect when the molecule under investigation has a velocity relative to observer or observing instrument. The case is related with gaseous samples where molecules are in random motion.

If a molecule is moving towards the measuring instrument with velocity μ , then frequency ν' of radiation 'seen' by the molecule is given by

$$\nu' = \nu \left(1 + \frac{u}{c}\right) \quad (1)$$

Where ν is the actual radiation frequency c velocity of light? If a molecule is moving away from the measuring instrument, the frequency of radiation 'seen' by the molecule is given by

$$\nu' = \nu \left(1 - \frac{u}{c}\right) \quad (2)$$

from eq (1), We have.

$$\frac{v-v'}{v} = \frac{\Delta v}{v} = \frac{-u}{c}$$

and from eq (2), We have

$$\frac{v-v'}{v} = \frac{\Delta v}{v} = \frac{u}{c}$$

The quantity Δv is the Doppler broadening. It is observed that depending up on the direction of motion of the molecule relative to instrument, the observed frequency becomes higher or lower than the actual frequency. It can be shown that the Doppler broadening of spectral line of a molecule of mass m is given by.

$$\frac{\Delta v}{v} = \left(\frac{2}{c}\right) \left(2kT \ln \frac{2}{m}\right)^{\frac{1}{2}} \text{-----}(3)$$

from eq (3) we get

$$\frac{\Delta v}{v} \propto T^{1/2}$$

Thus, Doppler broadening can be reduced by working with cold gaseous samples.

iii) Intensity of spectral lines: -

The intensity of a spectral line is determined by (i) The Boltzmann population of energy levels and (ii) The transition probability between the energy level.

According to Boltzmann, N_0 is the number of molecules in ground state, then at temperature T , N is excited state molecular given.

$$N = N_0 e^{-\frac{\Delta E}{kT}}$$

Where

ΔE = The energy difference between ground state and excited state,
 k = Boltzmann constant. The relative population at equilibrium is given as

$$\frac{N}{N_0} = e^{-\frac{\Delta E}{kT}}$$

If ΔE is large N/N_0 small. As at room temperature most molecules are in ground state, first excited states are more populated than second and other excited states. The transition probability means the probability of transition between two energy levels. These transitions are determined by selection rules, Allowed transition yield spectral lines with greater intensity than forbidden transition

1.5 Molecular spectra: -

Molecular spectra arise from three types of transition 'Viz' rotational, vibration and electronic transitions. The total energy of a molecule, according to Born- Oppenheim's approximation is given by

$$E = E_{tr} + E_{rot} + E_{vib} + E_{el} \quad (1)$$

The energy is sum of translational energy E_{tr} , rotational energy E_{rot} , Vibration energy, E_{vib} , electronic energy, E_{el}

All other energy is quantized except the translational energy and

$$E_{el} \gg E_{vib} \gg E_{rot} \gg E_{tr}$$

Neglecting E_{tr} as it is very small, we can write Born- Oppenheim's approximation as

$$E = E_{rot} + E_{vib} + E_{el}$$

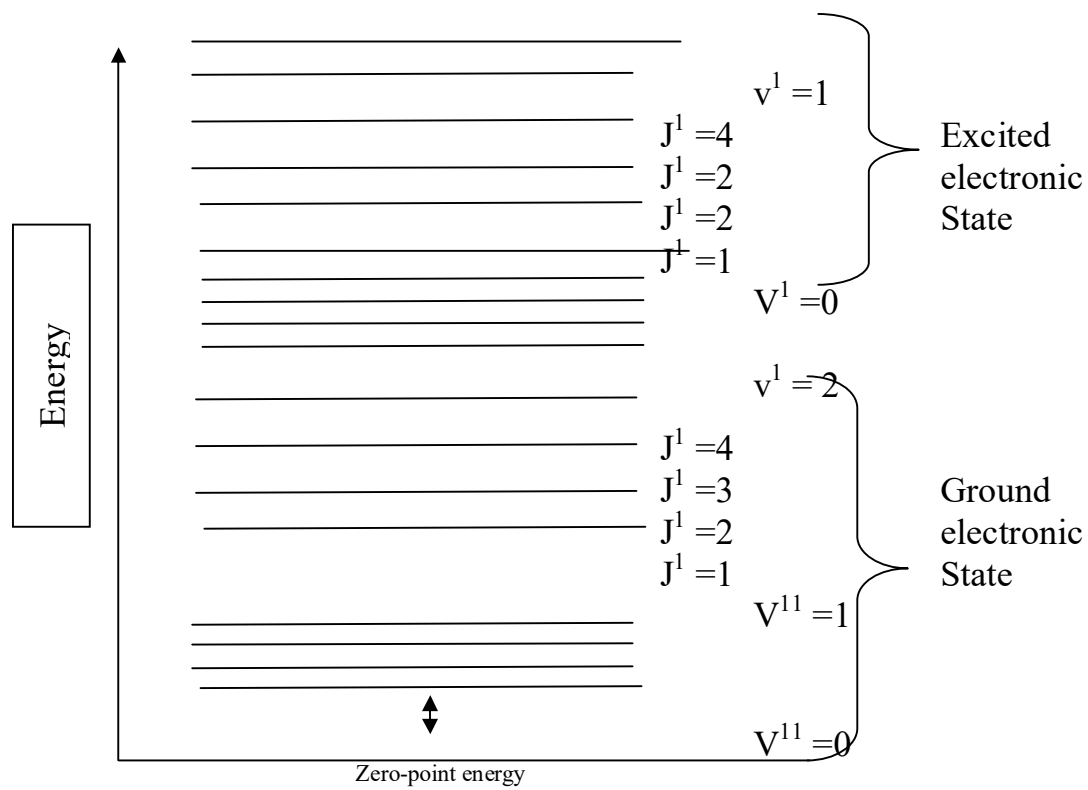
For diatomic molecule, rotational energy arises when the molecule rotates about an axis perpendicular to the internuclear axis and passing through centre of gravity of the molecule.

Vibrational energy is associated with the to and fro motion of the nuclei of the molecule such that centre of gravity does not change.

Electronic energy is associated with transition of an electron from ground state energy level to an excited state energy level of molecule by absorption of photon.

Associated with each electronic state are a series of vibrational energy levels (v) and associated with each vibrational energy level are series of rotational energy levels (J) as shown, single prime is higher energy level and double prime is lower energy level.

The rotational spectra obtained is microwave region vibrational region and electron spectra in the ultraviolet (UV) and visible regions of electromagnetic spectrum



1.6 Rotational Spectra: -

Classification of molecules-

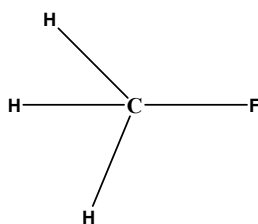
Body has three mutually perpendicular axes passing through centre of gravity, these are known as the principal axes of rotation. Thus body has three moments of inertia as I_A , I_B , I_C molecules are classified by their relative values of these three moments of inertia.

1. Linear molecule – In this all atoms in a molecule are arranged in a straight line such as HCl, carbon oxysulphide as H-Cl and O-C-S.

Now three directions of rotation are as follows.

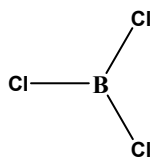
- a) About bond axis (I_A)
- b) end – over –end rotation in plane of paper (I_B)
- c) end- over –end rotation at right Here $I_B = I_C$ and I_A are very small; we assume that $I_A = 0$.

2. Symmetric Tops – Consider molecule $\text{CH}_3\text{-F}$ where 3H are bonded tetrahedral to C as follows.



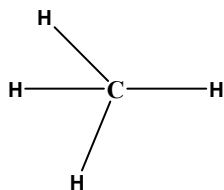
The moment of inertia about C – F bond is identical as $I_B = I_C$ and rotation about bond axis as is possible so $I_A \neq 0$ thus for symmetric tops, $I_B + I_C \neq I_A$ and $I_A \neq 0$.

There are two classes in this group, we have for CH_3F , $I_B + I_C > I_A$, then such molecule is called as prolate symmetric top, where as if $I_B + I_C < I_A$, then referred to as oblate symmetric top. example is BCl_3 in this $I_A + 2 I_B + 2 I_C$



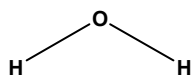
2. Spherical Tops- When molecule has all three moments of inertial identical, it is called as spherical tops, for ex CH₄

Spherical Top $I_A + I_B + I_C$

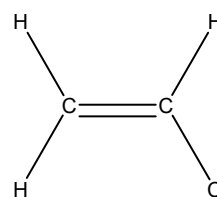


These molecules don't have dipole moments owing to their summity, so rotation alone can produce no dipole change and hence no rotational spectrum is observable.

- 3.



Water



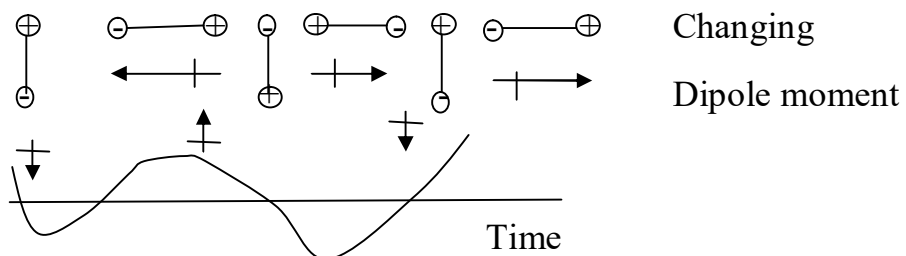
chloroethene

$$I_A \neq I_B \neq I_C$$

Note: -

The microwave region – HCl have permanent dipole moment H₂ and Cl₂ have zero dipole moment. During rotation of HCl about centre of gravity of the molecule so changes on H and Cl change places periodically and the component dipole moment in a given direction say upward direction fluctuates regularly. This fluctuation is plotted with time it is

exactly like fluctuating electric field of radiation, thus, interaction can occur energy absorbed or emitted gives rise to spectrum. If molecule have permanent dipole moment is microwave active so it is limited



1.7 Rotational spectra of diatomic molecule: -

Rotational energy is quantized. This means that rotational energy of a molecule has only certain discrete values as permitted by quantum rules, such values can be calculated by solving Schrödinger's equation for the system.

Consider a diatomic molecule in which M_1 , and M_2 are the masses of the two atoms and r_0 is the bond length, rotating about an axis passing through its centre of gravity, c.g.

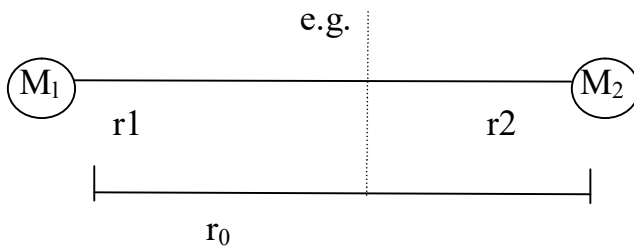


Fig. 1

From the definition of centre of gravity, moments must be equal

$$m_1 r_1 = m_2 r_2 \quad \text{-----(1)}$$

The moment of inertia I of a molecule is defined as

$$I = \sum m_i r_i^2 \quad \text{-----(2)}$$

Where

r_i = Distance of i^{th} particle from centre of gravity.

m_i = mass of i^{th} particle

For diatomic molecule, we have

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

$$I = m_1 r_1 r_1 + m_2 r_2 r_2$$

$$I = m_2 r_2 r_1 + m_1 r_1 r_2 \text{ from eq (1) } \quad \text{--- (1)}$$

$$I = r_1 r_2 (m_1 + m_2) \quad \text{--- (4)}$$

from fig.1. we have

$$r_0 = r_1 + r_2 \quad \text{--- (05)}$$

\therefore from eq (1) and (4) we have

$$m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$$

$$m_1 r_1 = m_2 (r_0 - r_1)$$

$$m_1 r_1 = m_2 r_0 - m_2 r_1$$

$$m_2 r_0 = m_1 r_1 + m_2 r_1 = r_1 (m_1 + m_2)$$

$$\therefore r_1 = \frac{m_2 r_0}{m_1 + m_2}$$

in same way

$$\therefore r_2 = \frac{m_1 r_0}{m_1 + m_2}$$

Substituting values of r_1 and r_2 in eq (04)

we get

$$I = \frac{m_2 r_0}{m_1 + m_2} \times \frac{m_1 r_0}{m_1 + m_2} m_1 + m_2$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 \text{-----(6)}$$

$$I = \mu r_0^2 \text{----(7)}$$

Where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is called as reduced mass.

By the use of Schrödinger's wave equation, we get rotational energy levels allowed to rigid diatomic molecule as

$$E_J = \frac{h^2}{8\pi^2 c} J(J + 1)$$

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

$h =$ Planck's constant

$I =$ Moment of inertia

The quantity J which can take integral values from zero upwards, is called as rotational quantum number, J values are obtained by Schrödinger's wave equation.

Equation (8) can also be written in other units of energy as cm^{-1}

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \text{-----(9)}$$

$$\bar{\nu} = \frac{\Delta E}{hc} \text{ cm}^{-1}$$

Where c is velocity of light in cm s^{-1}
from eq (9), we have

$$\varepsilon_j = B J(J+1) \text{ cm}^{-1} \text{ (10)}$$

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

Where B is rotational constant, is given by

$$B = \frac{h}{8\pi^2 I c} \text{-----(11)}$$

Using eq (10), we can show allowed energy levels diagrammatically as follows.



Fig.2 Allowed Rotational energy levels of a Rigid Atomic molecule

fig. 2 shows that for $J = 0$, $E_j = 0$ and $J = 1$, $\varepsilon_1 = 2B$, then rotating molecule has lowest angular momentum. As J value increases ε_j also increases.

Let us consider difference between the levels in order to explain spectrum. For ground rotational state $J = 0$, if the incident radiation is absorbed to raise it to $J = 1$ state, then energy absorbed will be

$$\varepsilon_{J=1} \rightarrow \varepsilon_{J=0} = 2B - 0 = 2B \text{ cm}^{-1} \text{ and therefore}$$

$\bar{\nu}_{J=1} \rightarrow \bar{\nu}_{J=0} = 2B \text{ cm}^{-1}$. The line will appear at $2B \text{ cm}^{-1}$.

If now molecule is raised from $J = 1$ to $J = 2$ level by absorption of radiation then

$$\varepsilon_{J=2} \rightarrow \varepsilon_{J=1} = 6B - 2B = 4B \text{ cm}^{-1}$$

$$\bar{\nu}_{J=1} \rightarrow \bar{\nu}_{J=2} = 4B \text{ cm}^{-1}.$$

The line will appear at $4B \text{ cm}^{-1}$. Now, in general, to raise the molecule from state J to next state $J + 1$, we have

$$\begin{aligned} \varepsilon_{J=J+1} \rightarrow \varepsilon_{J=J} &= B(J+1)(J+1+1) - BJ(J+1) \\ &= B(J+1)(J+2-J) \end{aligned}$$

$$= 2B(J+1) \text{-----(12)}$$

$$\bar{\nu}_{J=J} \rightarrow \bar{\nu}_{J=J+1} = 2B(J+1)$$

Thus, a series of rotational energy levels results in absorption spectrum consisting of lines at $2B, 4B, 6B, \text{ cm}^{-1}$ and similar lowering would result in identical emission spectrum. This is shown in following fig.

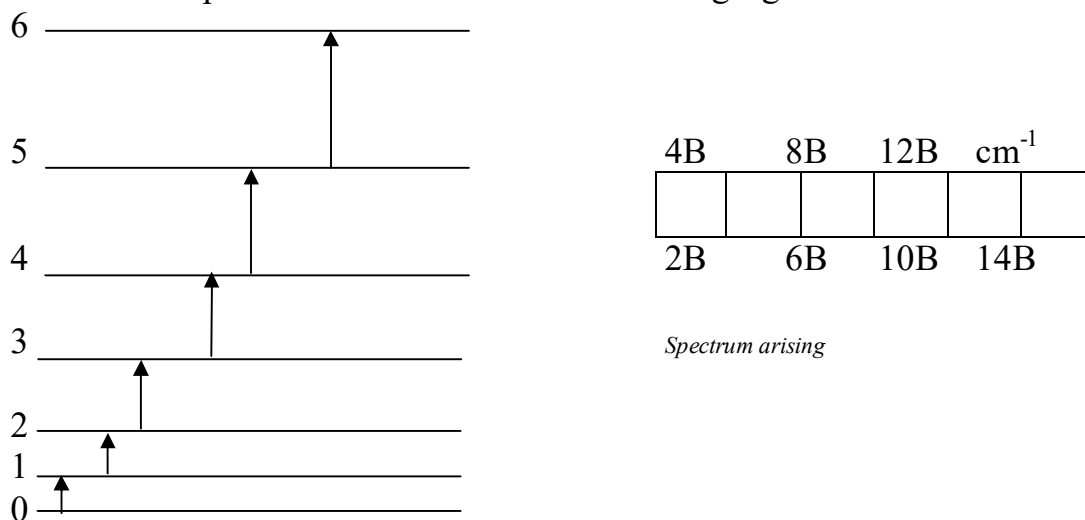


Fig.3

Allowed this pattern we have made one assumption that a transition can occur from a particular level. only to immediate neighbours either below or above. We have not considered transitions such as $J=0 \rightarrow J=2$, $J=2 \rightarrow J=4$ Thus, from Schrodinger's wave equation we have important rule that, we need only consider transition in which J changes by one unit and all other transitions

are spectroscopically forbidden. Such a result is called as a selection rule, and for rigid diatomic rotator as selection rule: $\Delta J = \pm 1$ -----(13)

Thus eq (12) gives the whole spectrum to be expected from rigid diatomic molecule.

