ICH 501 : Spectroscopic Techniques

UNIT I

Introduction:

→ Spectroscopy is the study of the interaction between matter and electromagnetic radiation as a function of wavelength

→ spectroscopy is the use of the absorption, emission or scanning of EMR by matter inorder to qualitative or quantitative study of matter.

→ When light of suitable frequency falls on a molec-le, transition occurs between different molecular energy levels.

Electromagnetic radiation :

Light is treated as an electromagnetic radiation. According to quantum mechanics, light exhibits dual nature, i.e., it behaves as a wave as well as a particle. Ligh is composed of tiny particles called photons. Energy of photon is calculated using the formula $E = h\nu$

Light radiation is a mixture of different wavelengths or frequency. Electromagnetic spectrum is an orderley arrangement of radiations according to their wavelengths.

EMR consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity.

Techniques in Spectroscopy:

1. Absorption spectroscopy

* When atoms or molecules absorb light, the incoming energy excites a structure to a higher energy level. The type of excitation depends on the light wavelength.

* An absorption spectrum is a way to represent the absorption of light as a function of wavelength.

* Absorption spectra obtained as dark band on a bright background.

2. Emission spectroscopy

* Emission occurs during transition from a higher level to a lower level.

* The substance first absorbs energy and then radiates (i.e., emits) this energy as light.

* Emission spectra obtained as bright band on a dark background

3. Scattering spectroscopy

* Scattering refers to light that is changed direction from its interaction with matter. It may or may not occur with energy transfer

* It differs from other spectroscopy types primarily because of speed. The scattering process is much faster than absorption or emission.

Intensity of Spectral lines

The intensity of spectral lines depends upon the total number of molecules undergoing transition between adjacent levels producing the spectrum. As the number of transition increase, the intensity increases. The intensity of spectral lines depend upon two factors

i) **Relative population of an energy level:** As the population of an energy level increases, the number of transition to the adjacent level increases. As a result of this the intensity of line corresponding to that transition. The population of an energy level is given by Boltzman distribution of molecules

$$\text{Intensity} \propto \frac{N_J}{N_0} = e^{-E_J/kT}$$

$$\text{But} \quad E_J = BJ(J+1)hc$$

$$\therefore \text{intensity} \propto e^{\frac{-BJ(J+1)hc}{kT}}$$

The equation shows that the population and hence the intensity decreases exponentially with increase in J value

ii) **Degeneracy of given energy state:** Existance of two or more states of same energy (degenerate levels) influence the intensity of spectral lines. As the number of degenerate state increases, the intensity decreases. The number of degenerate levels for particular J value is 2J+1. Thus, as J value increases, the number degenerate level increases.

The resultant spectral line is

$$\text{Intensity} \propto \frac{N_J}{N_0} = (2J+1) \cdot e^{\frac{-BJ(J+1)hc}{kT}}$$

The value of J for maximum population is

$$J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

Therefore transition to the level adjacent to J_{max} will be more intense.

Natural line width of Spectra

The natural line width of spectral line is determined by the Heisenberg uncertainty principle and the lifetime of the excited state. According to Heisenberg's uncertainty principle, the product of the uncertainty in the measurement of energy ΔE and time Δt is

$$\Delta E \cdot \Delta t \geq h/2\pi$$

Most excited states have lifetimes of 10^{-8} to 10^{-10} s, so the uncertainty in the energy of the electron slightly broadens the spectral line. This is called the natural line width and is in the order of 10^{-4} A°.

Spectral line Broadening

* The result of a radiative atomic transition from an upper to a lower energy level is radiation at a particular wavelength, as defined by

$$\lambda = \frac{hc}{E_2 - E_1}$$

where h is Planck's constant and c is velocity of light.

- However, atomic lines are not infinitely thin as ~~wold~~ would be expected
- There are a number of effects which control spectral line shape. A spectral line extends over a range of frequencies, not a single frequency (i.e., it has a non-zero line width). In addition, its centre may be shifted from its nominal central wavelength.
- There are several reasons for this broadening and shift.

1. Doppler broadening

- Doppler broadening is due to random kinetic motion toward and away from the detector, results in broadening of the spectral line on the order of 0.01 to 0.05 A°. The random atomic movement of the atoms is directly related to the temperature, which is why this broadening mechanism is called thermal- ~~broadening~~ Doppler effect.
- As we know from the Maxwell - Boltzmann statistics the speed of gas atoms follow Gauss equation,

$$\Delta \nu_D = \frac{\nu_0}{c}\sqrt{\frac{2kT}{m}}$$

- The equation shows that broadening increases with temperature and is higher for light atoms.

2. Pressure / Collision / Lorentz broadening

- * Collision with other atoms in the atomizer lead to pressure broadening, on the order of 0.05 A°
- * Collision randomize the phase of the emitted radiation. If it is frequent enough, shorten the lifetime of excited state
- * In this case, the spectral line characterized by a narrower spike and longer wings
- * Lorentz broadening increase with pressure and temperature. Thus $\Delta\nu$ increases with increase in T & P.

3. External field broadening

- * Magnetic or Electric external fields cause the Zeeman effect or the Stark effect with the splitting of the spectral lines and the final result of causing a broadening of the lines
- * Stark broadening occurs as a result of atoms encountering strong local electric fields.
- * In the presence of a magnetic field, Zeeman splitting of the electronic energy level also occurs.

Energy levels in a molecule

According to Born-Oppenheimer approximation, the total energy of a molecule is given by

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

Translational energy of a molecule is negligible; so

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

It is in the order $E_{rot} < E_{vib} < E_{el}$

Rotational Energy

- * This is the energy developed in a molecule as a result of rotation of the molecule about its axis.
- * When a molecule having permanent dipole moment rotates about its axis, an energy change occurs and this energy change is quantized. ($J = 0, 1, 2, 3 \cdots$)
- * An absorption of radiation of suitable frequency in the microwave region can cause transition between these energy levels. Hence the spectrum obtained is called microwave spectrum.

Vibrational Energy

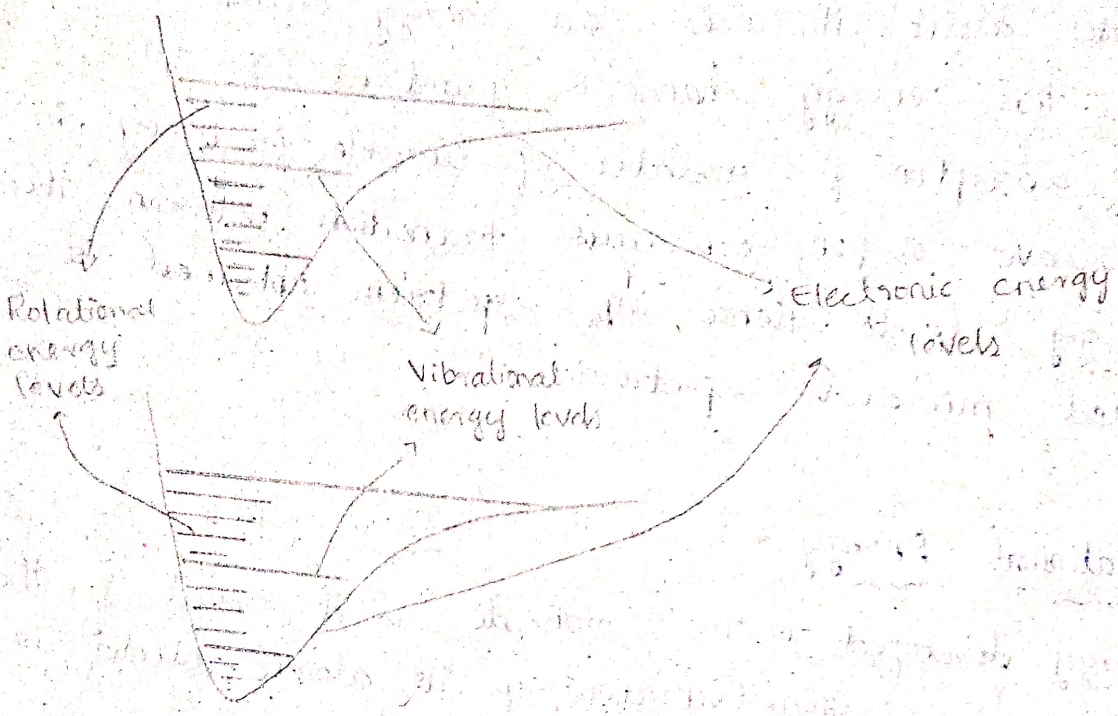
- * Energy developed in the molecule as a result of the to and fro motion (vibration) of its atomic nuclei is called vibrational energy
- * A change in dipole moment during different modes of vibration of the molecule, will cause energy changes in the molecule. These energy levels are quantized ($v = 0, 1, 2, 3 \cdots$)
- * An absorption of radiation of suitable frequency in the infrared region can cause transition between these energy levels. Hence the spectrum obtained is called Infrared spectrum.

Electronic Energy

- * It is the energy possesed by a molecule due to the transition of electrons between different energy levels.
- * During the transition of electrons from lower energy

to higher energy states, the energy is absorbed in the ultraviolet and/or visible region. Hence the spectrum obtained is called UV-visible spectrum.

Energy level diagram



Selection Rule

Selection rule for Rotational spectra : The selection rule for rotational spectrum is obtained by solving the Schrodinger wave equation. According to selection rule, only those transitions for which the rotational quantum number changes by one unit are allowed. i.e., the transition for which $\Delta J = \pm 1$ are allowed and the other transitions are forbidden.

Selection rule for Vibrational spectra : Solution of Schrodinger wave equation for a vibrating molecule indicates that only those transitions for which $\Delta V = \pm 1$ are allowed. All the remaining transitions are forbidden. Thus only those transitions for which V changes by one unit is allowed

Microwave Spectroscopy

→ It deals with the study of rotating molecules

→ The rotation of a three-dimensional body is quite complex. Therefore, to resolve it into rotational components about mutually ⊥r directions through the centre of gravity, i.e., principal axis of rotation.

→ Thus a body has 3 principal moments of inertia about the axis named I_A, I_B and I_C

1. Linear molecule

Eg:- HCl, OCS

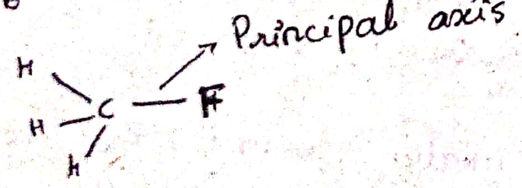
- * About the bond axis
- * End-over-end rotation in the plane of the paper
- * End-over-end rotation right angle to plane of paper

$I_A \approx 0$, $I_B = I_C$

2. Symmetric top

$I_A \neq 0$, $I_B = I_C$

Eg:- CH_3F



1. About the bond axis (C-F) ($I_A \neq 0$)
2. End-over-end rotation in the plane of the paper (I_B)
3. End-over-end rotation out of the plane of paper (I_C)

Classified as,

a) Prolate ⇒ $I_A > (I_B = I_C)$, Eg:- CH_3F

b) Oblate ⇒ $I_A < (I_B = I_C)$, Eg:- BCl_3

3. Spherical top

No dipole moment

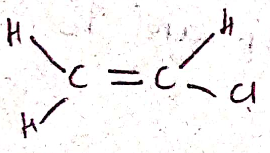
Eg: CH_4 , CO_2

$I_A = I_B = I_C$

4. Asymmetric

$I_A \neq I_B \neq I_C$

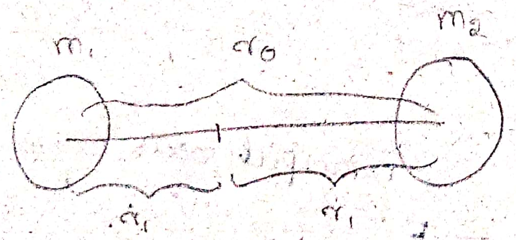
Eg :-



Rigid Rotor Model

* Consider a model which is a spinning dumbell

* The dumbell has two masses seperated by a fixed distance and spins around its centre q mass. This model can be further simplified using the concept q reduced mass



$r_0 = r_1 + r_2$

The moment q inertia w.r.t the centre q gravity is given by $I = m_1 r_1^2 + m_2 r_2^2$

$I = m_2 r_2 r_1 + m_1 r_1 r_2 \quad (\because m_1 r_1 = m_2 r_2)$

$= r_1 r_2 (m_1 + m_2)$ --(1) $(\because r_0 = r_1 + r_2$, $r_1 = r_0 - r_2)$

$m_1 r_1 = m_2 r_2$

$m_1 (r_0 - r_2) = m_2 r_2$

$$m_1 r_0 - m_1 r_2 = m_2 r_2$$

$$m_1 r_2 + m_2 r_2 = m_1 r_0$$

$$r_2 (m_1 + m_2) = m_1 r_0$$

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

Similarly $r_1 = \dfrac{m_2 r_0}{m_1 + m_2}$

$\therefore$ eqn (1) $\Rightarrow$

$$I = \left(\frac{m_1 r_0}{m_1 + m_2}\right)\left(\frac{m_2 r_0}{m_1 + m_2}\right)(m_1 + m_2)$$

$$= \frac{m_1 m_2 r_0^2}{(m_1 + m_2)^2}(m_1 + m_2)$$

$$I = \frac{m_1 m_2 r_0^2}{m_1 + m_2}$$

$$I = \mu r_0^2$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is reduced mass

* This equation defines the moment of inertia conveniently in terms of atomic masses and bond length

* The allowed rotational energy level for a rigid diatomic molecule is given by Schrodinger wave eqn

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

$$E_J = BJ(J+1)$$

J = rotational quantum number

B = rotational constant $= \dfrac{h}{8\pi^2 Ic}$

Consider the transition from J'' to J'.