Numerical – Gillion et al. Measured first line of CO at 3.84235 cm^{-1}

Hence to calculate bond length we have $B = 1.92118 \text{ cm}$.

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.626 \times 10^{-34}}{8(3.14)^2 1.92118 \times 3 \times 10^{10}} = 14.56954 \times 10^{-47}$$

Mass of C = $19.92168 \times 10^{-27} \text{ Kg}$

$$\text{O} = 26.56136 \times 10^{-27} \text{ Kg}$$

$$\text{H} = 1.00800 = 1.67343 \times 10^{-27} \text{ Kg}$$

$$\text{C} = 12.0000 \quad \text{O} = 15.9994$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{19.92168 \times 10^{-27} \times 26.56136 \times 10^{-27}}{19.92168 \times 10^{-27} + 26.56136 \times 10^{-27}}$$

$$\mu = 11.38365 \times 10^{-27} \text{ Kg}$$

$$r^2 = \frac{I}{\mu}$$

$$r^2 = \frac{14.56954 \times 10^{-47}}{11.38365 \times 10^{-27}} = 1.2799 \times 10^{-20} \text{ m}^2$$

Taking square root

$$r_{CO} = 0.1131 \text{ nm or } 1.131 \text{ \AA}$$

Numerical :-

1. The pure rotational spectrum of the gaseous molecule CN consists of series of equally spaced lines separated by 3.82 cm^{-1} , Calculate bond length of molecule $\mu = 1.0 \times 10^{-26} \text{ kg}$

Solution –

Given Data: As spectrum consist of equally spaced line,

$$\therefore 2B = 3.82 \text{ cm}^{-1}$$

$$B = 1.91 \text{ cm}^{-1}$$

$$\mu = 1.0 \times 10^{-26} \text{ kg}$$

$$c = 3 \times 10^{10} \text{ cms}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}^{-1}$$

Part I- Determine I using B

We have

$$B = \frac{h}{8\pi^2 I c} \text{ cm}^{-1}$$

$$\therefore I = \frac{h}{8\pi^2 B c} \text{ kgm}^2$$

$$I = \frac{6.626 \times 10^{-34}}{6.626 \times 10^{-34} \times 10^{-10}}$$

$$I = \frac{6.626 \times 10^{-34} \times 10^{-10}}{8 \times 3.14 \times 3.14 \times 1.91 \times 3}$$

$$I = \frac{6.626 \times 10^{-44}}{451.964064} = \frac{662.6 \times 10^{-46}}{451.964064}$$

$$I = 1.4660457 \times 10^{-46} \text{ Kgm}^2$$

Part II- Determine r_0

We have

$$I = \mu r_0^2$$

$$\therefore r_0^2 = \frac{I}{\mu}$$

$$= \frac{1.4660457 \times 10^{-46}}{1.0 \times 10^{-26}}$$

$$r_o = \sqrt{1.4660457 \times 10^{-10}} m$$

$$r_o = \sqrt{1.2108037 \times 10^{-10}} m$$

$$r_o = 1.2108037 \text{ \AA}$$

Thus, bond length of CN is 1.2108097 \AA

Numerical 2 :-

A pure rotational spectrum of gaseous molecule consists of series of equally spaced lines separated by 3.6 cm^{-1} . Calculate bond length of the molecule.

$$(\mu = 1.0 \times 10^{-23} g)$$

Solution :-

In rotational spectrum separation of lines is equal to $2B \text{ cm}^{-1}$

Given Data:

$$\therefore 2B = 3.6 \text{ cm}^{-1}$$

$$B = 1.8 \text{ cm}^{-1}$$

$$\mu = 1.0 \times 10^{-23} g = 1.0 \times 10^{-26} kg$$

$$\mu = 1.0 \times 10^{-26} kg$$

$$c = 3.10^{10} \text{ cms}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ J.s}$$

Part I Calculate I using B:

We have

$$B = \frac{h}{8\pi^2 Ic} \text{ cm}^{-1}$$

$$\therefore I = \frac{h}{8\pi^2 Bc} \text{ kgm}^2$$

$$\begin{aligned} \therefore I &= \frac{6.626 \times 10^{-34}}{8 \times 3.01 \times 3.14 \times 1.8 \times 3 \times 10^{-10}} \\ &= \frac{6.626 \times 10^{-34} \times 10^{-10}}{8 \times 3.14 \times 3.14 \times 1.8 \times 3} \end{aligned}$$

$$I = \frac{6.626 \times 10^{-44}}{425.93472} = \frac{662.6 \times 10^{-46}}{425.93472}$$

$$I = 1.555637 \times 10^{-46}$$

Part II: Calculate I using B

We have

$$I = \mu r_o^2$$

$$r_o^2 = \frac{I}{\mu}$$

$$= \frac{1.555637 \times 10^{-46}}{1.0 \times 10^{-26}}$$

$$= 1.555637 \times 10^{-46} \times 10^{+26}$$

$$r_o^2 = 1.555637 \times 10^{-20}$$

Taking square root

$$r_o = \sqrt{1.555637 \times 10^{-20}}$$

$$= 1.2472517 \times 10^{-10} m$$

$$r_o = 1.2472517 \text{ \AA}$$

1.8 Isotope effect:

When a particular atom in a molecule is replaced by its isotope the resulting substance is identical chemically with the original. There is no change in bond distance on isotopic substitution but there is a change in total mass and hence in moment of inertia and B value for the molecule.

Let us consider CO molecule, Isotope change from $^{12}\text{C } ^{16}\text{O}$ to $^{13}\text{C } ^{16}\text{O}$ there is mass increase and hence decrease in B value, if we designate B' value for ^{13}C then $B' < B$. This change will be reflected in rotational energy levels of molecule and shows lowering of ^{13}C Levels with respect to ^{12}C , for heavier species smaller separation between lines $2B'$ than that of lighter one $2B$.

This observation is very useful for the determination of precise atomic weights

For $^{12}\text{C } ^{16}\text{O}$ the $2B = 3.84235 \text{ cm}^{-1}$ and $^{13}\text{C } ^{16}\text{O}$, $2B' = 3.67337 \text{ cm}^{-1}$ thus B values are

$$B = 1.92118 \text{ cm}^{-1} \text{ and } B' = 1.83669 \text{ cm}^{-1}$$

thus

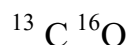
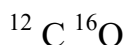
$$\frac{B}{B'} = \frac{h}{8\pi^2 I c} \times \frac{8\pi^2 I^1 c}{h} = \frac{I^1}{I} = \frac{\mu^1}{\mu} = 1.846$$

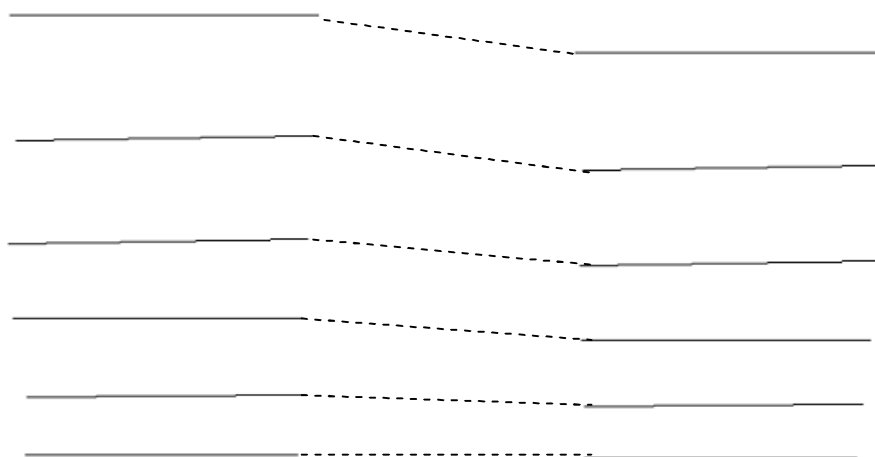
$$\frac{\mu^1}{\mu} = \frac{B}{B'} = \frac{1.92118}{1.83669}$$

$$\frac{\mu^1}{\mu} = 1.4046$$

$$1.4046 = \frac{15.9994 m^1}{15.9994 + m^1} \times \frac{12 + 15.9994}{12 \times 15.9994}$$

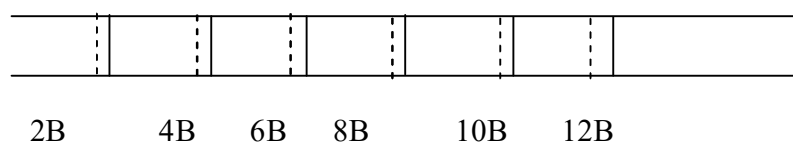
$M1 = 13.0007$ (0.02 % best value) The energy levels are





The effect of isotopic substitution on the energy levels of carbon monoxide

2B' 4B' 6B' 8B' 10B' 12B'



1.9 Qualitative Description of non-rigid Rotor:-

The Schrödinger's wave equation for nonrigid molecule and the rotational energy level are as follows

$$E_J = \frac{h^2}{8\pi^2J}J(J+1) - \frac{h^4}{32\pi^4I^2r^2k^2}J^4(J+1)^2 \text{ joule}$$

or

$$\varepsilon_J = \frac{E_J}{hc} = B J(J+1) - DJ^2 (J+1)^2 \text{ cm}^{-1}$$

Where B is rotational constant and D is centrifugal distortion constant D is given

$$\text{by } D = \frac{h^3}{32\pi^4I^2rk} \text{cm}^{-1}$$

D is positive quantity and applies for a simple harmonic force field only, but if the force field is enharmonic then expression becomes

$$\varepsilon_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 + \dots \dots \text{cm}^{-1}$$

Where H, K etc. are small constants depends up on geometry of the molecule they can be neglected. From the defining equations of B and D we have

$$D = \frac{16B^3\pi^2\mu c^2}{k} = \frac{4B^3}{\omega^2} \quad \boxed{\because k = 4\pi^2\bar{\omega}^2c^2}$$

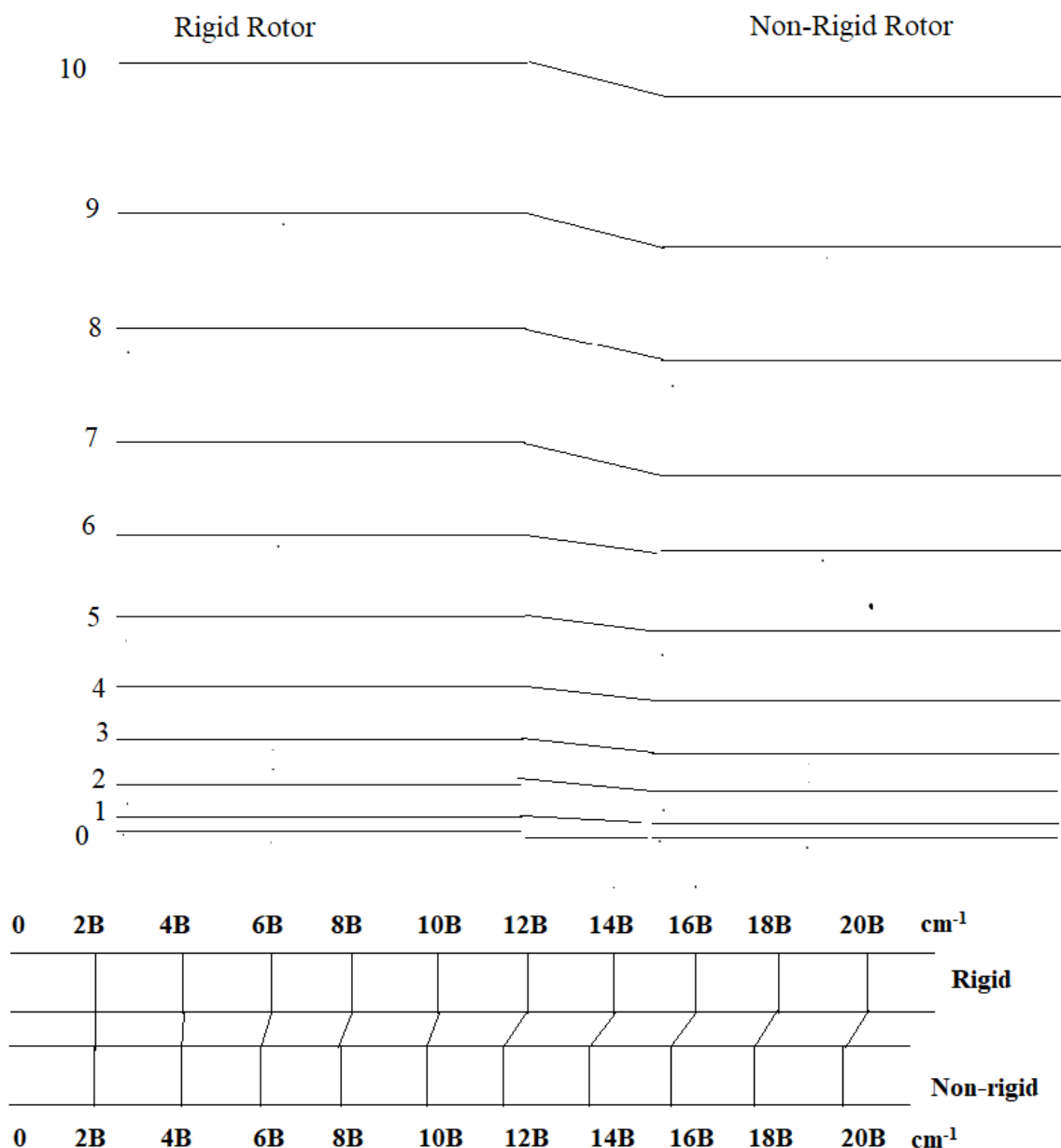
Where $\bar{\omega}$ is vibration frequency of bond, K is force constant. The value of D (order 10^{-3} cm^{-1}) is very small as compared with B value (10cm^{-1}) and is negligible when J value is less than J = 0 But for higher J value, J = 0 or more its value is appreciable.

Let us consider spectra of non-rigid diatomic molecule. The expression for the transitions as follows. It should be noted that $\Delta J = \pm 1$ thus

$$\begin{aligned} \varepsilon_{J=J+1} &\rightarrow \varepsilon_{J=J} \\ &= [B(J+1)(J+1+1) - D(J+1)^2(J+1+1)^2] - [BJ(J+1) \\ &\quad - DJ^2(J+1)^2] \end{aligned}$$

$$\begin{aligned}
 &= B[J + 1)(J + 2) - J(J + 1)] - D[(J + 1)^2(J + 2)^2 - J^2(J + 1)^2] \\
 &= 2B(J + 1) - 4D(J + 1)^3 \text{ cm}^{-1}
 \end{aligned}$$

$\bar{\nu}_J$ represents equally the upward transition from J to $(J+1)$, or downward from $(J+1)$ to J . The spectrum is similar to rigid rotor except each line is displaced slightly to low frequency and it increases with $(J+1)^3$ i.e. J value.



1.10 Vibrational Spectra:

The Energy of Diatomic Molecule:

A diatomic molecule formed by the combination of two atoms like HCl, here H atom, Cl atom rearrange themselves to form stable bond. The bond formation may be regarded as a balancing of forces arising out of the electron-electron and nucleus-nucleus repulsion and electron-nucleus attraction. The final result is the loss of energy. The two atoms settle at a mean inter nuclear distance such that these forces are just balanced and the total energy of system is a minimum. Squeezing the atoms closely together will cause the repulsive force to rise rapidly, while pulling them apart is resisted by the attractive force. Any attempt to distort the bond length requires an input of energy. If we plot energy against inter nuclear distance where we consider Cl atom is fixed on y-axis and imagine pushing and pulling of H atom closer to or further from the Cl atom, a bigger pushing pulling of H atom closer to or further from the Cl atom, a bigger push results in raising the energy more. The At equilibrium inter nuclear distance energy is minimum i.e. at req. or bond length.

The covalent bond in this case behave like spring and obeys Hooks law, and restoring force is given as

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

f – Restoring Force

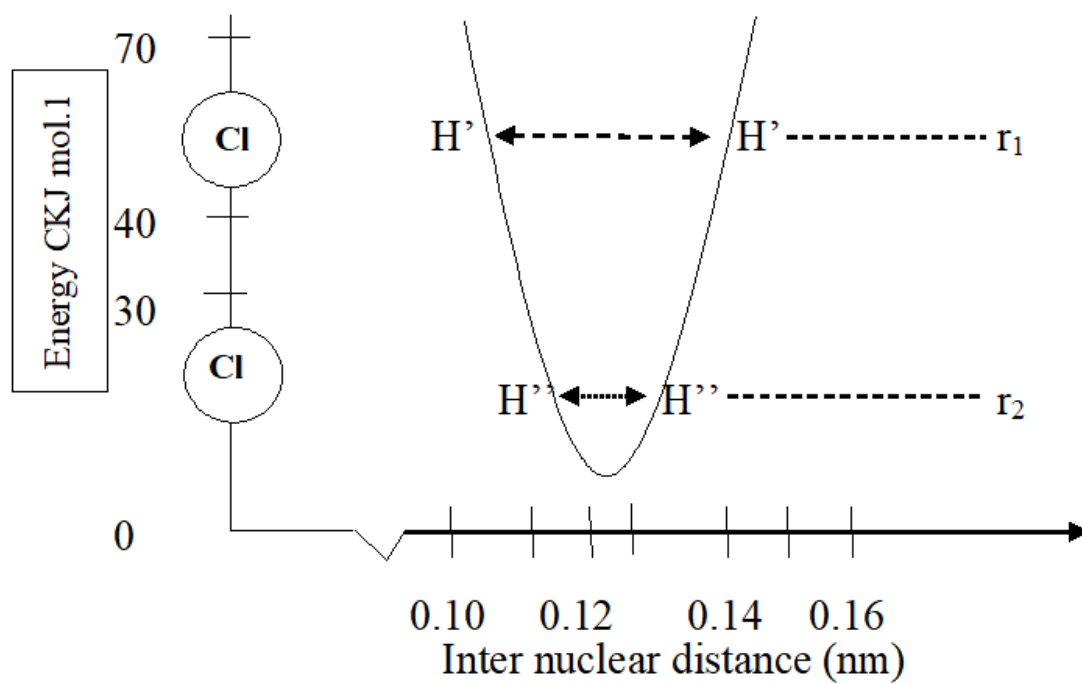
k – Force constant

r – Inter nuclear distance

In this case energy curve is parabolic and has the form.

$$E = \frac{1}{2}K(r - r_{eq})^2$$

Such model of vibrating diatomic molecule is called as simple harmonic



1.11 The Simple Harmonics Oscillator:-

When we plot energy against bond length for simple harmonic oscillator curve is a parabola. The zero of curve and equation at $r = r_{eq}$, and r_2 arises due to extension or compression of the bond, the figure shows that one atom (Cl) is fixed on axis at $r = o$ and other atom (H) will oscillate between H^1 and H^1 . During vibration heavy chlorine atom vibrates.

When energy of for ex HCl molecule increases to r_1 the oscillation will become more vigorous but note that vibration frequency depends on the mass of atoms and force constant (K) but does not depend on amount of distortion.

Classically the oscillation frequency is given by following equation

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz} \text{ ----- (1)}$$

Where,

μ – Reduced Mass

k – Force constant

Converting unit of frequency from Hz to cm^{-1} divide it by velocity of light C

$$\bar{\omega}_{osc} = \frac{\omega_{osc}}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Vibrational energies are quantized and allowed vibrational energy can be calculated from the Schrodinger's equation. For simple harmonic oscillator these are given as

$$E_v = \left(v + \frac{1}{2}\right) h \omega_{osc} \text{ Joules} \text{ ----- (3)}$$

$$v = 0, 1, 2, 3, \dots$$

V is vibrational quantum number converting units we get (divide it by hc)

$$\varepsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \frac{h\nu_{osc}}{hc}$$

$$\varepsilon_v = \left(v + \frac{1}{2}\right) \frac{h\nu_{osc}}{c} \text{ cm}^{-1}$$

$$\varepsilon_v = \left(v + \frac{1}{2}\right) \omega_{osc} e$$

The eq. (4) gives the only energies allowed to a simple harmonic vibrator. The lowest vibrational energy can be calculated by putting $v = 0$ thus

$$E_0 = \frac{1}{2} h\nu_{osc} \text{ joules}$$

or

$$\varepsilon_0 = \frac{1}{2} \omega_{osc} \text{ cm}^{-1}$$

The above expression shows that the diatomic molecule can never have zero vibrational energy the atoms can never be completely at rest relative to each other. The quantity $\frac{1}{2} h \nu_{osc}$ joule or $\frac{1}{2} \omega_{osc}$ is called as zero-point energy, it depends on classical vibrational frequency and hence strength of chemical bond and atomic masses.

Selection Rule:-

Schrodinger equation leads to simple selection rule for the harmonic oscillator undergoing vibrational changes $\Delta v = \pm 1$

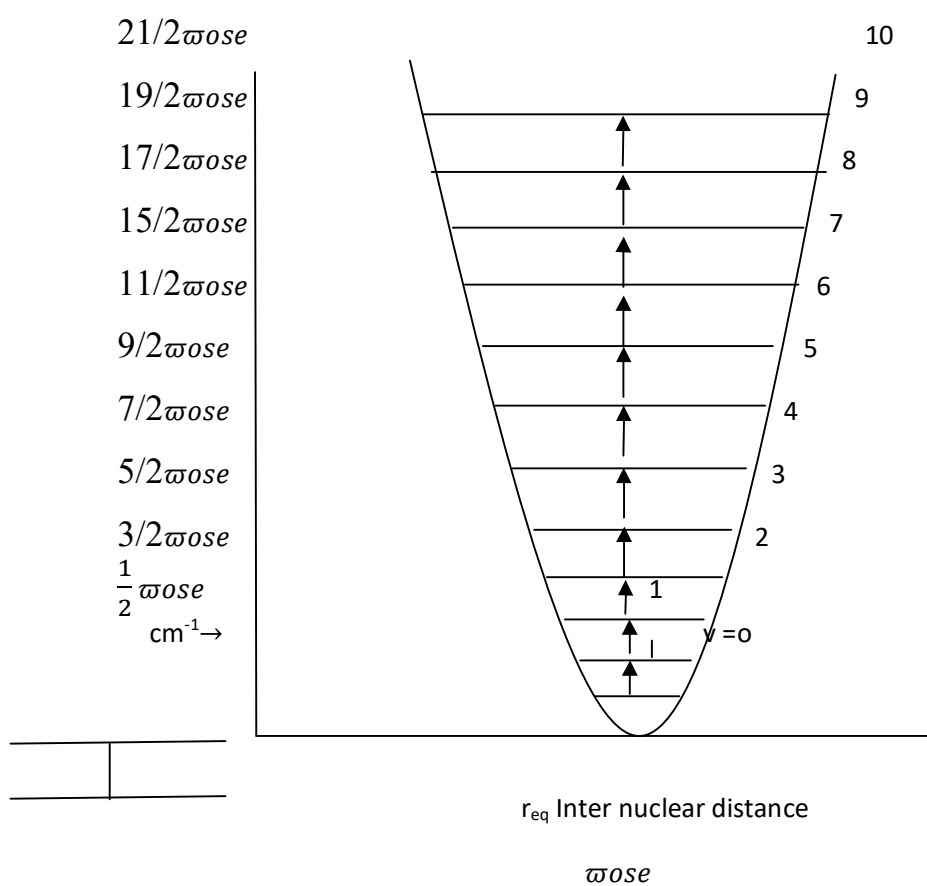
$\Delta v = +1$, Corresponds to the absorption spectra increase in vibrational quantum number.

$\Delta v = -1$, Corresponds to emission spectra. To obtain spectra we have one condition that vibrational energy changes will only give rise to spectrum. If the vibration can interact with radiation i.e. If the vibration involves a change in the dipole moment of the molecule Thus vibrational spectra is only observable in heteronuclear molecule since homo nuclear diatomic molecule have no dipole moment.

Applying selection rule, we have transition from v to $v+1$ is

$$\begin{aligned}\varepsilon_{\nu+1} \rightarrow \varepsilon_{\nu} &= \left(\nu + 1 + \frac{1}{2}\right) \omega_{osc} - \left(\nu + \frac{1}{2}\right) \omega_{osc} \\ &= \omega_{osc} \left[\nu + 1 + \frac{1}{2} - \nu \frac{1}{2}\right]\end{aligned}$$

$= \omega_{osc} \text{ cm}^{-1}$ for emission and $\varepsilon_{\nu} \rightarrow \nu + 1 = \omega_{osc} \text{ cm}^{-1}$ for absorption whatever the value of ν , $= \omega_{osc}$ is same. Thus, transition between any two neighbouring states will give rise to same energy change.



1.12 Force constant:

The force constant K of bond can be determined by using vibrational frequency or wave number, we know that vibrational frequency is

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

The vibrational ω_{osc} is known from IR spectrum of the molecule containing particular bond. The reduced mass μ can be given by equation

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ for m_1 & m_2 in kg. and If m_1 and m_2 are given as atomic masses then

$$\mu = \left(\frac{m_1 m_2}{m_1 + m_2} \right) \times \frac{1}{NA} \text{ gm/mole}$$

C is velocity of light (in cgs unit) i.e. $c = 3 \times 10^{10}$ cm/s then K can be given as

$$K = 4\pi^2 \omega_{osc}^2 c^2 \mu$$

1.13 The Anharmonic Oscillator Pure Vibrational Spectra:

Real molecule does not obey exactly Hooke's law. If the bond is stretched there comes a point at which it will break. The molecule dissociates into atom, when molecule is stretched greater than 10% of bond length much more complicated behaviour must be assumed, the shape of the energy curve for diatomic molecule, the ideal simple harmonic parabola is also shown by dashed lines.

The empirical expression was derived by P.M. Morse is called as Morse function

$$E = D_{eq} [1 - \exp \{r_{eq} - r\}]^2 \text{----(1)}$$

Where,

- E = Energy of anharmonic Oscillator
- D_{eq} = Constant for a particular molecule
- a = Constant for a particular molecule
- r_{eq} = Equilibrium bond distance or bond length.

r = Bond length during vibration

We can write

$$E = D_{eq} \cdot [1 - e^{a(r_{eq}-r_1)}]^2$$

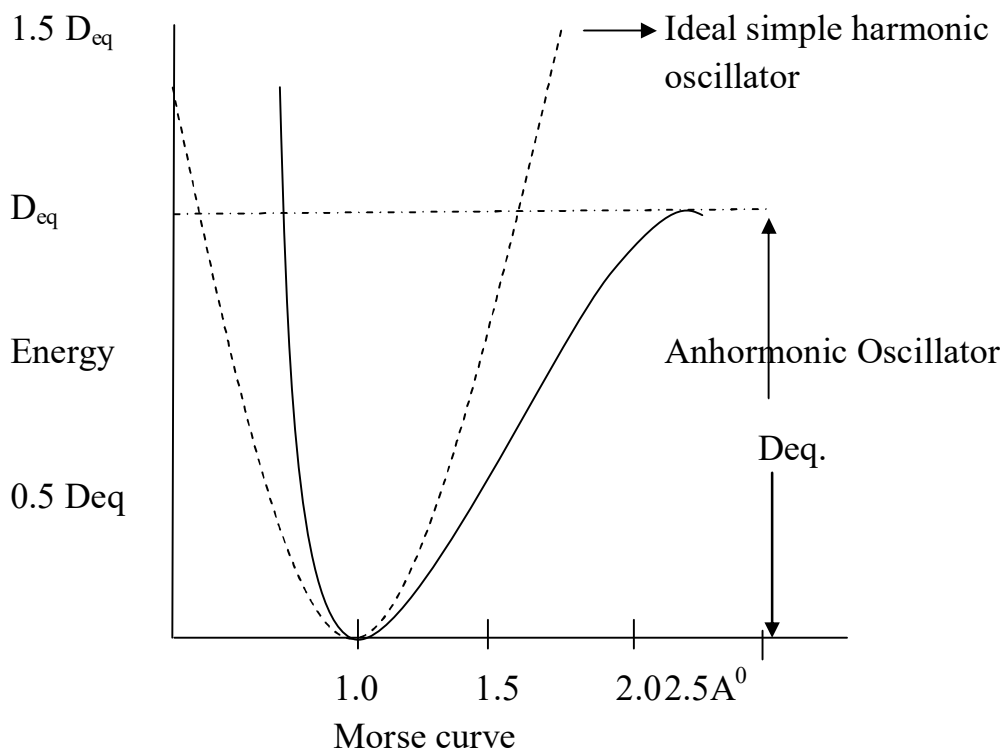
When eq (1) is used in the Schrödinger's equation for anharmonic oscillator the pattern of allowed vibrational energy level is found to be

$$\epsilon_v = \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right) \omega_e x_e \text{ cm}^{-1}$$

Where $V = 0,1,2,3, \dots$ ω_e = Oscillation frequency in cm^{-1}

x_e = anharmonicity constant for small bond stretch it is positive and 0.01.

The spacing between lines decreases with increase in V value.



From eq (2) we can write

$$\epsilon_v = \omega_e \left\{1 - x_e \left(v + \frac{1}{2}\right)\right\} \left(v + \frac{1}{2}\right) \text{-----(3)}$$

Comparing eq. (3) with equation of simple harmonic oscillator

$$\epsilon_v = \left(v + \frac{1}{2}\right) \omega$$

We get,

$$\omega_{osc} = \omega_e \left\{ 1 - x_e \left(v + \frac{1}{2} \right) \right\}$$

From eq.(5) we conclude that the anharmonic oscillator behaves like harmonic oscillator but when v value increases frequency decreases (ω_e)

If we put $v = -\frac{1}{2}$ then

$$\omega_{osc} = \omega_e \left\{ 1 - x_e \left(-\frac{1}{2} + \frac{1}{2} \right) \right\}$$

$$\omega_{osc} = \omega_e \text{ -----(6)}$$

thus ω_e , Oscillation frequency of anharmonic oscillator as (hypothetic) equilibrium frequency of anharmonic system.

Let us consider around state, $v = 0$

Then,

$$\omega_0 = \omega_e \left(1 - \frac{1}{2} x_e \right) \text{ cm}^{-1}$$

and

$$\epsilon_0 = \frac{1}{2} \omega_e \left(1 - \frac{1}{2} x_e \right) \text{ cm}^{-1}$$

The zero-point energy differs slightly from that of harmonic oscillator.