J'' - initial energy level

J' - higher energy level

$J' - J'' = 1 \Rightarrow J' = J'' + 1$

$$\Delta E_J = E_{J'} - E_{J''}$$

$$= BJ'(J'+1) - BJ''(J''+1)$$

$$= B\left[(J'(J'+1)) - J''(J''+1)\right]$$

$$= B\left[(J''+1)(J''+1+1) - J''(J''+1)\right]$$

$$= B\left[(J''+1)(J''+2) - J''(J''+1)\right]$$

$$= B\left[\cancel{J''^2} + 3J'' + 2 - \cancel{J''^2} - J''\right]$$

$$= B(2J'' + 2)$$

$$\Delta E_J = 2B(J''+1) \text{ Joules}$$

Another method :

Transition from $J \rightarrow J+1$

$$E_J = BJ(J+1)$$

$$E_{J+1} = B(J+1)(J+2)$$

$$E_{J+1} - E_J = B(J+1)(J+2) - BJ(J+1).$$

$$\Delta E_J = B(J+1)(J+2-J)$$

$$\Delta E_J = 2B(J+1) \text{ Joules}$$

Non - Rigid Rotor

The consideration of bond in a diatomic molecule as a rigid bond is only an approximation. However the bonds are non-rigid, i.e., all bonds are elastic to some extent. The ~~el~~ elasticity results in some changes which are as follows:

i) An elastic ~~bod~~ bond may have vibrational energy

ii) The quantities r & B vary during vibration

Spectrum of Non-rigid rotor

From Schrodinger equation for a non-rigid rotor in simple harmonic force field

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

k = force constant

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

$$= BJ(J+1) - DJ^2(J+1)^2 \quad \text{----} \quad (1)$$

where B is rotational constant and D is the centrifugal distortion constant which is a positive quantity

$$B = \frac{h}{8\pi^2 Ic} \text{ cm}^{-1}; \quad D = \frac{h^3}{32\pi^4 I^2 r^2 kc} \text{ cm}^{-1}$$

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

Relationship between B and D is

$$D = \frac{4B^3}{\bar{\omega}^2}$$

If $B = 10\ \text{cm}^{-1}$ & $\bar{\omega} = 10^3\ \text{cm}^{-1}$

$$D \approx \frac{(10\ \text{cm}^{-1})^3}{(10^3)^2} = \frac{10^3}{10^6} = 10^{-3}\ \text{cm}^{-1}$$

So $D << B$

i.e., D is much smaller than B

For smaller values of J, the correction term in eqn (1) is negligibly small.

For higher values of J, say 10 or more, the value of D may be appreciable.

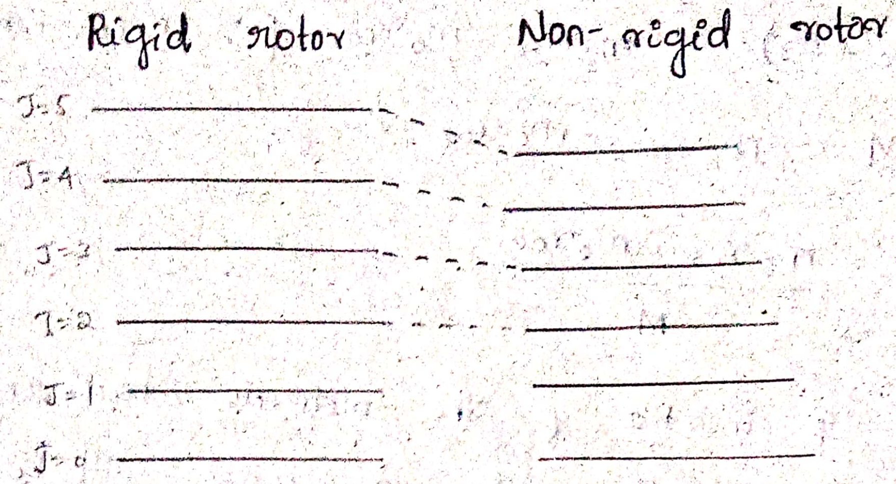
The selection rule $J = \pm 1$ is of course still valid

The spectral line given by the equation

$$BJ(J+1) - DJ^2(J+1)^2\ \text{cm}^{-1}$$

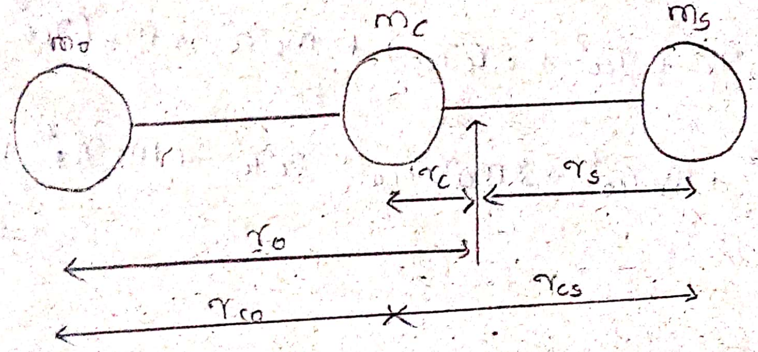
$$E_J = BJ(J+1) - DJ^2(J+1)^2\ \text{cm}^{-1}$$

If D is neglected, then spectral line occurs at interval of 2B



Linear polyatomic molecules

Consider linear unsymmetrical triatomic molecules such as OCS and HCN



Let us consider the rotation of OCS molecule r_o, r_c and r_s represents the atoms from the centre of gravity

$$r_o = r_c + r_{co}$$

$$r_s = r_{cs} - r_c$$

By considering the moment of inertia for end to end rotation

$$m_o r_o + m_c r_c = m_s r_s$$

$$m_o (r_c + r_{co}) + m_c r_c = m_s (r_{cs} - r_c)$$

$$m_o r_c + m_o r_{co} + m_c r_c = m_s (r_{cs} - r_c)$$

$$m_o r_c + m_c r_c + m_s r_c = m_s r_{cs} - m_o r_{co}$$

$$r_c(m_o + m_c + m_s) = m_s r_{cs} - m_o r_{co} \quad [\because m_o + m_c + m_s = M]$$

$$r_c M = m_s r_{cs} - m_o r_{co}$$

$$r_c = \frac{m_s r_{cs} - m_o r_{co}}{M}$$

The moment of inertia of the molecule about an axis passing through the centre of mass will be given by

$$I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2$$

$$= m_o(r_c + r_{co})^2 + m_c r_c^2 + m_s(r_{cs} - r_c)^2$$

$$= m_o(r_c^2 + r_{co}^2 + 2r_c r_{co}) + m_c r_c^2 + m_s(r_{cs}^2 + r_c^2 - 2r_{cs}r_c$$

$$I = m_o r_c^2 + m_o r_{co}^2 + 2m_o r_c r_{co} + m_c r_c^2 + m_s r_{cs}^2 + m_s r_c^2 + 2m_s r_{cs} r_c$$

$$I = m_o r_c^2 + m_c r_c^2 + m_s r_c^2 + m_o r_{co}^2 + m_s r_{cs}^2 - 2m_s r_{cs} r_c + 2r_c r_{co} m_o$$

$$= M r_c^2 + m_o r_{co}^2 + m_s r_{cs}^2 + 2r_c(m_o r_{co} - m_s r_{cs})$$

Substituting the value of r_c in above equation

$$= M\left[\frac{m_s r_{cs} - m_o r_{co}}{M}\right]^2 + m_o r_{co}^2 + m_s r_{cs}^2 + 2\left[\frac{m_s r_{cs} - m_o r_{co}}{M}\right](m_o r_{co} - m_s r_{cs})$$

$$= \frac{(m_s r_{cs} - m_o r_{co})^2}{M} + m_o r_{co}^2 + m_s r_{cs}^2 + 2\left[\frac{m_s r_{cs} - m_o r_{co}}{M}\right](m_o r_o - m_s r_{cs})$$