Selection Rule:-

The selection rule for anharmonic oscillator was found to be

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

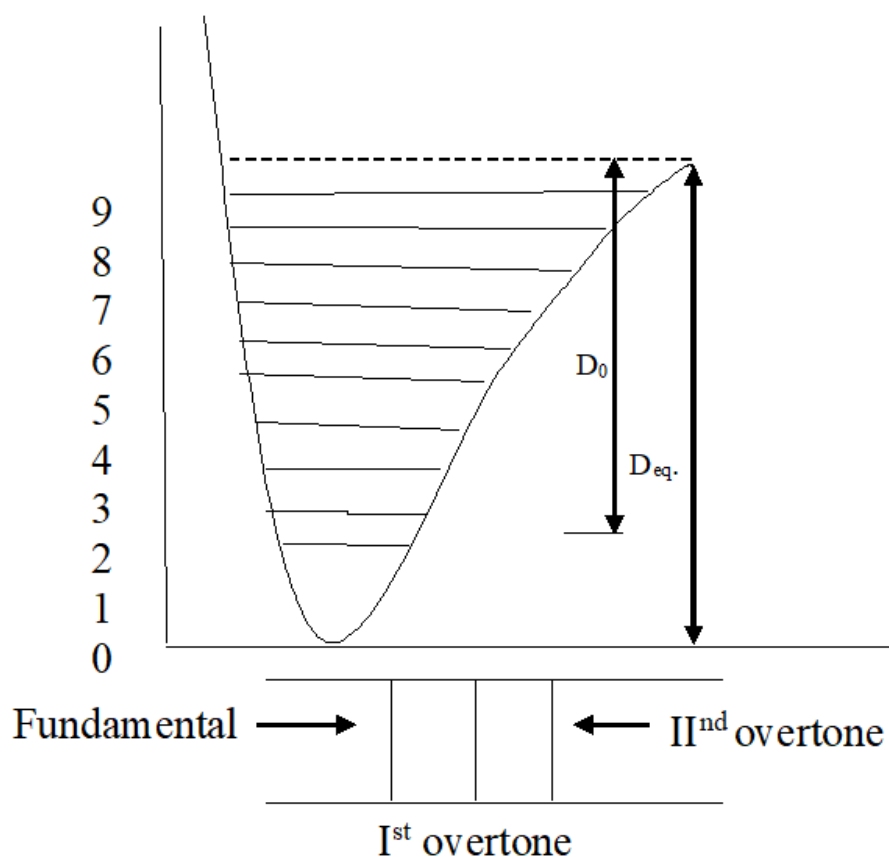
$$v = 0 \rightarrow v = 1, \Delta v = +1$$

$$\Delta \epsilon = \epsilon_{v=1} - \epsilon_{v=0}$$

$$\Delta \epsilon = \omega_e (1 - 2x_e) \text{ cm}^{-1} \text{ called as fundamental vibration.}$$

$$\Delta v = \pm 2$$

$$\Delta \epsilon = \epsilon_{v=0} - \epsilon_{v=2} = 2\omega_e (1 - 3x_e) \text{ cm}^{-1} \text{ called as First overtone}$$

**Numerical :-**

1. The fundamental vibrational frequency of HCl is 2886 cm^{-1} . Calculate the force constant of molecule if masses are

$$\text{H} = 1.67 \times 10^{-27} \text{ kg}$$

$$\text{Cl} = 58.06 \times 10^{-27} \text{ kg}$$

$$\omega_{\text{osc}} = 2886 \text{ cm}^{-1}$$

$$C = 3 \times 10^{10} \text{ cm/s}$$

Solution:-

Given data:

$$\text{H} = 1.673 \times 10^{-27} \text{ kg}$$

$$\text{Cl} = 58.06 \times 10^{-27} \text{ kg}$$

$$\omega_{\text{osc}} = 2886 \text{ cm}^{-1}$$

$$C = 3 \times 10^{10} \text{ cm/s}$$

Calculate μ

$$\begin{aligned} \mu &= \frac{m_1 m_2}{m_1 + m_2} = \frac{1.673 \times 10^{-27} \times 58.06 \times 10^{-27}}{1.673 \times 10^{-27} + 58.06 \times 10^{-27}} \\ &= 1.6261 \times 10^{-27} \text{ kg} \end{aligned}$$

We have

$$\begin{aligned} K &= 4\pi^2 \omega_{osc}^2 C^2 \mu \\ K &= 4 \times 3.14 \times 3.14 \times 2886 \times 2886 \times 3 \times 10^{10} \times 3 \times 10^{10} \\ &\quad \times 1.6261 \times 10^{-27} \\ &= 4 \times 3.14 \times 3.14 \times 2.886 \times 2.886 \times 10^6 \times 9 \times 10^{20} \\ &\quad \times 1.6261 \times 10^{-27} \\ &= 4 \times 3.14 \times 3.14 \times 2.886 \times 2.886 \times 0.9 \times 10^{27} \\ &\quad \times 1.6261 \times 10^{-27} \\ &= 480.7305 \text{ Nm}^{-1} \end{aligned}$$

2. The absorption of infrared radiation by CO molecule showed an absorption band at 2140 cm^{-1} . Calculate the bond force constant of the C-O Bond.

$$(\mu = 1.14 \times 10^{-26}) \text{ kg}$$

Given data :

$$\omega_{osc} = 2140 \text{ cm}^{-1}$$

$$C = 3 \times \frac{10^{10} \text{ cm}}{\text{s}}$$

$$\mu = 1.14 \times 10^{-26}$$

We have:

$$\begin{aligned}
K &= 4\pi^2 \bar{\omega}^2 \text{osc} \mu \\
&= 4 \times 3.14 \times 3.14 \times 3 \times 10^{10} \times 10^{10} \times 2140 \times 2140 \\
&\quad \times 1.14 \times 10^{-26} \\
&= 4 \times 3.14 \times 3.14 \times 9 \times 10^{20} \times 2.140 \times 2.140 \times 10^6 \\
&\quad \times 1.14 \times 10^{-26} \\
&= 4 \times 3.14 \times 3.14 \times 9 \times 2.14 \times 2.14 \times 10^{26} \\
&\quad \times 1.14 \times 10^{-26} \\
&= 1853.080 \text{ Nm}^{-1}
\end{aligned}$$

3. The fundamental vibration frequency of $\text{I} + \text{Cl}$ molecule was found to be at 2886 cm^{-1} Calculate force constant

$$(\mu = 1.661 \times 10^{-27}) \text{ kg}$$

Given data :

$$\bar{\omega} \text{osc} = 2886 \text{ cm}^{-1}$$

$$\mu = 1.66 \times 10^{-27} \text{ kg}$$

$$C = 3 \times \frac{10^{10} \text{ cm}}{\text{s}}$$

We have

$$\begin{aligned}
K &= 4\pi^2 C^2 \bar{\omega}_{\text{osc}}^2 \mu \\
&= 4 \times 3.14 \times 3.14 \times 3 \times 10^{10} \times 3 \times 10^{10} \times 2886 \times 2886 \\
&\quad \times 1.661 \times 10^{-27} \\
&= 4 \times 3.14 \times 3.14 \times 9 \times 10^{20} \times 2.886 \times 2.886 \times 10^6 \\
&\quad \times 1.661 \times 10^{-27} \\
&= 4 \times 3.14 \times 3.14 \times 0.9 \times 10^{21} \times 2.886 \times 2.886 \times 10^6
\end{aligned}$$

$$\begin{aligned} & \times 1.661 \times 10^{-27} \\ = & 491.0481 \text{ Nm}^{-1} \end{aligned}$$

4. Calculate the frequency of vibration of HF molecule if force constant for HF molecule is 967 Nm^{-1}

$$\begin{aligned} H &= 1.673 \times 10^{-27}, F = 31.55 \times 10^{-27} \\ [\mu &= 1.5887 \times 10^{-27}] \text{ kg} \end{aligned}$$

Given data :

$$\begin{aligned} K &= 967 \text{ Nm}^{-1} \\ \mu &= 1.5887 \times 10^{-27} \text{ kg} \\ C &= 3 \times 10^{10} \text{ cms}^{-1} \end{aligned}$$

We have

$$\begin{aligned} \omega_{osc} &= \frac{1}{2\pi C} \sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2\pi C} \times \sqrt{\frac{967}{1.5887 \times 10^{10}}} \\ &= \frac{1}{2 \times 3.14 \times 3 \times 10^{10}} \sqrt{608.6737 \times 10^{27}} \\ &= \frac{10^{13} \times 78.01754}{2 \times 3.14 \times 3 \times 10^{10}} = 4.14105 \times 10^{13} \times 10^{10} \\ \omega_{osc} &= 4141.05 \text{ cm}^{-1} \end{aligned}$$

1.14 Questions:

1. Derive an expression for rotational spectra of diatomic molecule?
2. Explain In brief Molecular spectra?
3. Derive an expression for energy level of rotational spectra of Diatomic molecule?
4. Prove that the difference between two successive lines of rotational spectra Is $2B$?
5. Derive an expression for energy level of vibrational spectra?
6. Define: a. Wavelength b. wave number c. frequency
7. Explain factors affecting Width of spectral lines?
8. Write a note on natural line width?
9. Explain In brief Intensity of spectral lines?
10. Prove $I = \mu r_0^2$
11. A pure rotational spectrum of gaseous molecule consists of series of equally spaced lines separated by 4.0 cm^{-1} . Calculate bond length of the molecule?
($\mu = 1.0 \times \times 10^{-23} \text{ gm}$)
12. What is isotopic effect on rotational spectra of diatomic molecule?
13. Derive an expression for energy level of pure vibrational spectra of Diatomic molecule?

14. The fundamental vibrational frequency of HCl is 2880 cm^{-1} . Calculate the force constant of molecule?
15. What is zero point energy ?
16. Explain in brief spectra of anharmonic oscillator?

Unit 2:Spectroscopy-II

2.1 Raman Spectroscopy

Raman Scattering :- If monochromatic radiation or radiation of very narrow frequency band is used, the scattered energy or radiation will almost consist of entirely of radiation of incident frequency called as Rayleigh scattering but in addition contain certain discrete frequencies above and below that of incident radiation will be scattered this is referred as Raman scattering .

When the scattered radiations have frequencies below the incident radiation frequency are called as Stokes lines.

When the scattered radiations have frequencies more than the incident radiation frequency are called as anti-stokes lines.

Normally scattered radiations consist of Rayleigh line, which are having highest intensity and stoker lines show very less intensity and lowest intensity is given by anti-Stokes lines.

2.2 Quantum theory of Raman effect :-

Raman Scattering may be most easily understood in terms of quantum theory of radiation consist of stream of Particles called photon with frequency V . The energy of photons is $E = h\nu$, where h is planks constant.

According to this theory photos are considered to undergo collisions with molecule and if the collisions is perfectlyelastic, they will be deflected unchanged. Thus, detector receive photon of energy $h\nu$, i.e radiation with frequency V , thus rayleigh line or rayleigh scattering is obtained. Elastic

scattering can be likened to a ball bearing striking a rigid table- The ball bearing bounces off the table, without any loss of energy.

ΔE joules must be equal to change in vibration or rotational or both energy levels of molecule. If molecule gains energy ΔE , the energy of scattered photon will be less and its energy is equal to $(h\nu - \Delta E)$ joules and the frequency of scattered photon will be lesser, i.e. $\left(\nu - \frac{\Delta E}{h}\right)$ thus we get

Stokes Lines.

But if molecule loses energy ΔE the scattered radiation got higher energy i.e. $(h\nu + \Delta E)$ joules and frequency of scattered radiation will be $\left(\nu + \frac{\Delta E}{h}\right)$, thus we get antismoke lines with higher frequency than the frequency of incident radiation.

The above inelastic process can be pictured in terms of ball striking drum. If the surface of drum is stationary when the ball bearing hits, it will start oscillating at its own normal frequency and the ball bearing will loss energy to drum and it will be reflected with less energy this resembles explanation of stokes lines. If the drum is already oscillating, the drum will give energy to ball bearing, the ball bearing flung off with increased energy. This give idea about anti stokes lines.

2.3 Classical Theory of the Raman effect :-

The classical theory of Raman effect also called the Polarizability theory. When a molecule is put into static electric field E associated with the electromagnetic radiation induces dipole moment u in the molecule and the molecule said to be polarized. The size of induced dipole moment μ depend up on magnitude of E and Polarizability of molecule, thus

$$\mu = \alpha E \text{-----} (1)$$

Where,

μ is induced dipole moment

α is polarizability of molecule.

When a sample of such molecules is subjected to a beam of radiation of frequency ν the electric field experienced by each molecule varies with equation.

$$E = E_0 \sin 2\pi \nu t \text{-----} (2)$$

Thus, the induced dipole also undergoes oscillation of frequency ν i.e. undergoes oscillations of frequency ν i.e.

$$\mu = \alpha E$$

$$\mu = \alpha E_0 \sin 2\pi \nu t \text{-----}(2)$$

Such an oscillating dipole emits radiation of its own oscillation frequency giving Rayleigh scattering.

If Polarizability α , varies due to internal motion such as vibration, then the oscillating dipole changes with ν vib with value.

$$\alpha = \alpha_0 + \beta \sin 2\pi \nu_{vib} t \text{-----}(4)$$

Where,

$$\mu = \alpha E$$

$$\mu = (\alpha_0 + \beta \sin 2\pi \nu_{vib} t)(E_0 \sin 2\pi \nu t)$$

$$\mu = (\alpha_0 E_0 \sin 2\pi \nu t + E_0 \beta (\sin 2\pi \nu_{vib} t)(\sin 2\pi \nu t))$$

using trigonometric relation,

$$\sin A \sin B = \frac{1}{2} \{ \cos(A - B) - \cos(A + B) \}$$

We have,

$$\mu = \left(\alpha_0 E_0 \sin 2\pi \nu t \right) + E_0 \beta \frac{1}{2} \left\{ \cos(2\pi \nu t - 2\pi \nu_{vib} t) - \cos(2\pi \nu t + 2\pi \nu_{vib} t) \right\}$$

$$\mu = \left(\alpha_0 E_0 \sin 2\pi \nu t \right) + \frac{1}{2} \left\{ \cos(2\pi(\nu - \nu_{vib})t) - \cos(2\pi(\nu + \nu_{vib})t) \right\} \text{-----(5)}$$

Thus, from eq (5), we found that the oscillating dipole has components $(\nu \pm \nu_{vib})$ as well as exciting frequency ν . Thus if oscillating dipole frequency decreases, we get Stokes lines and when oscillating dipole frequency increases, we get anti Stokes lines.

However, if there is no change in polarizability i.e. $B=0$, eq (5) gets the form of eq (4) and Rayleigh lines are obtained.

2.4 Pure Rotational Raman Spectra :-

The rotational energy levels of linear molecules have the form

$$E_J = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-2} (J=0,1,2,3,\dots)$$

But in Raman Spectroscopy, the precise determination of D , the Centrifugal distortion Constant, is not possible therefore neglecting the term containing D , if take simple form $E_J = BJ(J+1) \text{ cm}^{-2} (J=0,1,2,3,\dots)$ to represent energy levels.

The selection rule for pure rotational Raman Spectrum is

$$\Delta J = 0 \neq 2$$

Because the Raman work the rotational quantum number changes by two units which is due to symmetry of Polarizability ellipsoid.

Since $\Delta J = -2$ for correspond to Rayleigh scattering $\Delta J = -2$ for anti Stokes and $\Delta J = +2$ for Stokes lines.

Using $\Delta J = +2$ in eq (2) we get absorption lines called s branch

$$\begin{aligned} \Delta \epsilon_{J1} &= J + 1 - \epsilon_{J11} = J \\ &= B(J+2)(J+2+1) - B J (J+1) \text{ cm}^{-1} \\ &= B(J+2)(J+3) - B J (J+1) \\ &= B [(J+2)(J+3) - J(J+1)] \\ &= B [(J^2 + 3J + 2J + 6) - J^2 - J] \\ &= B (4J + 6) \text{ cm}^{-1} \text{ -----(3)} \end{aligned}$$

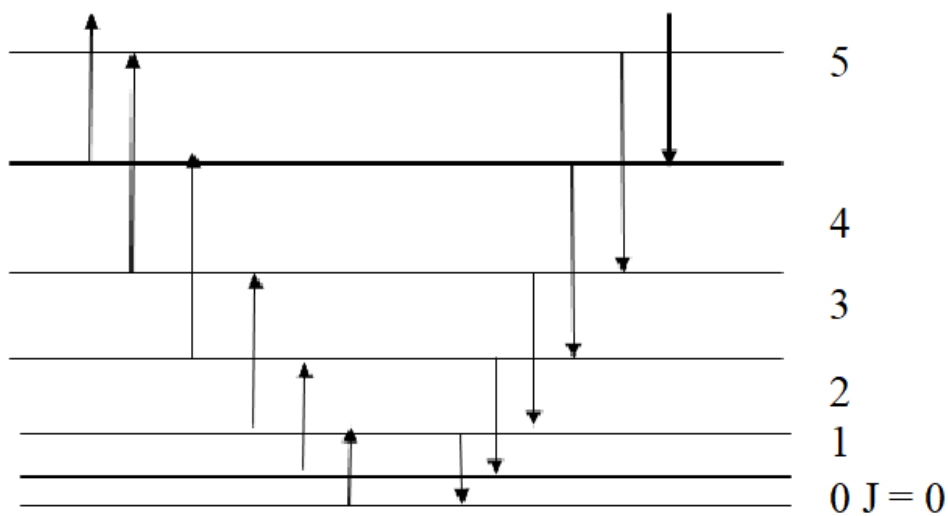
Since $\Delta J = 2$ we may label these lines as S branch and write

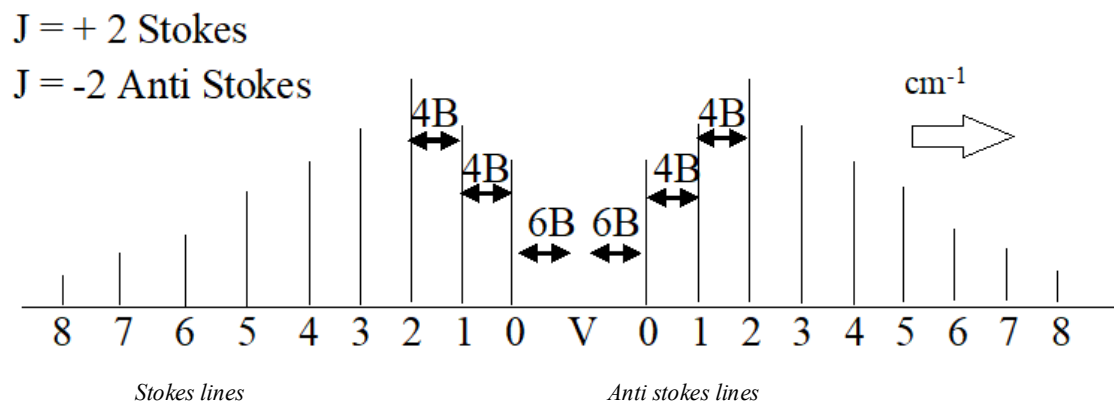
$\Delta \epsilon = B (4J + 6) \text{ cm}^{-1}$ -----(4) Where J is the rotational quantum number in lower state. Hence Raman Spectral lines appears at frequency $\nu_{exc} \neq \Delta \epsilon_s$ or $\nu_s = \nu_{exc} \neq B (4J + 6)$ -----(5) for Rayleigh Scattering $\Delta \epsilon_s = 0$

hence $\nu_s = \nu_{exc}$

For Stokes lines negative sign and for anti-Stokes we get positive sign in eq (5).

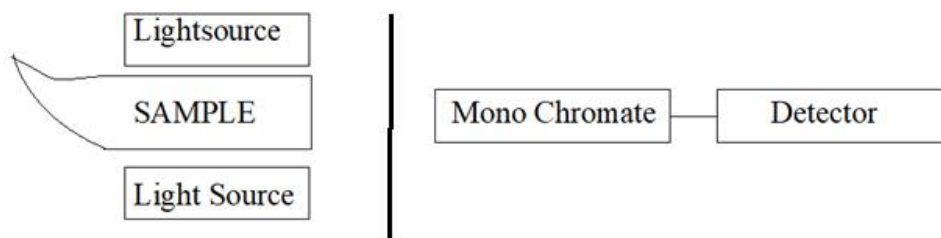
The Energy diagram and rotational Raman Spectrum is shown here.





First line obtained at $6B \text{ cm}^{-1}$ by putting value $J=0$ then the separation of successive lines is $4B \text{ cm}^{-1}$ by putting J values as $J=1,2,3,4$ -----in eq (5)

2.5 Experimental Raman Spectroscopy:



The Experimental set up for Raman Spectroscopy

The experimental setup for Raman Spectroscopy is shown above intense monochromatic radiation (single wavelength or frequency or colour) from a source consisting of a large spiral discharge tube with mercury electrodes is allowed to fall on the cell containing a gaseous or liquid sample. When the electric discharge passes through the tube (source mercury emits lines in its spectrum the most intense line at 4358 Å) (435.8 nm) Serve as exciting line ν_{exc}

The detector is either a photographic plate or photomultiplier. The horn shape of cell helps in reducing the direct reflection of source from the back of the cell. The Raman spectra of gases are generally weaker than those of liquids. If is necessary to use very long discharge Lamps and cells, the latter containing mirrors at both ends arranged so as to increase the effective path length of the cell.

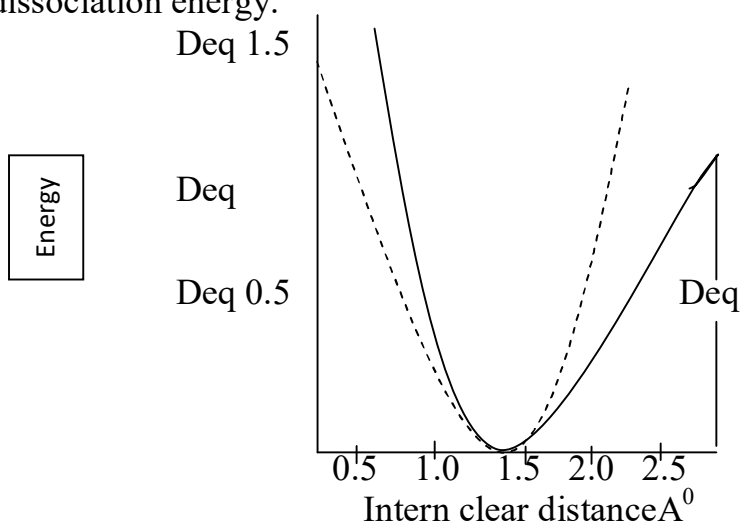
After the discovery of LASER in the late 1950 is new source of LASER are used which replace hg source. The LASER radiation is coherent and monochromatic i.e. it is a radiation of very high intensity with well-defined frequency. The line width is far smaller than that of mercury line. Using a LASER Raman Spectrometer, the spectrum of a sample can be easily recorded.

2.6 Electromagnetic Spectra

Concept of potential energy curve-

For real molecules, vibrational energy cannot be represented by hooks law, for these a purely empirical expression derived by P.M. Morse called the Morse function is used to explain shape of potential energy diagram.

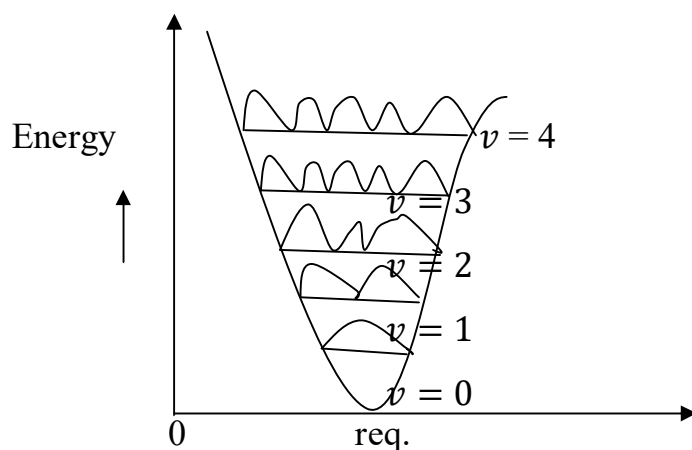
$E = D_{eq}[1 - \exp \{a (r_{eq} - r)\}]^2$ a is constant for molecule and D_{eq} is dissociation energy.



2.7 The Franck Condon Principle

This principle explains intensity of lines in vibration spectra during electronic transition spectra during electronic transition. Frank- Condon principle states that “ an electronic transition takes place so rapidly that a vibrating molecule does not change its intern clear distance appreciably during the transition.

Energy of diatomic molecule can be represented by mores curve in mores curve one atom is considered at an energy axis or at Y- axis at $r = 0$ and other is allowed to oscillate between the limits of curve. Classical theory Suggest oscillating atom would spend most of its time on curve at Turing point of its motion. Quantum theory agrees for this view for higher values of v and shows that for $v = 0$, the atom most likely at centre of its motion i.e. at equilibrium intern clear distance but for $v = 1, 2, 3, \dots$ most probable position steadily approach at the extremities for high V values, quintal and classical concept merges.

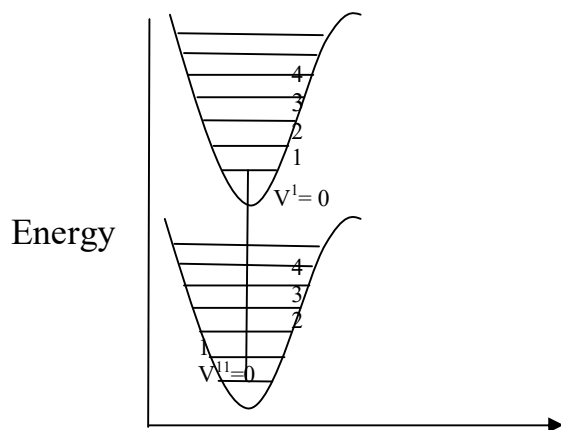


If a diatomic molecule undergoes electronic transitions to upper electronic state in which the excited molecule is stable can also be represented by mores curve. There is small difference in both curves of vibrational frequency bond length, dissociation energy just like morse curve.

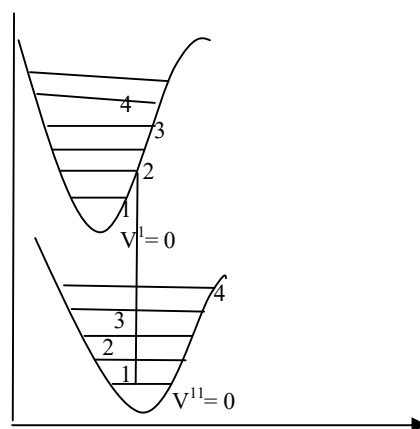
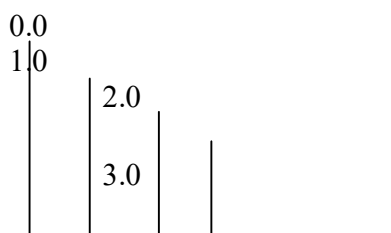
The intensity of vibrational lines can be discussed with four possibilities. here ground electronic state is represented as r'' and ground vibrational state as v'' Excited states are r' and v' respectively.

- a) When intern clear distances are equal in the upper and lower states the transition that can occur vertically on this diagram so molecules in ground state at $r'' = 0$ and $v'' = 0$ the excited state of vibration is $v' = 0$ & $r' = 0$, thus most probable transition will be (0,0) so most intense line will (0,0) and other transitions are (1,0), (2,0) diminish rapidly.

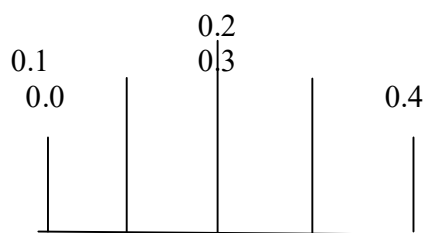
b)



a) Same intern clear distance

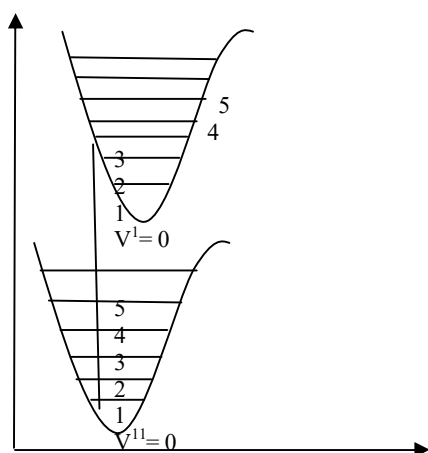


b) slight small distance

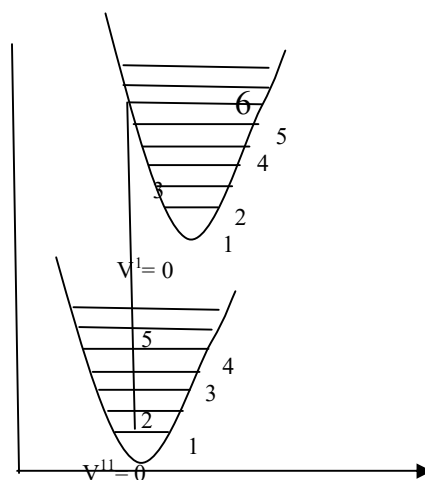


a) $an - 1$

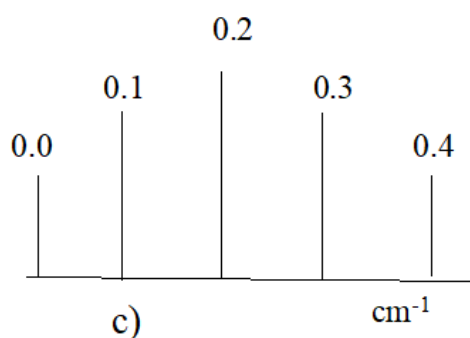
b) $cm - 1$



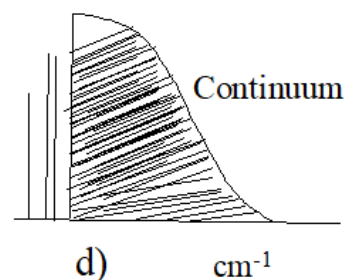
c) Slight large



d) Considerably larger greater



c)

cm⁻¹

d)

cm⁻¹

- c) Big b. shows the case where excited electronic separation than ground state A vertical transition from $v''=0$ to $v'=2$ is most likely to occur and have most intense line at (2,0) other lines diminishes such as (0,0), (1,0) etc.
- d) The excited electronic state has a slightly larger internuclear distance than ground state but resulting spectrum is same and most probable line at (2,0) other lines diminishes such as (0,0), (1,0) etc.
- e) In this the upper state separation that in the lower state and the vibrational level to which a transition takes place has high v' value. If further

transition occurred molecule dissociates as transition energy becomes more than dissociation energy.

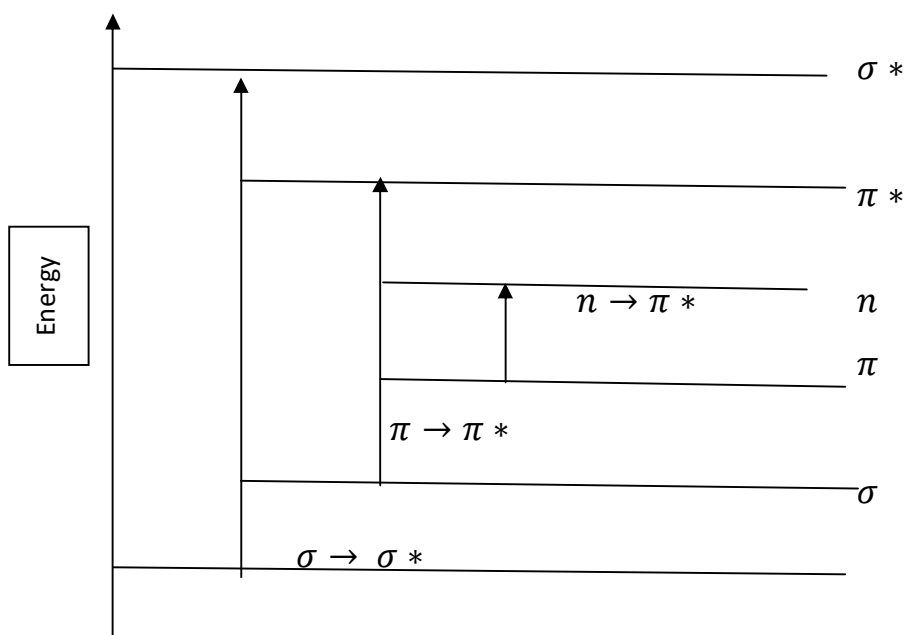
For such state the molecule will dissociate without any vibrations and since atoms are formed may take up any value of kinetic energy, the transitions are not quantized and a continuum result.

2.8 Type of Electronic Transitions-

In organic compound particularly those containing group like C=C, C=O, -N=N- and extensively conjugated systems form a special type of polyatomic molecules whose electronic spectra can be interpreted using Molecular Orbital Theory. According to MO Theory, the electron can be classified as σ , π or n (non bonding) depending up on MO's they occupy, For organic carbonyl compound, the electronic transitions involve promotion of the electronic in σ , π and n orbitals in ground State to σ^* and π^* Antibonding Molecular orbitals (ABMO'S) in the excited state. The transitions of type $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$ are allowed, n orbitals are non-bonding so there are no ABMO'S for n-orbitals.

The $\sigma \rightarrow \sigma^*$ transitions occurring in saturated hydrocarbon and other types of compounds in which all in single bonds or convent bond found in ultraviolet region, wavelength less than 150 nm (or high frequency) region as they ($\sigma \rightarrow \sigma^*$) involve high energy.

The $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$ transition found in UV region and visible region. The C=C and C=O show such transitions for aldehyde and Ketones found near 180 nm for $\pi \rightarrow \pi^*$, and at 285 nm for $n \rightarrow \pi^*$ transition for alkenes show $\pi \rightarrow \pi^*$, at 160-170 nm.