$$= \frac{m_s^2 r_{cs}^2 + m_o^2 r_{co}^2 - 2 m_s \cancel{r_{cs} \cdot m_o} r_{co}}{M} + m_o r_{co}^2 + m_s r_{cs}^2$$

$$+ \frac{2 m_s \cancel{r_{cs} m_o} r_{co} - 2 m_s r_{cs} m_s r_{cs} - 2 m_o r_{co} m_o r_{co} + 2 m_o r_{co} m_s r_{cs}}{M}$$

$$+ 2 m_o r_{co} \cdot m_s r_{cs}$$

$$= \frac{m_s^2 r_{cs}^2 + m_o^2 r_{co}^2}{M} + m_o r_{co}^2 + m_s r_{cs}^2 - \frac{2(m_s^2 r_{cs}^2) - 2(m_o^2 r_{co}^2)}{M}$$

$$= \frac{-m_s^2 r_{cs}^2 - m_o r_{co}^2 + 2 m_o r_{co} \cdot m_s r_{cs}}{M} + m_o r_{co}^2 + m_s r_{cs}^2$$

$$I = \frac{-[m_s r_{cs} - m_o r_{co}]^2}{M} + m_o r_{co}^2 + m_s r_{cs}^2$$

Q. Diatomic molecules such as CO, HF will show a rotational spectrum where as N_2, O_2, H_2 do not, why?

The main condition to show rotational spectra is that, the molecule should have permanent dipole moment. ~~hence~~ ~~shows~~ CO and HF possess permanent dipole moment hence shows rotational spectra, But homonuclear diatomic molecules like N_2, O_2, H_2 do not have permanent dipole moment.

Problems:

1. Calculate the rotational constant for

a. H_2 b. HCl

The bond length between H–H & H–Cl is 136 pm

⇒ Given, ~~for H_2~~

Bond length, $r = 136$ pm

$= 136 \times 10^{-12}$ ~~p~~m

W.K.T, $B = \frac{h}{8\pi^2 Ic}$

$I = \mu r^2$

$\mu = \frac{m_1 * m}{m_1 + m_2}$

For H_2, $m_1 = m_2 = 1.67 \times 10^{-27}$ Kg

$$\mu = \frac{(1.67 \times 10^{-27} \times 1.67 \times 10^{-27})}{1.67 \times 10^{-27} + 1.67 \times 10^{-27}}$$

$= 0.835 \times 10^{-27}$ Kg

$I = \mu r^2$

$= 0.835 \times 10^{-27} \times (136 \times 10^{-12})^2$

$= 1.5444 \times 10^{-47}$ Kg m²

$$B = \frac{h}{8\pi^2 Ic} = \frac{6.626 \times 10^{-34}}{8 \times (3.14)^2 \times 1.5444 \times 10^{-47} \times 3 \times 10^8}$$

$= 1813\ m^{-1}$

For HCl, $m_1 = 1.67 \times 10^{-27}$ Kg

$m_2 = 5.88 \times 10^{-26}$ Kg

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$= \frac{1.67 \times 10^{-27} \times 5.88 \times 10^{-26}}{1.67 \times 10^{-27} + 5.88 \times 10^{-26}}$$

$$= 1.623 \times 10^{-27} \text{ Kg}$$

$$I = \mu r^2 = 1.623 \times 10^{-27} \times (136 \times 10^{-12})^2$$

$$= 3.001 \times 10^{-47} \text{ Kgm}^2$$

$$B = \frac{h}{8\pi^2 Ic} = \frac{6.626 \times 10^{-34}}{8 \times (3.14)^2 \times 3.001 \times 10^{-47} \times 3 \times 10^8}$$

$$= 930.28 \text{ m}^{-1}$$

Q. For CO molecule, the first line in the spectrum is found to be 3.842 cm^{-1}. Calculate the bond length of CO.

Given,

$$2B = 3.842\ cm^{-1} \Rightarrow B = 1.921\ cm^{-1} = 192.1\ m^{-1}$$

W.K.T

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

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

$$= \frac{6.626 \times 10^{-34}}{8 \times (3.14)^2 \times 192.1 \times 3 \times 10^8}$$

$$I = 1.4557 \times 10^{-46}$$

$$I = \mu r^2$$

$$\mu = \frac{m_1 * m_2}{m_1 + m_2}$$

m_1 = mass of C $= 12 \times 1.677 \times 10^{-27}$ kg

m_2 = mass of O $= 16 \times 1.677 \times 10^{-27}$ kg

$$\mu = \frac{(12 * 16) \times (1.677 \times 10^{-27})^2}{(12 + 16 \times (1.677 \times 10^{-27}))} = 1.149 \times 10^{-26}\ kg$$

$$I = \mu r^2$$

$$r^2 = \frac{I}{\mu} = \frac{1.4557 \times 10^{-46}}{1.149 \times 10^{-26}}$$

$$= 1.2669 \times 10^{-20}$$

$$r = \sqrt{1.2669 \times 10^{-20}} = 1.1255 \times 10^{-10}\ m = 1.1255\ A^\circ$$

The rotational spectra of HF has the lines 4190 m^{-1} apart. Calculate the moment of inertial & bond length for HF molecule. [Given ; $m_H = 1$ amu, $m_F = 19$ amu, $c = 2.998 \times 10^8$ m/s , $h = 6.626 \times 10^{-34}$ JS]

Given,

$2B = 4190\ m^{-1}$

$B = 2095\ m^{-1}$

w.K.T , $B = \dfrac{h}{8\pi^2 I c}$

$$I = \frac{h}{8\pi^2 B c} = \frac{6.626 \times 10^{-34}}{8 \times (3.142)^2 \times 2095 \times 3 \times 10^8}$$

$= 1.3357 \times 10^{-47}$ Kg m^2

$I = \mu r^2$

$\mu = \dfrac{m_1 m_2}{m_1 + m_2}$, where $m_1 = 1 \times 1.677 \times 10^{-27}$ Kg

$m_2 = 19 \times 1.677 \times 10^{-27}$ Kg

$$\mu = \frac{(1 \times 19) \times (1.677)^2 \times 10^{-54}}{(1+19) \times (1.677 \times 10^{-27})}$$

$\mu =$ ~~5.6648×10^{-28} Kg~~ 1.5931×10^{-27} Kg

$\therefore r^2 = \dfrac{I}{\mu}$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.3357 \times 10^{-47}}{\cancel{5.6648}\ 1.5931 \times 10^{-27}}}$$

= ~~1.5378×10^{-10} m~~ $= 9.1565\ A^\circ \times 10^{-11}$

= ~~$1.5378\ A^\circ$~~ $= 0.9156\ A^\circ$

The microwave spectrum of HI molecule consist of the series of equidistant lines with spacing of 12.8 cm^{-1}. Calculate the bond length for HI (Given mH = 1 amu, mI = 127 amu)

Given, $2B = 12.8\ cm^{-1}$

$B = 6.4\ cm^{-1} = 640\ m^{-1}$

w.K.T. $B = \frac{h}{8\pi^2 I c}$

$I = \frac{h}{8\pi^2 BC} = \frac{6.626 \times 10^{-34}}{8 \times (3.142)^2 \times 640 \times 3 \times 10^8}$

$I = 4.3696 \times 10^{-47}\ kgm^2$

$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1 \times 127) \times (1.677)^2 \times 10^{-54}}{(1+127) \times 1.677 \times 10^{-27}}$

$= 1.6638 \times 10^{-27}\ kg$

$I = \mu r^2$

$r = \sqrt{\frac{I}{\mu}}$

$= \sqrt{\frac{4.3696 \times 10^{-47}}{1.6638 \times 10^{-27}}}$

$= 1.6205 \times 10^{-10}\ m$

$r = 1.6205\ A^\circ$

Isotopic Effect on Rotational Spectra

If ~~ca~~ ^{12}C carbon is replaced by ^{13}C isotope, the reduced mass of the molecule will increased since moment of inertia I is ~~pr~~ directly proportional to μ, inertia also increases.