Question

1. Define : a. Stokes lines b. Anti-stokes lines c. Rayleigh lines
2. Explain in brief Quantum theory of Raman effect?
3. Explain classical theory of Raman effect?
4. Derive an expression for rotational Ramanspectrum?
5. Explain experimental set up of Raman spectra?
6. Explain Frank Condon Principle?
7. Explain different types of electronic transitions?
8. What is morse curve?

Unit: 3 Chemical Kinetics

3.1 Third Order Reaction:

The study of velocity of chemical reactions is considered as chemical kinetics. The study of chemical kinetics involves rate of reaction, rate law and factors affecting rate of chemical reactions. In previous class we studied basics of chemical kinetics lets proceed to next level.

Third Order reaction with equal concentration of reactants:

Let us consider a third – order reaction of type $3A \rightarrow P$

Let, a be the initial concentration of A and x is amount of A that has reacted at time t , so that at time t amount of A is $(a - x)$ the rate equation is

$$\text{Rate, } r = \frac{dx}{dt} = k_3(a - x)^3$$

Where,

k_3 is third order rate constant

$$\frac{dx}{dt} = k_3(a - x)^3$$

Separating variables,

$$= \frac{1}{(a-x)^3} dx = k_3 dt \quad (2)$$

On integrating eq (2), we get,

$$= \int \frac{1}{(a-x)^3} dx = \int k_3 dt$$

$$\frac{1}{2(a-x)^2} = k_3 t + c \quad (3)$$

Where, C is integration constant.

To determine the value of C , we have initial condition, at $t = 0, x = 0$, so that

$$\frac{1}{2(a-0)^2} = k_3 \times 0 + c$$

$$\Rightarrow c = \frac{1}{2a_2}$$

Put this value of C in eq (3), we get,

$$\begin{aligned} \frac{1}{2(a-x)^2} &= k_3 t + \frac{1}{2a^2} \\ \therefore k_3 t \frac{1}{2(a-x)^2} &= \frac{1}{2a^2} \\ &= \frac{2a^2 - 2(a-x)^2}{2a^2 \times 2(a-x)^2} = \frac{2(a^2 - (a-x)^2)}{2a^2 \times 2(a-x)^2} \\ &= \frac{a^2 - a^2 + 2ax - x^2}{2a^2(a-x)^2} \\ k_3 t &= \frac{2ax - x^2}{2a^2(a-x)^2} \end{aligned}$$

$$k_3 = \frac{1ax}{2t} \times \frac{x(2a-x)}{a^2(a-x)^2} \text{ _____ (4)}$$

Eq (4) is the rate equation of third order reaction.

Characteristics of Third order Reactions:

1] Unit of rate constant of third order reaction :

We have,

$$\begin{aligned} k_3 &= \frac{1}{2t} \frac{x(2a-x)}{a^2(a-x)^2} \\ \therefore k_3 &= \frac{1}{\text{sec} \frac{\text{mole/lit} \times \text{mole/lit}}{(\text{mole/lit})^2 (\text{mole/lit})^2}} \\ &= \frac{1}{\text{sec} \frac{1}{(\text{mole/lit})^2}} \\ &= (\text{mole/lit})^2 \text{Sec}^{-1} \\ &= \text{lit})^2 \text{mole}^{-2} \text{Sec}^{-1} \end{aligned}$$

2] Relation between k_3 and half-life period $t_{1/2}$

The time required to complete a definite fraction of the third order reaction is inversely proportional to the square of the initial concentration of reactant.

This may be seen by putting, $x = \frac{a}{2}$, at $t_{1/2}$ in the rate equation thus,

$$k_3 = \frac{1}{2t} \left[\frac{x(2a-x)}{a^2(a-x)^2} \right] \text{ we, get,}$$

$$k_3 = \frac{1}{2t_{1/2}} \left[\frac{\frac{a}{2}(2a - \frac{a}{2})}{a^2(a - \frac{a}{2})^2} \right]$$

$$= \frac{1}{2t_{1/2}} \left[\frac{\frac{a}{2} \times \frac{3a}{2}}{a^2 \times \frac{a^2}{4}} \right] = \frac{3}{1} \times \frac{1}{t_{1/2}} \times \frac{1}{a^2}$$

$$t_{1/2} = \left(\frac{3}{2k_3} \right) \times \frac{1}{a^2}$$

$$\therefore t_{1/2} \propto \frac{1}{a^2}$$

Similarly, it can be proved that the time taken for the completion of any definite fraction of a reaction varies inversely with the square of initial concentration.

Examples:-

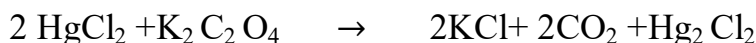
- i) There are only five examples (gas phase) of third order and each involves nitric oxide as one of reactant.





ii) Reactions in solutions :

Noyes and cattle showed that the reduction of ferric chloride by stannous chloride was of the third order.

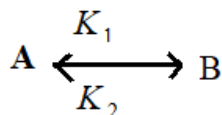


3.2 Opposing Reactions

There are certain reactions in which the products of a chemical change react to form the original reactant. Such reactions are known as counter, reversible or opposing reactions.

In opposing reactions, the rate of the reaction depends upon rate of backward and forward reaction.

Consider the simplest case when both the forward and backward reactions



are of the first order.

Where,

K_1 = Rate constant of forward reaction.

K_2 = Rate constant of back forward reaction.

Suppose 'a' is initial concentration of A. After some time t , x gm of molecules of A have decomposed to form B. Then concentration of A at time t , is $a - x$ and concentration of B is x , thus.

Rate of forward reaction = $k_1(a - x)$

Rate of back forward reaction = k_2x

\therefore The net rate of production of B is, i.e. $\frac{dx}{dt}, \frac{dx}{dt} = k_1(a - x) - k_2x$

At equilibrium, the net rate is zero, i.e. $\frac{dx}{dt} = 0$,

$$\therefore k_1(a - x_e) - k_2x_e = 0$$

$$k_2x_e = k_1(a - x_e)$$

$$k_2 = \frac{k_1(a - x_e)}{x_e}$$

Where, x_e is concentration of B at equilibrium Substituting the value of K_2 from eq (5) in eq (4), we get.

$$\frac{dx}{dt} = k_1(a - x) - \frac{k_1(a - x_e)}{x_e}x$$

$$\frac{dx}{dt} = k_1a - k_1x - \frac{k_1ax}{x_e} + \frac{k_1x_e}{x_e}$$

$$\frac{dx}{dt} = k_1a - k_1x - \frac{k_1a}{x_e}x + k_1x$$

$$= k_1a - \frac{k_1a}{x_e} = k_1a \left(-1 + \frac{1}{x_e}\right)$$

$$\frac{dx}{dt} = k_1a \left(\frac{x_e - x}{x_e}\right)$$

$$\frac{dx}{dt} = \frac{k_1a}{x_e} (x_e - x)$$

Separating variables, we get,

$$\frac{dx}{x_e - x} = \frac{k_1a}{x_e} dt$$

Integrating eq (6), we get,

$$-\ln(x_e - x) = \frac{k_1a}{x_e}t + c$$

Where, C is integration constant, to find value of C put initial conditions at

$$t = 0, x = 0.$$

$$-\ln(x_e - o) = \frac{k_1 a}{x_e} \times o + c$$

$$\Rightarrow = -\ln x_e \quad \text{_____} \quad (8)$$

Putting this value in eq (7), we get,

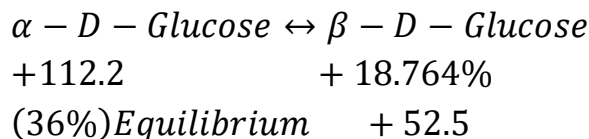
$$-\ln(x_e - x) = \frac{k_1 a}{x_e} t \ln x_e$$

$$\ln x_e - \ln(x_e - x) = \frac{k_1 a}{x_e} t$$

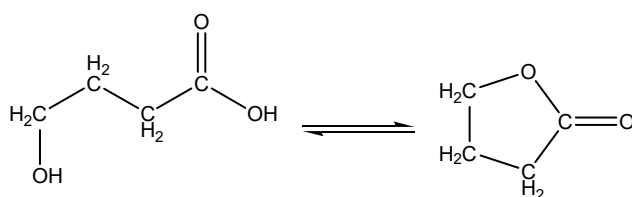
$$\frac{k_1 a}{x_e} t = \ln\left(\frac{x_e}{at}\right) \ln\left(\frac{x_e}{x_e - x}\right) \quad \text{_____} \quad (9)$$

Thus, value of k_1 can be calculated if x_e, x and t are known. Eq (9) represent rate equation for opposing reaction.

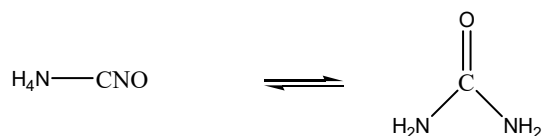
Examples : i) Mutarotation of α -D-glucose into β -D-glucose.



ii) Conversion of γ -hydroxybutyric acid into lactone

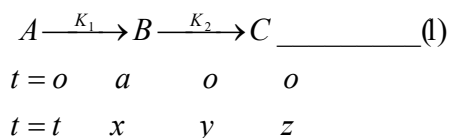


iii) Conversion of ammonium cyanate into urea



3.3 Consecutive Reactions

In such reactions, the products obtained in the first stage react with each other or with the reactants to form new products. This means consecutive reaction proceed instapes. For example



If a is initial concentration of A and let X, Y and Z denote concentration of A, B and C after time t we can write $x + y + z = a + \dots$ (2)

The rate of disappearance of A is

$$-\frac{dx}{dt} = k_1 x \quad (3)$$

Where, k_1 is rate constant for first stage ($A \rightarrow B$)

$$-\frac{dx}{x} = k_1 dt \quad (4)$$

Integrating eq (4), we get

$$-\ln x = k_1 t + I_c$$

I_c is integration constant,

When $t = 0, x = a$, we get

$$\begin{aligned} -\ln a &= k_1 \cdot 0 + I_c \\ I_c &= \ln a \end{aligned} \quad (5)$$

$$\begin{aligned} \therefore -\ln x &= k_1 t - \ln a \\ \ln x - \ln a &= -k_1 t \\ \ln \frac{a}{x} &= -k_1 t \\ x &= a e^{-k_1 t} \end{aligned} \quad (6)$$

Rate of formation if C is given by

$$\frac{dz}{dt} = k_2 y \quad (7)$$

K_2 is rate constant for formation of C from B

Rate of formation of B is K_1x and rate of decomposition of B to C is given by $K_2 y$, the rate at which B accumulates $\left(\frac{dy}{dt}\right)$ is given as,

$$\frac{dy}{dt} = \frac{-dx}{dt} - \left(\frac{+dz}{dt}\right) = \frac{-dy}{dt} = \frac{-dx}{dt} \text{-----(8)}$$

from eq (3), eq (7) & eq (8), we get $\frac{dx}{dt} = k_1x - k_2y$ -----(9)

Putting the value of x in eq (9), we get, $\frac{dy}{dt} = k_1xe^{-k_1t} - k_2y$

This is a linear differential equation of the first order, the solution of this is

$$y = ae^{-kt} \left[\frac{k_1 e^{(k_2-k_1)t}}{(k_2-k_1)} - \frac{k_1}{(k_2-k_1)} \right]$$

$$y = \frac{k_1 a}{(k_2-k_1)} x e^{-k_2t} (e^{k_2t} x e^{-k_2t} - 1)$$

$$y = \frac{k_1 a}{(k_2-k_1)} (e^{-k_2t} \times e^{k_2t} \times e^{-k_1t} - e^{-k_2t})$$

$$y = \frac{k_1 a}{(k_2-k_1)} (e^{k_2t} - \times e^{-k_2t}) \text{-----(10)}$$

But $x + y + z = a$

$$\therefore z = a - x - y$$

$$\therefore z = a - ae^{-k_1t} - \frac{k_1 a}{(k_2-k_1)} (e^{-k_1t} - e^{-k_2t})$$

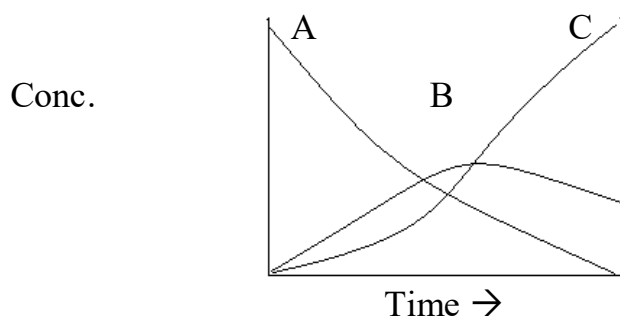
$$z = \frac{a}{(k_2-k_1)} (k_2-k_1) - e^{-k_1t} (k_2-k_1) - k_1 (e^{-k_1t} - e^{-k_2t})$$

$$z = \frac{a}{(k_2-k_1)} (k_2-k_1-k_2e^{-k_1t} + k_1e^{-k_1t} - k_1e^{-k_1t} + k_1e^{-k_2t})$$

$$z = \frac{a}{(k_2 - k_1)} (k_2 - k_2 e^{-k_1 t} - k_1 + k_1 e^{-k_2 t})$$

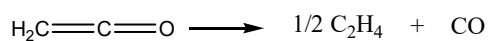
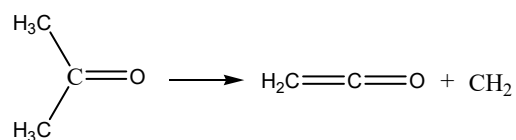
$$z = \frac{a}{k_2 - k_1} (k_2 - k_2 e^{-k_1 t}) - (k_1 - k_1 e^{-k_2 t})$$

If x, y and z are plotted against functions of time for $a = 1$, $k_1 = 0.01$ & $k_2 = 0.02$. The curves corresponding are shown.

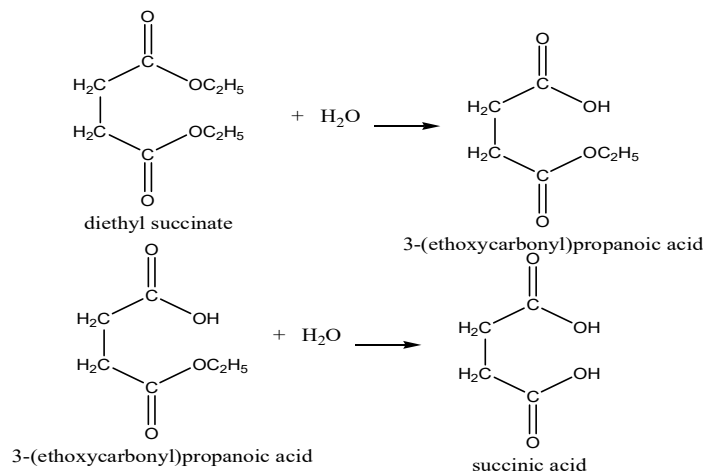


Examples :

i) Thermal decomposition of Acetone

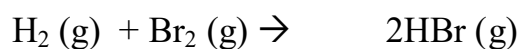


ii) Hydrolysis of ester of dibasic acid

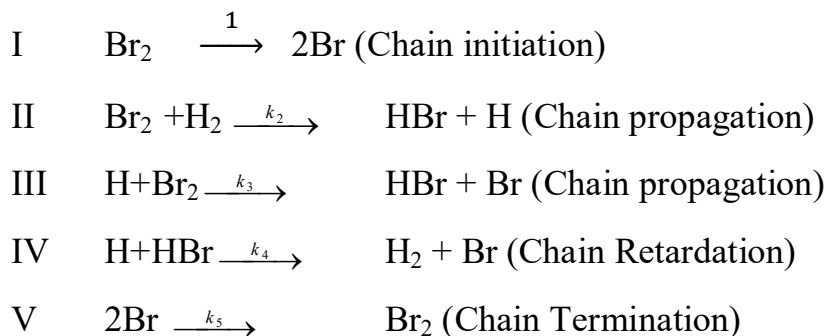


3.4 Kinetics of Chain Reactions

A typical chain reaction is that between H_2 and Br_2 as



Its mechanism:



Here,

$K_1, K_2, K_3, K_4,$ & K_5 are rate constants various steps can be discussed as
 Step 1- Chain Initiation: Bromine molecules acquires energy due to collision to dissociate into two Br radicals. Step II & step III Chain propagation: Steps II & III are Chain propagation steps. Here chain consumes Br, converting H_2 and

Br₂ into HBr and regenerating Br, Step IV Chain Retardation – In this step chain is inhibited by HBr, thus decreases the rate of its formation.