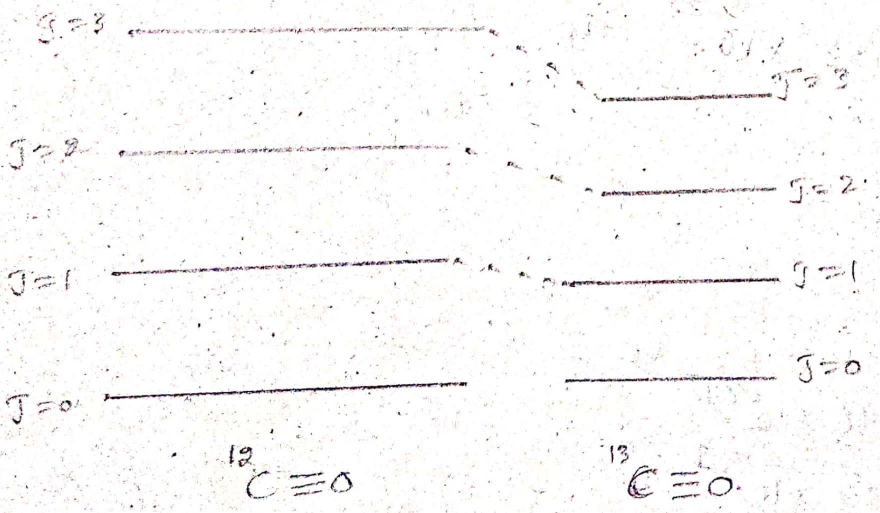
From the below equation,

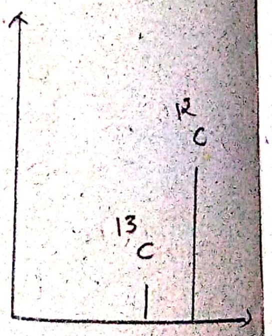
$$B = \frac{h}{8\pi^2 I c}$$

$$B \propto \frac{1}{I}$$

Rotational constant is inversely proportional to I

Therefore, as the inertia increases, B value decreases, i.e., the spacing between the lines in the spectrum of ^{13}C carbon monoxide will decrease.





Stark Effect

- splitting of the spectral lines in presence of external electric field is called Stark effect
- consider a linear rotational active molecule (which possess dipole moment) which is kept in an external ~~magnet~~ ~~mo~~ electric field will have rotational motion. Thus it possess angular momentum J

1) If the external electric field is perpendicular to the angular momentum of the molecule, then the dipole moment of the molecule will be twisted.

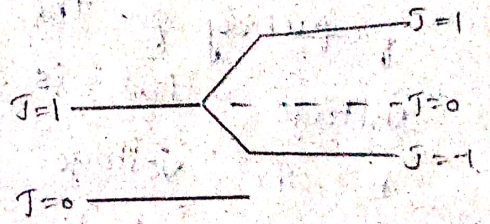
- When the dipole moment alligns with electric field, the rotation becomes faster.

2) When electric field is applied parellel to the angular momentum J, then the dipole moment of the molecule will be perpendicular to the electric field.

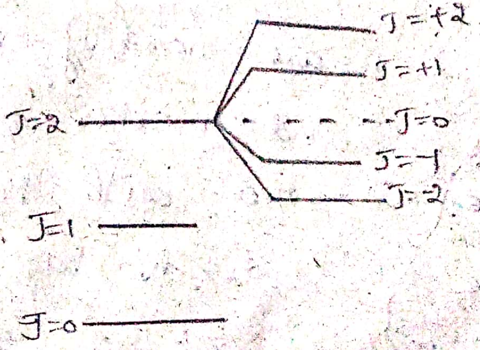
Thus the rotational energy level of the molecule will be splitted

Energy level splitting = $2J+1$

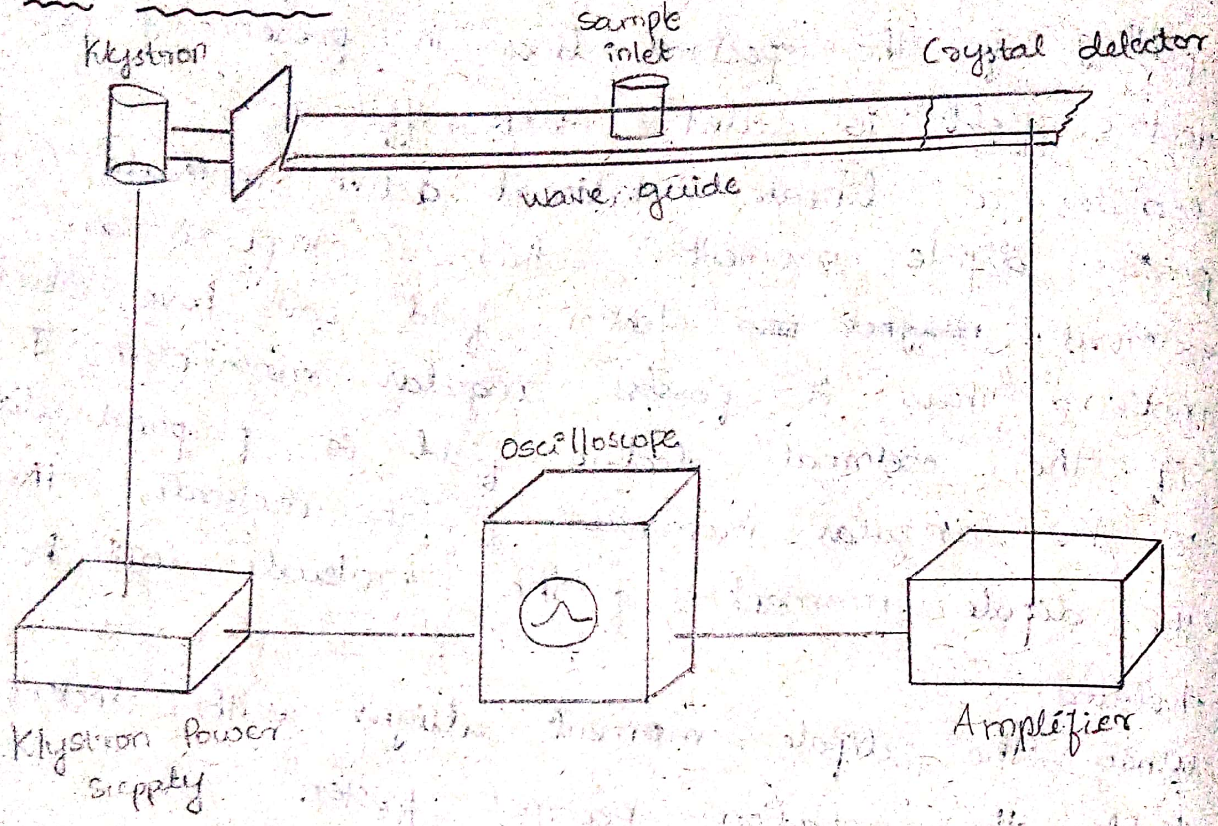
when $J=1$, $2\times1+1 = 3$



when $J=2$, $2\times2+1 = 5$



Instrumentation



Source and Monochromator

Beam delection, Sample & Samp
space, Detectors, Spectrum analyzer

Reflex klystron valve is the main source of radiations in microwave region. As the klystron valve emits radiation of a very narrow frequency range, it acts as its own monochromator. Furthermore, the frequency of the emitted radiations depends on the voltage that is applied to the klystron valve. As the voltage is varied over a given range, the emitted radiation can thus be made to sweep through a region of the microwave range.

Klystron are readily available from 3000 to 5000 Mc/s and weaker signals upto 25000 Mc/S may be obtained with harmonic generators.

One slight disadvantage of the klystron valve is that it radiates out very small energy which is of the order q 30 milliwatts. However since the energy radiated is concentrated into very narrow frequency band, a sharply tuned detector may be activated to produce a strong signal.

The beam direction:

The radiation emitted by klystron cannot be handled with mirrors and lenses, but can be most advantageously transmitted through hollow metallic conductors q such geometry that the electric and magnetic fields can be utilized to the greatest extent. These are known as wave guides. These are hollow tubes q copper or silver q rectangular cross section inside which the radiation is confined. In order to maintain the direction q the beam as well as its focusing, the wave guides may be bent or tapered. The wave guides are generally evacuated because if air is present, considerable absorption q the radiation will occur. The wave guides used in microwave spectrometer is now commonly used in chemical research facilities.

Sample and sample space

The sample is placed in a piece q evacuated wave guide, which is closed at both ends by thin mica windows. Round holes are made in the tube for evacuation purposes and for introduction q the gas under test. The pressure q the gas is adjusted to make the absorption line sharp

The sample must be in the gaseous state for studying in the microwave region. The pressures is of the order of 0.01 mm mercury are generally required to give absorption spectrum. Many solids or liquids substances can be studied by the microwave techniques provided, their vapour pressure are above the value of 0.01 mm of mercury.

Detector:

A quartz crystal is generally used as a detector. It is mounted on a cartbridge made up of tungsten whisker held in point contact with the crystal. In place of crystal detector, an ordinary superheterodyne radio receiver can be used provided it may be tuned to the appropriate high frequency. But a simple quartz crystal is more sensitive and easier to use.

Spectrum analyzer

It consists of an amplifier of detected energy and an indicator which may be either a cathode ray oscillograph or a pen-and ink-recorder. The vibrations emitted by the quartz crystal produce an electric signal which is amplified and then displayed as a pattern on a oscilloscope screen or a recording on a chart by the pen-and-ink recorder

Working

Monochromatic radiations of various wavelengths in the microwave region emitted by klystron valve are allowed to pass through the sample space containing the gaseous sample of the substance under investigation. Then the radiations are made to conduct along a rectangular tube called a wave guide. After this, the radiations are recieved by the quartz crystal detector which is situated at the far end of the waveguide. After recieving the radiations from the waveguide it vibrates and produces an electrical signal which is amplified by the amplifier and then displayed either as a recording on chart or as a pattern on an oscilloscopic screen. The pattern obtained on the chart or on screen of the oscillograph enables one to determine the frequency or the range of frequencies of the detected microwave radiation.

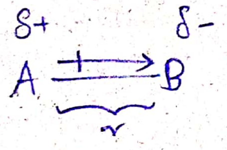
The microwave spectrometer described above is usually used for the measurements of the highest accuracy because the absorption lines are narrow and fairly faithful in shape and relative intensities. The use of oscilloscope posses serious problem that the amplifiers bandwidth cannot be narrowed to remove noice, thus the sensitivity is not exceptionally high. At the same time the new lines for unknown substances cannot be obtained very easily unless their frequencies are known within narrow limits.

By changing the frequancy of the oscillator and observing the intensity of transmitted beam, moment of inertia and internuclear distances upto ±0002 A° can be

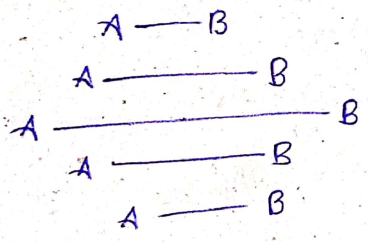
Calculated - Data obtained for bond lengths and bond angles calculated for linear molecules and symmetrical top molecules by microwave spectroscopy.

Vibrational Spectroscopy

Consider a molecule AB



During the vibration of the molecule, the distance b/w A and B will increase and it will decrease. Therefore, the magnitude of the dipole moment will change whereas the direction of the ~~[illegible]~~ dipole moment will not be changed.



The magnitude of the dipole moment is given by $\bar{\mu} = q \cdot r$

r - internuclear distance

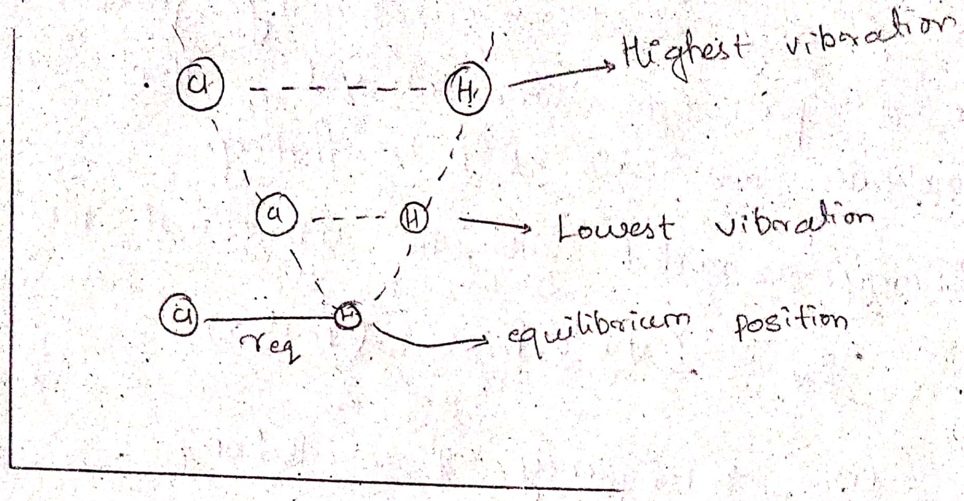
q - charge of the atom.

* During stretching or compression, the internuclear distance is changing wherein q remains the same.

* Whenever there is a periodicity in change in the magnitude of the dipole moment, the frequency of incident EM radiation matches with the frequency of vibration, the molecule will absorb energy and it undergoes transition.