Step V – Chain Termination- This removes Br atoms and Br atoms are converted back to Br₂.

The atoms H and Br are responsible for propagating the Chain are called as chain carriers.

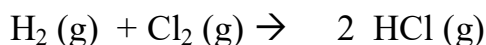
Rate law at 500 – 1500k is

$$r = \frac{d[HBr]}{dt} = k^1 [Br_2]^{1/2}$$

Rate law at steady state can be given as $\frac{d[H]}{dt} = \frac{d[Br]}{dt} = 0$

3.5 Kinetics of photochemical Reactions

1. Hydrogen-chlorine reaction:



Mechanism:

1. $Cl_2 + hv \xrightarrow{k_1} 2 Cl$
2. $Cl + H_2 \xrightarrow{k_2} HCl + H$
3. $H + Cl_2 \xrightarrow{k_3} HCl + Cl$
4. $Cl \text{ (at the walls)} \xrightarrow{k_4} \frac{1}{2} Cl_2$

According to mechanism

$$\frac{d[HCl]}{dt} = k_2 [Cl] [H_2] + k_3 [H] [Cl_2] \quad (1)$$

Applying steady state principle to [Cl]

$$\frac{d[Cl]}{dt} = k_1 I_1 - k_2 [Cl] [H_2] + k_3 [H] [Cl_2] - k_4 [Cl] = 0 \quad (2)$$

I_a is intensity of radiation, Applying steady state principle to $[H]$

$$d \frac{[H]}{dt} = k_2 [cl] [H_2] - k_3 [H] [cl_2] = 0 \quad (3)$$

Adding eq (2) and eq (3), we get,

$$k_1 I_a - k_4 [cl] + k_2 [cl] [H_2] + k_3 [H] [cl_2] - k_4 [cl] + k_2 [cl] [H_2] - k_3 [H] [cl_2] = 0$$

$$k_1 I_a - k_4 [cl] = 0, \text{ so that,}$$

$$[cl] = \frac{k_1 I_a}{k_4} \quad (4)$$

Substituting this value in eq (3), we get

$$k_2 = \frac{k_1 I_a}{k_4} [H_2] - k_3 [H] [cl_2] = 0$$

$$k_3 [H] [cl_2] = \frac{k_1 k_2}{k_4} I_a [H_2]$$

$$[H] = \frac{k_1 k_2}{k_3 k_4} \frac{I_a [H_2]}{[cl_2]} \quad (5)$$

Substituting the values of eq (4) & eq (5) in eq (1), we get

$$r = \frac{d[Hcl]}{dt} = k_2 \frac{k_1 I_a}{k_4} [H_2] + k_3 \frac{k_1 k_2}{k_3 k_4} \frac{I_a [H_2]}{[cl_2]} [cl_2]$$

$$= \frac{k_1 k_2}{k_4} I_a [H_2] + \frac{k_1 k_2}{k_4} I_a [H_2]$$

$$d \frac{[Hcl]}{dt} = \left(\frac{2k_1 k_2}{k_4} \right) I_a [H_2]$$

$$d \frac{[Hcl]}{dt} = K I_a [H_2]$$

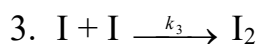
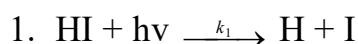
$$\text{Where, } k = \left(\frac{2k_1 k_2}{k_4} \right)$$

Thus, rate law is directly proportional to intensity I_a of radiation.

The quantum yield is between 10^4 - 10^6

2. Kinetic of Decomposition of HI:

The following mechanism has been suggested for the photochemical decomposition of HI,



The rate law for the composition of HI is given by

$$-d \frac{[\text{HI}]}{dt} = k_1 I a + k_2 [\text{H}][\text{HI}] \quad (1)$$

Applying steady state principle to [H],

$$d \frac{[\text{H}]}{dt} = k_1 I a - k_2 [\text{H}][\text{HI}] \quad (2)$$

$$\therefore k_2 [\text{H}][\text{HI}] = k_1 I a \quad (2)$$

Substituting this value in eq (1), we get,

$$-d \frac{[\text{HI}]}{dt} = k_1 I a + k_1 I a = 2k_1 I a \quad (3)$$

Eq (3) is rate equation for decomposition of HI.

The quantum yield of the reaction is given by

$$\begin{aligned} \phi &= \frac{\text{Rate of disappearance of HI}}{\text{Rate of absorption of } \vec{\epsilon} \text{ light}} \\ &= \frac{-d[\text{HI}]}{dt} = \frac{2k_1 I a}{k_1 I a} \quad (2) \\ \phi &= 2 \end{aligned}$$



3 Kinetic of Anthracene Reaction

Anthracene in benzene solution dimerises and simultaneously fluoresces when irradiated with light of certain frequency. The frequency of radiation emitted in fluorescence is $V^2 \lambda$. The following two mechanisms have been proposed for the reaction 'A' stands for Anthracene.

Mechanism I

1. $A + hv \xrightarrow{k_1} A^*$ (excitation)
2. $A^* + A \xrightarrow{k_2} A_2$ (Dimerization)
3. $A^* + hv \xrightarrow{k_3} A + hv^1$ (Fluorescence)

Mechanism II

1. $A + hv \xrightarrow{k_1} A^*$ (excitation)
2. $A^* + A \xrightarrow{k_2} A_2$
 $\xrightarrow{-k_2}$
3. $A^* \xrightarrow{k_3} A + hv^1$ (Fluorescence)

Using Mechanism, I

Applying steady state principle to

$$[A^*], \frac{d[A^*]}{dt} = k_1 I_a - k_2 [A^*][A] - k_3 [A^*] = 0 \quad (1)$$

I_a is intensity of radiation

$$k_2 [A^*][A] + k_3 [A^*] = k_1 I_a$$

$$[A^*] (k_2 [A] + k_3) = k_1 I_a$$

$$[A^*] = \frac{k_1 I_a}{k_2 [A] + k_3} \quad (2)$$

The rate of formation of dimer $[A_2]$ is $r = \frac{d[A_2]}{dt} = k_2 [A^*][A]$ _____(3)

Substituting the value of eq (2) in eq (3) $\frac{d[A_2]}{dt} = \frac{k_2 k_1 I_a}{k_2 [A] + k_3} [A]$ _____(4)

Eq(4) represents the rate of formation of A_2

The quantum yield for the formation of the dimer is given by

$$\begin{aligned} \phi_{A_2} &= \frac{\text{Number of moles of } A_2 \text{ formed}}{\text{Number of einsteins absorbed}} \\ &= \frac{\frac{d[A_2]}{dt}}{I_a} = \frac{k_2 k_1 \times I_a \times [A]}{k_2 [A] + k_3 I_a} \phi(A_2) = \frac{k_1 k_2 [A]}{k_2 [A] + k_3} \text{ _____(5)} \end{aligned}$$

The quantum yield is independent of intensity of the light absorbed. Eq (5) Can also be written as

$$\phi(A_2) = \frac{k_1 [A]}{[A] + \frac{k_3}{k_2}}$$

If $[A] \gg \frac{k_3}{k_2}$, we can write

$$\phi(A_2) = k_1$$

The quantum yields independent $[A]$. of

If $[A] \ll \frac{k_3}{k_2}$ then

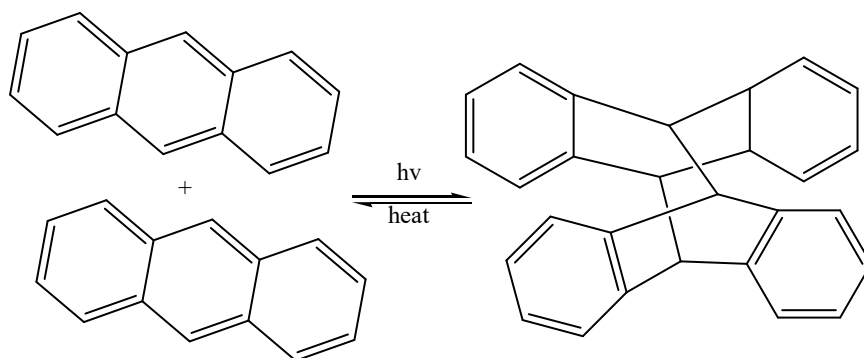
$$\phi(A_2) = \left(\frac{k_1 k_2}{k_3} \right) [A]$$

Thus $\phi(A_2)$ increases with increase in the concentration $[A]$ of the monomer.

Using the second mechanism, it can be shown that,

$$\phi(A_2) = \frac{k_1 k_2 [A] - k_2 k_3 [A_2] I_a^{-1}}{k_2 [A] + k_3}$$

The quantum yield depends up on the intensity of light absorbed.



Dimerization of Anthracene

Questions:

1. Derive an expression for third order reaction rate constant with equal concentration of all reactants?
2. Explain in brief opposing reactions?
3. Derive an expression for consecutive reactions?
4. Explain in brief kinetics of chain reactions?
5. explain kinetics of decomposition of HI?
6. Explain kinetics of formation of HCl?
7. Explain kinetics of formation of dimer of anthracene?

Unit 4: Distribution Law

4.1 Introduction: -

If we take two non-miscible solvent A and B in a beaker, they form separate Layers. When a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to Solvent B and from solvent B to Solvent A. Finally, a dynamic equilibrium, is set up at equilibrium rate at which molecules of X pass from one solvent to other is balanced. It is found that at equilibrium.

Concentration of X in A = a constant

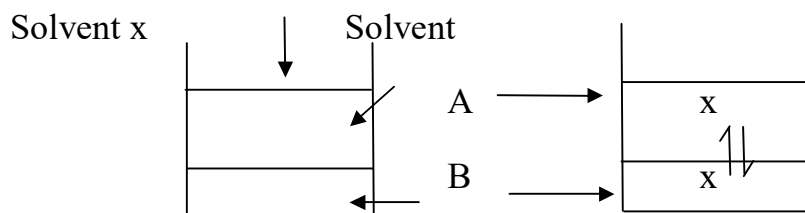
Concentration of X in B

4.2 Nernst's Distribution Law:

Nernst in 1891 gave distribution of a solute between two-miscible solvent. This is called Nernst Distribution Law or Distribution Law.

If a solute X distributes itself between two non-miscible solvent A and B at constant temperature and X is in the same molecular condition in both solvents.

$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = K_D$$



If C_1 is concentration of solute in (X) solvent A and C_2 the concentration in solvent B then,

$$\frac{C_1}{C_2} = K_D$$

Where K_D or K is called distribution co-efficient of partition co-efficient or distribution ratio.

4.3 Solubility's and Distribution Law: -

When solute is shaken with two non-miscible solvents at equilibrium both the solvent is saturated with the solute. Solubility also represents concentration we can write.

$$\frac{C_1}{C_2} = \frac{S_1}{S_2} = K_D$$

When S_1 and S_2 are solubilities of solution in two solvents

We can calculate solubility.

4.4 Explanation of Distribution Law: -

This is an equilibrium Law, at equilibrium rate R_1 at which molecules X pass from solvent A to B is proportional to its concentration C_1 in solvent A and the rate R_2 at which the molecules X pass from solvent B to A is proportional to its concentration C_2 in B. At equilibrium rates are equal Thus

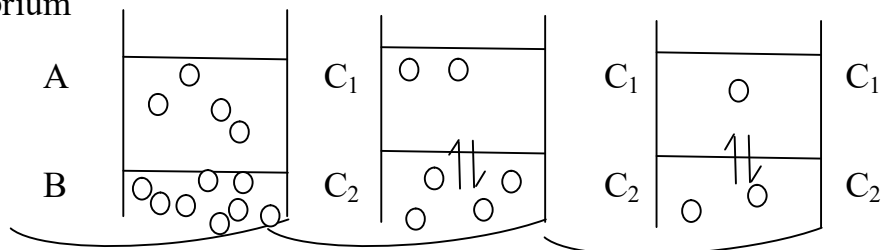
$$R_1 \propto C_1$$

$$R_1 = K_1 C_1 \quad K_1 \text{ Constant}$$

$$R_2 \propto C_2$$

$$R_2 = K_2 C_2 \quad K_2 \text{ constant.}$$

At equilibrium



This is Nernst Distribution Law

Equation At constant temperature K_D is constant.

4.5 Limitation of Distribution Law: -

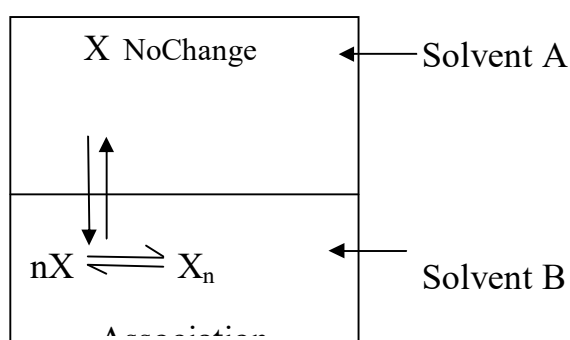
Following are limitations or conditions which are necessary for application of Nernst Distribution Law

- 1) Constant Temperature: The temperature is kept constant throughout the experiment.
- 2) Same molecules state: The molecular state of the solute is the same in the two solvent. The law does not hold if there is association or dissociation of the solute in one of the solvents.
- 3) Equilibrium concentrations: The concentrations of the solute are noted after the equilibrium has been established.
- 4) Dilute solutions: The concentration of the solute in the two solvents is low. The law does not hold when the concentration is high.
- 5) Non-miscibility of solvents: The two solvent are non-miscible or only slightly soluble in each other. The extent of mutual solubility of the solvents remains unaltered by the addition of solute to them.

4.6 Association and Dissociation of Solute in Solvent

1) When solute undergoes Association:

Suppose the solute present as simple molecules X in solvent A. But in solvent B. n molecules of X associate to form X_n molecules. Assuming that a few single molecules of X are also present in solvent B, then the equilibrium that exist in the two solvents are shown in as follows,

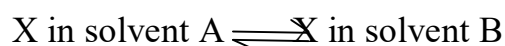


Let C_1 be the Conc. of X in A

C_3 be the conc. Of X in B

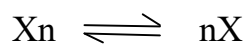
C_2 be the Conc.of X_n in B

Applying the distribution law, the equilibrium



$$\frac{C_1}{C_3} = K_D \text{ (1)}$$

Applying Mass law to the chemical equilibrium



$$\frac{[X]^n}{[X_n]} = K_c$$

$$\frac{[C_3]^n}{C_2] = K_c \text{-----}(2)$$

Taking n^{th} root of both sides in eq. (2)

$$\frac{C_3}{\sqrt[n]{C_2}} = \sqrt[n]{K_c} \text{-----}(3)$$

$$C_3 = \sqrt[n]{C_2} \times \sqrt[n]{K_c}$$

Substitute value of C_3 in eq (1)

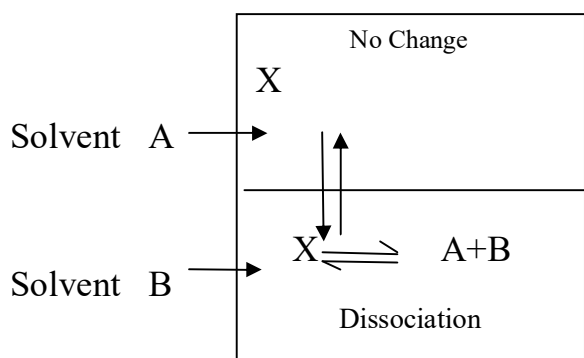
$$\frac{C_1}{\sqrt[n]{C_2}} = K_D \times \sqrt[n]{K_c} = K \text{ (a constant)}$$

Thus, when association occurs in one solvent, the distribution equation is modified as

$$\frac{C_1}{\sqrt[n]{C_2}} = K_D$$

(2) When solute undergoes Dissociation:

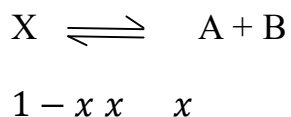
Suppose the solute is present as normal molecules X in solvent A. But it dissociates in to A+B in Solvent B as shown



Let C_1 be the concentration of X in solvent A.

C_2 be the total concentration of X (Dissociated and undissociated) in solvent B.

If the degree of dissociation in solvent B is x



Hence the concentration of undissociated molecules in solvent B is

$$C_2(1-x)$$

Applying Distribution Law to normal molecules in the two solvents

$$\frac{C_1}{C_2(1-x)} = K_D$$

This is the modified distribution Law equation when there is dissociation in one of the solvents

Ex. Succinic acid and oxalic Acid shows dissociation in water. The solvents are ether and water. The value of x can be determined by measuring electrical conductance of solution in water.