Eg:- Consider HCl molecule

The mass of the chlorine is comparatively higher than that of H_2, position of hydrogen will be changed during the vibration



Hydrogen and chlorine will be in equilibrium distance of r_{eq}, inorder to minimize the attractive force and the repulsive force

If we compress the bond by pulling the hydrogen towards chlorine, then chlorine will try to repell the hydrogen and there will a motion which is similar to that of a spring motion, mean to say that the molecule will start vibrating.

Whenever the position of one atom is changed w.r.t other, there will be a restoring force applied in opposite direction. Then according to the Hooke's law

$$-F \propto x$$

$$F = -kx$$

k - Force constant

Harmonic oscillator

If any object is undergoing periodic motion in a particular time interval, then such molecules are said to be oscillating.

Energy associated with the vibrational motion is

$$E_v = (v + \tfrac{1}{2}) h \omega_{osc} \quad (\text{Joules})$$

ω_{osc} → Frequency of oscillation.

The number of oscillations per second is represented by ω_{osc} and is given by

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \quad Hz$$

This expression gives ω_{osc} in Hz. To get it in cm^{-1},

$$\text{w.k.T} \quad \frac{1}{\lambda} = \frac{\nu}{c}$$

$$\Rightarrow \bar{\nu} = \frac{\nu}{c}$$

$$\therefore \bar{\omega}_{osc} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \quad cm^{-1}$$

~~To get energy in terms~~

Energy of the oscillation in terms of cm^{-1} could be written as

$$\varepsilon_v = \frac{(v+\frac{1}{2})h\cdot\omega_{osc}}{hc} \qquad \left[\because \bar{\nu} = \frac{E}{hc}\right]$$

$$= \frac{(v+\frac{1}{2})\,\omega_{osc}}{c}$$

$$\varepsilon_v = (v+\tfrac{1}{2})\,\bar{\omega}_{osc} \quad cm^{-1}$$

If we take the values for vibrational quantum number from 0 – 4, the energy for different vibrational energy levels will be equal to

For $v = 0$, $\varepsilon_0 = (0+\frac{1}{2})\,\bar{\omega}_{osc}$

$$= \frac{\bar{\omega}_{osc}}{2} \quad cm^{-1}$$

$v = 1$, $\varepsilon_1 = \frac{(1+\frac{1}{2})\,\bar{\omega}_{osc}}{2}$

$$= \frac{3\,\bar{\omega}_{osc}}{2} \quad cm^{-1}$$

$v = 2$, $\varepsilon_2 = \frac{5}{2}\,\bar{\omega}_{osc} \quad cm^{-1}$

$v = 3$, $\varepsilon_3 = \frac{7}{2}\,\bar{\omega}_{osc} \quad cm^{-1}$

If we take the difference in energy of $v = 1$ and $v = 0$, then,

$$\frac{3}{2}\,\bar{\omega}_{osc} - \frac{1}{2}\,\bar{\omega}_{osc} = 1\,\bar{\omega}_{osc}$$

which shows that the vibrational spectrum obtained for a molecule will be spaced at equal distance from one another, i.e., with the distance of $1\,\bar{\omega}_{osc}$

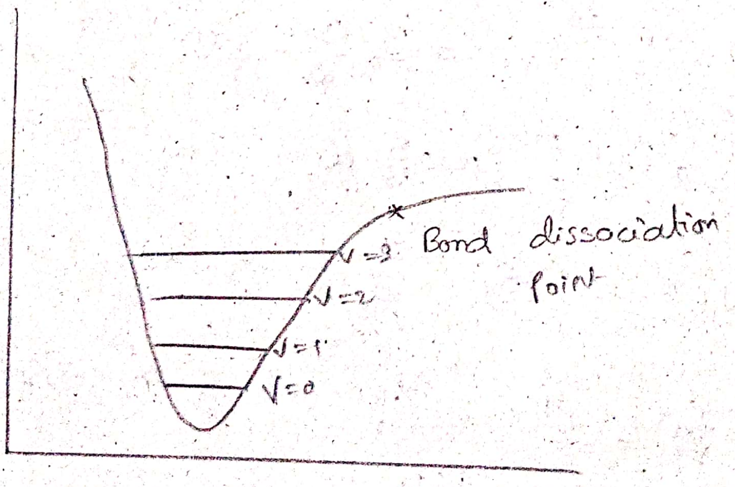
Zero point energy

For the value of $V=0$,

$$\varepsilon_0 = \left(0+\tfrac{1}{2}\right)\bar{\omega}_{osc} = \frac{\bar{\omega}_{osc}}{2}\ cm^{-1}$$

which means that, vibrational energy cannot be equal to zero. The energy at this point is called zero point energy.

In the case of anharmonic oscillation, the extent of vibration will be limited because observed for non-ideal anharmonic oscillation is observed for non-ideal molecule in which after certain vibrations, the bond between the atom will break at a point called bond dissociation point.



The energy for anharmonic oscillation is given by the formula

$$\varepsilon_{\text{anharmonic oscillation}} = \left(V+\tfrac{1}{2}\right)\bar{\omega}_{osc} - \left(V+\tfrac{1}{2}\right)^2 \bar{\omega}_{osc}\, X_e\ cm^{-1}$$

$$\mathcal{E}_1 - \mathcal{E}_0 = \left(\frac{3}{2}\bar{\omega}_{osc} - \left(\frac{3}{2}\right)^2 \bar{\omega}_{osc}\, x_e\right) - \left(\frac{1}{2}\bar{\omega}_{osc} - \left(\frac{1}{2}\right)^2 \bar{\omega}_{osc}\, x_e\right.$$

$$= \frac{3}{2}\bar{\omega}_{osc} - \frac{9}{4}\cdot\bar{\omega}_{osc}\, x_e - \frac{1}{2}\bar{\omega}_{osc} + \frac{1}{4}\bar{\omega}_{osc}\cdot x_e$$

$$= \bar{\omega}_{osc} - 2\bar{\omega}_{osc}\cdot x_e$$

$$\boxed{\Delta\mathcal{E}_{0-1} = \bar{\omega}_{osc}(1 - 2x_e) \quad cm^{-1}}$$

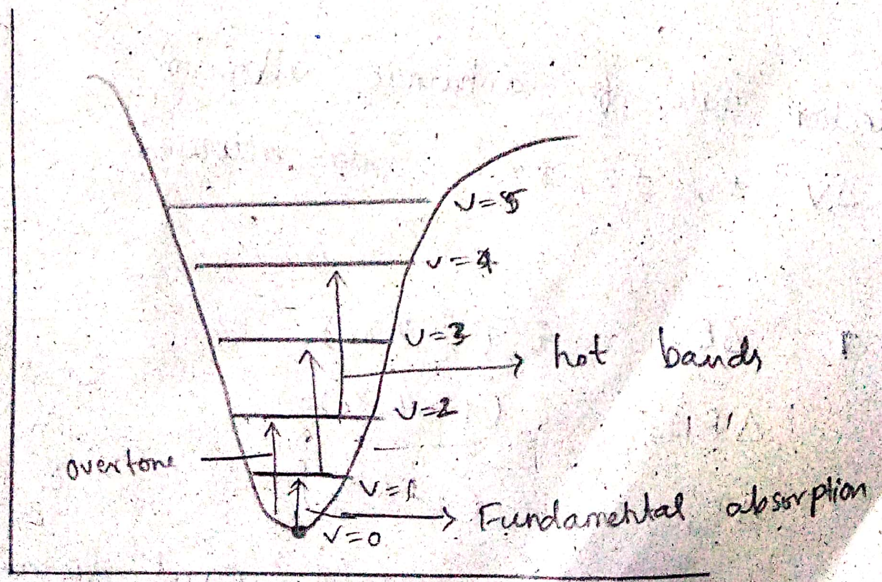
$$\mathcal{E}_0 - \mathcal{E}_2 = \frac{5}{2}\bar{\omega}_{osc} - \left(\frac{5}{2}\right)^2 \bar{\omega}_{osc}\cdot x_e - \frac{1}{2}\bar{\omega}_{osc} - \left(\frac{1}{2}\right)^2 \bar{\omega}_{osc}\, x_e$$