Henry's Law:- A form of Distribution Law Henry's law states that at a constant temperature the solubility of a gas in a liquid is proportional to the pressure of the gas above it.

It can be expressed as

$$C = Kp$$

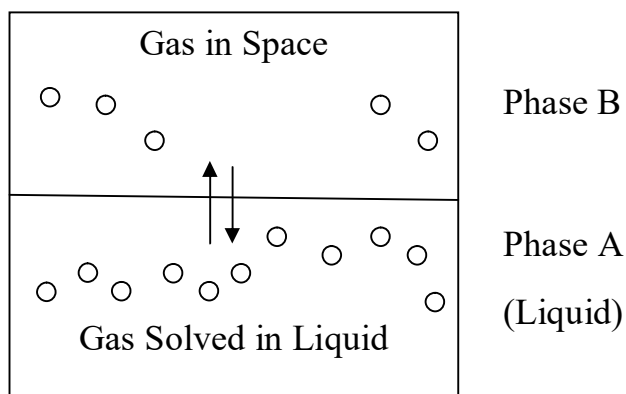
Where,

C = Solubility (or concentration)

K = constant

P = pressure of the gas.

K is called as Henry constant



Distribution diagram illustrating Henry Law.

Let us consider vessel containing liquid and gas is shaken, at equilibrium the gas can be regarded as distributed between liquid phase A and the space above liquid surface i.e. Phase B

Let C_1 be the concentration of gas in phase B

C be the concentration of gas in phase A

Applying distribution Law

$$\frac{C}{C_1} = K_D \text{ (a constants)}$$

But molar concentration of gas is proportional to its pressure p .

Hence,

$$\frac{C}{C_1} = K_D \text{ (a constant)}$$

or $C = KP$

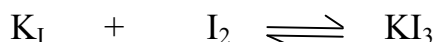
This is Henry's Law equation. This law holds good for dilute solutions of gases which do not react with the solvent.

Solubility of each gas is proportional to its partial pressure.

4.7 Determination of Equilibrium Constant from Distribution Co-efficient

Distribution law is useful in determining equilibrium constant of a reaction when one of reaction is soluble in two non-miscible solvents

Let's us consider reaction



This reaction can be carried in water and benzene mixture as I₂ is soluble in both water and benzene.

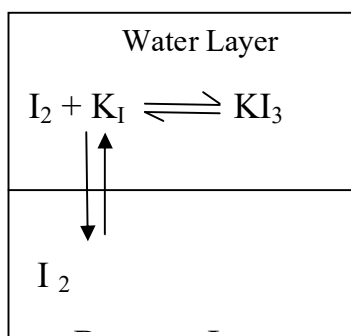
Procedure:-

1) To find the distribution co-efficient of I₂-

Iodine is shaken with water and benzene in a bottle. The concentration of Iodine in two layers is determined by titration against standard thiosulphate solution.

Thus,

$$\frac{\text{Concentration of } I_2 \text{ in water}}{\text{Concentration of } I_2 \text{ in Benzene}} = K_D$$



- 2) To find the equilibrium constant by using value of K (Distribution coefficient)

Aqueous solution of KI whose concentration is 'a' is shaken with Iodine in a bottle. Now add some benzene and shake bottle. On standing equilibrium is set up as shown above.

Let 'b' is concentration of I_2 in benzene and 'c' be the concentration of free I_2 and reacted iodine as KI_3 .

K is distribution co-efficient as determined earlier then,

$$\frac{\text{Concentration of } I_2 \text{ in water}}{\text{Concentration of } I_2 \text{ in Benzene}} = K_D$$

$$\therefore \text{Concentration of } I_2 \text{ (free state)} = Kb$$

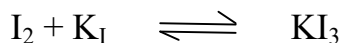
In water layer

Hence, conc. of KI_3 in water layer = c - Kb

\therefore Concentration of KI in

$$\begin{aligned} \text{Water layer} &= a - (c - Kb) \\ &= a - c + Kb \end{aligned}$$

Now equilibrium constant of the reaction



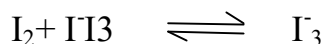
$$K_C = \frac{[KI_3]}{[I_2][KI]}$$

$$K_C = \frac{c - Kb}{(a - c + kb)kb}$$

Thus, equilibrium constant can be calculated.

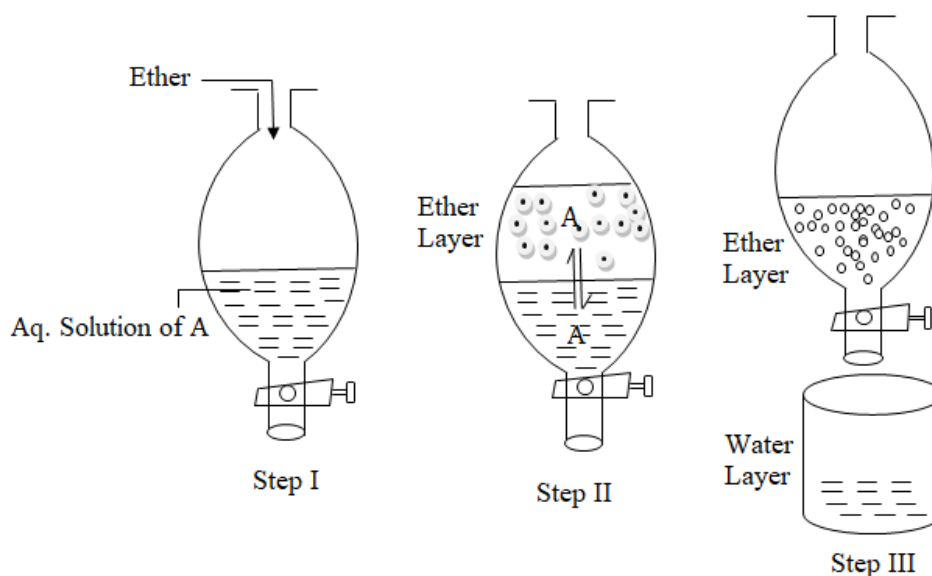
4.8 Study of Complex Ion:-

If the value of K_c comes out to be constant by taking different concentration, of KI and I_2 to start with, it proves the existence of KI_3 or the complex ion I_3^-



Thus, the distribution law is helpful in the study of complex ions.

4.9 Extraction with a solvent:-



The extraction of an organic substance from an aqueous solution is probably the most important application of distribution law, the process is carried out by shaking the aqueous solution with non-miscible organic solvent as ether in a separatory funnel. The distribution ratio is in favour of ether, most of the organic compound passes into ether layer. On standing ethereal layers and aqueous layers separate in funnel. The lower aqueous layer runs out leaving behind ethereal layer. This is transferred to distillation flask; ether is distilled

over while organic compound is left as residue in the flask. If desired the process may be repeated by using fresh ether.

The other common solvent used are hexane, benzene chloroform acetone Carbon tetrachloride etc.

The greater the distribution ratio is in favour of organic solvent; the greater will be the amount extracted in any one operation.

4.10 Liquid Chromatography(Partition Chromatography)

This technique is used for separation of a mixture of small amounts of organic substance. The operation is carried in glass tube packed with an inert solid material (silica) soaked in solvent 1 (Water) The mixture paste is applied to the column top Then the layer of another liquid, immiscible solvent (hexane) solvent 2, is allowed to flow down the column. A film of solvent- 1 held by silica forms stationary liquid phase, while the running solvent- 2 the mobile liquid phase. Each component of the mixture distributes itself between the stationary liquid phase and the mobile liquid phase, Thus

$$\frac{C_s}{C_m} = K_D$$

C_s = Concentration in stationary liquid phase.

C_m = Con. in mobile liquid phase.

Different components in organic mixture have different distribution coefficients. They pass into mobile phase in order of their distribution coefficients

The component with higher distribution coefficient in mobile phase (S_1) is extracted (eluted) first and is the first to move down the column. The location of the components is easy if they are coloured.

4.11 Applications of Distribution Law

1) Solvent Extraction

This is the process used for the separation of organic substance from aqueous solution is shaken with ether in a separator funnel. Most of organic substance pass in to ether due to favourable distribution constant. Ether layer is separated and distilled off to get organic compound. The process of extraction is more efficient when multiple extraction is preferred to simple extraction.

2) Partition chromatography

This method is used to separate mixture of organic compounds. A paste of organic compound is applied on top of column of soaked silica. Another immiscible solvent hexane is allowed to flow down the column. Various compounds are get extracted in order of distribution constant and are collected separately.

$$\frac{C_s}{C_m} = K_D$$

3) Desilverization of lead (Parkes process):

This method is used to separate silver, from lead (argentiferous lead) added, Zinc and Lead form two immiscible liquids at high temperature. The value to K_D is 300 in favour of Zinc of silver at 800°C . Most of silver pass into zinc layer, on cooling alloy of zinc-silver separates. The Zn-Ag alloy is distilled Zn easily distilled out leaving silver behind.

The lead layer still contains unextracted Ag, this is treated with fresh Zinc to recover most of silver. This is an example of solvent extraction.

4) Confirmatory Test- For Br_2 – and I_2 –:

The salt solution is treated with chlorine water. Small quantity of Br_2 or I_2 is liberated due to Chlorine water, the solution is then shaken with chloroform, on standing chloroform layer forms the lower layer. The For Br_2 or I_2 are highly soluble in chloroform, pass in to chloroform give red colour for Br_2 and violet colour for I_2

5) Determination of Association:

When a substance is associated in solvent B and exit as simple molecules in solvent A then distribution law is modified as

$$\frac{CA}{\sqrt[n]{CB}} = K$$

Where,

n = No. of molecules which are combined to form an associated molecule.

6) Determination of Dissociation:

When a substance act as normal in solvent 1 and substance dissociated in solvent 2, the distribution law is modified as

$$\frac{C_1}{C_2 C_1^{-x}} = K \text{ (a constant)}$$

C_1 Conc. of substance in solvent 1

C_2 Conc. of Substance in solvent 2

x– Degree of dissociation , determined by conductivity measurements.

7) Determination of Solubility Suppose that.

Solubility of I_2 in benzene is to be determined I_2 is shaken with water and benzene at equilibrium concentration of I_2 in water & benzene are determined and K_D is calculated

$$\frac{C_b}{C_w} = K_D$$

But $\frac{C_b}{C_w} = K_D$

thus, S_b can be calculated.

8) Deducing the Formula of a complex I on (I_3)

If one of reactant is soluble in two immiscible solvent then this method is utilized in first step K_D is determine separately for I_2 in water- benzene. Then in second part aq. KI is treated with I_2 to form KI_3 or $I_3^-(I_2 + I^-)$ then this is treated with benzene. after equilibrium is reached. the conc. is of free I_2 , remaining KI and formed KI_3 Substituting those values in law of mass action eq. we get.

$$\frac{[I_3^-]}{[I][I^-]} = K$$

The constant value of K for each set of different conc. of KI & I_2 confirms formation of complex ion I_3^-

9) Distribution Indicator :

In iodine titrations, the end point is detected by starch which turns blue. A greater sensitivity can be obtained by use of Distribution indicator for ex. a few drops of chloroform or CCL_4 is added as distribution indicator to

solution. The bulk of any iodine passes into the organic layer (Chloroform or CCl_4 layer) imparts intense violet colour to it.

= X=X=X=X=X

4.12 Numerical

1) Distribution Law $\frac{C_1}{C_2} = K_D$

Numerical: A solid X is added to a mixture of benzene and water. After shaking well & allowing to stand 10 ml of benzene layer was found to contain 0.13 gm of X and 100 ml water layer is found to contain 0.22 gm of X Calculate of the value of distribution co-efficient solution.

$$\text{Conc. of X in benzene} = C_B \frac{[\text{Amount of X in gm}]}{\text{Volume in ml}} = K$$

$$C_B = \frac{0.13}{10} = 0.13 \text{ gm/ml}$$

$$C_w = \text{Conc. of X in water} = \frac{0.22}{100} = 0.0022 \text{ gm/ml}$$

According to distribution law, $K_D = \frac{C_B}{C_w}$ in water

$$K_D = \frac{0.13}{0.0022} = 5.9$$

Numerical: 2 In the distribution of succinic acid between ether and water at 15°C , 20 ml of ethereal layer contains 0.092 gm of the acid. Find out weight layer in equilibrium with it. If the distribution co-efficient for succinic acid in between water & ether is 5.2

Given Data: $K_D = 5.2$

Let, wt. of Succinic Acid in aqueous layer is Xgm.

Conc. of Acid in aqueous layer $\frac{X}{50}$ gm/ ml

Conc. of Acid in ethereal layer $\frac{0.092}{20}$ gm/ ml

$$\text{But } K_D = \frac{C_{Water}}{C_{ether}} = 5.2$$

$$\frac{\frac{X}{50}}{\frac{0.092}{20}} = 5.2$$

$$\therefore X = 5.2 X = \frac{0.092}{20} X 50$$

$$X = 1.196 \text{ gm}$$

Numerical 3.

An aqueous solution of succinic acid at 15°C , containing 0.07 gm in 10 ml is in equilibrium with an ethereal solution which has 0.013 gm in 10 ml. The acid has its normal molecular weight in both the ethereal solution which is in equilibrium with an aqueous solution containing 0.024 gm in 10 ml?

Solution:

Conc. in aqueous solution $C_w \frac{0.07}{10} \text{ gm/ml}$

Conc. in ethereal solution $C_E \frac{0.013}{10} \text{ gm/ml}$

$$\therefore K_D = \frac{0.07/10}{0.013/10} = 5.38$$

$$X = 1.196 \text{ gm}$$

Conc. of in aqueous solution in second case = $\frac{0.024}{10} \text{ gm/ml}$

Let X be the concentration in ethereal layer

$$\therefore K_D = \frac{C_w}{C_E}$$

$$5.38 = \frac{0.024}{10}$$

$$\begin{aligned}\therefore X &= \frac{0.024}{10 \times 5.38} \\ X &= 0.00044 \text{ gm/ml}\end{aligned}$$

Numerical 4.

At 25⁰C an aqueous solution of iodine containing 0.0516 gm/lit is in equilibrium with CCl₄ solution containing 4.412 gm/ lit. The solubility of Iodine in water at 25⁰C is 0.34 gm lit, find the solubility of Iodine in CCl₄.

Solution:

$$C_w = 0.0516 \text{ gm/lit}$$

$$C_{CCl_4} = 4.412 \text{ gm/lit}$$

$$\therefore K_D = \frac{C_{CCl_4}}{C_w} = \frac{4.412}{0.0516}$$

$$= 85.5$$

Calculation of Solubility:

$$\frac{S_{CCl_4}}{S_w} = K_D$$

$$\begin{aligned}\therefore S_{CCl_4} &= K_D \times S_w \\ &= 85.5 \times 0.34 \\ &= 29.07 \text{ gm/lit}\end{aligned}$$

==**==**==**==*

NUMERICALS BASED ON ASSOCIATION**Numerical 5.**

When benzoic acid was shaken with mixture of Benzene and water at constant temperature, the following results were obtained.

Conc. of acid in water C_1	0.015	0.022	0.029	C_2
Conc. of acid in Benzene	0.24	0.55	0.93	

Comment on result.

Solution:

Calculating C_1/C_2 for each case

$$\frac{0.015}{0.24} = 0.0625, \frac{0.022}{0.55} = 0.04, \frac{0.029}{0.93} = 0.03188$$

Thus, the distribution co-efficient is not constant. Therefore, benzoic acid does not exist as single molecule in both solvents.

On Calculating $C_1/\sqrt{C_2}$, we have,

$$\frac{0.015}{\sqrt{0.24}} = \frac{0.015}{0.489897} = 0.03061$$

$$\frac{0.022}{\sqrt{0.55}} = \frac{0.022}{0.741619} = 0.296647$$

$$\frac{0.029}{\sqrt{0.93}} = \frac{0.029}{0.96436} = 0.030071$$

The constant value of distribution constant now arrived; it suggests that Benzoic acid is associated into double molecules in the benzene layer.

Question

1. Derive Nernst Distribution law?
2. Define Henry Law?
3. State Nernst Distribution law ? Give Its Important applications?
4. Deduce Nernst Distribution law in case of I) Association of solute in one of Its solvent. II) Dissociation of solute in one of the phases
5. Explain In brief applications of Nernst Distribution law?
6. Explain In brief Solvent extraction?
7. Explain application of Nernst Distribution law to column chromatography?
8. how Nernst distribution law Is useful in the determination of equilibrium constant?