$$= \frac{5}{2}\bar{\omega}_{osc} - \frac{25}{4}\bar{\omega}_{osc}\cdot x_e - \frac{1}{2}\bar{\omega}_{osc} + \frac{1}{4}\bar{\omega}_{osc}\cdot x_e$$

$$= 2\bar{\omega}_{osc} - 6\,\bar{\omega}_{osc}\cdot x_e$$

$$\boxed{\Delta\mathcal{E}_{0-2} = 2\bar{\omega}_{osc}(1 - 3x_e)}$$

Since ground state have more number of molecules, so there is more vibration and transition from 0-1 state is more. This absorption ~~is~~ band is called fundamental absorption band.



Morse PE diagram

The transition from 0-2 is called first overtone.
The transitions 1-3, 2-4 etc are called hot bands.

The energy of hot band is

$$\varepsilon_{1-3} = \frac{7}{2}\bar{\omega}_{osc} - \left(\frac{7}{2}\right)^2 \bar{\omega}_{osc} \cdot x_e - \left[\left(\frac{3}{2}\right)\bar{\omega}_{osc} - \left(\frac{3}{2}\right)\bar{\omega}_{osc} \cdot x_e\right]$$

$$= \frac{7}{2}\bar{\omega}_{osc} - \frac{49}{4}\bar{\omega}_{osc} \cdot x_e - \frac{3}{2}\bar{\omega}_{osc} + \frac{9}{4}\bar{\omega}_{osc} \cdot x_e$$

$$= 2\bar{\omega}_{osc} - 10\,\bar{\omega}_{osc} \cdot x_e$$

$$= 2\bar{\omega}_{osc}(1 - 5x_e)$$

$$\varepsilon_{2-4} = \frac{9}{2}\bar{\omega}_{osc} - \left(\frac{9}{2}\right)^2 \bar{\omega}_{osc} x_e - \left[\frac{5}{2}\bar{\omega}_{osc} - \left(\frac{5}{2}\right)^2 \bar{\omega}_{osc} x_e\right]$$

$$= \frac{9}{2}\bar{\omega}_{osc} - \frac{81}{4}\bar{\omega}_{osc} x_e - \frac{5}{2}\bar{\omega}_{osc} + \frac{25}{4}\bar{\omega}_{osc} x_e$$

$$= 2\bar{\omega}_{osc} - 14\,\bar{\omega}_{osc} \cdot x_e$$

$$= 2\bar{\omega}_{osc}(1 - 7x_e)$$

Selection rule for anharmonic vibration

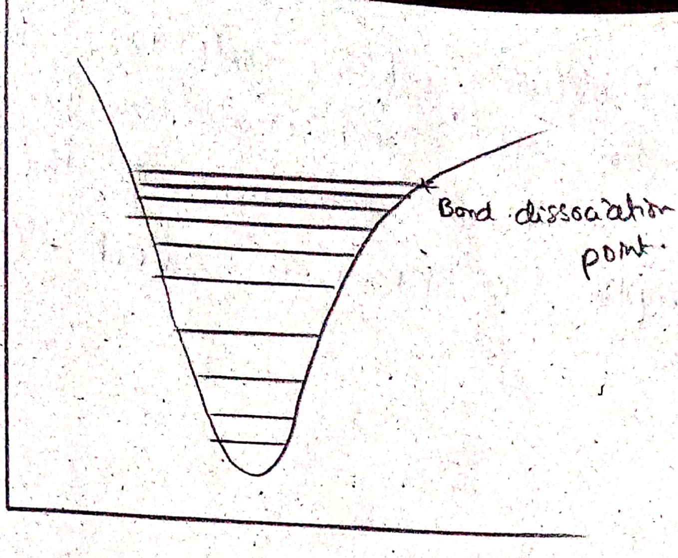
$\Delta v = \pm 1, \pm 2, \pm 3 \ldots$ are allowed.

W.K.T, $\Delta \varepsilon_{0-1} = \bar{\omega}(1 - 2x_e)$

$\Delta \varepsilon_{1-2} = \bar{\omega}(1 - 4x_e)$

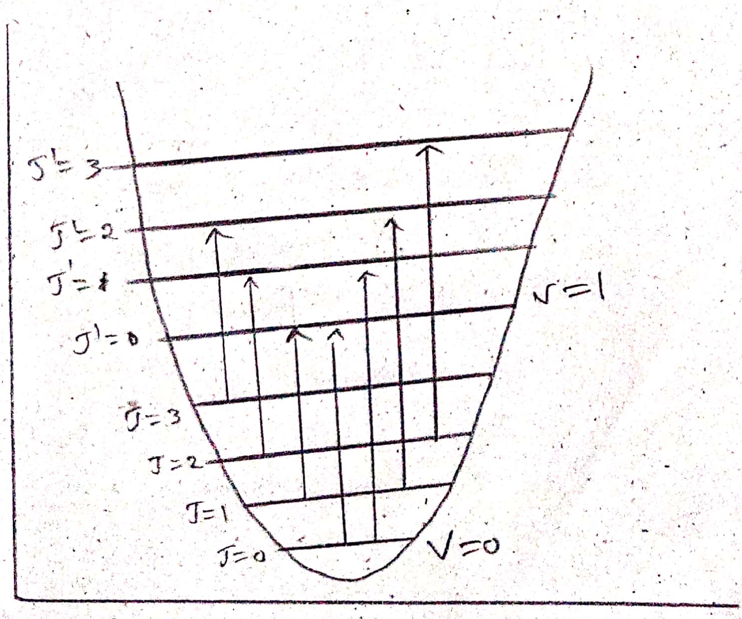
$\Delta \varepsilon_{2-3} - \bar{\omega}(1 - 6x_e)$

So; as energy state increases, band distance decreases



Rotational - Vibrational spectra

- when transition takes place from $V=0$ to $V=1$ without disturbing rotational energy, $J=0 \rightarrow J'=0$, This ~~ba~~ branch is called Q branch
- Other transition, $J=1 \rightarrow J'=0$, $J=2 \rightarrow J'=1$ etc are called P branch. Here $\Delta J=-1$. The transition with $J=+1$ is called R branch
- The transition



$$\varepsilon_{R,V} = BJ(J+1) + \left(\left(V+\tfrac{1}{2}\right)\bar{\omega}_{osc} - \left(V+\tfrac{1}{2}\right)^2 \bar{\omega}_{osc} x_e\right)$$

Consider a molecule which undergoes both vibration & rotation. the vibrational energy does not alter the rotational movement of the molecule - this assumption is known as Born - Oppenheimer approximation.